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Time-resolved cavity ringdown study of the Si and SiH₃ surface reaction probability during plasma deposition of *a*-Si:H at different substrate temperatures

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Time-resolved cavity ringdown spectroscopy (τ -CRDS) has been applied to determine the surface reaction probability β 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 β is discussed in detail. It is shown that Si is mainly lost in the gas phase to SiH₄ [reaction rate $k_r = (3.0 \pm 0.6) \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$], while the probability for Si to react at an *a*-Si:H surface is $0.95 < \beta_{\text{Si}} < 1$ for a substrate temperature of 200°C. SiH₃ is only lost in reactions with the surface and measurements of β of SiH₃ for substrate temperatures in the range of 50–450°C show that $\beta_{\text{SiH}_3} = (0.30 \pm 0.03)$, 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 sciencelike 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 conformality of deposition profiles obtained both experimentally and by simulation.^{5–11} However, this procedure in which films were deposited in trenches and cavitylike structures yields only a value of the surface reactivity averaged overall 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,^{12–18} 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 ringdown 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 (τ -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 τ -CRDS directly measures ab-

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sorptions, it also yields information on the (line-integrated) absolute density of the species observed without the need for an elaborate calibration procedure.

In this paper, we will discuss the determination of the loss rates of silane (SiH_4) radicals (Si and SiH_3) from the time evolution of the radical densities as obtained with τ -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 τ -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 SiH_4 -based plasma used for the deposition of hydrogenated amorphous silicon ($a\text{-Si:H}$). This system is ideally suited for such a study, as in the literature, extensive experimental and theoretical effort has been put into elucidating the $a\text{-Si:H}$ growth process. Nonetheless, as addressed in the following section, some important issues have not yet fully been established. This paper 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_3 radical.

The paper is structured as follows: Sec. II summarizes the previous work performed on the surface reaction probability of the different silane radicals on an $a\text{-Si:H}$ 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 SiH_3 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 $a\text{-Si:H}$ 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 $a\text{-Si:H}$ from SiH_4 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.^{28,29} The work was pioneered almost two decades ago by Gallagher, Matsuda, and Perrin.^{6,7,10,30,31} They constructed a first growth model of $a\text{-Si:H}$ with several possible surface reactions of the SiH_3 radical, based on indications that SiH_3 has the highest density of all reactive species in the SiH_4 plasma.^{32,33} The model was derived primarily from measurements of the deposition rate and the overall surface reactivity for changing substrate temperature⁶ and doping gas concentration,⁷ 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 SiH_3 , will react at the surface. Two classes of surface reactions were identi-

fied: 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 $\beta = s + \gamma$. An example of a sticking reaction that was included in the growth model is the adsorption of SiH_3 on a surface dangling bond, while examples of recombination reactions are the abstraction of a surface H by a surface SiH_3 creating a volatile SiH_4 and the recombination of two surface SiH_3 radicals forming a volatile disilane (Si_2H_6) molecule. This preliminary growth model has been fruitful and has contributed greatly to the understanding of $a\text{-Si:H}$ growth.

Following on this early work, more dedicated experiments of the silane radical densities have demonstrated that SiH_3 has indeed the highest plasma density,^{34–36} 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 mentioned in Sec. I, revealing β values of $\sim 0.2\text{--}0.3$,^{6,8,10–13,20,25} ~ 0.6 ,¹⁶ and ~ 0.95 (Ref. 2–4) for SiH_3 , SiH_2 , and SiH , respectively. Combining the β values for all plasma species with their densities has yielded that SiH_3 is the dominant precursor for device quality $a\text{-Si:H}$ film growth under most conditions. The values of β have also enabled sophisticated numerical models of SiH_4 plasmas that emphasize on $a\text{-Si:H}$ deposition.^{37–39} McCurdy *et al.* have measured the dependence of β of SiH on the substrate temperature,² 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 β 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^{40–44} and molecular dynamics simulations,^{41,45–48} which address the surface reactions at the atomistic scale. For SiH_3 , only indirect information is available about the dependence of β on the substrate temperature from the early study of Matsuda *et al.*⁶ This study, though, suffers from the uncertainty that the measured β values are averaged overall plasma species.⁸ On the other hand, all direct measurements of β_{SiH_3} have been obtained for a single substrate temperature^{12,20} and these data are insufficient to conclude on a consistent set of β values of SiH_3 for different substrate temperatures. Considering the fact that SiH_3 is the key precursor for deposition of $a\text{-Si:H}$, however, accurate information on the substrate temperature dependence of β_{SiH_3} is vital for obtaining detailed insight into the SiH_3 surface reactions. Another issue is the surface reaction probability of Si . β of Si is generally regarded to be unity,^{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 $a\text{-Si:H}$; however, under certain conditions, such as hot wire chemical vapor deposition and reactive magnetron sputter deposition of $a\text{-Si:H}$ as well as plasma deposition of $\mu\text{c-Si:H}$ under high H_2 dilution, the role of Si seems to be significant.^{28,50–52}

