A novel diagnostic approach for studying silicon thin film growth
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A NOVEL DIAGNOSTIC APPROACH
FOR STUDYING SILICON THIN FILM GROWTH

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CHAPTER 1

INTRODUCTION

I. INTRODUCTION TO THIN FILM GROWTH

Over the past century, thin films have become an intrinsic part of everyday life. The visible applications are wide-ranging across many fields; from microelectronics to automobile parts, and from windows on skyscrapers to the metallic coating on the inside of potato chip bags. The reason for this increase in thin film applications is the broad range of film properties that can be accessed by thin film growth. These film properties may be chemical, mechanical, electrical, or optical in nature, while the deposition process may aim to optimize specific film properties such as composition, purity, morphology, thickness, microstructure, electrical or thermal conductivity, optical absorption or transmission, adhesion, wear, reactivity, etc. Moreover, a thin film coating on a bulk material may change or enhance the functionality of the bulk material by changing its surface properties, such as the scratch resistance or O₂-permeability. This opens up new possible applications for available bulk materials.

In thin film growth from the vapor phase, a flux of gas phase species impinges on a substrate and reacts with the surface to deposit a film. The deposition techniques utilized to grow thin films may involve physical and chemical processes. For instance, in physical vapor deposition (PVD), typically individual atoms or perhaps small clusters of atoms that originate from a liquid or solid source impinge on a solid surface at which they stick and form a film. In this case, surface reactions are commonly induced by the reactive nature of the atoms or clusters, while the substrate is often held at room temperature. In contrast, in chemical vapor deposition (CVD) a film is usually deposited from a (stable) gas that undergoes a chemical reaction at the surface. In this process, heating of the substrate is generally used to activate and control the chemical reactions of the precursor gas. Our interest lies in a specific kind of CVD, in which the film growth takes place by reactive gas phase species, as for example created with a plasma or a hot filament.
Gas phase composition  
Film properties  
Surface composition  
Gas phase reactions  
Surface reactions and diffusion  
Subsurface and bulk processes

**Fig. 1.** Schematic representation of the growth process of thin films. The different aspects of the growth process, which include the gas phase composition, the surface composition, and the film properties, are shown in relation with their input parameters on the left and their internal physical and chemical processes on the right. The gas phase composition may be dominantly determined by gas phase activation of the precursor gases, as for example achieved using a plasma or a hot wire.

(plasma-enhanced CVD or hot-wire CVD, respectively). Key to these deposition methods is the fact that the dissociation of the precursor gases basically takes place in the gas phase, which generally results in a large variety of reactive gas phase molecules, atoms, radicals, and ions. As a consequence, gas phase activation of the precursor gases enables the deposition of high quality films at lower substrate temperatures than those typically used in conventional CVD. Alternatively, thin film synthesis by means of gas phase activation of precursors may also share PVD-like processes, such as surface bombardment by energetic gas phase species.

In general, the growth process of thin films can be broken down in three aspects, which include the gas phase composition, the surface composition, and the film properties, as schematically illustrated in Fig. 1. These aspects may exhibit strong mutual correlations, while they are also influenced by their internal physical and chemical processes. As an example for CVD, the chemical nature of the surface determines which gas phase species can react at the surface. On the other hand, the surface chemical nature itself is determined by the governing reactions that take place at the surface. This example illustrates that, in order to understand the thin film growth process, the following general research questions should be answered: What are the relevant gas phase species for the growth process?, What are the microscopic surface reaction steps (of these gas phase species) that lead to film growth?, and How are the film properties determined by these gas phase species and their surface reactions?

For thin film synthesis by gas phase activation of precursors, the answers to the above-mentioned questions may be very different than for conventional CVD or PVD, as can be reasoned as follows. CVD is generally performed at high substrate temperatures to create reactive surface sites, such as open bonds, at which the stable gas phase species can react. At these high substrate temperatures, the gas phase species can often diffuse relatively easily towards the energetically most-favorable surface sites to contribute there to film growth. This typically results in smooth surfaces and consequently in dense materials. On the other hand, gas phase activated synthesis of thin films is usually performed at substrate temperatures between room temperature and 400 °C. At these substrate temperatures, it is commonly found that most bonds at the surface are terminated, for instance by hydrogen, and the surface reactions are induced by the reactivity of the gas phase species. As a result, the surface reactions also occur at energetically less-favorable sites, leading to an increased surface roughness. Therefore, the benefit of using a lower substrate temperature may come at the expense of a lower film density. With these characteristics of thin film synthesis by gas phase activation in mind, the above-mentioned general research questions are explored in more detail.
1) What are the relevant gas phase species for the growth process?

The first aspect in answering this question is the flux of gas phase species towards the surface. The flux is determined by the composition and densities of the species, while the species' transport properties to the substrate can also have a significant influence. Determination of the gas phase densities may be a real challenge for plasma-enhanced and hot-wire CVD due to the diverse composition of (reactive) species that is typically created through a variety of gas phase reactions. Apart from the flux of species to the surface, it is also necessary to know the species' surface reactivity to establish the relevance of a species for film growth. Often a species that is very reactive at the surface has a relatively low gas phase density, because it is easily lost at the surface. Therefore, despite its low density its relevance for the growth process may be large. This may call for sensitive gas phase diagnostics that are able to detect low-density reactive species.

2) What are the microscopic surface reaction steps that lead to film growth?

The reactions that take place at the surface depend (to a large extent) on the chemical nature of the surface. Therefore, determination of the surface chemical nature is the first step in unraveling the microscopic surface reaction steps that lead to film growth. For thin film synthesis by gas phase activation for which the chemical bonds at the surface are typically terminated, an important question is whether the (reactive) gas phase species require active surface sites for film growth to take place. The surface kinetics and chemistry may also cover physical mechanisms such as surface bombardment by energetic gas phase species and surface diffusion mechanisms. Closely linked to surface diffusion is the morphology of the surface. In many thin film growth systems, surface diffusion of the growth precursors towards energetically more favorable surface sites is considered to be the key process for controlling the surface roughness to obtain dense films.

3) How are the film properties determined by the gas phase species and their surface reactions?

The general aim in thin film growth is to optimize the film properties, usually for a specific technological application. To this end, fundamental insight into the dominant gas phase species and their governing surface reactions alone does not suffice, but should be compared to the resulting film properties. Such a comparison can reveal correlations between the various aspects of the growth process and the film properties. These correlations, in turn, can be utilized to optimize the film properties, for example, by changing the process conditions to promote the production of a specific gas phase species.

II. GOAL AND FOCUS OF THE THESIS WORK

To obtain a fundamental understanding of the growth process, the various aspects of thin film growth that have been addressed above need to be studied by dedicated experiments. The work in this thesis focuses on the thin film synthesis by gas phase activation, for which the deposition pressure is typically in the range of 1–100 Pa and the deposition occurs in the "harsh" environment of reactive ions, radicals, and atoms. The large variety of possible surface reactions under these conditions explains why the fundamental insight into these growth systems is lagging behind that of some CVD systems, where the growth process can be studied under much better-defined conditions. Therefore, the goal of this thesis work is to implement a novel diagnostic approach for studying the growth process of thin film synthesis by gas phase activation. This approach, which is addressed below, is employed to the specific deposition system of hydrogenated amorphous silicon (a-Si:H) that has been chosen as a model system throughout the thesis work due to its exemplary role in the deposition of silicon-based films and other covalent systems. An overview of the previous research on a-Si:H thin film growth is given in Frame A, while its technological relevance is outlined in Frame B.
FRAME A: PREVIOUS RESEARCH ON a-Si:H THIN FILM GROWTH

The use of hydrogenated amorphous silicon (a-Si:H) films in electronic applications such as flat panel displays and solar cells (see Frame B) requires a low density of defects such as dangling bonds in the amorphous silicon matrix, because these defects act as recombination centers for electron transport in the final device. Already in the late 1960s, it was found that a low defect density is achieved by the incorporation of hydrogen in the growing film to saturate the dangling bonds, whereas an energetic ion bombardment should be avoided as it creates additional dangling bonds. Therefore, high-quality a-Si:H films are commonly synthesized by gas phase activation of a SiH4 containing gas mixture under conditions of low ion bombardment. The material properties of optimized a-Si:H films were found remarkably similar for the various deposition methods used, such as an rf capacitively-coupled plasma, the so-called ‘expanding thermal plasma’, and hot-wire CVD. Apart from its technological applications, a-Si:H is also interesting from a fundamental standpoint being a simple amorphous covalent material, while its similar chemical structure to c-Si provides the opportunity to benefit from the extensive literature on c-Si surface processes. As a result, the growth process of a-Si:H has been studied in detail over the past two decades, even to such an extent that it has basically become a model system for understanding thin film growth of silicon-based films, such as microcrystalline silicon and various silicon alloys (a-Si,Ox:H, a-Si,Ny:H, a-Si,Cy:H, etc…). For instance, (indirect) measurements of a relatively high surface reactivity and gas phase density of SiH3−10 led to the general belief that the growth process of high-quality films is dominated by SiH3 radicals, although other species such as SiH4 and H radicals may also be significant. At the same time, the growing a-Si:H surface was found almost fully hydrogen terminated at the typical growth temperature of 250 °C with an estimated surface dangling bond density of (much) less than 1%. Several growth models of a-Si:H were proposed, most of which were based on the SiH3 radical (see, e.g., Fig. A). Most growth models assumed that SiH3 will eventually stick on a surface dangling bond as these are assumed to be the most-reactive sites on the surface (see, e.g., reaction (1c) in Fig. A). Moreover, surface diffusion of an intermediate SiH3 surface-state has often been introduced to explain the apparent contradiction between the relatively high surface reactivity of SiH3 and the low surface dangling bonds density as well as the remarkable smoothness of the a-Si:H films. Alternatively, direct insertion of SiH3 into a strained Si-Si surface bond was proposed to explain SiH3 adsorption without the need for surface dangling bonds (reaction (2) in Fig. A). Recently, various other views on a-Si:H film growth have been proposed in the literature, to which this thesis work has also contributed, as also initiated by the recent availability of ab-initio calculations and molecular dynamics simulations.

Fig. A. Two specific a-Si:H growth models, based on the SiH3 radical, that received much attention in the literature: (1) an SiH3 impinges on the a-Si:H surface to assume a diffusion state (1a) and subsequently produces a surface dangling bond by H abstraction (1b) or adsorbs on a previously-created dangling bond (1c); and (2) SiH3 insertion into a strained Si-Si surface bond resulting in a five-fold coordinated Si atom that may also diffuse over the surface.
The diagnostic approach for studying thin film synthesis by gas phase activation of precursors that has been implemented in this thesis work covers the following aspects, as shown schematically in Fig. 2:

(i) Although a variety of (surface) diagnostics are readily available for studying thin film growth, in our approach dedicated diagnostics are developed that are able to address the key research questions of thin film synthesis by gas phase activation, such as “What is the role of surface dangling bonds for radical absorption?”. Preferentially, the deposition process is studied in real time and non-intrusively to address issues such as surface diffusion and to rule out relaxation effects of the surface after the deposition. As a consequence, there is a clear preference for “all-optical” diagnostics.

(ii) The diagnostics are applied to the same growth system to yield an extensive characterization of the various aspects of the film growth. Each diagnostic can only reveal limited information, however, by applying multiple diagnostics there is a good possibility to unravel the governing growth processes.

(iii) The growth process is preferentially studied under well-defined conditions. By identifying and isolating the key (reactive) gas phase species responsible for film growth, the surface reactions of these key species can be studied in detail. For instance, the deposition process may be mimicked using radical beams of those species that govern the growth.

![Fig. 2. Schematic representation of the diagnostic approach used for studying thin film synthesis by means of gas phase activation of precursors, as illustrated for the model system of a-Si:H deposition (dark and light balls depict Si and H atoms, respectively). The diagnostic approach covers three aspects: (i) real-time and all-optical diagnostics are developed to address specific questions on the growth process; (ii) the diagnostics are applied to the study of the same growth system on the new ultra-high vacuum setup; and (iii) the deposition takes place under well-defined conditions, e.g., a-Si:H deposition can be mimicked by a SiH$_3$ and H beam because these are the most important growth precursors. In this thesis work three of such diagnostics have been developed, i.e. (a) time-resolved cavity ringdown spectroscopy ($\tau$-CRDS) to measure the surface reactivity of gas phase species by monitoring the time-evolution of the species’ density in front of the substrate, (b) evanescent-wave cavity ringdown spectroscopy (EW-CRDS) that uses a monolithic folded optical cavity for in-situ and real-time detection of surface and bulk dangling bonds, and (c) real-time spectroscopic ellipsometry (RTSE) to yield information on surface diffusion mechanisms by monitoring the surface roughness evolution.](image-url)
FRAME B: TECHNOLOGICAL RELEVANCE OF SILICON THIN FILMS

Silicon thin films and a-Si:H thin films in particular are the key components in two prominent upcoming technologies, i.e. TFT-LCDs (thin-film transistor liquid crystal displays) and (flexible) solar cells. Meanwhile, other applications of silicon thin films such as photoreceptors and light emitting diodes remain important.

The electronic display market is being taken over by TFT-LCDs, as shown in Fig. B(a).\textsuperscript{19-21} TFT-LCD is the most versatile form of display technology, with, e.g., the latest sixth-generation facilities producing a-Si:H TFTs on 1.5\times1.8 m\textsuperscript{2} substrates. From its base in notebooks where its has a 100% share, TFT-LCD technology is taking over the desktop monitor market where a 90% share is predicted by 2007.\textsuperscript{22} The newest target market for TFT-LCDs is the 2.5 times larger consumer television segment, where a doubling of the current market share is expected in 2006.\textsuperscript{23} Other billion-dollar markets of TFT-LCD include digital still cameras, camcorders, and handheld games as well as the fast-growing small displays market.

Another expanding market for silicon thin films is photovoltaics (PV) with PV shipments averaging an annual growth of \~35\% over the last five years and a predicted annual growth of \~30\% for the upcoming decades, as shown in Fig. B(b).\textsuperscript{22-25} This leads to a predicted PV share of \~6\% and \~25\% for the world's energy and electricity supply, respectively, in 2040.\textsuperscript{23} Figure B(b) shows that within the PV market the share of silicon thin film solar cells increases from \textless10\% today to a possible dominant market share at 2030. Meanwhile, the electricity costs of future silicon thin film solar cells are estimated to drop below most conventional electricity sources, however, silicon thin film solar cells have the inherent advantage of a clean, silent, nontoxic, non-hydrocarbon based, and reliable energy production and the possibility for roll-to-roll production of (large area) flexible solar cells.

Because both markets are becoming mature, the profit margins on modules will drop. Therefore, the challenges for silicon thin film growth lie in more cost-effective production strategies using high deposition rates and large area substrates. In order to meet these challenges, a fundamental understanding of the microscopic surface reactions during silicon thin film growth will be required.

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Fig. B. (a) The iSuppli/Stanford Resources' forecast\textsuperscript{28} for the global annual revenue of the electronic display market, broken down by technology, including cathode-ray tube (CRT), thin-film transistor liquid crystal displays (TFT-LCD) for which predominantly silicon thin films are used, and other flat panel displays (FPD). (b) The European Photovoltaic Industry Association's forecast\textsuperscript{27} for the global annual shipment of photovoltaic modules in units of peak-Watts (Wp), broken down by technology, including c-Si and silicon thin film solar cells as well as "new concept" solar cells that are at present mostly at the basic research stage.
Chapter 1

III. OVERVIEW OF THE RESEARCH

Specifically, in this thesis work, three all-optical and real-time diagnostic techniques have been designed and implemented to study the deposition of a-Si:H. Two of the diagnostic techniques are based on the ultra-sensitive cavity ring-down spectroscopy (CRDS) method, which is an established technique for measuring the absolute density of (reactive) gas phase species: time-resolved CRDS for determining the surface reactivity of gas phase species and evanescent-wave CRDS for probing surface species. Moreover, real-time spectroscopic ellipsometry has been employed to investigate surface diffusion mechanisms while, in addition, a new ultra-high vacuum reactor has been constructed to carry out these and other future dedicated experiments.

The method of time-resolved cavity ring-down spectroscopy (τ-CRDS) [Fig. 2(a)] has been developed as a direct diagnostic to measure the surface reactivity of (low-density) gas phase species under regular thin film processing conditions. In addition, combination of the species' reactivity with their absolute gas phase density from CRDS yields their deposition flux. Specifically, τ-CRDS yields the surface reaction probability $\beta$ of a species from time-resolved measurements of a time-modulated gas phase density in front of the substrate. The feasibility of τ-CRDS is demonstrated in Chapter 2 for a-Si:H deposition, while in Chapter 3 the $\beta$ values of Si and SiH$_3$ on the a-Si:H surface are measured for different substrate temperatures. Combination of these results with additional measurements of the a-Si:H system and atomistic simulations of SiH$_3$ in the literature yields SiH$_3$ as the dominant a-Si:H growth precursor (Chapter 3) and shows new insights into the SiH$_3$ surface reactions (Chapter 4).

Chapters 5 and 6 present evanescent-wave cavity ringdown spectroscopy (EW-CRDS) [Fig. 2(b)] as a generic diagnostic for measuring absolute surface number densities of surface species with sub-monolayer sensitivity, while it also provides information on the orientation of the transition moments of the species on the surface. In particular, EW-CRDS is developed as a sensitive probe for in-situ and real-time detection of surface and bulk dangling bonds by probing the electronic sub-gap states of a material (Chapter 5), while a feasibility study of EW-CRDS for probing surface species is presented in Chapter 6 for the case of three chloroethylenes adsorbed on a silicon dioxide surface.

Chapter 7 presents a dedicated ultra-high vacuum setup that enables future surface science-like studies of thin film growth and the growth of a-Si:H in particular by using the here-presented and other diagnostics. In these studies, the deposition process is mimicked by well-defined radical beams (SiH$_3$ and H beams for a-Si:H film growth), as shown in Fig. 2. As a first step for studying the growth of a-Si:H in this new setup, Chapter 8 presents an extensive characterization of the a-Si:H material properties deposited in the new setup using real-time spectroscopic ellipsometry (RTSE) and several ex-situ film diagnostics, while RTSE is shown to be a valuable tool for detailed material characterization during thin film growth.

Finally, Chapter 9 establishes RTSE [Fig. 2(c)] a diagnostic that can yield detailed information on surface diffusion mechanisms by monitoring the surface roughness evolution during thin film growth. A study of the a-Si:H film growth for different substrate temperatures yields important insights into the initial nucleation behavior of a-Si:H and the surface diffusion processes occurring on small and large lateral length scales. In addition, the description of the roughness evolution in terms of a generic nonlinear stochastic growth equation is discussed as well as the consequences of the results for the governing atomistic surface reactions regarding surface diffusing growth precursors and active surface sites.
IV. OUTLOOK

The possibilities of these diagnostics are of course not limited to the growth system of a-Si:H. While all of these diagnostics can directly or relatively easily be applied to other silicon growth systems, they can also be adapted to other covalent systems or other thin film growth systems in general. At the same time, with the experimental arrangements described in this thesis it is now possible to address some of the key questions on the growth process of a-Si:H by employing the various diagnostics in the new ultra-high vacuum setup to monitor the a-Si:H film growth.

One such prominent issue for a-Si:H that can now be addressed is the role of dangling bonds for the growth of a-Si:H. EW-CRDS enables the direct measurements of the density of dangling bonds at the surface (and in the bulk), while the surface dangling bond density can also be measured using the surface-sensitive technique of second harmonic generation (SHG), which is being developed in our group for this purpose. Moreover, the study of the surface dangling bond density can be complemented by measuring the surface silicon hydride bond (SiH_x) composition at the a-Si:H surface, using attenuated total reflection Fourier transform infrared spectroscopy.

Another long-standing debate in the a-Si:H literature is whether the incorporation of SiH_3 radicals occurs through an intermediate surface state of the SiH_3 radical that may diffuse over the surface. EW-CRDS seems to be a promising diagnostic to directly detect the possible SiH_3 surface states that have been suggested in the literature, such as physisorbed SiH_3 and five-fold coordinated SiH_3. This can for example be done by probing a Si-H vibrational overtone such that the high chemical specificity of overtone absorption is utilized to distinguish between the various Si-H bonds at the surface while keeping sufficient sensitivity. Moreover, the dynamics of such an SiH_3 state on the surface may also be studied: While RTSE yields a general insight into the surface diffusion mechanisms that are active during a-Si:H film growth, the surface diffusion properties of a specific SiH_3 surface state may be probed directly by employing the excellent time and spatial resolution of EW-CRDS to monitor the evolution of the species’ density in time after manipulating the species’ spatial density distribution on the surface.

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W. M. M. Kessels, J. P. M. Hoefnagels, P. J. van den Oever, Y. Barrell, and M. C. M. van de Sanden, Surf. Sci. 547, L865 (2003); Chapter 4 of this thesis.
CHAPTER 2

TIME-RESOLVED CAVITY RING-DOWN SPECTROSCOPIC STUDY
OF THE GAS PHASE AND SURFACE LOSS RATES
OF Si AND SiH₃ PLASMA RADICALS

ABSTRACT

Time-resolved cavity ringdown spectroscopy has been applied to determine gas phase and surface loss rates of Si and SiH₃ radicals during plasma deposition of hydrogenated amorphous silicon. This has been done by monitoring the temporal decay of the radicals’ densities as initiated by a minor periodic modulation applied to a remote SiH₄ plasma. From pressure dependence, it is shown that Si is reactive with SiH₄ [(1.4±0.6)×10⁻¹⁶ m⁻³ s⁻¹ reaction rate constant], while SiH₃ is unreactive in the gas phase. A surface reaction probability β of 0.9 < β ≤ 1 and β = 0.30±0.05 has been obtained for Si and SiH₃, respectively.

For basic understanding and modeling of plasma deposition processes, information on the density as well as the surface reactivity of the plasma species is essential. The surface reaction probability $\beta$ of the species has often been obtained indirectly, e.g., from measurements of a macroscopic compound value of $\beta^4$, or under process conditions different from the actual plasma deposition process, e.g., by measurements in an afterglow plasma$^{1-4}$ or from a molecular beam scattering experiment.$^5$ In this Chapter, we will present a technique to obtain the gas phase and surface loss rates of radicals during plasma deposition, here particularly in the case of high rate deposition of hydrogenated amorphous silicon.$^6$ In this technique, the highly sensitive cavity ring-down spectroscopy (CRDS) method$^7$ is used to map the temporal decay of an increased radical density by means of time-resolved absorption measurements. This so-called ‘additional radical density’ is created in a continuously operated remote silane plasma by applying a minor periodic modulation to the applied plasma power. Although time-resolved CRDS has been employed previously to obtain gas phase loss rates of radicals,$^8$ in this work we apply the technique also to determine surface loss rates of the radicals. This yields simultaneously information on the surface reaction probability $\beta$ and the density of the radicals under the specific plasma conditions. Using this method, it is shown that Si is mainly lost in the gas phase to SiH$_4$, whereas SiH$_3$ is only lost via diffusion to and reactions at the surface.

In the expanding thermal plasma technique (ETP) [Fig. 1(a)] a remote expanding Ar-H$_2$ plasma is created in which SiH$_4$ precursor gas is injected downstream. To detect (low-density) radicals such as SiH$_3$ and Si in this highly-diluted SiH$_4$ plasma the CRDS technique has previously been employed; SiH$_3$ has been identified at the $^3\Delta_1 \leftarrow ^3\Delta_1$ broadband transition ranging from ~200 to ~260 nm,$^9$ whereas Si radicals have been probed at the $4s^3P_{0,1,2} \leftarrow 3p^3P_{0,1,2}$ transition around 251 nm.$^{10}$ This has yielded typical densities of SiH$_3$ and Si of $\sim 5 \times 10^{18}$ m$^{-3}$ and $\sim 10^{15}$ m$^{-3}$, respectively.$^{11,12}$ In the time-resolved CRDS ($\tau$-CRDS) measurements, a minor periodic modulation of the radical densities is produced by applying 5 Hz, 2.5% duty cycle rf pulses to the substrate in addition to the continuously operating ETP. The power in the rf

![Fig. 1. (a) The ETP setup equipped with the cavity ring-down spectroscopy system, which is aligned at 5 mm in front of the substrate. A pulsed rf bias can be applied to the substrate holder. (b) A timing scheme illustrating the modulation of the radical density and the synchronization of the CRDS laser pulses.](image-url)
pulse is 63 Watt and the bias voltage is between -40 and -120 V with a fall off time of less then 20 \( \mu s \). The additional absorption \( A_{\text{rf}} \) due to the radicals generated by the rf pulse is obtained from the difference in absorption at some point \( \Delta t \) in the rf afterglow and at a point long after the influence of the rf pulse has extinguished [see Fig. 1(b)]. Every CRDS trace is handled separately by means of a new ‘state-of-the-art’ 100 MHz, 12 bit data acquisition system\(^{13}\) and an averaged \( A_{\text{rf}} \) is obtained as a function of the time \( \Delta t \) in the afterglow of the rf pulse.

A typical \( \tau\)-CRDS measurement for Si and SiH\(_3\) is shown in Fig. 2. A duty cycle of 2.5 % has been used in order to obtain a good signal-to-noise ratio in the additional Si and SiH\(_3\) absorption, while possible powder formation due to the ‘anion-confining’ rf plasma sheath is suppressed.\(^{14}\) Figure 2 shows that both Si and SiH\(_3\) decrease single exponentially, which is expected from the radicals’ mass balance when the loss term is linear in the radical density.\(^{15}\) The corresponding loss rate \( \tau^{-1} \) depends linearly on the gas phase loss on one hand and the loss due to diffusion to and reactions at the surface on the other hand:\(^{15}\)

\[
\tau^{-1} = k_r n_x + \frac{D}{\Lambda^2} \quad (1)
\]

In this equation, \( k_r \) is the gas phase reaction rate with species \( x \) with density \( n_x \), \( D \) is the diffusion coefficient for the specific radical in the Ar-H\(_2\)-SiH\(_4\) mixture,\(^{16}\) and \( \Lambda \) is the effective diffusion length of the radical. The latter depends on diffusion geometry and on the radical’s surface reaction probability \( \beta \).\(^{15}\)

As revealed by Fig. 2, Si is lost typically a factor of 10 faster than SiH\(_3\) in the Ar-H\(_2\)-SiH\(_4\) plasma. As will be shown below, this is mainly due to the difference in the gas phase loss processes that need to be considered first before surface loss rates of the radicals can be deduced. For Si and SiH\(_3\) in the ETP plasma the only candidate for a significant gas phase loss is SiH\(_4\).\(^{16}\) To investigate this reaction channel, the loss rate of Si and SiH\(_3\) has been obtained as a function of the SiH\(_4\) density (Fig. 3) keeping the total pressure and thus the diffusion term in Eq. (1) nearly constant. The SiH\(_4\) density has been calculated from the SiH\(_4\) partial pressure using a kinetic gas temperature of 700K and including a correction for the local SiH\(_4\)
Fig. 3. The Si and SiH$_3$ loss rate as a function of the SiH$_4$ density at constant total pressure of 0.27 mbar. The error bars represent the statistical error in the decay time as shown in Fig. 2.

The loss rate of SiH$_3$ in Fig. 3 is independent of the SiH$_4$ density, which indicates no gas phase loss of SiH$_3$, while the loss rate of Si increases linear with the SiH$_4$ density. The slope reveals a reaction rate constant of Si($^3$P) with SiH$_4$ of $k_r = (1.4\pm0.6) \times 10^{-16}$ m$^3$s$^{-1}$. In the error analysis of this reaction rate the small statistical error in the loss rates as well as the following systematic uncertainties have been considered: The variation in the diffusion term in Eq. (1) can be neglected for the small SiH$_4$ dilutions used in Fig. 3, while the local SiH$_4$ density correction affects $k_r$ only slightly. The uncertainty in $k_r$ is mainly determined by the gas temperature, which has been estimated to be (700±200) K from plasma model calculations. The value of $k_r$ is somewhat lower than the value of $k_r = (3.5\pm1.0) \times 10^{-16}$ m$^3$s$^{-1}$ and $k_r = (4.4\pm1.0) \times 10^{-16}$ m$^3$s$^{-1}$ as obtained, respectively, by Tanaka et al. at ~350K in an rf plasma and Matsui et al. at 295K in a photolysis experiment. The value of Tanaka et al. is in relatively good agreement with our value considering the assumptions made (in both cases) on, e.g., the gas temperature and thermalization of Si, while the unaccounted presence of disilane in continuous rf plasmas could also easily account for the discrepancy. The comparison with the value of Matsui et al., which has been determined in a somewhat indirect way using a pre-assumed chemistry model, might not be so straightforward since it was obtained under a ~50 times higher He background pressure.

In order to deduce the surface reaction probability $\beta$ of Si and SiH$_3$ from the diffusion term in Eq. (1), a semi-empirical expression for the cylinder symmetrical geometry has been assumed to determine the effective diffusion length $\Lambda$, as has been proposed by Chantry et al. However, the diffusion geometry in the ETP reactor, although cylinder symmetric, is not as well defined as for example in an rf parallel plate reactor. In our approach we have assumed that the diffusion of the radicals in radial direction can be neglected in respect to the diffusion in axial direction. Although this assumption introduces the main uncertainty in $\beta$, larger than the uncertainty due to the radical’s temperature, the assumption is validated by the fact that within the 5 ms duration of the rf pulse the additional radicals do not have sufficient time to reach the outer reactor wall, while the additional density saturates due to axial diffusion to the substrate (see caption of Fig. 2). Moreover, on the basis of arguments such as plasma model calculations and light emission measurements, it is assumed that the additional radicals are produced and confined close to the substrate and that the transport to the substrate is diffusion dominated. Consequently, from the pressure balance it follows that the production term of a radical (proportional to the local SiH$_4$ density and the electron density) in the rf pulse under steady state conditions is equal to the radical density over its loss rate (i.e., $n/\tau$). The electron density remains fairly constant for the conditions used yielding therefore information on the local SiH$_4$ density.
dependence of the decay time of SiH₃ (Fig. 4) and the SiH₄ diffusion coefficient the parameters describing the axial diffusion geometry can be obtained: Figure 4 reveals a good linear dependence of the decay time of SiH₃ on the total pressure and therefore Eq. (1) has been fitted to the data points setting the gas phase loss term to zero. The surface reaction probability follows from the offset in Fig. 4 yielding a value of β=0.30±0.05 for SiH₃ in the ETP plasma. This value is in good agreement with the estimated β for SiH₃ from indirect measurements as obtained previously with the ‘aperture-well assembly’ method applied under similar conditions in the same setup. The value is also in good agreement with a β of SiH₄ of β=0.28±0.03 as determined by Perrin et al. by time-resolved threshold ionization mass spectrometry in an rf plasma with a 100% on-off modulation. Furthermore, by applying the same axial diffusion geometry to the measurements of Si (while taking into account the gas phase loss to SiH₄), a lower limit of 0.9 has been obtained for β of Si, yielding therefore 0.9<β≤1. Although this is the first direct experimental evidence for a nearly unity surface reaction probability of Si, a β of ~1 is generally assumed for the Si radical on the basis of its hydrogen deficiency.

In conclusion, it has been shown that the time-resolved cavity ring-down experiment applied on a remote plasma is capable of obtaining radical loss rates during the actual plasma deposition process. From partial and total pressure series, it has been shown that Si is highly reactive in the gas phase with SiH₄ whereas its surface reaction probability β is 0.9<β≤1. SiH₃ on the other hand is unreactive with SiH₄ and has a surface reaction probability of β=0.30±0.05 which is in good agreement with previously reported values. In the future, the geometrical model will be refined such that the β values of these and other silane radicals can be determined at very high accuracy and as a function of plasma and surface conditions.

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CHAPTER 3

TIME-RESOLVED CAVITY RING-DOWN STUDY
OF THE SI AND SIH₃ SURFACE REACTION PROBABILITY
DURING PLASMA DEPOSITION OF a-Si:H
AT DIFFERENT SUBSTRATE TEMPERATURES

ABSTRACT

Time-resolved cavity ring-down spectroscopy (τ-CRDS) has been applied to determine the surface reaction probability $\beta$ of Si and SiH₃ radicals during plasma deposition of hydrogenated amorphous silicon (a-Si:H). In an innovative approach, our remote Ar-H₂-SiH₄ plasma is modulated by applying pulsed rf power to the substrate and the resulting time-dependent radical densities are monitored to yield the radical loss rates. It is demonstrated that the loss rates obtained with this τ-CRDS technique equal the loss rates in the undisturbed plasma and the determination of the gas phase reaction rates of Si and SiH₃ as well as their surface reaction probability $\beta$ is discussed in detail. It is shown that Si is mainly lost in the gas phase to SiH₄ [reaction rate $k_r = (3.0\pm0.6)\times10^{-16}$ m$^3$s$^{-1}$], while the probability for Si to react at an a-Si:H surface is $0.95 < \beta_{Si} < 1$ for a substrate temperature of 200 °C. SiH₃ is only lost in reactions with the surface and measurements of $\beta$ of SiH₃ for substrate temperatures in the range of 50–450 °C show that $\beta_{SiH_3} = 0.30\pm0.03$, independent of the substrate temperature. The implications for a-Si:H film growth are discussed.

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I. INTRODUCTION

In the field of plasma materials processing, the plasma properties are not only determined by the plasma composition and the volume interactions, but also by interactions of the plasma species with the surrounding surface and substrates. Often expressed in terms of the surface reaction probability or surface loss probability, the macroscopic surface reactivity of plasma species, such as radicals, is of interest as it captures the various reactions taking place at the surface. In plasma modeling, incorporation of surface reactivities can be imperative to account for the effects of destruction and creation of plasma species at the reactor wall. The surface reactivity also reflects the (relative) importance of the species for surface processes. For example in plasma deposition, the surface reactivity determines the contribution of the different species to film growth. Moreover, measurements of the surface reactivity of plasma species in dedicated experiments (e.g., as a function of substrate temperature) can yield fundamental insight into the reactions taking place at the surface.

Values of the surface reactivity of plasma radicals have been obtained for some time in surface science-like experiments, studying the interaction of molecular beams with the surface under well-defined conditions.\(^1\)\(^-\)\(^4\) In a real plasma environment with a large variety of species, however, numerous different reactions can occur at the surface at the same time and therefore the values for the surface reactivity may differ significantly from those obtained by the molecular beam experiments. As an early solution to circumvent this problem for the field of plasma deposition, values of the surface reactivity have been determined from the comparison of the conformity of deposition profiles obtained both experimentally and by simulation.\(^5\)\(^-\)\(^11\) However, this procedure in which films were deposited in trenches and cavity-like structures, yields only a value of the surface reactivity averaged over all plasma species contributing to film growth. As a consequence, considerable effort has been put into the development of techniques and methods that measure directly the surface reactivity of a specific radical and which are generally applicable during plasma processing. These techniques are based on the measurement of the time evolution or the spatial profile of the radical density and utilize various plasma diagnostics, such as threshold ionization mass spectrometry,\(^12\)\(^-\)\(^15\) laser-induced fluorescence spectroscopy,\(^16\)\(^-\)\(^18\) actinometry,\(^19\) and various kinds of absorption spectroscopy.\(^20\)\(^-\)\(^24\) In addition to these techniques, we have reported recently that time-resolved density measurements by means of cavity ring-down laser absorption spectroscopy (CRDS) can also be used to measure the surface reactivity of plasma radicals.\(^25\) CRDS is a particularly powerful absorption technique to measure low-density radicals, because the decay time of the light intensity in a high-finesse optical cavity and not the light intensity itself is utilized as the absorption-sensitive observable.\(^26\) Enhanced sensitivity for small absorption values is increased further due to the effective multipassing of the light pulse in the optical cavity and the insensitivity of the decay time to light intensity fluctuations. The time-resolved version of CRDS (\(^\tau\)-CRDS) exploits the same enhanced sensitivity, while inherently it is a versatile diagnostic with a short time resolution that can be applied to basically all absorbing plasma species.\(^27\) Moreover, because \(^\tau\)-CRDS measures directly absorptions, it also yields information on the (line-integrated) absolute density of the species observed without the need for an elaborate calibration procedure.

In this Chapter, we will discuss the determination of the loss rates of silane (\(\text{SiH}_4\)) radicals (\(\text{Si}\) and \(\text{SiH}_3\)) from the time-evolution of the radical densities as obtained with \(^\tau\)-CRDS. From these loss rates, values of the gas phase reaction rates as well as the surface reactivity are extracted, as addressed in detail. Furthermore, the accuracy of the method is carefully assessed including experimental aspects, such as the role of the gas temperature. The strength of \(^\tau\)-CRDS will be illustrated for an experimental method that has the advantage that it determines the values of the surface reactivity during the plasma deposition process.
from a minor modulation of the radical density due to a pulse of rf power with respect to its steady-state density in the regularly operating plasma. The measurements are performed on a SiH₄-based plasma used for the deposition of hydrogenated amorphous silicon (a-Si:H). This system is ideally suited for such a study, as in the literature, extensive experimental and theoretical effort has been put into elucidating the a-Si:H growth process. Nonetheless, as addressed in the next section, some important issues have not yet fully been established. This Chapter will resolve two of such issues, i.e. the value of the surface reactivity of the Si radical and the temperature dependence of the surface reactivity of the SiH radical.

The Chapter is structured as follows: Sec. II summarizes the previous work performed on the surface reaction probability of the different silane radicals on an a-Si:H surface, while Sec. III gives a brief overview of the theory of diffusional transport of plasma radicals to the surface. Section IV describes the experimental procedure of the time-resolved CRDS measurements. The main results on the values of the surface reactivity of Si and SiH₃ are discussed in Sec. V, together with a careful assessment of the experimental accuracy of the τ-CRDS method. The implications of the results on a-Si:H film growth are also discussed. Finally, in Sec. VI the general conclusions are summarized.

II. THE SURFACE REACTION PROBABILITY OF SILANE RADICALS: PREVIOUS WORK

The deposition of a-Si:H from SiH₄ plasmas is probably the most studied plasma system in terms of the surface reactivity of the radicals investigated and the specific surface reactions leading to film growth proposed. The work was pioneered almost two decades ago by Gallagher, Matsuda, and Perrin. They constructed a first growth model of a-Si:H with several possible surface reactions of the SiH₃ radical, based on indications that SiH₃ has the highest density of all reactive species in the SiH₄ plasma. The model was derived primarily from measurements of the deposition rate and the overall surface reactivity for changing substrate temperature and doping gas concentration, where the overall surface reactivity was measured using the aforementioned indirect method of evaluating the conformality of deposition profiles. The surface reaction probability β was introduced as the probability that a plasma radical, such as SiH₃, will react at the surface. Two classes of surface reactions were identified: either the radical creates a chemical bond at the surface that leads to film growth (i.e. sticking with sticking probability s), or the radical recombines with species at the surface forming a stable molecule that desorbs into the gas phase (i.e. recombination with recombination probability γ), with β = s + γ. An example of a sticking reaction that was included in the growth model is the adsorption of SiH₃ on a surface dangling bond, while examples of recombination reactions are the abstraction of a surface H by a surface SiH₃ creating a volatile SiH₄ and the recombination of two surface SiH₃ radicals forming a volatile disilane (Si₂H₆) molecule. This preliminary growth model has been fruitful and has contributed greatly to the understanding of a-Si:H growth.

Following on this early work, more dedicated experiments of the silane radical densities have demonstrated that SiH₃ has indeed the highest plasma density at least for the specific plasmas investigated. Moreover, direct measurements of β for the silane radicals have been carried out by means of the various diagnostics mentions in Sec. I, revealing β values of ~0.2–0.3, ~0.6, and ~0.95 for SiH₃, SiH₂, and SiH, respectively. Combining the β values for all plasma species with their densities has yielded that SiH₃ is the dominant precursor for device quality a-Si:H film growth under most conditions. The values of β have also enabled sophisticated numerical models of SiH₄ plasmas that emphasize on a-Si:H deposition. McCurdy et al. have measured the dependence of β of SiH on the substrate temperature; however, other direct measurements of β as a function of changing surface conditions have been rare. Such measurements are essential to identify the surface reactions of a radical during plasma
deposition. For example, measurements of the dependence of $\beta$ on the substrate temperature can be used to elucidate possible surface reactions on the basis of their thermal activation. This can be done in conjunction with recent density functional theory calculations\textsuperscript{40-44} and molecular dynamics simulations\textsuperscript{41,45-48} which address the surface reactions at the atomistic scale. For SiH\textsubscript{3}, only indirect information is available about the dependence of $\beta$ on the substrate temperature from the early study of Matsuda \textit{et al.}\textsuperscript{6} This study, though, suffers from the uncertainty that the measured $\beta$ values are averaged over all plasma species.\textsuperscript{8} On the other hand, all direct measurements of $\beta_{\text{SiH}_3}$ have been obtained for a single substrate temperature\textsuperscript{12,20} and this data is insufficient to conclude on a consistent set of $\beta$ values of SiH\textsubscript{3} for different substrate temperatures. Considering the fact that SiH\textsubscript{3} is the key precursor for deposition of a-Si:H, however, accurate information on the substrate temperature-dependence of $\beta_{\text{SiH}_3}$ is vital for obtaining detailed insight into the SiH\textsubscript{3} surface reactions. Another issue is the surface reaction probability of Si. $\beta$ of Si is generally regarded to be unity,\textsuperscript{34,49} but this has never been confirmed experimentally by any of the established diagnostics, as summarized in the Introduction. Si is usually not considered in the growth models of a-Si:H, however under certain conditions, such as hot wire chemical vapor deposition and reactive magnetron sputter deposition of a-Si:H as well as plasma deposition of µc-Si:H under high H\textsubscript{2} dilution, the role of Si seems to be significant.\textsuperscript{28,50-52}

As outlined in the Introduction, these open issues for SiH\textsubscript{3} and Si will be addressed in this Chapter and will be used to demonstrate the strength of $\tau$-CRDS for measuring surface reaction probabilities. In this respect, it is interesting to note that (ground state) SiH\textsubscript{3} radicals cannot be detected by laser-induced fluorescence spectroscopy (the first electronically excited state of SiH\textsubscript{3} is a non-radiative, predissociative state\textsuperscript{53}), whereas SiH\textsubscript{3} is easily detected with absorption spectroscopy. On the other hand, Si radicals are relatively difficult to measure with mass spectrometry (mainly due to its high reactivity in the gas phase), whereas CRDS is relatively sensitive to Si due to the large absorption cross-sections of the atomic transitions.

III. THEORETICAL ASPECTS OF GAS PHASE AND SURFACE LOSS

This section presents a brief overview of the theoretical background that is needed to obtain the radical surface reaction probability $\beta$ from the time evolution of the radical density after a pulse of rf power (cf. Sec. IV). The theoretical description as derived by Chantry\textsuperscript{54} is followed and summarized for the case of our plasma reactor with a cylinder symmetrical geometry.

Assuming that self-recombination reactions can be neglected, the time-dependent mass balance of a radical density $n$ in a small volume element can be written as:\textsuperscript{54}

$$\frac{dn}{dt} = P - \frac{n}{\tau},$$

(1)

where $P$ is the volume production term and $n/\tau$ is the volume loss term with $\tau$ the loss time of the radical, corresponding with the loss rate $\tau^{-1}$. After a pulse of rf power, at the moment when the production term has vanished, the density describes a single exponential decay with the exponential decay time equal to $\tau$. This loss time $\tau$ can incorporate three possible loss channels for the radicals in the plasma: loss due to reactions in the gas phase with loss time $\tau_{\text{gas}}$, loss at the surface with loss time $\tau_{\text{surf}}$, and loss by pumping with loss time $\tau_{\text{pump}}$. 

The pumping loss can often be neglected for reactive species, while the gas phase loss rate can be expressed in terms of

\[ \tau_{\text{gas}}^{-1} = k, n_x, \]  

(3)

with \( k \) the gas phase rate constant for reactions of the radicals with a species \( x \) with a density \( n_x \). The surface loss due to diffusion to and reaction at the surface can be accurately approximated by

\[ \tau_{\text{surf}} = \frac{\Lambda_0^2}{D} \left( \frac{4}{v} \left( 1 - \frac{\beta}{2} \right) \right) \]  

(4)

with \( v = \sqrt{k_b T_{\text{gas}}} \) the kinetic velocity with Boltzmann constant \( k_b \), mass of the radical \( m \), and gas temperature \( T_{\text{gas}} \). The radical’s diffusion constant \( D \), assumed position-independent, is inversely proportional to the pressure \( p \) and has a \( T_{\text{gas}} \)-dependent pre-factor that can be calculated using the Chapman-Enskog diffusion theory including the Lennard-Jones parameters.\(^{55}\) The diffusion geometry in Eq. (4) is accounted for by the ‘geometrical’ diffusion length \( \Lambda_0 \) and the volume-to-area ratio of the diffusion volume \( l_0 \). The parameters \( \Lambda_0 \) and \( l_0 \) can be expressed in terms of the radius \( R \) and height \( H \) of the cylindrical diffusion volume:

\[ \Lambda_0 = \left[ \left( \frac{n_x}{H} \right)^2 + \left( \frac{2.405}{R} \right)^2 \right]^{-1} \]

and

\[ l_0 = \frac{HR}{2(H + R)}. \]

(5)

Combining Eqs. (4) and (5), \( \beta \) can be calculated from \( \tau_{\text{surf}} \) when \( H, R, \) and \( T_{\text{gas}} \) are known.

IV. EXPERIMENTAL SETUP

A schematic representation of the experimental setup is shown in Fig. 1 and basically three elements of the setup can be distinguished: the expanding thermal plasma (ETP) reactor in which the SiH\(_4\) plasma is created, the cavity ring-down spectroscopy setup, and the various additional components necessary to carry out the time-resolved measurements.

A. The Expanding Thermal Plasma

The ETP reactor\(^{56-58}\) consists of a cascaded arc plasma source and a low-pressure deposition chamber. In the cascaded arc, a current controlled dc discharge at 22.5 A is maintained at ~0.4 bar using an Ar and H\(_2\) flow of 27.5 and 2.5 sccs (standard cubic centimeter per second), respectively. The dc discharge produces a thermal Ar-H\(_2\) plasma that expands into the deposition chamber. By regulating the pumping speed, the pressure in the reactor can be controlled between 0.09–0.54 mbar, corresponding to a residence time in the reactor of ~0.4–2.4 s. At ~5cm from the arc exit, a pure SiH\(_4\) flow of 0.5–2.5 sccs is injected into the expanding plasma. Due to the expansion, the electron temperature is reduced to ~0.1–0.3 eV and therefore, electron-induced dissociation of SiH\(_4\) can be neglected, as presented in our previous work.\(^{35,57,59}\) Instead, the SiH\(_4\) is dissociated by reactive ionic or atomic species emanating from the plasma source. As
described elsewhere, for the conditions used in this Chapter, atomic hydrogen is dominating the dissociation of SiH₄ leading mainly to the creation of SiH₃ radicals. Si and other radicals are also produced, but at a much lower rate, leading to a much lower density. The SiH₄ plasma flows towards a substrate with an area of 10×10 cm², located at 35 cm from the arc exit. For the conditions used in this Chapter, ion bombardment can be neglected as the low electron temperature leads to a small floating potential of -2 V of the a-Si:H surface, while there are indications that the flux of atomic hydrogen towards the substrate is relatively low compared to the flux of the silane radicals. The substrate temperature can be accurately controlled from room temperature to 450 °C. Heating of the substrate by the plasma is reduced to less then 15 °C from its starting temperature due to good thermal contact between the substrate and the substrate holder by means of a small helium back flow.

B. Cavity ring-down spectroscopy

An optical cavity with a cavity length of 108 cm is created using two highly reflective mirrors (reflectivity R ≈ 0.99 at 251 nm), positioned on either side of the plasma reactor (Fig. 1). The cavity is aligned at an axial position of ~5 mm from the substrate in order to probe the radicals directly in front of the substrate. A Sirah Precisionscan D dye laser, pumped by a Nd:YAG laser (Spectra Physics, Quanta Ray DCR11), is operated on a Coumarin 500 dye in order to produce 10 Hz, 6-7 ns laser pulses at ~502 nm that are frequency doubled by a beta-Barium Borate crystal to ~251 nm with a line width of ~1.0 pm. The dye laser is temperature stabilized within 0.1 °C to consistently control the wavelength within ~0.2 pm. After passing a neutral-density filter to reduce the light intensity, the laser pulses are introduced into the CRDS cavity. The light intensity in the cavity decays exponentially due to intrinsic cavity losses and possible absorption losses. Light, leaking out the cavity through the second mirror, is detected by a photomultiplier (Hamamatsu R928) after passing an interference bandpass filter centered at 250 nm to reduce stray light. With a repetition rate up to 2 kHz, every CRDS transient is individually digitized and processed (i.e. a weighted least-squares fit to the logarithm of the transient) by means of a state-of-the-art 100 MHz, 12 bit data acquisition system (TU/eDACS, Ref. 62) yielding the exponential decay time of the light intensity in the cavity. A measurement of the difference in this decay time with and without a plasma as a function of the laser wavelength yields the absorption spectrum of the plasma in absolute sense. Dividing the absorption values by the absorption cross-section yields the line-integrated density of the species. When the
radial density profile has also been determined, the spatially-resolved radical density in front of the substrate can be computed directly from the line-integrated density.

In our previous work, CRDS has been employed to detect SiH$_3$ and Si radicals in the ETP and to determine their gas phase densities.\textsuperscript{35,49,60} SiH$_3$ has been measured at the $\tilde{A} \tilde{A}_1 \leftarrow \tilde{X} \tilde{A}_1$ transition, which yields a broadband featureless absorption spectrum ranging from $\sim$200 to $\sim$260 nm, as shown in Fig. 2. SiH$_3$ has unambiguously been identified in our plasma from the good agreement with the normalized absorption spectra of SiH$_3$ reported by Baklanov et al.\textsuperscript{64} and Lightfoot et al.\textsuperscript{65} (Fig. 2) as well as from the good agreement with threshold ionization mass spectrometry measurements of SiH$_3$.\textsuperscript{60} Si has been measured from the atomic line spectrum of the Si 4s $^3P_0,1,2 \leftarrow ^3P_2$ transition at $\sim$251 nm,\textsuperscript{66} which lies superimposed on the SiH$_3$ spectrum, as is shown in the inset of Fig. 2. From a measurement of the radial density profile,\textsuperscript{60} typical densities of SiH$_3$ and Si of $10^{18} \sim 10^{19}$ m$^{-3}$ and $10^{15} \sim 10^{16}$ m$^{-3}$, respectively, have been found in the ETP. In this Chapter, both Si and SiH$_3$ are detected around 250.7 nm: Si at the 4s $^3P_2 \leftarrow ^3P_1$ transition at 250.69 nm with peak absorption cross-section of $4.17 \times 10^{-17}$ m$^2$,\textsuperscript{66} and SiH$_3$ at the underlying broadband spectrum with an absorption cross-section of $\sim 4.9 \times 10^{-22}$ m$^2$, as reported recently by Baklanov et al.\textsuperscript{64} This recent and more accurate absorption cross-section of SiH$_3$ differs only slightly from the previously-used absorption cross-section of Lightfoot et al.\textsuperscript{65}

### C. Time-resolved measurements

In a $\tau$-CRDS measurement, the radical density close to the substrate is modulated by applying pulsed rf power to the substrate, while the time evolution of the absorption induced by the rf-generated radicals is mapped using CRDS. Here, these two aspects are described.

To apply rf power to the substrate, a Hewlett Packard 8116A function generator is used to create a 20.1 MHz sine wave signal. The signal is subsequently amplified by a 10 Watt and 100 Watt amplifier (Henry Electronics 100B-30) and is impedance matched to the substrate holder by a L-type matching network. The forward power, measured with a Bird 4410A power meter between the amplifier and matching network, was kept constant at 63 Watt, unless stated otherwise, while the reflected power was reduced to <0.1 Watt for all measurements. The dc bias voltage on the substrate, as measured with a high
Fig. 3. Wavelength scans showing the absorption due to the Si 4s 3P_2 ← 3P_1 transition at 250.69 nm superimposed on the broadband SiH3 absorption, for 2 cases: (a) ETP plasma and (b) ETP plasma together with continuous rf power applied to the substrate. At the beginning and end of the wavelength scans, the plasma has been turned off to obtain the baseline loss in the CRDS cavity, which corresponds to zero absorption.

voltage probe, is typically between -50 V and -100 V for the plasma settings used in this Chapter. A Stanford DG535 delay generator is used to gate the function generator in order to generate 5 Hz rf pulses with a duty cycle of typically 2.5%. It is noted that the dc bias voltage falls off within 20 µs after the rf power is turned off, as has been measured with the high voltage probe.

To test the influence of the rf power on the radical densities in front of the substrate, the absorption of Si and SiH3 has been measured with CRDS at ~5 mm from the substrate during regular operation of the ETP plasma. Two cases have been considered: with and without continuous rf power applied to the substrate. Figure 3 shows the measured absorption values as a function of the wavelength. The figure clearly shows that both the absorption due to Si (absorption peak) and due to SiH3 (broadband absorption) increase due to the rf power. This demonstrates that the radical density in front of the substrate indeed increases compared to the steady-state density in the ETP plasma, when applying rf power to the substrate.

The procedure to obtain a time-resolved measurement of the radical density is explained on the basis of the timing scheme shown in Fig. 4. The rf pulses at 5 Hz [Fig. 4(a)] modulate the SiH3 radical density with respect to the steady-state density in the ETP plasma [Fig. 4(b)]. Starting at the steady-state ETP density, the density increases due to the rf pulse and decreases back to the steady-state ETP density after the rf pulse has ended. The increased radical density at a certain time ∆t (defined with respect to the end of the rf pulse) is determined from a combination of two CRDS measurements: a first CRDS transient is measured at ∆t [laser pulse (1) in Fig. 4(c)], while a reference CRDS transient is measured at a time after the influence of the rf pulse has extinguished [laser pulse (2) in Fig. 4(c)]. The difference between the two CRDS transients is only due to the radicals generated by the rf pulse and is used to determine the so-called ‘rf-generated absorption’, A_rf. To map the time-dependent radical density, A_rf is measured as a function of ∆t.

Experimentally, a combination of two delay generators (Fig. 1) is used to synchronize the laser pulses to the rf pulses: the Nd:YAG laser (lamp switch and Q-switch) and the TU/eDACs system are both triggered continuously at 10 Hz, while within each period of two trigger pulses the function generator receives a start trigger and an end trigger, thereby producing rf pulses at 5 Hz. The end trigger is fixed at a constant delay after the start trigger throughout the experiment in order to generate rf pulses of constant duty cycle, while the rf pulses are shifted in time with respect to the laser pulses (by changing the start delay) in order to set the time ∆t of a measurement of A_rf. Every CRDS transient obtained is processed...
separately in real time by the TU/e DACS system to suppress low-frequency (<5 Hz) noise sources, and for every ∆t, typically, an average of 128 A_{rf}'s is obtained to further reduce the noise in A_{rf}. In a complete τ-CRDS measurement, a software program (LabVIEW programming language, National Instruments) fully-automatically obtains an averaged A_{rf} and then scans to the next ∆t to map the evolution of the radical density in time.

V. RESULTS AND DISCUSSION

A. Radical loss times

A typical τ-CRDS measurement of the rf-generated absorption, A_{rf}, as a function of the time ∆t in the rf pulse is shown in Fig. 5(a). Two cases are displayed: the wavelength fixed at 250.69 nm to measure simultaneously Si at the 4s 3P_{2} ← 3p 3P_{1} peak and SiH_{3} at the underlying broadband spectrum and the wavelength fixed at 250.68 nm to measure only SiH_{3}. The figure shows that A_{rf} at 250.68 nm, which correlates directly to the time evolution of the rf-generated SiH_{3} radicals, increases and reaches steady-state in the rf pulse and decreases back to zero after the rf pulse is turned off. The decay of A_{rf} of SiH_{3} for ∆t > 0 is shown in more detail in the semi-logarithmic plot of Fig. 5(b). Figure 5(a) also shows that A_{rf} at 250.69 nm changes due to a change in the density of Si as well as of SiH_{3}. It is clear that A_{rf} at 250.69 nm responds much faster to the rf pulse than A_{rf} at 250.68 nm, which indicates a much faster increase and decrease of the Si density than that of SiH_{3}. In order to investigate the decay of the Si density separately, the difference between A_{rf} at 250.69 nm and 250.68 nm of Fig. 5(a) has been calculated for each ∆t. This difference, which is only due to the time evolution of the rf-generated Si radicals, has also been plotted for ∆t > 0 in the semi-logarithmic plot of Fig. 5(b).

Figure 5(b) clearly shows that the rf-generated absorption of both Si and SiH_{3} decrease single exponentially, as expected from the theoretical considerations in Sec. II. In fact, a single exponential decay has been observed for all measured decay curves of Si and SiH_{3} presented in this Chapter, which confirms the assumption made in Sec. II that self-recombination reactions can be neglected. The exponential decay times obtained from Fig. 5 are 0.226±0.007 ms and 1.93±0.05 ms for Si and SiH_{3}, respectively. The decay
times are much longer than the time-resolution of a CRDS measurement (~1 \(\mu\)s) and the fall off time of the dc bias after switching off the rf power (<20 \(\mu\)s). Consequently, it is concluded that the decay times as obtained with \(\tau\)-CRDS correspond to the loss times of the radicals in the plasma during plasma deposition.

In principle, the rf power supplied to the substrate can affect the ETP plasma conditions and/or surface conditions such that the measured loss times are different from the loss times in the undisturbed ETP plasma. For instance, an increased ion bombardment on the surface might significantly alter the surface loss time, \(\tau_{\text{surf}}\). In order to investigate such an influence of the rf power, the dc bias voltage on the substrate [Fig. 6(a)], the rf-generated SiH\(_3\) density, \(n_{\text{rf-SiH}_3}\), as reached at the end of the rf pulse [Fig. 6(b)], and the loss time of SiH\(_3\), \(\tau_{\text{SiH}_3}\), [Fig. 6(c)] have been measured for different rf powers. Figure 6(a) shows indeed that the dc bias voltage on the substrate increases from nearly zero to about -67 V for increasing rf power, corresponding to an increased ion bombardment on the surface. Figure 6(b) shows that the rf-generated SiH\(_3\) density increases in front of the substrate with increasing rf power. This is, however, only a minor change in the plasma, as the absolute value of \(n_{\text{rf-SiH}_3}\) remains below the steady-state SiH\(_3\) density of \(7\times10^{18}\) m\(^{-3}\) in the ETP plasma. More importantly, Fig. 6(c) shows that \(\tau_{\text{SiH}_3}\) is independent of the applied rf power up to 77 Watt. Apparently, the plasma and surface conditions are not changed from the undisturbed ETP plasma to such an extent that the resulting loss times are affected. This conclusion is certainly true for an rf power of 63 Watt, as used in all further \(\tau\)-CRDS measurements reported in this Chapter. In addition, from the reproducibility of the loss time in Fig. 6(c) it is found that the standard deviation in the determination of the loss time with \(\tau\)-CRDS is 6%.

The influence of the rf power has also been investigated from a series of \(\tau\)-CRDS measurements at 250.68 nm, similar the one of Fig. 5, for varying duty cycles in the range of 1 to 40% (not shown). Most importantly, it was found that the loss time of SiH\(_3\) is independent of the duty cycle within its uncertainty. However, two boundary conditions were identified that define an optimal duty cycle with respect to the accuracy in \(\tau_{\text{SiH}_3}\). For a duty cycle below ~1.5%, the rf-generated absorption \(A_{\text{rf}}\) of SiH\(_3\) does not reach steady-state in the rf pulse. This leads to a lower \(A_{\text{rf}}\) at the end of the rf pulse and consequently a lower
Fig. 6. (a) The dc bias voltage $V_{bias}$, (b) the rf-generated SiH$_3$ density, $n_{rf-SiH3}$, at the end of the rf pulse (for $\Delta t<0$), as calculated assuming a homogeneous radial SiH$_3$ density profile with a diameter of 30 cm in accordance with Ref. 60, and (c) the loss time $\tau$ of SiH$_3$ as a function of the applied rf power in the pulse. The dashed lines are guides to the eye. For reference, an rf power of 63 Watt is used in all other $\tau$-CRDS measurements reported in this Chapter.

signal-to-noise ratio in $\tau_{SiH3}$, when this data of $A_{rf}$ is used to determine the loss time. For rf pulses with a duty cycle above ~5%, the decay in $A_{rf}$ for $\Delta t>0$ becomes double exponentially. Presumably, the plasma is disturbed to such an extent that cluster and dust particles are generated and confined in the rf confining electric field in front of the substrate. Scattering on and absorption of the laser light by these powder particles can cause this double exponential decay in $A_{rf}$. The loss time of the powder particles has been found to be in the order of the residence time of the reactor, which is much longer than the loss time of SiH$_3$. Therefore, $A_{rf}$ of SiH$_3$ can easily be distinguished from $A_{rf}$ of the powder particles. Still, the double exponential decay in $A_{rf}$ reduces the accuracy in the determination of $\tau_{SiH3}$. Consequently, the highest accuracy in the loss time of SiH$_3$ (and of Si) is found for a duty cycle of about 2.5%.

It is concluded that the loss times of the radicals obtained with $\tau$-CRDS correspond to the loss times in the undisturbed ETP plasma and can be used to obtain information about the loss processes of the radicals during regular plasma deposition. Our interest lies in the determination of the surface reaction probability $\beta$ of Si and SiH$_3$. It is clear from the values of the loss times of Fig. 5 that pumping loss can be neglected, however, before $\beta$ of Si and SiH$_3$ can be studied, first the gas phase loss processes of Si and SiH$_3$ need to be investigated.

B. Gas phase loss of SiH$_3$ and Si

An assessment of all possible gas phase reactions of Si and SiH$_3$ with other plasma species, based on reaction rates reported in the literature combined with measured or estimated densities in our Ar-H$_2$-SiH$_4$ plasma, has yielded that SiH$_4$ is the only candidate for a significant gas phase loss rate of Si and SiH$_3$. If these radicals react with SiH$_4$, if follows from Eq. (3) that the loss rate of Si and SiH$_3$ should be linear with the SiH$_4$ density. The loss rate, $\tau^{-1}$, of Si and SiH$_3$ has therefore been measured for five different SiH$_4$ flows, while keeping the total pressure constant at 0.27 mbar. In order to determine the gas phase reaction rates of Si and SiH$_3$ with SiH$_4$, however, first the local SiH$_4$ density in the detection volume, i.e. at 5 mm from the substrate, needs to be calculated for each SiH$_4$ flow.

As a first approximation, the SiH$_4$ densities have been calculated from the SiH$_4$ partial pressure using the ideal gas law for a total pressure of $p=0.27$ mbar and a kinetic gas temperature of $T_{gas}=1500$ K, as
Table I. For the different SiH$_4$ flows admixed in the plasma, the SiH$_4$ density, $n_{\text{SiH}_4,\text{uncorr}}$, as calculated directly from the SiH$_4$ partial pressure, while neglecting SiH$_4$ consumption in the plasma; the Si density at the end of the rf pulse, $n_{\text{Si,rf}}$, as generated by the rf power; and the loss time of Si, $\tau_\text{Si}$, are given. From $n_{\text{Si}}$ and $\tau_\text{Si}$, the production rate of Si radicals in the rf plasma, $P_\text{Si}$, has been calculated. $P_\text{Si}$ has been used to determine the local SiH$_4$ density in front of substrate, $n_{\text{SiH}_4,\text{corr}}$, that is corrected for SiH$_4$ consumption in the plasma.