As outlined in the Introduction, these open issues for

SiH_3 and Si will be addressed in this paper and will be used to demonstrate the strength of τ -CRDS for measuring surface reaction probabilities. In this respect, it is interesting to note that (ground state) SiH_3 radicals cannot be detected by laser-induced fluorescence spectroscopy (the first electronically excited state of SiH_3 is a nonradiative, predissociative state⁵³), whereas SiH_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 transition.

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 β from the time evolution of the radical density after a pulse of rf power (cf. Sec. IV). The theoretical description as derived by Chantry⁵⁴ 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 as⁵⁴

$$\frac{dn}{dt} = P - \frac{n}{\tau}, \quad (1)$$

where P is the volume production term and n/τ is the volume loss term with τ the loss time of the radical, corresponding with the loss rate τ^{-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 τ . This loss time τ can incorporate three possible loss channels for the radicals in the plasma: loss due to reactions in the gas phase with loss time τ_{gas} , loss at the surface with loss time τ_{surf} , and loss by pumping with loss time τ_{pump} :

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{gas}}} + \frac{1}{\tau_{\text{surf}}} + \frac{1}{\tau_{\text{pump}}}. \quad (2)$$

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

$$\tau_{\text{gas}}^{-1} = k_r n_x, \quad (3)$$

with k_r 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 by⁵⁴

$$\tau_{\text{surf}} = \frac{\Lambda_0^2}{D} + \frac{4l_0(1-\beta/2)}{v} \quad (4)$$

with $v = \sqrt{8k_b T_{\text{gas}}/\pi m}$ the kinetic velocity with Boltzmann constant k_b , mass of the radical m , and gas temperature T_{gas} . The radical's diffusion constant D , assumed position independent, is inversely proportional to the pressure p and has a T_{gas} -dependent prefactor that can be calculated using the Chapman-Enskog diffusion theory including the Lennard-

FIG. 1. Schematic representation of the expanding thermal plasma (ETP) setup used for plasma deposition of a -Si:H. For the τ -CRDS measurements, the setup has been equipped with a cavity ringdown spectroscopy setup including a TUEdACS data acquisition system, a rf power supply and delay generator for application of pulsed rf power to the substrate, and an additional delay generator for synchronization of the laser shots to the pulses of rf power.

Jones parameters.⁵⁵ The diffusion geometry in Eq. (4) is accounted for by the “geometrical” diffusion length Λ_0 and the volume-to-area ratio of the diffusion volume l_0 . The parameters Λ_0 and l_0 can be expressed in terms of the radius R and height H of the cylindrical diffusion volume:

$$\Lambda_0^2 = \left[\left(\frac{\pi}{H} \right)^2 + \left(\frac{2.405}{R} \right)^2 \right]^{-1} \quad (5a)$$

and

$$l_0 = \frac{HR}{2(H+R)}. \quad (5b)$$

Combining Eqs. (4) and (5), β can be calculated from τ_{surf} , when H , R , and T_{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 ringdown 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 and 0.54 mbar, corresponding to a residence time in the reactor of ~ 0.4 – 2.4 s. At ~ 5 cm 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,^{57,58} for the conditions used in this paper, atomic hydrogen is dominating the dissociation of SiH_4 leading mainly to the creation of SiH_3 radicals. Si and other radicals are also produced, but at a much lower rate, leading to a much lower density.⁴⁹ The SiH_4 plasma flows towards a substrate with an area of $10 \times 10 \text{ cm}^2$, located at 35 cm from the arc exit. For the conditions used in this paper, ion bombardment can be neglected as the low electron temperature leads to a small floating potential of -2 V of the $\alpha\text{-Si:H}$ surface,⁵⁹ while there are indications that the flux of atomic hydrogen towards the substrate is relatively low compared to the flux of the silane radicals.⁶⁰ The substrate temperature can be accurately controlled from room temperature to 450°C . Heating of the substrate by the plasma is reduced to less than 15°C from its starting temperature⁶¹ due to good thermal contact between the substrate and the substrate holder by means of a small helium back flow.

B. Cavity ringdown spectroscopy

An optical cavity with a cavity length of 108 cm is created using two highly reflective mirrors (reflectivity $R \approx 0.99$ at 251 nm), positioned on either side of the plasma reactor (Fig. 1). The cavity is aligned at an axial position of $\sim 5 \text{ mm}$ 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 (YAG—yttrium aluminum garnet) 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 $\sim 502 \text{ nm}$ that are frequency doubled by a beta-barium borate crystal to $\sim 251 \text{ nm}$ with a linewidth of $\sim 1.0 \text{ pm}$. The dye laser is temperature stabilized within 0.1°C to consistently control the wavelength within $\sim 0.2 \text{ pm}$. 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.

FIG. 2. Parts of the SiH_3 absorption spectrum of the $\tilde{A}^2A'_1 \leftarrow \tilde{X}^2A_1$ electronic transition, as measured in the ETP, compared to the normalized absorption spectra as reported by Baklanov and Krasnoperov (see Ref. 64) and Lightfoot *et al.* (see Ref. 65) both given in arbitrary units. Inset: absorption lines of the $4s^3P \leftarrow 3p^2^3P$ transition of Si around 251 nm, superimposed on the broadband SiH_3 spectrum (dashed line).

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.^{35,49,60} SiH_3 has been measured at the $\tilde{A}^2A'_1 \leftarrow \tilde{X}^2A_1$ transition, which yields a broadband featureless absorption spectrum ranging from ~ 200 to $\sim 260 \text{ nm}$,⁵³ as shown in Fig. 2. SiH_3 has unambiguously been identified in our plasma^{35,63} from the good agreement with the normalized absorption spectra of SiH_3 reported by Baklanov and Krasnoperov⁶⁴ and Lightfoot *et al.*⁶⁵ (Fig. 2) as well as from the good agreement with threshold ionization mass spectrometry measurements of SiH_3 .⁶⁰ Si has been measured from the atomic line spectrum of the Si $4s^3P_{0,1,2} \leftarrow 3p^2^3P_{0,1,2}$ transition at $\sim 251 \text{ nm}$,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,⁶⁰ typical densities of SiH_3 (Ref. 35 and 60) and Si (Ref. 49) of $10^{18}\text{--}10^{19} \text{ m}^{-3}$ and $10^{15}\text{--}10^{16} \text{ m}^{-3}$, respectively, have been found in the ETP. In this paper, both Si and SiH_3 are detected around 250.7 nm: Si at the $4s^3P_2 \leftarrow 3p^2^3P_1$ transition at 250.69 nm with peak absorption cross section of $4.17 \times 10^{-17} \text{ m}^2$,⁶⁶ and SiH_3 at the underlying broadband spectrum with an absorption cross section of $\sim 4.9 \times 10^{-22} \text{ m}^2$, as reported recently by Baklanov and Krasnoperov.⁶⁴ This new and more accurate absorption cross section of SiH_3 differs only slightly from the previously used absorption cross section of Lightfoot *et al.*⁶⁵

C. Time-resolved measurements

In a τ -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 W and 100 W 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 net-

FIG. 3. Wavelength scans showing the absorption due to the $\text{Si } 4s^3P_2 \leftarrow 3p^2^3P_1$ transition at 250.69 nm superimposed on the broadband SiH_3 absorption, for two 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.

work, was kept constant at 63 W, unless stated otherwise, while the reflected power was reduced to <0.1 W for all measurements. The dc bias voltage on the substrate, as measured with a high voltage probe, is typically between -50 V and -100 V for the plasma settings used in this paper. 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 $20 \mu\text{s}$ 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 SiH_3 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 SiH_3 (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 SiH_x 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 Δt (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 Δt [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-

FIG. 4. Timing scheme of a τ -CRDS measurement. The 5 Hz, 2.5% duty cycle rf pulses (a) are synchronized to the 10 Hz laser pulses (c). Also shown is a schematic representation of the time-dependent radical density (b) that is modulated by the application of the rf power pulses to the substrate with respect to the steady-state density in the ETP plasma. The additional absorption of the radicals generated by the rf pulses, A_{rf} , is obtained from the difference between an absorption measurement in the afterglow of the rf pulse [measurement (1) at time Δt] and an absorption measurement sufficiently long after the rf pulse [measurement (2)], when the influence of the rf pulse has extinguished.

called “rf-generated absorption,” A_{rf} . To map the time-dependent radical density, A_{rf} is measured as a function of Δt .