<table>
<thead>
<tr>
<th>SiH$_4$ flow (sccs)</th>
<th>$n_{\text{SiH}_4,\text{uncorr}}$ ($10^{19}$ m$^{-3}$)</th>
<th>$n_{\text{Si,rf}}$ ($10^{15}$ m$^{-3}$)</th>
<th>$\tau_\text{Si}$ (s)</th>
<th>$P_\text{Si}=n_{\text{Si,rf}}/\tau_\text{Si}$ ($10^{13}$ m$^{-3}$ s$^{-1}$)</th>
<th>$n_{\text{SiH}_4,\text{corr}}$ ($10^{19}$ m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.1</td>
<td>1.8</td>
<td>4.3×10$^4$</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>1.0</td>
<td>4.2</td>
<td>2.5</td>
<td>1.7×10$^4$</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>1.5</td>
<td>6.2</td>
<td>2.8</td>
<td>8.3×10$^5$</td>
<td>3.5</td>
<td>4.1</td>
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<td>2.5</td>
<td>5.0×10$^5$</td>
<td>5.0</td>
<td>5.8</td>
</tr>
<tr>
<td>2.5</td>
<td>10.0</td>
<td>3.1</td>
<td>3.7×10$^5$</td>
<td>7.8</td>
<td>9.0</td>
</tr>
</tbody>
</table>

measured directly from the Doppler broadening of the Si line profiles (cf. Appendix). These SiH$_4$ densities, which are not corrected for consumption of SiH$_4$ by the plasma, are given in Table I as $n_{\text{SiH}_4,\text{uncorr}}$. Consumption of SiH$_4$ by the plasma can significantly reduce the SiH$_4$ densities and needs to be corrected for. On the basis of a direct measurement of the SiH$_4$ consumption under similar plasma operating conditions, a SiH$_4$ consumption of 10% is assumed for the highest SiH$_4$ flow of 2.5 sccs. This yields a local SiH$_4$ density in front of the substrate that is corrected for SiH$_4$ consumption of $n_{\text{SiH}_4,\text{corr}}=9.0×10^{19}$ m$^{-3}$, as reported in Table I. For the other SiH$_4$ flows, the relative magnitude of $n_{\text{SiH}_4,\text{corr}}$ is calculated utilizing the fact that the production of Si radicals by the rf power, $P_\text{Si}$, occurs dominantly through electron impact dissociation of SiH$_4$ with reaction rate $k_\text{e-SiH}_4$.

$$P_\text{Si} = k_\text{e-SiH}_4 n_{\text{SiH}_4} n_e.$$ \hspace{1cm} (6)

The local electron density, $n_e$, is assumed to be independent of $n_{\text{SiH}_4}$, because the bias voltage is independent of the SiH$_4$ flow (not shown). Therefore, $P_\text{Si}$ scales linearly with $n_{\text{SiH}_4}$. Using Eq. (1), the values of $P_\text{Si}$ have been determined from the Si density at the end of the rf pulse, $n_{\text{Si,rf}}$, divided by the loss time of Si, $\tau_\text{Si}$. These values have been used to scale the values of $n_{\text{SiH}_4,\text{corr}}$ relative to the value of $n_{\text{SiH}_4,\text{corr}}$ of $9.0×10^{19}$ m$^{-3}$ for the SiH$_4$ flow of 2.5 sccs (Table I).

Figure 7 shows the loss rates of Si and SiH$_3$ versus the local SiH$_4$ density $n_{\text{SiH}_4,\text{corr}}$. For SiH$_4$, it is clear that the loss rate is independent of the SiH$_4$ density and it can be concluded that SiH$_4$ is not lost in the gas phase to SiH$_4$ in our plasma. This is in agreement with a gas phase reaction rate of SiH$_3$ with (deuterated) SiH$_4$ of $k_\text{Si-SiH}_4=(4±2)×10^{-20}$ m$^3$ s$^{-1}$.$^{48}$ The reproducibility of the loss rates of SiH$_4$ in Fig. 7 yields again a standard deviation in $\tau_\text{Si}$ of 6%. For Si, Fig. 7 shows that the loss rate depends strongly on the SiH$_4$ density, revealing clearly a linear behavior. This linear dependence in the SiH$_4$ density is in agreement with Eq. (3) and validates the correction for SiH$_4$ consumption as presented in Table I. The slope in Fig. 7 yields the reaction rate of Si($^3$P$_1$) with SiH$_4$, $k_\text{Si-SiH}_4=(3.0±0.6)×10^{-16}$ m$^3$ s$^{-1}$.$^{1}$ The direct uncertainty in the error-weighted fit of Fig. 7 is 2.5%, however, the error bar in $k_\text{Si-SiH}_4$ also takes into account the uncertainty in the SiH$_4$ consumption and the gas temperature. The loss time of Si has also been measured for the two other ground states of Si (transitions 4s $^3$P$_1$ $→$ 3p$^2$ $^3$P$_0$ and 4s $^1$P$_1$ $→$ 3p$^2$ $^1$P$_2$) and it has been found that the loss times of the

$^{1}$ In Ref. [25], a lower $T_{\text{gas}}$ of 700K was assumed based on fluid dynamics simulations for different plasma conditions. In the Appendix, it is shown that $T_{\text{gas}}$ is (1500±200) K. Using this improved value of $T_{\text{gas}}$, the value of $k_{\text{e-SiH}_4}$, $\beta_\text{Si}$, and the reference data point of $P_\text{Si}$(Si) at 200°C (Fig. 9) have been recalculated with respect to Ref. [25].
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Fig. 7. The loss rate $\tau^{-1}$ of Si and SiH$_3$ as a function of the local SiH$_4$ density in front of substrate at a constant pressure of 0.27 mbar, an Ar flow of 27.5 sccs, a H$_2$ flow of 2.5 sccs, and an arc current of 22.5 A. The local SiH$_4$ density in front of substrate has been calculated from the SiH$_4$ partial pressure and corrected for the local SiH$_4$ consumption. The error bars correspond to the statistical error in the loss time $\tau$.

triplet ground states of Si are equal within their uncertainty, indicating a single value of $k_r$, in agreement with Ref. 69. The value of $k_r$ corresponds well with the values of $k_r$ in the range of $(2.1 - 6.6) \times 10^{-16}$ m$^3$s$^{-1}$ reported in the literature, an overview of which is given in Ref. 69. The main conclusion of this section is that in our plasma Si is mainly lost to SiH$_4$, while SiH$_3$ is not lost by gas phase reactions at all.

C. Surface loss of SiH$_3$ and Si

As gas phase loss can be neglected for SiH$_3$, the loss time as measured with $\tau$-CRDS equals directly the surface loss time, i.e. $\tau_{\text{SiH}_3} = \tau_{\text{surf}}$ [Eq. (2)]. Combining Eqs. (4) and (5) with the expressions of the kinetic velocity $v$ and diffusion constant $D$, the diffusion theory$^{6}$ presented in Sec. III predicts that $\tau_{\text{surf}}$ scales linearly with the total pressure, $p$, with a slope that depends on the geometrical parameters $R$ and $H$ and the gas temperature $T_{\text{gas}}$. Moreover, the value of $\tau_{\text{surf}}$ at zero total pressure corresponds to the loss time of the radical in the so-called "free-fall" limit and depends on $R$, $H$, $T_{\text{gas}}$ and the parameter of interest, i.e. the surface reaction probability $\beta$. Therefore, to obtain $\beta$ of SiH$_3$, $\tau_{\text{SiH}_3}$ has been measured as a function of the total pressure $p$ for an Ar-H$_2$-SiH$_4$ plasma with Ar, H$_2$, and SiH$_4$ flows of 27.5, 2.5, and 1.0 sccs, respectively, and an arc current of 22.5 A. This measurement has been repeated for six different substrate temperatures, $T_{\text{sub}}$.

Figure 8 shows the measured values of $\tau_{\text{SiH}_3}$ as a function of $p$ for the six different $T_{\text{sub}}$. The figure shows clearly that, for each of the six data sets, $\tau_{\text{SiH}_3}$ depends linearly on $p$ in agreement with the diffusion theory of Sec II. Therefore, each data set of $\tau_{\text{SiH}_3}$ has been fitted to Eq. (4) in order to obtain the value of $\beta_{\text{SiH}_3}$ at the corresponding $T_{\text{sub}}$. To perform these fits, the kinetic velocity $v$ and diffusion constant $D$ have been calculated for the above-mentioned Ar-H$_2$-SiH$_4$ mixture,$^{55}$ using the experimentally obtained values of the gas temperature $T_{\text{gas}}$. These values of $T_{\text{gas}}$ have been obtained from the Doppler broadening of the Si line profiles and $T_{\text{gas}}$ has been found to be $1500 \pm 200$ K, independent of $T_{\text{sub}}$ (cf. Appendix). The fact that $T_{\text{gas}}$ is not affected by $T_{\text{sub}}$ suggests that the diffusion profile with parameters $R$ and $H$ is also not affected by $T_{\text{sub}}$. Because the slope of $\tau_{\text{SiH}_3}$ versus $p$ is defined only by the parameters $R$, $H$, and $T_{\text{gas}}$, it should also be

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$^1$ The time-dependent mass balance of Sec. III applies to the rf-generated density, independent of the steady-state density profile of the ETP plasma, because the diffusion of the rf-generated density is only determined by the gradients in the rf-generated density.
Fig. 8. The loss time $\tau$ of SiH$_3$ as a function of the total pressure in the reactor for six different substrate temperatures in the range of 50–450 °C, for an Ar, H$_2$, and SiH$_4$ flow of 27.5, 2.5, and 1.0 sccs, respectively, and for an arc current of 22.5 A. The six data sets with their uncertainties have been fitted simultaneously with one combined slope but with individual offsets.

The values of $\tau_{\text{surf}}$, obtained by extrapolating the fits in Fig. 8 to zero pressure, can now be used to calculate the values of $\beta_{\text{SiH}_3}$, when the geometrical parameters $R$ and $H$ are known. The values of $R$ and $H$ can be deduced independently from the value of the shared slope of the fits in Fig. 8 under the assumption that the diffusion in radial direction can be neglected with respect to the diffusion in axial direction, i.e. $R/H \gg 1$. This assumption is made plausible based on the following line of reasoning. Within the 5 ms duration of the rf pulse the rf-generated radicals do not have sufficient time to reach the outer reactor wall, therefore effectively yielding $R=\infty$. On the other hand, it is seen from Fig. 5(b) that the rf-generated absorption reaches steady-state within 5 ms, which can only be attributed to the temporal saturation of the axial diffusion profile as a result of rf-generated radicals diffusing to and reacting with the substrate. Moreover, additional information, such as plasma model calculations$^{60}$ and spatial profiles of the light emission in front of the substrate, indicate that the rf-generated radicals are produced and confined close to the substrate and that the transport to the substrate must be diffusion dominated. Therefore, under the assumption of $R/H \gg 1$, a value of $H=8 \text{ cm}$ has been deduced from the shared slope of the fits, enabling the values of $\tau_{\text{surf}}$ at zero pressure to be used to calculate $\beta_{\text{SiH}_3}$. The resulting values of surface reaction probability of SiH$_3$, $\beta_{\text{SiH}_3}$, as a function of the substrate temperature, are shown in Fig. 9. The main observation in this figure is the absence of a trend in $\beta_{\text{SiH}_3}$ as a function of $T_{\text{sub}}$. Furthermore, because $\beta_{\text{SiH}_3}$ is independent of the substrate temperature, the values of $\beta_{\text{SiH}_3}$ in Fig. 9 can be averaged, yielding an averaged $\beta_{\text{SiH}_3}$ of 0.30±0.03.

In addition to the results of $\beta_{\text{SiH}_3}$, the value of $\beta_{\text{Si}}$ at $T_{\text{sub}}=200$ °C has been obtained from a measurement of the loss time $\tau$ of Si as a function of pressure. As Si is lost to SiH$_4$ in the gas phase with

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1 The value of $H$ reflects the axial gradient of the rf-generated density profile (determined by the surface reaction probability $\beta$ of the substrate) at the position of the measurement, i.e. at 5 mm from the substrate, and should not be confused with the axial dimension of the rf-generated density profile.
$k_r = (3.0 \pm 0.6) \times 10^{-16} \text{ m}^3 \text{s}^{-1}$, the measured loss times have first been corrected for gas phase loss to obtain the surface loss rates, $\tau_{\text{surf}}$. Similar to the case of SiH$_3$, the values of $\tau_{\text{surf}}$ versus $p$ have been fitted to Eq. (4) under the assumption of $R/H \gg 1$, while using the values of $v$ and $D$ as calculated for the diffusion of Si radicals in the Ar-H$_2$-SiH$_4$ mixture. With the obvious restriction that $\beta_{\text{Si}} \leq 1$, this procedure yields $0.95 < \beta_{\text{Si}} \leq 1$.

Before the implications of these results on $\beta_{\text{SiH}_3}$ and $\beta_{\text{Si}}$ are discussed, first, the uncertainties in the derivation of $\beta$ are assessed. The error in $\beta_{\text{SiH}_3}$ in Fig. 9 is ~15%, corresponding to the statistical error in the offset of the fits in Fig. 8. This error is significantly larger than the errors in $\tau$ and $p$ (~6% and < 3%, respectively) due to the extrapolation to zero pressure. This demonstrates that it is necessary to measure $\tau$ within a sufficiently large pressure range in order to obtain accurate values of $\beta$. In our particular situation, the error in the $\beta$ has been reduced by almost a factor of 2 by using the fitting procedure of one shared slope, which is possible whenever $T_{\text{gas}}$ is independent of $T_{\text{sub}}$. The reproducibility in $\beta_{\text{SiH}_3}$ is illustrated in Fig. 9 by an additional measurement of $\beta_{\text{SiH}_3}$ at $T_{\text{sub}} = 200$°C, obtained previously under exactly the same experimental conditions.

In addition to statistical errors, a number of systematic errors are potentially introduced in the derivation of $\beta$, i.e. the uncertainty in the derivation of Eq. (4), in the gas temperature, and in the assumption of $R/H \gg 1$. In the derivation of Eq. (4), Chantry used a simple empirical approximation of the reactor’s fundamental mode diffusional length, which introduces a maximum systematic error in $\beta$ of 3%, as calculated from the error analysis in Ref. 54. The uncertainty of 200 K in the value of $T_{\text{gas}}$ of 1500 K also introduces a maximum systematic error in $\beta$ of 3%. Finally, the assumption of $R/H \gg 1$ yields potentially the largest uncertainty in $\beta$, where it is noted that a deviation from this assumption would result in a lower value of $\beta$. Although the uncertainty in $\beta$ due to this assumption is difficult to assess, a decrease in $\beta$ of more than 10% seems unlikely. For Si, the uncertainty in the gas phase reaction rate with SiH$_4$ could introduce an additional systematic uncertainty in the derivation of $\beta$ compared to the case of $\beta_{\text{SiH}_3}$. Finally, it is noted that the observation in Fig. 9 of a $T_{\text{sub}}$-independent $\beta_{\text{SiH}_3}$ is not affected by any potential systematic error in $\beta_{\text{SiH}_3}$.

Our values of $\beta$ are further evaluated by a comparison with values of $\beta$ reported in the literature that have either been obtained under similar experimental conditions or by means of a diagnostic that yields $\beta$ directly. The values of $\beta_{\text{SiH}_3}$ are in perfect agreement those obtained previously by Kessels et al. for three
substrate temperatures using the indirect method of the ‘aperture-well assembly’ under similar conditions in our ETP setup, see Fig. 9. Our $\beta_{\text{SiH}_3}$ values are also in perfect agreement with the value of $\beta_{\text{SiH}_3} = 0.28 \pm 0.03$ at $T_{\text{sub}} = 300$ °C as determined by Perrin et al.\textsuperscript{12} by time-resolved threshold ionization mass spectrometry in an rf plasma, in which the SiH$_3$ density was modulated by turning the rf plasma completely on and off. A somewhat lower value of $\beta_{\text{SiH}_3}$ of 0.15 has been found at room temperature in an rf plasma during plasma deposition of a-Si:H using infrared laser absorption spectroscopy.\textsuperscript{20} However, the authors consider their measured value of $\beta_{\text{SiH}_3}$ to be too small, since the spatial density profile of SiH$_3$ used to obtain $\beta_{\text{SiH}_3}$ is sensitive to the volume production of SiH$_3$. In perspective, the different values of $\beta_{\text{SiH}_3}$ correspond surprisingly well considering the difference in diagnostics and in a-Si:H deposition methods used. For Si, no direct comparison with literature values can be made, however, a surface reaction probability that is nearly unity is generally expected for Si.\textsuperscript{34,49}

D. Implications for a-Si:H film growth

In this section, our results on $\beta$ for Si and SiH$_3$ are discussed with respect to the importance of the various plasma species for a-Si:H film growth and the key surface reactions ruling the a-Si:H growth process.

For SiH$_3$, a value for $\beta_{\text{SiH}_3}$ of 0.30±0.03 has been found, which is in good agreement with previously reported values. It has been speculated previously that a value of $\beta_{\text{SiH}_3}$ of ~0.3−0.4 reflects the probability that a SiH$_3$ approaches the surface with its dangling bond oriented towards the surface.\textsuperscript{10} For Si, the surface reaction probability has now been measured for the first time and a $\beta_{\text{Si}}$ of >0.95 is found. A $\beta_{\text{Si}}$ of unity has been inferred previously based on the hydrogen deficiency of Si.\textsuperscript{34,49} The presence of merely dangling bonds for Si compared to the one dangling bond for SiH$_3$ makes that Si is more reactive than SiH$_3$ on the surface as well as in the gas phase, as shown in this Chapter. This line of reasoning is further corroborated by comparing our values of $\beta_{\text{Si}}$ and $\beta_{\text{SiH}_3}$ with the reported values of $\beta_{\text{SiH}}$ and $\beta_{\text{SiH}_2}$ of ~0.95 and ~0.6, respectively. Furthermore, the argument can be extended to the stable SiH$_4$ molecule, which has a surface reaction probability of <10$^{-4}$, even on a H-free c-Si surface.\textsuperscript{70} Therefore, we conclude from our measurements that there is a general trend that the surface reaction probability $\beta$ of the silane radicals increases with increasing number of dangling bonds, as shown in Table II. This trend is in agreement with the observations from molecular dynamics (MD) simulations.\textsuperscript{45−48}

To get an indication of the relative importance of the different radicals to a-Si:H film growth, the Si growth flux due to a specific radical, $\Gamma_{\text{Si}}$, (i.e. the number of Si atoms deposited per second by the specific radical) can be estimated from the value of $\beta$ and the density $n$ in the plasma:\textsuperscript{34}

$$\Gamma_{\text{Si}} = \frac{1}{4} n v \frac{s}{1 - \beta/2}. \quad (7)$$

In this equation, $\frac{1}{4} n v$ is the thermal flux impinging on the surface and $s$ is the sticking probability with $s \leq \beta$. The value of $s$ is not precisely known for the silane radicals, but is generally assumed $s = \beta/2$ for SiH$_3$ and $s = \beta$ for SiH$_2$, SiH and Si$^{6,12,20,34,36,70}$. Combining these estimates of $s$ with the values of $\beta$ and the typical densities in the ETP and rf plasma under conditions where device quality a-Si:H is grown, as presented in Table II, yields the Si growth fluxes for the different silane radicals. Although an exact calculation of the Si growth fluxes is prevented by the uncertainty in absolute density measurements (caused by the need for accurate cross-sections as well as elaborate calibration procedures or spatial density profiles), it is nevertheless apparent that SiH$_3$ is the key growth precursor for plasma deposition of a-Si:H, whereas the contribution of other radicals is limited to a few percent or lower. While this conclusion has been deduced on the assumption of $s = \beta/2$ for SiH$_3$, a value of $s_{\text{SiH}_3}$ of more than 0.01 is needed at the least
TABLE II. An overview of the surface reaction probability $\beta$ and typical density of the different silane radicals in the ETP and rf plasma for conditions where device quality a-Si:H is grown.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\beta$</th>
<th>Density in ETP plasma$^a$</th>
<th>Density in rf plasma$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>$&gt;0.95^c$</td>
<td>$2\times10^{13}$</td>
<td>$1\times10^{15}$</td>
</tr>
<tr>
<td>SiH</td>
<td>$-0.95^c$</td>
<td>$3\times10^{13}$</td>
<td>$2\times10^{13}$</td>
</tr>
<tr>
<td>SiH$_2$</td>
<td>$-0.6^d$</td>
<td>$10^{11}$</td>
<td>$1\times10^{15}$</td>
</tr>
<tr>
<td>SiH$_3$</td>
<td>0.3$^f$</td>
<td>$7\times10^{13}$</td>
<td>$3\times10^{13}$</td>
</tr>
<tr>
<td>SiH$_4$</td>
<td>$&lt;1\times10^{3}$ $^g$</td>
<td>$1\times10^{23}$</td>
<td>$1\times10^{21}$</td>
</tr>
</tbody>
</table>

$^a$ References 35, 49, and 60.
$^b$ The rf plasma densities, taken from Ref. 34 for an rf power of 0.05 W/cm$^2$, are representative for rf plasmas in general (Refs. 12, 16, 20, and 33).
$^c$ This work.
$^d$ References 2–4.
$^e$ References 16.
$^f$ This work and Refs. 6, 8, 10–13, 20, and 25.
$^g$ Reference 70.

In view of SiH$_3$ being the key growth precursor for a-Si:H growth, we have measured $\beta$ of SiH$_3$ as a function of the substrate temperature to study the growth process of a-Si:H. No dependence of $\beta_{\text{SiH}_3}$ on the substrate temperature has been found (Fig. 9), consistent with the observations from MD simulations. To obtain $\beta$ values in an rf plasma, Matsuda et al.$^6$ employed the aforementioned indirect method of evaluating the conformality of deposition profiles. This method, however, yields only compound values of $\beta$ that are averaged over all plasma species coming to the surface. In an effort to overcome this problem, they installed a mesh in front of the surface in order to select preferentially SiH$_3$ radicals to come to the surface. Using this configuration, they found that the compound value of $\beta$ is independent of $T_{\text{sub}}$ (from room temperature up to 500 °C) with a $\beta$ of 0.26±0.05. While the rf plasma is modified by the application of the mesh, the good agreement with our results of $\beta_{\text{SiH}_3}$ indicates that their measurements have been performed under SiH$_3$ dominated conditions. Along the same line of reasoning, the compound values of $\beta$ of $\sim$0.3 for three substrate temperatures obtained indirectly with the ‘aperture-well assembly’ method by Kessels et al. in the ETP setup$^8$ (see Fig. 9) imply that the specific ETP plasma conditions used are SiH$_3$ dominated. These findings corroborate the conclusion that SiH$_3$ is the dominant growth precursor for a-Si:H film growth. More importantly, as our values of $\beta_{\text{SiH}_3}$ have been obtained from direct measurements of SiH$_3$ and during regular plasma deposition of a-Si:H, our measurements remove any remaining uncertainty about the independence of $\beta_{\text{SiH}_3}$ on the substrate temperature.

The substrate temperature dependence of the surface reaction probability of a radical is of interest as it can yield information on the thermal activation of the surface reactions of the radical. With a $\beta_{\text{SiH}}$ of approximately unity, SiH virtually always reacts to the substrate and therefore the experimental observation$^7$ of a substrate temperature independent $\beta_{\text{SiH}}$ was not unexpected. Applying the same argument to Si, no dependence of $\beta_{\text{Si}}$ on the substrate temperature is expected. For SiH$_3$, however, the independence
of $\beta_{\text{SiH}}$ on the substrate temperature is less obvious and is shown to have direct implications for the dominant reactions of SiH$_3$ with the a-Si:H surface. Either the surface reactions are all individually independent of $T_{\text{sub}}$, or the surface reactions do depend on $T_{\text{sub}}$, but their thermal activation cancel out. The latter seems improbable due the typical exponential dependence of the reaction rates on the activation barrier. To narrow the constraints on the possible surface reactions of SiH$_3$ further, first the substrate temperature dependence of the surface silicon hydride coverage of a-Si:H is addressed. Two similar studies for different a-Si:H deposition systems$^{71,72}$ have shown that the hydrogen coverage of the a-Si:H surface changes drastically with increasing $T_{\text{sub}}$: from a surface that is covered with tri-hydride (−SiH$_3$) bonds at $T_{\text{sub}}<150$ °C to a di-hydride (=SiH$_2$) covered surface at intermediate temperatures to a mono-hydride (=SiH) covered surface at $T_{\text{sub}}>300$ °C. This observation is in sharp contrast with the substrate temperature independence of $\beta_{\text{SiH}}$. The sticking probability $s$ of SiH$_3$ is investigated next. Although a direct measurement of $s_{\text{SiH}_3}$ is unfeasible, insight on $s_{\text{SiH}_3}$ can be obtained from the Si growth flux $\Gamma_{\text{Si}}$ as can be calculated from the product of the deposition rate and the Si atomic density in the a-Si:H film. In this reasoning, it is assumed that all Si atoms in the film are deposited by SiH$_3$ radicals coming to the surface, as argued above. Figure 10 shows the Si growth flux as a function of substrate temperature, measured for 2 different pressures with all other conditions equal to the measurement conditions of $\beta_{\text{SiH}}$. It is seen that $\Gamma_{\text{Si}}$ is independent of $T_{\text{sub}}$, in good agreement with two previous measurements of $\Gamma_{\text{Si}}$ in the ETP plasma under slightly different plasma settings.$^{8,73}$ Apart from $\Gamma_{\text{Si}}$, it has been shown in this Chapter that for these plasma conditions also the density $n$, the gas temperature $T_{\text{gas}}$, and thus also the thermal velocity $v$ are independent of $T_{\text{sub}}$. Therefore, it follows from Eq. (7) that $s_{\text{SiH}_3}$ must also be independent of the substrate temperature. Moreover, in the case that $s<\beta$, if follows that the recombination probability $\gamma$ of SiH$_3$ must also be independent of $T_{\text{sub}}$. To conclude, the substrate temperature independence of all three macroscopic surface reaction parameters, $\beta$, $s$, and $\gamma$, of SiH$_3$ puts strict boundary conditions on the possible surface reactions ruling a-Si:H film growth, especially when taking into account the strong substrate temperature dependence of the surface silicon hydride composition.

A candidate model that describes a-Si:H growth within these boundary conditions has been proposed in Ref. 71. There, it is argued that SiH$_3$ contributes to a-Si:H growth via a 2-step reaction mechanism. First, a gaseous SiH$_3$ abstracts a surface hydrogen directly from the a-Si:H surface by means of the Eley-Rideal reaction:

$$\text{SiH}_3 + \text{Si} \rightarrow \text{SiH}_2 + \text{SiH}$$

This reaction is known to be fast and efficient, and it is assumed that the surface hydrogen is readily available for abstraction. The second step involves the reaction of the abstracted SiH* with the surface to form the a-Si:H film:

$$\text{SiH} + \text{Si} \rightarrow \text{SiH}_2$$

The resulting SiH$_2$ is then incorporated into the a-Si:H film, contributing to its growth.

This two-step mechanism is consistent with the substrate temperature independence of $\beta_{\text{SiH}}$, $s_{\text{SiH}_3}$, and $\gamma$, and it provides a plausible explanation for the observed growth behavior of a-Si:H films.
process, thereby forming a dangling bond. From MD simulations, it has been found that this process has a reasonably low activation energy (~0.09 eV) and can explain the substrate temperature independence of $\gamma$. Then, a second Si$H_3$ sticks on the dangling bond to contribute to a-Si:H film growth. This second step, which may or may not involve surface diffusion of Si$H_3$, has no activation barrier, corresponding to a substrate temperature independent $s$. As $\beta = \gamma + s$, this 2-step reaction mechanism also implies a substrate temperature independent $\beta$. Although this is only one possible growth model that complies with the boundary conditions, the model clearly demonstrates the far-reaching implications of our experimental findings on the growth mechanism of a-Si:H.

VI. CONCLUSIONS

It has been shown that time-resolved cavity ring-down spectroscopy (τ-CRDS) yields accurate measurements of the loss time of radicals in the plasma with a standard deviation of ~6%. Moreover, the experimental method of modulating the radical density, by applying a minor pulse of rf power to the substrate, with respect to its steady-state density in the regularly operating plasma leads to loss times of the radicals that equal the loss times in the undisturbed plasma. Therefore, the loss times can be used to obtain the gas phase reactions rates and the surface reaction probabilities of the radicals during the actual plasma deposition process. A careful assessment of the applicability and the measurement accuracy of the method including experimental aspects, such as the role of the gas temperature, has yielded a statistical error in the surface reaction probability of ~15% and a potential systematic error of less than ~16%.

The capabilities of the τ-CRDS method have been demonstrated on a Ar-H$_2$-Si$H_4$-based plasma used for the deposition of hydrogenated amorphous silicon (a-Si:H). It has been found that Si is highly reactive with Si$H_4$ in the gas phase [$k_r=(3.0\pm0.6)\times10^{-16} \text{ m}^3 \text{s}^{-1}$] and that it has a surface reaction probability $\beta$ with the a-Si:H surface of $0.95 < \beta_{Si} < 1$. Si$H_3$ is only lost by diffusion to and reaction at the a-Si:H surface and the values of $\beta_{SiH_3}$, obtained for substrate temperatures in the range of 50–450 °C, are in good agreement with previously reported findings. It has been found that $\beta_{SiH_3}$ is independent of the substrate temperature with an averaged value of $\beta_{SiH_3}$ of 0.30±0.03. On the basis of these observations, the growth process of a-Si:H has been addressed.

ACKNOWLEDGMENTS

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The kinetic gas temperature, $T_{\text{gas}}$, has been determined from the Doppler broadening of the Si $4s\,^3P_2 \leftarrow ^3P_1$ atomic transition. The measured absorption profile is a convolution of the Gaussian Doppler profile and the Lorentzian line width profile of the laser and is consequently fitted to a Voight profile to extract the Doppler width, as is shown in the inset of Fig. 11. The obtained Doppler width is used to determine the temperature of the Si atoms in the $^3P_1$ ground state. This temperature of the ground state of Si is equal to $T_{\text{gas}}$, as the average number of collisions of a Si atom with other gas particles (mainly Ar) upon detection ensures thermal equilibrium. Moreover, it has been verified that optical saturation of the Si transition, leading to an apparent increase in the Doppler width, is avoided in the experiments. To this end, the laser light intensity in the cavity has been chosen sufficiently low (laser pulse energy in the cavity is $E < 1 \times 10^{-8}$ J/pulse, as calculated from the measured laser pulse energy before the cavity and the transmission of the first cavity mirror).

The values of $T_{\text{gas}}$ are shown in Fig. 11 as a function of the substrate temperature $T_{\text{sub}}$. The dependence of $T_{\text{gas}}$ on $T_{\text{sub}}$ has been investigated for a SiH$_4$ flow of 0.5 sccs. This condition has been chosen for its relatively high Si density in the ETP plasma, which leads to a high accuracy in the determination of $T_{\text{gas}}$. The horizontal fit through the data points shows that $T_{\text{gas}}$ is independent of $T_{\text{sub}}$ with a $T_{\text{gas}}$ of ~1850 K for this particular SiH$_4$ flow. Three additional measurements at $T_{\text{sub}}=200 \, ^\circ\text{C}$ have been obtained for two different pressures and for a SiH$_4$ flow of 1.0 sccs, which corresponds to the measurement conditions of $\beta_{\text{SiH}_3}$ and $\beta_{\text{Si}}$. These measurements yield an (averaged) value for $T_{\text{gas}}$ of 1500±200 K that is independent of the pressure. A $T_{\text{gas}}$ of 1500 K is in perfect agreement with measurements of the rotational energy distribution of SiH under comparable plasma conditions in the same setup. Therefore, a $T_{\text{gas}}$ of 1500±200 K that is independent of $T_{\text{sub}}$ is assumed for the measurements of $\beta$ throughout the Chapter.

** It is noted that CRDS yields a line-integrated value of $T_{\text{gas}}$, whereas the spatially resolved $T_{\text{gas}}$ is needed. Fluid dynamics calculations show, however, that the specific radial $T_{\text{gas}}$ profile at a distance of 5 mm from the substrate is such that these two values of $T_{\text{gas}}$ are equal within the uncertainty reported. This is especially true, as most Si radicals are located within the radius of the substrate, where $T_{\text{gas}}$ is constant.

APPENDIX: DETERMINATION OF THE KINETIC GAS TEMPERATURE

Fig. 11. The kinetic gas temperature $T_{\text{gas}}$ as determined from the Doppler broadening of the Si $4s\,^3P_2 \leftarrow ^3P_1$ transition at 250.69 nm (inset) as a function of the substrate temperature $T_{\text{sub}}$. The dashed line shows a fit through the measurements obtained for a SiH$_4$ flow of 0.5 sccs, yielding $T_{\text{gas}}=1850\pm80$ K. Three additional gas temperatures have been measured at $T_{\text{sub}}=200 \, ^\circ\text{C}$ for a SiH$_4$ flow of 1.0 sccs and for two pressures. These additional measurements shows an average temperature of $T_{\text{gas}}=1500\pm200$ K.
REFERENCES

71 W. M. M. Kessels, J. P. M. Hoefnagels, P. J. van den Oever, Y. Barrell, and M. C. M. van de Sanden, Surf. Sci. 547, L865 (2003); Chapter 4 of this thesis.
CHAPTER 4

TEMPERATURE DEPENDENCE
OF THE SURFACE REACTIVITY OF SiH₃ RADICALS
AND THE SURFACE SILICON HYDRIDE COMPOSITION
DURING AMORPHOUS SILICON GROWTH

ABSTRACT

For hydrogenated amorphous silicon (a-Si:H) film growth governed by SiH₃ plasma radicals, the surface reaction probability $\beta$ of SiH₃ and the silicon hydride ($=\text{SiH}_x$) composition of the a-Si:H surface have been investigated by time-resolved cavity ring-down and attenuated total reflection infrared spectroscopy, respectively. The surface hydride composition is found to change with substrate temperature from $=\text{SiH}_3$-rich at low temperatures to $\equiv\text{SiH}$-rich at higher temperatures. The surface reaction probability $\beta$, ranging between 0.20 and 0.40 and with a mean value of $\beta = 0.30 \pm 0.03$, does not show any indication of temperature dependence and is therefore not affected by the change in surface hydride composition. It is discussed that these observations can be explained by a-Si:H film growth that is governed by H abstraction from the surface by SiH₃ in an Eley-Rideal mechanism followed by the adsorption of SiH₃ at the dangling bond created.

* Published as W. M. M. Kessels, J. P. M. Hoefnagels, P. J. van den Oever, Y. Barrell, and M.C.M. van de Sanden, Surf. Sci. 547, L865 (2003).
Understanding of the growth kinetics of thin films is a major effort in materials science. Especially when the films are synthesized by gas phase activation of molecules such as in plasma enhanced chemical vapor deposition, the situation is rather complex due to the large variety of plasma species and broad range of possible surface reactions. For hydrogenated amorphous silicon (a-Si:H) film growth by SiH₄ plasmas, however, it is generally assumed that the growth process of high-quality films is dominated by SiH₃ radicals. The growth process of a-Si:H is therefore described by surface reactions of SiH₃, but only recently the proposed surface reactions have risen above the level of speculations due to the availability of ab-initio calculations and molecular dynamics (MD) simulations. The objective of this Chapter is to obtain more insight into the surface reactions of SiH₃ radicals that rule a-Si:H growth from experimental investigations of the SiH₃ surface reactivity and the chemical nature of the a-Si:H surface during growth.

The SiH₃ surface reactivity, expressed in terms of the surface reaction probability β, has been addressed in several studies. However, the reported β-values of SiH₃ are either determined for one single substrate temperature only or are derived from the conformity of particular deposition profiles and are therefore indirect. In this Chapter, we report on direct measurements of β of SiH₃ during regular deposition conditions and for different substrate temperatures. Furthermore, we consider the temperature dependence of the sticking probability s of SiH₃, with sticking being one of the possible SiH₃ reactions that can take place at the surface (with s ≤ β). The results will be related to the a-Si:H surface composition in terms of the surface silicon hydrides (–SiHₓ). The observations will be used to discuss the surface reactions of SiH₃ as proposed based on density-functional-theory (DFT) calculations and MD simulations in the literature.

The experiments have been carried out in a remote SiH₄ plasma created by the expanding thermal plasma method. The deposition process using this method is characterized by three aspects which are beneficial for the present study: (i) under regular plasma conditions, a-Si:H growth is governed almost completely by SiH₃ radicals; (ii) the growth process is not affected by ion bombardment because of the low self-bias (<2 V); and (iii) surface reactions by H radicals are expected to be of minor importance because the H flux to the a-Si:H surface is much smaller than the SiH₃ flux.

The surface composition of the a-Si:H has been deduced from in-situ attenuated total reflection infrared spectroscopy experiments, similar to those described in Ref. 13. The experiments involve the deposition of a-Si:H films on a GaAs internal reflection element while surface specificity has been obtained by ion-induced desorption of the surface hydrogen. The spectra measured in the Si-H stretching region reveal narrow absorption lines which reflect the –SiHₓ presence at the surface and which are identified on the basis of crystalline silicon literature. Figure 1 gives the –SiHₓ surface composition of a-Si:H for three substrate temperatures: the a-Si:H surface at 100 °C contains mainly trihydrides (–SiH₃) and is balanced by dihydrides (≡SiH₂) whereas at 250 °C the –SiH₃ hydrides have disappeared and the monohydrides (≡SiH) have become dominant. At 400 °C the surface contains only ≡SiH hydrides. These results obtained for SiH₃
Fig. 2. The SiH\textsubscript{3} loss time \(\tau_{\text{SiH}_3}\) as measured by the time-resolved cavity ring-down measurements as a function of the pressure for substrate temperatures between 50 and 450 °C. The lines are fits to the data using a gas temperature of 1500 K for all substrate temperatures.

governed growth conditions are in good agreement with a previous study in an inductively coupled plasma,\textsuperscript{14} which revealed that the \(\text{–SiH}_x\) surface composition is governed by thermally activated decomposition reactions. These reactions convert the surface hydrides from \(\text{–SiH}_3\) to \(\equiv\text{SiH}_2\) to \(\equiv\text{SiH}\) for increasing temperature.

The surface reaction probability \(\beta\) of SiH\textsubscript{3} has been determined by time-resolved cavity ring-down measurements monitoring the decrease in SiH\textsubscript{3} density at a distance of 5 mm from the substrate after a minor periodic modulation of the SiH\textsubscript{3} density. The experimental procedure is described in Ref. 15 in which it is also demonstrated that SiH\textsubscript{3} is not reactive in the gas phase. Information on \(\beta\) is therefore obtained by measuring the SiH\textsubscript{3} loss time to the surface at different pressures, as shown in Fig. 2 for substrate temperatures between 50 to 450 °C. The loss time of SiH\textsubscript{3} can be expressed by

\[
\tau_{\text{SiH}_3} = \frac{\Lambda_0}{D} + \frac{4l_0}{v_0} \left( \frac{1 - \beta/2}{\beta} \right)_{\text{SiH}_3},
\]

with \(D\) the diffusion coefficient and \(v_0\) the thermal velocity of SiH\textsubscript{3} and \(\Lambda_0\) and \(l_0\) geometrical factors.\textsuperscript{6} The increase of \(\tau\) with pressure is therefore due to slower diffusion at higher pressures (lower \(D\)) while \(\beta\) can be deduced from the extrapolated loss time at zero pressure which reflects the “free-fall” limit of the SiH\textsubscript{3} radicals.\textsuperscript{15} The SiH\textsubscript{3} thermal velocity \(v_0\) has been calculated from the gas temperature (1500±200 K, independent of the substrate temperature) obtained from Doppler linewidth studies of Si radicals in the plasma, while \(l_0\) has been deduced from the slope of the linear fits of the data in Fig. 2.

The resulting values for \(\beta\) of SiH\textsubscript{3} are shown in Fig. 3. The surface reaction probability \(\beta\) ranges from 0.20 to over 0.40 with a mean value of \(\beta=0.30\pm0.03\) and without any indication of temperature dependence for the temperature range and conditions studied. The \(\beta\) values show also good agreement with those obtained previously by indirect means under SiH\textsubscript{3} dominated conditions\textsuperscript{5} and with the \(\beta\) value at 300 °C determined in a radiofrequency plasma using time-resolved mass spectrometry.\textsuperscript{6} The temperature independence of \(\beta\) is consistent with the results obtained by the aforementioned indirect investigations based on the conformality of deposition profiles.\textsuperscript{5} Furthermore, the temperature independence is also in accordance with the results from MD simulations (discussed below) that revealed \(\beta=0.18.\textsuperscript{16}\)

Direct experimental determination of the sticking probability \(s\) of SiH\textsubscript{3} (with \(s \leq \beta\)) is unfeasible in the present experiment but information on the temperature dependence of \(s\) can be obtained from the Si growth flux as shown in Fig. 4.\textsuperscript{5,9} The growth flux, which can be expressed by:
Fig. 3. The surface reaction probability $\beta$ of SiH$_3$ derived from the data in Fig. 2. The dashed line represents the average of the values of $\beta$. Data points presented in the literature by Perrin et al.\textsuperscript{6} and Kessels et al.\textsuperscript{9} are also indicated.

\[ \Gamma_{Si} = \frac{1}{m_a} \frac{s}{\Gamma - \beta/2} \]

for SiH$_3$ governed growth, shows no clear dependence on the substrate temperature while also the density $n$ of SiH$_3$ in front of the substrate and $v_a$ are independent of substrate temperature. As a consequence, also $s$ of SiH$_3$ is substrate temperature independent. This temperature dependence of both $\beta$ and $s$, which might simply indicate that $s=\beta$, puts strict constraints on the surface reactions of SiH$_3$, particularly because the surface –SiH$_x$ composition changes drastically. We will use this information to obtain more insight into the dominant surface reactions of SiH$_3$. Although several surface reactions have been proposed in the literature, we will limit ourselves to three reactions for which evidence exists from both DFT calculations and MD simulations.

The first reaction [Fig. 5(a)] is the adsorption of SiH$_3$ on a surface dangling bond.\textsuperscript{16} This reaction has no activation energy barrier and its occurrence is generally accepted. However, its significance in a-Si:H growth (in the case that SiH$_3$ absorbs directly from the gas phase) is usually considered to be limited because it is often assumed that the surface density of dangling bonds on a-Si:H is very low.\textsuperscript{4} The second reaction [Fig. 5(b)] is the abstraction of a surface H atom by SiH$_3$ creating a surface dangling bond. Such an abstraction reaction has been considered to be important since the first growth mechanisms of a-Si:H were proposed because it leads to new sites for SiH$_3$ adsorption. Recently, evidence has been presented that this H abstraction takes place by an Eley-Rideal reaction by SiH$_3$ from the gas phase and not by “physiosorbed” SiH$_3$ on the a-Si:H surface.\textsuperscript{17-19} Although several values have been calculated,\textsuperscript{18,19} Ramalingam et al. found an activation energy of 0.09 eV for H abstraction by DFT and MD simulations.\textsuperscript{17} This small activation energy indicates that H abstraction by SiH$_3$ is relatively weakly temperature dependent. The third reaction [Fig. 5(c)] is the insertion of SiH$_3$ into a strained Si-Si bond at the surface. This insertion reaction, proposed on the basis of experimental work,\textsuperscript{20} leads to SiH$_3$ adsorption without a surface dangling bond being involved. The insertion reaction creates a five-fold coordinated Si atom\textsuperscript{16} and Walch et al. found activation energies in the range of 0.7-0.9 eV for a Si(001)$\times$(2×1) surface.\textsuperscript{21} Furthermore, they found that insertion occurs less frequently than H abstraction, which is consistent with the higher activation energy for insertion.

We will address the consequences of the results obtained for the surface –SiH$_x$ composition and $s$ and $\beta$ for these three surface reactions to identify their importance in a-Si:H growth. If the insertion reaction has a similar magnitude for the activation energy for a-Si:H as for the Si(001)$\times$(2×1) surface (which is not necessarily the case due to the different surface structure), the relatively high activation energy implies that the occurrence of insertion is highly temperature dependent. If SiH$_3$ insertion relies also on the presence of
dimer-like strained Si-Si bonds, the reaction is even more likely at high temperatures, when the surface is composed of –SiH instead of higher hydrides. As a consequence, a-Si:H film growth that is governed by SiH$_3$ insertion is expected to have a strong temperature dependence and therefore our results on $\beta$ and $s$ suggest that an insertion reaction as proposed in Refs. 20 and 21 is not very important.

The reaction in which SiH$_3$ adsorbs on a surface dangling bond has zero activation energy. This will lead to a temperature independent sticking probability $s$ when the density of surface dangling bonds available for adsorption is temperature independent. The (nearly) temperature independent creation mechanism of dangling bonds by the Eley-Rideal reaction in Fig. 5(b) is helpful in fulfilling this condition although there is one apparent complication. On the basis of the surface –SiH$_x$ composition it is expected that more H atoms are present at the surface at low temperatures which might imply that SiH$_3$ has a higher probability to abstract H at lower temperatures. However, it should be realized that not all surface H atoms are available for H abstraction because this would lead to an exponential increase in surface sites. Moreover, the fact that at lower substrate temperatures more H atoms are incorporated into the a-Si:H implies that not all surface H atoms are subject to H abstraction by SiH$_3$. Therefore, it is plausible that the number of dangling bonds created at the surface and consequently the surface dangling bond density is not significantly temperature dependent. The combination of H abstraction by SiH$_3$ and adsorption of SiH$_3$ on the created dangling bonds can therefore explain the temperature independence of both $\beta$ and $s$ while it also clarifies why $\beta$ and $s$ are not affected by the surface –SiH$_x$ composition.

The H abstraction and SiH$_3$ adsorption reactions need to balance each other \(i.e., s = \frac{1}{2} \beta\) when other surface recombination reactions of SiH$_3$ can be excluded) and this implies a rather high surface dangling bond density during a-Si:H growth$^7$ when adsorption takes place directly by SiH$_3$ from the gas phase.

![Fig. 5. Possible SiH$_3$ surface reactions during a-Si:H film growth as reported in the literature. (a) Adsorption of SiH$_3$ from the gas phase onto a dangling bond. (b) Abstraction of an H atom by SiH$_3$ in an Eley-Rideal process creating a dangling bond and a gaseous SiH$_4$ molecule. (c) Insertion of SiH$_3$ into a strained surface Si-Si bond. The five-folded coordinated Si-atom can dissociate by the transfer of a H atom from the SiH$_3$ radical to a surface Si atom.](image)
However, at the moment we cannot exclude that SiH$_3$ can also adsorb on other surface sites and can find dangling bonds by surface diffusion.$^{16,22}$ Such an adsorption mechanism reduces the number of surface dangling bonds but has no consequences for the abovementioned reaction mechanism as long as the H abstraction reaction is the rate-limiting step. Furthermore, the surface mobile species can contribute to surface smoothening which is very important for a-Si:H film growth.$^{19,22,23}$

In summary, it has been made plausible that the balance between H abstraction by SiH$_3$ in an Eley-Rideal mechanism and the adsorption of SiH$_3$ on the dangling bonds created can explain the observations that $s$ and $\beta$ are substrate temperature independent and not affected by the temperature dependent surface SiH$_x$ composition. These two reactions can therefore be mainly responsible for a-Si:H growth from SiH$_3$ radicals when reactions by other plasma species (SiH$_n$ ($n \leq 2$), H, etc.) can be neglected.

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ABSTRACT

A monolithic folded cavity is an optical resonator that employs ultrahigh-reflectivity mirrors and a total internal reflection (TIR) interface for the use in evanescent wave cavity ring-down spectroscopy (EW-CRDS). Such a monolithic folded cavity has been carefully designed and characterized to provide sufficient sensitivity to detect defect-related absorptions, such as surface and bulk dangling bonds, in-situ and real-time during a-Si:H film growth of hydrogenated amorphous silicon (a-Si:H). To find the optimized design parameters, a number of considerations have been addressed, including the polarization-dependent electric field strengths in the evanescent wave emanating from the TIR surface and in the a-Si:H film, the stability criteria for a stable optical cavity, the beam spot size inside the cavity, and the different optical loss terms that constitute the total intrinsic loss of the folded cavity. Moreover, the distribution of cavity modes has been carefully optimized to obtain the lowest measurement uncertainty in the ring-down time. Preliminary ex-situ EW-CRDS measurements of a folded cavity, fabricated with the optimized design parameters, showed an ultra-low minimum detectable absorption of \( \Delta \lambda_{\text{min}} \approx 0.21 \) ppm/pass for single laser shots at its center coating wavelength of \( \lambda_c = 1202 \) nm, which easily satisfies the sensitivity requirements.

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I. INTRODUCTION

Cavity ring-down spectroscopy (CRDS)\(^1\) allows for highly-sensitive absolute absorption measurements and has been applied in recent years to an increasing number of applications, mainly in the gas phase.\(^2,3\) In the most common approach, CRDS uses pulsed laser excitation of a stable optical cavity formed by two highly reflective, concave dielectric mirrors with reflectivity \(R\). The mean lifetime, the so-called ‘ring-down time’ \(\tau\), of the photons trapped in such a high-finesse cavity yields the absolute absorption of an analyte present in the cavity with a very high sensitivity.\(^4\) The minimal detectable optical loss for single laser shots is 
\[
L_{\text{min}} = L_0 \times \sqrt{2} \sigma \tau^{-1},
\]
where \(L_0 = (1 - R)\) is the intrinsic optical loss of the cavity without analyte and \(\sigma / \tau\) is the measurement uncertainty in the determination of \(\tau\). Typical values for \(\sigma / \tau\) and \(L_0\) are \(10^{-2}\) and \(10^{-3}\)–\(10^{-4}\), respectively, yielding a single-shot minimal detectable optical loss in the order of ppm’s, while these values can be reduced with \(1 / \sqrt{n}\) by averaging over \(n\) CRDS transients.

Our aim is to use CRDS for the real-time and in-situ detection of defect-related absorptions during thin film growth. A particular application is the thin film growth of hydrogenated amorphous silicon (a-Si:H). The detection of defect-related absorptions in a-Si:H has already been demonstrated in our group by probing the sub-gap states of a-Si:H using ex-situ CRDS; first at a single wavelength (1.16 eV),\(^4\) followed by a full spectral analysis (0.7–1.7 eV) for a series of a-Si:H films with thicknesses in the range of 4–98 nm.\(^5\) The next step is to extend the defect-related absorption spectroscopy to real-time and in-situ application during thin film growth of a-Si:H with an emphasis on polarization-dependent and surface-sensitive studies of the growth process. This calls for a new and dedicated design of the CRDS cavity.

Extension of CRDS to thin films and to adsorbed surface species has recently been demonstrated by Engeln et al.\(^6,7\) and Pipino et al.\(^8–10\) respectively, and was soon followed by others.\(^5,11–19\) Compared to gas phase CRDS, where the analyte is confined between the mirrors, CRDS of thin films requires the inclusion of intra-cavity elements, because in most cases the use of the cavity mirrors as a substrate is not feasible. To maintain a low intrinsic cavity loss, some configurations have positioned the intra-cavity interfaces at the Brewster angle.\(^8,13–15,17,19\) For instance, an optically transparent substrate coated with a thin film has been placed inside the cavity at the Brewster angle.\(^13\) The advantage of total transmission at the Brewster angle for transverse magnetic (TM) polarization excludes, however, a low-loss cavity configuration for transverse electric (TE) polarization, thereby prohibiting polarization-dependent studies. Moreover, the three interfaces of the (ambient/substrate/thin-film/ambient) stack should all be under the Brewster angle,\(^15\) which is only possible by applying very precise index-matching between the substrate and thin film over the full wavelength range required for the measurement. For the case of a-Si:H, which has a refractive index above 3.5 in the visible and infrared, the best candidate substrate for index-matching is germanium with an absorbance of \(10^{2}\) cm\(^{-1}\),\(^13\) thereby prohibiting a very low intrinsic cavity loss.

An alternative configuration places the substrate perpendicular to the optical axis of the cavity.\(^4–7,12\) This easy-to-work-with configuration is usually avoided due to interference effects in the (substrate/thin-film) stack that cause the light intensity and consequently also the apparent absorption in the thin film to be a function of the wavelength and the position in the film. These interference effects, however, can be modeled easily and can even be used to deduce additional information on the depth profile of absorbers in

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\(^{1}\) The line-integrated density of analyte absorbers in the cavity is closely approximated by the optical loss due to absorption, \(A\), divided by the absorption cross-section, \(\sigma\). The absorption loss \(A\), in turn, is measured from the difference between the ring-down time with and without analyte in the cavity.
Moreover, the large reflections at the intra-cavity interfaces are no problem at perpendicular orientation, as all of the reflected and almost all of the scattered light remains stable in the cavity (contrary to the Brewster angle configuration). Therefore, this interesting configuration allows for a low intrinsic loss of $\mathcal{L}_0 \approx 10^{-4}$, making it a sensitive tool for measuring absorptions of adsorbed species and thin films. Unfortunately, at normal incidence the electric field of both polarizations is parallel to the interfaces, prohibiting polarization-dependent studies. In addition, the required optical access from the front and back of the substrate complicates in-situ application.

A sophisticated alternative that allows for polarization-dependent studies is to use the evanescent wave (EW) emanating from a total-internal-reflection (TIR) surface to probe the adsorbate at the TIR surface. This technique, called evanescent-wave CRDS (EW-CRDS)\textsuperscript{2, 6, 8, 10, 13, 16, 21, 22}, utilizes the extremely low-loss ($R \approx 10^{-6}$) broadband reflection that TIR provides for both TM and TE polarization. Measurement sensitivity is further improved due to the fact that the electric field amplitude in the evanescent wave is enhanced with respect to the incoming beam. Additionally, EW-CRDS holds the benefit that the evanescent wave has an electric field in all three directions, allowing for sensitive measurements of the average tilt angle of the absorbers with the surface.\textsuperscript{10} EW-CRDS can be achieved by introducing an intra-cavity element that includes a TIR surface, such as a Pellin Broca prism\textsuperscript{8} or a Dove prism.\textsuperscript{15} In these intra-cavity elements,\textsuperscript{8, 15} however, it was found that loss at the other facets of the intra-cavity element, although placed at the Brewster angle, drastically increased the intrinsic cavity loss (to $\mathcal{L}_0 \approx 10^{-2}$). Yet EW-CRDS can also be achieved by a class of cavities called 'monolithic resonators' that consist of a single solid material thereby excluding the need for intra-cavity interfaces. Small in size, these resonators can easily be designed for in-situ application. A particularly appealing example is the monolithic TIR-ring resonator,\textsuperscript{9, 21} in which the light in the cavity is confined only by a number of total internal reflections. Free of optical coatings that limit the bandwidth, the monolithic TIR-ring resonators can provide an intrinsic loss that is only limited by bulk losses, while one or more facets of the resonator can be used to probe the analyte at the TIR surface with the evanescent wave. Photon-tunneling, however, is required to excite a TIR-ring resonator, which makes the TIR-ring resonator cumbersome to work with. Therefore, a monolithic resonator was developed\textsuperscript{10} that combines the easy applicability of using dielectric mirrors to optically excite the cavity with a TIR-surface to exploit the advantages of EW-CRDS in probing an analyte at the surface. The easiest configuration for such a combined monolithic resonator is the so-called 'folded cavity' (FC),\textsuperscript{10, 18} shown in Fig. 1.

![Fig. 1. Schematic illustration and photograph of a monolithic folded cavity (FC). Light is coupled in and out of the cavity through two highly reflective, planar dielectric mirrors, which form a stable optical cavity of length $L$ together with the total internal reflection (TIR) at the spherically curved surface that has a radius of curvature $R$. TIR will occur at this ultra-smooth, convex surface only when the angle of incidence $\theta_i$ is larger than the critical angle $\theta_c = \arcsin(n_2/n_1)$, where $n_1$ and $n_2$ are the refractive index of the folded cavity and the ambient, respectively. Also shown is the evanescent wave emanating from the convex surface that is used to probe the adsorbate or the thin film.](image)
This Chapter describes the design process of such a monolithic folded cavity for the specific purpose of measuring defect-related absorptions in-situ and real-time during thin film growth of a-Si:H. To this end, first some general theory of the electric field in the evanescent wave and in the thin film on top of the TIR surface is treated in Sec. II. Then, using the work of Pipino on the TIR-ring resonator as a starting point, the basic design consideration of the folded cavity are discussed in Sec. III, which include the stability criteria for forming a stable resonator, the beam spot size inside the optical cavity, the different optical loss terms that constitute the total intrinsic loss \( \varepsilon_0 \), and the measurement uncertainty \( \sigma_\tau \). In Sec. IV, these different considerations are combined to decide on the optimum values for the folded cavity design parameters. In Sec. V, the first ex-situ measurements with the folded cavity are presented as a proof of principle and the maximum achievable sensitivity for measuring defect-related absorptions in a-Si:H is estimated. Finally, the general conclusions are given in Sec. VI.

The optimum values of the folded cavity design parameters that enable the highest sensitivity for in-situ and real-time detection of defect-related absorptions in a-Si:H are (Sec IV): a wavelength of peak mirror reflectivity of \( \lambda_c = 1200 \) nm; a bulk material of ultra pure fused silica with a very low bulk attenuation coefficient of a few dB/km and a refractive index of \( n = (1.44805 \pm 0.00001) \) at 1200 nm and room temperature; an angle of incidence of \( \theta_i = 45^\circ \); a cavity length of \( L = 2 \) cm; and a radius of curvature of \( R_c = 9 \) cm. Moreover, the TIR surface should be "super-polished" (\( \sigma_{RMS} \approx 0.5 \) Å). These values are given here, as they will be used in Secs. II and III to elucidate the theoretical considerations by means of a number of specific calculations, which will be clearly marked within text boxes equal to this one.

II. TOTAL INTERNAL REFLECTION THEORY

As mentioned above, in an EW-CRDS experiment with the folded cavity, the evanescent wave at the total internal reflection (TIR) surface will be used to probe the absorbing medium located at the interface. Moreover, by means of the evanescent wave also gas phase absorptions in front of the interface can be probed and, therefore, should be taken into account. In an EW-CRDS experiment, the difference in ring-down time with and without absorbing medium in the evanescent wave yields the optical loss per pass, \( A \). The absorption coefficient \( \alpha \) of the analyte, however, is of interest and relates to \( A \) as:

\[
A = \int \alpha(z, \lambda) I(z, \lambda) dz = \int \alpha(z, \lambda) |E(z, \lambda)|^2 dz,
\]

where \( I = |E|^2 \) is the light intensity with \( E \) the electric field vector with amplitude \( \hat{E} = |E| \). The integration of Eq. (1) is performed over the full length of the evanescent wave, starting at the TIR-surface, i.e. \( z = 0 \). In general, \( \alpha(z, \lambda) \) depends not only on the wavelength \( \lambda \), but also has a spatial dependence on the distance from the TIR-surface, \( z \). At the same time, the light intensity \( I(z, \lambda) \), which also depends on \( z \) because \( I(z, \lambda) \) decreases exponentially with \( z \) in the evanescent wave, can be enhanced or decreased due to interference in a thin film at the TIR-surface. Also, the light intensity \( I(z, \lambda) \) reduces due to absorption in the absorbing medium. Therefore, in order to obtain \( \alpha(z, \lambda) \) from the CRDS measurements, the electric field amplitudes \( \hat{E}(z, \lambda) \) in the evanescent wave need to be known for the different polarizations and as a function of \( z \). Conversely, when \( \hat{E}(z, \lambda) \) is known, Eq. (1) yields information on the spatial dependence of the absorbers.

For internal reflection (\( n_1 > n_2 \) with \( n_1 \) and \( n_2 \) the refractive index of the medium 1 and 2, corresponding to the incident and refracted beam), total internal reflection (TIR) occurs only when the incidence angle \( \theta \) exceeds the critical angle \( \theta_c \). The existence of TIR can be seen from the Fresnel
Equations that describe the reflection coefficient, \( r \), and transmission coefficient, \( t \), i.e. \( r = \frac{\hat{E}_r}{\hat{E}_i} \) and \( t = \frac{\hat{E}_t}{\hat{E}_i} \), with \( \hat{E}_i \), \( \hat{E}_r \), and \( \hat{E}_t \), the (complex) amplitude of the electric fields \( E_i \), \( E_r \), and \( E_t \) of the incoming, reflected and transmitted beam, respectively. Both \( r \) and \( t \) are different for perpendicular (or transverse electric TE) and parallel polarization (or transverse magnetic TM), for which the electric field vibrates perpendicular or parallel to the plane of incidence, respectively. For the case of TIR, the Fresnel equations for the reflection coefficient can be expressed as:

\[
\begin{align*}
    r_{TE} &= \frac{\hat{E}_r}{\hat{E}_i} = \frac{\cos \theta_i - i\sqrt{\sin^2 \theta_i - n_2^2}}{\cos \theta_i + i\sqrt{\sin^2 \theta_i - n_2^2}} \\
    r_{TM} &= \frac{\hat{E}_r}{\hat{E}_i} = \frac{-n_2^2 \cos \theta_i - i\sqrt{\sin^2 \theta_i - n_2^2}}{-n_2^2 \cos \theta_i + i\sqrt{\sin^2 \theta_i - n_2^2}}
\end{align*}
\]

with \( n_2 = n_2 / n_1 \) and \( \sin^2 \theta_i - n_2^2 \geq 0 \) (Snell's law). Since the real and imaginary part of the numerator and denominator are equal, except for the sign, the magnitudes of the numerator and denominator are equal and \( r \) has unit amplitude, constituting a total internal reflection. The phase shift upon total internal reflection, \( \phi \), may be investigated by expressing Eq. (2) in complex polar form, as:

\[
\begin{align*}
    n_{TE,TM} &= e^{-i\zeta} = e^{-i(2\zeta)}
\end{align*}
\]

with \( \tan \zeta_{TE} = \sqrt{\sin^2 \theta_i - n_2^2} / (\cos \theta_i) \) and \( \tan \zeta_{TM} = \sqrt{\sin^2 \theta_i - n_2^2} / (n_2^2 \cos \theta_i) \) for the TE and TM mode, respectively. Then, the phase shift upon TIR \( \phi \) is found by writing \( r = e^{\pi i} \), i.e. \( \phi = 2\zeta \), yielding for TE and TM polarization:

\[
\begin{align*}
    \phi_{TE} &= -2\arctan \left( \frac{\sqrt{\sin^2 \theta_i - n_2^2}}{\cos \theta_i} \right) \\
    \phi_{TM} &= -2\arctan \left( \frac{\sqrt{\sin^2 \theta_i - n_2^2}}{n_2^2 \cos \theta_i} \right)
\end{align*}
\]

At the critical angle \( \theta_c \), where \( \sin \theta_c = n_2 \), \( \phi_{TE} \) and \( \phi_{TM} \) are zero, while \( \phi_{TE} \) and \( \phi_{TM} \) increase monotonic with \( \theta_i \) towards \( \pi \) at \( \theta_i = 90^\circ \).

As the beam is totally reflected, interference between the incoming and reflected waves results in a standing wave pattern of the electric field in the denser medium perpendicular to the totally reflecting interface (z-direction), as shown in Fig. 2. This interference pattern is a function of the TIR phase shifts.

The amplitude of the electric field \( \hat{E}_{TE} = |\hat{E}_{TE}| \) for TE polarization in the denser medium, normalized to the amplitude of the incoming beam, as a function of \( z \) is given by:

\[
\hat{E}_{TE} = \hat{E}_i \cos \left( k_z z + \sqrt{\phi_{TE}} \right)
\]

where \( k_z = n_1 k_0 \cos \theta_i \) is the z-component of the wave vector in medium 1 of the incident beam, which relates to the wavelength in vacuum through \( k_0 = 2\pi / \lambda_0 \). The normalized electric field amplitude for TM polarization is best described by its components in \( x \) and \( z \) direction:

\[
\begin{align*}
    \hat{E}_{x} &= 2 \cos \theta_i \cos(k_z z + \sqrt{\phi_{TM}} - \gamma_z) \\
    \hat{E}_{z} &= 2 \sin \theta_i \cos(k_z z + \sqrt{\phi_{TM}}) \\
    \hat{E}_{TM} &= \sqrt{\hat{E}_x^2 + \hat{E}_z^2}
\end{align*}
\]

1 Eqs. 5 and 6 are expressed differently from the equations given in Refs. 24 and 25.
From Eqs. (4)–(6), the electric field amplitudes in the denser medium $\hat{E}_{x0}$, $\hat{E}_{y0}$, and $\hat{E}_{z0}$ at the interface can be obtained as a function of the incident angle by setting $z = 0$, as is shown in Fig. 3. At the critical angle, $\varphi_{\text{TE}} = \varphi_{\text{TM}} = 0$ and $\hat{E}_{x0}$ has a node, while $\hat{E}_{y0}$ and $\hat{E}_{z0}$ have an antinode at the interface. The magnitude of $\hat{E}_{x0}$ and $\hat{E}_{z0}$ decreases monotonically with increasing $\theta_i$ towards zero at $\theta_i = 90^\circ$. $\hat{E}_{y0}$ on the other hand, increases rapidly for increasing angle up to a maximum and subsequently follows the trend of $\hat{E}_{x0}$ and $\hat{E}_{z0}$ and goes to zero at an angle of $\theta_i = 90^\circ$.