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 Δt of a measurement of A_{rf} . Every CRDS transient obtained is processed separately in real time by the TU/eDACS system to suppress low-frequency (<5 Hz) noise sources, and for every Δt , 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 Δt 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 Δt 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 $4s^3P_2 \leftarrow 3p^2^3P_1$ peak and SiH_3 at the underlying broadband $\tilde{A}^2A'_1 \leftarrow \tilde{X}^2A_1$ 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 $\Delta t > 0$ is shown in more detail in the semilogarithmic plot of Fig. 5(b). Figure 5(a) also shows that A_{rf} at 250.69 nm changes

FIG. 5. (a) A typical τ -CRDS measurement of the rf-generated absorption, A_{rf} , as a function of the time Δt for two cases: the wavelength kept constant at 250.69 nm, i.e., resonant to the Si $4s\ ^3P_2 \leftarrow 3p^2\ ^3P_1$ peak, and the wavelength kept constant at 250.68 nm, i.e., off-resonant to the Si peak (see Fig. 3). $\Delta t = 0$ ms is assigned to the moment that the rf pulse is turned off. Within the rf pulse (i.e., at $\Delta t < 0$), the densities of Si and SiH₃ reach a steady-state value. (b) Semilogarithmic plot for $\Delta t > 0$ of the rf-generated absorption of Si, as determined by point-to-point subtraction of the two data sets of Fig. 5(a), and the rf-generated absorption of SiH₃. The lines depict linear least-squares fits of the decay curves and are used to deduce the values of the loss time τ . The ETP plasma settings are an Ar, H₂, and SiH₄ flow of 27.5, 2.5, and 1 SCCS, respectively, a pressure of 0.36 mbar, and an arc current of 22.5 A. The rf settings are a power of 63 W, a dc bias voltage of -65 V, and a duty cycle of 2.5%.

due to a change in the density of Si as well as of SiH₃. 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 SiH₃. 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 Δt . This difference, which is only due to the time evolution of the rf-generated Si radicals, has also been plotted for $\Delta t > 0$ in the semilogarithmic plot of Fig. 5(b).

Figure 5(b) clearly shows that the rf-generated absorption of both Si and SiH₃ 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 SiH₃ presented in this paper, 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 SiH₃, respectively. The decay times are much longer than the time resolution of a CRDS measurement (~ 1 μ s) and the falloff time of the dc bias after switching off the rf power (< 20 μ s). Consequently, it

FIG. 6. (a) The dc bias voltage V_{bias} , (b) the rf-generated SiH₃ density, n_{rf-SiH_3} , at the end of the rf pulse (for $\Delta t < 0$), as calculated assuming a homogeneous radial SiH₃ density profile with a diameter of 30 cm in accordance with Ref. 60, and (c) the loss time τ of SiH₃ as a function of the applied rf power in the pulse. The dashed lines are guides to the eye. For reference, a rf power of 63 W is used in all other τ -CRDS measurements reported in this paper.

is concluded that the decay times as obtained with τ -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, τ_{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 SiH₃ density, n_{rf-SiH_3} , as reached at the end of the rf pulse [Fig. 6(b)], and the loss time of SiH₃, τ_{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 SiH₃ 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_{rf-SiH_3} remains below the steady-state SiH₃ density of 7×10^{18} m⁻³ in the ETP plasma. More importantly, Fig. 6(c) shows that τ_{SiH_3} is independent of the applied rf power up to 77 W. 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 a rf power of 63 W, as used in all further τ -CRDS measurements reported in this paper. 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 τ -CRDS is 6%.

The influence of the rf power has also been investigated from a series of τ -CRDS measurements at 250.68 nm, similar to the one of Fig. 5, for varying duty cycles in the range of 1%–40% (not shown). Most importantly, it was found that the loss time of SiH₃ 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 τ_{SiH_3} . For a duty cycle below $\sim 1.5\%$, the

rf-generated absorption A_{rf} of SiH_3 does not reach steady state in the rf pulse. This leads to a lower A_{rf} at the end of the rf pulse and consequently a lower signal-to-noise ratio in τ_{SiH_3} , when this data of A_{rf} is used to determine the loss time. For rf pulses with a duty cycle above $\sim 5\%$, 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.⁶⁷ 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 τ_{SiH_3} . 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 τ -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 β 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 β 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 literature⁵⁵ 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 , it follows from Eq. (3) that the loss rate of Si and SiH_3 should be linear with the SiH_4 density. The loss rate τ^{-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 $T_{\text{gas}}=1500$ K, as 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,³⁶ 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 $n_{\text{SiH}_4, \text{corr}}=9.0$

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, $n_{\text{Si}, \text{rf}}$, as generated by the rf power; and the loss time of Si, τ_{Si} , are given. From n_{Si} and τ_{Si} , the production rate of Si radicals in the rf plasma, P_{Si} , has been calculated. P_{Si} has been used to determine the local SiH_4 density in front of substrate corrected for SiH_4 consumption in the plasma, $n_{\text{SiH}_4, \text{corr}}$.

SiH_4 flow (SCCS)	$n_{\text{SiH}_4, \text{uncorr}}$ (10^{19} m^{-3})	$n_{\text{Si}, \text{rf}}$ (10^{15} m^{-3})	τ_{Si} (s)	$P_{\text{Si}}=n_{\text{Si}, \text{rf}}/\tau_{\text{Si}}$ ($10^{19} \text{ m}^{-3} \text{ s}^{-1}$)	$n_{\text{SiH}_4, \text{corr}}$ (10^{19} m^{-3})
0.5	2.1	1.8	4.3×10^{-4}	0.4	0.5
1.0	4.2	2.5	1.7×10^{-4}	1.5	1.7
1.5	6.2	2.8	8.3×10^{-5}	3.5	4.1
2.0	8.2	2.5	5.0×10^{-5}	5.0	5.8
2.5	10.0	3.1	3.7×10^{-5}	7.8	9.0

$\times 10^{19} \text{ m}^{-3}$, 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_{Si} , occurs dominantly through electron impact dissociation of SiH_4 with reaction rate $k_{e-\text{SiH}_4}$:

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

The local electron density, n_e , is assumed to be independent of n_{SiH_4} , because the bias voltage is independent of the SiH_4 flow (not shown). Therefore, P_{Si} scales linearly with n_{SiH_4} . Using Eq. (1), the values of P_{Si} have been determined from the Si density at the end of the rf pulse, $n_{\text{Si}, \text{rf}}$, divided by the loss time of Si, τ_{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 $9.0 \times 10^{19} \text{ m}^{-3}$ 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_3 , it is clear that the loss rate is independent of the SiH_4 density and it can be concluded that SiH_3 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 $k_r \leq (4 \pm 2) \times 10^{-20} \text{ m}^3 \text{ s}^{-1}$.⁶⁸ The reproducibility of the loss rates of SiH_3 in Fig. 7 yields again a standard deviation in τ 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

FIG. 7. The loss rate τ^{-1} of Si and SiH_3 as a function of the SiH_4 density 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 SiH_4 density has been calculated from the SiH_4 partial pressure and corrected for the local SiH_4 consumption, as explained in the text. The error bars correspond to the statistical error in the loss time τ .

FIG. 8. The loss time τ 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 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 $\text{Si}(^3P_1)$ with SiH_4 , $k_r = (3.0 \pm 0.6) \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$.⁶⁹ The direct uncertainty in the error-weighted fit of Fig. 7 is 2.5%, however, the error bar in k_r 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 $4s\ ^3P_1 \leftarrow 3p^2\ ^3P_0$ and $4s\ ^3P_2 \leftarrow 3p^2\ ^2P_1$) and it has been found that the loss times of the triplet ground states of Si are equal within their uncertainty, indicating a single value of k_r , in agreement with Ref. 70. The value of k_r corresponds well with the values of k_r in the range of $(2.1\text{--}6.6) \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$ reported in the literature, an overview of which is given in Ref. 70. 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 τ -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 theory⁷¹ presented in Sec. III predicts that τ_{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_{gas} . Moreover, the value of τ_{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_{gas} and the parameter of interest, i.e., the surface reaction probability β . Therefore, to obtain β of SiH_3 , τ_{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_{sub} .

Figure 8 shows the measured values of τ_{SiH_3} as a function of p for the six different T_{sub} . The figure shows clearly that, for each of the six data sets, τ_{SiH_3} depends linearly on p in agreement with the diffusion theory of Sec II. Therefore, each data set of τ_{SiH_3} has been fitted to Eq. (4) in order to

obtain the value of β_{SiH_3} at the corresponding T_{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_{gas} . These values of T_{gas} have been obtained from the Doppler broadening of the Si line profiles and T_{gas} has been found to be 1500 ± 200 K, independent of T_{sub} (cf. Appendix). The fact that T_{gas} is not affected by T_{sub} suggests that the diffusion profile with parameters R and H is also not affected by T_{sub} . Because the slope of τ_{SiH_3} versus p is defined only by the parameters R , H , and T_{gas} , it should also be independent of T_{sub} . As a consequence, the slopes of the six data sets of τ_{SiH_3} should be equal, as is also corroborated by the lack of any correlation between the slopes of the six fits and T_{sub} . Therefore, to increase the accuracy in the fits, the six data sets have been refitted to Eq. (4) with individual offsets, but with one shared slope. These fits are shown in Fig. 8.