Going from dense to rare medium, $\hat{E}_{x0}$ and $\hat{E}_{y0}$ remain equal, whereas $\hat{E}_{z0}$ is increased with a factor of $1/n_{21}^2$ (Fig. 3), as follows directly from the Maxwell equations that dictate that the electric field parallel to an interface and the displacement field ($\mathbf{D} = \varepsilon \mathbf{E} = n^2 \mathbf{E}$) perpendicular to an interface should be continuous across the interface. In the rare medium, the $z$-component of the wave vector of the transmitted beam is imaginary for the case of TIR, causing the electric field amplitudes $\hat{E}_{x}$, $\hat{E}_{y}$, and $\hat{E}_{z}$ to decay exponentially for increasing distance from the interface (while the evanescent wave has the frequency of the incoming wave), as shown in Fig. 2:

Fig. 3. The electric field amplitudes in the x, y, and z direction normalized to the amplitude of the incoming beam (calculated at the interface $z = 0$) for the case of a silica-ambient interface $n_{21}^2 = (1/1.44805)$ at $\lambda_c = 1200$ nm). As defined in the inset, the component in the y direction corresponds to the polarization perpendicular to the plane of incidence, i.e., $\hat{E}_y = \hat{E}_{\text{TE}}$, whereas the parallel polarization ($\hat{E}_{\text{TM}}$) has a component in the x and z direction with $\hat{E}_{z\text{TM}} = \sqrt{\hat{E}_{x\text{TM}}^2 + \hat{E}_{z\text{TM}}^2}$. $\hat{E}_x$ and $\hat{E}_y$ are continuous across the interface, while $\hat{E}_z$ is enhanced with a factor of $1/n_{21}^2$ going into the rarer medium (the main figure shows $\hat{E}_z$ in the dense medium as well as in the rare medium).
\[
E_{x,0:z} = E_{x,0,0:0} \exp \left( -\frac{z}{d_p} \right) \tag{7}
\]

with \( E_{x,0,0:0} \) the electric field at the totally reflecting interface in the rare medium and \( d_p \) the penetration depth:

\[
d_p = \frac{\lambda_0}{2\pi \sin \theta_i - n_{tf}} \tag{8}
\]

with \( \lambda_0 = \lambda_1 / n_i \) the wavelength in medium 1. The penetration depth increases monotonically with decreasing \( \theta_i \) up to an infinitely large penetration depth at the critical angle \( \theta_c \). The latter is an anomaly from the intrinsic assumption of an infinite plane wave, whereas in reality the penetration depth is always finite due to nonspecular effects of a finite beam near the critical angle (Sec. III).

For a fused silica-ambient interface with \( n_{tf} = (1/1.44805) \) at \( \lambda_c = 1200 \text{ nm} \), the penetration depth is \( \sim 1257 \text{ nm} \) for \( \theta_i = 45^\circ \), while the penetration depth decreases to \( 272 \text{ nm} \) at \( 80^\circ \).

For the case that the second medium is non-absorbing and that the TIR is not frustrated, i.e. no material with a refractive index \( n_3 > n_1 \) is placed inside the evanescent wave, no net energy flows into the rarer medium, i.e. the Poynting vector is imaginary. Therefore, the presence of the evanescent wave does not contradict energy conservation.

Combination of Eqs. (4)–(8) enables a complete calculation of the electric field in the evanescent wave in three directions as a function of the distance from the interface \( z \). It is noted that in this calculation, absorption losses have been neglected, i.e. the imaginary part of the refractive index has been neglected with respect to the real part. However, even for an absorption loss of \( A = 0.1 \) per pass, the calculation of \( A \) with Eq. (1) using the electric field calculated with Eqs. (4)–(8) deviates only 10\% from the exact calculation.\(^{26}\) Hence, for our case, where the absorption loss \( A \) is in the order of hundreds of ppm's per pass at maximum, the calculation of the electric field with Eqs. (4)–(8) can be assumed exact.

Nota Bene: Figure 3 illustrates clearly that the evanescent wave has an electric field in three directions. This enables molecular orientation measurements and other polarization-dependent absorption spectroscopy experiments.\(^{9,18}\) For example, a transition moment perpendicular to the surface will only be detected by TM polarized light. Figure 3 also illustrates clearly the enhancement of the electric fields in the evanescent wave with respect to the incoming wave due to the positive interference at the interface [factor of 2 in the Eqs. (5) and (6)], thereby improving measurement sensitivity.

Often, the folded cavity will have a lower refractive index than the thin film of analyte on the folded cavity, as shown schematically in Fig. 4. In that case, TIR does not occur at the folded cavity-thin film (fc-tf) interface, but can still occur at the thin film-ambient (tf-amb) interface. This is a direct result of the conservation of momentum, which imposes that the component of the wave vector parallel to the interface is continuous across the interface:

\[
n_{fc} \sin \theta_{f,c} = n_{tf} \sin \theta_{f,t} = n_{amb} \sin \theta_{amb}, \tag{9}
\]

where the subscripts 'fc', 'tf', and 'amb' denote 'folded cavity', 'thin film', and 'ambient', respectively. Eq. (9) shows that the condition for TIR at the tf-amb interface is \( \theta_{f,t} > \sin^{-1}(n_{amb} / n_{fc}) \), independent of \( n_{fc} \).

When a film of a-Si:H is deposited on our folded cavity (\( \theta_i = 45^\circ \), \( n_{fc} = 1.44805 \), \( n_{amb} = 1 \), and \( n_{tf} \approx 3.65 \) at \( \lambda_c = 1200 \text{ nm} \) for a-Si:H\(^{27}\)), it is found that \( \sim 66\% \) and \( \sim 89\% \) of the light intensity will penetrate the thin film for TE and TM polarization, respectively.
It is noted that absorption losses in the film are not taken into account in Eq. (10); however, this is justified for our case with an absorption loss \( A \) in the thin film well below 0.001 ppm/pass, as discussed above. Moreover, for films with a thickness of less than a few monolayers, the assumption used to derive the macroscopic Maxwell equations from the microscopic Maxwell equations, i.e. an average over a sufficient number of molecules, breaks down as does Eq. (10).

To illustrate the interference effects in the thin film, Figure 5 shows the normalized electric field amplitudes in the thin film as a function of the film thickness \( d \) at three positions in the film: \( z = z_0 = 0 \), \( z = d/2 \), and \( z = d \), as calculated with Eq. (10) for TE and TM polarization and for the \( x \) - and \( z \) -component of the TM polarization, using \( \theta_c = 45^\circ \), \( n_{ee} = 1.45 \), \( n_{em} = 3.65 \), \( n_{amb} = 1 \), and \( \lambda_c = 1200 \) nm. As the incident angle in the thin film is \( \theta_c = 45^\circ \), \( E_z \) is on average smaller than \( E_x \). For increasing thickness, e.g., during deposition, the electric field amplitudes at a certain position \( z_0 \) and thus the absorption loss \( A \) measured with EW-CRDS...
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0 1 2 0 1 2 0 1 2 0 1 00 200 300 400

\[ \begin{align*}
\hat{y} &= \hat{T}_E \\
\hat{x} &= \hat{T}_M \\
z &= \hat{d}/2 \\
z &= \hat{d}\end{align*} \]

Electric field amplitude

Film thickness (nm)

Fig. 5. The electric field amplitudes in the thin film normalized to the amplitude of the incoming beam for TE and TM polarization and the x- and z-component of the TM polarization calculated with Eq. (10) as a function of the film thickness for three positions in the thin film: at the fc-tf interface \((z = 0)\), halfway in the thin film \((z = d/2)\), and at the tf-amb interface \((z = d)\). The input parameters used in the calculations of Eq. (10) are \(\theta_i = 45^\circ\), \(n_{fc} = 1.44805\) at \(\lambda_c = 1200\) nm, \(n_{tf} = 4\), \(n_{amb} = 1\), and \(\lambda_c = 1200\) nm. Absorption losses in the film are not taken into account in Eq. (10).

will oscillate in time. Finally, the electric field in the evanescent wave emanating from the thin film at \(z = d\) can be calculated with Eq. (7) by inserting for \(E_{x0, y0, z0}\) the electric field amplitude at \(z = d\) from Eq. (10).

III. GENERAL CONSIDERATIONS FOR THE FOLDED CAVITY DESIGN

In this section, the various considerations involved in designing a folded cavity for use in an EW-CRDS experiment are discussed, starting with some general concepts, such as the stability criteria of a folded cavity and the beam spot size inside the cavity. Subsequently, the optical loss terms of the folded cavity that make up the total intrinsic loss \(\mathcal{L}_0\) as well as the measurement uncertainty in the ring-down time \(\sigma/\tau\) will be considered, as they both determine the minimum detectable absorption of our folded cavity measurement technique through \(\mathcal{L}_{min} = \mathcal{L}_0 \times \sqrt{2\sigma/\tau}\) (Sec. I). The intrinsic loss is determined by the design of the folded cavity, whereas \(\sigma/\tau\) depends mostly on the signal detection and digitization characteristics.

A. Stability criteria

Calculations using ray-transfer matrices are a convenient method to describe a generalized ray in an arbitrary optical system, consisting of translations, reflections, refractions, etc. In fact, all geometric beam properties in an optical system are incorporated in the transfer matrix. This method will therefore be used to determine the conditions under which the monolithic folded cavity is stable. It is noted that these stability conditions remain equally valid when diffraction is included. In fact, a detailed diffraction analysis shows that a number of transverse amplitude distributions – the transverse TEM\(_{mn}\) modes that are discussed below – can resonate stably in an optical cavity that fulfills the stability criteria.\(^{29}\) In the method of ray-transfer matrices, the ray is characterized by the distance from the optical axis, \(y\), and the angle with the optical axis, \(\phi\). The ray transfer matrix describes the changes in \(y\) and \(\phi\) as the ray makes its way through the optical system. For example, the transformation of an input ray with \(y_0\) and \(\phi_0\) into an output ray with \(y_1\) and \(\phi_1\) due to a simple translation of length \(L\) is:
where $M_T$ is the translation matrix and the so-called "paraxial approximation", i.e. $\tan(\phi) = \phi$, is used. This is assumption is justified as it is shown below that the cavity modes (i) propagate close to the optical axis and (ii) are weakly divergent. In the same way, a reflection at a concave spherical mirror with radius of curvature $R$ is described by the reflection matrix $M_R$:

$$
\begin{pmatrix}
\pm 1 & 0 \\
-2/R & \pm 1
\end{pmatrix}
$$

with $+$ and $-$, respectively, for the perpendicular (or sagittal, $s$) and parallel (or tangential, $t$) plane relative to the plane of incidence, which can be arbitrarily chosen for a reflection at normal incidence. For reflection at a planar mirror ($R = \infty$), Eq. (12) converges to the unity matrix $I$ (more specifically $I$ and $-I$ for the sagittal and tangential plane, respectively), which seems to indicate that no reflection takes place. This can be understood as the matrix method only expresses the distance and angle relative to the optical axis, whereas it does not incorporate the change of direction of the optical axis itself. Therefore, a reflection at a planar mirror located under an angle $\theta_i$ with the optical axis, is also described by the unity matrix. A reflection under an angle $\theta_i$ with a spherically curved mirror is described by Eq. (12), however, the radius of curvature $R$ needs to be replaced by the effective radius of curvature $R_{\text{eff}}$, i.e. the radius of curvature as experienced by the rays of light, which is different for the sagittal and tangential plane:

$$
R_{\text{eff},s} = \frac{R}{\cos(\theta_i)} \quad \text{and} \quad R_{\text{eff},t} = R \cdot \cos(\theta_i),
$$

respectively. For an optical system that consists of $N$ transformations, the ray-transfer matrix $M$ representing the entire optical system is a multiplication of the matrices of the individual optical components in reverse order:

$$
M = M_N \cdots M_3 \cdots M_2 = \begin{pmatrix} A & B \\ C & D \end{pmatrix}
$$

In order to obtain the stability conditions of the folded cavity, first, the ray-transfer matrix for a round-trip through the folded cavity, $M_{FC}$, is computed using cavity length $L$ and an effective radius of curvature $R_{\text{eff}}$ at the TIR surface, which is defined by Eq. (13). A round-trip for a ray that has just entered the folded cavity through the first planar mirror consists of, in consecutive order, a translation of distance $L/2$ towards the TIR surface, a reflection from the TIR surface, a translation of distance $L/2$ towards the second planar mirror, a reflection at the second planar mirror, a translation of distance $L/2$ towards the TIR surface, a reflection from the TIR surface, a translation of distance $L/2$ towards the first mirror, and finally a reflection at the first planar mirror, yielding:

$$
\begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix} \begin{pmatrix}
\pm 1 & 0 \\
0 & \pm 1
\end{pmatrix} \begin{pmatrix}
\pm 1 & 0 \\
0 & \pm 1
\end{pmatrix} \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix} \begin{pmatrix}
\pm 1 & 0 \\
0 & \pm 1
\end{pmatrix} \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix} \begin{pmatrix}
\pm 1 & 0 \\
0 & \pm 1
\end{pmatrix} \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix}
$$

$$
= \begin{pmatrix}
\pm 1 & 0 \\
0 & \pm 1
\end{pmatrix} \begin{pmatrix}
\pm 1 & 0 \\
0 & \pm 1
\end{pmatrix} \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix} \begin{pmatrix}
\pm 1 & 0 \\
0 & \pm 1
\end{pmatrix} \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix}
$$

$$
= \begin{pmatrix}
1-4 \frac{L}{R_{\text{eff}}} + 2 \frac{L^2}{R_{\text{eff}}^2} & 2L-3 \frac{L^2}{R_{\text{eff}}^2} + \frac{L^3}{R_{\text{eff}}^3} \\
\frac{4}{R_{\text{eff}}} - 4 \frac{L}{R_{\text{eff}}} & 1-4 \frac{L}{R_{\text{eff}}} + 2 \frac{L^2}{R_{\text{eff}}^3}
\end{pmatrix} = \begin{pmatrix} A & B \\ C & D \end{pmatrix}
$$
with appropriate substitutions of $R_{\text{eff}}$ [Eq. (13)] for the sagittal and tangential plane. Here, it should be noted that in order for an optical cavity to be stable, it is not necessary that each ray returns to the same distance and angle with the optical axis after each round-trip, i.e. $M_{FC}$ does not have to be unity. The stability condition requires only that the light is confined inside some finite boundary in such a way that all rays contribute to a reproducible amplitude distribution within the cavity. It is therefore necessary to compute the effect on a ray of an arbitrary large number of cavity round-trips and determine whether the components of the ray vector will remain real and finite. Following, $n$ round-trips in the folded cavity, i.e. $(M_{FC})^n$, are analyzed using Sylvester’s theorem:

$$
\begin{pmatrix}
A & B \\
C & D
\end{pmatrix}^n = \frac{1}{n \sin(\phi)} \begin{pmatrix}
A \sin(n\phi) - \sin(n-1)\phi & B \sin(n\phi) \\
C \sin(n\phi) & D \sin(n\phi) - \sin(n-1)\phi
\end{pmatrix} \text{ with } \sin(\phi) = \sqrt{1 - \frac{1}{2}(A+D)^2}.
$$

(16)

For $(M_{FC})^n$ to be real, $\sin(\phi)$ must also be real and, as $A$ and $D$ of Eq. (15) are both real, the stability criteria becomes:

$$
-1 < \frac{1}{2}(A+D) < 1 \text{ or } -1 < 1 - 4 \frac{L}{R_{\text{eff}}} + 2 \frac{L^2}{R_{\text{eff}}^2} < 1.
$$

(17)

This condition is fulfilled for the range of $L/R_{\text{eff}} \in (0,2)$, except for $L=R_{\text{eff}}$, for which the cavity is critically stable. This borderline stability is undesirable due to always-present fabricational errors in the cavity. As $R_{\text{eff}}$ is different for the sagittal and tangential plane [see Eq. (13)], there are two stability criteria that the radius of curvature $R_c$ must fulfill.

With an angle of incidence $\theta_i=45^\circ$ and $L=2$ cm, our folded cavity is optically stable in the sagittal and tangential plane for a radius of curvature of $R_c \in \{(\sqrt{2}, \infty) \cup (\sqrt{2}, \infty)\}$ and $R_c \in \{(\sqrt{2}, 2 \sqrt{2}) \cup (2 \sqrt{2}, \infty)\}$, respectively, in units of cm. Both stability criteria are clearly satisfied for $R_c=9$ cm (the specific value of 9 cm is mainly based also on considerations of the distribution of cavity modes in the folded cavity, as addressed below).

B. Beam spot size

Similar to a laser beam, the lowest order mode in the cavity, i.e. TEM$_{00}$ mode, has a Gaussian transverse amplitude distribution:

$$
E = E_0 e^{-\frac{w^2}{w_0^2}},
$$

(18)

where the beam spot size $w$ is a measure of the half-width of the TEM$_{00}$ mode. It can be shown that the TEM$_{00}$ mode, as well as any other TEM$_{mn}$ mode cavity mode, is completely characterized by its complex radius of curvature $q$:

$$
\frac{1}{q(z)} = \frac{1}{R(z)} + \frac{\lambda}{\pi w(z)^2}.
$$

(19)

which describes the change of the (real) radius of curvature of the wave front, $R(z)$, and the spot size $w(z)$ as the beam propagates along the $z$-axis. Briefly, some general features of Gaussian beams that will be necessary later are summarized here.$^{31}$

(i) At the focus, the wave front is planar ($R=\infty$) and the spot size $w$ is at a (local) minimum and is called the beam waist $w_0$.

(ii) The spot size will diverge as the beam propagates away from the focus, in either direction ($+z$ or $-z$),
however, the transverse amplitude distribution will remain Gaussian. This corresponds to a change in \( w(z) \) as a function of the distance from the focus, \( z \), given by

\[
w(z) = w_0 \left[ 1 + \left( \frac{z}{Z_R} \right)^2 \right].
\]

(20)

Here \( Z_R \) is the Rayleigh range, which is a measure of the Lorenztian intensity profile along the \( z \)-axis:

\[
Z_R = \frac{\pi w_0^2 n}{\lambda}.
\]

(21)

where \( \lambda / n \) is the wavelength in a medium of refractive index \( n \).

(iii) The divergence corresponds to the (initially plane) wave-fronts becoming spherical (again with symmetry about \( z = 0, w = w_0 \)) with radius of curvature given by:

\[
R(z) = z \left[ 1 + \left( \frac{Z_R}{z} \right)^2 \right].
\]

(22)

The modes in the folded cavity have, by definition, a matching planar wave front at both of the planar mirrors, while the radius of curvature of the modes at the TIR surface matches the effective radius of curvature, \( R_{	ext{eff}} \), experienced at the TIR surface. This means that the modes have a focus (node) at both of the planar mirrors and an antinode at the TIR surface, located \( L/2 \) from the focus. The Rayleigh range \( Z_R \) can thus be obtained by inserting \( z = L/2 \) in Eq. (22) and setting \( R(z) \) equal to \( R_{	ext{eff}} \), while inserting the resulting expression of \( Z_R, z = L/2 \), and Eq. (21) in Eq. (20) yields the beam waist at the focus \( w_{0,\text{mirror}} \):

\[
Z_R = \frac{1}{2} \sqrt{(2R_{	ext{eff}} - L)L} \quad \text{and} \quad w_{0,\text{mirror}} = \frac{\lambda}{2\pi} \sqrt{(2R_{	ext{eff}} - L)L}.
\]

(23)

Then, the spot size at the TIR surface \( w_{0,TIR} \) is directly calculated from \( w_{0,\text{mirror}} \) using Eq. (20). Through \( R_{	ext{eff}} \), the spot size at the focus and at the TIR surface differ in the sagittal and tangential plane. Therefore, the projected area of the sampling spot at the TIR interface is elliptical with an area of:

\[
A_{\text{TIR}} = \frac{\pi w_{0,TIR} w_{0,TIR}}{\cos(\theta_i)}.
\]

(24)

where the factor \( \cos(\theta_i) \) accounts for the projection of the beam onto the TIR surface, which is located under an angle \( \theta_i \), with the optical axis.

For our folded cavity with \( n = 1.44805 \) at \( \lambda_c = 1200 \text{ nm}, L = 2 \text{ cm}, R_c = 9 \text{ cm}, \) and \( \theta_i = 45^\circ \), a calculation of the Rayleigh range and spot size of the TEM\(_{00}\) mode at the mirror (focus) and at the TIR surface for the sagittal and tangential plane yields \( Z_{R,s} = 3.4 \text{ cm}, Z_{R,t} = 2.3 \text{ cm}, w_{0,\text{mirror},s} = 95 \mu\text{m}, w_{0,\text{mirror},t} = 78 \mu\text{m}, w_{0,TIR,s} = 99 \mu\text{m}, w_{0,TIR,t} = 85 \mu\text{m}, \) respectively, while the TIR sampling area is \( A_{\text{TIR}} = 0.037 \text{ mm}^2 \).

C. Optical loss terms

The photon decay time \( \tau \), also called the ring-down time, in a folded cavity is given as follows:

\[
\tau = \frac{t_p}{t_0 + A} = \frac{t_p}{t_{\text{bulk}} + t_{\text{surf}} + t_{\text{mirror}} + t_{\text{diff}} + A}.
\]

(25)
Here, \( t_p = nL/c \) is the light propagation time per pass in the optical cavity of length \( L \) having refractive index \( n \) and \( c \) is the speed of light, while \( A \) is the loss per pass due to analyte absorption. \( \mathcal{L}_0 \) is the total intrinsic loss per pass of the cavity, which can be divided into a number of contributions: loss due to bulk attenuation \( \mathcal{L}_{\text{bulk}} \) loss at the TIR surface due to surface scattering \( \mathcal{L}_{\text{surf}} \) and non-specular effects \( \mathcal{L}_{\text{nonspec}} \), loss at the two dielectric mirrors \( \mathcal{L}_{\text{mirror}} \), and loss due to diffraction at small apertures \( \mathcal{L}_{\text{diff}} \). As explained in Sec. I, the detection limit for measuring the absorption \( A \) is typically determined by the total intrinsic loss \( \mathcal{L}_0 \). Therefore, the loss terms are discussed individually here, in line with Ref. 21.

For a resonator of length \( L \) that is fabricated from a highly transparent material, the loss per pass due to bulk attenuation is well approximated by

\[
\mathcal{L}_{\text{bulk}} = \alpha \mathcal{L}_0,
\]

where \( \alpha \) is the bulk attenuation coefficient. Partly due to a continuing demand from the telecom industry, fused silica with a very low OH-content is now available which allows for a bulk attenuation coefficient of a few dB/km corresponding to a bulk loss of less than 10 ppm/cm. It should, however, be noted that the bulk OH absorption shows spectral regions with strong absorption lines with a bulk loss exceeding 10\(^4\) ppm/cm, as is addressed below, and, therefore, the very low absorption losses are only obtained in the intermediate regions. Because \( \mathcal{L}_{\text{bulk}} \) increases with increasing cavity length, \( \mathcal{L}_{\text{bulk}} \) will always dominate all the other terms in Eq. (25) for large cavities, i.e. for increasing cavity length the ring-down time \( \tau \) will saturate towards \( \tau \approx t_p/\mathcal{L}_{\text{bulk}} \). On the other hand, the gain in bulk loss by reducing the cavity size is counteracted by the simultaneous reduction of the ring-down time \( \tau \), which leads to an increase in the measurement uncertainty \( \sigma_\tau/\tau \). Moreover, for small cavities other loss terms might become more important than \( \mathcal{L}_{\text{bulk}} \). In choosing the cavity length, these effects need to be considered carefully.

The loss per pass due to surface scattering at the TIR surface, \( \mathcal{L}_{\text{surf}} \), can be estimated from

\[
\mathcal{L}_{\text{surf}} = \frac{4\pi n_0 \sigma_{\text{RMS}} \cos \theta_i}{\lambda_0} \]

where \( \lambda_0 \) is the wavelength in vacuum, \( \theta_i \) is the angle of incidence of the TIR surface, and \( \sigma_{\text{RMS}} \) is the root-mean-squared surface roughness. Current optical polishing techniques allow for fabrication of ultra smooth surface with \( \sigma_{\text{RMS}} \approx 0.5 \text{Å} \). It is noted that Eq. (27) yields an upper limit of the surface loss, because the possibility that scattered light remains stable in the optical cavity is not taken into account.

For our folded cavity with \( n = 1.44805 \) at \( \lambda_c = 1200 \text{ nm} \), \( \theta_i = 45^\circ \) and assuming \( \sigma_{\text{RMS}} = 0.5 \text{Å} \), a surface loss of \( \mathcal{L}_{\text{surf}} \leq 0.3 \text{ ppm/pass} \) is calculated, which is much lower than the bulk loss. However, when a layer of a-Si:H is deposited on the folded cavity, the surface roughness increases to \( \sigma_{\text{RMS}} \leq 10 \text{Å} \), resulting in an estimated surface loss \( \mathcal{L}_{\text{surf}} \leq 100 \text{ ppm/pass} \), as is addressed in Sec. IV.
The finite spot size of the cavity modes gives rise to a number of nonspecular effects\textsuperscript{31,36} at total internal reflection that leads to an additional loss at the TIR surface, $\mathcal{L}_{\text{nonspec}}$. Intuitively, this can be understood by considering that the Fresnel reflection coefficients [Eq. (2)] have been derived strictly for an infinite plane wave, while a finite beam can be seen in terms of an angular spectrum of plane waves, all of which experience a different phase and amplitude modification at reflection.\textsuperscript{36} When a finite beam undergoes total internal reflection in the vicinity of the critical angle, the conditions for TIR is no longer satisfied for a portion of the angular spectrum of plane waves, which leads to light being lost from the cavity due to transmission. For the specific case of total internal reflection of a Gaussian beam near the critical angle, Schiller deduced an expression for the transmission loss due to nonspecular effects:\textsuperscript{34}

$$
\mathcal{L}_{\text{nonspec}} = \frac{e^{-\xi^2}}{2\xi\sqrt{\pi}} \left[ 1 + \frac{1}{2\xi^2} + \cdots \right] \quad \text{with} \quad \xi = \frac{2n_i}{\lambda_c} w_0 \sin \left( \frac{\theta_i - \theta_c}{\sqrt{2}} \right),
$$

(28)

where $\theta_c = \arcsin(1/n_i)$ is the critical angle. It is easily seen from Eq. (28) that $\mathcal{L}_{\text{nonspec}}$ decreases very rapidly for increasing incident angle $\theta_i$ and thus $\mathcal{L}_{\text{nonspec}}$ only becomes important for incident angles very near the critical angle.

The critical angle for the interface between the folded cavity ($n_1 = 1.44805$ at $\lambda_c = 1200$ nm) with air ($n_2 = 1.0002$) is $\theta_c = 43.65^\circ$. At an angle of incidence of $\theta_i = 44^\circ$, the loss due to nonspecular effects is $\mathcal{L}_{\text{nonspec,s}} = 2$ ppm/pass and $\mathcal{L}_{\text{nonspec,t}} = 33$ ppm/pass for the $s$ and $t$ directions, respectively. For $\theta_i = 45^\circ$, however, these losses have been reduced to less than $10^{-48}$ ppm/pass.

The loss at one dielectric mirror, $\mathcal{L}_{\text{mirror}}$, consists of a combination of losses. The transmission loss is the light transmitted through the mirror, which is measured by the detector to obtain the ring-down time $\tau$. Light can also be lost in the multilayer mirror stack due to bulk absorption in the dielectric layers and due to scattering at the interfaces between the layers. Still the total loss at a mirror $\mathcal{L}_{\text{mirror}}$ can be very low, as has been shown by Hood et al.\textsuperscript{33} They demonstrated for a 37-layer stack of alternating high-index (Ta$_2$O$_5$, $n = 2.0411$) and low-index (SiO$_2$, $n = 1.445$) dielectric layers with a center wavelength at 852 nm a transmission loss and an (absorption plus scatter) loss of $4.3$ and $2.9$ ppm per roundtrip, respectively.

The mirrors of our folded cavity have been coated for a center wavelength of $\lambda_c = 1200$ nm. The reflectivity of the mirrors is specified as $R = 99.995\%$.\textsuperscript{35} The manufacturer has indicated, however, that their best effort mirror has a transmission loss and an (absorption plus scatter) loss of $\sim 5$ ppm and $\sim 0.02$ ppm, respectively, yielding a total loss of $\mathcal{L}_{\text{mirror}} = 10$–30 ppm/pass. Such a low transmission loss of $\sim 5$ ppm might reduce $\sigma/c$ due to insufficient light intensity at the detector, however, the transmission loss readily increases when scanning away from the center wavelength.

The final loss term investigated is the loss due to diffraction at small apertures, $\mathcal{L}_{\text{diff}}$. The diffraction loss for a Gaussian beam (TEM$_{00}$ cavity mode) at an aperture of radius $r$ is:\textsuperscript{39}

$$
\mathcal{L}_{\text{diff}} = 1 - \Phi_{\text{pw}} = e^{-2\pi r/w^2},
$$

(29)

where $\Phi_{\text{pw}}$ is the fractional power passing through the aperture and $w$ is the (local) spot size. When the aperture radius $r$ is $2.5w$ and $3w$, $\mathcal{L}_{\text{diff}}$ is $\sim 4$ ppm and $\sim 0.02$ ppm, respectively. However, Eq. (29) only takes into account the direct loss at the aperture, whereas the transmission loss is increased with a correction factor in the order of unity due to aperture diffraction effects caused by sharp-edged circular apertures (page 667 in Ref. 29). Moreover, it needs to be taken into account that higher order cavity modes have a broader irradiance pattern than the TEM$_{00}$ mode. In all, diffraction losses can surely be neglected for an aperture radius of $r = 5w$. It is noted that the diffraction that diffracted light remains stable in the cavity is not considered here.
As shown above, the spot size of the TEM$_{00}$ mode remains below 100 $\mu$m throughout the cavity. Therefore, diffraction losses can be neglected when all apertures have a radius exceeding 0.5 mm. Because there is no drawback in increasing the aperture sizes, our folded cavity has been designed with clear apertures of 1.5 mm, which clearly eliminates diffraction losses. At the TIR surface, a clear aperture perpendicular to the light beam of 3 mm corresponds to an elliptical area of the super-polished TIR-surface that has a width of 4.24 and 3 mm in the sagittal and tangential plane [Eq. (24)], respectively.

D. Measurement uncertainty $\sigma_{\tau}/\tau$

In CRDS, the minimum detectable absorption $\Delta_{\text{min}} = \tau_0 \times \sqrt{2\sigma_{\tau}/\tau}$ (Sec. I) is directly related to the measurement uncertainty in the ring-down time $\sigma_{\tau}/\tau$. For the most part, $\sigma_{\tau}/\tau$ is determined by instrumental aspects, such as light intensity on the detector and the measurement and processing of the CRDS signal. From a more fundamental point of view, however, $\sigma_{\tau}/\tau$ is also affected by the number of modes coupled into the cavity and enclosed within the detector area. Here, these different aspects are discussed.

1. Light intensity on the detector

In order to get as much of the light coming out of the cavity onto the detector, the light needs to be focused with a lens onto the detector. As mentioned above, the cavity modes of the folded cavity have their focus located at the planar mirrors with a corresponding waist size $w_{0,\text{mirror}}$ and Rayleigh range $R_{z,\text{mirror}}$ given by Eq. (23). Then, the lens position, detector position, and waist size $w_{0}'$ at the detector can be calculated from the general lens formula and magnification formula for a Gaussian beam:

$$\frac{1}{s/f} + \frac{(Z_{\text{R}}/f)^2}{(s/f-1)} = \frac{1}{s'} - \frac{1}{f}$$

and

$$m = \frac{w_0}{w_{0,\text{mirror}}} = \frac{1}{\sqrt{(1-(s/f))^2 + (Z_{\text{R}}/f)^2}}$$

with $f$ the focal length of the lens, $s$ and $s'$ the object and image distance from the lens, respectively. The position of the lens and the focal length used thus depend on the size of the detector area and, through $w_{0,\text{mirror}}$, on the design of the folded cavity. Because $w_{0,\text{mirror}}$ depends on the sagittal and tangential plane, the focal length will be different in the $s$ or $t$ plane.

For in-situ application of the folded cavity, the lens must be positioned 35 cm or more from the folded cavity. Using for example a lens with a focal length of 15 cm, the focus of the TEM$_{00}$ mode at the output mirror of our folded cavity ($w_{0,\text{mirror}},s \approx 95 \mu$m and $w_{0,\text{mirror}},t \approx 78 \mu$m) is projected into an image focus with a waist size of 58 and 71 $\mu$m and an image distance of 26.10 and 26.18 cm for the $s$ and $t$ plane, respectively. This is much smaller than the detector diameter of the photodiode of 0.3 mm (Appendix A), clipping less than $10^{-8}$ of the power of the TEM$_{00}$ mode [Eq. (29)] when perfectly aligned, which is far below the detection limit.

2. CRDS data acquisition system

In order to obtain the highest sensitivity in the measurement of the CRDS transient and thus in $\sigma_{\tau}/\tau$, a low-noise, high-gain, free-space InGaAs/PIN photodiode with a detector diameter of 0.3 mm is used.
together with a high sampling frequency, high resolution data acquisition system. The noise in $\sigma/\tau$ is reduced further by processing every CRDS transient separately in real time yielding individual ring-down times $\tau$. Details of the detector, the CRDS transient handling procedure, and the data acquisition system are presented in Appendix A, B, and C, respectively.

3. Cavity mode dependence of $\sigma/\tau$

It is common use in CRDS to try to control the spatial and temporal profile of the laser pulses that are coupled into the CRDS cavity as accurately as possible, aiming to excite as few cavity modes as possible. It is shown below, however, that single-mode excitation is generally not readily feasible for pulsed laser CRDS. For this common case of CRDS, called multiple mode excitation, it is argued that one should aim to couple in as many modes as possible, because the excitement of only a few modes is detrimental for $\sigma/\tau$. This is caused by the fact that in an optical cavity, each mode has its own resonance frequency and therefore has its own ring-down time, because the intrinsic loss and the absorption in the cavity usually both depend on the frequency and the spatial distribution. Therefore, multiple mode excitation results in a multiple exponential decay. The repeatability of this multiple exponential decay increases with the number of modes in the cavity. Here, after a derivation of the mode frequencies in the folded cavity, the implications of a distribution of excited modes on the measurement uncertainty $\sigma/\tau$ are investigated.

In the paraxial approximation, the wave equation in a homogeneous dielectric medium with refractive index $n$ has a set of solutions known as the transverse electromagnetic (TEM$_{mn}$) modes, whose order is given by two positive integers $(m,n)$. The spatial field amplitude $E(x,y,z,t)$ for these modes is written in terms of Hermite-Gaussian functions:

$$E(x,y,z,t) = E_0 \frac{W(z)}{w(z)} H_n \left( \frac{\sqrt{2} x}{w(z)} \right) H_m \left( \frac{\sqrt{2} y}{w(z)} \right) e^{-\frac{(x^2+y^2)}{w(z)^2}} e^{i \frac{(x^2+y^2)}{w(z)^2}} e^{-i \frac{2i \phi}{w(z)}} e^{-i \sigma t}$$

where the $z$-dependence of the transverse amplitude profile is completely determined by spot size $w(z)$ relative to the waist size $w_0$ and by the radius of curvature $R(z)$. Here, $Z_0$ is the Rayleigh range, $\phi$ is the angular frequency of the light, and $H_n(\xi)$ and $H_m(\xi)$ are Hermite polynomials of order $m$ and $n$. For the lowest order mode, i.e. the TEM$_{00}$ mode with $m=n=0$, $H_0(\xi)$ and $H_0(\xi)$ are equal to 1 and the solution for the spherical Gaussian beam profile defined by $\exp[-(x^2+y^2)/(w(z)^2)]$ is found. For the higher-order TEM$_{mn}$ modes ($m,n>0$), the spherical Gaussian beam profile is multiplied by the Hermite polynomials $H_n(\xi)$ and $H_m(\xi)$, thereby constructing the well-known burn patterns of higher-order TEM$_{mn}$ cavity modes. In fact, the transverse TEM$_{mn}$ modes form a set of orthogonal functions with real eigenvalues in the frequency space. As $R(z)$ changes slowly with $z$, the phase change along the $z$-direction of a TEM$_{mn}$ mode is predominantly determined by the second phase term of Eq. (32). The angular frequency of the modes in the cavity can be found by setting the total phase change of a roundtrip through the cavity equal to $2\pi q$ with $q$ the longitudinal mode number. For an etalon (or a gas phase CRDS cavity) this leads to modes of frequency

$$\omega_{\text{mode}} = \left( q\pi + \phi + (m+n+1)\arctan\frac{L}{Z_0} \right) \frac{c}{nL},$$

where $\phi$ is the phase shift upon reflection at the mirrors and $L$ is the cavity length. For a certain longitudinal mode number $q$, the different transverse modes have a slight frequency shift compared to the fundamental longitudinal mode, which is caused by the so-called Guoy phase shift $(m+n+1)\arctan(L/Z_0)$ that depends on transverse mode indices $m$ and $n$. For the case of the folded cavity, the Rayleigh range at the focus [Eq. (23)] is different for the saggital ($s$) and transversal ($t$) plane in the cavity due to the different effective radius of curvature $R_{eff}$ of the TIR surface, i.e. $R_{eff,s} = R_s \cos \theta$, and $R_{eff,t} = R_t \cos \theta$ [Eq. (13)]. This results in a
different Guoy phase for the two directions. Moreover, as explained in Sec. II, the TIR surface introduces an additional TIR phase shift, $\varphi$ [Eq. (4)], that is different for TE or TM polarization. Therefore, the modes frequencies of the folded cavity are given by:

$$
\omega_{\text{mode}} = \left( q\pi + \phi + \left( m + \frac{1}{2}\right) \arctan \left( \frac{2\sqrt{L}}{2 R_{\text{eff}} - L} \right) + \left( n + \frac{1}{2}\right) \arctan \left( \frac{2\sqrt{L}}{2 R_{\text{eff}} - L} \right) + \varphi_{\text{TE,TM}} \right) \frac{c}{nL},
$$

(34)

where $\varphi_{\text{TE,TM}}$ should be chosen either $\varphi_{\text{TE}}$ or $\varphi_{\text{TM}}$, depending on the polarization. The phase shift $\phi$ upon reflection at the mirrors for normal angle of incidence is of course equal for both sagittal and tangential planes as well as for both TE and TM polarizations.

For multiple mode excitation of the folded cavity (or any other cavity), the light intensity at the output mirror is determined by the interference between the different modes. As the phase changes with time as $\exp(-i\omega t)$, the differences in frequency, given by Eq. (34), results in time oscillations in the light intensity at the output mirror due to constructive and destructive interference. This so-called 'beating' between different mode frequencies is superimposed on the exponentially decaying signal envelope, i.e. the sum of the individual ring-down transients of each of the excited modes. The mode beats have a frequency equal to the difference in mode frequency between the modes, i.e. for longitudinal mode beating the beat frequencies are multiples of $\Delta f = c/2nL$. In principle, the exponential decay of the light in the cavity is not affected by mode beating and consequently the same ring-down time $\tau$ with and without beating should be found when averaging over a sufficiently large number of mode beats. In this case, where the round-trip time is much shorter than the ring-down time, the round-trip beating pattern can be filtered electronically to obtain the exponentially decaying signal envelope without significant distortions. Transverse mode beats, however, are spaced much closer to each other and consequently have much lower beat frequencies that are more difficult to filter out electronically. For the folded cavity, the beat frequencies of transverse mode beating are multiples of $\Delta f_{\text{st}} = c/2nL \times \arctan(\sqrt{2L/(2R_{\text{eff}} - L)})$, where $R_{\text{st}}$ and $\Delta f_{\text{st}}$ are different for the sagittal and tangential plane. In practice, multiple mode beats can occur at the same time yielding a complex round-trip beating pattern, making it nearly impossible to average over an exact number of oscillations for all the mode beats. Moreover, when scanning the wavelength, different modes will be excited resulting in different beat frequencies. Additionally, transverse mode beating can be introduced by the finite size of the detector, as for lower order transverse modes, which are more localized near the optical axis, a larger portion of the light intensity will be detected by a small detector than for higher order modes. It is thus concluded that the mode beating is very difficult to control. Unfortunately, as the influence of mode beating on the measured CRDS transient is highly unpredictable, it acts as a noise term on $\sigma/\tau$. The detrimental effect of mode beating on $\sigma/\tau$ is clearly illustrated below, where we will see that $\sigma/\tau$ can easily be a factor of $\sim 100$ higher for multiple-mode excitation than for single-mode excitation. It is shown next that the solution of single-mode excitation is too complicated for most applications, but that the effect of mode beating on $\sigma/\tau$ can be reduced by exciting as many modes as possible thereby averaging out the mode beating.

Single mode excitation offers a clear advantage as it yields a single exponential decay of the light in the cavity without the occurrence of mode beating, while it also offers superior laser light intensity stability. Therefore, in principle, the minimum $\sigma/\tau$ will be achieved for single mode excitation, as demonstrated by the reported value of $\sigma/\tau = 3 \times 10^{-7}$ for a cavity with $\tau = 10$ $\mu$s. Excitation of only one longitudinal mode, however, requires a bandwidth of the input laser smaller than the frequency shift between longitudinal modes. Moreover, excitation of only one transverse mode can only be achieved with careful mode matching, i.e. a single-mode input laser beam (in practice usually the TEM$_{00}$ mode) that is determined by its spot size $w(z)$ and radius of curvature $R(z)$, is focused such that at the input mirror $w$ and $R$ of the input laser match exactly $w$ and $R$ of the excited mode (for the folded cavity, the focus lies at the
input mirror, thus \( R_{\text{mirror}} = \infty \) and \( w = w_{0, \text{mirror}} \) as given by Eq. (23)). Therefore, single transverse mode excitation requires, besides precise alignment of the position and angle of the input laser beam to the optical axis of the cavity, also strict control of the spot size \( w(z) \) and radius of curvature \( R(z) \) of the laser beam. This is a complicated engineering problem when using a single-mode operating laser, but is nearly impossible when using a tunable pulsed laser system such as dye laser or optical parametric oscillator (OPO), which have multiple longitudinal and transverse modes in its output beam. In addition to the requirements on the laser system and the alignment, the length of the optical cavity should also be highly stable (a maximum cavity length variation of \( \leq 0.25 \) nm was calculated in Ref. 43). For the folded cavity this may be accomplished by accurate control of the temperature. For a cavity consisting of separate mirrors, however, the cavity length must be controlled actively at a fixed distance, as can be done, for instance, by mode-locking the cavity to an additional, frequency-stabilized single-mode continuous-wave laser.\(^{43}\)

When single-mode excitation is not achieved, a few cavity modes can be excited. In that case, pulse-to-pulse fluctuations in the composition of excited TEM\(_{mn} \) modes and in their relative intensities can be large due to pulse-to-pulse fluctuations of the laser profile or due to cavity vibrations. This results in large pulse-to-pulse fluctuations in the round-trip beating pattern as well as in the exponentially decaying signal envelope, yielding a much larger \( \sigma_\tau / \tau \) than for the case of single-mode excitation. Typically a single-shot value of \( \sigma_\tau / \tau \) of 1–5\% is found, up to two orders of magnitude higher than for single-mode excitation. Especially, when scanning over the frequency, the number of excited modes can change strongly depending on the overlap of the laser profile with the mode frequencies.

A solution to this problem is to couple in as many modes as possible, as also recognized by Meijer et al.\(^{44}\) In that case, as individual sets of modes show constructive or destructive mode beating, the ensemble of mode beats will roughly average out and a smooth exponentially decaying signal envelope will appear. Moreover, as there are always many modes in the cavity, scanning over the frequency will not drastically change the number of modes in the cavity. Consequently, the pulse-to-pulse fluctuations in \( \tau \) and thus the measurement uncertainty \( \sigma_\tau / \tau \) can be much smaller than for a few excited modes. The number of modes that are coupled into the cavity increases with the spectral and spatial width of the input laser. A broad-band laser with a broad spatial width is easy to obtain, while it has the additional advantage that a careful control of the spatial laser profile and a careful alignment of the laser beam with the cavity is not needed. It is noted that mode beating due to the finite size of the detector still needs to be avoided, limiting the spatial width of the laser profile. The number of modes that are coupled into the cavity increases also with the density of cavity modes in frequency space, thereby decreasing \( \sigma_\tau / \tau \). A uniform distribution of cavity modes in frequency space is more important, as this reduces the fluctuations in the number of cavity modes when scanning the frequencies. A uniform distribution of cavity modes also guarantees a constant large number of excited cavity modes. The density and uniformity of the cavity modes can be controlled by the design of the cavity. For the folded cavity, modes with a different longitudinal and transverse mode number are shifted multiples of \( \Delta f_l = c / 2 n L \) and \( \Delta f_{\nu j} = c / 2 n L \times \arctan \left( 2L / (2R_{\text{eff}} - L) \right) \), respectively, and therefore the distribution of modes can be controlled by carefully choosing the ratio of the cavity length \( L \) to the radius of curvature of the TIR surface \( R_c \). An example of such tuning of the radius of curvature for a given cavity length to obtain a dense, uniform distribution of cavity modes is given below. There, it is concluded that, when single-mode excitation cannot be achieved, one should choose a laser system to couple in as many modes as possible and design the cavity to yield a dense, uniform distribution of cavity modes.

**Tuning the distribution of cavity modes.**

For our folded cavity of fused silica \( (n = 1.44805 \text{ at } \lambda_c = 1200 \text{ nm}) \) with length \( L = 2 \) cm and angle of incidence \( \theta_i = 45^\circ \), the longitudinal modes are separated multiples of \( \Delta f_l = c / 2 n L = 5.2 \text{ GHz} \). The separation of the transverse modes in the sagittal and tangential plane are multiples of...
\[ \Delta f_s = \frac{c}{2nL} \times \arctan \left( \sqrt{\frac{2L}{(2R_c \cos(\theta) - L)}} \right) \] and \[ \Delta f_t = \frac{c}{2nL} \times \arctan \left( \sqrt{\frac{2L}{(2R_c \cos(\theta) - L)}} \right) \], respectively, and can be controlled by choosing the radius of curvature \( R_c \). Because the aim is a dense, uniform distribution of cavity modes frequencies, one first needs to know for which values of \( R_c \), two (or more) TEM\(_{mn}\) modes have the same frequency. This so-called 'degeneracy' of cavity modes occurs for the case that

\[ \Delta f_l = k \Delta f_s + l \Delta f_t, \]  

(35)

where \( k \) and \( l \) are integers. The solution to Eq. (35) is a set of radii of curvature, \( R_{c_{kl}} \), for which mode degeneracy will occur. These radii of curvature should be avoided to obtain a uniform distribution of modes in the cavity. This is illustrated in Fig. 6, which shows a so-called 'comb spectrum' of the TEM\(_{mn}\) modes of a folded cavity with \( n = 1.44805 \) at \( \lambda_c = 1200 \text{ nm} \), \( L = 2 \text{ cm} \), and \( \theta_i = 45^\circ \) for two cases (a) \( R_c = 9 \text{ cm} \) and (b) \( R_c = 5.08 \text{ cm} \). The figure shows clearly the difference in frequency shift between \( \Delta f_l \) and \( \Delta f_s \), which reflects the difference in Guoy phase shift between the sagittal and tangential plane. Moreover, it is noted that the absolute mode frequencies depend on the TE or TM polarization as well as the length and refractive index of the cavity [Eq. (34)], however, the comb spectra, which show the frequency shifts, are independent of these parameters.

Figure 6 shows clearly that the density of cavity modes is higher for \( R_c = 9 \text{ cm} \) than for \( R_c = 5.08 \text{ cm} \). In fact, the density of cavity modes increases monotonically with radius of curvature \( R_c \). The magnitude of \( R_c \), however, is usually restrained by other design and fabricational considerations. Nevertheless, small changes in \( R_c \) have a large impact on the uniformity of the cavity mode distribution. Figure 6(a) shows that for \( R_c = 9 \text{ cm} \), corresponding to \( \Delta f_s = 0.87 \text{ GHz} \) and \( \Delta f_t = 1.17 \text{ GHz} \), there is no mode degeneracy, i.e. the modes are uniformly distributed across the frequency space. On the other hand, for \( R_c = 5.08 \text{ cm} \) [Fig. 6(b)], which has been calculated with Eq. (35) using \( k = l = 2 \) and corresponds to \( \Delta f_s = 1.12 \text{ GHz} \) and \( \Delta f_t = 1.47 \text{ GHz} \), almost all modes are degenerate. When scanning the frequency spectrum to obtain an absorption spectrum, the fluctuations in the number of excited modes and thus in \( \tau \) are much larger for \( R_c = 5.08 \text{ cm} \) than for \( R_c = 9 \text{ cm} \). Therefore, to find a suitable value of \( R_c \) that yields a low measurement uncertainty \( \sigma_\tau / \tau \), all combinations of the integers \( k \) and \( l \) have been inserted into Eq. (35) to obtain the full set of radii of curvature, \( R_{c_{kl}} \), for which mode degeneracy occurs. This set of radii of curvature is shown in the inset of

![Fig. 6. Two so-called 'comb spectra' of the folded cavity, which show the frequency shift of the TEM\(_{mn}\) modes of order \( m + n \leq 14 \), relative to an arbitrary TEM\(_{00}\) mode, as calculated with Eq. (34) for a folded cavity with length \( L = 2 \text{ cm} \) and the radius of curvature of (a) \( R_c = 9 \text{ cm} \) and (b) \( R_{c_{22}} = 5.08 \text{ cm} \). In Fig. 6(a) the frequency shifts \( \Delta f_l = 5.2 \text{ GHz} \), \( \Delta f_s = 0.87 \text{ GHz} \) and \( \Delta f_t = 1.17 \text{ GHz} \) are indicated by arrows. The inset of Fig. 6(b) shows the set of radii of curvature, \( R_{c_{kl}} \), for which mode degeneracy occurs, as calculated with Eq. (35).](image-url)
Fig. 6(b). On the basis of this figure, a radius of curvature of $R_c = 9 \text{ cm}$ has been chosen [Fig. 6 (a)], which is significantly different from any value of $R_{c_k}$, while it is close to $R_c \approx 10 \text{ cm}$ to comply with other design considerations (Sec. IV).

The actual number of excited cavity modes is difficult to predict as it strongly depends on the degree of mode matching between the laser profile and the specific modes. However, of course only those cavity modes within the bandwidth of the laser can be excited. To illustrate the number of cavity modes that can be excited, the spectra are compared with the bandwidth of a number of specific laser systems. An optical parametric oscillator (OPO), an optical parametric oscillator with amplifier (OPA), a dye laser, and a Q-switched Nd:YAG laser that is injection seeded for operation in a single Gaussian TEM$_{00}$ mode typically have a bandwidth of $\sim 200$, $\sim 2.2$, $\sim 1$, and $\sim 0.09 \text{ GHz}$, respectively, although the bandwidths depend on the specific laser designs. The number of excited cavity modes scales with the bandwidth. Therefore, even though the OPO usually exhibits the largest pulse-to-pulse fluctuations in the laser profile, it is expected to yield the lowest value of $\sigma_{\tau}/\tau$. This counter-intuitive conclusion is in agreement with practical experiences.

IV. CHOICE FOR THE OPTIMUM FOLDED CAVITY DESIGN

The optical transition of the analyte of interest determines the probe wavelength $\lambda$ of operation and thereby the center wavelength of the folded cavity. The optical transition also determines the bulk material of the folded cavity as the bulk loss of material is generally strongly wavelength dependent. It is recalled from Sec. I that our aim is to design a folded cavity to enable real-time and in-situ detection of defect-related absorptions during thin film growth of hydrogenated amorphous silicon (a-Si:H). It has been demonstrated in Ref. 5 that defect-related absorptions, such as due to Si dangling bonds, can be probed at sub-gap energies in the range of $\sim 0.7$ to $\sim 1.4 \text{ eV}$ from a broadband absorption that exhibits a weak energy-dependence.

Therefore, the wavelength of maximum sensitivity for measuring dangling bonds is not so much determined by the absorption spectrum of the Si defects as it is determined by the intrinsic loss of the folded cavity. Consequently, the bulk material is chosen before the center coating wavelength. Fused silica is chosen as the material, because no other optical material matches its purity, yielding ultra-low bulk losses in the order of ppm's per cm over a wide spectral range. Moreover, the material is easily-polished allowing for an ultra-smooth surface roughness of $\sim 0.5 \text{ Å}$, while it is resistant to scratching and thermal shock. Furthermore, it has a very low thermal expansion coefficient, which facilitates temperature dependent studies. It is noted, however, that the ultra-low bulk losses are mainly achievable outside the energy regions of the relatively strong OH overtone and combination absorption bands. Regions of strong OH absorption are located, for instance, around $\sim 1400$ and $\sim 950 \text{ nm}$ (first and second overtone of the OH stretching mode) and induce large bulk OH losses as well as large surface losses, as caused by absorption of silanol (SiOH) structures at the H-terminated silica surface and by adsorbed water at the surface. While regions of strong OH absorption are best avoided, a few isolated surface silanol and water lines within the coating region are beneficial as they can enable a precise analysis of the surface state of the fused silica, especially as the energy of these transitions depends sensitively on the local environment of the surface groups.

In fact, the measurement sensitivity analysis of our folded cavity, addressed below, suggests that detection of OH (as well as CH) absorptions with submonolayer coverage could be possible even when probing higher overtone and combination transitions. Therefore, taking into account that the spectral width of the high reflectivity region of a dielectric coating is $\sim 15\%$ of the center wavelength, a center wavelength of the dielectric coating of $\lambda_c = 1200 \text{ nm}$ has been chosen. This yields a measurement range of at least 1125–1275 nm, while the estimated bulk loss at 1200 nm is $\ell_{\text{bulk}} \approx 5–20 \text{ ppm/cm}$. This wavelength range includes a number of optical transitions due to possible surface silanol groups, e.g., at $\sim 1225$ and
~1235 nm, and of adsorbed water, e.g., at ~1142 and ~1188 nm.\textsuperscript{47,48} Furthermore, also a number of CH transitions, e.g., the second CH stretching overtone at ~1190 nm,\textsuperscript{49} are located within the coating range, thereby allowing for various surface studies in the future.

The angle of incidence, $\theta_i$, is selected from a number of considerations. First, for decreasing angle of incidence towards the critical angle $\theta_c$, the electric field amplitude in the evanescent wave (rarer medium) for both polarizations ($E_{TE} = \hat{E}_i$, and $E_{TM} = \sqrt{\hat{E}_s^2 + \hat{E}_c^2}$) increases monotonically (Fig. 3), thereby increasing the measurement sensitivity. Second, for polarization-dependent studies, an angle of incidence as close as possible to the critical angle $\theta_c$ is preferred, as can be seen from Fig. 3: A transition moment perpendicular to the surface will only be detected by TM polarized light, independent of the other polarization.\textsuperscript{47,48} For both polarizations ($\hat{E}_i$), the transition moment parallel to the surface that is randomly oriented in azimuthal direction, the ratio of TE over TM absorption (i.e. the contrast in the polarization measurement) increases slowly for decreasing angle of incidence above $\theta_c = 50^\circ$, but increases sharply for $\theta_i$ approaching $\theta_c$ with no TM absorption (maximum contrast) at the critical angle. Third, for decreasing angle of incidence close to the critical angle, nonspecular losses $\sigma_{\text{nonspec}}$ become rapidly important (Sec. III). To exclude nonspecular losses, the angle of incidence should be chosen $>1^\circ$ above the critical angle, which is $\theta = -43.6^\circ$ for fused silica. Combining these considerations, an angle of incidence of $\theta = 45^\circ$ has been chosen, which also results in a straightforward design of the folded cavity. Moreover, to enable \textit{in-situ} use of the folded cavity our ultra-high vacuum setup has been designed with view ports under $45^\circ$ which is a convenient angle as view ports under $45^\circ$ can be shared by other diagnostics.

Selection of the unfolded length of the cavity $L$, is a trade-off between a lower bulk loss for a short cavity and a lower measurement uncertainty $\sigma_\tau/\tau$ for a longer cavity length. It is often experienced that $\sigma_\tau/\tau$ decreases with increasing $\tau$ up to $\tau = 1 \mu$s, but $\sigma_\tau/\tau$ remains roughly constant for $\tau$ increasing above $1 \mu$s. This lower limit of $\sigma_\tau/\tau$ can be understood from the fact that for large ring-down times $\sigma_\tau/\tau$ is no longer limited by the sampling resolution, but is determined by pulse-to-pulse fluctuations of the ring-down time $\tau$ itself. Therefore, the estimations of the different loss terms of the folded cavity (Sec. III) have been used to deduce the cavity length for which the ring-down time $\tau$ is more than $1 \mu$s for a wavelength range of ~1150 – ~1250 nm. This procedure yields a cavity length of $L = 2$ cm.

The radius of curvature $R_c$ needs to be chosen such that the stability condition for a stable resonator, i.e. $L/R_{\text{eff}} \in (0,1) \cup (1,2)$ in units of cm, is fulfilled. For $L = 2$ cm and $\theta_c = 45^\circ$, this leads to the constraint of $R_c \in (\sqrt{2}, 2\sqrt{2}) \cup (2\sqrt{2}, \infty)$ for combined stability in the sagittal and tangential plane. Within these constraints, $R_c$ is selected from the following considerations. In Sec. III, it was explained that the measurement uncertainty $\sigma_\tau/\tau$ decreases with the number of modes excited in the cavity, which increases for increasing $R_c$. Moreover, the different effective radius of curvature $R_{\text{eff}}$ in the sagittal and tangential plane (Sec. III) results in an astigmatic beam inside the cavity and therefore also an astigmatic beam that is coupled out of the folded cavity. An astigmatic beam is undesirable, because it results in a different focal plane position for each direction when focused by a spherical lens. The stronger the astigmatism, the further apart the two focal planes and the harder it is to focus the beam onto the detector. The degree of astigmatism reduces with increasing $R_c$. On the other hand, the fabrication uncertainty in the centration of the convex TIR surface is specified to be 10 arc minutes and increases for increasing $R_c$, while other fabrication uncertainties are less important. A centration error results in a shift of the (fixed) folded optical path of the folded cavity and therefore a shift of the TIR-spot, e.g., for $R_c = 10$ cm a centration error of 10 arc minutes results in a significant shift of the TIR-spot of ~0.3 mm. These considerations suggest a value of $R_c$ somewhere around 10 cm. In Sec. III, it was also explained that the measurement uncertainty $\sigma_\tau/\tau$ is decreases with an increasing uniformity of cavity modes in frequency space. Therefore, the precise value of $R_c$ is selected to yield a uniform distribution of cavity modes in frequency space. As shown in Sec. III, a radius of curvature of $R_c = 9$ cm meets the requirements for a low $\sigma_\tau/\tau$. 
Finally, the thickness of the folded cavity is only constrained by possible diffraction losses, as explained in Sec. III. There, it was argued that diffraction losses can be neglected when all apertures have a radius of at least 0.5 mm. To be safe, the radii of the clear apertures have been chosen 1.5 mm to include a margin for the shift of the (fixed) optical path due to a centration error and other fabricational errors. Including an additional fabricational margin of 1 mm above and below the aperture, the thickness of the folded cavity has been chosen at 5 mm.

The following optimum specifications of our folded cavity for detection of defect-related absorptions at $\lambda_c = 1200$ nm can be summarized:

1. The fused silica bulk material (suprasil 300, $n = 1.44805$ at $\lambda_c = 1200$ nm) with a path length of $L = 2$ cm yields an estimated bulk loss of $\mathcal{L}_\text{bulk} = 5 - 20$ ppm/pass. The convex surface has a radius of curvature of $R_c = 9$ cm, while its super-polished surface ($\sigma_{\text{RMS}} \approx 0.5$ Å) induces a surface loss $\mathcal{L}_\text{surf}$ of less than 0.3 ppm/pass for a clean surface. The mirror loss at the center wavelength of the coating is estimated to be $\mathcal{L}_\text{mirror} = 10 - 30$ ppm/pass in total, which includes a transmission loss of $\sim 5$ ppm/pass. The angle of incidence at the TIR surface is $\theta_i = 45^\circ$ and the clear apertures with a radius of 1.5 mm ensure that non-specular losses and diffraction losses can be neglected. These numbers of the different losses add up to a total intrinsic loss of $\mathcal{L}_0 = 20 - 50$ ppm/pass. Assuming a measurement uncertainty of $\sigma_{\tau/\tau} = 1\%$, a single-shot minimum detectable absorption of $\mathcal{L}_\text{min} = 0.2 - 0.5$ ppm/pass is obtained. However, $\sigma_{\tau/\tau}$ is expected to be lower than 1 %, because the choice for $R_c = 9$ cm yields a uniform distribution of cavity modes in frequency space.

2. These estimates of the loss terms can directly be compared with the monolithic folded cavity that was used by Pipino et al.\textsuperscript{18} to probe three chloroethylenes adsorbed at the TIR surface at their first CH stretching overtones at $\sim 1650$ nm. Specifications of this folded cavity are an unfolded per-pass length, a convex surface radius of curvature, and an angle of incidence at TIR surface of $L = 3$ cm, $R_c = 7.5$ cm, and $\theta_i = 45^\circ$, respectively. This longer path length of 3 cm and a thickness of 5 cm was chosen primarily to allow dosing of the TIR-spot by means of a gasket-sealed glass cell with liquid reservoir, while no care was taken in the choice of $R_c$ to obtain a uniform distribution of cavity modes. Their mirror reflectivity was specified at $R = 99.997\%$, but is probably also better estimated at $\mathcal{L}_\text{mirror} < 10$ ppm/pass, while for reasons that are the same as for our folded cavity surface, non-specular, and diffraction losses can be neglected for their cavity. Their main loss term was bulk loss at the suprasil 311 fused silica material,\textsuperscript{23} which has a $\sim 4$ times higher OH concentration than our suprasil 300 material,\textsuperscript{23} yielding an estimated bulk loss of $\mathcal{L}_\text{bulk} = 25 - 120$ ppm/pass. These numbers explain their reported total intrinsic loss of $\mathcal{L}_0 = 1.1 \times 10^4$ ppm/pass.\textsuperscript{18}

V. PROOF OF PRINCIPLE MEASUREMENTS

Using the afore-mentioned optimum design specifications of the folded cavity, a number of folded cavities have been fabricated by Research Electro-Optics.\textsuperscript{38} In this section, the estimated single-shot minimum detectable absorption of $\mathcal{L}_\text{min} = 0.2 - 0.5$ ppm/pass is compared to some preliminary ex-situ EW-CRDS measurements using the folded cavities. Tunable near-infrared (NIR) pulses are generated by an optical parametric oscillator (OPO) consisting of two beam-walk-compensating beta-Barium-Borate (BBO) crystals\textsuperscript{46} pumped by a 30 Hz, frequency-tripled, injection-seeded-Nd:YAG laser. As no grating is used in this laser system, the bandwidth of the NIR "idler" laser beam is $\sim 200$ GHz. Polarization and pulse-energy

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\textsuperscript{1} Additional design specifications are: pyramidal error between side surfaces within 30 arc seconds; centration of convex TIR surface within 10 arc minutes; and the surface quality and surface flatness of all optically-relevant surfaces are "superpolished" (0.5 Å) and "$\frac{1}{4}$ wavelength", respectively.
control of the NIR pulses are provided by a pair of Glan-Laser polarizing beam splitters with extinction ratios of $10^5$ separated by a double Fresnel rhomb rotator. The NIR pulses are focused by a lens onto the folded cavity to increase the spectral irradiance per cavity mode. However, no attempt has been made to mode match the spatially amorphous and temporally erratic idler beam, because mode matching prohibits a uniform distribution of cavity modes (Sec. III). The NIR ring-down transients emanating from the folded cavity are divided by a Glan-Laser polarizing beam splitter into a TE and TM polarized beam, which enables simultaneous detection of both polarization directions. Both beams are free-space focused with a doublet achromatic lens onto a high-speed InGaAs/PIN photodiode with an detector diameter of 0.3 mm (cf. Appendix A), where the lens and detector position have been determined using Eq. (35).