The values of τ_{surf} , obtained by extrapolating the fits in Fig. 8 to zero pressure, can now be used to calculate the values of β_{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 calculations⁶⁰ 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 $H = 8$ cm (Ref. 72) has been deduced from the shared slope of the fits, enabling the values of τ_{surf} at zero pressure to be used to calculate β_{SiH_3} . The resulting values of surface reaction probability of SiH_3 , β_{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 β_{SiH_3} as a function of T_{sub} . Furthermore, because β_{SiH_3} is independent of the substrate temperature, the values of β_{SiH_3} in Fig. 9 can be averaged, yielding an averaged β_{SiH_3} of 0.30 ± 0.03 .

In addition to the results of β_{SiH_3} , the value of β_{Si} at $T_{\text{sub}} = 200^\circ\text{C}$ has been obtained from a measurement of the loss time τ of Si as a function of pressure. As Si is lost to SiH_4 in the gas phase with $k_r = (3.0 \pm 0.6) \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$, the measured loss times have first been corrected for gas phase loss to obtain the surface loss rates τ_{surf} . Similar to the case of SiH_3 , the values of τ_{surf} versus p have been fitted to Eq. (4) under the assumption of $R/H \gg 1$, while using the values

FIG. 9. The surface reaction probability β of SiH_3 as a function of the substrate temperature, T_{sub} . The plasma settings are equal to the ones in Fig. 8. The horizontal dashed line depicts the averaged value of β_{SiH_3} of 0.30 ± 0.03 . Previously obtained values of β_{SiH_3} measured in the ETP setup by means of τ -CRDS (see Refs. 25 and 69) and the aperture-well assembly (see Ref. 8) have been added to the figure for comparison.

of ν and D as calculated for the diffusion of Si radicals in the $\text{Ar-H}_2\text{-SiH}_4$ mixture. With the obvious restriction that $\beta_{\text{Si}} \leq 1$, this procedure yields $0.95 < \beta_{\text{Si}} \leq 1$.⁶⁹

Before the implications of these results on β_{SiH_3} and β_{Si} are discussed, first, the uncertainties in the derivation of β are assessed. The error in β_{SiH_3} in Fig. 9 is $\sim 15\%$, corresponding to the statistical error in the offset of the fits in Fig. 8. This error is significantly larger than the errors in τ and p ($\sim 6\%$ and $< 3\%$, respectively) due to the extrapolation to zero pressure. This demonstrates that it is necessary to measure τ within a sufficiently large pressure range in order to obtain accurate values of β . In our particular situation, the error in β has been reduced by almost a factor of 2 by using the fitting procedure of one shared slope, which is possible whenever T_{gas} is independent of T_{sub} . The reproducibility in β_{SiH_3} is illustrated in Fig. 9 by an additional measurement of β_{SiH_3} at $T_{\text{sub}} = 200^\circ\text{C}$, obtained previously under exactly the same experimental conditions.^{25,69} In addition to statistical errors, a number of systematic errors are potentially introduced in the derivation of β , 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,⁵⁴ which introduces a maximum systematic error in β of 3%, as calculated from the error analysis in Ref. 54. The uncertainty of 200 K in the value of T_{gas} of 1500 K also introduces a maximum systematic error in β of 3%. Finally, the assumption of $R/H \gg 1$ yields potentially the largest uncertainty in β , where it is noted that a deviation from this assumption would result in a lower value of β . Although the uncertainty in β due to this assumption is difficult to assess, a decrease in β 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 β_{Si} compared to the case of β_{SiH_3} . Finally, it is noted that the observation in Fig. 9 of a T_{sub} -independent β_{SiH_3} is not affected by any potential systematic error in β_{SiH_3} .