Figure 7 shows the baseline loss of our folded cavity for TE and TM polarization as a function of the wavelength, i.e. without applying an analyte to the TIR surface. Prior to the measurements, the TIR surface has been cleaned by a standard cleaning procedure for super-polished surfaces as described in Ref. 8. The overall shape of the optical loss as a function of the wavelength reflects the wavelength-dependent reflectivity of the dielectric mirrors. The peak reflectivity is found at $\lambda_c = 1202$ nm, close to the specified wavelength of 1200 nm. The lowest optical loss of ~19 ppm (ring-down time of $\tau \approx 5$ µs) is found at 1202 nm and is in the low end of the estimation of the intrinsic loss of $\varepsilon_0 \approx 20$–50 ppm/pass (Sec. IV). The inset in Fig. 7 shows the noise in the optical loss at $\lambda_c = 1202$ nm for 75 CRDS transient averages. The standard deviation of the noise is ~0.025 ppm/pass. This yields a minimum detectable absorption of $\varepsilon_{\text{min}} \approx 0.21$ ppm/pass for single laser shots at 1202 nm. This value is noticeably low and almost surpasses the estimated minimal detectable absorption of $\varepsilon_{\text{min}} \approx 0.2$–0.5 ppm/pass (Sec. IV). The measurement uncertainty at $\lambda = 1202$ nm is $\sigma_\tau/\tau \approx 0.1\%$, which is very low considering the low light intensity at the detector due to a transmission loss through the mirrors at 1202 nm of ~5 ppm/pass (Sec. III). This is corroborated by the fact that at the side of the spectrum ($\lambda = 1245$ nm), where light intensity at the detector is much higher, the measurement uncertainty has reduced to $\sigma_\tau/\tau \approx 0.5\%$, even though the ring-down time $\tau$ has also reduced with a factor of ~2. Combining the value of $\sigma_\tau = 0.0125$ µs at $\lambda = 1245$ nm with $\tau = 5$ µs at $\lambda_c = 1202$ nm one obtains the principally-obtainable single-shot measurement uncertainty of $\sigma_\tau/\tau \approx 0.25\%$. This value is very

** The complete extent of the wavelength range has not yet been tested as a result of the possible hazard of damaging the detector due to the higher mirror losses near the edges of the wavelength range.
Fig. 8. Absorption spectrum of a surface species, attributed to the combination of the first OH overtone (2νOH) occurring near 1365 nm with the OH in-plane bending mode (δOH) occurring above 10 µm, as measured for TM polarization with 75 averages per data point in each scan and averaged over 7 individual scans (the original scans are shown in the inset). The absorption spectrum has been isolated from the other losses of the folded cavity by subtracting the baseline, which has been determined by third-order polynomial fit through the average of the 7 spectra in the inset with the peak omitted from the spectrum.

low for pulsed laser CRDS, particularly when considering that no care has been taken to precise control the spatial and temporal profile of the laser pulses or mode matching the laser beam to the cavity. Therefore, this high measurement sensitivity seems to be a result of the beneficial influence of the large numbers of modes coupled in the cavity by using the broad-band OPO system and the uniform distribution of cavity modes in frequency space.

Figure 7 also clearly shows the presence of a number of absorption peaks in the spectra. For a detailed analysis of these absorption peaks, the reader is referred to the work of Aarts et al. They argue that the absorption peaks correspond to surface OH molecular transitions and the position and area of the absorption peaks is used to deduce detailed information on the nature of the surface. Figure 8 shows the absorption peak at ~1234 nm, measured for TM polarization, in more detail. In Ref. 51, this peak is attributed to the combination of the first OH overtone (2νOH) occurring near 1365 nm with the OH in-plane bending mode (δOH) occurring above 10 µm and it is argued that the peak corresponds to a sub-monolayer coverage of surface OH species. Therefore, the signal-to-noise ratio of this absorption peak shown in Fig. 8, with a height of only ~1 ppm, clearly illustrates the sensitivity of the folded cavity measurement technique for detecting surface species with sub-monolayer coverage. Figure 7 also shows that the absorption peak for TE polarization is shifted towards a considerably lower wavelength compared to TM polarization, which shows that the OH species must be preferentially oriented on the surface. Both these features of the folded cavity measurement technique have been explicitly demonstrated in the above-mentioned adsorption study of three chloroethylenes on an earlier version of the fused silica folded cavity.

Finally, it is noted that a good long-term stability in the folded cavity measurements of the absolute ring-down time is obtained, as shown by the good overlap between different measurements in Figs. 7 and 8. While the monolithic nature of the folded cavity inherently possesses a good long-term stability, ever-present long-term laser instabilities are apparently not reflected in the ring-down time, which may be attributed to the large number of excited cavity modes.

In-situ application of the folded cavities on the ultra-high vacuum setup Galapagos has also been demonstrated. To this end, a sophisticated substrate holder was designed and built that provides rotational freedom of the folded cavity in all three directions for alignment purposes. The alignment procedure was adapted to the new substrate holder, but the alignment, performed with the vacuum vessel open, remains
fairly easy. Moreover, the folded cavity remained aligned during pump-down of the reactor as well as during subsequent heating of the folded cavity to 150 °C.

With the measurement sensitivity clearly established, the detection limit for measuring dangling bonds with our folded cavity can now be estimated. An important notion here, however, is that the loss due to surface scattering \( \sigma_{\text{surf}} \) is expected to increase rapidly due to the development of surface roughness during the deposition of an a-Si:H film on the folded cavity. Hoefnagels et al.\(^5\) have measured that under optimum a-Si:H deposition conditions the root-mean-square roughness \( \sigma_{\text{RMS}} \) does not exceed 10 Å, corresponding to a surface loss of \( \sigma_{\text{surf}} \approx 100 \text{ ppm/pass} \) (Sec. III). This upper limit yields a minimum detectable absorption of \( \sigma_{\text{surf}} \approx 0.5 \text{ ppm/pass} \), with \( \sigma_{\text{RMS}} \approx 0.5 \text{ Å} \). Moreover, it is noted that Hoefnagels et al.\(^5\) also demonstrated that under certain conditions and at a certain bulk layer thickness the surface roughness of the a-Si:H film can decrease to \( \sigma_{\text{RMS}} \approx 1 \text{ Å} \). This corresponds to a minimum detectable absorption of \( \sigma_{\text{surf}} \approx 0.2 \text{ ppm/pass} \) with an a-Si:H film on the folded cavity, which is essentially equal to the clean super-polished TIR surface. Aarts et al.\(^5\) have measured an absorption due to dangling bonds at the a-Si:H surface of \( \approx 200 \text{ ppm/pass} \). When such an a-Si:H surface would be deposited on the folded cavity, the upper limit estimate of the minimum detectable absorption of \( \sigma_{\text{surf}} \approx 0.5 \text{ ppm/pass} \) still yields an estimated single-shot signal-to-noise ratio of \( \approx 400 \) in measuring the surface dangling bonds. This indicates that there is a margin for the surface dangling bond density to be much lower or the surface roughness to be much higher, while still preserving sufficient sensitivity to measure the surface dangling bonds. Aarts et al.\(^5\) have also measured the absorption due to dangling bonds in the bulk of an a-Si:H film. This bulk dangling bond absorption was only \( \approx 0.1 \text{ ppm/pass} \) per nanometer film thickness due to the much lower density of dangling bonds in the bulk a-Si:H material. Then, the upper limit estimate of the single-shot signal-to-noise ratio for measuring bulk dangling bonds in a 10 nm thick a-Si:H film is \( \approx 2 \), but can easily be increased by averaging over multiple laser shots.

The last issue to be addressed is the cleaning of a deposited a-Si:H thin film from the super-polished fused silica surface, as the ability to remove a grown a-Si:H layer from the super-polished fused silica surface in order to recover the original folded cavities is desirable. To test different chemical solvents and cleaning strategies, a series of super-polished, planar fused silica substrates have been coated with a high-quality a-Si:H film with a thickness of \( \approx 1 \mu \text{m} \). While organic solvents as well as acidic (buffer) solutions were not effective in removing the a-Si:H, the following procedure was found to yield the most promising results: (i) Immersion for 24 hours in a regularly-refreshed basic buffer solution (pH = 10.00) of deionized water, boric acid \([\text{B(OH)}_2]\), and potassium hydroxide \([\text{KOH}]\) to remove the complete a-Si:H film; (ii) thorough rinsing with ultra-pure water; (iii) immersion in ultrahigh-purity methanol (<0.1 ppm residue after evaporation) for two hours; (iv) the ‘standard’ cleaning procedure for super-polished surfaces described in Ref. 8. This cleaning procedure has not yet been optimized in terms of temperature, pH level, length of exposure, etc. Nevertheless, no significant difference in the total intrinsic loss was found between planar substrates that were deposited on and subsequently cleaned and planar substrates that were exposure prolonged to ambient conditions and subsequently cleaned. This was concluded from measurements of the baseline loss when placing the substrates in a linear CRDS cavity conform Ref. 19. Furthermore, visual inspection of the surface scattering of a green He-Ne laser beam at normal incidence has revealed areas on the substrate that are as smooth as the substrates that come directly from the factory.

VI. GENERAL CONCLUSIONS

A monolithic folded cavity has been designed to enable evanescent-wave cavity ring-down spectroscopy (EW-CRDS) detection of defect-related absorptions in-situ and real-time during thin film growth of a-Si:H. To come to the final design, a number of design considerations have been addressed,
including (i) the polarization-dependent electric field strength for the different directions in the evanescent wave and in a thin film on top of the folded cavity; (ii) the beam spot size inside the cavity; (iii) the stability criteria for a stable optical cavity; and (iv) the different optical loss terms that constitute the total intrinsic loss of the folded cavity, i.e. loss due to bulk attenuation, scatter loss at the TIR surface, non-specular effects, loss at the two dielectric mirrors, and diffraction losses at the apertures; and (v) the measurement uncertainty in the ring-down time \( \sigma_r/\tau \). Combination of these design considerations has resulted in a set of optimized design parameters, that yielded an estimated minimum detectable absorption of \( \ell_{\text{min}} \approx 0.2−0.5 \) ppm/pass for single laser shots. A number of folded cavities with a center coating wavelength at \( \lambda_c = 1202 \) nm have been fabricated in accordance with these design parameters. Baseline EW-CRDS measurement showed that the actual single-shot minimum detectable absorption almost surpassed the estimate with \( \ell_{\text{min}} \approx 0.21 \) ppm/pass, This low minimum detectable absorption is owed in part to the low single-shot measurement uncertainty of \( \sigma_r/\tau \approx 0.5 \% \), which was attributed to (i) the large number of optical modes coupled in the cavity, (ii) the uniform distribution of cavity modes in frequency space, and (iii) the separate handling procedure of the CRDS transients with subsequent averaging over the ring-down times. Finally, the single-shot signal-to-noise ratio for measuring surface and bulk dangling bonds in a 10 nm thick a-Si:H film was estimated to be ~400 and ~2, respectively.

**APPENDIX A: DETECTOR**

The most appropriate detector for our purpose of measuring near-infrared signals with low-noise is the free-space, DC-coupled, InGaAs/PIN photodiode (New Focus, model 1811, Ref. 40) with a bandwidth of 125 MHz, a current gain of 40 V/mA, a large detector diameter of 0.3 mm, and a large bandwidth with flat response. The frequency responsivity of the New Focus 1811 InGaAs/PIN photodiode is shown in Fig. 9. The figure shows that up to a wavelength of \( \sim 1600 \) nm the detector is efficient. Above a wavelength of 1600 nm CRDS experiments become increasingly difficult. An additional home-built transimpedance amplifier\textsuperscript{53} with a bandwidth of \( \sim 47 \) MHz is used to match the output range of the photodiode to the input range of the TU/eDACS system, discussed below. It is noted that the upper bandwidth of \( \sim 50 \) MHz is beneficial because this allows CRDS transients (\( \tau \geq 1 \) \( \mu \)s corresponding to a frequency of \(< 1 \) MHz) to be transmitted, whereas fast intensity fluctuations due to longitudinal mode beating (Sec. III) and other noise sources are blocked.

![Fig. 9. Responsivity of the New Focus 1811 InGaAs/PIN photodiode as a function of the wavelength, as taken from the New Focus manual.\textsuperscript{40}](image_url)
Fig. 10. Distribution graph of 2\(^{15}\) measurements of the ring-down time \(\tau\), each deduced from a separate CRDS transient. In the experiment, the fundamental laser pulses at 1064 nm of a unseeded Nd:YAG laser are injected in an empty linear cavity with a length of 16 cm. The mean value and standard deviation of the distribution are \(\tau = (3427.2 \pm 0.3)\) ns and \(\sigma_\tau = (50.2 \pm 0.2)\) ns, respectively, while the dashed lines indicate the range of \(\tau\) within 4 \(\sigma_\tau\) from the \(\mu\). Due to instabilities in the laser, \(-0.5\%\) of the laser pulses are outside the specifications, resulting in values of \(\tau\) far outside the 4 \(\sigma_\tau\)-range, as can be clearly observed in the semi-logarithmic plot (inset).

**APPENDIX B: SEPARATE CRDS TRANSIENT HANDLING**

In this section, the procedure used to process the CRDS transient to obtain the ring-down time \(\tau\) is tested for its accuracy. In the common approach of CRDS, a number of measured CRDS transients that each have an individual ring-down time \(\tau\) are added up to form a summed CRDS transient. This is, for instance, done when averaging CRDS transients on an oscilloscope. Subsequently, the summed CRDS transient is fitted to obtain an averaged ring-down time, \(\tau_{av,a}\). This procedure is denoted as averaging procedure "\(a\)". However, from a fundamental point of view, it is easily seen that the averaged ring-down time, \(\tau_{av,a}\), is not equal to ring-down time, \(\tau_{av,b}\), that is obtained by averaging the individual ring-down times \(\tau\). The latter procedure is referred to as averaging procedure "\(b\)". A simple mathematical calculation for a distribution of \(\tau\)'s with a standard deviation of \(\sigma_\tau = 1\%\) learns that \(\tau_{av,a}\) is \(-0.1\%\) higher than \(\tau_{av,b}\). Furthermore, in averaging procedure \(a\) every transient is used, while it is well-known that occasionally laser pulses fall outside the laser specifications due to ever-present instabilities in laser systems. Therefore, laser manufacturers often only specify the laser characteristics for 99 out of 100 laser pulses. The "bad" laser pulses can have a very different beam profile or light intensity. Although CRDS is in principle independent of the light intensity, such bad laser pulses can still result in an erroneous ring-down time. This is demonstrated by a simple CRDS experiment, in which the fundamental laser pulses at 1064 nm of an unseeded Nd:YAG laser are injected in an empty linear cavity consisting of two mirror with \(R = 0.99985\) that are separated \(-16\) cm. Figure 10 shows the distribution of the 2\(^{15}\) ring-down times \(\tau\)'s with a mean value and standard deviation of \(\mu = (3427.2 \pm 0.3)\) and \(\sigma_\tau = (50.2 \pm 0.2)\) ns, respectively, corresponding to a single-shot measurement uncertainty of \(\frac{\sigma_\tau}{\mu} = (1.465 \pm 0.006) \times 10^{-2}\). Approximately, 0.5% of the laser pulses fall outside the 4 \(\sigma_\tau\)-interval, i.e. \((\mu - 4 \sigma_\tau \ldots \mu + 4 \sigma_\tau)\), much more than the expected 0.006% corresponding to a normal distribution. Therefore, in averaging procedure \(b\), all \(\tau\)'s outside the 4 \(\sigma_\tau\)-interval are considered "bad" and are discarded and only the good \(\tau\)'s within the 4 \(\sigma_\tau\)-interval are used to calculate of \(\tau_{av,b}\). Of course, in averaging procedure \(a\), the bad transients can not be discarded.

To investigate the influence of the averaging procedure \(a\) and \(b\) on the value of the measurement uncertainty \(\frac{\sigma_\tau}{\mu}\), a group of 16 transients has been measured and averaged with procedure \(a\) and \(b\) to obtain
Fig. 11. Distribution graph of the 16-times-averaged ring-down time $\tau_{av}$ as obtained by using averaging procedure a and b. In averaging procedure a, the 16 CRDS transients are added to a single CRDS transient, from which $\tau_{av,a}$ is deduced.

In averaging procedure b three steps are performed: (i) from the 16 transients the individual ring-down times $\tau_i$ are determined, (ii) the values of $\tau_i$ outside 4 $\sigma_\tau$ from $\tau_\tau$ are considered "bad" and are discarded, (iii) the remaining $\tau_i$'s are averaged to obtain $\tau_{av,b}$. The solid bars above the distribution graphs show the mean value $\tau_\tau$ and standard deviation $\sigma_\tau$ of the distribution graphs, yielding $\tau_{av,a} = (3429.3 \pm 0.4)$ ns and $\sigma_{av,a} = (17.6 \pm 0.3)$ ns for averaging procedure a and $\tau_{av,b} = (3432.0 \pm 0.3)$ ns and $\sigma_{av,b} = (12.7 \pm 0.2)$ ns for averaging procedure b.

The 16-times averaged ring-down time $\tau_{av,a}$ and $\tau_{av,b}$, respectively. This procedure has been repeated $2^{11}$ times to obtained a distribution graph of $2^{11} \tau_{av,a}$'s and a distribution graph of $2^{11} \tau_{av,b}$'s, shown in Figs. 11(a) and 11(b), respectively. The mean value $\tau_\tau$ and standard deviation $\sigma_\tau$ of these distribution graphs are $\tau_{av,a} = (3429.3 \pm 0.4)$ ns and $\sigma_{av,a} = (17.6 \pm 0.3)$ ns for distribution graph a and $\tau_{av,b} = (3432.0 \pm 0.3)$ ns and $\sigma_{av,b} = (12.7 \pm 0.2)$ ns for distribution graph b. The value of $\tau_{av,a}$ is ~0.1% higher than $\tau_{av,b}$ in agreement with the above-mentioned simple mathematical calculation, which clearly illustrates that average procedure a yields a principally wrong measurement of the ring-down time, resulting in a small error in the measured absolute absorption. Moreover, the single-shot measurement uncertainty can be obtained from $\sigma_{i/\tau} = \sqrt{0.03 \times \sigma_{av}} / \tau_{av}$ and is $\sigma_{i/\tau} = (2.05 \pm 0.03) \times 10^{-3}$ and $\sigma_{i/\tau} = (1.48 \pm 0.02) \times 10^{-3}$ for distribution graph a and b, respectively. The latter value of $\sigma_{i/\tau}$, obtained with averaging procedure b agrees perfectly with the value of $\sigma_{i/\tau}$ found above for the distribution graph of Fig. 10, whereas the former value of $\sigma_{i/\tau}$ is a factor 1.39 higher, reflecting the fact that the bad transients have not been discarded in averaging procedure a. In other words, a gain in sensitivity of 1.39 is obtained by using our separate CRDS transients handling procedure (procedure b) instead of the common approach of using an oscilloscope (procedure a). This gain in sensitivity depends on the number of CRDS transients that are being averaged, $N$. Therefore, Fig. 12 shows the gain in CRDS sensitivity as a function of $N$, where each data point is computed from a new set of CRDS transients. The gain in CRDS sensitivity increases with increasing $N$ and can readily become as large as 4 for high values of $N$. A gain in sensitivity of 4 corresponds to a 16 times shorter measurement time needed for averaging procedure b to yield the same measurement uncertainty $\sigma_{i/\tau}$.

Averaging each CRDS separately also opens up the possibility of suppressing low-frequency noise sources in the ring-down time. In general, a CRDS measurement of the absorption loss requires at least one measurement of $\tau$ with and one without the analyte in the cavity. Therefore, when the presence of the analyte can be switched on and off as fast as the repetition rate $f$ of the laser pulses, 2 laser pulses suffice to complete an absorption measurement and the noise with a frequency of lower than $f/2$ will be suppressed. For instance, in Ref. 54 the density of SiH radicals in the gas phase CRDS cavity is modulated at a rate of 5 Hz, half the laser frequency, suppressing noise components below 5 Hz.
APPENDIX C: DATA ACQUISITION SYSTEM

From an experimental point of view, averaging procedure b requires a data acquisition system that can digitize and process each individual CRDS transient in real time to compute the ring-down times $\tau_i$ and subsequently calculate averaged ring-down time $\tau_{av_b}$. The TU/eDACS data acquisition system meets these requirements. It is a highly versatile modular system that can be equipped with a number of function-specific modules to enable complicated real-time measurements and experimental control. A state-of-the-art 100 MHz, 12-bit transient recorder has been installed to digitize the CRDS transients, thereby overcoming the previously-unavoidable compromise in either time resolution or measurement precision. The time resolution can even be improved in an easy way by exchanging the transient recorder for the latest 400 MHz, 12-bit version. Equipped with a multi-purpose memory unit and a digital signal processor unit, the TU/eDACS system provides the ability to calculate the ring-down time $\tau$ by applying a weighted least-squares fit to the logarithm of the CRDS transient with a maximum repetition rate of up to 2 kHz. In the case that a high degree of freedom is wanted in processing the CRDS data, the CRDS transients can also be transported from the TU/eDACS system to a host computer by means of the Serial Highway protocol with a repetition rate of ~30 Hz, depending on the size of the transients. To obtain the individual ring-down times, the transients can then be processed on the host computer by a commercial measurement control software package, such as LabVIEW™, that also offers full operational control of the experiment.

REFERENCES


Fig. 12. The gain in sensitivity of the CRDS experiment, when using procedure b instead of procedure a to average the CRDS transients, as a function of the number of CRDS transients that have been averaged, $N$. Two CRDS cavity lengths have been used, i.e. 16 cm (open circle) and 36 cm (solid circle). The dashed line is a guide to the eye.
CHAPTER 6

ABSOLUTE SURFACE COVERAGE MEASUREMENT USING A VIBRATIONAL OVERTONE*

ABSTRACT

Determination of absolute surface coverage with sub-monolayer sensitivity is demonstrated using evanescent-wave cavity ring-down spectroscopy (EW-CRDS) and conventional CRDS by employing conservation of the absolute integrated absorption intensity between gas and adsorbed phases. The first C-H stretching overtones of trichloroethylene (TCE), cis-dichloroethylene (c-DCE), and trans-dichloroethylene (t-DCE) are probed using the idler of a seeded optical parametric amplifier having a 0.075 cm⁻¹ line width. Polarized absolute adsorbate spectra are obtained by EW-CRDS using a fused-silica monolithic folded resonator having a finesse of 28500 at 6050 cm⁻¹, while absolute absorption cross sections for the gas phase species are determined by conventional CRDS. A measure of the average transition moment orientation on the surface, which is utilized for the coverage determination, is derived from the polarization anisotropy of the surface spectra. Coverage measurement by EW-CRDS is compared to a mass-spectrometer-based surface-uptake technique, which we also employ for coverage measurements of TCE on thermally grown SiO₂ surfaces. To assess the potential for environmental sensing, we also compare EW-CRDS to optical waveguide techniques developed previously for TCE detection.


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I. INTRODUCTION

High-finesse optical resonators significantly enhance spectroscopic sensitivity, providing new opportunities for novel fundamental studies and applications. Cavity ring-down spectroscopy (CRDS) is a prevalent resonator-enhanced technique that uses the photon decay rate of an ultra-low-loss resonator to probe weak absorptions or low number densities. In essentially all implementations of CRDS, a stable optical resonator is employed, supporting low-diffraction-loss, self-replicating optical modes. A laser light pulse with carrier frequency $\omega$, is injected into the resonator to excite one or more modes that decay in intensity or “ring down” at a rate given by

$$\kappa(\omega) = \frac{1}{\tau(\omega)} = \frac{1}{t_r} \left[ \sum_i \ell_i(\omega) + \ell_{abs}(\omega) \right],$$

(1)

where $\Sigma \ell_i(\omega)$ is the sum of intrinsic resonator losses, $\ell_{abs}(\omega)$ is absolute analyte extinction, and $t_r = n L / c$ is the per-pass light propagation time in the resonator of length $L$ having refractive index, $n$. In practice, the decay times with and without analyte, $\tau(\omega)$ and $\tau_o(\omega) = t_r (\Sigma \ell_i(\omega))^{-1}$, respectively, are measured which determine $\ell_{abs}(\omega)$ with a minimum of two laser pulses. CRDS provides a typical dynamic range of $10^{-7} \leq \ell_{abs} \leq 10^{-3}$, where the detection limit is determined by the product of the total intrinsic loss and the fractional uncertainty in $\tau_o(\omega)$. While CRDS provides a considerable gain in sensitivity, facile measurement of absolute optical loss is also a significant capability, yielding absolute absorption cross sections, number densities, and reaction rate constants. Here, we exploit the sensitivity and absolute measurement capability of CRDS to determine absolute sub-monolayer surface number densities using a vibrational overtone.

While most CRDS studies have probed gas phase species using a conventional linear optical resonator, novel extensions of the technique have included studies of a sub-monolayer adsorbate, thin films, a thin liquid channel, bulk liquids, fibers, and nanoparticles, often employing unconventional resonator configurations. Guided by the Fresnel equations, some configurations have utilized the Brewster angle or total internal reflection (TIR) to admit intra-cavity elements or interfaces that facilitate sampling while maintaining a low intrinsic loss. In principal, the Brewster angle provides unit transmission through intra-cavity interfaces for modes with transverse magnetic (TM) polarization, although high losses are incurred for transverse electric (TE) modes, precluding determination of absorber orientation or absolute coverage on the element surface. Alternatively, TIR provides extremely low-loss ($\approx 10^{-6}$), broadband reflection for both TE and TM polarizations. Having an enhanced surface electric field with a tunable direction, the associated evanescent wave provides a well suited probe of adsorbrates, films, or particles as employed in evanescent-wave CRDS (EW-CRDS). EW-CRDS has been implemented through several resonator designs including direct extensions of the linear resonator with intra-cavity elements, a monolithic folded resonator, and a monolithic TIR-ring resonator, while whispering-gallery-mode spherical resonators could also be employed in a similar mode. Readily miniaturized with no intra-cavity interfaces, the monolithic resonators provide the lowest intrinsic loss (highest sensitivity), which is typically bulk-loss limited. Free of optical coatings that limit spectral bandwidth, the TIR-ring and spherical resonators are also broad-band devices, although a comparatively complicated photon-tunneling mechanism is utilized for excitation. The monolithic folded resonator, which permits direct excitation of cavity modes through a coated surface as in conventional CRDS, provides a very stable and convenient design, despite the coating-limited bandwidth. As both TE and TM modes have high finesse for the monolithic resonators, adsorbate orientation and absolute coverage can be probed.
The measurement of absolute surface coverage is fundamental to surface science, providing key information for the elucidation of adsorption geometries and reaction stoichiometries. A variety of strategies have been employed to measure absolute coverage including several mass-spectrometer-based techniques, Rutherford back-scattering spectrometry (RBS), X-ray methods, and STM. Many strategies require UHV or provide an indirect or ex-situ measurement. The development of an optical technique for absolute coverage measurement would eliminate the need for UHV and increase access to this often decisive information. In contrast to X-ray absorption cross-sections, optical absorption cross sections typically show large changes at a given wavelength between different chemical environments. Yet the integrated absorption being proportional to the oscillator strength of a transition is essentially conserved, showing relatively small variations between different chemical environments, which can often be modeled. However, while optical absorption is readily used for relative coverage measurements, determination of absolute coverage is complicated by baseline uncertainties and instrumental bandpass effects. As CRDS-based methods provide the absolute loss directly, baseline subtraction uncertainties are essentially eliminated given an isolated absorption band that is contained within the high-finesse bandwidth of the resonator, although some residual error can be incurred from low-frequency noise sources. CRDS also employs relatively narrowband laser sources that eliminate complications arising from finite bandpass effects, which are a major consideration in the determination of absolute intensities by conventional absorption methods. Therefore, the exploration of optical measurement of absolute coverage by CRDS-based techniques appears propitious with EW-CRDS in particular providing both sub-monolayer sensitivity and a requisite measure of surface orientation.

While for dipole-allowed electronic transitions sub-monolayer detection is readily achieved with EW-CRDS, sub-monolayer detection using most vibrational overtones is more challenging due to their comparatively small absorption cross-sections. Yet in the near IR where many vibrational overtones occur, the bulk attenuation of optical-communication-grade fused silica falls precipitously to achieve the well know minimum of $\lambda=1\times10^6$ loss/cm around $\sim1550$ nm, creating auspicious conditions for sub-monolayer detection by EW-CRDS. Further, in contrast to many electronic transitions, the absorption bandpasses of vibrational overtones for gas, liquid, and adsorbed phases typically fit within the coating-limited bandwidth often encountered in CRDS measurements, allowing unambiguous baseline subtraction for all phases. Hence, conservation of the integrated band intensity can be readily implemented using vibrational overtones in the NIR to determine absolute sub-monolayer surface coverages. Furthermore, vibrational overtones provide a high degree of chemical specificity and increased conformational resolution, while NIR operation assures fiber-optic compatibility for chemical sensing applications.

In the following, we demonstrate the measurement of absolute surface coverage using a narrowband, pulsed NIR source to probe the first C-H stretching overtones of trichloroethylene (TCE), cis-dichloroethylene (c-DCE), and trans-dichloroethylene (t-DCE). Conventional CRDS measurements provide absolute absorption cross sections for the overtone bands of the gas phase species, which for c-DCE and t-DCE are compared to recent ab initio local mode calculations. Using a fused-silica monolithic folded resonator, EW-CRDS measurements provide polarized spectra for the adsorbed chloroethylenes. The absolute surface coverages are found from conservation of the integrated band intensities using average molecular tilt angles that are derived from the polarization anisotropies of the adsorbate spectra. To emphasize the unique capabilities and limitations of absolute coverage measurement by EW-CRDS, we contrast the technique with a mass-spectrometer-based uptake method, which is also employed here for absolute coverage measurements of TCE on thermally grown SiO$_2$ on Si(100). In addition, as TCE is a prevalent environmental contaminant, the sensitivity of EW-CRDS for detection of TCE in the NIR is compared to previous waveguide-attenuated-total-reflectance measurements.
Fig. 1. In (a) the optical configuration for CRDS and EW-CRDS measurements is shown (TP, GL, DFR, BD, DM, L, HR, TRP, DC, and DET correspond to turning prism, Glan-Laser polarizing beam splitter, double Fresnel rhomb, beam dump, dichroic mirror, lens, high reflectivity mirror, tilt-rotation platform, dosing cell, and detector, respectively). An optical parametric oscillator/amplifier (OPO/OPA) provides near-IR pulses for the CRDS measurements, which employ the intra-cavity flow cell, and the EW-CRDS measurements, which employ a monolithic folded resonator (MFR). In (b) the monolithic, folded resonator is shown in more detail. Two high-reflectivity-coated planar surfaces and a convex TIR surface form the stable resonator, which is fabricated from a single block of high-purity fused silica. Light is injected into one planar surface and the residual transmission is detected through the second planar surface. An evanescent wave emanates from the apex of the TIR surface to form the sensing region, which has dimensions defined by the resonator-mode spot size.

II. EXPERIMENT

A schematic diagram of the experimental configuration used for both CRDS and EW-CRDS is shown in Fig. 1(a). The tunable NIR pulses are generated by an optical parametric amplifier (OPA) consisting of two beam-walk-compensating beta-barium-borate (BBO) crystals, pumped by a 10 Hz, frequency-tripled, injection-seeded -Nd:YAG laser, which also pumps a 0.075 cm\(^2\) line width optical parametric oscillator (OPO) that seeds the OPA at the signal wavelength. Initial separation of idler from signal is accomplished with a dichroic beamsplitter, while residual signal and pump-laser harmonics are extinguished beyond detection with glass filters. Polarization and pulse-energy control are provided by a pair of Glan-laser polarizing beamsplitters with extinction ratios of 10\(^5\) separated by a double Fresnel rhomb rotator. For both the CRDS and EW-CRDS measurements the NIR ring-down transients are free-space coupled to a high-speed, 125 MHz bandwidth, InGaAs detector with a 300 µm diameter. The output of the detector is digitized by a 12-bit, 50 MHz, PC-based data acquisition board. Individual ring-down times are extracted using a weighted least-squares fit and then averaged.

The gas phase CRDS measurements are performed with a linear resonator and an intra-cavity double-Brewster-window flow cell, similar to that described elsewhere. Gimbal-mounted concave mirrors with a radius of curvature of 1 m and a maximum reflectivity specified as R = 99.997 % at 1650 nm are separated by 37 cm to form the linear resonator. A mode-matching lens is employed to excite a small number of low-order modes. The intra-cavity flow cell consists of a pair of low-OH fused-silica optical flats (2.54 cm dia. \(\times\) 0.635 cm) with surface roughness of <0.1 nm rms on one side and \~0.4 nm rms on the other (WavePrecision, Moorpark, CA). The optical flats are gasket-sealed to a stainless-steel vacuum bellows with terminal flanges cut approximately at Brewster’s angle (~55.4\(^\circ\)). The modified flanges are supported by kinematic mounts to provide angular adjustment near Brewster’s angle. To generate a known concentration of analyte, a gravimetrically calibrated diffusion vial (0.5 cm orifice; 2.54 cm neck length) is
located inside a glass U-shaped tube having inlet and outlet ports, which is maintained at 30.3±0.1 °C in a temperature-controlled enclosure. A 250 liter liquid N\textsubscript{2} Dewar with a gas purifier ([H\textsubscript{2}O] ≤ 10\textsuperscript{10} mol/L) provides a dry nitrogen carrier gas stream through ¼ in., electro-polished, stainless-steel tubing to a mass flow controller (10–1000 cm\textsuperscript{3}/min) which delivers a known flow through the U-tube and subsequently the intra-cavity cell.

For the EW-CRDS measurements, a fused-silica (Amersil 311) monolithic folded resonator (REO, Boulder, CO) is employed similar to that described previously\textsuperscript{22,66} As shown schematically in Figure 1b, the folded resonator has two high-reflectivity-coated planar surfaces and a convex TIR surface. The unfolded per-pass length, convex surface radius of curvature, and incident angle, at the TIR surface, are 3.0 cm, 7.5 cm, and 45.0°, respectively. The reflectivity of the two planar, coated surfaces is specified as R=99.997 % at 1650 nm. The convex TIR and coated surfaces are polished to ~0.05 nm rms surface roughness. The incident beam with typically 1–3 mJ per pulse is weakly focused on the coated surface, although no particular effort is made to mode match the spatially amorphous and temporally erratic idler beam. The minimum loss per pass is 1.1×10\textsuperscript{-4}, which provides an adequately long ring-down time of 1.3 µs. The resonator is mounted on a platform that provides control of all degrees of freedom relative to the incident laser beam. The weakly astigmatic Gaussian output beam of the resonator is collected with an anti-reflection-coated doublet lens and imaged onto the high-speed InGaAs detector. The detector is mounted on a sub-platform that provides control of all degrees of freedom relative to the resonator. Gaussian beam calculations provide the initial cavity-to-lens and lens-to-detector distances for optimum signal collection at the 300 µm diameter detector. The TIR surface is dosed under equilibrium conditions at the room temperature (22.0±0.5 °C) vapor pressure of the haloethylenes (9.794×10\textsuperscript{3} Pa, 2.705×10\textsuperscript{4} Pa, and 4.443×10\textsuperscript{4} Pa, for TCE, c-DCE, and t-DCE, respectively at 25 °C)\textsuperscript{66} by employing a glass cell with a liquid reservoir that is gasket-sealed to the convex surface. For TCE, 18 TE-polarized spectra and 16 TM-polarized spectra were averaged, where each spectrum employed a 0.1 nm signal-wave step size and a 25 shot average/point. For c-DCE, 4 TE- and 4 TM-polarized spectra were averaged, while for t-DCE, 5 TE- and 3 TM-polarized spectra were averaged, both employing a 0.030 nm signal-wave step size and a 25 shot average/point. The absolute surface coverage for TCE on an SiO\textsubscript{2} surface is also determined from mass-spectrometer-based uptake measurements. The technique employed is similar to that described by Sanabia \textit{et al.}\textsuperscript{67} which is based on previous work by Yates and co-workers.\textsuperscript{43-45} Although differences in dosing and surface conditions complicate a direct comparison of the coverage results with the EW-CRDS measurements, it is useful to contrast the two techniques. The samples are formed from Si (100) single crystals, which are cleaned by the low temperature cleaning method of Ishizaka \textit{et al.}\textsuperscript{68} Oxidation of the Si surfaces is performed under the conditions reported by Watanabe \textit{et al.}\textsuperscript{69} to produce an oxide layer with an approximate thickness of 0.63 nm. The uptake measurements are conducted in a UHV system incorporating a temperature-controlled sample manipulator, a dosing system, and a quadrupole mass spectrometer. The dosing system consists of a gas manifold and injection system. The manifold contains a small, known volume (1.7 mL) which is pumped out by the UHV pumping system and then backfilled with sample vapor at a measured pressure (±133 Pa) and temperature (25±0.5 °C), thereby providing a known number of molecules, assuming ideal gas behavior. The known dose is then discharged through a stainless-steel (Type 316) nozzle with a 1/16 in. inner diameter onto the sample located approximately 1 cm away in the UHV chamber at normal incidence. To obtain the absolute coverage, the time-integrated mass spectrometer response to a dose of \(N_o\) molecules is determined under two conditions: 1) for TCE-saturated conditions (sample and surroundings) where no net adsorption is expected and 2) for a freshly cleaned sample surface. If the mass spectrometer response to dose \(N_o\) for a saturated-surface is \(f_{sat}(t)\) and for a clean surface is \(f_{cln}(t)\), then the absolute coverage is obtained from
\[
N_{\text{abs}} = \frac{N_s}{A_s} \left( 1 - \frac{\int f_{\text{sat}}(t)dt}{\int f_{\text{sat}}(t)dt} \right),
\]

where \( A_s \) is the sample area. In practice, the saturation response is determined for several dose sizes until a linear calibration curve is found, which indicates saturation is achieved. The slope of the calibration curve then provides \( (1/N_s) \int f_{\text{sat}}(t)dt \). The clean surface response is obtained after heating the sample to 610 °C for 5 minutes in the UHV system, followed by cooling to room temperature. A potential determinant error in the measurement comes from adsorption to adjacent surfaces that are also heated during the cleaning cycle. To examine this effect, the sample cleaning step is accomplished with two heating systems having different dimensions. In one, a W filament (8 in. length, 0.008 in. diameter) with ceramic insulation is used as a radiative heat source. Located below the sample under a Mo heat shield, the W filament heater can achieve a 970 K sample temperature for an 80 W input power. The second system employs a UHV compatible “button” heater (HeatWave Labs, Inc., Model 101137), with a 0.5 in. diameter Mo body, which provides an upper limit of 940 °C. The sample sizes used with the W filament and button heater were 1.32×0.51 cm and 0.89×0.89 cm, respectively. The relative standard deviation for a group of measurements using either heater is typically ~20–~30%.

III. RESULTS AND DISCUSSION

Figure 2 shows the absolute cross sections for the first C-H stretching overtones of TCE, c-DCE, and t-DCE. In Fig. 2(a), the cross section for TCE reveals a peak value of \( 8.31 \times 10^{-21} \) cm\(^2\)/molecule at \((6091.2 \pm 0.2) \) cm\(^{-1}\) along with a secondary maximum at \((6082.6 \pm 0.2) \) cm\(^{-1}\), though no rotational fine structure is observed. Using sub-Doppler optothermal spectroscopy (OTS), Platz and Demtröder similarly observed two peaks for TCE at 6092 cm\(^{-1}\) and 6084 cm\(^{-1}\) with line widths of ~10 cm\(^{-1}\), possessing no rotational fine structure. Because the lack of fine structure observed in Fig. 2(a) is confirmed by sub-Doppler OTS, molecular physics accounts for the lack of structure, clearly indicating that the 0.075 cm\(^{-1}\) laser line width does not significantly affect the band shape. Platz and Demtröder tentatively assigned the peaks to P- and R-branches, while the suppression of rotational fine structure was explained by invoking a broad radiationless-transition line width relative to the small rotational level spacing arising from the heavy Cl atoms. In Fig. 2(b), the absolute cross section for c-DCE is shown, which also reveals a distinct lack of rotational structure, whereas in Fig. 2(c), the results for t-DCE show partially resolved, rather broad rotational lines. Although we have not found independent confirmation that the observed lack of rotational structure or broad rotational peaks for c-DCE and t-DCE, respectively, are free of laser line width effects, we nonetheless assume the 0.075 cm\(^{-1}\) laser line width is sufficiently narrow for our purposes.

Table I shows the integrated absolute cross sections for TCE, c-DCE, and t-DCE as determined from the CRDS measurements in Fig. 2, along with calculated values for the DCE isomers taken from work of Takahashi et al. for comparison. From the CRDS measurements, the integrated absolute cross sections are determined by

\[
A_o = \frac{1}{n_s l c} \int L_{\text{abs}}(\omega) d\omega = \frac{\omega_o}{n_s l c} \int \omega L_{\text{abs}}(\omega) d\omega,
\]

where \( n_s \), \( l_c \), \( \omega_o \), and \( \Gamma_o \) are the number density, cell path length, wave number at band maximum, and the logarithmic integration of the absolute cross section, respectively. The integrated intensities can be determined by either integration with respect to frequency to yield \( A_o \) or by logarithmic integration to yield \( \Gamma_o \).
Fig. 2. The absolute cross-sections for the first C-H overtones of (a) TCE, (b) cis-DCE, and (c) trans-DCE are shown. The corresponding integrated cross sections are given in Table I. The inset in (b) shows the weak sideband occurring around 6010 cm$^{-1}$ for cis-DCE, which appears to reproduce the main feature.
Although we provide $A_o$ values for comparison to the calculations of Takahashi et al., we use $\Gamma_o$ to obtain absolute surface number densities for its theoretical advantages, although at high wavenumbers the difference is rather small. Takahashi et al. calculated the integrated cross sections for the C-H stretching overtones of c-DCE and t-DCE using a local mode model in which both the potential energy surface and the dipole moment function were determined from \textit{ab initio} calculations. These authors sought to explain the deviation of the t-DCE cross section from the trend observed by Burberry et al. of a characteristic (molecule-independent) integrated cross section per C-H bond for the second through sixth overtones. Finding the vibrational wavefunctions for two DCE isomers to be essentially identical, Takahashi et al. explained the experimental discrepancy through a significant difference in the calculated dipole moment functions. While their calculated intensities were found to consistently overestimate the available liquid phase experimental data, agreement improved considerably above the first overtones. Comparing $A_{\text{calc}}$ to $A_o$ in Table I, we also note that the calculated values overestimate the experimental values for the first overtone in the gas phase. Furthermore, the cis and trans integrated cross sections measured by CRDS are not as disparate as reported for higher overtones, having the ratio $(A_o)^{\text{cis}}/(A_o)^{\text{trans}} = 1.09$, which is closer to the ratio for the fundamentals of ~1.

Table I. Gas phase integrated absolute cross sections.

<table>
<thead>
<tr>
<th></th>
<th>$A_o$ a</th>
<th>$\Gamma_o$ b</th>
<th>$A_{\text{calc}}$ c,d</th>
<th>$\omega_o$ d</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>1.70</td>
<td>2.8</td>
<td>...</td>
<td>6091.1</td>
</tr>
<tr>
<td>c-DCE</td>
<td>2.50</td>
<td>4.11</td>
<td>3.10</td>
<td>6075.7</td>
</tr>
<tr>
<td>t-DCE</td>
<td>2.28</td>
<td>3.77</td>
<td>2.37</td>
<td>6077.3</td>
</tr>
</tbody>
</table>

a Units of $10^{-19}$ cm/molecule.

b Units of $10^{-23}$ cm$^2$/molecule.

c From Ref. 62.

d Position of band maximum in cm$^{-1}$.

Figure 3 shows the absolute evanescent wave (EW) absorption spectra for the haloethylenes obtained with the folded resonator for TE and TM polarizations, after subtraction of the resonator intrinsic loss. The insets of Fig. 3(a) show the raw data for TCE and the baseline intrinsic loss, prior to subtraction. The baseline loss was established by fitting the average of multiple scans to a third-order polynomial. Small, constant baseline offsets as seen for TM polarization in the Fig. 3(a) inset, which likely arise from surface contamination, were removed. The EW spectra consist of contributions from both adsorbed species and gas phase species. Superimposed on each EW spectrum in Fig. 3 is the estimated gas phase contribution (grey lines) to the spectrum, which is determined using the peak absolute cross section for each species from Figure 2 and the calculated effective thickness for TM and TE evanescent waves. For the fused-silica folded resonator with a 45° angle of incidence at the TIR surface, the effective thickness for TM polarization is precisely twice the value for TE polarization. In Fig. 4, the gas phase contributions are subtracted from the EW spectra, revealing only the adsorbed-phase contribution. The subtraction was performed by aligning the relatively narrow gas phase peaks and applying minor adjustments to the estimated gas phase signal magnitude while maintaining the ×2 multiplier between the TE and TM polarizations. The minor adjustments to the wavelength axis of the gas phase spectra used for subtraction arise mainly from the wavelength repeatability of the OPO and the scanning procedure, while intensity adjustments are likely required to correct for the actual versus calculated EW effective thickness and the actual partial pressure of haloethylene in the evanescent wave compared to the estimated ambient vapor pressure. Alignment of the rotational structure between the gas phase and EW spectra for t-DCE is shown.
Fig. 3. The evanescent wave absorption spectra for (a) TCE, (b) cis-DCE, and (c) trans-DCE are shown as measured by EW-CRDS with the monolithic folded resonator. Both gas phase and surface-bound species contribute to the spectra. The estimated gas phase contributions (heavy solid lines) are superimposed on the EW spectra.
Fig. 4. The TE- and TM-polarized evanescent wave absorption spectra for surface-adsorbed (a) TCE, (b) cis-DCE, and (c) trans-DCE are shown as obtained after subtraction of the gas phase contributions from the EW-CRDS spectra shown in Fig. 3. The bars indicate the estimated full-width at half-maximum intensity.
Table II. Integrated intensities, peak positions, and line widths for the adsorbed chloroethylenes

<table>
<thead>
<tr>
<th></th>
<th>$\Gamma_{TE}$</th>
<th>$\Gamma_{TM}$</th>
<th>$\rho$</th>
<th>$\omega_b$</th>
<th>$\Delta\omega_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>2.92</td>
<td>2.41</td>
<td>1.21</td>
<td>6066.0</td>
<td>28.6</td>
</tr>
<tr>
<td>c-DCE</td>
<td>4.34</td>
<td>3.22</td>
<td>1.34</td>
<td>6053.1</td>
<td>30.0</td>
</tr>
<tr>
<td>t-DCE</td>
<td>4.47</td>
<td>3.55</td>
<td>1.26</td>
<td>6050.7</td>
<td>29.0</td>
</tr>
</tbody>
</table>

$^a 10^{-8}$ cm$^2$.

$^b$ Position of band maximum in cm$^{-1}$.

$^c$ Bandwidth in cm$^{-1}$ of adsorbate spectrum after subtraction of gas phase contribution.

in the insets of Fig. 3(c), which aided the gas phase subtraction in that case. In general, the adsorbed-phase spectra for the three haloethylenes in Figs. 4(a)−4(c) show single, symmetrical peaks which are shifted to lower wavenumbers relative to the gas phase spectra with essentially identical peak positions for TE and TM within experimental error. Furthermore, there is a distinct polarization anisotropy for all three species as the TE polarizations show consistently stronger absorption compared to TM.

The polarization anisotropy of the adsorbed-phase spectra indicates a significant degree of orientation for the adsorbates, which must be considered to obtain the absolute coverage. Table II gives the integrated absolute intensities for the three adsorbed species and two polarizations. From the dichroic ratio of TE-to-TM-polarized intensities, $\rho = \Gamma_{TE}/\Gamma_{TM}$, a measure of the average orientation of the transition moment can be determined. A molecule in the evanescent field with a molecular transition moment given by $\mu(\theta, \varphi) = |x \sin \theta \cos \varphi + y \sin \theta \sin \varphi + z \cos \theta|$ interacts with the surface electric field $E(0, \varphi, \theta, n_r, n_o)$ according to $\Gamma \propto \langle |\mu(0, \varphi, 0, \theta)| \rangle$, where the angle brackets denote averaging over a distribution of orientations specified in the polar and azimuthal surface coordinates, $\theta$ and $\varphi$, respectively (defined in the inset of Fig. 5). The surface electric field is assumed to be described by the Fresnel equations for a given polarization, angle of incidence $\theta_i$, resonator refractive index $n_r$, and ambient refractive index, $n_o$. If the distribution of orientations is assumed to be isotropic in $\varphi$, then the distribution function can be expanded in Legendre polynomials, $P_n$, according to

$$N(x) = \sum_{n=0}^{\infty} C_n P_n(x) = \sum_{n=0}^{\infty} \left( \int_{-1}^{1} N(\xi) P_n(\xi) d\xi \right) P_n(x),$$  \hspace{1cm} (4)

where $x = \cos \theta$ and $0 \leq \theta \leq \pi/2$. Mirror symmetry about the equatorial surface plane requires all $C_n = 0$ for $n$ odd, while absorption is further restricted to measurement of the “order parameter”, $C_2$, only. If the distribution function is unimodal with a small angular dispersion, so that $N(\cos \theta)$ can be approximated as $\delta(\cos \theta_0 - \cos \theta)$, then $C_2 = P_2(\cos \theta_0)$, which yields an average polar tilt angle $\theta_0 = \cos^{-1}(2C_2 + 1)/3$, as commonly used in studies of oriented polymer films and adsorbed biomolecules. Employing this assumption, the value of $C_2$ and $\theta_0$, can be determined from $\rho$, which we find is given by

$$\rho = \frac{\Gamma_{TE}}{\Gamma_{TM}} \frac{I_{TE}}{I_{TM}} \left( \frac{1 - C_2(\theta_0)}{I_{TE} + I_{TM}} + \frac{2I_{TE} - I_{TM}C_2(\theta_0)}{I_{TE} + I_{TM}} \right),$$  \hspace{1cm} (5)

where $I_i = |E_i|^2/|E_{ni}|^2$, $i = x,y,z$ are the calculated electric field intensities at the TIR surface relative to the incident field intensity. Using $\theta_i = 45^\circ$ and $n_r(1640 \text{ nm}) = 1.442$ for the folded resonator, we find the relative field intensities to be $I_x = 0.28$, $I_y = 3.85$, and $I_z = 7.42$, which change negligibly over the absorption band. A plot of $\theta_0$ versus $\rho$ is shown in Fig. 5 along with the experimentally determined values of $\rho$ for TCE, c-DCE, and t-DCE. Note that $\theta_0$ remains relatively constant over the interval $0 \leq \theta_0 \leq 60^\circ$, which leads to a
Fig. 5. The average angle of orientation \( \theta_{o} \) for the transition moment is plotted as a function of the dichroic ratio, \( \rho = \Gamma_{TE}/\Gamma_{TM} \). The experimental data points for the three haloethylenes are marked and defined in the legend.

relatively large error in \( \theta_{o} \) for a given error in \( \rho \) over this interval. Further, a given value of \( C_{2} \) determined from \( \rho \) can correspond to a wide variety of distributions, especially when \( C_{2} \) is in the center of its range, which extends over the interval \([-0.5,1]\). Indeed for \( C_{2}=0 \), an assumed \( \delta \)-function distribution leads to an orientation angle of \( \theta_{o}=54.7^\circ \), while \( C_{2}=0 \) is also consistent with an isotropic distribution. However, the experimental data for the haloethylenes occur around \( C_{2}=-0.4 \), where \( \theta_{o}(\rho) \) levels off, which suggests the three adsorbates are distinctly oriented and a meaningful orientation angle can be determined with confidence, at least within the assumption of a unimodal distribution. The transition moment tilt angles are found to be \( \theta_{o}(\rho)=74\pm2^\circ \), \( 75\pm2^\circ \), and \( 76\pm2^\circ \) for TCE, c-DCE, and t-DCE, respectively, relative to the TIR-surface normal, where the error limits are estimated from the variability of the integrated intensities.

The corresponding molecular orientations can be identified given the transition moment direction relative to a molecular axis. In the gas phase, TCE, c-DCE, and t-DCE have \( C_{s} \), \( C_{2v} \), and \( C_{2h} \) symmetries, respectively. For TCE, a normal coordinate perspective requires the transition moment to be in the molecular plane, since the transition operator must transform as \( A' \) to connect totally symmetric ground and excited states. The transition moments of the DCE isomers are also in-plane in the local mode model of Takahashi et al. Therefore, if the transition moments are all in-plane, the three haloethylenes have their molecular planes oriented on average nearly parallel to the mean plane of the ultra-smooth TIR surface. As the tilt angles are comparable for the three species, the different molecular symmetries apparently result in indistinguishable adsorption geometries within experimental error.

Given the integrated gas phase cross sections, the adsorbed-phase integrated intensities, and the average orientations of the transition moments, absolute surface coverages can be obtained by invoking conservation of the integrated intensity with adsorption. Although the oscillator strength of a transition is conserved between gaseous and condensed phases, the integrated intensity is affected by changes in the local field. However, correction factors can be derived to account for local field effects, which predict the ratio of integrated gas-to-liquid phase cross sections to be \(<2\). As noted, here we assume the Fresnel equations describe the local electric field at the TIR surface, which neglects adsorbate coupling and surface image-dipole effects. Since the TE surface spectra have higher signal-to-noise ratio than the TM spectra, we employ these for the absolute coverage calculations. With \( E_{TE}=I_{y} \), we find the absolute number density of adsorbed molecules at the TIR surface to be given by

\[
N_{abs} = \frac{2\cos \theta_{o} \int c_{abs} \cos \theta_{o} \sin \theta_{o} \sin \phi \, d\omega}{3I_{y} \sin^{2} \omega_{o}}.
\]
where the factor of 3 in the denominator arises from orientation averaging of the gas phase absolute cross section and the factor of 2 in the numerator arises from azimuthal averaging over the surface distribution. Given spectra with sufficiently high signal-to-noise ratio, the major source of uncertainty in Eq. (6) lies in the evaluation of orientation, although as discussed above the uncertainty is smallest for highly oriented systems having $C_2$ near the periphery of its range [-0.5,1]. Using Eq. 6, we find $N_{abs}=1.41\times10^{14}$ molecules/cm$^2$, $1.40\times10^{14}$ molecules/cm$^2$, and $1.59\times10^{14}$ molecules/cm$^2$ for TCE, c-DCE, and t-DCE, respectively. If the underlying site density is defined by close-packed, planate TCE molecules ($N_0\approx1.23\times10^{15}$ sites/cm$^2$), then the saturation coverages are found to be 11.5%, 11.4%, and 12.9% for TCE, c-DCE, and t-DCE, respectively.

For adsorbed TCE on oxidized Si(100) surfaces, the mass-spectrometer-based uptake measurements yielded absolute coverages of $(1.0\pm0.2)\times10^{14}$ molecules/cm$^2$ and $(0.4\pm0.1)\times10^{14}$ molecules/cm$^2$ for the W filament and “button” heaters, respectively, where the quoted errors are standard deviations. As previously noted, the discrepancy between the results for the two heaters could arise from adsorption to adjacent, inadvertently cleaned surfaces, which could account for the larger coverage obtained for the larger W filament heater. Since the EW-CRDS measurements are performed under equilibrium conditions and ambient humidity where significant surface Si-OH formation and adsorbed water can be expected, a direct comparison to the mass-spectrometer-based measurements is difficult. However, it is valuable to contrast the techniques. A key difference between the uptake measurements and EW-CRDS is the accessible pressure range, which is restricted to UHV in the former case and very broad in the latter case. The EW-CRDS approach also probes the species of interest directly at the surface within a spatial region that is precisely defined by the resonator properties, whereas the uptake approach infers the surface coverage from remote measurements in which the effective surface dimensions may be ill-defined by the cleaning step. However, an approach using EW-CRDS or some variation of CRDS requires the surface of interest to be integral to a resonator, while the uptake measurements can be applied to an arbitrary substrate. Furthermore, any approach based on conservation of integrated intensity requires an isolated absorption band and may require a local field correction.

Finally, we compare the detection capability of EW-CRDS to previous efforts in which evanescent wave NIR absorption was employed for TCE detection. Ache and co-workers explored extensively the detection of TCE with the first C-H overtone using a long-effective-path-length planar waveguide, which improved on the sensitivity of their previous optical-fiber sensor by a factor of 120. Polysiloxane coatings were employed with these devices to reversibly enrich the local concentration of TCE in the evanescent wave. The chemical composition of the polysiloxane polymers was also varied to identify optimal conditions for sensing as determined by the TCE partition coefficient and polymer refractive index. Furthermore, it was shown that competing absorption from C-H groups of the polymer could be essentially eliminated through efficient deuteration. The gas phase detection limit for TCE obtained using the optimized planar waveguide with a polysiloxane coating was found to be $0.1$ mmol/L or $\sim2$ parts-per-thousand in the gas phase at atmospheric pressure. By comparison, EW-CRDS also provides an equivalent detection limit determined by the minimum detectable absorption of $1\times10^{-7}$ based on a 0.1 % relative decay time precision (1σ for ensembles of 25 averaged laser shots per point) and a $1\times10^{-4}$/pass intrinsic loss. Yet this detection limit is obtained by EW-CRDS without a TCE-enriching polymer. As shown in Fig. 6, the EW-CRDS response to adsorption of TCE on the silica surface of the folded resonator is also reversible with a response time of $<1$ min. The addition of an enriching polymer layer to an EW-CRDS-based TCE detection scheme could lower detection limits significantly. The use of a low-scatter-loss, deuterated polysiloxane film should permit a low intrinsic loss to be maintained. The polysiloxane layer, which can be thick relative to the evanescent wave decay length for an appropriate resonator design, should also serve to protect the sensing surface and eliminate interference from particulates. A significant additional
Fig. 6. Reversibility of the EW-CRDS measurement of TCE detection is demonstrated by modulating TCE exposure while monitoring the TE-polarized absorption.

IV. CONCLUSIONS

This work is significant to both fundamental surface science and the development of chemical sensors. The measurement of the absolute surface coverage by EW-CRDS can potentially provide absolute reaction rates on films or particles, similar to gas phase CRDS kinetics studies. Sub-monolayer coverages can be probed without the need for ultra-high vacuum as long as the total system intrinsic loss is sufficiently small. In connection with the development of new chemical sensors, EW-CRDS provides a significant advance in detection sensitivity in the NIR, along with comparable selectivity to the mid-IR. While further improvements appear feasible, the detection limit achieved in this initial effort using an unclad folded resonator is comparable to that obtained using an optimized planar waveguide with an analyte-enriching surface coating.

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REFERENCES

CHAPTER 7

NEW ULTRA-HIGH VACUUM SETUP FOR STUDYING RADICAL-SURFACE INTERACTION DURING THIN FILM GROWTH*

ABSTRACT

A new vacuum setup is presented which is designed for studying the surface science aspects of thin film growth and in particular the growth process of hydrogenated amorphous silicon (a-Si:H). Key features of the setup are (i) an atomic hydrogen source (H-source), an electron cyclotron resonance (ECR) plasma source, and a hot wire radical source to mimic the plasma deposition process by well-defined radical (and ion) beams, (ii) full optical access to the substrate for real-time monitoring of surface processes by advanced optical diagnostics, and (iii) well-defined process conditions, such as ultra-high vacuum, high-purity gasses, and accurate control of the substrate temperature, $T_{\text{sub}}$. The H-source has been characterized in terms of its relative H flux by real-time spectroscopic ellipsometry measurements of the H-induced etch rate of hydrogenated amorphous carbon (a-C:H) films. Moreover, the absolute H flux from the H-source has been quantified by a comparison of the data with the absolute H flux from a similar, calibrated H-source in the literature. The absolute H flux was used to measure the H-induced etch yield of a-C:H at $T_{\text{sub}}=230 \, ^\circ\text{C}$ and a-Si:H at $T_{\text{sub}}=85 \, ^\circ\text{C}$ yielding $(2.0 \pm 0.1) \times 10^{-2}$ C atoms per H atom and $(5.1 \pm 0.5) \times 10^{-3}$ Si atoms per H atom, respectively. Utilizing the a-C:H etch yield, the ECR- and hot wire source, when operated on $\text{H}_2$, have been extensively characterized by means of H-induced etch experiments of a-C:H films. This has lead to insight into the operation of the sources as well as into their operation ranges.

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I. INTRODUCTION

Gaining understanding of the surface processes is a major effort in thin film growth. Over the last two decades, one of the most extensively studied systems is the thin film deposition process of hydrogenated amorphous silicon (a-Si:H), a material that is commonly deposited by plasma or hot filament activation of SiH$_4$ containing gas mixtures. This material has been studied to such an extent that it has basically become a model system for understanding thin film growth.1-2 Throughout the years, the investigations have become more advanced and sophisticated although most of the experiments have been carried out under regular, but sometimes rather well-defined operating conditions for a-Si:H deposition.3-9 For instance, it has been demonstrated in some cases that the SiH$_3$ radical is the dominant silicon-containing growth precursor for high quality a-Si:H film growth.7,10-14 This has lead to the general believe that high quality a-Si:H films are grown under SiH$_3$-dominated conditions.1,2 Several surface reactions have been proposed for the SiH$_3$ radical that have mainly been concentrated on the adsorption mechanism of SiH$_3$ and the possible surface diffusion process of the radical. The latter aspect is considered to be the explanation for the remarkably high smoothness of a-Si:H films. It is noted, however, that the role of atomic hydrogen (and of ions) in the growth process might also be significant.1,2,15

To reach the next level of understanding, i.e. insight into the surface reactions on the atomic scale, surface science-like studies under well-defined and idealized conditions will be required. Such studies can, for example, be carried out by mimicking a-Si:H film growth using several well-defined radical beams. This approach has been found fruitful for c-Si plasma etching16 and the deposition of hydrogenated amorphous carbon (a-C:H).17 In this Chapter, we present a new experimental setup for beam studies of thin film growth and the growth process of a-Si:H in particular. In the design of this setup, three basic criteria have been taken into account:

1) With well-defined radical (and ion) beams, film growth under regular deposition conditions can be mimicked. The radical beams should preferentially be mono-radical and accurately quantified in terms of their flux. For a-Si:H deposition, radical beams of SiH$_3$ and H are most appropriate. The system should be flexible in providing the radical beam sources with various feed gases, while isotope counterparts of some feed gases should be available to allow for isotope exchange studies.

2) The growth process needs to be investigated by advanced in-situ diagnostics with a clear preference for “all-optical” techniques which are able to monitor film growth non-intrusively and in real time. Furthermore, the techniques should be innovative to answer questions of a-Si:H film growth, such as “What is role of surface Si dangling bonds for radical absorption?”.

3) The substrate, onto which the thin film is deposited, is the key object within the setup and should therefore be easily accessible by (optical) diagnostics, while different substrate types, materials, and sizes should be applicable. This feature makes the setup distinct from the setups used in the above-mentioned beam studies. Moreover, the substrate should remain clean for a sufficiently long time to allow enough time for sensitive measurements of the surface state, thereby setting strict demands on the level of vacuum reached by the setup.

The setup Galapagos, which meets these requirements, is presented in Sec. II. The setup is equipped with three radical sources, i.e. an atomic hydrogen source, an electron cyclotron resonance plasma source, and a hot wire radical source. The principle of operation of these sources is explained in Sec. III. The behavior of the sources under different source operating conditions is carefully investigated in Sec. IV. Utilizing the fact that the radical sources can all be operated on H$_2$ to produce H atoms, the absolute H flux from the sources
is measured by H-induced etch experiments of a-C:H and a-Si:H films using real-time spectroscopic ellipsometry. Finally, the general conclusions are presented in Sec. V.

II. EXPERIMENTAL APPARATUS

A. Vacuum system

The setup is entitled Galapagos, which is an acronym for General Apparatus for Layer Analysis using Plasma Assisted Growth Of Semi-conductors. A side view picture and schematic top view of the setup are shown in Fig. 1(a) and 1(b), respectively. The setup consists of two vacuum chambers that are separated by a flange that holds the substrate. The "deposition" chamber contains the radical sources, while the "backside" chamber allows for optical access of the substrate from the backside. The chambers are separately pumped by a turbomolecular pump (a Pfeiffer TPU 261P, 210 l/s, and a Pfeiffer TPU 170, 170 l/s, are used to pump the deposition and backside chamber, respectively). The pressure in the deposition chamber can be controlled by means of a regulating valve and by changing the rotation speed of the turbomolecular pump. Both vacuum chambers have been equipped with a combined pirani/cold cathode pressure gauge (Pfeiffer Vacuum, PKR261) as well as a Bayard-Alpert gauge (AML, PGC2D) for pressure measurements\(^1\) in the range of \(5 \times 10^{-9} - 1000 \text{ mbar}\) and \(3 \times 10^{-11} - 10^{-3} \text{ mbar}\), respectively. The setup is completely ultrahigh vacuum (UHV) compatible and both vacuum chambers have been equipped with an infrared heating lamp (Halogen Photo Optic Lamp, 1000 W) to bake out the setup (not shown in Fig. 1). A shutter is integrated in the setup to shield the substrate from contaminants during bake-out and during start up of the radical sources. Using only the infrared heating lamps, a pressure of \(\sim 10^{-9}\) mbar is reached after a full night of baking. A pressure of \(10^{-10}\) mbar should be reachable after an extensive bake-out procedure that includes external heating tapes. The quality of the vacuum is monitored with a residual gas analyzer (RGA, Pfeiffer Vacuum, QME 200), which yields the mass-resolved spectrum of the gas phase species showing possible contaminants levels, while the RGA is also used as a helium leak detector. The high-purity process conditions that are achieved in Galapagos result in low levels of contaminants in the deposited a-Si:H films, as is discussed in Sec. IV. The setup is fully automated by a programmable logic control, which provides user process control, automated safety procedures, and data history logging.

B. Substrate

The substrate is positioned in a flange that is screwed in place between both vacuum chambers [Fig. 1(b)]. As the substrate and the substrate holder do not serve as a vacuum seal, this configuration allows for complete freedom in choice of substrate types, materials, and sizes, as well as in the design of the substrate holder to allow for optical access of the substrate from the front and the back side. Moreover, the system is flexible for new types of substrates as a new substrate requires at the most a new substrate holder design. The substrate can be heated radiatively from the backside by a Boralectric\textsuperscript{TM} heater (Advanced Ceramics Corporation, Flat PBN Boralectric\textsuperscript{TM} Heater, HTR 1002, 1440 W, see Fig. 1(b)) that allows for substrate temperatures in the range of \(T_{\text{sub}} = RT - 800 \degree C\). The substrate temperature is actively controlled by a proportional, integral, derivative (PID) temperature controller (Eurotherm 2500) using an input temperature measurement from a thermocouple glued directly on (or close by) the substrate. Figure 2 shows the

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\(^1\) When using H\(_2\), the pressure readings has been corrected for the (partial) pressure of H\(_2\) in accordance with the manuals of the pressure gauges.
Fig. 1. Side view picture (a) and schematic top view (b) of the new UHV setup Galapagos together with pictures of the radicals sources in operations, i.e. (c) the electron cyclotron resonance (ECR) plasma source, as seen from a reflection on the substrate in the substrate holder, (b) the thermal source for atomic H beam production (H-source), and (e) the hot wire source. The schematic top view [Fig. 1(b)] shows several of the optical diagnostics that can be used to study the radical-surface interaction processes, i.e. gas phase cavity ring-down spectroscopy (CRDS) to measure (low-density) gas phase species in front of the substrate and time-resolved CRDS to obtain the surface reactivity of the gas phase species; real-time spectroscopy ellipsometry (RTSE) to monitor the optical and structural material properties as well as the surface roughness evolution; attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) to detect bulk and surface absorptions, such as due to silicon hydride bonds; and evanescent-wave cavity ring-down spectroscopy (EW-CRDS) and second harmonic generation (SHG) to detect, e.g., (surface) dangling bonds, etc.
Fig. 2. The response of the substrate temperature $T_{\text{sub}}$ for a change in the set point from room temperature to $T_{\text{sub}} = 250 \, ^\circ\text{C}$, as measured by the input thermocouple of the PID-controller that is glued directly on the c-Si substrate. The substrate temperature is within $2 \, ^\circ\text{C}$ from the set point in less than 10 min, as indicated by the dashed line. The inset shows the response of the substrate temperature upon opening and closing of the shutter due to the PID-controller.

C. Radical sources and gas supply

Currently, the setup is equipped with three radical sources (cf. Fig. 1). The three source are discussed in detail in Secs. III en IV, but are briefly introduced here. A thermal atomic H source (H-source) is present to produce a well-defined H flux by means of a hot capillary.$^{19,20}$ An electron-cyclotron-resonance (ECR) plasma source that can be operated in “atom-mode”, “low-energy ion mode”, and “hybrid mode” and can serve multiple purposes.$^{21}$ It can be used to produce an ion ($\text{Ar}^+$) beam, while also efforts are being taken to develop the source as a (low flux) SiH$_3$ radical beam. Finally, a hot wire radical source is present to deposit a-Si:H films at reasonable deposition rate under SiH$_3$-dominated conditions when operating on SiH$_4$ gas. When operated on H$_2$, the hot wire can be used for in-situ chamber cleaning and conditioning. The three sources are positioned on linear shifts with bellows (Fig. 1) such that the source-substrate distance can be varied in the range of 5.4–15.4 cm, 11–21 cm, and 6.8–16.8 cm for the H-source, ECR-source, and hot wire radical source, respectively. This enables an independent control of the radical fluxes towards the substrate without changing any of the source operating conditions. Therefore, the linear shifts enable well-defined studies of the flux-dependence of surface processes.
The radical sources can be operated on a variety of feed gases. To enable a large degree of freedom for future fundamental studies, a gas supply system has been installed that yields a high flexibility in the supply of different gases to the radical sources, as shown in Fig. 3. For the present connection of the gases to the radical sources, the H-source can be supplied with H₂ and D₂, the ECR-source can be supplied with H₂, D₂, and Ar to the "plasma chamber" and SiH₄, Si₂D₄, and Si₃H₆ to the "precursor inlet" (see Sec. III for the explanation of ECR-source), while the hot wire can be operated on all of these gases by injection into the background. The deuterated gasses D₂ and SiD₄ have been added with respect to the regularly-used hydrogenated gases H₂ and SiH₄ to allow for isotope exchange studies. Moreover, a spare connection for a lecture bottle is available for variable gases. The spare connection has been used up to now for CF₄, NH₃, and O₂ gas and is presently connected to the ECR precursor inlet. Furthermore, argon gas can be supplied directly to the reactor to vent the system. It is noted that the connection of the gases to the radical sources is flexible for changes, while the specialty gases that are supplied by lecture bottles can easily be changed without venting the system (Fig. 3). Higher gas flows can be set automatically with mass flow controllers (MFC), while very low gas flows can be set with leak valves. The specified purities of gases used are listed in the upper right inset of Fig. 3. The purity level of the gases is increased by using specific H₂/D₂, SiH₄/Si₂D₄/Si₃H₆, and inert gas purifiers (Aeronex Gatekeeper SS-35KF−H−4R, SS-35KF−SK−4R, and SS-35KF−I−4R, respectively) in the gas supply lines that remove gaseous contaminants, such as O₂, CO, CO₂, H₂O, and non-methane hydrocarbons to less then 1 ppm. Finally, it is noted that the gas supply system is completely built up of components that are specifically designed for UHV applications.

D. In-situ and real-time diagnostics

As illustrated in Fig. 1(b), the setup has multiple ports for optical access to the substrate. This enables real-time monitoring of surface processes by advanced optical diagnostics. For instance, real-time spectroscopic ellipsometry (RTSE) can be applied from the front side (at an angle of 60° with the substrate...
normal) to monitor the optical and structural material properties of the growing film as well as the evolution of the surface roughness.\textsuperscript{25-26} Infrared spectroscopy can be applied from the backside (at an angle of 45° with the substrate normal) using an attenuated total reflection (ATR) crystal for enhanced sensitivity. The technique can also be applied from the front side by means of a direct reflection on the substrate. Infrared spectroscopy can, for instance, be applied for H-depth profiling and to determine the H surface coverage (of a-Si:H).\textsuperscript{8,9,27} Evanescent-wave cavity ring-down technique (EW-CRDS)\textsuperscript{28,29} can be applied from the backside optical port at 45° with the substrate normal and can be used, among other things, for detection of defect-related absorptions (in a-Si:H) at subgap energies.\textsuperscript{30} Surface and defect states can also be studied from the front side of the substrate (at 35° with the substrate normal) using the surface-sensitive technique of second harmonic generation (SHG).\textsuperscript{31,32} Furthermore, gas phase cavity ring-down spectroscopy (CRDS) can be applied in front of the substrate to measure (low-density) gas phase species,\textsuperscript{33,34} while time-resolved CRDS can yield the surface reactivity of the gas phase species.\textsuperscript{7,35} Finally, the residual gas analyzer can be used for thermal-programmed desorption studies.

### III. PRINCIPLE OF OPERATION OF THE RADICAL SOURCES

#### A. Atomic hydrogen source

The basic element in the H-source is a long thin tungsten capillary (length 6 cm, inner diameter 1 mm), as shown in Fig. 4. A heating filament, which is coiled concentric around the capillary at a radial distance of ~2 mm from the capillary, is fed by a current, \( I_{\text{fil}} \), from a 600 W DC power supply in order to radiatively heat the last ~2.5 cm of the capillary. This yields a maximum capillary temperature of \( T_{\text{cap}} \approx 2400 \text{ K} \). Calibration of \( T_{\text{cap}} \) as a function of \( I_{\text{fil}} \) is provided by the manufacturer.\textsuperscript{36} The capillary is surrounded by molybdenum heat shields and a water-cooled copper jacket to prevent radiative heating of the substrate. At the end of the H-source, a small opening in the copper jacket allows the mixture of H and \( \text{H}_2 \) to effuse into the direction of the substrate, as seen in Fig. 1(d). The capillary ends in the water cooled jacket at 0.6 cm from the end of the source. The H-source is equal to the H-source of Tschersich and Von Bonin, described in detail in Refs. 19 and 20, with the exception that their H-source incorporates electron

![Fig. 4. Schematic drawing of the atomic hydrogen source with the tungsten capillary and concentric heating coil. The capillary is surrounded by molybdenum heat shields and a water-cooled copper jacket. Also indicated are the two set parameters, i.e. the \( \text{H}_2 \) flow and the current through the heating coil, \( I_{\text{fil}} \).](image-url)
impact heating of the capillary enabling a maximum temperature of $T_{\text{cap}} = 2600$ K. Using mass spectrometry, Tschersich and Von Bonin have carefully measured the absolute H flux emanating from their version of the H-source as a function of $T_{\text{cap}}$ and the H$_2$ flow through the capillary. In Sec. IV, it will be shown that our H-source yields the same absolute H flux for the same setting of $T_{\text{cap}}$ and H$_2$ flow. To establish this correlation, a detailed understanding of the H-source is required. Therefore, the principle of operation of the H-source is summarized here from the work of Tschersich and Von Bonin.\textsuperscript{19,20}

The absolute H flux from the H-source at the position of the substrate is determined by three parameters, i.e. the H$_2$ flow through the capillary, the degree of dissociation of H$_2$ molecules in the capillary, $\alpha_{H_2}$, and the beam profile of the H flux emanating from the source, as is explained next. The production rate of H atoms in the capillary is equal to the H$_2$ flow times the degree of dissociation $\alpha_{H_2}$, where $\alpha_{H_2}$ depends on $T_{\text{cap}}$ and the H$_2$ flow. For the reaction $H_2 \rightarrow H + H$, the degree of dissociation $\alpha_{H_2} = p_{H_2}/(p_{H_2} + 2p_{H_2})$ in a hypothetical closed chamber at thermodynamical equilibrium can be calculated with:\textsuperscript{17}

$$\alpha = \frac{K_p(F)}{\sqrt{3}p_{\text{eq}}/p^0 + K_p(F)},$$  

(1)

where $K_p = p_{H_2}^2/(p_{H_2} \times p^0)$ is the equilibrium constant, $p_{H_2}$ and $p_{H_2}$ are the partial pressure of H and H$_2$, respectively, $p_{\text{eq}} = p_{H_2} + p_{H_2}$ is the total pressure, and $p^0 = 1$ bar. The equilibrium constant $K_p$ is tabulated\textsuperscript{38} and can, in the temperature range of interest, be calculated from the fit function:

$$\log(K_p) = 6.304 - \frac{22760 \text{ K}}{T}.$$  

(2)

The degree of dissociation $\alpha_{H_2}$ for our H-source cannot be measured directly. However, Tschersich has found that the relative H flux from the H-source as a function of $T_{\text{cap}}$ and the H$_2$ flow could well be fitted with Eqs. (1) and (2) (while taking the influence of the H$_2$ flow on the beam profile into account) when adopting $p_{\text{eq}}$ as a fit parameter.\textsuperscript{20} The H-source can therefore be regarded as a chamber with a small orifice at thermodynamical equilibrium at temperature $T_{\text{cap}}$ and at a pressure $p_{\text{eq}}$, where $p_{\text{eq}}$ corresponds to a position in the H-source not far from the end of the capillary. The resulting degree of dissociation as a function of $T_{\text{cap}}$ for the four H$_2$ flows used by Tschersich is shown in Fig. 5. The figure clearly shows that

![Graph showing degree of dissociation as a function of $T_{\text{cap}}$](image)

Fig. 5. The degree of dissociation of H$_2$, $\alpha_{H_2}$, as a function of the capillary temperature $T_{\text{cap}}$ for four different H$_2$ flows (given in sccm) through the capillary. The figure has been reproduced from Ref. 20, where the values of $\alpha_{H_2}$ were calculated using Eqs. (1) and (2).
$\alpha_{H_2}$ decreases with increasing $H_2$ flow. Tschersich\textsuperscript{20} has attributed this effect to Le Chatelier's principle,\textsuperscript{10} which states that, when a system in equilibrium is compressed, the system will adjust itself to minimize the increase in pressure. This results in a decrease of the dissociation rate of one $H_2$ into two $H$. The figure also shows that $\alpha_{H_2}$ increases with increasing capillary temperature $T_{cap}$. For $T_{cap} \leq 2000$ K, this increase is nearly exponential. For very high $T_{cap}$, the degree of dissociation saturates towards unity as nearly all $H_2$ is converted into two $H$.

The $H$ flux at a certain substrate position is equal to the production rate of $H$ atoms in the capillary multiplied by the probability that an $H$ atom will flow to the specific substrate position, as determined by the beam profile. The normalized angular distributions of the $H$ flux with respect to the capillary axis have been measured by Tschersich and Von Bonin for their $H$ source using mass spectrometry.\textsuperscript{19} The results are shown in Fig. 6 for the same $H_2$ flows as in Fig. 5. These measurements enabled Tschersich\textsuperscript{20} to determine the absolute $H$ flux from his $H$-source by combining the $\sim 100\%$ $H_2$ dissociation for a low $H_2$ flow and high $T_{cap}$ (Fig. 5) with the corresponding relative angular distribution for the same $H_2$ flow (Fig. 6). This procedure yielded the absolute $H$ flux with an estimated uncertainty of only $\sim 20\%$. Three features are noted in the data of Fig. 6. First, the $H$-source provides a relative narrow beam compared to a cosine angular distribution (dashed line in the figure) that describes the random emission of a particle from a planar surface. Second, the width of the angular distribution decreases continuously with decreasing pressure, yielding a $H$ beam with a half width at half maximum (HWHM) at a polar angle of $13^\circ$, $7^\circ$, $5^\circ$, and $4^\circ$ for a $H_2$ flow of $4.2 \times 10^{-1}$, $9.2 \times 10^{-2}$, $8.1 \times 10^{-3}$, and $1.9 \times 10^{-3}$ sccm. Third, at the lowest $H_2$ flow the on-axis intensity is attenuated. These features will be described next.

The specific shape of angular distributions in Fig. 6 is caused by the transport of species inside the capillary. This transport occurs via gas phase collisions as well as via adsorption at the wall followed by reemission according to a cosine distribution and progresses along a linear pressure gradient ending in a molecular flow regime at the end of the capillary (Ref. 40 and references therein). The shape of the angular distributions can be understood by dividing all species that impinge on the substrate into two groups based on their last collision that determined their final trajectory. The first group of species obtained their final trajectory from a reemission from the inner capillary wall somewhere within the molecular-flow regime at the end of the capillary. This results in a hollow angular distribution, because the probability for reemission

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig6}
\caption{Normalized $H$ flux as a function of the polar angle $\theta$, as measured using mass spectrometry for four different $H_2$ flows (given in sccm) and a capillary temperature of $T_{cap} = 2600$ K. The lines depict fits based on a model describing $H_2$ dissociation in a capillary\textsuperscript{19} and serve only to extrapolate to the on-axis intensity to which the data are normalized. The figure has been reproduced from Ref. 19.}
\end{figure}
from the wall with a direction nearly parallel to the capillary axis is very small. The second group of species obtained their final trajectory from a gas phase collision. Therefore, these species originate from deep within the capillary, where the flow is dominated by gas phase collisions, and their angular distribution is peaked around the axis of the capillary. As a consequence, the total angular distributions of the H-source, as shown in Fig. 6, obtain their width from the angular distribution of the first group, while their on-axis intensity is determined by the angular distribution of the second group. When the H$_2$ flow is decreased, the transition point in the capillary between the collision-dominated regime and the molecular-flow regime is pushed further inwards. This has little effect on the angular distribution of the second group of species that was already peaked. The angular distribution of the species directed by a final wall collision, however, becomes narrower as the average position at which the species have their final reemission from the inner capillary surface moves further inside the capillary. Therefore, the width of the combined angular distributions, shown in Fig. 6, decrease with decreasing H$_2$ flow.

For the measurements with the H-source, presented in this Chapter, the H-source is aimed at the center of the substrate and, therefore, the H flux at the substrate consists to a close approximation only of H atoms belonging to the second group, i.e. the H atoms that were dissociated at the wall deep within the capillary and that obtained their final trajectory towards the substrate by a gas phase collision. For our H-source as well as for the H-source of Tschersich and Von Bonin only the last ~2.5 cm of the capillary is heated uniformly. Therefore, when the last wall collision occurs on average deeper than ~2.5 cm within the capillary, where the local capillary temperature is lower than the set value of $T_{\text{cap}}$, i.e. the degree of H$_2$ dissociation is lower than expected on the basis of Fig. 5. On the other hand, the off-axis H intensity is not or barely attenuated for the lowest H$_2$ flow, because the H atoms contributing to the off-axis angular distribution had their last wall collision closer to the capillary exit, where the local capillary temperature is (nearly) equal to $T_{\text{cap}}$. This effect explains the attenuation of the on-axis H intensity for the lowest H$_2$ flow of Fig. 6. More importantly, it shows that the H atoms that reach the substrate can originate from deep within the capillary.

B. ECR-source

The electron cyclotron resonance (ECR) plasma source\textsuperscript{21,41} is a versatile source that can generate various ion and radical beams through operation on different feed gases. The ECR plasma source is schematically shown in Fig. 7. Microwaves with a frequency of 2.45 GHz and a maximum power of 200 W are generated in the magnetron and are coupled via a cylindrical resonator cavity (inner diameter ~106 mm, length ~130 mm) to a coaxial antenna, which guides the microwave into the vacuum up to end of the antenna, where the microwaves are coupled into the alumina (Al$_2$O$_3$) plasma chamber (inner diameter ~26 mm, length ~34 mm). A plasma is ignited [see Fig. 1(c)] by the microwave-induced excitation of free electrons in the feed gas. The electrons are confined in radial direction due to the electron cyclotron resonance condition. That is to say, the radial component of the oscillating electric field at 2.45 GHz is resonantly matched to a stationary axial magnetic field of 87 mT, generated by four water-cooled permanent magnets in a quadrupole configuration (Fig. 7). This leads to a electron cyclotron rotation around the magnetic field lines that confines the electrons in the plasma. The plasma chamber is closed off with one or more semi-transparent grid(s) that increase(s) the pressure in the plasma chamber compared to the pressure in the reactor. Therefore, the plasma can be operated at a reactor pressure of as low as $\lesssim$2.5×10$^{-6}$ mbar when using a grid with only a few small holes.\textsuperscript{41} Under typical ECR plasma operating conditions, the heavy particles, that are not confined by the ECR conditions, have only a few or no gas phase reactions before they reach the wall or are emitted through one of the holes in the grid(s) towards the substrate. This leads to an ECR beam profile with a HWHM of ~15° [from visual observation of the spatial deposition
Given in more detail are (a) the side-view and (b) the front-view of the ECR plasma chamber. Microwaves at a frequency of 2.45 GHz are coupled by the antenna into the alumina plasma chamber, which is surrounded by four water-cooled permanent magnets, generating a quadrupole magnetic field of 87 mT. All components of the ECR-source are ultra-high vacuum compatible and the source can be fully baked, because the permanent magnets are outside the vacuum and can be removed for baking. Discharges between the antenna and the outer cylinder at higher operating pressures are prevented by differential pumping using a 56 l/s turbo pump.

The ECR-source can be operated in different modes, i.e. the so-called "ion mode", "atom mode", and "hybrid mode", which differs in the number of grids used, the number of holes and their size in the grid, and the voltage applied on the grid(s). In ion mode, the plasma chamber is closed by two metal grids (e.g., two molybdenum grids with 85 holes of 2 mm diameter), as shown schematically in Fig. 7. Positive ions are accelerated out of the plasma chamber towards the substrate due to a voltage difference between the anode grid (on the plasma side) and the extractor grid. The voltage can be varied independently at a voltage of up to +2 keV and -1 keV, respectively, yielding an ion beam with an energy in the range of 50-1000 eV. The acceleration towards the substrate results in a narrowing of the ECR-beam to a HWHM of ~4° and a large increase of the on-axis ion flux in the beam of up to ~10^17 cm^-2 s^-1. Because the neutral flux is not increased, the relative density of neutral species in the beam is low. It has been demonstrated that a low energy (50 eV) Ar^-beam, produced by operating of the ECR-source in ion mode on Ar gas, can be used to completely remove the native oxide and carbaceous contaminations of a (InAs) substrate wafer without altering the wafer properties. A low energy Ar^-beam can also be used to carefully strip all the surface hydrogen from an a-Si:H surface to create a bare surface that is covered by dangling bonds, in line with experiments described in Refs. 9 and 27. Removal of the surface hydrogen is an important tool for measurements of the surface SiHₓ bonds of a-Si:H with ATR-FTIR as well as for the measurements of the surface dangling bonds with EW-CRDS and SHG. Furthermore, higher energy ion beams can be used to independently investigate the influence of ion bombardment on a-Si:H deposition as a function of the ion energy.

![Schematic representation of the electron cyclotron resonance (ECR) plasma source.](image)
In the atom mode, the two metal grids are replaced by a single dielectric [e.g. alumina (Al₂O₃)] grid with many small holes, to which no voltage is applied. For the grid with 270 holes of 0.2 mm diameter that has been used for all measurements presented in this Chapter, the holes cover only ~1.5% of the surface area of the grid, resulting in a plasma chamber pressure that is a factor ~50 higher than the reactor pressure. Therefore, the particles collide on average many times with the inner walls of the plasma chamber before exiting through one of the holes in the grid. Due to these many wall collisions the ions are effectively neutralized and, consequently, the beam consists predominantly of neutral species. In addition, an ion trap is present (Fig. 7) that can be supplied with a voltage difference up to 10 keV (~5 keV and +5 keV) over ~3 cm to deflect virtually all of the ions (with a typical ion energy of ~10–~20 eV) from the beam towards the substrate. The final mode of the ECR-source is the hybrid mode, which combines the two metal grids with the dielectric grid. This configuration yields effectively the same beam composition as the ECR source in atom mode, however, an ion flux can be added to the beam by setting a voltage over the metal grids.

As a final point, the ECR source has a second gas inlet (not shown in Fig. 7) that enables the injection of precursor gasses, such as SiH₄, SiD₄, and Si₂H₆ (see Fig. 3), into the plasma emanating from the plasma chamber in the direction of the substrate. This precursor inlet opens up additional degrees of freedom for creating a (mono-)radical beam. For instance, a SiH₄ reaction chamber at the end of the ECR-source has been designed to create a mono-SiH₃ beam for deposition of a-Si:H (Sec. IV).

C. Hot wire radical source

The hot wire radical source consists of a single ~5.5 cm long, coiled tungsten filament with a diameter of 0.45 mm that is clamped between two copper electrodes [Fig. 1(e)]. The filament is resistively heated by a dc current. The temperature of the hot wire, \( T_{HW} \), has been measured with a color-temperature optical pyrometer (Pyro-werk, Mikro-pyrometer, 2981) as well as with an infrared radiation thermometer (Chino, IR-AHS) taking into account the reflection and absorption at the glass window, the emissivity of tungsten, and the projected area of the hot wire. For instance, a dc current of ~11 A yields a temperature of \( T_{HW} = (2325 \pm 200) \) K. At such a high filament temperature the gas phase molecules that collide with the hot wire are thermally dissociated. The radicals produced in this process may reach and react at the substrate or may, depending on the pressure, react in the gas phase to create new species (Sec. IV). An important feature of the hot wire is the relatively high radical fluxes that can be achieved (Sec. IV). The high flux of H atoms that is produced by immersing the hot wire in a relatively high H₂ pressure is ideal for reactor cleaning by means of H-induced etching. Moreover, a high H flux has been found well suited for conditioning the reactor surface and/or the substrate prior to an experiment, which has lead to very reproducible results of the initial phase of a-Si:H growth. Moreover, H-induced etching can also be used to remove a layer of a-Si:H from a substrate to enable reuse of the substrate in a next experiment without breaking the vacuum. As SiO₂ is not etched by H, the removal of a-Si:H stops at the native oxide layer of a-cSi substrate or at any optical substrate element made from quartz or fused silica (e.g., the folded cavity used in EW-CRDS). Because the dissociated atoms and molecules are emitted in random direction from the hot filament surface, a shield has been installed just behind the hot wire [Fig. 1(b)] to prevent deposition in the direction opposite from the substrate. Finally, it is noted that the hot wire can also be used to deposit a-Si:H by operating the hot wire in SiH₄ (or Si₂H₆) gas, as discussed in detail in Sec. IV, while deposition of micro-crystalline and poly-crystalline silicon can be achieved by a heavy dilution of SiH₄ in H₂.
IV. CHARACTERIZATION OF RADICAL SOURCES

In this section, the operation of the three radical sources in the Galapagos setup is characterized. First, the relative H flux from the H-source under different source operating conditions is measured by means of H-induced etch experiments of a-C:H and a-Si:H films. In these experiments, the etch process is monitored by real-time spectroscopic ellipsometry (RTSE). To determine the absolute H flux from the H-source, the trends in the H flux are compared with the trends in the H flux from the (similar) H-source of Tschersich and Von Bonin,\textsuperscript{19,20} thereby establishing a relation between the etch rate of a-C:H and the absolute H flux. Moreover, the H-induced etch yield of a-C:H and a-Si:H are determined. The ECR-source and the hot wire source can also be operated on H\textsubscript{2} gas to generate H atoms. By utilizing the above-mentioned relation, the ECR-source and hot wire source are characterized in terms of their absolute H flux by means of RTSE measurements of the H-induced etch rate of a-C:H.

A. Real-time spectroscopic ellipsometry experiments

For the H-induced etch experiments of a-C:H, a batch of hard a-C:H ("diamond-like carbon") films with a thickness of \(-400\) nm and a density of \(1.7\) g/cm\(^3\) have been deposited on native-oxide covered c-Si substrates.\textsuperscript{45} These depositions have been carried out in the so-called "expanding thermal plasma" setup, while using equal operating conditions for all films.\textsuperscript{45} The H-induced etch experiments of these a-C:H films have been monitored by real-time spectroscopic ellipsometry (RTSE) using a Woollam M2000U ellipsometer (\(0.7−5.0\) eV) at a fixed angle of incidence of \(-60^\circ\) with the substrate normal. Sets of 100 full RTSE spectra, each with a duration of 50 ms, have been averaged to enhance sensitivity. RTSE requires model-based analysis\textsuperscript{25} to extract H-induced etch rate of a-C:H from the RTSE data. To this end, a simple three-layer model (ambient / surface roughness layer / bulk a-C:H layer / native oxide layer / semi-infinite c-Si substrate) was found adequate to model the optical response of our a-C:H films. In the model, standard dielectric functions are used for the semi-infinite c-Si substrate and the native oxide layer, the dielectric function of the bulk a-C:H layer is described by the Tauc-Lorentz formalism,\textsuperscript{46} and the optical response of the surface roughness is modeled by the commonly-used Bruggeman effective medium approximation of 50% voids and 50% bulk a-C:H.\textsuperscript{25} Therefore, the model has the following fit parameters: the four Tauc-Lorentz fit parameters (\(A \approx 20\) eV, \(\Gamma \approx 5\) eV, \(E_0 = 6\) eV, and \(E_g \approx 0.9\) eV for our a-C:H films), the native oxide layer thickness (\(-20\) Å), the bulk layer thickness, \(d_b\), and the surface roughness layer thickness, \(d_s\). For each of the a-C:H films, the Tauc-Lorentz parameters as well as the native oxide layer thickness were measured with RTSE prior to the H-induced etch experiments (using the procedure described in Ref. 25) and were kept constant during the etch experiments. The H-induced etch rate of a-C:H is determined from the change of \((d_b + \frac{1}{2} d_s)\) as a function of the etch time.

For the H-induced etch experiments of a-Si:H, the RTSE data only provided satisfactory fits by adding a porous sub-surface layer to the model, in agreement with.\textsuperscript{22,49,50} In fact, the formation of a porous, hydrogen-rich sub-surface layer has been found to be a necessary condition for a-Si:H etching\textsuperscript{49} and has been explained by H atoms that penetrate into the bulk a-Si:H layer breaking a significant fraction of Si−Si bonds and terminating the dangling bonds.\textsuperscript{23} The thickness of the sub-surface layer was found to saturate at \(-100\) Å for \(T_{sub}=85\) °C, somewhat higher than the saturated sub-surface layer thickness of \(-70\) Å for \(T_{sub}=100\) °C found in Ref. 49.
As a first experiment, the H-induced etch rate of a-C:H, \( R_{etch} \), has been measured as a function of the distance \( r \) between the front side of the H-source and the substrate (Fig. 8), as set with the linear shift of the H-source, for a \( H_2 \) flow of 0.40 sccm and \( T_{cap} = 2130 \) K. The substrate temperature has been set at \( T_{sub} = 230 \) °C for all H-induced etch experiments of a-C:H, presented in this Chapter. As the diameter of the capillary is only 1 mm, the H-source is expected to have a point source behavior. To test the \( 1/r^2 \)-dependence of \( R_{etch} \), \( 1/\sqrt{R_{etch}} \) has been plotted on the left ordinate of Fig. 8. A linear dependence of \( R_{etch} \) with \( r \) is found, as illustrated by the good linear fit, corroborating the expected point source behavior. The intersect of the linear fit with the x-axis is found at a negative value of \( r \), i.e. \( r_0 = (-3.1 \pm 0.3) \) cm, indicating that the H radicals are produced within the H-source. The inset shows a schematic drawing of the front end of the H-source (cf. Fig. 4), represented such that the dimensions correspond to the x-axis.

B. Atomic hydrogen source

As a first experiment, the H-induced etch rate of a-C:H, \( R_{etch} \), has been measured as a function of the distance \( r \) between the front side of the H-source and the substrate (Fig. 8), as set with the linear shift of the H-source, for a \( H_2 \) flow of 0.40 sccm and \( T_{cap} = 2130 \) K. The substrate temperature has been set at \( T_{sub} = 230 \) °C for all H-induced etch experiments of a-C:H, presented in this Chapter. As the diameter of the capillary is only 1 mm, the H-source is expected to have a point source behavior. To test the \( 1/r^2 \)-dependence of \( R_{etch} \) for the case of a point source, \( 1/\sqrt{R_{etch}} \) has been plotted on the left ordinate of Fig. 8. A linear dependence of \( 1/\sqrt{R_{etch}} \) with \( r \) is found, as illustrated by the good linear fit, corroborating the expected point source behavior. The intersect of the linear fit with the x-axis is found at a negative value of \( r \), i.e. \( r_0 = (-3.1 \pm 0.3) \) cm. Taking into account that the capillary ends 0.6 cm from the front side of the H-source (Fig. 4), this values implies that the origin of the H atom trajectories lies on average at 2.6 cm within the capillary. This is in agreement with the fact that the on-axis H flux from the H-source consists of those H atoms that obtained their final trajectories towards the substrate by a gas phase collision in the collision-dominated regime deep within the capillary (Sec. III). In addition, Fig. 8 shows that the etch rate of a-C:H varies from 0.67 to 3.5 Å/min by varying the distance between the H-source and the substrate from 15.5 to 5.4 cm. This illustrates the ability to vary solely the H flux by setting the linear shift without changing any of the source operating conditions. Finally, the fact that a good \( 1/r^2 \)-dependence of \( R_{etch} \) is obtained also demonstrates that the etch rate of a-C:H depends linearly on the H flux. Therefore, measurements of the a-C:H etch rate can be used as a relative measure of the H flux. Next, the absolute H flux from the H-source is determined.

Tschersich has quantified his version of the H-source in terms of the absolute H flux.\(^{20}\) Our H-source is similar to this quantified H-source with the only difference being the heating mechanism of the capillary (Sec. III). Therefore, it is expected that both sources yield the same absolute H flux for a certain \( T_{cap} \) and \( H_2 \) flow. To verify this, the etch rate of a-C:H, \( R_{etch} \), has been measured as a function of \( T_{cap} \) for a \( H_2 \) flow of
The etch rate of a-C:H, $R_{\text{etch}}$, as a function of (a) the capillary temperature of the H-source, $T_{\text{cap}}$, as measured for a H$_2$ flow of 0.002 sccm at two different days (squares and triangles) and (b) as a function of the H$_2$ flow for $T_{\text{cap}} = 2130$ K. For both plots the distance of the H-source to the substrate is set at 5.4 cm. In both figures, the thick gray line depicts the absolute H flux, as measured by Tschersich for a similar H-source under the same operating conditions, while the thickness of the gray lines indicates the estimated uncertainty in the relative H flux. The right ordinates of the figures (a) and (b) show the value of the absolute H flux and have been scaled linearly to the left ordinate without offset to obtain the best overlap with the data points.

0.002 sccm, as shown in Fig. 9(a). Starting at a low $T_{\text{cap}}$, the etch rate of a-C:H increases up to $T_{\text{cap}} \approx 2200$ K above which $R_{\text{etch}}$ saturates to a constant value of $R_{\text{etch}} \approx 0.5 \text{ Å/min}$. This saturation of $R_{\text{etch}}$ with $T_{\text{cap}}$ should scale linearly with the saturation of the degree of H$_2$ dissociation $\alpha_{\text{H}_2}$ with increasing $T_{\text{cap}}$, as shown in Fig. 5 for the lowest H$_2$ flow of $1.9 \times 10^{-5}$ sccm. Therefore, the measurements of $R_{\text{etch}}$ in Fig. 9(a) are compared with the measurements of the absolute H flux by Tschersich under the same operating conditions. The absolute H flux is represented in Fig. 9(a) by the thick gray line and right ordinate, where the thickness of the gray line indicates the estimated uncertainty in the relative H flux. The right ordinate has been scaled linearly without offset to the left ordinate to obtain the best overlap with $R_{\text{etch}}$. The trend of our measurements of $R_{\text{etch}}$ agrees with the trend of the absolute H flux measurements within uncertainties. It is noted that the (low) H$_2$ flow of 0.002 sccm is set by regulating the needle valve (Sec. II) to obtain the corresponding H$_2$ pressure in the reactor, and, therefore, can have a significant uncertainty due to the uncertainty in the pressure measurements for H$_2$ gas and to a lesser extent in the pumping speed of H$_2$ gas. This uncertainty in the H$_2$ flow may change the trend of $R_{\text{etch}}$ with the H$_2$ flow somewhat. Nevertheless, the agreement in Fig. 9(a) is good enough to state on the basis of Fig. 5 that the degree of dissociation of H$_2$ in our capillary is more than 80% for the highest capillary temperature of $T_{\text{cap}} = 2375$ K.

In a second experiment, the etch rate of a-C:H has been measured as a function of the H$_2$ flow for $T_{\text{cap}} = 2130$ K, as shown in Fig. 9(b). It is noted that the H$_2$ flows in Fig. 9(b) are controlled accurately by a mass flow controller (Sec. II) and, therefore, the comparison of $R_{\text{etch}}$ with the absolute H flux determined by Tschersich is more reliable for Fig. 9(b) than for Fig. 9(a). This is emphasized by the perfect agreement between $R_{\text{etch}}$ and the absolute H flux (thick gray line) in Fig. 9(b). The agreement in both Fig. 9(a) and Fig. 9(b) demonstrates that our H-source and the one of Tschersich have the same H$_2$ dissociation behavior as a function of $T_{\text{cap}}$ and the H$_2$ flow. It is therefore concluded that the absolute H fluxes as measured by Tschersich [and shown on the right ordinates of Figs. 9(a) and 9(b)] also apply to our H-source. As a consequence, combining the individual ranges of the H flux with $T_{\text{cap}}$, the H$_2$ flow, and the distance $r$ (Figs. 8 and 9) yields a total range for the absolute H flux from the H-source of $~10^{12} - 10^{16}$ cm$^{-2}$s$^{-1}$.

The observation that the absolute H flux calibration by Tschersich applies also to our H-source enables a quantitative determination of the relation between the etch rate of a-C:H and the absolute H flux. To this end, the values of $R_{\text{etch}}$ [left ordinate of Fig. 9(b)] have been plotted in Fig. 10(a) as a function of the

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**Fig. 9.** The etch rate of a-C:H, $R_{\text{etch}}$, as a function of (a) the capillary temperature of the H-source, $T_{\text{cap}}$, as measured for a H$_2$ flow of 0.002 sccm at two different days (squares and triangles) and (b) as a function of the H$_2$ flow for $T_{\text{cap}} = 2130$ K. For both plots the distance of the H-source to the substrate is set at 5.4 cm. In both figures, the thick gray line depicts the absolute H flux, as measured by Tschersich for a similar H-source under the same operating conditions, while the thickness of the gray lines indicates the estimated uncertainty in the relative H flux. The right ordinates of the figures (a) and (b) show the value of the absolute H flux and have been scaled linearly to the left ordinate without offset to obtain the best overlap with the data points.

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**Fig. 10.** The etch rate of a-C:H, $R_{\text{etch}}$, as a function of (a) the capillary temperature of the H-source, $T_{\text{cap}}$, and (b) as a function of the H$_2$ flow, as determined by Tschersich for a similar H-source under the same operating conditions, while the thickness of the gray lines indicates the estimated uncertainty in the relative H flux. The right ordinate of the figures (a) and (b) show the value of the absolute H flux and have been scaled linearly to the left ordinate without offset to obtain the best overlap with the data points.
Fig. 10. (a) The etch rate of a-C:H, \( R_{\text{etch}} \), as a function of the H flux towards the substrate for \( T_{\text{cap}} = 2130 \) K and \( T_{\text{sub}} = 230 \) °C, where each data point has been measured at a different \( H_2 \) flow as shown in Fig. 9(b). Similar to the etch rate of a-C:H shown in figure (a), figure (b) shows the etch rate of a-Si:H as a function of the H flux towards the substrate for a \( H_2 \) flow of 0.43 sccm and \( T_{\text{sub}} = 85 \) °C. Each data point has been measured at a different capillary temperature, as indicated in the figure. The right ordinates of the figures show the etched C flux and etched Si flux from the a-C:H and a-Si:H substrate, respectively.

values of the H flux [right ordinate of Fig. 9(b)]. A good linear dependence is found as illustrated by the linear fit, where the small offset of the fit from the origin reflects the systematic uncertainties in all measurements involved. Taking this systematic uncertainty into account together with the estimated uncertainty of ~20% in absolute H flux by Tschersich (Sec. III), a relation between \( R_{\text{etch}} \) and the absolute H flux can be extracted from the slope of the linear fit:

\[
H \text{ flux (cm}^3\text{s}^{-1}) = (7 \pm 2) \times 10^{14} R_{\text{etch}} (\text{Å/min}).
\]

Equation (3) allows for the determination of the absolute H flux from the a-C:H etch rate, which will be used below to characterize the ECR-source and the hot wire radical source in terms of their absolute H flux.

Figure 10(a) can also be used to obtain the H-induced etch yield of a-C:H. To this end, the a-C:H etch rate and the carbon density in the film of \( 8.5 \times 10^{22} \) cm\(^{-3} \) (calculated from the a-C:H film density of 1.7 g/cm\(^3 \)) have been used to calculate the etched C flux from the substrate, as plotted at the right ordinate of Fig. 10(a). The relation between the etched C flux and the H flux reveals an etch yield of a-C:H of \( (2.0 \pm 0.6) \times 10^{-2} \), i.e. ~50 H atoms are needed to etch one C atom. This value corresponds well with the etch yield of \( (2.0 \pm 0.7) \times 10^{-2} \) at \( T_{\text{sub}} = 380 \) °C reported by Schwarz-Selinger et al., who also used a hot capillary H-source. In their work, the absolute H flux was also determined using mass spectrometry following the above-mentioned method of Tschersich. Other reported values of the etch yield of a-C:H at \( T_{\text{sub}} \approx 30 \) °C range from ~2.5×10\(^{-3}\) to ~4×10\(^{-2}\). Following Schwarz-Selinger et al., we attribute these differences to the large uncertainty in the H flux in those references and conclude that our value of the etch yield with its small uncertainty is reliable.

This method to obtain the etch yield can also be applied to obtain the etch yield of a-Si:H by atomic hydrogen. To this end, the H-induced etch rate of an a-Si:H layer, deposited with the hot wire (see below), has been measured as a function of the H flux from the H-source for \( T_{\text{sub}} = 85 \) °C. For these measurements, the H flux was varied by changing \( T_{\text{cap}} \) for a fixed \( H_2 \) flow of 0.43 sccm. The results are shown in Fig. 10(b). Contrary to H-induced etching of a-C:H, H-induced etching of a-Si:H occurs through the formation of a void-rich, hydrogen-rich sub-surface layer, as discussed above. The uncertainty in the dielectric function of this additional layer leads to the larger error bars in Fig. 10(b) compared to Fig. 10(a). Nevertheless, a good linear dependence of the a-Si:H etch rate with the H flux is observed. Using the silicon density in the a-Si:H film of ~5.2×10\(^{22} \) cm\(^{-3} \) an etch yield of a-Si:H of \( (5.1 \pm 1.5) \times 10^{-3} \) at \( T_{\text{sub}} = 85 \) °C is...
found. The good agreement with the literature, i.e. values of $\sim 2.5 \times 10^{-3}$ and $\sim 1 \times 10^{-2}$ at $T_{\text{sub}} = 85 ^\circ C$ have been reported for the etch yield of a-Si:H in two studies by the same group, supports again the reliability of our measurement of the etch yield. The expected reliability of both the a-C:H and a-Si:H etch yield supports in turn the reliability of the above-mentioned calibration procedure of the absolute H flux from the H source.

Finally, it is noted that no difference has been observed between the H-induced and D-induced etch yield of a-Si:H in agreement with the literature where no isotope effect for this etch process is mentioned. This result has been deduced from a separate etching experiment, where the a-Si:H etch rate as well as the optical material properties remained unchanged under alternating between an H flux and a D flux. An isotope independent a-Si:H etch yield is important for performing well-defined H-D exchange experiments, e.g. with ATR-FTIR to probe the Si-H and Si-D bonds in the a-Si:H film and on the surface. Moreover, the experiments show that the thermal dissociation of H$_2$ and D$_2$ into H and D, respectively, inside the H-source is equally efficient. Therefore, the absolute D flux can be set by using the calibration graphs of the H-source for the H flux, i.e. Figs. 8 and 9.

C. ECR-source

To gain insight into the plasma operation of the ECR-source, the absolute H flux has been measured under various operating conditions by means of the above-mentioned method of H-induced etching of a-C:H films. For these experiments, the ECR has been operated in the "atom mode", using an alumina grid, for which the open area of the holes is only $\sim 1.5\%$ of the surface area of the grid (Sec. III). As the ECR-source has been operated on pure H$_2$ as well as a mixture of H$_2$ and Ar, first, the influence of Ar ions on the a-C:H films has been investigated. To this end, the ECR-source has been operated on a pure argon plasma. No a-C:H etching or modification of the a-C:H surface has been observed (not shown), even without the use of the ion trap. This could mean that Ar ions (and metastables) do not modify the a-C:H films at all. More likely, it means that ions (and metastables) do not reach the substrate when the ECR-source is operated in the atom mode due the large number of ion-neutralizing wall collisions that the species on average undergo before reaching the substrate (Sec. III). More important, the measurement shows that the H-induced etch rate of a-C:H films is still a valid probe to obtain the absolute H flux when the ECR plasma is operated on a mixture of H$_2$ and Ar.

To characterize the ECR plasma operation on H$_2$, first the influence of the magnetron current, $I_{\text{magn}}$, has been investigated. It has been found (not shown) that the a-C:H etch rate and therefore also the H flux increases monotonically and fairly linear with $I_{\text{magn}}$ up to the maximum magnetron current of 100 mA. A similar trend of the H flux with $I_{\text{magn}}$ has been found for an H$_2$ flow of 1.0 and 3.0 sccm. For a fixed pressure in the plasma chamber, this monotonically increase in the H flux is explained by an increase of the degree of dissociation of H$_2$ with increasing magnetron current.

Figure 11 shows the measurements of the H-induced etch rate of a-C:H as a function of the distance $r$ between the front of the ECR-source and the substrate, as set with the linear shift of the ECR-source. The experimental settings are: a H$_2$ flow and Ar flow of 3.0 and 0.5 sccm, respectively, $I_{\text{magn}} = 100$ mA, and $T_{\text{sub}} = 230 ^\circ C$. To test the $1/r^2$-dependence of $R_{\text{etch}}$ for the case of a point source, $1/\sqrt{R_{\text{etch}}}$ has been plotted on the left ordinate of Fig. 11. A linear dependence of $1/\sqrt{R_{\text{etch}}}$ with $r$ is found, illustrated by the linear fit, demonstrating the point source behavior. The intersect of the linear fit with the x-axis is found at a negative

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Data set 2 has been measured with a leak in the ECR plasma chamber, reducing the chamber pressure. Nevertheless, the value of $R_{\text{etch}}$ of data set 2 showed clear a $1/r^2$-dependence of $R_{\text{etch}}$ and, therefore, have been multiplied with a factor of 1.5 to correspond to data set 1.
value of $r$, i.e. $r_0 = (-3 \pm 1)$ cm. Taking into account the length of the plasma chamber of $\sim 3.4$ cm (Sec. III), this value of $r_0$ indicates that the particle trajectories originate on average from a position close to the antenna (Fig. 7). This seems to reflect the fact that the H atoms, once produced, can have various trajectories to reach the substrate, e.g., via a gas phase reaction or via a reflection from the back side wall of the plasma chamber, because the mean free path of H in the plasma chamber is $\sim 16$ mm for the conditions of Fig. 11. In addition, Figure 11 shows that the a-C:H etch rate and therefore also the H flux can be varied with a factor of $\sim 4$ by adjusting the linear shift without altering any of the plasma operating conditions. Finally, the figure shows that the reproducibility is fairly good, but not as good as the reproducibility of the H-source.

Some insight into the ECR plasma operation in the atom mode is obtained from H-induced a-C:H etch experiments as a function of the H$_2$ flow with and without an additional Ar flow of 0.5 sccm, as shown in Fig. 12. On the right ordinate, the absolute H flux calculated from the a-C:H etch rate by the use of Eq. (3) is plotted. In this study, the ECR-source is operated at the minimum distance of 11 cm between the ECR-source and the substrate and at the maximum magnetron source current of 100 mA. Therefore, the figure shows directly the maximum H flux of $\sim 10^{15}$ cm$^{-2}$s$^{-1}$ that can be obtained with the ECR-source in atom mode for the flow conditions used. For a pure H$_2$ plasma, Fig. 12 shows that there exists a lower limit for the H$_2$ flow, below which no sustained plasma operation is possible due to a too low plasma pressure. The lower limit plasma pressure has been calculated to be $\sim 3 \times 10^{-3}$ mbar from a balance between the inflow of H$_2$ into the plasma chamber and the outflow of a mixture of H and H$_2$. Above a H$_2$ flow of 0.5 sccm, the H flux increases with increasing H$_2$ flow, while the H flux saturates at a H$_2$ flow of $\sim 2$ sccm and possibly even decreases for H$_2$ flows above 2 sccm. This saturation and possible decrease in the H flux might be explained by a decrease of the electron temperature, caused by a decrease of the electron mean free path with increasing plasma pressure, resulting in a decrease of electron-impact ionization and dissociation rate...
Fig. 12. The etch rate of a-C:H, $R_{\text{etch}}$, as a function of the H$_2$ flow into the ECR-source with (open circles) and without (closed circles) an additional Ar flow of 0.5 sccm. The operating conditions are $I_{\text{mag}} = 100$ mA, a minimum distance of the ECR-source to the substrate of 11 cm, while the grid of the ECR source contains 270 holes of 0.2 mm diameter. The dashed lines are guides to the eye. The right axis shows the absolute H flux at the a-C:H substrate, as calculated from the a-C:H etch rate using Eq. (3).

of H$_2$, because both reactions have a high activation barrier. In all, the window of operation of a pure H$_2$ plasma seems to be fairly small.

Figure 12 also shows the measurements of the H flux as a function of the H$_2$ flow for an additional Ar flow of 0.5 sccm. This Ar flow leads to a partial pressure of $\sim 1.2 \times 10^{-2}$ mbar, which is higher than the lower limit plasma pressure to sustain plasma operation. Therefore, no lower limit for the H$_2$ flow is observed for an Ar flow of 0.5 sccm. Figure 12 also shows that the H flux is increased for each H$_2$ flow when 0.5 sccm Ar is admixed to the H$_2$ plasma. The H flux does also not saturate for H$_2$ flows up to 3 sccm. Apparently, the production of H is more efficient with admixture of an Ar flow. These observations might be explained by the fact that plasma operation and H production is facilitated when Ar is present, possibly due to the presence of Ar ions and metastables. In all, Figure 12 clearly show that the H flux, or any other flux of the ECR plasma, can be optimized by tuning the plasma chemistry.

D. Hot wire radical source

Hot wire operation on H$_2$ gas has been examined as a function of the two main control parameters, i.e. the hot wire temperature $T_{\text{HW}}$ and the H$_2$ pressure, by H-induced etching of a-C:H films. The measurements of the a-C:H etch rate and, correspondingly, the H flux are shown in Fig. 13 and show directly that a high H flux of $1.5 \times 10^{16}$ cm$^{-2}$s$^{-1}$ can be obtained with the hot wire. Figure 13(a) shows that the H flux increases monotonically with $T_{\text{HW}}$, seemingly in an exponential manner. Figure 13(b) shows that the H flux increases also with increasing H$_2$ pressure, however, the H flux seems to saturate for higher H fluxes. These two trends can be understood when considering that the H atoms, produced at the hot wire, do not react in the gas phase. Therefore, the H flux at the substrate is equal to the production rate of H atoms at the tungsten hot wire multiplied by the probability that an H atom is reemitted from the hot wire in the direction of the substrate. Similar to the case of the H-source, the production rate of H atoms at the hot wire can be computed by multiplying the degree of dissociation of H$_2$ $\alpha_{\text{H}}$ at the hot wire (Fig. 5) with the H$_2$ flux towards the hot wire, where $\alpha_{\text{H}}$ can be calculated from Eqs. (1) and (2) by setting $p_{\text{eq}}$ equal to the H$_2$ pressure (Sec. III), while the H$_2$ flux towards the hot wire scales with the H$_2$ pressure. Moreover, the H production rate at the hot wire should scale linearly with the measured H flux, because, contrary to the H-
source, the beam profile of the H flux from the hot wire can be assumed independent of the H$_2$ flow. Therefore, Figure 13 shows the calculations of the relative H production rate (solid lines) as a function of the hot wire temperature $T_{HW}$ and the H$_2$ pressure, where the calculated values have been scaled linearly to the left axis without offset to obtain the best overlap with the data points. A good correspondence is found between the measured H-flux and calculated H production rate, which clearly shows that the dissociation of H$_2$ into H atoms at the tungsten hot wire is indeed described by Eqs. (1) and (2).

By means of H-induced etching of a-C:H, the H flux has also been measured as a function of the distance between the hot wire and the substrate (not shown), as set by changing the linear shift of the hot wire (Fig. 1). These measurements showed that H flux can be changed with a factor of ~17 without altering any of the hot wire operating conditions by varying the distance $r$ from 6.8 to 16.8 cm. By combining the trends of the H flux with $T_{HW}$, the H$_2$ pressure, and the distance $r$, the hot wire can provide an H flux in the range of ~2 × 10$^{11}$ to ~2 × 10$^{16}$ cm$^{-2}$ s$^{-1}$. The maximum H flux at the substrate can be increased further by increasing the H$_2$ pressure or $T_{HW}$ or by decreasing the minimum distance of the hot wire.

E. Deposition of a-Si:H

To deposit a-Si:H by the ECR-source, Si-containing precursor gasses, such as SiH$_4$, SiD$_4$, or Si$_2$H$_6$, can be injected through the second gas inlet into the reactive ECR beam, as discussed in Sec. III. Indeed, a-Si:H deposition has been obtained, in accordance with Ref. 56, by injecting a SiH$_4$ flow into the H-H$_2$ beam emanating from the plasma chamber, when operating the ECR-source in atom mode on H$_2$ gas. By this method, SiH radicals are created in the ECR beam via the hydrogen abstraction reaction H + SiH$_4$ → H$_2$ + SiH$_3$. Because it is expected that all other gas phase reaction can be neglected, the only reactive species flowing towards the substrate are H and SiH$_3$. Therefore this method can potentially be extended to create a mono-SiH$_3$ beam by optimizing the SiH$_3$ flux with respect to the H flux, based on two considerations. First, by increasing the pressure of H and SiH$_4$, the hydrogen abstraction reaction of SiH$_4$ becomes more effective yielding an increase in the SiH$_3$ flux, while decreasing the H flux. Second, the reaction probability of SiH$_3$ at an a-Si:H surface is fairly low ($\beta \approx 0.3$, Refs. 7, 9, and 35), while that of H is near unity. Therefore, collisions with a wall (that is automatically covered with a-Si:H due to SiH$_3$ deposition) will enhance the ratio between the SiH$_3$ and H flux. Based on these considerations, a SiH$_3$...
measurements showed that the density of tungsten in the a-Si:H films was below the detection limit of \( n_W \approx 5 \times 10^{17} \) cm\(^{-3}\). The low contamination levels of the a-Si:H films demonstrates the high-purity process conditions that can be achieved in Galapagos.

Deposition of a-Si:H can also be achieved by operating the hot wire in SiH\(_4\) gas. This technique, called hot wire chemical vapor deposition (HW-CVD), and is well-established in the literature\(^{44,60-65}\). It will therefore only briefly be explained here. For \( T_{\text{HW}} \approx 1800\) K, the majority of the SiH\(_4\) molecules colliding with the heated tungsten filament are decomposed into one Si and four H atoms.\(^{4,60}\) However, when increasing \( T_{\text{HW}} \) towards \( T_{\text{HW}} \approx 2300\) K, SiH\(_4\) decomposition into Si\(_2\)H\(_6\) and SiH\(_3\) radicals also becomes significant.\(^{62}\) For very low pressures, the SiH\(_4\) decomposition products produced at the filament will reach the surface and can contribute to a-Si:H film growth. When the SiH\(_4\) pressure is increased, the deposition rate increases due to the higher flux of SiH\(_4\) to the hot wire. At the same time, gas phase reactions become important. For a sufficiently large SiH\(_4\) gas density, the H atoms produced at the hot wire react with SiH\(_4\) in the gas phase to form H\(_2\) and SiH\(_3\) radicals.\(^{14,57,61}\) The SiH\(_3\) radicals are stable in the gas phase\(^{4,33,58}\) and, therefore, can reach the substrate. The Si atoms produced at the filament react in the gas phase with SiH\(_4\) to form Si\(_2\)H\(_4\) or other possible Si reaction products\(^{14,15,41-65}\). A minimum SiH\(_4\) pressure is thus necessary to react out the Si atoms before they reach the substrate. Increasing the SiH\(_4\) pressure beyond this minimum SiH\(_4\) pressure increases the concentration of the Si reaction products to such an extent that a significant fraction reacts further with SiH\(_4\) to yield large Si\(_x\)H\(_y\) \((x>2)\) radicals\(^{44,63}\) that are detrimental for the a-Si:H film quality.\(^{61}\) Therefore, there exists an optimum regime at intermediate pressures, for which the flux of radical at the surface is dominated by SiH\(_3\) radicals without the presence of the large, detrimental radicals. This intermediate pressure regime yields the optimum a-Si:H film quality\(^{61}\) and is obtained when the product of the SiH\(_4\) pressure and the distance from the hot wire to the substrate is in the range of \(-0.04 \text{--} -0.10\) mbar-cm, as determined experimentally.\(^{61}\) For the minimum distance between the hot wire and the substrate in our setup of 6.8 cm, the optimum regime is obtained for a SiH\(_4\) pressure of \(5.9 \times 10^{-2} \text{--} 1.5 \times 10^{-2}\) mbar. Using, therefore, a pressure of \(1.1 \times 10^{-2}\) mbar and \(T_{\text{HW}} = (2325 \pm 200)\) K, a series of a-Si:H films have been deposited at substrate temperatures in the range of 70—450 °C.\(^{21,28}\) It has been shown in Ref. 25 that high quality a-Si:H is grown under these conditions for \(T_{\text{sub}} = 250\text{—}450\) °C, in agreement with Ref. 61.

One aspect of this a-Si:H deposition series is highlighted here. Elastic recoil detection analysis combined with Rutherford back scattering (RBS) measurements of the a-Si:H films showed that the densities of the contaminants in the films were very low (atomic densities of C, N, and O of \(n_C \approx 5 \times 10^{17}\), \(n_N \approx 4 \times 10^{17}\), and \(n_O \approx 2 \times 10^{16}\) cm\(^{-3}\), respectively, compared to a Si and H density of \(n_Si \approx 4.8 \times 10^{25}\) and \(n_H \approx 5 \times 10^{26}\) cm\(^{-3}\), respectively).\(^{25}\) Especially, the oxygen density is notably low.\(^{66,67}\) These low impurities have been attributed\(^{25}\) to the low base pressure of \(10^{-9}\) mbar, to the preparation steps performed before the deposition runs, i.e. an overnight bake-out procedure followed by a intensive two-hour hot wire hydrogen etch to clean and condition the substrate and reactor walls (Sec. III), and to the gas purifier in the SiH\(_4\) supply line (Sec. II) that prevents the inflow of oxygen during the depositions. Moreover, the RBS measurements showed that the density of tungsten in the a-Si:H films was below the detection limit of \(n_W \approx 5 \times 10^{17}\) cm\(^{-3}\).
V. GENERAL CONCLUSIONS

A new vacuum setup designed for studying the surface science aspects of thin film growth and in particular the growth process of hydrogenated amorphous silicon has been presented. In an innovative reactor design, the substrate is located centrally between two vacuum chambers, making the substrate optically accessible from the front and back side through the various optical vacuum ports. This enables real-time monitoring of surface processes by advanced optical diagnostics. The process conditions, which include ultra-high vacuum, high-purity gases, and an accurate substrate temperature control, are well-defined and yield notably low contaminants in the deposited a-Si:H films. Finally, the plasma deposition process is mimicked by well-defined radical (and ion) beams. To this end, an atomic hydrogen source, an electron cyclotron resonance plasma source, and a hot wire radical source have been installed on the setup and can be supplied with a large number of feed gases, including isopes for future isotope labeling studies. Moreover, the three sources are positioned on linear shifts to allow for variation of the radical fluxes without altering the operating conditions.

For each of the three sources, the principle of operation has been addressed and tested from measurements of the relative H flux by operating the source on H\textsubscript{2} gas. Additionally, the H-source, the ECR source, and the hot wire have been characterized in terms of their absolute H flux, yielding a total range of the absolute H flux of \( \sim 10^{12} \text{--} 10^{16} \text{ cm}^{-2}\text{s}^{-1} \), \( \sim 10^{13} \text{--} 10^{15} \text{ cm}^{-2}\text{s}^{-1} \), and \( 2 \times 10^{11} \text{--} 2 \times 10^{16} \text{ cm}^{-2}\text{s}^{-1} \), respectively. A number of well-defined radical (and ion) beams can be produced by the three sources. The atomic hydrogen source produces a well-defined H beam (or D beam) with known beam profile and absolute H flux (or D flux). Using this H beam, the H-induced etch yield of a-C:H at \( T_{\text{sub}} = 230 \degree \text{C} \) and a-Si:H at \( T_{\text{sub}} = 85 \degree \text{C} \) has been measured with high precision, yielding \( (2.0 \pm 0.1) \times 10^{-2} \) C atoms per H atom and \( (5.1 \pm 0.5) \times 10^{-3} \) Si atoms per H atom, respectively. The electron cyclotron resonance plasma source can be used to create a well-defined ion beam or to deposit a-Si:H, while the source is currently being optimized as a SiH\textsubscript{3} source. Finally, the hot wire radical source has proven to deposit good-quality a-Si:H under SiH\textsubscript{3}-dominated flux conditions, while the source is also suited for reactor cleaning, in-situ a-Si:H removal, and reactor and substrate conditioning prior to an experiment.

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CHAPTER 8

REAL-TIME SPECTROSCOPIC ELLIPSMETRY
CHARACTERIZATION OF A-Si:H DEPOSITED BY HOT WIRE CVD
AT DIFFERENT SUBSTRATE TEMPERATURES

ABSTRACT

We have applied real-time spectroscopic ellipsometry (RTSE) as well as a number of ex-situ diagnostics to characterize hydrogenated amorphous silicon (a-Si:H) deposited at substrate temperatures in the range of $T_{\text{dep}} = 70-450$ °C. The a-Si:H films have been grown by hot wire chemical vapor deposition (HWCVD) from undiluted silane (SiH$_4$) gas. After a careful validation of our RTSE data analysis approach, a comparison of the RTSE results with the ex-situ results has yielded a detailed characterization of the optical and structural properties of the a-Si:H films. For instance, it has been found that high quality a-Si:H films are grown with HWCVD in the range of $T_{\text{dep}} = 250-450$ °C with an optimum around ~300 °C. Moreover, a number of correlations between material parameters have been found. Therefore, while RTSE directly yields the dielectric function, film thickness, and surface roughness evolution, these correlations also enable the real time determination of structural material properties of a-Si:H from RTSE, including absolute values of the total mass density and the hydrogen concentration and relative information on the silicon-hydride bonding configuration, bond-length distribution, and disorder in the film. The comparative study also yields some general insight into the dependence of the optical and structural properties of a-Si:H on the substrate temperature.

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I. INTRODUCTION

The development of multichannel ellipsometers has enabled real-time spectroscopic ellipsometry (RTSE), a powerful diagnostic that yields the optical material properties of the growing film from its dielectric function.\textsuperscript{1–4} RTSE can also be applied to investigate the surface roughness evolution during thin film growth. As such, RTSE has been applied extensively to study the nucleation, coalescence, and growth of Group IV thin films, including hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon (μc-Si:H), as done by Collins \textit{et al.} for rf plasma enhanced chemical vapor deposition (PECVD)\textsuperscript{5,6} and by Levi \textit{et al.} for hot wire chemical vapor deposition (HWCVD)\textsuperscript{7–10} In addition, RTSE has the potential of providing insight into the structural material properties and even the electronic material properties from the correlations between these properties and the dielectric function.

Having a detailed knowledge of the material properties of the growing a-Si:H films is an essential condition for conducting dedicated studies of the surface processes during a-Si:H growth under well-defined conditions in our new ultrahigh-vacuum setup.\textsuperscript{11,12} Therefore, our first aim is to perform an extensive material characterization with RTSE of a-Si:H films deposited by HWCVD at substrate temperatures in the range of 70–450 °C. To this end, the RTSE data is analyzed by the same procedure as used by Collins \textit{et al} on their RTSE data\textsuperscript{5,6} to allow for a direct comparison between the RTSE results. Additional material characterization is obtained by analyzing the grown a-Si:H films with a number of \textit{ex-situ} diagnostics, i.e. Raman spectroscopy, Fourier transform infrared spectroscopy, elastic recoil detection analysis combined with Rutherford back scattering analysis, and atomic force microscopy. A second aim of this study is to find correlations between different material parameters by comparing the RTSE results with the results of the \textit{ex-situ} diagnostics. Using these correlations, RTSE can be extended to provide \textit{in-situ} and real-time information on the structural material properties during the growth of a-Si:H films, deposited under the same or different operating conditions, or even during the growth of different silicon thin films. As a final aim, the study will also serve to gain general insights into the dependence of the optical and structural material properties of a-Si:H on the substrate temperature, a key parameter for the material quality. Although various studies on a-Si:H material properties as a function of different growth conditions have been reported in the literature, correlations between optical and structural a-Si:H properties are often scattered across the literature and obscured by the differences in deposition technique and growth conditions used. Our extensive investigation of a set of a-Si:H films that only differ in the substrate temperature during deposition yields information on the substrate temperature dependence of the material properties in a natural way.