Our values of β are further evaluated by a comparison with values of β reported in the literature that have either

been obtained under similar experimental conditions or by means of a diagnostic that yields β directly. The values of β_{SiH_3} are in perfect agreement with those obtained previously by Kessels *et al.*⁸ for three substrate temperatures using the indirect method of the "aperture-well assembly" under similar conditions in our ETP setup, see Fig. 9. Our β_{SiH_3} values are also in perfect agreement with the value of $\beta_{\text{SiH}_3} = 0.28 \pm 0.03$ at $T_{\text{sub}} = 300^\circ\text{C}$ as determined by Perrin *et al.*¹² by time-resolved threshold ionization mass spectrometry in a rf plasma, in which the SiH_3 density was modulated by turning the rf plasma completely on and off. A somewhat lower value of β_{SiH_3} of 0.15 has been found at room temperature in a rf plasma during plasma deposition of $a\text{-Si:H}$ using infrared laser absorption spectroscopy.²⁰ However, the authors consider their measured value of β_{SiH_3} to be too small, since the spatial density profile of SiH_3 used to obtain β_{SiH_3} is sensitive to the volume production of SiH_3 . In perspective, the different values of β_{SiH_3} correspond surprisingly well considering the difference in diagnostics and in $a\text{-Si:H}$ 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.^{34,49}

D. Implications for $a\text{-Si:H}$ film growth

In this section, our results on β for Si and SiH_3 are discussed with respect to the importance of the various plasma species for $a\text{-Si:H}$ film growth and the key surface reactions ruling the $a\text{-Si:H}$ growth process.

For SiH_3 , a value for β_{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 β_{SiH_3} of $\sim 0.3\text{--}0.4$ reflects the probability that a SiH_3 approaches the surface with its dangling bond oriented towards the surface.¹⁰ For Si, the surface reaction probability has now been measured and a β_{Si} of > 0.95 is found. A β_{Si} of unity has been inferred previously based on the hydrogen deficiency of Si.^{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 paper. This line of reasoning is further corroborated by comparing our values of β_{Si} and β_{SiH_3} with the reported values of β_{SiH} and β_{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 $< 10^{-3}$, even on a H-free $c\text{-Si}$ surface.⁷³ Therefore, we conclude from our measurements that there is a general trend that the surface reaction probability β 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.^{45–48}

To get an indication of the relative importance of the different radicals to $a\text{-Si:H}$ film growth, the Si growth flux due to a specific radical, Γ_{Si} (i.e., the number of Si atoms deposited per second by the specific radical) can be estimated from the value of β and the density n in the plasma:⁵⁴

TABLE II. An overview of the surface reaction probability β and typical density of the different silane radicals in the ETP and rf plasma for conditions where device quality *a*-Si:H is grown.

Species	β	Density in ETP plasma ^a (m ⁻³)	Density in rf plasma ^b (m ⁻³)
Si	>0.95 ^c	2×10^{15}	1×10^{16}
SiH	$\sim 0.95^d$	3×10^{16}	2×10^{16}
SiH ₂	$\sim 0.6^e$	$\sim 10^{17}$	1×10^{16}
SiH ₃	0.3 ^f	7×10^{18}	3×10^{17}
SiH ₄	$\leq 1 \times 10^{-3g}$	1×10^{20}	1×10^{21}

^aReferences 35, 49, and 60.

^bThe rf plasma densities, taken from Ref. 34 for a rf power of 0.05 W/cm², are representative for rf plasmas in general (Refs. 12, 16, 20, and 33).

^cThis work.

^dReference 2–4.

^eReference 16.

^fThis work and Refs. 6, 8, 10–13, 20, and 25.

^gReference 73.

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

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 $s \approx \beta/2$ for SiH₃ and $s = \beta$ for SiH₂, SiH, and Si.^{6,12,29,34,36,73} Combining these estimates of s with the values of β 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 SiH₃ 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 $s \approx \beta/2$ for SiH₃, a value of s_{SiH_3} of more than 0.01 is needed at the least to account for the *a*-Si:H growth rates observed. On the other hand, the densities of the other radicals are clearly not high enough to explain the *a*-Si:H growth rates even with an s of unity. These findings are in perfect agreement with a contribution of SiH₃ to *a*-Si:H film growth of $(90 \pm 10)\%$, as found in the ETP plasma using a different approach,³⁵ and with Ref.36.

In view of SiH₃ being the key growth precursor for *a*-Si:H growth, we have measured β of SiH₃ as a function of the substrate temperature to study the growth process of *a*-Si:H. No dependence of β_{SiH_3} on the substrate temperature has been found (Fig. 9), consistent with the observations from MD simulations.⁴⁶ To obtain β values in a 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 β that are averaged overall 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 SiH₃ radicals to come to the surface. Using this configuration, they found that the compound value of β is independent