To give a generic validity to the obtained results, the series of a-Si:H films has been deposited by HWCVD from undiluted silane (SiH\textsubscript{4}) gas under "optimum HWCVD deposition conditions".\textsuperscript{13} Under these conditions the deposition flux is dominated by SiH\textsubscript{3} radicals.\textsuperscript{13,14} SiH\textsubscript{3}-dominated growth conditions are generally believed to result in device-quality a-Si:H films\textsuperscript{15–17} and it will be show below that high quality a-Si:H films are indeed obtained under these conditions. In addition, the material properties of optimized a-Si:H films are generally found to be remarkably independent of the deposition method used.\textsuperscript{13} Therefore, it is expected that the results presented in this Chapter are representative for HWCVD a-Si:H growth and a-Si:H deposition in general.

The Chapter is structured as follows. After presenting the experimental details in Sec. II, the validity of our RTSE data analysis approach as well as the accuracy of the RTSE results are carefully examined in Sec. III on a three times repeated a-Si:H deposition at a substrate temperature of 250 °C. The RTSE results obtained from the series of a-Si:H deposition runs at different substrate temperatures are presented in Sec.
IV and the optical material properties are deduced. In Sec. V, the optical material properties are compared to the structural properties obtained from the ex-situ diagnostics to deduce useful correlations as well as general trends of a-Si:H material properties with the substrate temperature. Finally, the general conclusions are presented in Sec. VI.

II. EXPERIMENTAL DETAILS

A-Si:H films with a thickness of 2000–3000 Å have been deposited using HWCVD at five different substrate temperatures, referred to as the deposition temperature $T_{dep}$, in the range of $T_{dep}=70$–450 °C while all other experimental conditions were kept constant. The deposition runs took place in an ultrahigh-vacuum compatible setup dedicated for fundamental studies (presented in detail in Refs. 11 and 12), which has as main features a low-contaminant background (base pressure $<10^{-9}$ mbar, purity of SiH$_4$ gas specified at $>99.995\%$ with sub-ppm levels of O$_2$, CO, CO$_2$, H$_2$O, and non-methane hydrocarbons due to additional gas purification), an accurately controlled substrate temperature (within 2 °C), a shutter to shield the substrate, and a good accessibility to the substrate for “all-optical” diagnostic techniques. The hot wire (a single ~5.5 cm long, coiled tungsten filament with a diameter of 0.45 mm) was operated in undiluted SiH$_4$ at a dc current of 11A (voltage of 7.7 V), resulting in a temperature of the hot wire of $2050\pm200$ °C. The SiH$_4$ flow rate was set at 3.0 standard cm$^3$/min (sccm) and the pressure within the deposition chamber was controlled at $1.1\times10^{-2}$ mbar. By positioning the hot wire at 6.8 cm from the substrate, the conditions are within the region of “optimum HWCVD operating conditions” as reported by Molenbroek et al.$^{13,14}$ In order to condition the reactor and the substrate prior to each deposition, an overnight bake-out procedure was performed, in which the reactor and substrate were heated overnight to 120 °C and 450 °C, respectively (with the shutter closed). This bake-out procedure ensured a background pressure prior to deposition of $\leq10^{-9}$ mbar, but it also changed the substrate condition, as discussed in Sec. III. The bake-out procedure was followed by a two-hour HWCVD hydrogen etch (with the shutter closed) just prior to the deposition to remove any residual water from the reactor walls.

The a-Si:H deposition runs were monitored in real time using a rotating compensator spectroscopic ellipsometer (J. A. Woollam, Inc. M2000U), at a fixed angle of incidence of ~60° with respect to the substrate normal. The photodiode-array-based detection system is capable of collecting a full spectroscopic ellipsometry (SE) spectra consisting of 662 wavelengths in the range of 245–1700 nm (0.75–5.04 eV) in 50 ms. This extended wavelength range assures the measurement of all roughness wavelengths present on the surface, as demonstrated in Ref. 19. For the deposition runs presented in this study, sets of 100 full SE spectra were averaged to yield sufficient sensitivity to accurately measure the surface roughness development during the early stages of the a-Si:H growth. The choice for a high sensitivity, however, comes at the expense of a relatively low time-resolution of 11 sec (which includes real-time numerical calculations for data analysis). The model used to extract the thickness and opto-electronic parameters of the different layers from the RTSE data is treated in detail in Sec. III.

The grown a-Si:H films have also been analyzed by a number of ex-situ diagnostics. Information on the microstructure of the films has been determined at the Delft University of Technology from Raman spectroscopy. Polarized Raman scattering spectra were obtained over an integration time of 300 s by means of a home-built Raman spectroscopy setup (see, e.g., Ref. 20). This setup uses a 180° backscatter geometry that includes a doubled Nd:YVO$_4$ laser at 532 nm with a reduced laser power of 2 mW in a spot size of ~1 µm and a Spex 340E monochromator with a liquid nitrogen cooled CCD camera. Two holographic supernotch filters were used to separate the Raman signal from the Rayleigh scattering signal. Furthermore,
The density and bonding configuration of hydrogen in the a-Si:H films has been investigated with Fourier transform infrared spectroscopy (FTIR) measurements in transmission mode using a Bruker Vector Fourier Transform Spectroscope with a frequency range of ν = 370–7000 cm⁻¹ and a resolution of 4 cm⁻¹. The silicon-hydride modes (Si-H₆) were probed at the three characteristic absorption peaks in a-Si:H: the wagging mode (WM) at ~640 cm⁻¹, the low stretching mode (LSM) at 1980–2030 cm⁻¹, and the high stretching mode (HSM) at 2060–2160 cm⁻¹, where the nomenclature of Ref. 22 is followed. It is generally believed that every bonded hydrogen atom in a-Si:H contributes to the wagging mode and, depending on its local environment in the film, also contributes either to the LSM or to the HSM. Consequently, the total hydrogen density in the film can be obtained from the product of the integrated absorption strength of the wagging mode peak, \( I_{WM} \), times the proportionality constant \( A_{WM} \), whereas the density of Si-H₆ bonds contributing to the LSM and HSM is equal to \( I_{LSM}A_{LSM} \) and \( I_{HSM}A_{HSM} \), respectively. Acknowledging the debate in the literature about the precise values of \( A_{WM} \), \( A_{LSM} \), and \( A_{HSM} \), here, Ref. 22 was followed and the values of \( A_{WM} = 1.6 \times 10^{19} \) cm⁻² and \( A_{LSM} = A_{HSM} = 9.1 \times 10^{19} \) cm⁻² were adopted. The choice for these values is validated from the fact that for our measurements at various \( T_{dep} \), the hydrogen concentration obtained from the wagging modes, [\( H \)\]_{WM} = \( I_{WM}A_{WM} \), corresponds closely to that obtained from the stretching modes, [\( H \)\]_{LSM} = \( I_{LSM}A_{LSM} \) + \( I_{HSM}A_{HSM} \). Moreover, the average between [\( H \)\]_{WM} and [\( H \)\]_{LSM}, i.e. [\( H \)\]_{FTIR}, corresponds well with [\( H \)\]_{ERD} obtained from ERD, as shown below.

Finally, the surface topography of the a-Si:H films has been analyzed using a vibration-stabilized NT-MDT Solver P47 atomic force microscope (AFM). The AFM scans, with three different scan sizes of \( L = 1 \times 1 \), 2×2, and 3×3 μm², were carried out in air in the non-contact mode with a resonant frequency of ~200 kHz using c-Si cantilever probes with a nominal tip radius of 5–10 nm. One such set of 3 AFM scans was measured for \( T_{dep} = 70 \) and 250 °C, while 2 such sets were measured for \( T_{dep} = 150, 350, \) and 450 °C. From each AFM scan, the root-mean-square (RMS) roughness \( w(L) \) has been calculated. Typical AFM scans are shown in Ref. 19, in which also the precise calculation procedure of \( w(L) \) is given that includes the average over smaller window sizes \( l \) within each scan size \( L \). In Ref. 19, it is also shown that the AFM results do not depend on the scan size \( L \). Therefore, for each \( T_{dep} \), the values of the \( w(L) \) were averaged.

III. RTSE DATA ANALYSIS APPROACH

In this section, the validity of our RTSE data analysis approach and the accuracy of the RTSE results is investigated. Spectroscopic ellipsometry (SE) yields the ratio \( \rho \) of the complex Fresnel reflection coefficients \( r_p \) and \( r_s \) of \( p \)- and \( s \)-polarized light, respectively, upon interaction with the sample:
The ratio $\rho(E)$ can be expressed in the conventional ellipsometry parameters $\Psi(E)$ and $\Delta(E),$ which are all functions of the photon energy of the light $E$. A real-time SE (RTSE) measurement yields a set of $\Psi(E)$ and $\Delta(E)$ at each scan time $i$ during the deposition, i.e. $<\Psi(E)_{\text{exp}},\Delta(E)_{\text{exp}}>$.

In order to extract the structural and optical material properties of the film as a function of time, model-based analysis is required. In this analysis, a parameterized optical model of the sample structure is generated that consists of several layers each with an individual dielectric function $\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$.

The optical response of this model in terms of $\Psi(E)$ and $\Delta(E)$ is simulated using the Fresnel equations. The simulated $\Psi(E)$ and $\Delta(E)$ are then compared with the measured $\Psi(E)$ and $\Delta(E)$ in the fitting procedure and the goodness-of-fit is expressed by the mean square error (MSE). The model parameters are adjusted iteratively using the Levenburg-Marquardt optimization to minimize the MSE. For all the deposition runs presented in this Chapter, a consistent single-phase a-Si:H material was observed throughout the film growth, as is shown below. Therefore, the a-Si:H films could well be represented by a simple two-layer model (ambient / surface roughness layer / bulk a-Si:H layer / semi-infinite substrate) with only two time-dependent fit parameters, i.e. the surface roughness thickness $d_s$ and the bulk thickness $d_b$, as shown in Fig. 1. The individual models of the different layers are described next.

A. Substrate.

All films were grown on c-Si substrates covered with a native oxide layer, which could well be simulated with a (ambient / SiO$_2$ layer / semi-infinite c-Si substrate) model when using standard dielectric functions at the appropriate $T_{\text{dep}}$ to model the semi-infinite c-Si substrate and the SiO$_2$ layer. Prior to each deposition, an overnight bake-out procedure was performed (Sec. II) that changed the substrate condition, as deduced from in-situ and ex-situ SE measurements. Before the bake-out procedure, an apparent thickness of the native oxide layer of $\sim$17-19 Å was observed. After the bake-out procedure, a native oxide layer with a thickness of $(9 \pm 1)$ Å remained. The difference is explained by the removal of adsorbed water and other contaminants from the substrate, leaving the bare native oxide layer as a very reproducible starting point for the a-Si:H deposition runs. During the a-Si:H deposition runs, the native oxide layer is assumed to be unaffected by the over-deposition of a-Si:H. This assumption has been verified from a separate etch study of an a-Si:H film by H atoms generated by the hot wire, which showed that the remaining native oxide layer thickness after complete removal of the a-Si:H film changed (increased) by less than a monolayer. This observation is in agreement with the literature$^6,24$ and with a very low surface reaction probability of H on a native-oxide-covered c-Si substrate.$^{25}$

In the RTSE model of Fig. 1 that is used to model the a-Si:H deposition runs, the c-Si substrate with
native oxide layer is implemented using a so-called 'virtual substrate'. This virtual substrate is the pseudodielectric function $\langle \varepsilon(E) \rangle = \langle \varepsilon_1(E) \rangle + i \langle \varepsilon_2(E) \rangle$ of the native-oxide-covered c-Si substrate, as calculated directly from $\langle \varepsilon(E)_{\text{exp}} \rangle$ using the Fresnel equations of a single interface (ambient / substrate):

$$\langle \varepsilon \rangle = \sin^2 \theta \left[ 1 - \left( \frac{\rho - 1}{\rho + 1} \right)^2 \tan^2 \theta \right],$$

where $\langle \varepsilon(E)_{\text{exp}} \rangle$ has been measured just prior to the start of the deposition at the specific $T_{\text{dep}}$. Therefore, the virtual substrate is an exact representation of the optical response of the substrate during the deposition. The above-mentioned (ambient / SiO$_2$ layer / semi-infinite c-Si substrate) model, however, is only a (good) approximate representation of the optical response of the substrate and introduces an additional uncertainty in the RTSE model. Therefore, the use of the virtual substrate is preferred.

**B. Bulk a-Si:H layer**

The a-Si:H material is described by the Tauc-Lorentz (TL) formalism, which is the most widely used parameterization of the optical functions of amorphous semiconductors. In the TL formalism, the imaginary part of the dielectric function $\varepsilon_2(E)$ is determined by the product of the Tauc law and the Lorentz oscillator model.$^{1,26}$ The Tauc law is a description of $\varepsilon_2(E)$ above the band gap due to the joint density of states of a semiconductor:$^{27}$

$$\varepsilon_2(E) = A_T (E - E_g)^2 / E^2,$$

where the constants to be fit are the optical band-gap $E_g$ and the amplitude $A_T$. The Lorentz oscillator model describes the $\varepsilon_2(E)$ of a collection of non-interacting atoms, which in the case of a single transition is characterized by the peak position $E_0$, the broadening term $\Gamma$, and the amplitude $A_L$: $^{28}$

$$\varepsilon_2(E) = \frac{A_L E_0 \Gamma}{(E^2 - E_0^2)^2 + \Gamma^2 E^2}. $$

The TL formalism combines the Tauc joint density of states with the Lorentz oscillator model, yielding $^{1,26}$

$$\varepsilon_2(E) = \left\{ \begin{array}{ll}
AE_0 \Gamma (E - E_g)^2 / (E^2 - E_0^2)^2 + \Gamma^2 E^2 & E > E_g, \\
0 & E \leq E_g.
\end{array} \right.$$

Therefore, the imaginary part of the dielectric function $\varepsilon_2(E)$ is described by the four TL parameters, $E_0$, $E_g$, $\Gamma$, and the amplitude $A$ (i.e. the product of $A_T$ and $A_L$), all with units of energy. The real part of the dielectric function $\varepsilon_1(E)$ is obtained from a Kramers-Kronig integration of $\varepsilon_2(E)$:$^{28}$

$$\varepsilon_1(E) = \varepsilon_1(\infty) + \frac{2}{\pi} \int_{E_g}^{\infty} \frac{\varepsilon_2(z)}{z^2 - E^2} \, dz,$$

where $P$ is the Cauchy principal part of the integral. It is noted that the value of $\varepsilon_1(\infty)$ is kept principally fixed at 1.$^{28}$ It is recognized that the dielectric function of a-Si:H can also be described by the so-called Cody-Lorentz (CL) formalism,$^{29}$ in which the Tauc joint density of states of Eq. (3) is replaced by an expression that is based on the Cody joint density of states $\varepsilon_2(E) = A_T (E - E_g)^2$, i.e.:

$$\varepsilon_2(E) = \frac{A_T (E - E_g)^2}{(E - E_g)^2 + E_0^2}, $$
where $A_c$ and $E_g$ are the amplitude and the optical gap, respectively, and $E_p$ is an extra fit parameter that defines a transition energy. As discussed below, the TL formalism has been tested against the CL formalism.

C. Surface roughness.

The dielectric function of the surface roughness layer $\varepsilon_s$ was modeled as a layer consisting of 50% voids and 50% of the underlying material using the Bruggeman effective medium approximation (EMA):

$$f_v \frac{\varepsilon_v - \varepsilon_{as}}{\varepsilon_v + 2\varepsilon_{as}} + f_a \frac{\varepsilon_{as} - \varepsilon_v}{\varepsilon_{as} + 2\varepsilon_v} = 0,$$

where $f_v$ and $f_a$ are the volume fractions of the randomly distributed constituents ($f_v = f_a = 0.5$ in this case) and $\varepsilon_v$ and $\varepsilon_{as}$ are the dielectric functions of the voids ($\varepsilon_v = 1 + i\varepsilon$) and the bulk a-Si:H material, respectively. Therefore, there are no fit parameters in $\varepsilon_s$; only the thickness of the surface roughness layer, $d_s$, is fitted. In several studies, it has been shown that for a-Si:H the surface roughness layer on top of the bulk layer is best modeled using this EMA with 50% voids and that inclusion of additional free parameters, such as the void volume fraction, is not beneficial.

D. Fit procedure

The post-deposition RTSE analysis of an a-Si:H deposition consists of two fitting steps. In the first fitting step, the dielectric function of the a-Si:H bulk layer as well as the bulk thickness $d_b$ and surface roughness $d_s$ are obtained from a so-called 'single time frame' (STF) fit of the final RTSE time frame of the deposition run at a bulk thickness of ~2000-3000 Å, i.e. $<\Psi(E_{exp})\Delta(E_{exp})>$final. At these thicknesses, the high-energy part of the spectrum (>3 eV) is opaque, while the low-energy part of the spectrum (<2eV) is still transparent and shows interference fringes. Therefore, after a first guess of the fit parameters, the Levenburg-Marquardt optimization is able to simultaneously find the optimum $d_s$ from the interference fringes at the low-energy part of the spectrum, the optimum $d_b$ from the high-energy part of the measured spectrum, and the optimal TL (or CL) parameters from the total $<\Psi(E_{exp})\Delta(E_{exp})>$final spectrum. In the second fitting step, the evolution of $d_b$ and $d_s$ as a function of deposition time $t$, i.e. $<d_{b_{new}}d_{s_{new}}>$, is determined by assuming fixed TL (or CL) parameters throughout the deposition process. The accuracy of this assumption of a bulk thickness independent dielectric function of a-Si:H is examined below.

It is noted that the dielectric functions of more complex models, such as µc-Si:H where the microstructure of the film changes as a function of bulk thickness, are generally optimized by performing an elaborate global minimization (GM) procedure, which is a simultaneous optimization over all the RTSE time frames of the deposition. Because, in principle, the choice for a certain fit procedure could have a large impact on the obtained RTSE results, the STF fit procedure is tested below against the more rigorous GM procedure.

E. Justification of the RTSE data analysis approach

First the RTSE model and the fit procedure have been explained, now the accuracy of our RTSE data analysis approach is tested. To this end, Figure 2 shows the evolution of the surface roughness layer thickness $d_s$ and the bulk layer thickness $d_b$ as a function of deposition time $t$ for the three times repeated a-Si:H deposition at $T_{dep} = 250$ °C. The RTSE data has been fitted with the STF fit procedure applied to the
two-layer TL model, as described above. In the first ~17 s, the surface roughness increases up to a value of ~13 Å (the initial growth of a-Si:H on the native oxide surface occurs through the formation of islands that coalesce at ~17 s, Ref. 19), whereas after ~17 s bulk film growth starts at a constant growth rate of ~77 Å/min. During bulk growth, the surface roughness is first observed to decrease and subsequently to increase again as a result of surface smoothening mechanisms that are active during the a-Si:H growth, as addressed in detail in Ref. 19. In this Chapter, however, not so much the trends of \( d_s \) and \( d_b \) with the deposition time are important, as is the fact that a very good agreement is found between the three a-Si:H deposition runs.

An equally good reproducibility is seen in Fig. 3, which shows the real \( \varepsilon_1(E) \) and imaginary \( \varepsilon_2(E) \) part of the dielectric function of the three deposition runs of Fig. 2 (indicated by \( a_1, a_2, \) and \( a_3 \) in Fig. 3), while Table I shows the corresponding optimized TL-parameters at \( T_{dep}=250 \) °C. The dielectric functions \( a_1, a_2, \) and \( a_3 \) agree within their 90% confidence limits. This good agreement in both Figs. 2 and 3 reflects the typical run-to-run reproducibility to grow a-Si:H layers with a certain dielectric function and the measurement sensitivity of our rotating compensator spectroscopic ellipsometer. The good agreement also reflects the accuracy of our RTSE data analysis approach including the STF fit procedure. Having shown the statistical accuracy of our RTSE data analysis, the approach is subsequently examined for potential systematic errors in the assumptions of the model and in the fit procedure, by means of three specific tests.

1. First, the most basic assumption of our RTSE model is tested, which implies that a consistent single-phase a-Si:H material is grown throughout the deposition. To this end, the depth profile of the dielectric function has been obtained by performing a separate STF fit on each time frame \( i \), \( <\Psi(E)_{\exp}\Delta(E)_{\exp}>_i \), yielding a simulated \( <\Psi(E)_{\text{sim}}\Delta(E)_{\text{sim}}>_i \) with six optimized fit parameters \( (A, \Gamma, E_0, E_g, d_s, d_b) \) for each time frame. Initially, the 90% confidence limits of the four TL parameters improve rapidly with increasing bulk layer thickness, but the 90% confidence limits saturate towards their final value at the end of the deposition. More important, for each time frame, the four TL parameters correspond with their final values within their 90% confidence limits. As an illustration, curve \( b_1 \) in Fig. 3 shows the dielectric function at the minimum in the surface roughness at a deposition time of \( t\approx130\) Å, i.e. \( <\varepsilon_1(E)_{\text{sim}}\Delta(\varepsilon)_2_{\text{sim}}>_i \) calculated from the optimized TL parameters obtained from the STF fit of \( t\approx130\) Å. A very good agreement between dielectric function \( a_i \) and \( b_i \) in Fig. 3 is observed. Only a small deviation in \( \varepsilon_1(E) \) and \( \varepsilon_2(E) \) is observed for \( E<2.5\) eV (see inset of Fig. 3), which is still within the 90% confidence limits that are relatively large for the STF fit at \( t\approx130\) Å. It is thus concluded that a-Si:H with a (nearly) constant dielectric function is deposited throughout the deposition process. Therefore, it is appropriate to
CHAPTER 8

1.6 1.8 2.0

0 1 2 3 4 5 6

-10 -5 0 5 10 15 20 25

c
c

Photon energy E (eV)

Real part of dielectric function ε1

Imaginary part of dielectric function ε2

Fig. 3. The real ε1(E) and imaginary ε2(E) part of the dielectric function of the three a-Si:H deposition runs at Tdep = 250 °C shown in Fig. 2. The dielectric functions have been obtained by using four different fit procedures a–d, where the subscript denotes the a-Si:H deposition run. In procedure a, the 'single time frame' (STF) fit procedure has been applied to fit the two-layer RTSE model of Fig. 1 with the bulk a-Si:H layer described by the Tauc-Lorentz (TL) formalism. Procedures b–d all differ in a single aspect from procedure a: in procedure b the STF fit has been performed at the position of the dip in the surface roughness at d0 = 160 Å instead of at the end of the deposition run; in procedure c the Cody-Lorentz formalism is used instead of the Tauc-Lorentz formalism; and in procedure d the global minimalization (GM) procedure is used instead of the STF fit procedure. The inset shows a magnification of ε2(E) in the band-gap region.

simulate the total a-Si:H deposition, before and after the minimum in the surface roughness, with one optical model.

(2) Second, the Tauc-Lorentz formalism to model the a-Si:H bulk dielectric function is tested against the Cody-Lorentz formalism.39 To this end, curve c1 in Fig. 3 has been calculated from the same a-Si:H deposition run as curve a1, but in the simulations of curve c1 the TL formalism in the RTSE model has been replaced with the CL formalism, as explained above. A very good agreement between the two formalisms is observed for the full energy range, although a small deviation is seen for E > 4.5 eV. Particularly, the inset of Fig. 3 shows that the agreement between the two formalisms is excellent near the band-gap.† The surface roughness evolution as a function of time agrees also within the 90% confidence limits. Even though the Cody-Lorentz formalism uses five instead of the four TL parameters to describe the imaginary part of the dielectric function, no significant improvement of the obtained mean squared errors of the fits has been observed.† Therefore, it is concluded that the dielectric function of our a-Si:H material is well described by the TL formalism in agreement with Refs. 34 and 35. The extra fit parameter is therefore not deemed beneficial. In fact, the TL formalism is preferred over the CL formalism, as the four TL fit parameters are less correlated, resulting in a faster Levenburg-Marquardt optimization, while trends of the fit parameters with deposition settings are not obscured by correlation effects.39

(3) Finally, the single time frame (STF) fit procedure is tested against the global minimalization (GM) procedure,5,9 explained above. To this end, curve d1 in Fig. 3 has been calculated from the same a-Si:H deposition run as curve a1, but in the calculation of curve d1 the fit parameters of the CL formalisms

† We believe that the three arguments for the use of the CL over the TL formalism in the simulation of amorphous semiconductors39 are unimportant for our a-Si:H material, as briefly explained here. First, the same value of the optical gap Eg is found for the two formalisms within their uncertainties, while the highest consistency in the value of Eg is found from extrapolating the Tauc plot (and not the Cody plot), in agreement with Ref. 39. Second, as also recognized in Ref. 29, inclusion of the Urbach Tail in either the TL or the CL formalisms is not necessary to accurately model a-Si:H films. Third, we have modeled all a-Si:H deposition runs with ε1(∞) fixed at 1 (Sec. III) and found good fits and, therefore, found no reason to assume the TL description does not include all electronic transitions.
Table I. The optimized values of the four TL parameters $A$, $\Gamma$, $E_a$, and $E_b$ (not corrected for their dependence on the analysis temperature $T_{an}$), as well as the growth rate $F$, for the a-Si:H films grown at deposition temperature $T_{dep}$. The bottom row shows the values of the linear dependence of the different TL parameters on $T_{an}$ (referred to as "$T_{an}$-depen." given in units of $10^4$ eV/K). The values of $T_{an}$-depen. have been deduced from the post-deposition SE analysis of the grown a-Si:H films at different $T_{an}$.

<table>
<thead>
<tr>
<th>$T_{dep}$ (°C)</th>
<th>A (eV)</th>
<th>$\Gamma$ (eV)</th>
<th>$E_a$ (eV)</th>
<th>$E_b$ (eV)</th>
<th>$F$ (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70±2</td>
<td>171±2</td>
<td>2.58±0.04</td>
<td>3.79±0.02</td>
<td>1.78±0.02</td>
<td>102.2±0.4</td>
</tr>
<tr>
<td>150±2</td>
<td>187±2</td>
<td>3.72±0.02</td>
<td>3.68±0.01</td>
<td>1.72±0.01</td>
<td>84.9±0.4</td>
</tr>
<tr>
<td>250±2</td>
<td>183±3</td>
<td>2.29±0.02</td>
<td>3.60±0.01</td>
<td>1.57±0.01</td>
<td>78.0±0.4</td>
</tr>
<tr>
<td>250±2</td>
<td>185±3</td>
<td>2.29±0.02</td>
<td>3.59±0.01</td>
<td>1.58±0.02</td>
<td>76.5±0.4</td>
</tr>
<tr>
<td>250±2</td>
<td>180±3</td>
<td>2.27±0.02</td>
<td>3.58±0.01</td>
<td>1.55±0.02</td>
<td>77.4±0.4</td>
</tr>
<tr>
<td>500±2</td>
<td>176±2</td>
<td>2.27±0.02</td>
<td>3.50±0.01</td>
<td>1.46±0.01</td>
<td>80.2±0.4</td>
</tr>
<tr>
<td>200±2</td>
<td>165±2</td>
<td>2.25±0.02</td>
<td>3.55±0.03</td>
<td>1.40±0.03</td>
<td>77.7±0.4</td>
</tr>
<tr>
<td>500±2</td>
<td>168±3</td>
<td>2.24±0.02</td>
<td>3.53±0.04</td>
<td>1.37±0.02</td>
<td>83.3±1.5</td>
</tr>
<tr>
<td>$T_{an}$-depen.</td>
<td>4.7±0.3</td>
<td>3.1±0.3</td>
<td>-1.0±0.1</td>
<td>-3.8±0.1</td>
<td>N/A</td>
</tr>
</tbody>
</table>

have been optimized by performing the more rigorous GM procedure. Dielectric functions $a_1$ and $d_1$ show a perfect agreement over the full energy range taking into account the confidence limits, even for the near band-gap energy region where the absorptions are small. An equally good agreement is found for the values of $d_a$ and $d_b$ as a function of the deposition time. Apparently, the Levenburg-Marquardt optimization is well capable of finding simultaneously the correct TL fit parameters and the values of $d_a$ and $d_b$ from a single set of $\Delta\Psi(E, \omega)$, $\Delta(E)$, from a film of appropriate thickness that contains opaque and transparent regions, as is done in the STF fit procedure performed on the final RTSE time frame of the deposition run. It is therefore concluded that the use of the elaborate global minimization procedure is not required for our single-phase a-Si:H material.

In conclusion, the RTSE data analysis approach, which includes the two-layer model with TL and EMA formalism to represent the bulk and surface a-Si:H layers as well as the STF fit procedure to find the optimum TL parameters, has been examined. It has been verified that this analysis is capable of finding the unique solution of the bulk dielectric function together with the bulk and surface roughness layer thickness ($d_a$ and $d_b$) as a function of the deposition time. In addition, the validity of the analysis has explicitly been verified for the other a-Si:H deposition runs by random examinations of the other a-Si:H deposition runs using one of the alternative fit procedures $b$-$d$. Therefore, this analysis has been applied to all a-Si:H deposition runs presented in this Chapter.

F. In-situ post-deposition SE analysis

The dielectric function of a-Si:H changes as a function of the analysis temperature $T_{an}$ due to thermal disorder effects in the material, as is the case for the c-Si substrate. Therefore, a direct comparison of the optical properties of a-Si:H films grown at different deposition temperatures $T_{dep}$ is only possible when the influence of the thermal disorder effects on the TL parameters due to a different $T_{an}$ is corrected for. To determine the $T_{an}$-dependence of the TL-parameters, in-situ post-deposition SE analysis has been performed, in which the dielectric function of the grown a-Si:H films is analyzed at temperatures between room temperature and $T_{dep}$. To model a SE measurements at $T_{an}$, the same (ambient / surface roughness
layer / bulk a-Si:H layer / semi-infinite substrate) model has been used as described above except for two differences. First, the thicknesses $d_1$ and $d_2$ are assumed independent of $T_m$ and are taken equal to the final values of $d_1$ and $d_2$ at the end of the a-Si:H deposition. Second, the dielectric function of the native-oxide-covered c-Si substrate also changes with $T_m$ due to thermal disorder effects in the two layers. The dependence of this dielectric function on $T_m$ is corrected for by using a virtual substrate obtained at the appropriate $T_m$ as explained above, prior to the a-Si:H deposition. The main result from this in-situ post-deposition SE analysis was that the TL parameters depend linearly on $T_m$ (within uncertainty), in agreement with Refs. 36 and 38. The values of the linear $T_m$-dependence of the TL parameters are shown in the bottom row of Table I. In addition, the linear $T_m$-dependence of the optical band-gap $E_{\text{opt}}$, a parameter describing the optical band-gap similar to $E_g$ (see Sec. IV), has been determined and is found to be $dE_{\text{opt}}/dT_m = (3.7 \pm 0.2) \times 10^{-4}$ eV/K, in good agreement with $dE_g/\Delta T_m = (3.8 \pm 0.2) \times 10^{-4}$ eV/K (Table I). These two values are also in fair agreement with $dE_{\text{opt}}/\Delta T_m = 4.3 \times 10^{-4}$ eV/K and $dE_{\text{opt}}/dT_m = 4.7 \times 10^{-4}$ eV/K as found for $T_m \geq 200$ K from continuous-wave luminescence and absorption measurements. It is noted that $dE_{\text{opt}}/\Delta T_m$ converges towards zero when $T_m$ approaches 0 K. In Sec. IV, these values of the $T_m$-dependence of the TL parameters are used to correct the TL parameters that are given in Table I to their room temperature values, which enables a direct comparison of TL parameters obtained for depositions at different $T_{\text{dep}}$ as well as a direct comparison with the ex-situ diagnostics results obtained at room temperature.

IV. OPTICAL MATERIAL PROPERTIES FROM RTSE

In this section, the optical material properties of the a-Si:H films deposited at $T_{\text{dep}} = 70, 150, 250, 350$, and 450 °C are investigated. To this end, first the RTSE measurements are presented. Figure 4 shows the evolution of the surface roughness layer thickness $d$, as a function of the deposition time $t$. The real $\varepsilon_1(E)$ and imaginary $\varepsilon_2(E)$ part of the dielectric function that correspond to the deposition runs of Fig. 4 are shown in Fig. 5, while the corresponding TL-parameters are shown in Table I. It is noted that the values of the TL-parameters in Table I are not yet corrected for their $T_m$-dependence. In addition, the deposition rates are given in Table I, however, it is noted that the values of the deposition rate mainly reflect the so-called hot wire aging effects, obscuring the dependence of the deposition rate on $T_{\text{dep}}$. The surface roughness evolution in Fig. 4 is in good agreement with the data reported by Collins et al. for a-Si:H deposited by rf PECVD and with the data reported by Levi et al. for HWCD deposition of a-Si:H.

The optical material properties of the a-Si:H films are investigated as a function of the deposition temperature from the dependence of the $(T_m$-dependence corrected) TL parameters on $T_{\text{dep}}$, as shown in Fig. 6. The optical band-gap, $E_g$, is a very important parameter of a-Si:H films with respect to its opto-electronic properties. It has even been suggested to categorize amorphous silicon materials according to their band-gap, as applications often require a specific value of the band-gap. The band-gap is given directly by the TL parameter $E_g$, however, there exist also a number of other methods to determine the optical band-gap. The Tauc band-gap is the most-widely used description for the optical band-gap of a-Si:H and is, therefore, also plotted in Fig. 6. Following Ref. 39, the Tauc band-gap has been determined from the extrapolation to zero ordinate of the linear fit of $[\mu^2 \varepsilon_2(E)]^{1/2}$ in the range of the optical absorption coefficient $\alpha$ of $3 \times 10^3 < \alpha < 3 \times 10^7$ cm$^{-1}$. Both $E_g$ and $E_{\text{Tauc}}$ show a monotonic decrease with increasing $T_{\text{dep}}$.

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1 In fact, the dependence of the native-oxide-covered c-Si substrate on the analysis temperature $T_m$ has only been measured for one a-Si:H film. The small run-to-run differences between different substrates are accounted for by a small additional SiO$_2$ substrate layer with a thickness between -1 and 1 Å that is assumed independent of $T_m$. 

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being much smaller for c-Si than for a-Si:H.

Figure 6 shows that \( E_g = (2.02 \pm 0.03) - \gamma(T_{dep})(K) \) and \( E_{Tauc} = (2.04 \pm 0.03) - \gamma(T_{dep})(K) \), and a good agreement in absolute values is observed. In addition, the optical band-gap has been determined from the dielectric function: from the Tauc plot (i.e. \( \frac{E_T}{E_g} \approx \frac{1}{2} \) vs. \( E \)) yielding \( E_{Tauc} \) and from the Cody plot (i.e. \( \epsilon(E) \) vs. \( E \)) yielding \( E_{Cody} \). Moreover, the dielectric function \( \epsilon(E) \) itself can be obtained in two ways: by using the TL and CL formalism in the RTSE model. For each deposition run, all values of the band-gap including \( E_g \) were found to be within \( \pm 0.03 \) eV from \( E_{Tauc} \): both values of \( E_{Tauc} \) correspond within \( \pm 0.01 \) eV, while the values of \( E_{Cody} \) and \( E_g \) are systematically 0.01–0.02 eV higher and 0.02–0.03 eV lower, respectively, than \( E_{Tauc} \). The use of the CL formalism yielded an increased scatter in \( E_{Tauc} \) and \( E_{Cody} \). For all five band-gaps, the \( T_{dep} \)-dependence was found in agreement with \( \frac{dE_{Tauc}}{dT_{dep}} = (6.6 \pm 0.5) \times 10^{-4} \) eV/K.

The broadening term \( \Gamma \) of the Lorentz oscillator [Eq. (4)] reflects the order in the material with \( \Gamma \) being much smaller for c-Si than for a-Si:H. Therefore, \( \Gamma \) is likely to be influenced by the bond length, bond angle, and disorder of the a-Si:H matrix. Moreover, it is also expected that \( \Gamma \) scales inversely to the excited state lifetime for transitions of electrons and holes deep within the conduction and valence band.

Figure 6 shows that \( \Gamma \) decreases for increasing \( T_{dep} \) with a strong decrease in \( \Gamma \) for \( T_{dep} \leq 250 \) °C and a slow decrease in \( \Gamma \) for \( T_{dep} \geq 250 \) °C. This suggests that the order in the a-Si:H material increases with increasing deposition times in the range of \( t = 100–250 \) s. These speckles emerged at the substrate-a-Si:H layer interface, as deduced from the evolution of the RTSE data, while the presence of crystallites in the bulk of the film is also excluded from the clear evidence presented in this Chapter that all films are completely amorphous. As a consequence, the simulated values of \( d_s \) and \( d_b \) showed artifacts for deposition times in the range of \( t = 100–250 \) s, however, the values of \( d_s \) could still be obtained with reasonable precision by imposing that a linear bulk growth continued in this time range.
The absolute value of Γ observed in Fig. 6 is relatively low for $T_{\text{dep}} \geq 250 ^\circ C$, which might indicate a relatively low disorder in the films compared to what is commonly reported in the literature.

The peak energy $E_0$ of the Lorentz oscillator [Eq. (4)] shows a clear decrease with $T_{\text{dep}}$ for $T_{\text{dep}} \leq 250 ^\circ C$, while it remains approximately constant for $T_{\text{dep}} \geq 250 ^\circ C$ (Fig. 6). The peak energy $E_0$ is expected to increase from 3.6 to 4.15 eV as the film evolves from a-Si:H to µc-Si:H. The fact that all values of $E_0$ are below 3.8 eV, strongly suggests that the films deposited are amorphous.

The Tauc-Lorentz amplitude $A$ is the product of $A_T$ and $A_L$ with $A_L$ the amplitude of the Lorentz oscillator [Eq. (4)], which is a measure for the Si-Si bond density in the a-Si:H material. Figure 6 shows that the TL amplitude $A$ increases for increasing $T_{\text{dep}}$ up to a maximum at $T_{\text{dep}} = 250 ^\circ C$, after which $A$ decreases slowly for increasing $T_{\text{dep}}$. Although the trend of $A$ with $T_{\text{dep}}$ may well be obscured by the trend of $A_T$ as well as $E_g$ [Eq. (5)] with $T_{\text{dep}}$, this trend of $A$ suggest a maximum in the Si-Si bond density at $T_{\text{dep}} = 250 ^\circ C$.

V. COMPARISON WITH EX-SITU DIAGNOSTICS

To gain insight into the material properties, the trends of the optical material parameters from RTSE with the deposition temperature will be compared with post-deposition analysis of the (same) a-Si:H films performed with a number of a ex-situ diagnostics. In addition, this comparative study will be used to explore the extent of information that RTSE can yield on the structural material properties of a-Si:H. Moreover, it is also interesting to investigate general trends of the a-Si:H material properties with the deposition temperature. Additional information is obtained by investigating the surface roughness evolution from RTSE.

A. Raman spectroscopy

In order to obtain information on the microstructure in the a-Si:H films, ex-situ Raman spectroscopy has been applied to the a-Si:H films. Figure 7 shows the Raman Si-Si spectra for our a-Si:H films deposited at $T_{\text{dep}}$ values in the range of 70–450 °C. First of all, it can be seen that all five spectra have essentially the same shape, which includes all the peaks that are characteristic for the relaxed matrix of the a-Si:H material: the four broad peaks at ~150, ~310, ~410, and ~480 cm$^{-1}$ are assigned to the transverse acoustic (TA), longitudinal acoustic (LA), longitudinal optical (LO), and transverse optical (TO) Si-Si phonon vibrations.
Fig. 6. The four parameters in the Tauc-Lorentz formalism describing the dielectric function of a-Si:H plotted as a function of the deposition temperature \( T_{\text{dep}} \). These include the amplitude \( A \), the broadening term \( \Gamma \), and the peak position \( E_0 \) that describe the Lorentz oscillator, and the optical band-gap parameter \( E_g \) that describes the Tauc joint density of states. Also plotted is the Tauc band-gap \( E_{\text{Tauc}} \). All values shown have been corrected to room temperature for their intrinsic dependence on \( T_{\text{dep}} \). The error bars correspond to the uncertainty in the fits of the RTSE data. The lines are guides to the eye.

modes, as shown in the inset of Fig. 7, while the small peak at \(~600\) cm\(^{-1}\) is due to the Si-H\(_x\) wagging mode. Clearly, no sharp peak at \(~520\) cm\(^{-1}\), which corresponds to the TO phonon mode in c-Si, is present and, therefore, no \( \mu \)-Si:H fractions are expected to be present in the films. Moreover, also no peak at \(~510\) cm\(^{-1}\) is observed in our spectra, while it has been argued that nano-crystallites in the film can be identified by a peak at this position.\(^{45}\) It is therefore concluded that our a-Si:H films are completely amorphous, as was already found indirectly from the low values of the peak position \( E_0 \) of the Lorentz oscillator as well as from the good fits of the RTSE data with our simple two-layer optical model of pure a-Si:H material.

The full width at half maximum (FWHM\(_{\text{TO}}\)) and center frequency (\( \omega_{\text{TO}} \)) of the TO peak correlate directly to the root-mean-square bond-angle variation \( \Delta \theta \) in the a-Si:H films,\(^{46}\) which is a measure for the degree of disorder in the a-Si:H matrix. To determine FWHM\(_{\text{TO}}\) and \( \omega_{\text{TO}} \), the Raman spectra have been fitted with a convolution of the four Gaussian peaks representing the four phonon modes in line with Ref. 44, as shown in the inset of Fig. 7. The value of FWHM\(_{\text{TO}}\) decreases linearly with \( T_{\text{dep}} \) while \( \omega_{\text{TO}} \) increases monotonically with \( T_{\text{dep}} \) showing a steeper increase for \( T_{\text{dep}} < 250 \) °C than for \( T_{\text{dep}} > 250 \) °C (not shown). More interesting than FWHM\(_{\text{TO}}\) and \( \omega_{\text{TO}} \) is the bond-angle variation \( \Delta \theta \), however, the relation of \( \Delta \theta \) with FWHM\(_{\text{TO}}\) and \( \omega_{\text{TO}} \) is still under debate in the literature.\(^{46-48}\) Beeman \textit{et al.} found from model calculations\(^{47}\) that FWHM\(_{\text{TO}}\)(cm\(^{-1}\)) = \( 15 + 6 \times \Delta \theta_{\text{450°C}} \). This relation is most-widely used in the literature to calculate \( \Delta \theta \) and found indirect experimental support.\(^{48}\) More recently, a comprehensive study by Vink \textit{et
Fig. 7. Raman Si-Si spectrum of the a-Si:H films for deposition temperature in the range of 70–450 °C (for clarity the spectra have been shifted vertically by multiples of 100 counts). The Raman spectra consist of four Si-Si phonon modes, \(^i\)e. the transverse acoustic (TA), longitudinal acoustic (LA), longitudinal optical (LO), and transverse optical (TO) Si-Si phonon mode at \(\sim 150\), \(\sim 310\), \(\sim 410\), and \(\sim 480\) cm\(^{-1}\), respectively, while the small peak at \(\sim 600\) cm\(^{-1}\) is due to the Si-H wagging mode. To obtain the line width, FWHM\(_{\text{TO}}\) and center frequency, \(\omega_{\text{TO}}\) of the TO phonon mode, the spectra are fitted with a convolution of four Gaussian line profiles in line with Ref. 44, as shown in the inset.

Comparing a number of models showed that the dependence of FWHM\(_{\text{TO}}\) as well as of \(\omega_{\text{TO}}\) on \(\Delta\theta\) is probably best modeled using a semi-experimental approach, yielding the relations: FWHM\(_{\text{TO}}\)(cm\(^{-1}\)) = 18.4 + 6.6\(\times\)\(\Delta\theta_{\text{BEEM}}\)(°) and \(\omega_{\text{TO}}\)(cm\(^{-1}\)) = 505.5 – 2.5\(\times\)\(\Delta\theta_{\text{BEEM}}\)(°). All three relations have been used to calculate \(\Delta\theta\) as a function of \(T_{\text{dep}}\), as shown in Fig. 8. While the absolute values of \(\Delta\theta\) differ significantly between the different methods used, as was recognized by Vink et al.,\(^{46}\) a fair agreement in the trend of \(\Delta\theta\) with \(T_{\text{dep}}\) is found. The bond-angle variation and therefore also the degree of disorder in the a-Si:H material decreases monotonically with increasing substrate temperature. While \(\Delta\theta_{\text{BEEM}}\) decreases linearly with \(T_{\text{dep}}\), \(\Delta\theta_{\text{BEEM}}\) shows a fast decrease for \(T_{\text{dep}}\leq250\) °C and a slower decrease for \(T_{\text{dep}}\geq250\) °C. The absolute values of \(\Delta\theta\) calculated with the Beeman relation\(^{47}\) can be compared with literature values of \(\Delta\theta\) obtained with the same relation. A bond-angle variation of \(\sim 7°\) for \(T_{\text{dep}}\geq250\) °C is very low compared to the value of \(8–9°\) that are typically reported for rf PECVD of a-Si:H.\(^{48,49}\) This suggests high-quality optical a-Si:H material for \(T_{\text{dep}}\geq250\) °C with a maximum roughly at \(T_{\text{dep}}\approx400\) °C. Using a value of \(\Delta\theta=7°\), the distribution of Si-Si bond lengths in our a-Si:H material can be estimated\(^{48}\) to have an average value of \(\bar{\tau} = 2.360\) Å and a variance of \(\sigma_{\tau} = 0.027\) Å, compared to \(\bar{\tau} = 2.371\) Å and \(\sigma_{\tau} = 0.046\) Å for a-Si and \(\bar{\tau} = 2.352\) Å for c-Si. Therefore, because roughly a quarter of all Si-Si bonds in a-Si:H are shorter than the c-Si bond-length, the change from c-Si to a-Si:H is not so much reflected in the averaged increase of the bond length as it is reflected in the increase of the spread in the bond lengths.

The Tauc-Lorentz broadening term \(\Gamma\) also reflects the degree of disorder in the a-Si:H matrix (Sec. IV). Therefore, \(\Delta\theta_{\text{FSPM}}\) obtained with the Beeman relation, is plotted as a function of \(\Gamma\) in the inset in Fig. 8. This figure provides a direct way to obtain the bond-angle variation \(\Delta\theta\) from a RTSE measurement.

B. FTIR

Fourier transform infrared spectroscopy (FTIR) has been applied to probe the silicon-hydride modes in the a-Si:H films, yielding the hydrogen concentration \([H]\)\(_{\text{FTIR}}\), as explained in Sec. II. Figure 9 shows \([H]\)\(_{\text{FTIR}}\) from FTIR together with the hydrogen concentration from ERD, \([H]\)\(_{\text{ERD}}\) that is discussed below, as
The root-mean-square bond angle variation, $\Delta \theta$, as a function of the deposition temperature $T_{dep}$. The values of $\Delta \theta_{FWHM}$ and $\Delta \theta_\omega$ have been calculated from the line width, FWHM$_{FWHM}$, and center frequency, $\omega_{TO}$, respectively, of the TO phonon mode of the Raman spectra of Fig. 7 using the Beeman relations:

$$FWHM_{FWHM}(\text{cm}^{-1}) = 15 + 6 \times \Delta \theta_{TO}(\text{°})$$

and

$$\omega_{TO}(\text{cm}^{-1}) = 18.4 + 6.6 \times \Delta \theta_{TO}(\text{°})$$

The inset shows $\Delta \theta_{TO}$, obtained with the Beeman relation, as a function of the Tauc-Lorentz parameter $\Gamma$. The solid lines have been fitted, while the dashed lines are guides to the eye.

As the hydrogen concentration is one of the main parameters of a-Si:H films, we aim to find a general relation between our RTSE measurements and the measurements of [H] enabling future calculations of [H] from the RTSE measurements alone. Encouraged by the strong influence of [H] on $\varepsilon_2(E)$ and on the density of states, the Tauc band-gap $E_{Tauc}$, the energy position of the peak value of $\varepsilon_2$, $E_{\varepsilon_2,peak}$, and the...
Fig. 10. The Tauc band-gap $E_{\text{Tauc}}$, the energy position of the peak value of $\varepsilon_2$, $E_{\text{2,peak}}$, and the value of $\varepsilon_2$ at the peak, $\varepsilon_2(E_{\text{2,peak}})$, as a function of the hydrogen concentration $[\text{H}]$. The values of $E_{\text{Tauc}}$ of $E_{\text{2,peak}}$ and $\varepsilon_2(E_{\text{2,peak}})$ and of $[\text{H}]$ have been taken directly from Fig. 6, Figs. 3 and 5, and Fig. 9, respectively. The lines depict the weighted average fits of $E_{\text{Tauc}}(\varepsilon) = (1.49 \pm 0.02) + (16.4 \pm 1.6) \times 10^{-3} [\text{H}](\%)$, $E_{\text{2,peak}}(\varepsilon) = (3.41 \pm 0.02) + (24.2 \pm 1.5) \times 10^{-3} [\text{H}](\%)$, and $\varepsilon_2(E_{\text{2,peak}}) = (31.5 \pm 0.5) - (0.56 \pm 0.04) [\text{H}](\%)$. The relationship $E_{\text{Tauc}}(\varepsilon) = 1.50 \times 10^{3} [\text{H}](\%)$, which has been recalculated from the data of Cody et al.\textsuperscript{41}, is depicted by the dashed line.

value of $\varepsilon_2$ at the peak, $\varepsilon_2(E_{\text{2,peak}})$, are given in Fig. 10 as a function of [H]. Both $E_{\text{Tauc}}$ and $E_{\text{2,peak}}$ show a clear linear increase with increasing [H], while $\varepsilon_2(E_{\text{2,peak}})$ shows a clear linear decrease with increasing [H]. From the weighted averaged fit through the data points of $E_{\text{Tauc}}$, it is found that the Tauc band-gap depends on [H] as $E_{\text{Tauc}}(\varepsilon) = (1.49 \pm 0.02) + (16.4 \pm 1.6) \times 10^{-3} [\text{H}](\%)$. Besides the good agreement of the slope with the literature values of $a$-Si:H of $\sim 19$ meV/at.% from Ref. 54 and $\sim 14$–$20$ meV/at.% from Ref. 53, the fit also corresponds perfectly with the accurate linear relation of $E_{\text{Tauc}}(\varepsilon) = 1.50 \times 10^{3} [\text{H}](\%)$ (dashed line in Fig. 10) found by Cody et al.\textsuperscript{41} from a detailed analysis of the Tauc band-gap as a function of the hydrogen concentration for a large number of $a$-Si:H films deposited with four different deposition techniques. Figure 10 also shows that the peak of $\varepsilon_2(E)$ varies with the hydrogen concentration as $E_{\text{2,peak}}(\varepsilon) = (3.41 \pm 0.02) + (24.2 \pm 1.5) \times 10^{-3} [\text{H}](\%)$. This slope of $(24.2 \pm 1.5)$ meV/at.% corresponds well with the literature values for $a$-Si:H of $\sim 23$ meV/at.% and $\sim 20$ meV/at.% reported for HWCVD\textsuperscript{10} and for magnetron sputter deposition\textsuperscript{42}, respectively. Furthermore, Fig. 10 shows that the value of $\varepsilon_2(E)$ at the peak depends on [H] as $\varepsilon_2(E_{\text{2,peak}}) = (31.5 \pm 0.5) - (0.56 \pm 0.04) [\text{H}](\%)$. This relation of $\varepsilon_2(E_{\text{2,peak}})$, however, is not in agreement with the slope of $(0.33 \pm 0.1)$ found by Feng et al.\textsuperscript{52} The analysis seems to suggest that the dependences of $E_{\text{Tauc}}$ and $E_{\text{2,peak}}$ on [H] are generic features of $a$-Si:H, independent of deposition conditions, while $\varepsilon_2(E_{\text{2,peak}})$ does not seem to possess this quality. Therefore, the relations of $E_{\text{Tauc}}$ and $E_{\text{2,peak}}$ with [H] (and especially the precise relation of Cody et al.) enable a quantitative calculation of the hydrogen concentration in the $a$-Si:H films from the dielectric function obtained with RTSE.

Apart from [H], the FTIR measurements also contain information on the local environment of the H atoms in the $a$-Si:H films. To this end, the difference between the integrated IR absorption of the low stretching mode (LSM), $I_{\text{LSM}}$, and that of the high stretching mode (HSM), $I_{\text{HSM}}$ (Sec. II) is investigated. The difference between $I_{\text{LSM}}$ and $I_{\text{HSM}}$ is conveniently represented by the microstructure factor $R^*$, defined as $R^* = I_{\text{LSM}}/(I_{\text{LSM}} + I_{\text{HSM}})$. From the literature, it is seen that device-quality $a$-Si:H material generally exhibits $R^* < 0.1$, while $a$-Si:H material of lower electro-optical quality typically has a value of $R^*$ larger than 0.1. This can be understood from the contribution of the different bonding configurations of the hydrogen in the film. On one hand, it is widely accepted that the monohydrides (i.e. an isolated H atom attached to a Si atom that has three Si-Si back bonds, =SiH) that are located in a monovacancy or divacancy
(i.e. one or two missing Si atoms in the matrix) contribute to the $I_{\text{LSM}}$. On the other hand, all dihydrides (i.e. two hydrogen atoms attached to a single Si atom that has two Si-Si back bonds, =SiH$_2$, a configuration that appears mainly in larger vacancies or voids) contribute to the $I_{\text{IWM}}$. The assignment of other silicon-hydride modes is still under debate in the literature, e.g., it is expected that monohydrides that are located at the edges of polymer-like $m$-vacancy (i.e. a chain of $m$ missing Si atoms) contribute to the $I_{\text{IWM}}$, while other monohydride configurations that are associated with larger vacancies contribute to the $I_{\text{RSM}}$. Figure 9 shows that $R^*$ decreases from $R^* = 0.3$ at $T_{\text{dep}} = 70$ °C to $R^* < 0.08$ for $T_{\text{dep}} \geq 250$ °C. A minimum in $R^*$ is found at $T_{\text{dep}} = 350$ °C, where $R^*$ is as low as 0.04, suggesting high-quality a-Si:H material. These results suggest that for $T_{\text{dep}} \geq 250$ °C virtually all hydrogen is located at mono- or divacancies, while for lower temperatures also larger vacancies or voids are present in the films. This conclusion corresponds perfectly with the conclusion found by Smets et al. that a-Si:H with a [H] of less than 14% contains predominantly divacancies decorated with hydrogen, while for [H] > 14% the a-Si:H material also contains microscopic voids. The presence of vacancies and voids in the film may be correlated to the disorder in the a-Si:H material, because $I_{\text{LSM}}$ and $I_{\text{IWM}}$ show a similar decrease with $T_{\text{dep}}$ as the Tauc-Lorentz broadening term $\Gamma$ and the bond-angle variation $\Delta \theta$. Let us therefore examine $R^*$ in more detail. Starting at $T_{\text{dep}} = 70$ °C, the decrease of $I_{\text{IWM}}$ with increasing $T_{\text{dep}}$ corresponds to a decrease of the number of voids in the material. This decrease of the number of voids may be related with the large beneficial effect on the order in the a-Si:H matrix as observed by a fast decrease of $\Gamma$ and $\Delta \theta$. For increasing $T_{\text{dep}}$ above 250 °C, $I_{\text{IWM}}$ has become roughly zero and the density of voids is negligible. At the same time, $I_{\text{LSM}}$ continues to decrease with increasing $T_{\text{dep}}$ above 250 °C, which corresponds to a decrease in the number of mono- and di-vacancies. This decrease of the number of vacancies may be responsible for the slight decrease in the a-Si:H disorder, as seen from $\Gamma$ and $\Delta \theta$ for $T_{\text{dep}} \geq 250$ °C. Therefore, the similar trend of $I_{\text{LSM}}$ and $I_{\text{IWM}}$ and of $\Gamma$ and $\Delta \theta$, with the deposition temperature may be explained by the following picture: vacancies (especially mono- or divacancies) can easily be incorporated in the a-Si:H films without altering the surrounding a-Si:H matrix much, whereas voids that are generally larger have a larger detrimental influence on the order in the film.

C. ERD/RBS

The atomic densities of all species present in the a-Si:H films have been obtained from elastic recoil detection (ERD) analysis combined with Rutherford back scattering (RBS) analysis, as explained in Sec. II. Table II shows the atomic densities of Si, H, C, N, and O as a function of the deposition temperature along with the total atomic density $n_{\text{tot}}$ and the total mass density $\rho$ of the films. The contaminant levels of C, N, and O are discussed below. The hydrogen concentration determined from ERD was already discussed above, showing a fair agreement with the hydrogen concentration as obtained from FTIR, [H]$_{\text{FTIR}}$ (Fig. 9). The Si atomic density, $n_{\text{Si}}$, increases for increasing $T_{\text{dep}}$ up to $T_{\text{dep}} = 250$ °C, after which it remains approximately constant. Related to $n_{\text{Si}}$ and showing a similar trend with $T_{\text{dep}}$ is the total mass density $\rho_{\text{RTSE}}$ of the films determined from the ERD and RBS data, which is an interesting parameter as it is a regarded as a direct measure of the a-Si:H material quality. Therefore, it would be very interesting to compare the values of $\rho_{\text{RTSE}}$, with independent values of the total mass density, especially when deduced from the RTSE results. This is possible by using the Clausius-Mossoti relation to obtain the total mass density $\rho_{\text{LSM}}$ from the IR refractive index $n_{\text{IR}}$ and the hydrogen concentration in the film [H].

The Clausius-Mossoti description states that at long wavelengths the IR refractive index can be written in terms of the individual harmonic dipole oscillators in the material, i.e. the Si-Si and Si-H bonds for a-Si:H. For a-Si:H with a 100% amorphous fraction, the Clausius-Mossoti relation equals:}
Table II. The density of Si, H, C, N, and O, i.e. $n_\text{Si}$, $n_\text{H}$, $n_\text{C}$, $n_\text{N}$, $n_\text{O}$, respectively, that are present in the a-Si:H films, as determined from Rutherford back scattering and elastic recoil detection analysis. Also shown are the total atomic density $n_\text{tot}$ and the total mass density $\rho$ of the a-Si:H films. The surface and interface oxygen densities have been eliminated in the determination of the bulk oxygen density $n_\text{O}$. Boron may also be present in all but one films, as an ERD signal (that is about equal to the noise level) has been observed (typical density would be $n_\text{B}=(3\pm4)\times10^{17}$ cm$^{-3}$).

<table>
<thead>
<tr>
<th>$T_\text{dep}$ (°C)</th>
<th>$n_\text{Si}$ ($10^{22}$ cm$^{-3}$)</th>
<th>$n_\text{H}$ ($10^{23}$ cm$^{-3}$)</th>
<th>$n_\text{C}$ ($10^{19}$ cm$^{-3}$)</th>
<th>$n_\text{N}$ ($10^{15}$ cm$^{-3}$)</th>
<th>$n_\text{O}$ ($10^{27}$ cm$^{-3}$)</th>
<th>$n_\text{tot}$ ($10^{27}$ cm$^{-3}$)</th>
<th>$\rho$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>4.4±0.2</td>
<td>8.7±0.9</td>
<td>7.9±0.6</td>
<td>3.2±0.7</td>
<td>1.7±0.3</td>
<td>5.3±0.3</td>
<td>2.09±0.10</td>
</tr>
<tr>
<td>150</td>
<td>4.4±0.2</td>
<td>7.4±0.7</td>
<td>2.9±0.4</td>
<td>2.2±0.6</td>
<td>1.3±0.2</td>
<td>5.2±0.3</td>
<td>2.10±0.10</td>
</tr>
<tr>
<td>250</td>
<td>4.8±0.2</td>
<td>6.5±0.7</td>
<td>5.6±0.7</td>
<td>3.9±0.7</td>
<td>2.2±0.3</td>
<td>5.5±0.3</td>
<td>2.29±0.11</td>
</tr>
<tr>
<td>350</td>
<td>4.8±0.2</td>
<td>4.4±0.4</td>
<td>3.8±0.5</td>
<td>3.3±0.8</td>
<td>1.9±0.3</td>
<td>5.3±0.3</td>
<td>2.28±0.11</td>
</tr>
<tr>
<td>450</td>
<td>4.9±0.2</td>
<td>3.2±0.3</td>
<td>4.0±0.7</td>
<td>3.1±2.3</td>
<td>10.1±0.7</td>
<td>5.2±0.3</td>
<td>2.31±0.12</td>
</tr>
</tbody>
</table>

*This deposition was performed under a somewhat increased base pressure.

\[
\rho_{\text{RTSE}} = \frac{n_\text{Si}}{n_\text{H}} \frac{2m_\text{Si}}{n_\text{H}} \left[ 2\alpha_{\text{Si-Si}} + \frac{[\text{H}]}{[\text{H}]} \left( \alpha_{\text{Si-H}} - \frac{1}{2} \alpha_{\text{Si-Si}} \right) \right],
\]

(9)

where $m_\text{Si}$ is the mass of a Si atom and $\alpha_{\text{Si-Si}}$ and $\alpha_{\text{Si-H}}$ are the bond polarizabilities in the a-Si:H matrix, which have been estimated at $\alpha_{\text{Si-Si}}=1.96\times10^{-24}$ cm$^3$ and $\alpha_{\text{Si-H}}=1.36\times10^{-24}$ cm$^3$.$^{56,57}$ In this calculation of $\rho_{\text{RTSE}}$, the value of $n_\text{H}$ in the infrared can be obtained from $n_\text{H}(\text{cm}^{-3})=\rho_{\text{RTSE}}/\rho_{\text{Si}}$, where $\rho_{\text{RTSE}}$ is taken at the lowest energy in Figs. 3 and 5, while the extinction coefficient $k$ can be neglected below the band-gap.

The hydrogen concentration in the film has been calculated from the Tauc band-gap using the Cody relation $E_{\text{Tauc}}(\text{eV})=1.50 + (15.0\pm0.6)\times10^{-3} \times [\text{H}]/[$Si$]$. By inserting $n_\text{H}$ and [H] in Eq. (9), the values of $\rho_{\text{RTSE}}$ for different $T_\text{dep}$ have been determined solely from RTSE results (it is noted that the use of $[\text{H}]_{\text{ERD}}$ or $[\text{H}]_{\text{ERD}}$ of Fig. 9 instead of [H] obtained with the Cody relation results in negligible differences in $\rho_{\text{RTSE}}$).

Figure 11 shows $\rho_{\text{ERD}}$ and $\rho_{\text{RTSE}}$ as a function of $T_\text{dep}$. The trend of $\rho_{\text{RTSE}}$ with $T_\text{dep}$ and the absolute values of $\rho_{\text{RTSE}}$ show a good agreement with $\rho_{\text{ERD}}$. Moreover, on the bases of the error bars it is inferred that $\rho_{\text{RTSE}}$ is obtained with much higher accuracy than $\rho_{\text{ERD}}$. Figure 11 shows that for $T_\text{dep} \geq 250$ °C the total mass density approaches the value of $\rho_{\text{a-Si}} = 2.29$ g/cm$^3$ of a-Si.$^{58}$ Therefore, the a-Si:H material for $T_\text{dep} \geq 250$ °C is very dense, while the material decreases in density for decreasing $T_\text{dep}$ below 250 °C but remains fairly dense.

Following Remes et al.$^{56}$ the dependence of the total mass density on the hydrogen content is simulated using two simple models to calculate the density of a-Si:H based on the density of a-Si. In the mono-vacancy model, single silicon atoms in the a-Si matrix are each replaced by four hydrogen atoms. Therefore, the mono-vacancy model yields the most densely-packed a-Si:H material without interstitial H atoms. In the di-vacancy model sets of two neighboring silicon atoms in the a-Si matrix are replaced by six hydrogen atoms. Both models are scaled to saturate to a density of $\rho_{\text{a-Si}} = 2.29$ g/cm$^3$ for unhydrogenated a-Si. The mono- and di-vacancy model are depicted in Fig. 11 by the upper and lower thin dotted lines. The fact that the measured total mass density $\rho_{\text{RTSE}}$ (and $\rho_{\text{ERD}}$) is somewhat higher than the mono-vacancy model for $T_\text{dep} \geq 250$ °C is probably explained by a systematic error either in $\rho_{\text{RTSE}}$ or in $\rho_{\text{a-Si}}$ as used in the literature.$^{56}$ The slope of $\rho_{\text{RTSE}}$ (and $\rho_{\text{ERD}}$) with $T_\text{dep}$, however, is more interesting as it does not suffer from systematic errors. For $T_\text{dep} \geq 250$ °C, the slope shows a better correspondence with the di-vacancy model than with the mono-vacancy model. This suggests that for $T_\text{dep} \geq 250$ °C mainly di-vacancies are present in the a-Si:H films. For $T_\text{dep}$ below 250 °C, a sharp drop of both $\rho_{\text{RTSE}}$ and $\rho_{\text{ERD}}$ is observed for $T_\text{dep} = 150$ °C.
The total mass density \( \rho \) as a function of the deposition temperature \( T_{dep} \). The total mass density has been deduced in two ways: from the sum over all species in the film as measured with ERD and RBS (Table I), i.e. \( \rho_{ERD} \), and from a calculation of the Clausius-Mossoti relation [Eq.(9)], i.e. \( \rho_{RTSE} \), using the IR refractive index \( n_{IR} \) and the hydrogen concentration in the film [H] that have both been obtained from RTSE. The dashed line is a guide to the eye, while the solid line depicts the upper limit of \( \rho = 2.29 \text{ g/cm}^3 \) of a-Si (for c-Si \( \rho = 2.33 \text{ g/cm}^3 \)). The upper and lower thin dotted line depict the mono- and di-vacancy model, respectively.

and even more for \( T_{dep} = 70 \text{ °C} \). This drop cannot be explained by the di-vacancy model and even less by the mono-vacancy model. It seems, therefore, that for \( T_{dep} \leq 150 \text{ °C} \), a significant part of the hydrogen is bonded in other configurations than mono-vacancies or di-vacancies, such as larger vacancies or voids. These observations correspond precisely with the observations of Smets et al.\(^{55}\) and with the conclusions drawn from \( R^* \) in Fig. 9, i.e. for \( T_{dep} \geq 250 \text{ °C} \) the hydrogen is predominantly bonded as monohydrides in mono- or di-vacancies, whereas for \( T_{dep} \leq 150 \text{ °C} \) also larger vacancies or voids are present in the films.

Next, the contaminants in the a-Si:H films are addressed from the ERD measurements of Table II. A low impurity level is important for conducting well-defined studies of the surface processes, while even very small levels of contaminants can be detrimental for the opto-electronic properties of the a-Si:H films.\(^{59,60}\) Table II shows that, besides Si and H, also C, N, and O have been found in the films with atomic densities of \( n_C \approx 5 \times 10^{20} \text{ cm}^{-3} \), \( n_N \approx 4 \times 10^{18} \text{ cm}^{-3} \), and \( n_O \approx 2 \times 10^{16} \text{ cm}^{-3} \), respectively. All contaminant levels are low, however, the oxygen density \( n_O \) is particularly low.\(^{59,60}\) This is illustrated from a number of ultra-high vacuum studies reported in the literature that were unsuccessful in lowering, specifically, the level the oxygen in the film below \( 10^{18} \text{ cm}^{-3} \) (see Ref. 60 and references therein). Only one extensive study to grow ultra-pure a-Si:H succeeded to obtain the much lower contamination levels of \( n_C = n_N = 10^{15} \text{ cm}^{-3} \) and \( n_O = 10^{14} \text{ cm}^{-3} \).\(^{60}\) Our low impurity level seems to be a direct result of the overnight bake-out procedure and the subsequent two-hour HWCVD hydrogen etch to clean the substrate and reactor walls prior to each deposition (Sec. III), while the gas purifier in the SiH\(_4\) supply line prevent an inflow of, specifically, O\(_2\), CO, CO\(_2\), and H\(_2\)O during deposition.\(^{12}\)

D. AFM

The last parameter to be studied is the surface roughness layer thickness. To this end, the final roughness layer thickness \( d_s(\text{RTSE}) \) at the end of the deposition obtained with RTSE is compared with the root-mean-square roughness \( d_s(\text{AFM}) \) obtained with AFM (Sec. II). Figure 12 shows \( d_s(\text{RTSE}) \) and \( d_s(\text{AFM}) \) as a function of the deposition temperature \( T_{dep} \) and a fairly good agreement between \( d_s(\text{RTSE}) \) and \( d_s(\text{AFM}) \) is found. Both \( d_s(\text{RTSE}) \) and \( d_s(\text{AFM}) \) show a monotonic decrease with increasing \( T_{dep} \) with a
is grown at \(T_{\text{dep}}\) and unable to follow the contours for electronic performance and stability of the a-Si:H material for applications such as solar cells. The empirical correlation of Collins therefore, the evolution of the surface roughness during the a-Si:H deposition (Figs. 2 and 4) is significantly larger than those of \(d_s\) (AFM). The relation between \(d_s\) (RTSE) and \(d_s\) (AFM) is still under debate in the literature, as clearly illustrated from the fact that two different relations for a-Si:H have been reported in the literature \(^{31,61,62}\) i.e. \(d_s\) (RTSE) = \(1.5 \times d_s\) (AFM) + 4 Å and \(d_s\) (RTSE) = 0.88 \(d_s\) (AFM) + 4.9 Å. Our values of \(d_s\) (RTSE) versus \(d_s\) (AFM) for \(T_{\text{dep}} \leq 150\) °C correspond well with the first relation, whereas the data for \(T_{\text{dep}} \geq 250\) °C is in good agreement with the second relation. This transition at \(T_{\text{dep}} \approx 250\) °C may be another indication for a transition from a low roughness regime (\(T_{\text{dep}} \geq 250\) °C) where AFM is able to yield the full roughness to a higher roughness regime (\(T_{\text{dep}} \leq 150\) °C) where the roughness is underestimated. Taking into account that both RTSE and AFM yield very low values of \(d_s\) for \(T_{\text{dep}} \geq 250\) °C, it is fair to conclude that the surface roughness layer thickness obtained with RTSE is reliable, in agreement with the findings in Sec IV. Therefore, the evolution of the surface roughness during the a-Si:H deposition (Figs. 2 and 4) is investigated to gain insight into the a-Si:H material properties, as addressed next.

Collins et al. \(^{5,6,13,63}\) have found an empirical correlation between the position of the so-called ‘a-Si → a-Si roughening transition’ and the opto-electronic properties of the a-Si:H material. The a-Si → a-Si roughening transition, or so-called ‘dip’ in the surface roughness \(d_s\), is identified in Figs. 2 and 4 as the transition at a bulk thickness of \(d_{b,\text{dip}}\) = 100 Å from a decrease of \(d_s\) in time to an increase of \(d_s\) in time. The dip in the roughness is quantified by the position of the dip, \(d_{s,\text{dip}}\), and by the depth of the dip, \(\Delta d_s\), defined as the difference between \(d_s\) at the onset of bulk growth (dashed line in Figs. 2 and 4) and \(d_s\) in the dip. The empirical correlation of Collins et al. states that a higher \(\Delta d_s\) and \(d_{s,\text{dip}}\) corresponds to a better electronic performance and stability of the a-Si:H material for applications such as solar cells. \(^{5,6,13,63}\) Figs. 2 and 4 show that both \(\Delta d_s\) and \(d_{s,\text{dip}}\) cannot be identified for \(T_{\text{dep}} = 70\) °C, but increase rapidly for increasing \(T_{\text{dep}}\) towards \(T_{\text{dep}} = 250\) °C, where a clear maximum is reached. For \(T_{\text{dep}}\) increasing above 250 °C, both \(\Delta d_s\) and \(d_{s,\text{dip}}\) gradually decrease again, but remain well above the values of \(T_{\text{dep}} = 150\) °C. Therefore, the empirical correlation of Collins et al. suggests that the best opto-electronic and most stable a-Si:H material is grown at \(T_{\text{dep}}\) = 250 °C with a fast and slow decrease in material quality towards lower and higher \(T_{\text{dep}}\).
respectively. A similar trend of $\Delta d$, with $T_{dep}$ with a maximum at $T_{dep} = 250$ °C as well as a similar absolute values of $\Delta d$, have been found by the group of Collins for PECVD of a-Si:H.\textsuperscript{33} Collins et al. explained their empirical correlation by a surface equilibration driven by diffusion that establishes a well-ordered Si network with a low density of defects (i.e. weak bonds and coordination defects).\textsuperscript{33} For the case of the high precursor surface diffusion length at $T_{dep} = 250$ °C, this surface equilibration results in optimum electronic-grade a-Si:H. The lower precursor surface diffusion length at other temperatures, however, leads to a more defective surface microstructure during growth, which results in more bulk defects that limit the electronic device quality of the a-Si:H.\textsuperscript{33} If this explanation by Collins et al. is true, then the surface roughness evolution from RTSE (and in particular the values of $\Delta d$, and $d_{b,dep}$) is a qualitative measure for the defect density in the a-Si:H film.

VI. CONCLUSIONS

A series of a-Si:H films has been deposited at $T_{dep} = 70, 150, 250, 350$, and 450 °C by means of HWCVD of undiluted SiH$_4$ and has been analyzed by RTSE as well as by a number of ex-situ diagnostics. As a first step, our RTSE data analysis approach has been carefully validated and its accuracy has been demonstrated. Subsequently, the optical material properties of the a-Si:H films from RTSE have been determined and compared with results from the ex-situ diagnostics to conduct a detailed characterization of the a-Si:H films. All a-Si:H films are completely amorphous. The bond-angle variation $\Delta \theta$ decreases monotonically with increasing $T_{dep}$ and is $\sim 7\degree$ for $T_{dep} \geq 250$ °C, which is low compared to the value of 8–9° typically reported for a-Si:H (both values calculated with the Beeman relation). The total mass density $\rho$ shows a sharp increase for increasing $T_{dep}$ below 250 °C and a saturation towards an a-Si:H material that is approximately as dense as a-Si ($\rho_{a-Si} = 2.29$ g/cm$^3$) for $T_{dep} \geq 250$ °C. The Tauc band-gap decreases linearly with $T_{dep}$ and for $T_{dep} = 250$ °C a value of $E_{\text{Tauc}} = 1.67$ eV was found, which is equal or slightly lower than literature values for typical high-quality a-Si:H material. The hydrogen concentration $[H]$ increases monotonically with decreasing $T_{dep}$ and corresponds well with the literature in terms of the absolute values and its trend with $T_{dep}$. A study of the silicon-hydride bonding configuration showed that for $T_{dep}$ above 250 °C, essentially all hydrogen is bonded as monohydrides, presumable in di-vacancies, while for decreasing $T_{dep}$ below 250 °C, the fraction of dihydrides that resides in voids increases sharply. Finally, the surface roughness at the end of the deposition was found to decrease with increasing $T_{dep}$ towards a very low value of $\sim 10\AA$ for $T_{dep} \geq 250$ °C. All these findings are consistent with high quality a-Si:H material for $T_{dep} \geq 250$ °C. Moreover, the low microstructure factor of $R^* < 0.1$ for $T_{dep} \geq 250$ °C also indicates high-quality a-Si:H material, as do the large values of the position of the dip, $d_{b,dep}$, and the depth of the dip, $\Delta d$, that are obtained for $T_{dep} \geq 250$ °C and especially for $T_{dep} = 250$ °C. From these measurements, we conclude that the optimum in the a-Si:H material quality is approximately at $T_{dep} = 300$ °C.

In addition, RTSE has been explored as a future tool for providing extended in-situ, real-time material characterization during the growth of a-Si:H films to reduce the need for ex-situ diagnostics in the future. To this end, a number of correlations between material parameters have been found that enable the future determination of structural parameters from the RTSE results. The amorphicity of the films can be determined from the value of the peak energy of the Lorentz oscillator $E_0$, while the bond-angle variation $\Delta \theta$ can be obtained from the Tauc-Lorentz broadening term $\Gamma$ by using the inset in Fig. 8. A consistent single phase material can be deduced from a dielectric function that is constant during the deposition. Two useful relations have been deduced to determine the hydrogen concentration in the film $[H]$ from the Tauc-band gap as well as from the peak value of $e_{2}(E)$ using $E_{\text{Tauc}}(eV) = 1.50 + (15.0 \pm 0.6) \times 10^{-3} \times [H](\%)$ and $E_{2,\text{peaks}}(eV) = (3.41 \pm 0.02) + (24.2 \pm 1.5) \times 10^{-3} \times [H](\%)$, respectively. Subsequently, the total mass density can
be obtained from the IR refractive index $n_{IR}$ and $[\text{H}]$ by using the Clausius-Mossoti relation [Eq. (9)]. Finally, the empirical correlation of Collins et al. can be used to obtain relative information on the opto-electronic properties of the a-Si:H material from $d_{\text{dep}}$ and $\Delta d_i$ and, therefore, indirect information on the bulk defect density.

Finally, some general insight has been gained into the dependence of the optical and structural material properties of a-Si:H on the substrate temperature $T_{\text{dep}}$, a key parameter for the material quality. The total mass density seems to be inversely related to the hydrogen concentration $[\text{H}]$ with the total mass density and $[\text{H}]$ showing the opposite trend with $T_{\text{dep}}$. For low $[\text{H}]$, the increase of $[\text{H}]$ seems to correspond to an increase of $d_i$ and $\Delta d_i$ in the film, while the stronger increase of $[\text{H}]$ above ~14% seems to correspond to the onset of larger vacancies and voids, in agreement with the literature. The hydrogen bonding configuration seems to be related also to the disorder in the film. The origin of such a relation may lie in a small effect on the a-Si:H matrix due to incorporation of (small) vacancies compared to a larger detrimental influence on the film order due to incorporation of (larger) voids. Finally, the defect density in the film does not simply relate to the above trends with a minimum at $T_{\text{dep}} \approx 250 ^\circ C$ and a slow and fast increase towards higher and lower $T_{\text{dep}}$, respectively.

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CHAPTER 9

TEMPERATURE DEPENDENCE STUDY
OF THE SURFACE ROUGHNESS EVOLUTION:
SURFACE DIFFUSION PROCESSES DURING a-Si:H GROWTH

ABSTRACT

The surface roughness evolution of hydrogenated amorphous silicon (a-Si:H) growth at substrate temperatures between 70 and 450 °C has been studied by real-time spectroscopic ellipsometry (RTSE) and ex-situ atomic force microscopy (AFM). Data analysis is performed (i) by comparison with previous RTSE work by Collins and co-workers [Sol. Energy Mater. Sol. Cells 78, 143 (2003)]; (ii) by formulation of a stochastic, non-linear growth equation; and (iii) by applying the concept of dynamic scaling to the post-initial a-Si:H growth and to the post-deposition AFM scans. Our results at 250 °C are in excellent agreement with reported studies in the literature, including the observed self-affine post-initial growth. Our substrate temperature dependent studies, however, reveal some new insights. The initial nucleation behavior is fully determined by the substrate. The post-nucleation surface smoothens and subsequent roughens as a result of a surface diffusion mechanism that stabilizes the nucleation-induced roughness features at small lateral length scales, but that is unable the stabilize the upcoming roughness features at large length scales. Analysis of this surface roughness transition in the framework of the growth equation is discussed in terms of a two-species growth mechanism, in which a mobile growth precursor can only contribute to film growth at active growth sites that may also diffuse. Analysis of the growth equation also suggests a novel interpretation of the post-initial growth phase, which shows a monotonic decrease in the growth exponent $\beta$ from ~0.18 to ~0.05 with increasing substrate temperature. We conjecture that a conserved non-linear term rules the post-initial surface smoothening, resulting in a pseudo Edward-Wilkinson scaling behavior in the high temperature limit.

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I. INTRODUCTION

Fundamental and technologically relevant information on the surface processes during thin film growth can be obtained by studying the evolution of the surface roughness as a function of bulk thickness with real-time spectroscopic ellipsometry (RTSE). Such studies give insight into the microstructural evolution of the film and the corresponding surface processes, including nucleation, initial growth, surface roughening, surface smoothing, and surface diffusion mechanisms. For the deposition of hydrogenated amorphous silicon (a-Si:H), the surface roughness evolution has been studied previously by Collins et al. for rf plasma enhanced chemical vapor deposition (PECVD) and by Levi et al. for hot wire chemical vapor deposition (HWCVD). In an attempt to unravel the governing surface processes during a-Si:H film growth, we present a first dedicated investigation of the surface roughness evolution during a-Si:H growth as a function of the substrate temperature in the range of $T_{\text{sub}} = 70-450^\circ\text{C}$.

The governing surface processes have also been investigated by employing the concept of dynamic scaling, which states the general idea that the width of an interface may depend in a self-affine manner upon the length and time as $w(t, l) = l^\beta f(t/\xi_l(t))$, where $\beta$ is the growth exponent, $l$ is the size of the measurement window, and $\xi_l(t)$ is the lateral correlation length. $\xi_l(t)$ is the lateral distance within which the surface heights are correlated through the growth process. The scaling function $f(u)$ has two limiting cases. For $u \gg 1$, $f(u)$ is constant and the interface width develops in time as $w(t) \propto t^\alpha$. This situation applies to RTSE, for which the measurement window in the order of 1 mm is much larger than $\xi_l(t)$. Therefore, the growth exponent $\beta$ can be obtained from RTSE by fitting the surface roughness evolution of the a-Si:H film growth. For $u \ll 1$, the scaling function $f(u)$ behaves as $u^\alpha$ with $\alpha$ the roughness exponent, equal to $\alpha = z^\beta$, thus the interface width scales as $w(t) \propto t^\alpha$. This regime can be accessed by scanning the surface topography with a scan size $l$ smaller than $\xi_l(t)$, as can be done with atomic force microscopy (AFM) or scanning tunneling microscopy (STM). Therefore, to obtain the values of $\alpha$, our a-Si:H films have been analyzed ex situ by AFM as a function of the scan size $l$. One notable outcome of the dynamic scaling hypothesis is the existence of universality in which the essential features of roughness evolution, i.e., the scaling exponents $\alpha$, $\beta$, and $z$, depend on certain symmetries and the dimensionality of the system, but not on the detailed interactions. This has made it possible to divide growth processes into a number of universality classes according to the values of these scaling exponents.

Here, three well-known universality classes are given as an example. For a two-dimensional surface, the simplest universality class is “random deposition” (RD) in which the randomly arriving particles stick at impact on the surface without any subsequent surface smoothing mechanism. For the RD universality class $\beta = z/2$, while $\alpha$ and $z$ are undefined. On the other hand, ultimate surface smoothing is found when the randomly arriving particles are allowed to stick at the lowest height position within a certain lateral distance from the impact position. The corresponding universality class “random deposition with relaxation” (RDR) has scaling exponents $\beta = 0$ and $z = 1$. An intermediate universality class is represented by “random deposition with surface diffusion” (RDD), for which the particles are allowed to diffuse to an energetically more favorable surface site (e.g. the nearest step-like surface site) that is, however, not necessarily the lowest height position. The RDD universality class exhibits the growth exponents $\beta = 0.25$, $\alpha = 1$, and $z = 4$. Therefore, through the essential mechanisms that govern the evolution of the interface width, the universality classes with their unique scaling exponents enable a correlation between experimental growth systems, such as the deposition of a-Si:H, and theoretical

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1 The growth exponent $\beta$ is different from the surface reaction probability $\beta$ used in Chapters 2, 3, and 4.
treatments of the growth process, such as stochastic differential equations and simulations. It should be noted though that the scaling behavior of the essential mechanisms that govern the growth process is only observed in the long-time, long-scale asymptotic limit, where the influence of initial or local mechanisms can be neglected.\textsuperscript{7} Stochastic differential equations describing the growth process have been proposed successfully to various fields of deposition, such as molecular-beam epitaxy (MBE)\textsuperscript{20,23,25–30} and physical vapor deposition (PVD),\textsuperscript{24,31–34} as well as etching.\textsuperscript{35–37} The construction of these growth equations have lead to a greater understanding of the governing growth processes. Therefore, in this Chapter, an attempt will be made to construct a specific growth equation that is able to describe the full surface roughness evolution during a-Si:H film growth, as assessed by RTSE and AFM.

The a-Si:H films have been deposited from undiluted silane (SiH\textsubscript{4}) by means of HWCVD. For HWCVD, an ion bombardment that may strongly influence the surface diffusion process\textsuperscript{38} is not present. Moreover, the a-Si:H films are deposited under "optimum HWCVD conditions",\textsuperscript{39} where the deposition flux is dominated by SiH\textsubscript{3} radicals.\textsuperscript{39,40} SiH\textsubscript{3}-dominated growth of a-Si:H results in smooth surfaces, which is generally attributed to surface diffusion of the SiH\textsubscript{3} growth precursor.\textsuperscript{41,42} Moreover, it is generally believed that SiH\textsubscript{3}-dominated growth conditions result in device quality a-Si:H films,\textsuperscript{41–43} a feature that has also been demonstrated for the a-Si:H films presented here.\textsuperscript{44} The material properties of optimized a-Si:H films are generally found to be remarkably independent of the deposition method used.\textsuperscript{45} Therefore, it is expected that the results presented in this Chapter are representative for HWCVD a-Si:H growth and a-Si:H deposition in general. Insight in the governing a-Si:H growth processes is gained, among others, from an empirical correlation between the surface roughness evolution and the surface diffusion length found by Collins\textsuperscript{8,13} et al.\textsuperscript{9,12} For that reason, our RTSE data has been analyzed in line with the work of Collins et al.\textsuperscript{9,12}

The Chapter is structured as follows. After the experimental details in Sec. II, the different growth phases observed during a-Si:H film growth are identified in Sec. III, in line with the work of Collins and co-workers. Section III is followed by a more detailed qualitative analysis of the different growth phases, for instance, by employing the concept of dynamic scaling. In Sec. IV, the surface roughness evolution is analyzed more quantitatively by proposing a specific growth equation that can describe the full surface roughness evolution. In addition, the surface roughness evolution during initial a-Si:H growth is simulated numerically based on this growth equation. In general, it is found that a-Si:H film growth exhibits many similarities with other deposition systems reported in the literature. There are also some distinct differences, however, which are discussed in Sec. V. Finally, the general conclusions are presented in Sec. IV.

II. EXPERIMENTAL DETAILS

The a-Si:H films were deposited using HWCVD at five different substrate temperatures in the range of \( T_{\text{sub}} = 70–450 \) °C with all other experimental conditions kept constant. The depositions took place in an ultrahigh-vacuum compatible setup dedicated for fundamental studies (described in detail in Refs. 46 and 47), which has as main features a low-contaminant background (base pressure <10\textsuperscript{-9} mbar, purity of SiH\textsubscript{4} gas specified at >99.995% with sub-ppm levels of O\textsubscript{2}, CO, CO\textsubscript{2}, H\textsubscript{2}O, and non-methane hydrocarbons due to additional gas purification), an accurately controlled substrate temperature (within 2 °C), and a good accessibility of the substrate for "all-optical" diagnostic techniques. The hot wire (a single ~5.5 cm long, coiled W filament with a diameter of 0.45 mm) was operated in undiluted SiH\textsubscript{4} at a dc current of 11 A resulting in a temperature of the hot wire of 2050±200 °C. The SiH\textsubscript{4} flow rate was set at 3.0 standard cm\textsuperscript{3}/min and the pressure within the deposition chamber was controlled at 1.1×\texttimes10\textsuperscript{-2} mbar. With a hot-wire to substrate distance of 6.8 cm, the conditions are within the region of "optimum operating conditions" as
reported by Molenbroek et al. Under these conditions, deposition rates of $R_d = 102.2, 84.9, 77.4, 80.2,$ and $77.7$ Å/min were obtained for $T_{sub} = 70, 150, 250, 350,$ and $450$ °C, respectively, resulting in a final thickness of $2000–3000$ Å after ~30 min. of growth. It is noted that the dependence of the deposition rate on $T_{sub}$ is obscured by so-called ‘hot wire aging effects’. The depositions were carried out on crystalline Si (c-Si) substrates covered with a native oxide. Before deposition, the substrates were baked overnight at a temperature of $450$ °C. This procedure was found to remove the adsorbed water layer (and other contaminants) and leave a bare native oxide layer with a thickness of $(9\pm1)$ Å, as concluded from RTSE.

The deposition processes were monitored by real-time spectroscopic ellipsometry (RTSE) using a near-infrared extended ellipsometer (Woollam M2000U) with a wavelength range of 250-1700 nm, at a fixed angle of incidence of $-60^\circ$ from the substrate normal. Throughout every deposition run, 100 full SE spectra, each with a duration of 50 ms, were averaged per data point in order to measure the surface roughness with sufficient sensitivity, thereby sacrificing the time-resolution needed to monitor the nucleation phase. To extract the bulk thickness, $d_b$, and the surface roughness, $d_s$, as a function of the deposition time from the RTSE data, a simple two-layer model (ambient / surface roughness layer / bulk a-Si:H layer / semi-infinite substrate) was used for the a-Si:H, as shown in Fig. 1. In this model, the optical response of the bulk layer is described by the Tauc-Lorentz formalism, while the optical response of the surface roughness is modeled by the common Bruggeman effective medium approximation of 50% voids and 50% bulk a-Si:H, as commonly used and accepted in the field. The optical properties of the films [i.e. the real and imaginary part of the dielectric function $\varepsilon_1(E)$ and $\varepsilon_2(E)$] used in the Tauc-Lorentz formalism were obtained from the RTSE data at the end of the deposition, where the films are opaque. These optical properties were assumed constant during film growth, which was tested to be true within their 90% confidence limits. The c-Si substrate with native oxide was accounted for in the model by using a so-called ‘virtual substrate’, which is a direct numerical inversion of the dielectric functions of the c-Si substrate with native oxide, as measured just prior to the start of the deposition. The validity of the optical model used for a-Si:H, the description of the Tauc-Lorentz formalism; the use of a virtual substrate; and the optimization procedure for finding the bulk dielectric function was assured from a detailed comparison with different modeling approaches reported in the literature. It was also corroborated by a detailed comparison of the optical film properties obtained from RTSE with the film properties obtained from ex-situ material characterization. It is noted that all films were found to be completely amorphous. In order to obtain the growth exponent $\beta$, the surface roughness evolution at the final stages of the a-Si:H depositions (i.e. in the long-time, long-scale asymptotic limit) has been fitted to relation $d_s \propto t^\beta$. This relation is equivalent to the relation $\frac{d_s}{d_b}(t) \propto t^\beta$, given in Sec. I, because the deposition rate is constant for each a-Si:H deposition.

The surface topography of the a-Si:H films was analyzed ex situ using a vibration-stabilized NT-MDT Solver P47 AFM. The AFM scans were carried out in air in non-contact (tapping) mode with a resonant frequency of $\sim 200$ kHz using c-Si cantilever probes with a nominal tip radius of 5–10 nm. AFM

![Fig. 1. Optical model that is used to analyze the spectroscopic ellipsometry data of the a-Si:H depositions.](image-url)
scans of the films were obtained for three scan sizes 1×1, 2×2, and 3×3 µm². For \( T_{\text{sub}} = 70 \) and 250 °C, one set of 3 AFM scans was performed, while 2 sets of 3 AFM scans were performed for \( T_{\text{sub}} = 150, 350, \) and 450 °C. For each \( T_{\text{sub}} \), a typical AFM surface topographical scan of 2×2 µm² is shown in Fig. 2. In order to obtain the roughness exponent \( \alpha \) (Sec. 1), the AFM scans were analyzed to yield the root-mean-square (RMS) roughness \( w(l) \) of the surface roughness spectrum as a function of the window size \( l \) in the range of 10 nm to \( L \), because \( w(l) \) should scale \( l \) as \( w(l) \propto l^{\alpha_{\text{RMS}}} \) in the range of \( l \ll \xi \) (Sec. 1). Here, \( w(l) \) is calculated as \( w(l) = \langle (h(x) - \langle h \rangle)^2 \rangle^{1/2} \), where \( h(x) \) is the height at position \( x=(x,y) \), \( \langle ... \rangle \) denotes an average over \( x \) in a window of size \( l \), and \( \langle ... \rangle \) denotes an average over the ensemble of windows of size \( l \).

A typical measurement of \( w(l) \) as a function of \( l \) is shown in Fig. 2 on double-logarithmic scale, obtained from a 2×2 µm² AFM scan of the a-Si:H film deposited at \( T_{\text{sub}} = 450 \) °C. Also shown is the corresponding apparent linear fit to determine \( \alpha_{\text{RMS}} \) in the unsaturated regime \( (l \ll \xi) \), yielding \( \alpha_{\text{RMS}} = 0.34 \pm 0.02 \).

In order to assess whether the a-Si:H surface scales self-affine or multi-affine, the AFM scans were also analyzed by extracting the \( q \)th order height difference correlation functions \( G_q(l) \) from the surface roughness spectrum, which should scale with the window size \( l \) as \( G_q(l) \propto l^{\alpha_q} \) in the range of \( l \ll \xi \) with \( \alpha_q \)'s the local roughness exponents. Here, \( G_q(l) \) is defined as \( G_q(l) = \langle [h(x) - h(x-x')]^q \rangle^{1/2} \), where the overbar denotes an average over \( x \) in scan size \( L \) and \( \langle ... \rangle \) denotes an average over the ensemble of vectors \( x'. \) Figure 2 shows typical measurements of \( G_1(l) \) up to \( G_5(l) \) as a function of \( l \), obtained from the same 2×2 µm² AFM scan of the a-Si:H film deposited at \( T_{\text{sub}} = 450 \) °C. Also shown are the apparent linear fits to determine the values of \( \alpha_q \)'s in the unsaturated regime \( (l \ll \xi) \). The values of \( \alpha_q \)'s

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\( w(l) \) and \( G_q(l) \) (Å)

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Fig. 2. The root-mean-square roughness (RMS) \( w(l) \) and the \( q \)th order height difference correlation functions \( G_q(l) \) of the surface roughness spectrum as a function of the window size \( l \), obtained from a typical AFM scan of 2×2 µm² of the a-Si:H film deposited at \( T_{\text{sub}} = 450 \) °C. Also shown are the apparent linear fits of \( w(l) \propto l^{\alpha_{\text{RMS}}} \) and \( G_q(l) \propto l^{\alpha_q} \) in the range of \( l \ll \xi \) to obtain the values of the roughness exponents \( \alpha_{\text{RMS}} \) and \( \alpha_q \)'s, respectively. For each \( T_{\text{sub}} \), a typical AFM surface topographical scan of 2×2 µm² is shown in the top of the figure, where the reported range of the height scale denotes the gray scale range from black to white.
are equal within their uncertainty with no trend of \( \alpha_q \) with \( T_{\text{sub}} \) and are less than unity (with an average value of \( \alpha_q = 0.46 \pm 0.02 \)). These qualities of \( \alpha_q \)’s were found to be true for all AFM scans at all \( T_{\text{sub}} \). A single value of \( \alpha_q \) that is less than unity implies that the a-Si:H surface is self-affine statistically scale invariant, i.e. the Family-Vicsek scaling relation \( w(l,t) \propto l^\beta f(l/\xi(t)) \) is valid.\(^{19-22}\) This self-affine scaling behavior of all a-Si:H surfaces is further corroborated from the fact that the relation \( d_s \propto d_e^\alpha \) fits well to the surface roughness evolution at the final stages of a-Si:H depositions. Therefore, the scaling behavior can completely be classified by two scaling exponents, the growth exponent \( \beta \) and the roughness exponent \( \alpha \) (Sec. 1). In order to analyze the dynamic scaling behavior of our a-Si:H films below, besides the values of \( \alpha_q \) on the AFM scan size was found. Therefore, for each \( T_{\text{sub}} \), the values of \( \alpha_q \) were averaged as was done for the values of \( \alpha_{\text{ex-situ}} \). The resulting averaged values of \( \alpha_q \) and \( \alpha_{\text{ex-situ}} \) are given below.

Finally, \( \text{ex-situ} \) AFM analysis of the a-Si:H films is briefly compared to \( \text{in-situ} \) RTSE analysis of the a-Si:H film growth. From Fig. 2, the largest surface roughness wavelength of the surface roughness spectrum of our \( \sim 2000 \) Å thick a-Si:H films can be estimated to be in the order of 100 nm, as the surface roughness does not increase for a window size increasing above 100 nm. Therefore, all AFM scans, even the smallest \( 1 \times 1 \) \( \mu \text{m}^2 \) scans, as well as the spectroscopic ellipsometer with a wavelength range of 245–1700 nm probe all roughness wavelengths that are present on the surface. As a consequence, the saturated root-mean-square roughness \( w_{\text{sat}} \) for large window size \( (l >> \xi) \) from AFM can be compared to the final values of the surface roughness \( d_{e,\text{final}} \) from RTSE at the end of the a-Si:H depositions. This has been done in Ref. 44 and it was concluded that \( w_{\text{sat}} \) shows a fair agreement with \( d_{e,\text{final}} \), showing a similar trend with \( T_{\text{sub}} \) as well as a fair correspondence in absolute numbers, especially when considering the different relationships between \( w_{\text{sat}} \) and \( d_{e,\text{final}} \) reported in the literature.

III. QUALITATIVE SURFACE ROUGHNESS ANALYSIS

A. Introduction of the different growth phases observed

Figure 3 shows the variation of the surface roughness layer thickness \( d_s \) as a function of the bulk layer thickness \( d_e \) for four a-Si:H films deposited at 250 °C. The four films have been deposited under equal deposition conditions and, therefore, Fig. 3 reveals that the data has a good reproducibility. Moreover, the surface roughness evolution observed is in good agreement with RTSE results on a-Si:H film growth reported in the literature,\(^{5,18}\) as is discussed in detail in Refs. 46 and 50. The consensus in the observed trends of the roughness evolution between different groups provides additional confidence in the reliability of the RTSE data, as does the good agreement of the material properties obtained from the RTSE data with those determined by \( \text{ex-situ} \) material characterization of the a-Si:H films.\(^{44}\) Using the interpretation of the surface roughness evolution by Collins and co-workers as a starting point, several growth phases can be distinguished in the surface roughness evolution of the a-Si:H growth process. The growth phases are denoted in Fig. 3 by the Roman numbers and are schematically illustrated in Fig. 4.

I. The nucleation phase and the moment of island coalescence: The growth of a-Si:H on a native-oxide covered c-Si substrate is generally assumed to initiate through the formation of islands, where the islands are usually represented by hemisphere-like structures. This heterogeneous surface is reflected in a relatively
large surface roughness. In the study presented here, the relatively large RTSE data acquisition time (Sec. II) prevents a detailed study of the nucleation phase, however, still some specific conclusions about the nucleation mechanism can be drawn, as discussed below. The nucleation phase continues up to the moment of island coalescence, \( t_{\text{coal}} \) (IIb.), at which point bulk growth initiate. At the moment of island coalescence, the surface roughness is approximately \( d_{s,\text{coal}} \approx 13 \, \text{Å} \) (Fig. 3), which corresponds to the final height of the islands that form on the substrate just before coalescence occurs. In the case of hemisphere-like islands, the final radius of the islands is roughly equal to the final height reached and a nucleation density of \( \sim 15 \times 10^{12} \, \text{cm}^{-2} \) can be calculated from the data in Fig. 3.

II. The smoothing phase and the so-called "dip" in the surface roughness: the decrease of the surface roughness in the first \( \sim 150 \, \text{Å} \) of bulk growth is attributed to surface diffusion, which smoothens out the surface roughness provided that the surface diffusion process is active with a sufficiently long surface diffusion length. The surface smoothing continues until a minimum in the surface roughness is reached that is referred to as the "dip" in the surface roughness (IIb.), which occurs before the onset of the roughening phase (III.). Collins and co-workers have found an empirical correlation between the position of the dip and the opto-electronic properties of the a-Si:H material. This empirical correlation states that a long postponement of the dip towards a large film thickness, \( d_{b,\text{dip}} \), and a large initial decrease of the surface roughness, \( \Delta d_{s} \), correspond to a high electronic performance and stability of the a-Si:H material for applications such as solar cells.\(^8,9,12,13\)

III. The roughening phase and the a-Si \( \rightarrow \) a-Si roughening transition: after reaching a bulk thickness of \( \sim 160 \, \text{Å} \), the surface roughness increases sharply again, denoted as the roughening phase. This clearly shows that, in the roughening phase, the surface diffusion process is no longer effective in smoothening the surface roughness. The transition between surface smoothing and surface roughening is also referred to as the "amorphous-to-amorphous (a-Si \( \rightarrow \) a-Si) roughening transition"\(^9,12\) because before and after the transition the material that is grown is amorphous. For our a-Si:H depositions, additional RTSE data analysis has confirmed that indeed (the same) amorphous material is grown before and after the transition.\(^44\)

VI. The stable growth phase: at a certain thickness of the surface roughness \( d_{s} \approx 8 \, \text{Å} \), the strong increase in the surface roughness levels off, which can only be explained by the onset of a "smoothening
Fig. 4. Schematic illustration of the different growth phases encountered during the deposition of an a-Si:H film that includes: the nucleation phase at the substrate (Ia.) and the moment of island coalescence (Ib.); the smoothening phase (Iia.) that ends in the so-called "dip" in the surface roughness (Iib.); the roughening phase (IIIb.); and the stable growth phase (IV). The following parameters are schematically indicated in the figure: the surface roughness in general ds, at the moment of island coalescence ds,coal, and in the dip ds,dip; the average lateral distance between the a-Si:H islands ls; and the average radius of the a-Si:H islands rs; the surface diffusion length ζ on the a-Si:H islands ζisl on the native oxide surface ζSiOx, and on the homogeneous a-Si:H surface ζ0; and the characteristic surface roughness wavelength λisl and most unstable surface roughness wavelength λm.

mechanism”. The surface roughness evolution of a-Si:H in this stable growth phase is in the long-time, long-scale asymptotic scaling limit and, therefore, the dynamic scaling behavior of the stable growth phase can be studied by investigating the growth exponent β as explained in Sec. I.

While in this section the interpretation of Collins and co-workers was adopted to identify the different growth phases that are encountered during an a-Si:H deposition, in the following sections these growth phases will be carefully reanalyzed without presumptions in order to gain insight into the surface processes that govern the observed surface roughness evolution. To this end, a-Si:H film have been grown at substrate temperatures in the range of Tsub = 70–450 °C. The surface roughness evolution as a function of the bulk thickness of these depositions is shown in Fig. 5. In this figure, the surface roughness evolution shown for Tsub = 250 °C is an average of the four deposition runs shown in Fig. 3.

B. Nucleation phase and the moment of island coalescence

Figures 3 and 5 show that for all substrate temperatures the surface roughness ds increases to a thickness of ds,coal = (13±1) Å before any bulk thickness db has formed. After the moment of island coalescence, however, the surface roughness decreases, at least for Tsub ≥ 250 °C. This transition from an increase to a decrease of the surface roughness can only be explained by the (abrupt) transition from heterogeneous growth, i.e. growth of a-Si:H islands on the native oxide-covered c-Si substrate, to homogeneous growth, i.e. growth of a-Si:H on a-Si:H. Initial growth by means of island formation has been explained previously by a larger a-Si:H–native oxide interface energy than a-Si:H–air interface energy.

Despite the limited time-accuracy of the RTSE measurements, it can be deduced that the deposition rate of a-Si:H during the nucleation phase before the moment of island coalescence is almost four times lower than that during the bulk growth after the moment of island coalescence (the deposition rate is
Fig. 5. Surface roughness evolution for a-Si:H deposited at substrate temperatures in the range of $T_{\text{sub}} = 70$–$450$ °C. The data shown for $T_{\text{sub}} = 250$ °C are the averaged values of the four deposition runs at $T_{\text{sub}} = 250$ °C shown in Fig. 3. It is noted that for $T_{\text{sub}} = 450$ °C, the accuracy in $d_s$ for times in the range of $t = 100$–$250$ s ($d_b = 130$–$320$ Å) was reduced, as discussed in Ref. 44.

defined as the increase of $d_b + \frac{1}{2} d_s$ in time). This observation is true for all $T_{\text{sub}}$ and an a-Si:H deposition rate that is much lower on native oxide than on an a-Si:H substrate is in agreement with Ref. 52. The only logical explanation is that primarily those a-Si:H growth precursors that land on or in close proximity of an a-Si:H island contribute to growth. Conversely, the majority of the species that land on the native oxide surface are either reflected from the surface or are desorbed from the surface before finding a growth site. This leads to the following conclusions. First, the growth precursors adsorbed at the surface (from hereon called "adatoms") have a surface diffusion length on the native oxide surface, $\zeta_{\text{SiOx}}$ (schematically shown in Fig. 4), that is smaller than the average lateral distance between the islands, $l_{\text{isl}}$, i.e. $\zeta_{\text{SiOx}} < l_{\text{isl}}$ (because otherwise the species that are not reflected would still reach an a-Si:H island and contribute to growth). Second, because $l_{\text{isl}} > \zeta_{\text{SiOx}}$, the position and size of the a-Si:H islands is not determined by $\zeta_{\text{SiOx}}$, but by the native oxide surface itself. In other words, the growth of a-Si:H islands can only initiate at specific growth sites on the native oxide surface, such as point defects. The second conclusion is corroborated by the experimental observations addressed next.

It is expected that the surface diffusion length on the native oxide surface $\zeta_{\text{SiOx}}$ depends strongly on $T_{\text{sub}}$, as surface diffusion is generally a strongly activated process. For instance, it will be shown below that the surface diffusion length on the homogeneous a-Si:H surface, $\zeta_0$ (Fig. 4), depends strongly on $T_{\text{sub}}$. The initial surface roughness at coalescence, $d_{\text{coal}}$, however, was found to be independent of the substrate temperature with a value of $d_{\text{coal}} = (13 \pm 1)$ Å. Moreover, $d_{\text{coal}}$ is also independent of pressure, as is concluded from four additional a-Si:H depositions at a much lower pressure of $p = 1 \times 10^{-5}$ mbar and at $T_{\text{sub}} = 150$, 250, 350, and 450 °C (not shown). These additional measurements show a value of $d_{\text{coal}} = (14 \pm 1)$ Å that is also independent of $T_{\text{sub}}$. At the low pressure of $p = 1 \times 10^{-6}$ mbar, the a-Si:H growth precursors are the direct silane decomposition products at the hot wire, i.e. predominantly Si and H. For increasing pressure up to the pressure of Figs. 3 and 5 ($p = 1.1 \times 10^{-5}$ mbar), not only the deposition flux increases, but also gas phase reactions gradually replace Si and H by predominantly SiH$_3$. It is therefore concluded that $d_{\text{coal}}$ is independent of (a) the specific a-Si:H growth precursors, (b) the surface diffusion length of the adatoms on the native oxide surface, $\zeta_{\text{SiOx}}$, and (c) the deposition flux. This implies that the
lateral distance between the a-Si:H islands on the native oxide surface $l_{iso}$ is completely determined by the native oxide surface itself, i.e. the surface density of the growth sites, and not by the deposition conditions.

In this case, where the distance between the islands $l_{ij}$ is independent of $T_{sub}$, the only way to obtain the same surface roughness at coalescence $d_{coal}$ is when the shape of the islands is (approximately) independent of $T_{sub}$. Because the effective surface diffusion length of the adatoms on the a-Si:H islands, $\zeta_{isl}$ (Fig. 4), is likely to have a large influence on the shape of the islands, it seems inevitable that $\zeta_{isl}$ is also independent of $T_{sub}$. This may seem to contradict a surface diffusion length on the homogeneous a-Si:H surface $\zeta_{si}$ that depends strongly on $T_{sub}$. However, it could just mean that for all $T_{sub}$ the surface diffusion length of the adatoms on the a-Si:H islands is restricted to the length scale of the island, i.e. $\zeta_{isl} = 1/2 \pi r_{isl}$ with $r_{isl}$ the radius of the island (Fig. 4) and $\zeta_{isl} \leq \zeta_{si}$. As a consequence, the adatoms will diffuse towards the energetically most favorable position on the a-Si:H island and, therefore, the surface energy of the a-Si:H islands is in or close to thermodynamical equilibrium. A surface energy in thermodynamical equilibrium combined with a larger a-Si:H–native oxide interface energy than a-Si:H–air interface energy would lead to a-Si:H islands with a hemisphere-like shape. In the case of hemispheres, the surface roughness at the moment of island coalescence of $d_{coal} \approx 13$ Å yields an average radius of the hemispheres of $r_{isl} \approx 13$ Å and a surface roughness spectrum with a characteristic surface roughness wavelength $\lambda_{isl}(\approx 26$ Å).

The obtained insights into the initial stages of a-Si:H growth can be compared with observations reported in the literature. It is a long-standing dispute in the literature, whether a-Si:H growth on a native oxide surface initiates through the formation of islands or not.54−56 No evidence for island formation was found in AFM55 and STM56 images of the initial a-Si:H growth. However, islands that have a radius of as small as $\approx 13$ Å can not easily be resolved with an AFM tip with a radius of 50−100 Å55 or even with an STM tip with a tip radius of $\approx 20$ Å.56 On the other hand, those reports in the literature of AFM55,56 and STM56 images of the initial a-Si:H growth that do show a-Si:H islands, also show islands that are larger than the tip radius used. Moreover, post-initial AFM54 and STM56 measurements of the growing a-Si:H feature sizes also indicate island formation. Finally, the existence of a-Si:H islands is always observed with (spectroscopic) ellipsometry5−8,14,19,51,61 which is sensitive to even the smallest islands.

The conclusion that the surface roughness at the moment of island coalescence of $d_{coal} = (13 \pm 1$) Å is independent of $T_{sub}$, the pressure, the a-Si:H growth precursors, $\zeta_{sub}$, and the deposition flux is in agreement with the various RTSE measurements across the literature: the value of $d_{coal}$ is generally found to be independent of H$_2$-admixing within the uncertainty limits up to a silane dilution ratio $R = [\text{H}_2]/[\text{SiH}_4]$ of $R \leq 5$.8,10,12,13,18,17 while this value is often also found to be independent of other deposition conditions, such as the substrate temperature.8,9,61 Typically, the value of $d_{coal}$ obtained from RTSE1 is in the range of $13−22$ Å.8−18,49 Our somewhat lower value may be explained by the extensive bake-out procedure prior to every a-Si:H deposition (Sec. II), causing (near complete) desorption of H$_2$O from the native oxide surface that may increase the areal density of (reactive) growth sites. In a similar way, the observed decrease of $d_{coal}$ with increasing rf power for PECVD a-Si:H growth on native-oxide-covered c-Si52 may be explained by an increase of the density of reactive growth sites with increasing ion energy.

The very small spread in $d_{coal} = (13 \pm 1$) Å can also be attributed to the extensive bake-out procedure, because the native oxide surface is brought in a very well-defined state before every a-Si:H deposition. The $T_{sub}$-independent value of $d_{coal}$ implies an effective homogeneous a-Si:H "substrate" at the moment of island coalescence that is independent of $T_{sub}$. The start of a-Si:H bulk growth from this reproducible a-Si:H substrate with a large, nucleation-induced surface roughness works in our advantage, because it enables an accurate study of the surface smoothing processes as a function of $T_{sub}$ as addressed next.

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1 Earlier work using single wavelength ellipsometry shows much larger values of $d_{coal}$ in the range of 30−70 Å.5,51,61
C. Smoothening phase and the so-called "dip" in the surface roughness

Figure 5 shows that the surface roughness evolution that starts after the moment of island coalescence depends on the substrate temperature: for substrate temperatures $>150$ °C the surface roughness first decreases, whereas for substrate temperatures $<150$ °C the surface roughness monotonically increases. The observed surface smoothening for $T_{sub} > 150$ °C is not at all obvious, as the surface of a growing film has the general tendency to become rougher in time due to ever-present roughening mechanisms, such as the noise in the deposition flux, as will be discussed below. The origin of the surface smoothening lies in the surface roughness that remains after the moment that the islands coalesce into a homogeneous a-Si:H surface. This surface roughness is much larger than would be the case when the a-Si:H deposition was started on a flat a-Si:H surface under the same deposition conditions with the same roughening mechanisms. Moreover, on the homogeneous a-Si:H surface, the surface diffusion of the adatoms is no longer restricted by the size of the island. Therefore, on the homogeneous a-Si:H surface with a large nucleation-induced roughness, the adatoms will feel a strong force to diffuse towards the energetically most favorable positions on the surface, which are the valleys, resulting in surface smoothening. Smoothening of an initially rough surface has been observed in literature for a number of deposition systems and has, in most of these cases, been tentatively explained by a temperature-dependent surface diffusion mechanism.

When all adatoms have a surface diffusion length that is long enough to reach a valley and contribute there to film growth, surface smoothening would be almost instantaneous, because there would be virtually no growth outside the valleys making the roughening mechanisms inoperative. Figure 5 shows, however, that the case of an almost instantaneous surface diffusion does not apply to any of our depositions. Still, when the surface diffusion length on the homogeneous a-Si:H surface $\zeta_0$ is long enough that most (not all) of the adatoms reach a valley, surface smoothening will be observed when the surface smoothening is more effective than the roughening mechanisms. This situation seems to be the case for $T_{sub} > 150$ °C. When the surface diffusion length decreases further, the surface diffusion becomes less effective up to the point where the surface diffusion is no longer able to control the roughening mechanisms, which seems to be the case for $T_{sub} < 150$ °C. Apparently, the surface diffusion length $\zeta_0$ increases for increasing substrate temperature from 70 to 250 °C. An increase of $\zeta_0$ with $T_{sub}$ is expected, because surface diffusion is generally an activated process. More specifically, following Collins and co-workers, the surface diffusion length $\zeta_0$ can be approximately estimated with respect to the characteristic surface roughness wavelength $\lambda_{isl}$ based on whether surface smoothing or roughening occurs. When assuming $\lambda_{isl}=26$ Å for the case of hemispheres (Sec. II), this procedure yields $\zeta_0 < \lambda_{isl}$ for $T_{sub}=70$ °C, $\zeta_0 \gg \lambda_{isl}$ for $T_{sub}=150$ °C, and $\zeta_0 >> \lambda_{isl}$ for $T_{sub} \geq 250$ °C.

The surface smoothening for $T_{sub} > 150$ °C continues until a minimum in the surface roughness is reached that is referred to as the "dip" in the surface roughness (IIb). Collins and co-workers have found an empirical correlation between the position of the dip and the opto-electronic properties of the a-Si:H material grown. This empirical correlation states that a long postponement of the dip, $d_{sub dip}$, and a large initial decrease of the surface roughness, $\Delta d_{s}$, correspond to a high opto-electronic performance and stability of the a-Si:H material for applications such as in solar cells. More importantly, Collins et al. interpret their empirical correlation in terms of the surface diffusion length $\zeta_0$, which is expected to increase with increasing $d_{sub dip}$ and $\Delta d_{s}$. In this description, the postponement of the dip $d_{sub dip}$ is defined as the bulk thickness at the position of the dip, while the initial decrease of the surface roughness $\Delta d_{s}$ is defined as the difference in surface roughness at the moment of island coalescence $d_{sub coal}$ and at the position of the dip $d_{sub dip}$. Using these definitions, the values of the values of $\Delta d_{s}$ and $d_{sub dip}$ have been determined from Figs. 3 and 5 and are given in Table I. Both $\Delta d_{s}$ and $d_{sub dip}$ are not defined for $T_{sub} = 70$ °C, but they increase (rapidly) for increasing $T_{sub}$ towards $T_{sub} \approx 250$ °C, where a maximum is reached. For increasing substrate temperature above 250 °C, both $\Delta d_{s}$ and $d_{sub dip}$ gradually decrease again, but remain well above the values of...
TABLE I. Given for the different substrate temperature $T_{\text{sub}}$ are the postponement of the “dip”, $d_{\text{sub, dip}}$, and the initial decrease of the surface roughness, $\Delta d_0$, that define the position of the dip in Figs. 3 and 5. Also given are the values of the characteristic surface roughness wavelength $\lambda_{\text{sc}}$ and the critical surface roughness wavelength $\lambda_c$ that correspond to the best effort simulations shown in Fig. 7. The reported uncertainties of $\lambda_{\text{sc}}$ and $\lambda_c$ reflect the range of values that yield good fits for the simulations on the basis of Eq. (5), when assuming the $T_{\text{sub}}$-independent values of $j=1.17$ Å and $S_0=1$ Å.

<table>
<thead>
<tr>
<th>$T_{\text{sub}}$ (°C)</th>
<th>$d_{\text{sub, dip}}$ (Å)</th>
<th>$\Delta d_0$ (Å)</th>
<th>$\lambda_{\text{sc}}$ (Å)</th>
<th>$\lambda_c$ (Å)</th>
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<td>(31.2±0.3)</td>
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<tr>
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<tr>
<td>450</td>
<td>103±8</td>
<td>9.7±0.7</td>
<td>(23.0±0.3)</td>
<td>(25.0±0.3)</td>
</tr>
</tbody>
</table>

$T_{\text{sub}}=150$ °C. For the case that the empirical correlation of Collins et al. would also apply to our a-Si:H depositions, then the best a-Si:H material should be obtained at $T_{\text{sub}}=250$ °C with a fast and slow decrease of material quality to lower and higher $T_{\text{sub}}$, respectively, which would be in agreement with external material characterization measurements. Moreover, for this case, the surface diffusion length $\zeta_0$ should increase sharply with increasing $T_{\text{sub}}$ from $T_{\text{sub}}=70$ °C to $T_{\text{sub}}=250$ °C, in accordance with the above-mentioned trend in $\zeta_0$, while $\zeta_0$ should decrease gradually for increasing $T_{\text{sub}}$ from 250 °C to 450 °C. Such a maximum of $\zeta_0$ at $T_{\text{sub}}=250$ °C would be in agreement with the literature. A possible decrease of $\zeta_0$ for $T_{\text{sub}}\geq250$ °C may be a result of a change in the chemical nature of the a-Si:H surface with increasing $T_{\text{sub}}$, for instance, associated to the change in surface silicon hydride composition with changing $T_{\text{sub}}$. It may seem extraordinary that the surface roughness dampens for $T_{\text{sub}}=150$ °C to such an extent that an almost atomically flat surface ($d_i=1.5–3$ Å) remains in the dip, whereas after the dip the surface roughness rises very rapidly, seemingly exponentially. However, such a fast roughening after an initial smoothening has been reported previously in the literature for a-Si:H growth as well as for MBE growth. A fast surface roughening in general has been explained previously by a number of theories, including shadowing effects with possible reemission, random fluctuations in the binding energy in an amorphous matrix, and the inability of the surface diffusion mechanism to stabilize roughness features at large lateral length scales. The first two theories are estimated to be unimportant for our a-Si:H depositions due to the very low surface roughness around the dip and the very low surface roughness increase in the stable growth phase ($T_{\text{sub}}$, as discussed below. The third theory, however, has been proven effective in explaining the initial stages of growth in a number of different growth systems and therefore will be explored here to explain the trends in the surface roughness for different $T_{\text{sub}}$ for the case of a-Si:H film growth (Fig. 5). To this end, the surface roughness wavelengths that comprise the surface roughness spectrum are investigated based on only two assumptions. First, in the absence of any smoothening mechanism(s), the amplitude of all possible roughness wavelengths will always increase due to ever-present roughening mechanisms and, importantly, small roughness wavelengths develop more rapidly than larger roughness wavelengths. As the specific nature of the roughening mechanism(s) is left undetermined for now, this assumption corresponds to the generally-accepted believe of growing interfaces. Second, in accordance with the discussion above, surface smoothening is assumed to be caused by a surface diffusion process that is characterized by a finite surface diffusion length $\zeta_0$, where $\zeta_0$ may depend on the substrate temperature.

D. Roughening phase and the a-Si $\rightarrow$ a-Si roughening transition

It may seem extraordinary that the surface roughness dampens for $T_{\text{sub}}=150$ °C to such an extent that an almost atomically flat surface ($d_i=1.5–3$ Å) remains in the dip, whereas after the dip the surface roughness rises very rapidly, seemingly exponentially. However, such a fast roughening after an initial smoothening has been reported previously in the literature for a-Si:H growth as well as for MBE growth. A fast surface roughening in general has been explained previously by a number of theories, including shadowing effects with possible reemission, random fluctuations in the binding energy in an amorphous matrix, and the inability of the surface diffusion mechanism to stabilize roughness features at large lateral length scales. The first two theories are estimated to be unimportant for our a-Si:H depositions due to the very low surface roughness around the dip and the very low surface roughness increase in the stable growth phase ($T_{\text{sub}}$, as discussed below. The third theory, however, has been proven effective in explaining the initial stages of growth in a number of different growth systems and therefore will be explored here to explain the trends in the surface roughness for different $T_{\text{sub}}$ for the case of a-Si:H film growth (Fig. 5). To this end, the surface roughness wavelengths that comprise the surface roughness spectrum are investigated based on only two assumptions. First, in the absence of any smoothening mechanism(s), the amplitude of all possible roughness wavelengths will always increase due to ever-present roughening mechanisms and, importantly, small roughness wavelengths develop more rapidly than larger roughness wavelengths. As the specific nature of the roughening mechanism(s) is left undetermined for now, this assumption corresponds to the generally-accepted believe of growing interfaces. Second, in accordance with the discussion above, surface smoothening is assumed to be caused by a surface diffusion process that is characterized by a finite surface diffusion length $\zeta_0$, where $\zeta_0$ may depend on the substrate temperature.
As discussed above, at the moment of island coalescence, the surface roughness has a characteristic surface roughness wavelength $\lambda_{isl}$ that corresponds to the average size of the islands ($\lambda_{isl} \approx 26$ Å for the case of hemispheres) and, subsequently, to the average distance between the valleys on the a-Si:H surface after the moment of island coalescence. As also discussed above, surface smoothening occurs for $T_{sub} > 150$ °C, because the surface diffusion length $\zeta_0$ is long enough that most of the adatoms reach a valley to contribute there to film growth. In other words, for $T_{sub} > 150$ °C, $\lambda_{isl}$ is (much) smaller than $\zeta_0$. Continuing this line of reasoning, there must exist an (unknown) critical surface roughness wavelength $\lambda_c$, related to $\zeta_0$ (with $l_d < \lambda_c < \zeta_0$), that is defined by the fact that all roughness wavelengths below $\lambda_c$ are stabilized by the surface diffusion mechanism, whereas all roughness wavelengths $> \lambda_c$ will increase undisturbed as the surface diffusion mechanism is not effective on these large length scales. The observed a-Si → a-Si roughening transition can now be explained by the increase of these long, unstable roughness wavelengths $> \lambda_c$ that start dominating the surface roughness at a certain bulk thickness: Initially, the long roughness wavelengths $> \lambda_c$ have a small amplitude and the initial surface roughness is dominated by the nucleation-induced surface roughness with wavelength $\lambda_{isl}$. This initial surface roughness first decreases with increasing bulk thickness, because the short, stable wavelengths $< \lambda_c$ are damped. The surface smoothening continues up to the dip, at which thickness the unstable wavelengths $> \lambda_c$ have gained sufficiently in amplitude to start dominating the surface roughness. After the dip, the unstable wavelengths continue to increase, causing the strong surface roughness increase as observed in the roughening phase (Fig. 5).

The change of the position of the dip with changing substrate temperature, i.e. the decrease of $d_{dip}$ and $\Delta d_l$ with increasing $T_{sub}$ above $T_{sub} = 250$ °C (Table I), can now be understood in light of this competition between the decrease of the short, stable wavelengths $< \lambda_c$ and the increase of the long, unstable wavelengths $> \lambda_c$ and the fact that $\lambda_c$ must scale with $\zeta_0$. For decreasing $\lambda_c$, the number of unstable wavelengths that are larger than $\lambda_c$ increases. Moreover, these additional unstable wavelengths are smaller and thus will increase more rapidly with thickness. Therefore, when $\zeta_0$ and thus also $\lambda_c$ decrease with increasing $T_{sub}$ above 250 °C, the unstable wavelengths will dominate the surface roughness at an earlier thickness for $T_{sub} = 450$ °C compared to $T_{sub} = 250$ °C. This leads to the earlier rise of the surface roughness for $T_{sub} = 450$ °C and results in a decrease of $d_{dip}$ and $\Delta d_l$ for increasing $T_{sub}$ above $T_{sub} = 250$ °C, as observed in Fig. 5 and Table 1. This provides a physical explanation for the empirical correlation by Collins et al. that the values of $d_{dip}$ and $\Delta d_l$ scale with the surface diffusion length $\zeta_0$.

The remarkably flatness of the a-Si:H surface in the dip (d ≈ 1.5–3 Å) for $T_{sub} \geq 250$ °C that is followed by the sharp increase in the surface roughness in the roughening phase (Fig. 5) suggests that the increase of the long, unstable wavelengths is exponential with thickness, as also observed for MBE growth of InAs. An exponential increase would also explain, why the slope of the surface roughness increase during the roughening phase looks identical for $T_{sub} = 250$, 350, and 450 °C. A detailed analysis of the smoothening phase and roughening phase on the basis of a possible continuum growth equation, including exponential fits of the roughening phase, is given in Sec. IV.

E. Stable growth phase

At some thickness during the roughening phase (at a bulk thickness of around 300 Å), the (exponential) increase of the surface roughness levels off (Figs. 3 and 5) entering the so-called "stable growth phase" (IV.), during which only a relatively small increase of the surface roughness with bulk thickness is observed. While this transition is present for all $T_{sub}$, for $T_{sub} \geq 250$ °C the stable growth phase seems to set in at a fixed surface roughness of ≈10 Å rather than a fixed bulk thickness. The occurrence of this transition can only be explained by the onset of an additional smoothening mechanism that is effective
in stabilizing (to a large extent) the long, unstable wavelengths >λc. Therefore, the surface roughness evolution during the stable growth phase is governed by surface processes that are active in the long-time, long-scale asymptotic limit. This provides the opportunity for investigating these surface processes by studying the scaling characteristics of the growing a-Si:H surface, as explained in Sec. I. Because it was demonstrated in Sec. II that the Family-Vicsek scaling relation \( w(t) \propto f(\xi) \) applies to our a-Si:H surfaces in the stable growth phase, the roughness exponents \( \alpha \) and the growth exponent \( \beta \) have been determined from the AFM and RTSE results, respectively, using the procedures described in Sec. II. The resulting values of \( \alpha \) and \( \beta \) are shown in Fig. 6 as a function of the substrate temperature \( T_{\text{sub}} \).

Figure 6 shows that the value of growth exponent \( \beta \) decreases monotonically for increasing \( T_{\text{sub}} \) from \( \beta = 0.18 \) at \( T_{\text{sub}} = 70 \, ^\circ\text{C} \) to \( \beta = 0.05 \) at \( T_{\text{sub}} = 450 \, ^\circ\text{C} \). This trend is in good agreement with the measurements of \( \beta \) for a-Si:H film growth reported in the literature that show the consistent trend of a monotonic decrease of \( \beta \) with increasing \( T_{\text{sub}} \), i.e. a transition from \( \beta = 0.5 \) at \( T_{\text{sub}} = 50 \, ^\circ\text{C} \) to \( \beta = 0.25 \) at \( T_{\text{sub}} = 300 \, ^\circ\text{C} \) to \( \beta = 0.07 \) at \( T_{\text{sub}} = 500 \, ^\circ\text{C} \).\(^{5,54,60,71}\) The trend seems to be independent of the deposition rate.\(^5\) It is noted that for all \( T_{\text{sub}} \) our values of \( \beta \) are quite low compared to most literature values. The roughness exponent \( \alpha \) has been determined in two ways, yielding \( \alpha_2 \) and \( \alpha_{\text{RMS}} \) (Sec. II), and Fig. 6 shows that the values of \( \alpha_2 \) are typically ~0.1 higher than the values of \( \alpha_{\text{RMS}} \) which was already addressed in Sec. II. The general trend of \( \alpha_2 \) and \( \alpha_{\text{RMS}} \), however, is the same: \( \alpha \) decreases from \( \alpha = 0.5 \) for \( T_{\text{sub}} = 70 \, ^\circ\text{C} \) to \( \alpha = 0.3 \) at \( T_{\text{sub}} = 350 \, ^\circ\text{C} \), but seems to increase again to \( \alpha = 0.4 \) for \( T_{\text{sub}} = 450 \, ^\circ\text{C} \), although the uncertainty in \( \alpha \) seems considerable. This trend of \( \alpha \) with \( T_{\text{sub}} \) as well as the absolute values of \( \alpha \) are in good agreement with \( \alpha \) values reported in Ref. 72, although there the uncertainty in \( \alpha \) was also large. In general, our values of \( \alpha \) and \( \beta \), as well as our values of the final surface roughness of our grown a-Si:H films (not shown), are quite low compared to most values reported in the literature.\(^{5,54,60,71}\) This seems to suggest that the surface smoothing processes are more effective for our "optimum HWCVD conditions" (Sec. I) than for other a-Si:H deposition techniques.

\(^{5}\) Of course, the roughness wavelengths >\( \lambda_c \) are, by definition, not unstable with respect to this additional smoothing mechanism, however, the terminology of "long, unstable wavelengths >\( \lambda_c \)" will be continued throughout the Chapter.
To investigate the surface smoothening processes that govern the stable growth phase, the measured values of $\alpha$ and $\beta$ are compared with the $\alpha$ and $\beta$ of the universality classes introduced in Sec. I, i.e. "random deposition" (RD) with $\alpha = \infty$ and $\beta = \frac{1}{2}$, "random deposition with surface diffusion" (RDD) with $\alpha = 1$ and $\beta = 0.25$, and "random deposition with surface relaxation" (RDR) with $\alpha = \beta = 0$. Our values of $\alpha$ and $\beta$ clearly show that for every $T_{\text{sub}}$ the stable growth phase does not correspond to the pure random deposition and that one or more surface smoothening mechanisms must be active. Our values of $\alpha$ and $\beta$ are also much lower than $\alpha = 1$ and $\beta = 0.25$ for RDD. Therefore, surface diffusion cannot be the (only) governing smoothening mechanism, which is additional evidence that an other smoothening mechanism must be active during the stable growth phase. It seems, however, that RDR is not this other smoothening mechanism, because the measured values of $\alpha$ and $\beta$ are significantly higher than $\alpha = \beta = 0$. A number of alternative universality classes with each their own set of $\alpha$ and $\beta$ values have been suggested in the literature, among which the lowest values of the scaling exponents are found for the Kardar-Parisi-Zhang (KPZ) growth model with $\alpha = 0.38$ and $\beta = 0.24$ and the growth model proposed by Lai, Das Sarma and Villain with $\alpha = \frac{3}{8}$ and $\beta = 0.2$. Some of these universality classes may explain the low values of $\alpha$ in Fig. 6. However, to the best of our knowledge, no universality classes, has yet been proposed in the literature with a value of $\beta$ in the range of $0 < \beta < 0.2$. Even more importantly, each of the universality classes has a fixed value of $\alpha$ and $\beta$, whereas the measurements of $\alpha$ and $\beta$ show a clear dependence of $\alpha$ and $\beta$ on the substrate temperature (Fig. 6).

The fixed values of $\alpha$ and $\beta$ for the universality classes are a direct result of the fact that the universality classes describe a growth process by means of a single (smoothening) mechanism that is assumed to be instantaneous, i.e. corresponding to an infinite temperature. In reality, however, surface smoothening mechanisms, such as surface diffusion, are temperature-activated processes. Therefore, at a finite temperature, the effectiveness of a surface smoothening mechanism will be reduced with respect to its effectiveness in the corresponding universality class, resulting in higher values of $\alpha$ and $\beta$ than those of the corresponding universality class. Moreover, a change of the effectiveness of the surface smoothening mechanism with changing substrate temperature will also induce a change in the value of $\alpha$ and $\beta$. Taking this into account, the very low values $\alpha < 0.5$ and $\beta = 0.05$ for $T_{\text{sub}} \geq 350 \, ^\circ\text{C}$ imply most likely that, for the high temperature limit, a-Si:H film growth in the long-time, long-scale asymptotic limit is governed by RDR but with a reduced effectiveness of the surface relaxation due to the finite substrate temperature, resulting in values of $\alpha$ and $\beta$ above zero. Therefore, one explanation for the decrease of $\beta$ with increasing substrate temperature (Fig. 6) may be the increase in effectiveness of the surface relaxation. Alternatively, it was argued above that surface diffusion is effective in stabilizing the short, stable wavelengths $< \lambda_c$, and there is no reason to assume that this mechanism stops working in the stable growth phase. Therefore, a second explanation of the decrease of $\beta$ with increasing $T_{\text{sub}}$ may be that the gradual transition from an a-Si:H growth regime at low $T_{\text{sub}}$ that is governed by surface diffusion (RDD) to an a-Si:H growth regime at high $T_{\text{sub}}$ that is governed by surface relaxation (RDR). This second explanation may possibly also explain the the minimum in $\alpha$ at $T_{\text{sub}} = 350 \, ^\circ\text{C}$, because surface diffusion was argued above to be most effective at $T_{\text{sub}} = 250 \, ^\circ\text{C}$, while the effectiveness of surface relaxation is expected to increase with increasing $T_{\text{sub}}$. A gradual cross-over between different universality classes was also proposed by Smets et al., who explained the transition from $\beta = 0.5$ at $T_{\text{sub}} = 50 \, ^\circ\text{C}$ to $\beta = 0.25$ at $T_{\text{sub}} = 300 \, ^\circ\text{C}$ to $\beta = 0.07$ at $T_{\text{sub}} = 500 \, ^\circ\text{C}$ by the gradual cross-over from RD at low $T_{\text{sub}}$ to RDD at intermediate $T_{\text{sub}}$ towards RDR at high $T_{\text{sub}}$.

Finally, the underlying mechanism of surface relaxation is discussed for the case of a-Si:H film growth. Surface relaxation is generally regarded as a process that reduces the surface tension that is contained in the roughness features on the surface. For a-Si:H film growth, bulk diffusion can be neglected, therefore, a surface tension driven surface relaxation mechanism should occur somehow through the surface processes of the adatoms on the a-Si:H surface. One possible view may be that the surface
tension pushes all individual surface diffusion trajectories of the adatoms a small extent towards the valleys on the surface, resulting in a net diffusion flux towards the valleys, despite the fact that the separation between the valleys can be much greater than the surface diffusion length $\zeta_0$. This would explain how surface relaxation is able to stabilize (to a large extent) the long, unstable wavelengths $>\lambda_c$. In this view, surface relaxation may be regarded as a correction term on the surface diffusion mechanism.

IV. QUANTITATIVE SURFACE ROUGHNESS ANALYSIS USING GROWTH EQUATIONS.

In this section, the surface roughness evolution will be investigated in more detail by attempting to produce a specific continuum growth equation that is able to explain the full evolution of the surface roughness shown in Figs. 3 and 5. Initially, we will follow the work of Raible, Linz, and Hänggi (RLH), who proposed a minimum nonlinear stochastic growth equation for the specific case of amorphous thin film growth: Starting from the well-established phenomenological approach that is based on stochastic nonlinear partial differential equations, while using the symmetry principles relevant for amorphous film growth, the condition of a conserved growth (discussed below), and an expansion in the gradients of the single-valued surface height profile $h(x,t)$, RLH obtained the following functional form for the lowest-order nonlinear stochastic growth equation for a 2-dimensional surface, referred to as the "RLH growth equation":

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h - \kappa \nabla h - \epsilon_0 \nabla^2 (\nabla h)^2 + \eta(x,t), \quad (1)$$

where $h$ is the difference in height with the average height on the surface that moves along in the growth direction, $\nabla = (\partial / \partial x, \partial / \partial y)$, and $\nu$, $\kappa$, and $\epsilon_0$ are scalar material-dependent prefactors. The term $\eta(x,t)$ represents the stochastic fluctuations in the deposition flux, which are assumed to be Gaussian white:

$$\langle \eta(x,t) \rangle = 0; \quad \langle \eta(x,t)\eta(x',t') \rangle = 2D \delta^2(x-x') \delta(t-t'), \quad (2)$$

where $\delta(x)$ is the Dirac delta function and $2D$ refers to the variance of the noise term and is proportional to the deposition rate. When the deposition noise is the only term present, i.e. $\partial h / \partial t = \partial h = \eta(x,t)$, random deposition (RD) will occur with $d_s \propto d_b^{1/2}$. The Laplacian term $(\nu \nabla^2 h)$ in Eq. (1) can appear due to a variety of physical origins. For $\nu<0$, the term $\nabla^2 h$ leads to surface smoothing and can be interpreted as surface relaxation caused by surface tension. In the case that only the Laplacian term is competing with $\eta(x,t)$, one obtains the so-called Edwards and Wilkinson (EW) equation, i.e. $\partial h / \partial t = \nu \nabla^2 h + \eta(x,t)$ with scaling exponents $\alpha = \beta = 0$. The EW equation is generally believed to belong to the universality class of RDR (Sec. I) due to the similarity in relaxation mechanism and the coincidence of the same scaling exponents in both one and two dimensions. The same Laplacian term with positive $\nu$ has also been introduced to describe the equilibrium between deposition and desorption of particles on and from the surface, respectively, a mechanism that also leads to surface smoothing. In our case, however, desorption of growth precursors from the a-Si:H surface is expected to be negligible at the low substrate temperatures used, as corroborated by recent experiments. While RLH did not need to include diffusive noise $\eta_d(x,t)$ in their RLH equation to simulate their measurements, we believe that diffusive noise is also unimportant for the a-Si:H growth processes studied in this Chapter. For the initial stages of film growth, this assessment is based on the considerations presented by Krug and Rost. For the later stages of film growth, diffusive noise is deemed unimportant, because the governing roughness mechanisms are active on length scales that are larger than the surface diffusion length, as argued throughout the Chapter.
value of $v$ is negative, the Laplacian term leads to surface roughening. Such a term was introduced by Villain\textsuperscript{7} to explain the growth of moundlike surface structures in MBE due to a potential barrier at the step edges of the crystalline lattice. However, for amorphous film growth, this effect is also deemed unimportant.\textsuperscript{32} A growth instability represented by the Laplacian term with $v < 0$ can still appear as a result of (a) the finite size of the atoms, as arriving atoms are attached to the surface at a position separated from their center of mass\textsuperscript{49,70} and (b) particle deflection caused by interatomic attraction.\textsuperscript{32,34} Mathematically, growth instabilities (a) and (b) are equivalent\textsuperscript{11}, but it is argued in Ref. 34 that the deflection effect (b) must be considered as the genuine underlying mechanism for that growth instability. Moreover, growth instability (b) has recently been demonstrated experimentally.\textsuperscript{76} For our purpose, it is not really important, which exact physical mechanism is responsible for the Laplacian term, as it will not be possible to extract its physical origin from our data. It is important, however, that a Laplacian term with $v < 0$ must be present in Eq. (1) to explain the a-Si $\rightarrow$ a-Si roughening transition, as will be seen below.

The term $-\kappa \nabla^4 h(x)$ with $\kappa > 0$ is included in Eq. (1) to represent the surface diffusion mechanism. Herring proposed that the chemical potential for an atom on a homogeneous surface is proportional to the curvature of the surface,\textsuperscript{71} while Mullins applied Herring's chemical potential to calculate a surface evolution having the form $\partial h / \partial t = -\kappa \nabla^4 h(x)$.\textsuperscript{78} This mathematical description of surface diffusion is generally accepted and is the dominant smoothing term introduced in continuum models in use today. The case where deposition noise is only counteracted by surface diffusion, i.e. $\partial h / \partial t = -\kappa \nabla^4 h + \eta(x,t)$, yields the scaling exponent $\alpha = 1$, and $\beta = 1/4$ for the long-time, long-scale limit and, therefore, this equation is believed to belong to the universality class RDD (Sec. 1).\textsuperscript{21,23,25}

To this point, the terms treated, i.e. $\eta(x,t)$, $\nu \nabla^2 h$ and $-\kappa \nabla^4 h(x)$, were all linear, reflecting the fact that each roughness wavelength develops independently. It is generally observed with AFM and STM, however, that the feature size on the a-Si:H surface increases with bulk thickness.\textsuperscript{34,39,66,72,79} This suggests the presence of a non-linear term in our growth equation.\textsuperscript{71} The lowest order non-linear term that complies with the symmetry principles for amorphous film growth is the unconserved Karadar-Parisi-Zhang (KPZ) nonlinearity, i.e. $\omega_2 (\nabla h)^2$ with $\omega_2 > 0$.\textsuperscript{32} This term indeed causes the dominant roughness wavelength to increase, because the larger protrusions on the surface increase at the expense of the smaller ones\textsuperscript{\dagger\dagger} (schematically illustrated in the stable growth phase IV, in Fig. 4). The unconserved KPZ term does, however, not satisfy the condition of a conserved growth. Conserved terms, such as $\nu \nabla^2 h$ and $-\kappa \nabla^4 h(x)$, reorganize the interface height $h$ (that has been normalized to the average height on the surface) such that the total mass remains unchanged. In contrast, unconserved terms add material to the interface and the amount of added material increases with increasing effectiveness of the unconserved term, i.e. with increasing surface roughness, irrespective of whether voids or overhangs are present in the film or not. As a consequence, unconserved growth is only allowed in the presence of desorption of surface species from the surface or another mechanism that can influences the rate of material deposition. As mentioned above, desorption is expected to be negligible for our a-Si:H depositions, while no other surface process that can influences the rate of material deposition has been identified for amorphous film growth. Moreover, the deposition rate is constant throughout our a-Si:H deposition,\textsuperscript{44} while the surface roughness is clearly not (Figs. 3 and 5). Therefore, the unconserved KPZ nonlinearity is expected to be unimportant. Alternatively, the conserved term $-\omega_2 \nabla^2 (\nabla h)^2$ that is included in the RLH growth equation also causes the dominant wavelengths to increase in a similar manner as $\omega_2 (\nabla h)^2$.\textsuperscript{32} Therefore, it has been suggested that the term $-\omega_2 \nabla^2 (\nabla h)^2$, referred to as the "conserved KPZ nonlinearity", is an important term for growth processes.\textsuperscript{21,26} Indeed, it can be simply derived from the slope dependent adatom concentration that the

\textsuperscript{\dagger\dagger} The exact mathematical description of growth instabilities (a) and (b) introduces an additional fourth-order term in Eq. (1). This additional fourth-order term can, however, be neglected under practical deposition conditions.\textsuperscript{32,33}
conserved KPZ nonlinearity is always present as a correction term (with $\omega_1 > 0$) of the surface diffusion term $-\kappa \nabla^4 h(x)$ as can be seen as follows. The deposition flux per surface area and consequently the adatom areal concentration is lower for a steep slope, resulting in a net surface diffusion towards the steep slope from the surrounding surface. It has been observed in the simulations of the RLH growth equation by Raible et al.\textsuperscript{32} that this mechanism produces a surface morphology that resembles the morphology of a cauliflower\textsuperscript{80} with its steepest slopes located in the valleys or pits. Therefore, the conserved KPZ nonlinearity $-\omega \nabla^2 (\nabla h)^2$ leads to surface smoothening, as the deposition rate in the growth direction is enhanced for the valley ($\partial_t h > 0$) at the price of a lower deposition rate of the surrounding surface ($\partial_t h < 0$). For a-Si:H (as well as for many other thin film growth systems\textsuperscript{80}), a cauliflower-like surface is generally observed from AFM images\textsuperscript{54,57,58,72,81} and STM images\textsuperscript{56,59,60,79,81} and is also seen in the AFM scans for our a-Si:H depositions shown in Fig. 2. Therefore, the mechanism described by the conserved KPZ nonlinearity $-\omega \nabla^2 (\nabla h)^2$ may well be responsible for the cauliflower-like surface morphology of a-Si:H.

### A. Linear, deterministic growth equation to model initial growth

It was hypothesized in Sec. III that the smoothening of an initially rough surface (with $\lambda_{isl} \approx 26$ Å for the case of hemispheres) into the dip with an almost atomically flat surface followed by a strong surface roughening is caused by a competition between the decrease of small, stable wavelengths $<\lambda_c$, which initially dominate the lateral surface geometry, and the increase of large, unstable wavelengths $>\lambda_c$. It will now be attempted to substantiate these qualitative findings from the mathematical description of the RLH growth equation.

An important result from the different one- and two-dimensional simulations of Raible et al.\textsuperscript{32} is that the conserved KPZ nonlinearity and the deposition noise in the RLH growth equation [Eq. (1)] are not important for the initial stages of the surface growth. In other word, the early stages of film growth are governed by the linear, deterministic limit of the RLH growth equation:

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h - \kappa \nabla^4 h \quad \text{with} \quad \nu < 0.$$  \hspace{1cm} \text{(3)}

This conclusion has been corroborated by the success of Eq. (3) to describe a number of experimental findings in the literature.\textsuperscript{29,33,69,70} In particular, Gyure et al. measured with AFM an initial surface roughness evolution for MBE growth of InAs that is quite similar to ours for a-Si:H growth (Fig. 3). They concluded that Eq. (3), in which the Laplacian term was introduced to represent the potential barrier at the step edges,\textsuperscript{27} was adequate to quantitatively describe the AFM measurements, while nonlinear terms were estimated to be unimportant until much later times. Krug and Rost\textsuperscript{30} concluded from the same AFM data that deposition noise $\eta(x,t)$ and diffusive noise $\eta_d(x,t)$ do not substantially contribute to the surface roughness in the early stages of the film growth, while the nonlinear terms were also deemed unimportant. Encouraged by the success of Eq. (3), here, Eq. (3) will be used to analyze the initial surface roughness evolution of Figs. 3 and 5.

Mazor et al., Gyure et al. and Raible et al. all come to essentially the same conclusions when analyzing Eq. (3).\textsuperscript{29,33,69,70} There exists a critical roughness wavelength $\lambda_c = 2\pi/k_c = 2\pi \sqrt{\nu |\nabla|}$, below which all wavelengths are damped out due to surface diffusion, while all wavelengths $>\lambda_c$ are unstable and grow exponentially. This can easily been seen by inserting $\sin(k \cdot x)$ as an initial trial perturbation in Eq. (3). This sinusoidal perturbation shows an exponential increase or decrease in time according to

$$\exp\left((-\nu k^2 - \kappa k^4)t\right)$$  \hspace{1cm} \text{(4)}
with $k = |k|$. It also follows from Eq. (4) that there exists a maximum unstable wavelength

$$\lambda_{un} = \sqrt{2} \lambda_c = 2 \sqrt{2} \pi \sqrt{\kappa}$

which is the fastest growing wavelength that will eventually dominate the surface roughness (see Fig. 4). It thus seems that Eq. (3) provides us with the mathematical description of our qualitative findings of Sec. III. Therefore, an attempt will be made to simulate the surface roughness evolutions shown in Fig. 5. To this end, the values of $d_s$ have been replotted in Fig. 7 as a function of the deposition time $t$ from the moment of island coalescence ($t \geq t_{coal}$). The a-Si:H surface at the moment of island coalescence with surface roughness $d_{s,coal}$ is incorporated into the simulations as the initial boundary condition by means of a spatial roughness spectrum $S_0(k) = S_0(k) = \langle \hat{h}(k,0) \rangle$, where $k = |k|$, $\hat{h}(k,0)$ is the Fourier spectrum of $h(r,t)$, and $\langle \ldots \rangle$ denotes an average over the ensemble of vectors $k$. In accordance with the discussions in Sec. III, the surface roughness at the moment of island coalescence is assumed to be dominated by a single characteristic roughness wavelength $\lambda_{isl} = 2 \pi / k_{isl}$ with amplitude $\Delta$. All other wavelengths are probably best represented by a white noise roughness spectrum with a low (constant) amplitude $\hat{S}_0$, in accordance with Ref. 29. This yields the initial spatial roughness spectrum of $S_0(k) = \hat{S}_0 + \Delta \times \delta(k-k_{isl})$, where $\delta(x)$ is the Dirac delta function. The values of $\hat{S}_0$ and $\Delta$ are chosen such that the simulated initial surface roughness $d_s(t=0)$ equals the surface roughness at the moment of island coalescence $d_{s,coal}$, i.e., $d_{s,coal} = 13.0$ Å for all $T_{sub}$ except for $T_{sub} = 150$ °C where $d_{s,coal} = 14.5$ Å (Fig. 7). The value of $\hat{S}_0$ is unknown and is therefore incorporated into the simulations as a fitting parameter. However, because the contribution of white noise to the initial surface roughness $d_s(t=0)$ is less than 0.1 Å for all reasonable values of $\hat{S}_0$, the values of $\Delta$ can be calculated with $\Delta = \lambda_{isel} d_{s,coal} / (2 \pi)^2$ in order to set the initial surface roughness $d_s(t=0)$ equal to $d_{s,coal}$. Then, the evolution of the surface roughness $d_s(t)$ can be obtained by numerically integrating $S_0(k)$ over all wavenumbers:

$$d_s(t) = \int \frac{d}{dk} \left\{ \frac{1}{2} \kappa S_0(k) \exp \left\{ 2(-\nu k^2 - \kappa k^4) t \right\} \right\} dk.$$

(5)

**Fig. 7.** Simulations of the surface roughness layer thickness as a function of deposition time $t$ from the moment of island coalescence for $T_{sub} = 70$–450 °C. The RTSE data points of Fig. 5 have been replotted as a function of the time $t$ after the moment of island coalescence. The surface roughness has been simulated by numerical integration of an initial surface roughness spectrum that is dominated by a single roughness wavelength $\lambda_{isel} = 2 \pi / k_{isel}$ of amplitude $\Delta$ on top of a white noise background spectrum with amplitude $\hat{S}_0$, i.e., $S_0(k) = \hat{S}_0 + \Delta \times \delta(k-k_{isel})$. The simulations incorporate only three fitting parameters, given in Table 1: $\lambda_{isel}$, $\lambda_{c}$, and the $T_{sub}$-independent parameter $\hat{S}_0$. 
Here, $\lambda_{\text{cutoff}}$ is the smallest wavelength present on the surface and has been assumed $\lambda_{\text{cutoff}} = 5$ Å. However, it has been tested that the value of $\lambda_{\text{cutoff}}$ has negligible influence on the simulated results as long as $\lambda_{\text{cutoff}} < \lambda_c$. The critical roughness wavelength $\lambda_c$ is incorporated in the simulations through the value of $\kappa$, i.e. $\lambda_c = 2\pi\sqrt{\kappa/\nu}$, while the value of $\nu$ is assumed based on the following arguments. For the case that the Laplacian term $\nabla^2 h$ represents the above-mentioned growth instability (a) of Mazor et al.\textsuperscript{66,70} (i.e. roughening due to the finite size effect of the arriving atoms that are attached to the surface at a position separated from their center of mass), then $\nu = -j \times R_d$ with $R_d$ the deposition rate and $j$ half the interatomic distance, which is $j = 1.17$ Å for a Si-Si bond. For the case that $\nabla^2 h$ corresponds to the growth instability (b) of Raible et al.\textsuperscript{32,34} (i.e. roughening due to particle deflection caused by interatomic attraction), then $\nu = -b \times R_d$ with $b$ the interatomic attraction distance. The value of $b$ is not known for a-Si:H. For vapor deposition of ZrAlCu films, however, Raible et al.\textsuperscript{32} found the value of $b$ to be $\sim 1$ Å.\textsuperscript{34} Because $b = 1$ Å agrees with $j = 1.17$ Å within uncertainty limits, the more precise value of $j = 1.17$ Å is used in our simulations. Subsequently, the values of the deposition rate $R_d$ (Sec. II) are used to calculate $\nu$ with $\nu = -j \times R_d$. In all, the simulations incorporate only three fitting parameters, i.e. $\lambda_{\text{cutoff}}, \lambda_c, \hat{S}_0$. Moreover, $\hat{S}_0$ is assumed independent of $T_{\text{sub}}$ because there is no reason to assume why the amplitude of the white noise spectrum would depend on $T_{\text{sub}}$ (in fact, it has been argued in Sec. III that the a-Si:H surface at the moment of island coalescence is remarkably independent of $T_{\text{sub}}$ and is well reproduced between different a-Si:H depositions).

Figure 7 shows our best effort simulations, as obtained by assuming the $T_{\text{sub}}$-independent value of $\hat{S}_0 = 1$ Å\textsuperscript{2}. The simulations show a very good agreement with the RTSE data with respect to the trend in the surface roughness evolution during the early stages of a-Si:H film growth, the dependence of this trend on $T_{\text{sub}}$, and the absolute values of the simulated surface roughness. Even the sharp transition from surface smoothing to surface roughness at the dip is well captured by the simulations. Only the roughening phase of $T_{\text{sub}} = 150$ °C is not quite as well simulated. It is noted that the data could also be fitted well for other $T_{\text{sub}}$-independent values of $j$ and $\hat{S}_0$ in the range of 0.9–1.5 Å and 0.5–5 Å\textsuperscript{4}, respectively. This range of $\hat{S}_0$ around $\hat{S}_0 = 1$ Å\textsuperscript{2} seems reasonable in comparison to, e.g., a white noise spectrum with amplitude $\hat{S}_0 = 0.5$ Å\textsuperscript{4} as measured with AFM for an InAs(001) substrate after oxide desorption.\textsuperscript{29} The fact that the surface roughness evolution during the early stages of a-Si:H film growth can be simulated so well with the linear, deterministic growth equation of the RLH growth equation gives a strong confirmation of the validity of our hypothesis that the early stages of a-Si:H growth are governed by the competition between the decrease of the short, stable wavelengths $<\lambda_c$ and the increase of the long, unstable wavelengths $>\lambda_c$.

The values of the fit parameters $\lambda_{\text{cutoff}}$ and $\lambda_c$ that correspond to the best effort simulations of Fig. 7 are given in Table I. For a given choice of an $T_{\text{sub}}$-independent value of $j$ and $\hat{S}_0$, the absolute uncertainty in the values of $\lambda_{\text{cutoff}}$ and $\lambda_c$ is assessed at $\pm 0.3$ Å for all $T_{\text{sub}}$, except for $T_{\text{sub}} = 150$ °C where the uncertainty is $\pm 0.5$ Å. The value of characteristic roughness wavelength $\lambda_{\text{cutoff}}$ seems independent of $T_{\text{sub}}$. In particular, $\lambda_{\text{cutoff}}$ does not increase with $T_{\text{sub}}$ as the highest value of $\lambda_{\text{cutoff}}$ is found at $T_{\text{sub}} = 70$ °C. This corroborates the conclusion stated in Sec. III that the nucleation of a-Si:H islands on a native oxide substrate is completely determined by the substrate and not by the deposition conditions. The weighted average of the best fit values of $\lambda_{\text{cutoff}}$ is $\lambda_{\text{cutoff}} = (26.2 \pm 0.5)$ Å. Although the error bar could be significantly larger due to (unknown) uncertainties in $j$ and $\hat{S}_0$, a value of $\lambda_{\text{cutoff}}$ close to 26 Å ($= 2 \times d_{\text{coal}}$) supports our conclusion that the a-Si:H islands on a native oxide substrate could well be hemispheres. Moreover, the fact that the trends in the surface roughness can be fitted well by using a delta peak in the initial boundary condition, i.e. $S_d(k) = \hat{S}_0 + \Delta \delta(k-k_{\text{cut}})$, is an indication that the distribution of the island sizes has a very small width. In fact, various guesses of $S_d(k)$ have been tested, including one or multiple distributions of island sizes with various widths and peak positions, however, the exact trends in the RTSE data could only be reproduced well by using a very small width in the distribution of the island sizes. This small width corroborates the small spread in the measured
values of surface roughness at the moment of island coalescence, $d_{\text{coal}}$ (Sec. III). The values of the critical roughness wavelength $\lambda_c$ given in Table I and the resulting implications for the surface diffusion mechanism during a-Si:H film growth are discussed in Sec. V.

**B. Full RLH growth equation to describe the stable growth phase**

The simulations in Fig. 7 predict a continuing exponential growth of the long, unstable wavelengths $>\lambda_c$ for increasing bulk thickness after the dip, whereas the RTSE data clearly show that this strong increase in the surface roughness levels off in agreement with the low values of the surface roughness found by AFM (Fig. 2). The latter can only be explained by the onset of an additional smoothening mechanism that is able to stabilize (to a large extent) the long, unstable wavelengths $>\lambda_c$. Moreover, this onset seems to occur at a fixed surface roughness, at least for $T_{\text{sub}} \geq 250 \degree C$. To investigate the nature of this additional smoothening mechanism, the full non-linear stochastic RLH growth equation [Eq. (1)] is reexamined.

To this point, the conserved KPZ nonlinearity $-\alpha_0 V^2(\vec{\nabla}h)^2$ has been neglected with respect to the surface diffusion term $-\kappa V^4 h$, because the fourth order derivative is more effective for steep local slopes that occur on small lateral length scales. However, larger wavelengths have smaller slopes ($\partial h / \partial x < 1$). Therefore, with increasing roughness wavelength, the effectiveness of the $-\kappa V^4 h$ term decreases much faster than the effectiveness of the conserved KPZ nonlinearity. Hence, the latter may well become the dominant smoothening mechanism during the stable growth phase. The fact that the conserved KPZ nonlinearity $-\alpha_0 V^2(\vec{\nabla}h)^2$, which is a correction term of the surface diffusion term $-\kappa V^4 h(x)$ as explained above, may be active on length scales much larger than the surface diffusion length $\zeta_0$ can be understood as follows. The conserved KPZ nonlinearity introduces a diffusion current towards the valleys on the surface as a result of a slope dependent adatom concentration. When a large roughness wavelength is divided into sections of length $\zeta_0$, within each section the conserved KPZ nonlinearity will push the surface diffusion on average towards the side of the section that has the steepest slope. For the cauliflower-like surface of a-Si:H, the results is a net diffusion towards the valleys, even when the separation between the valleys is much larger than the surface diffusion length $\zeta_0$. Therefore, the microscopic mechanism of $-\alpha_0 V^2(\vec{\nabla}h)^2$ seems to be quite similar to that the suggested microscopic mechanism for surface relaxation during a-Si:H film growth within the universality class RDR (Sec. III). Raible et al. have tested the influence of the conserved KPZ nonlinearity $-\alpha_0 V^2(\vec{\nabla}h)^2$ from one and two-dimensional simulations. When simulating the linear, deterministic growth equation [Eq. (3)], they also observed that the unstable modes $>\lambda_c$ continue to grow exponentially with increasing bulk thickness and that the surface is getting increasingly dominated by the most unstable mode $\lambda_c$ until only this mode exists on the surface. However, when the conserved KPZ nonlinearity was included in the simulations, they found that the conserved KPZ nonlinearity is able to level off this exponential surface roughness increase. This occurs even when the deposition noise $\eta(x,t)$ is also included in the simulations. Moreover, the simulations of Raible et al. also show that the conserved KPZ nonlinearity sets in at a fixed surface roughness instead of a fixed deposition time or bulk thickness.

The question of course remains, whether the RLH growth equation [Eq. (1)] that includes the conserved KPZ nonlinearity is able to yield the very low values of the roughness exponent $\alpha$ and the growth exponent $\beta$ during the stable growth phase and the trend of $\alpha$ and $\beta$ with $T_{\text{sub}}$ (Fig. 6). In Sec. II, this data of $\alpha$ and $\beta$ has been qualitatively explained in Sec. III by the onset surface relaxation. Unfortunately, an exact solution of the values of the scaling parameters $\alpha$, $\beta$, and $z$ in the long-time, long-scale asymptotic limit is not known for the RLH growth equation. However, a case will be made that the RLH growth equation may indeed yield these low values of $\alpha$ and $\beta$.

Let us first analyze the individual smoothening terms of the RLH equation under the influence of the deposition noise, starting with the surface diffusion:
\[
\frac{\partial h}{\partial t} = -\kappa \nabla^4 h + \eta(x,t). 
\]  
(6)

For the case that the growing surface is self-affine, the values of \( \alpha \) and \( \beta \) in the long-time, long-scale asymptotic limit of Eq. (6) can be obtained exactly by applying the scaling approach, explained in Ref. 7: a self-affine growing surface should be invariant under the transformation of \( x \rightarrow bx \), \( h \rightarrow b^\alpha h \), and \( t \rightarrow b^{1-z}t \) with \( z = \alpha/\beta \). As a result of the transformation, the terms \( \partial_t h \) and \( \nabla^4 h \), which have the dimension of \([\text{height/time}]\) and \([\text{height/length}^4]\), respectively, transform to \( b^{1-z-\alpha} \partial_t h \) and \( b^{4-2z} \nabla^4 h \), while it can be shown that \( \eta(x,t) \) transforms to \( b^{-z/2} \eta(x,t) \) for a two-dimensional surface, yielding:

\[
\frac{\partial h}{\partial t} = -b^{-z} b^{4-2z} \kappa \nabla^4 h + b^{4-z} \eta(x,t).
\]  
(7)

Equation (7) can only be equal to Eq. (6) when both exponents of \( b \) equal zero, i.e. \( z = 4 \), \( \alpha = 1 \), and \( \beta = 1/4 \). As these values are equal within uncertainty limits to the ones of the universality class "random deposition with surface diffusion", RDD is generally believed to be described by Eq. (6).\textsuperscript{7,23,25} In the same way, the values of \( \alpha \) and \( \beta \) of the conserved KPZ nonlinearity\textsuperscript{21} can be estimated from the transformation:

\[
\frac{\partial h}{\partial t} = -\omega \nabla^2 (\tilde{h})^2 + \eta(x,t) \rightarrow \frac{\partial h}{\partial t} = -b^{2-\alpha} \omega \nabla^2 (\tilde{h})^2 + b^{2-\alpha} \eta(x,t)
\]  
(8)

yielding \( z + \alpha = 4 \) and \( z/2 - \alpha = 1 \) and thus \( z = 10/3 \), \( \alpha = 2/3 \), and \( \beta = 1/5 \). These values of the scaling exponents are fairly close to the ones found in Fig. 6. The fact that these values are lower than the ones found for surface diffusion indicates that the conserved KPZ nonlinearity is a stronger smoothing mechanism in the long-time, long-scale asymptotic limit. In fact, when both smoothing terms are combined, i.e.

\[
\frac{\partial h}{\partial t} = -\nu \nabla^2 h - \omega \nabla^2 (\tilde{h})^2 + \eta(x,t),
\]  
(9)

the values \( z \), \( \alpha \) and \( \beta \) remain \( z = 10/3 \), \( \alpha = 2/3 \), and \( \beta = 1/5 \) in the long-time, long-scale asymptotic limit, as has been deduced with a more complicated method.\textsuperscript{7,26} This is again an indication that there is a transition from the initial growth regime, dominated by surface diffusion, towards the asymptotic limit dominated by the conserved KPZ nonlinearity, in accordance with our RTSE data. To this point, the roughening term \( \nu \nabla^2 h \) with \( \nu < 0 \) has been neglected, but it should of course be added to Eq. (9) to determine the asymptotic behavior of the full RLH growth equation. As mentioned above, an exact solution of \( z \), \( \alpha \) and \( \beta \) is not known for the full RLH growth equation. Therefore, instead of directly investigating the RLH growth equation with conserved KPZ nonlinearity \( -\omega \nabla^2 (\tilde{h})^2 \), insight into the RLH growth equation is obtained by first regarding the unconserved KPZ nonlinearity \( \omega \nabla^2 (\tilde{h})^2 \). For the unconserved KPZ nonlinearity, the scaling approach yields:

\[
\frac{\partial h}{\partial t} = \omega \nabla^2 (\tilde{h})^2 + \eta(x,t) \rightarrow \frac{\partial h}{\partial t} = b^{2-\alpha} \omega \nabla^2 (\tilde{h})^2 + b^{2-\alpha} \eta(x,t)
\]  
(10)

resulting in the scaling exponents \( z = 2 \) and \( \alpha = \beta = 0 \). When the unconserved KPZ nonlinearity is used in the RLH equation instead of the conserved KPZ nonlinearity, the stochastic version of the Kuramoto-Sivashinsky (SK) equation is obtained:

\[
\frac{\partial h}{\partial t} = \nu \nabla^2 h - \omega \nabla^2 (\tilde{h})^2 - \kappa \nabla^4 h + \eta(x,t) \text{ with } \nu < 0,
\]  
(11)
which has been studied in detail because it is believed to describe the roughness development during sputtering.\textsuperscript{28,35,36,82} For this growth equation, the notable result has been found that the unconserved KPZ nonlinearity $\eta_t(\nabla h)^2$ is capable of balancing the negative Laplacian term such that the effective scaling behavior in the long-time, long-scale asymptotic limit corresponds to a pseudo Edward-Wilkinson scaling behavior. In other words, the effective scaling behavior of Eq. (11) in the asymptotic limit exhibits the same scaling behavior as the Edward-Wilkinson equation $\partial_t h = \nabla^2 h + \eta(x,t)$ with positive $\nu$, i.e. $z = 2$ and $\alpha = \beta = 0$.\textsuperscript{28,35,36,82} Apparently, the unconserved KPZ nonlinearity $\eta_t(\nabla h)^2$ is able to cancel the roughening effects of the Laplacian term with negative $\nu$.

Whether other nonlinearities, such as the conserved KPZ nonlinearity $-\alpha \nabla^2 (\nabla h)^2$, also possess this quality to reduce or even cancel the roughening effects of the negative Laplacian term in the asymptotic limit is still unresolved in the literature.\textsuperscript{28,42} It seems well possible that the scaling behavior of the RLH growth equation in the asymptotic limit is equal to the one of Eq. (9) with scaling exponents $z = 10/3$, $\alpha = 2/3$ and $\beta = 1/5$, or it could even be equal to the asymptotic EW scaling behavior with $\alpha = \beta = 0$. Such reasoning is supported by the simulations of Raible et al.\textsuperscript{31} that show that the conserved KPZ nonlinearity is able to stabilize the long, unstable wavelengths $>\lambda_c$. Moreover, the SK and RLH equation also show a similar behavior with respect to the onset, at which the non-linear term becomes the dominant term governing the surface roughness development. This onset of the asymptotic scaling behavior occurs at a fixed surface roughness of $\sim 5 - 10$ Å for both the SK and RLH equation.\textsuperscript{32,33} Furthermore, the addition of the conserved KPZ nonlinearity in the RLH equation was found necessary to explain the saturation of the surface roughness during physical vapor deposition of ZrAlCu films.\textsuperscript{33} In all, it has been made plausible that the RLH growth equation with its conserved KPZ nonlinearity is a promising candidate to yield the very low values $\alpha < 0.5$ and $\beta = 0.05$ for $T_{\text{sub}} \geq 350$ °C and, more generally, to describe the "stable growth phase" of a-Si:H film growth.

In order to explain the substrate temperature dependence of the values of $\alpha$ and $\beta$ in Fig. 6, it was suggested in Sec. III that the surface diffusion and surface relaxation mechanisms during a-Si:H film growth are temperature-activated processes. This is in contrast to the universality classes that only include a single smoothening mechanism that is assumed to be instantaneous, i.e. having an infinite temperature and a fixed value of $\alpha$ and $\beta$. This perspective of a temperature-activated surface diffusion and surface relaxation can be extended in a natural way to the RLH growth equation by allowing the prefactors of the surface diffusion term $-\kappa \nabla^2 h(x)$ and the conserved KPZ nonlinearity $-\alpha \nabla^2 (\nabla h)^2$ to be temperature-dependent. From the linear, deterministic simulations, it was already seen that the prefactor $\kappa$ is directly related to the temperature-dependent critical roughness wavelength $\lambda_c$ through $\kappa = v \lambda_c^2 / 2 \pi$, where $\lambda_c$ is closely related to the temperature-dependent surface diffusion length $\zeta_p$. There is also no reason, why the prefactor $\alpha_0$ of the conserved KPZ nonlinearity $-\alpha_0 \nabla^2 (\nabla h)^2$ should not depend on the temperature. In fact, it was recognized above that the microscopic mechanism of the conserved KPZ nonlinearity may be quite similar to the suggested microscopic mechanism of surface relaxation during a-Si:H film growth (Sec. III). Therefore, $\alpha_0$ may well have a similar temperature-dependence as the one suggested for surface relaxation, i.e. a monotonic increase of $\alpha_0$ with $T_{\text{sub}}$. If this is the case, the combination of the temperature-dependent $\kappa$ and $\alpha_0$ in the RLH growth equation may explain the trends of $\alpha$ and $\beta$ with $T_{\text{sub}}$ (Fig. 6) in a similar way as the temperature-activated surface diffusion and surface relaxation mechanisms. That is to say, the trends of $\alpha$ and $\beta$ with $T_{\text{sub}}$ may be explained by the same two possible explanations that have been proposed in Sec. III: the monotonic decrease of $\beta$ with increasing $T_{\text{sub}}$ is either explained by the increase of effectiveness of surface relaxation with increasing $T_{\text{sub}}$ or by the gradual cross-over from surface diffusion as the governing smoothening mechanism at low $T_{\text{sub}}$ to surface relaxation at high $T_{\text{sub}}$. Some additional support for the second explanation comes from the values of the dynamic exponent $z = \alpha / \beta$ (Fig. 6), which is roughly equal to $-4$ for low $T_{\text{sub}}$ in close correspondence with surface diffusion (RDD), while $z$ increases
towards \( z = 6-8 \) for \( T_{\text{sub}} \geq 250 ^\circ \text{C} \) indicating a cross-over to another governing smoothening mechanism. The value of \( z = 6-8 \) has not yet been resolved, but might be associated to the RLH equation with pseudo EW scaling behavior in the asymptotic limit or might be a consequence of the temperature-activated surface smoothening mechanisms.

V. IMPLICATIONS FOR A-Si:H GROWTH

It was seen in Sec. III that the smoothening rates for \( T_{\text{sub}} > 150 \) \(^\circ\)C after the moment of island coalescence are relatively low (Figs. 3 and 5). As a consequence, the simulations of the linear, deterministic limit of the RLH growth equation [Eq. (3)] in Sec. IV yielded low values of the critical roughness wavelength \( \lambda_c \) of \( \lambda_c \approx 30 \) Å (Table 1). In this section, the critical roughness wavelength \( \lambda_c \), its relation with the surface diffusion length \( \zeta_0 \), and the resulting implications for the surface diffusion mechanism during a-Si:H film growth are discussed.

In their analysis of Eq. (3), Mazor et al.\(^{69,70}\) assign \( \lambda_c \) tentatively to the surface diffusion length \( \zeta_0 \) based on the fact that the roughness wavelengths \( \approx \lambda_c \) are damped due to surface diffusion, while all wavelengths \( > \lambda_c \) are unstable and grow exponentially. When this assumption of \( \zeta_0 = \lambda_c \) is applied to our a-Si:H film growth, it would mean that the surface diffusion length \( \zeta_0 \) is equal to \( \lambda_c \approx 30 \) Å (Table 1). This is lower than expected. In fact, the typical rate of surface smoothening and the typical values of \( d_{\text{coal}} \) and \( d_{\text{dip}} \) found by the group of Collins\(^{8-14}\) for a variety of PECVD a-Si:H depositions on a native-oxide-covered c-Si substrate for substrate temperatures in the range of \( T_{\text{sub}} = 200-260 \) \(^\circ\)C are very similar to our values in Figs. 3 and 5. Therefore, when simulations of the same linear, deterministic limit of the RLH growth equation Eq. (3) would be applied to the surface roughness evolution of these depositions, this procedure would yield values of the surface diffusion length \( \zeta_0 \) that are also roughly equal to \( \lambda_c \approx 30 \) Å and approximately independent of the conditions used. A surface diffusion length \( \zeta_0 \) during a-Si:H film growth of \( \approx 30 \) Å is much lower than expected from alternative, more direct measurements of \( \zeta_0 \) by Collins and Yang\(^{6}\) and Gerbi and Abelson.\(^{62}\) Both groups deposited (high-quality) a-Si:H under regular operating conditions on an intentionally rough substrate with a measured dominant wavelength of \( \approx 70 \) and \( \approx 80 \) Å, respectively, and found that the initial roughness remarkably smoothed out. This implies that the surface diffusion length \( \zeta_0 \) must be (much) larger than \( \zeta_0 \approx 70-80 \) Å for the deposition conditions used, but most likely also for regular a-Si:H deposition conditions in general. The combination of a surface diffusion length that is (much) larger than \( \zeta_0 \approx 70-80 \) Å and a general value of \( \lambda_c \approx 30 \) Å is in contradiction with the assumption of \( \zeta_0 = \lambda_c \) and therefore it is concluded that \( \zeta_0 \) is not equal to \( \lambda_c \) for a-Si:H film growth. This conclusion is corroborated by the fact that the best fit value of \( \lambda_c \) of \( T_{\text{sub}} = 70 ^\circ\text{C} \) is higher than of \( T_{\text{sub}} = 450 ^\circ\text{C} \) (Table 1), while clearly the surface diffusion mechanism is more effective at \( T_{\text{sub}} = 450 ^\circ\text{C} \). Apparently, although the early stages of a-Si:H film growth are well described by the linear, deterministic limit of the RLH growth equation [Eq. (3)], the relation between \( \lambda_c \) and \( \zeta_0 \) is more complex than \( \zeta_0 = \lambda_c \) and, therefore, this relation is investigated in more detail next.

The surface diffusion term \(-\nabla \mu \cdot \overrightarrow{h}\) is a mathematical description deduced for a one-element system, in which an adatom seeks the local minimum chemical potential \( \mu(\mathbf{x},t) \) that depends on the curvature of the surface, i.e. \( \mu(\mathbf{x},t) \propto -\nabla^2 \mu \).\(^{77,78}\) As a consequence, an adatom that has its impact on the surface at a distance from a valley that is within the range of the surface diffusion length will always reach the position of minimum chemical potential in the valley, where it contributes to film growth. As mentioned above, for our a-Si:H depositions at \( T_{\text{sub}} \geq 250 ^\circ\text{C} \), the rate of surface smoothening is relatively slow. In practical terms, a slow surface smoothening rate implies that the number of sticking events is only slightly higher in a surface
valley than on a surface top. However, for the a-Si:H depositions of $T_{\text{sub}} \geq 250 \, ^\circ\text{C}$, it was argued in Sec. III that the surface diffusion length must be much larger than the distance between the valleys, i.e. $\zeta_0 > \lambda_{\text{isl}}$. The combination of the condition of $\zeta_0 > \lambda_{\text{isl}}$ with a sticking frequency that is only slightly enhanced in the valleys can only be explained when sticking events can not take place on any surface site (as is basically assumed for a one-element system), but can only take place on active surface sites. For a-Si:H, this seems to be a consequence of the fact that the a-Si:H surface is (almost) completely terminated with hydrogen, while a-Si:H growth is generally believed to take place at the few open surface bonds, the so-called 'dangling bonds', because these are the most reactive sites on the surface.\textsuperscript{41,42} Therefore, a slow surface smoothening rate can be explained with a distribution of dangling bonds on the surface that is only slightly higher in a surface valleys than on a surface tops. Such a distribution may be generated by a slightly preferential creation rate of dangling bonds in the valleys or by random creation of dangling bonds on the surface followed by a (relatively slow) surface diffusion of the dangling bonds towards the valleys. It is noted that both generation mechanisms seem to be compatible with the two creation mechanisms of surface dangling bonds on the a-Si:H surface that are most-often reported in the literature.\textsuperscript{41,42,64} i.e. the creation of a dangling bond via the abstraction of a surface H by a SiH\textsubscript{3} radical that is diffusing over the a-Si:H surface and the creation of a dangling bond via a direct abstraction of a surface H from a SiH\textsubscript{3} radical from the gas phase in an Eley-Rideal type of reaction. Irrespective of the precise mechanism, a distribution of dangling bonds that is only slightly enhanced in the valleys can explain the observed trends in the surface roughness evolution in Fig. 5 based on the following two-species surface diffusion picture of a-Si:H: a growth precursor lands on the a-Si:H surface, diffuses over the surface until it finds a dangling bond to contribute to film growth, where the distribution of dangling bond can be assumed static compared to the fast surface diffusion of the adatoms. In this picture, the surface diffusion length of the adatoms may be much larger than the distance between the valleys, i.e. $\zeta_0 > \lambda_{\text{isl}}$, which would lead to an even distribution of adatoms on the surface. Only in the case of such an even distribution of adatoms, the rate of surface smoothening is solely determined by the surface distribution of dangling bonds and is independent of $\zeta_0$. This may be the case for $T_{\text{sub}} \geq 250 \, ^\circ\text{C}$, which would explain the equal surface smoothening rate observed (for these substrate temperatures a surface diffusion length of $\zeta_0 > \lambda_{\text{isl}}$ was estimated in Sec. III). When the surface diffusion length decreases and the condition of $\zeta_0 > \lambda_{\text{isl}}$ is no longer met (for $T_{\text{sub}} < 250 \, ^\circ\text{C}$), then the faster depletion of adatoms in the valleys can no longer be sufficiently regenerated, leading to a lower surface density of adatoms in the valleys and, consequently, resulting in a decrease in the surface smoothening rate. (Eventually, for negligible surface diffusion length, random growth occurs, even when the density of dangling bonds is much higher in the valleys.) This explains the much lower or even absent surface smoothening rate for $T_{\text{sub}} = 150 \, ^\circ\text{C}$ and 70 \, ^\circ\text{C}. Therefore, within this two-species surface diffusion picture for a-Si:H growth, a roughness wavelength $\lambda_c$ is only stable when the condition of $\zeta_0 > \lambda_{\text{isl}}$ is met. As a consequence, for all roughness wavelengths shorter than the critical roughness wavelength $\lambda_c$, the condition of $\zeta_0 > \lambda_{\text{isl}}$ is met, while for all wavelength >$\lambda_{\text{isl}}$, this condition is not met. Within this two-species surface diffusion picture for a-Si:H growth, the critical roughness wavelength $\lambda_c$ itself is, by definition, also (much) smaller than $\zeta_0$, but does scale with $\zeta_0$. In that case, the increase of the delay of the $a$-Si $\rightarrow$ a-Si roughening transition and subsequent roughening phase for substrate temperatures in the order of 450, 350 and 250 \, ^\circ\text{C} (Fig. 5) corresponds to an increase in $\lambda_c$ and thus to an increase in $\zeta_0$. This would mean that the delay of the onset of the roughening phase is a \textit{qualitative} measure for the surface diffusion length $\zeta_0$. Moreover, for the case of a $T_{\text{sub}}$-independent surface smoothening rate as observed for $T_{\text{sub}} \geq 250 \, ^\circ\text{C}$ in Fig. 5, the delay of the onset of the roughening phase scales directly to the depth of the dip $\Delta d$, and the postponement of the $d_{\text{ad},\text{tot}}$. This would therefore mean that the value of $\Delta d$ and $d_{\text{ad},\text{tot}}$ are also qualitative measures for the surface diffusion length. All these findings are in perfect agreement with the findings in Sec. III, which gives additional support that the two-species surface diffusion picture in which the growth precursor can only contribute to film growth at an active surface site could be well be valid.
VI. GENERAL CONCLUSIONS

A first extensive investigation of the substrate temperature dependence of the surface roughness evolution has been conducted to study the surface processes during a-Si:H film growth, such as initial film growth, surface roughening and smoothening, and surface diffusion mechanisms. To this end, purely amorphous films have been deposited from undiluted silane by HWCVD for substrate temperatures in the range of $T_{\text{sub}} = 70 - 450 ^\circ \text{C}$. The surface roughness layer thickness has been monitored in time by real-time spectroscopic ellipsometry (RTSE) using the same RTSE analysis approach as used by Collins and co-workers.\textsuperscript{9} After the nucleation, the surface smoothen for the case of $T_{\text{sub}} > 150 ^\circ \text{C}$. This surface smoothening continues up to the a-Si $\rightarrow$ a-Si roughening transition, which occurs at a bulk layer thickness in the range of 9-15 nm with the optimum of ~15 nm at 250 °C. The surface roughness increases rapidly after the a-Si $\rightarrow$ a-Si roughening transition, but levels off at the onset of the stable growth phase. In general, our results at 250 °C are in excellent agreement with previous work, e.g., by Collins et al.\textsuperscript{9} on RF-PECVD deposited a-Si:H. In addition, analysis of the so-called “stable growth phase” by RTSE and ex-situ AFM demonstrates a self-affine growth in good agreement with previous results on a-Si:H growth by, e.g., Smets et al.\textsuperscript{5}

Our temperature dependence studies, however, have revealed some new insights into the growth mechanism of a-Si:H. First of all, the initial roughness of the islands was found to be close approximation independent of the substrate temperature and other experimental settings indicating a nucleation behavior that is fully determined by the substrate. A detailed analysis of the surface roughness evolution after nucleation, based on qualitative arguments as well as on a stochastic growth equation, yield essentially the same conclusions: the minimum in the surface roughness at the a-Si $\rightarrow$ a-Si roughening transition is explained by the competition between the decrease of the nucleation-induced, short roughness wavelengths due to surface diffusion and the exponential increase of unstable roughness wavelengths that are longer than the surface diffusion length. The position of this minimum and its substrate temperature dependence have been completely explained by the substrate temperature dependence of the surface diffusion length, thereby clarifying an empirical correlation found earlier by Collins and co-workers.\textsuperscript{8,13} In addition, a quantitative analysis of the surface roughness evolution in the framework of the stochastic growth equation suggests that the usual mono-radical surface diffusion picture of surface smoothening needs to be replaced, for example, by a two-species surface diffusion picture in which the growth precursor can only contribute to film growth at active surface sites. This two-species picture contains the possibility that both the growth precursor and the active surface site diffuse.

Analysis based on the concept of dynamic scaling also suggests a novel interpretation of the stable growth phase. The monotonic decrease of the growth exponent $\beta$ with increasing $T_{\text{sub}}$ and the low values of the roughness exponents $\alpha$ may be explained either by the increase of effectiveness of the surface relaxation mechanism with increasing $T_{\text{sub}}$ or by the gradual cross-over from surface diffusion as the governing smoothening mechanism at low $T_{\text{sub}}$ to surface relaxation at high $T_{\text{sub}}$. The same results can be obtained from the stochastic growth equation that includes a conserved non-linear term that seems able to explain the stabilization of the long, unstable roughness wavelengths. We conjecture that this conserved non-linear term rules the surface smoothening, resulting in a pseudo Edward-Wilkinson scaling behavior in the high temperature limit.
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A NOVEL DIAGNOSTIC APPROACH FOR STUDYING SILICON THIN FILM GROWTH

SUMMARY

In the deposition of thin films, the material properties are formed through the interaction of gas phase species with the growing surface. The resulting surface kinetics and chemistry is determined by the reactivity of the different gas phase species as well as by the surface chemical nature and may involve physical and chemical mechanisms such as surface bombardment by energetic gas phase species and surface diffusion mechanisms. Therefore, to obtain a fundamental understanding of the growth process of thin films, these various aspects need to be studied by dedicated experiments, which are preferably carried out non-intrusively and in real-time during the deposition. The work in this thesis focuses on several of such dedicated experiments for the specific case that film growth takes place by reactive gas phase species, as for example created with a plasma or a hot filament. Three all-optical and real-time diagnostic techniques have been designed and implemented and they have been employed for the specific deposition system of hydrogenated amorphous silicon (a-Si:H), which has an exemplary role in the deposition of silicon-based films and other covalent systems. Two of the diagnostic techniques are based on the ultra-sensitive cavity ring-down spectroscopy (CRDS) method, which is an established technique for measuring low-density gas phase species: time-resolved CRDS for determining the surface reactivity of gas phase species and evanescent-wave CRDS for probing surface species. Real-time spectroscopic ellipsometry has been employed to investigate surface diffusion mechanisms while, in addition, a new ultrahigh vacuum reactor has been constructed to carry out these and other future dedicated experiments.

The method of time-resolved cavity ring-down spectroscopy (τ-CRDS) has been developed as a direct diagnostic to measure the surface reactivity of (low-density) gas phase species under regular thin film processing conditions. In τ-CRDS, the surface reaction probability $\beta$ of a species is determined from time-resolved measurements of a time-modulated gas phase density in front of the substrate. For a-Si:H deposition in the so-called 'expanding thermal plasma', time-modulation of the gas phase densities was achieved by applying a pulsed rf power to the substrate. The probability for the Si radical to react at the a-Si:H surface was measured to be $0.95 \lesssim \beta_{\text{Si}} \lesssim 1$ at 200 °C, while $\beta$ of SiH$_3$ was found independent of the substrate temperature in the range of 50–450 °C with an averaged value of $\beta_{\text{SiH}_3} = 0.30 \pm 0.03$. Combination of this data with the absolute gas phase densities from CRDS has revealed that SiH$_3$ is the key growth precursor for a-Si:H film growth. These results together with measurements of the a-Si:H growth rate and the surface silicon hydride (SiH$_x$) composition put strict constraints on the surface reactions of SiH$_3$ that govern a-Si:H film growth. The results have therefore been used to discuss the growth mechanism of a-Si:H on the basis of SiH$_3$ surface reactions proposed in the literature.

The novel technique of evanescent-wave cavity ring-down spectroscopy (EW-CRDS) has been developed into a sensitive probe for in-situ and real-time detection of defect-related absorptions in thin films, such as due to dangling bonds. To this end, a monolithic folded optical cavity made of fused-silica
has been carefully designed to provide sufficient sensitivity to detect surface and bulk dangling bonds during a-Si:H film growth. Preliminary ex-situ measurements showed a finesse of the folded cavity of \( \sim 165000 \) at 1200 nm, which easily satisfies the sensitivity requirements. Furthermore, as an initial study to explore the potential of EW-CRDS for probing surface species, the first C-H stretching overtones of three different chloroethylenes adsorbed on the fused silica surface of a folded cavity have been probed in an ex-situ study. This study has demonstrated that EW-CRDS is a generic diagnostic for measuring absolute surface number densities of surface species with sub-monolayer sensitivity, while EW-CRDS can also provide the orientation of the transition moments of the species on the surface.

To carry out such dedicated experiments on surface species and to investigate the reactions of the \( \text{SiH}_3 \) growth precursor at the a-Si:H surface, an ultrahigh vacuum setup has been designed and constructed that allows for surface science-like studies of thin film growth. Key features of the setup are (i) three radical sources to mimic the plasma deposition process by means of well-defined radical beams, (ii) full optical access to the substrate for the real-time optical diagnostics, and (iii) well-defined processing conditions. As a first step for studying the growth of a-Si:H in this new setup, the material properties of a-Si:H films deposited by hot wire CVD have been extensively characterized by real-time spectroscopic ellipsometry (RTSE) and several ex-situ film diagnostics.

Insight into surface diffusion mechanisms during a-Si:H growth has been obtained by monitoring the surface roughness evolution as a function of film thickness with RTSE for substrate temperatures ranging from 70–450 °C. This study has yielded insight into the initial nucleation behavior of a-Si:H, the transition from surface smoothening to roughening, and the surface diffusion processes occurring on small and large lateral length scales. In addition, the description of the roughness evolution in terms of a generic nonlinear stochastic growth equation has been discussed as well as the consequences of the results for the atomistic surface reactions with regard to surface diffusing growth precursors and growth sites.
SAMENVATTING

In de depositie van dunne films worden de filmeigenschappen gevormd door de interactie van gasfasedeeltjes met het aangroeiende oppervlak. De resulterende oppervlakkinetiek en -chemie wordt bepaald door de reactiviteit van de verschillende gasfasedeeltjes alsmede door de chemische aard van het oppervlak en kan fysische en chemische mechanismen omvatten zoals oppervlakkettenbombardelement door energetische gasfasedeeltjes en oppervlakteverspringmechanismen. Om fundamentele kennis over het aangroeiproces van dunne films te vergaren, dienen die reden de verschillende aspecten te worden bestudeerd in gerichte experimenten, die bij voorkeur worden uitgevoerd op een niet-verstorende en directe wijze tijdens de depositie. Het werk in dit proefschrift concentreert zich op een aantal van zulke gerichte experimenten voor het specifieke geval dat de filmangroei plaatsvindt door reactieve gasfasedeeltjes, zoals bijvoorbeeld gecreëerd met een plasma of een heet filament. Drie geheel-optische en directe diagnostieken zijn ontworpen en geïmplementeerd en ze zijn toegepast op het specifieke depositiesysteem van gehydrogeeneerd amorf silicium (a-Si:H), dat een voorbeeldfunctie heeft voor de depositie van siliciumhoudende films en andere covalente systemen. Twee van deze diagnostieken zijn gebaseerd op de ultragevoelige "cavity ring-down" spectroscopie (CRDS) methode, welke een bewezen techniek is voor het meten van gasfasedeeltjes met een lage dichtheid: tijdsopgeloste CRDS voor het bepalen van de oppervlakteverspringreactiviteit van gasfasedeeltjes en "evanescent-wave" CRDS voor het bemonsteren van deeltjes en chemische bindingen aan het oppervlak. Spectroscopische ellipsometrie is toegepast tijdens de filmangroei om oppervlakteverspringmechanismen te onderzoeken en daarnaast is er een ultrahoog vacuümopstelling geconstrueerd om deze en andere toekomstige experimenten uit te voeren.

De methode van tijdsopgeloste "cavity ring-down" spectroscopie (t-CRDS) is geïntroduceerd als een directe diagnostiek om de oppervlakteverspringreactiviteit van gasfase deeltjes (met lage dichtheid) te meten onder reguliere depositiecondities. In t-CRDS wordt de oppervlakteverspringkans β van een deeltje bepaald uit tijdsopgeloste metingen van een tijdsgemoduleerde gasfasedichtheid voor het substraat. Voor a-Si:H depositie in het zogenaamde expanderende thermische plasma is de modulatie van de gasfasedichtheden in de tijd bewerkstelligd door het aanbrengen van een gepulst rf vermogen op het substraat. De gemeten kans voor het Si radicaal om te reageren met het a-Si:H oppervlak is 0.95 < β_{Si} < 1, terwijl aangetoond is dat β van SiH₃ onafhankelijk is van de substraattemperatuur in het bereik van 50–450 °C met een gemiddelde waarde van β_{SiH₃}=0.30±0.03. Combinatie van deze data met de absolute gasfasedichtheden, bepaald met CRDS, heeft duidelijk gemaakt dat SiH₃ de belangrijkste precursor is voor dunne filmangroei van a-Si:H. Deze resultaten, samen met metingen van de aangroei snelheid van a-Si:H en de oppervlaktecompositie van silicium-waterstofbindingen (SiH₄), leggen strikte randvoorwaarden op aan de mogelijke oppervlakteverspringreacties van SiH₃ die bepalend zijn voor de dunne filmangroei van a-Si:H. De resultaten zijn daarom gebruikt om het aangroeimechanisme van a-Si:H te bediscussiëren op basis van de oppervlakteverspringreacties van SiH₃ die zijn voorgesteld in de literatuur.
De nieuwe "evanescent-wave" CRDS (EW-CRDS) techniek is ontwikkeld tot een gevoelige diagnostiek voor directe en in-situ detectie van defectgerelateerde absorpties in dunne films, zoals ten gevolge van open bindingen (zogenaamde "dangling bonds"). Om dit te bewerkstelligen is op nauwkeurigewijze een monolithische "gevouwen" optische trilholte ontworpen met het doel voldoende gevoeligheid te behalen om dangling bonds aan het oppervlakte en in de film te kunnen detecteren tijdens filmaangroei. Initiële ex-situ metingen hebben een finesse van de gevouwen trilholte van ~165000 bij 1200 nm aangetoond, waarmee deze gemakkelijk voldoet aan de gestelde eisen aan de gevoeligheid. Bovendien zijn, in een initiële studie om de potentie van EW-CRDS voor het detecteren van oppervlakteffecten te onderzoeken, de C-H vibrationele overgangen van drie verschillende chloroethylenen bemonsterd op hun dubbele vibrationele frequentie. In deze ex-situ studie zijn de chloroethylenen geadsorbeerd op het synthetisch kwartsoppervlak van de gevouwen trilholte. Deze studie heeft aangetoond dat EW-CRDS een generieke diagnostiek is voor het meten van absolute oppervlakte dichtheden van geadsorbeerde deeltjes met een bezettingsgraad van minder dan een monolaa g. Tevens is aangetoond dat EW-CRDS ook informatie over de oriëntatie van de transitiemomenten van de deeltjes aan het oppervlak kan verschaffen.

Om gerichte experimenten aan oppervlakteeffecten uit te voeren en om de reacties van de SiH₃ precursors aan het a-Si:H oppervlak te onderzoeken, is er een ultrahoog vacuümoostelling ontworpen en geconstrueerd die oppervlaktefysica-achtige experimenten van dunne filmaangroei mogelijk maakt. De voornaamste kenmerken van de opstelling zijn (i) drie radicaalbronnen om het plasmadepositieproces na te bootsen met goedgedefinieerde radicaalbundels, (ii) volledige optische toegang tot het substraat voor de optische diagnostieken die toegepast kunnen worden tijdens de aangroei van de dunne films, en (iii) goedgedefinieerde depositiecondities. Als eerste stap voor het bestuderen van het a-Si:H aangroeiproces in de nieuwe opstelling, zijn er a-Si:H films gedeponemd met een heet filament en zijn de materiaaleigenschappen van de films uitgebreid gekarakteriseerd met tijdsopgeloste spectroscopische ellipsometrie en verschillende ex-situ diagnostieken.

Inzicht in oppervlakte.diffusiemechanismen tijdens de aangroei van a-Si:H is verworven door het monitoren van de evolutie van de oppervlaktruwheid als een functie van de film dikte met spectroscopische ellipsometrie voor substraattemperaturen in het bereik van 70–450 °C. Deze studie heeft inzichten opgeleverd in het initiële nucleatiegedrag van a-Si:H, de overgang van oppervlaktevervlakkings naar -verruwing, en de oppervlakte diffusieprocessen die op kleine en grote laterale lengteschaal actief zijn. Daarnaast is de beschrijving van de evolutie van de ruwheid in termen van een generieke niet-lineaire stochastische aangroeivergelijking bediscussieerd, alsmede de consequenties van de resultaten voor de atomaire oppervlakte reacties met betrekking tot over het oppervlak diffunderende precursors en reactieve aangroeiplaatsen.
LIST OF PUBLICATIONS RELATED TO THIS WORK

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