of T_{sub} (from room temperature up to 500°C) with a β of 0.26 ± 0.05 . While the rf plasma is modified by the application of the mesh, the good agreement with our results of β_{SiH_3} indicates that their measurements have been performed under SiH₃ dominated conditions. Along the same line of reasoning, the compound values of β of ~ 0.3 for three substrate temperatures obtained indirectly with the aperture-well assembly method by Kessels *et al.* in the ETP setup⁸ (see Fig. 9) imply that the specific ETP plasma conditions used are SiH₃ dominated. These findings corroborate the conclusion that SiH₃ is the dominant growth precursor for *a*-Si:H film growth. More importantly, as our values of β_{SiH_3} have been obtained from direct measurements of SiH₃ and during regular plasma deposition of *a*-Si:H, our measurements remove any remaining uncertainty about the independence of β_{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 β_{SiH} of approximately unity, SiH virtually always reacts to the substrate and therefore the experimental observation² of a substrate temperature independent β_{SiH} was not unexpected. Applying the same argument to Si, no dependence of β_{Si} on the substrate temperature is expected. For SiH₃, however, the independence of β_{SiH_3} on the substrate temperature is less obvious and is shown to have direct implications for the dominant reactions of SiH₃ with the *a*-Si:H surface. Either the surface reactions are all individually independent of T_{sub} , or the surface reactions do depend on T_{sub} , but their thermal activation cancels out. The latter seems improbable due to the typical exponential dependence of the reaction rates on the activation barrier. To narrow the constraints on the possible surface reactions of SiH₃ 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^{74,75} have shown that the hydrogen coverage of the *a*-Si:H surface changes drastically with increasing T_{sub} : from a surface that is covered with trihydride (—SiH_3) bonds at $T_{\text{sub}} < 150^\circ\text{C}$ to a dihydride (=SiH_2) covered surface at intermediate temperatures to a monohydride (≡SiH) covered surface at $T_{\text{sub}} > 300^\circ\text{C}$. This observation is in sharp contrast with the substrate temperature independence of β_{SiH_3} . The sticking probability s of SiH₃ is investigated next. Although a direct measurement of s_{SiH_3} is unfeasible, insight on s_{SiH_3} can be obtained from the Si growth flux Γ_{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 SiH₃ radicals coming to the surface, as argued above. Figure 10 shows the Si growth flux as a function of substrate temperature, measured for two different pressures with all other conditions equal to the measurement conditions of β_{SiH_3} . It is seen that Γ_{Si} is independent of T_{sub} , in good agreement with two previous measurements of Γ_{Si} in the ETP plasma under slightly different plasma settings.^{8,76} Apart from Γ_{Si} , it has been shown in this paper that for these plasma conditions also the density n , the gas temperature

FIG. 10. The Si growth flux Γ_{Si} as a function of the substrate temperature T_{sub} for 0.27 and 0.36 mbar and all other conditions equal to the measurement conditions of β_{SiH_3} . The Si growth flux is calculated from the product of the Si atomic density in the *a*-Si:H film and the deposition rate, both determined from Fourier transform infrared spectroscopy measurements of the *a*-Si:H films and corroborated by elastic recoil detection analysis.

T_{gas} , and thus also the thermal velocity v are independent of T_{sub} . Therefore, it follows from Eq. (7) that s_{SiH_3} must also be independent of the substrate temperature. Moreover, in the case that $s < \beta$, it follows that the recombination probability γ of SiH_3 must also be independent of T_{sub} . To conclude, the substrate temperature independence of all three macroscopic surface reaction parameters, β , s , and γ , 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. 74. There, it is argued that SiH_3 contributes to *a*-Si:H growth via a two-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 process,^{41,46} thereby forming a dangling bond. From MD simulations it has been found that this process has a reasonably low activation energy (~ 0.09 eV) (Ref. 41) and can explain the substrate temperature independence of γ . Then, a second SiH_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 SiH_3 , has no activation barrier,⁴⁶ corresponding to a substrate temperature independent s . As $\beta = \gamma + s$, this two-step reaction mechanism also implies a substrate temperature independent β . 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 ringdown spectroscopy (τ -CRDS) yields accurate measurements of the loss time of radicals in the plasma with a standard deviation of $\sim 6\%$. 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. There-

fore, the loss times can be used to obtain the gas phase reaction 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 $\sim 15\%$ and a potential systematic error of less than $\sim 16\%$.

The capabilities of the τ -CRDS method have been demonstrated on a $\text{Ar-H}_2\text{-SiH}_4$ -based plasma used for the deposition of hydrogenated amorphous silicon (*a*-Si:H). It has been found that Si is highly reactive with SiH_4 in the gas phase [$k_r = (3.0 \pm 0.6) \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$] and that it has a surface reaction probability β with the *a*-Si:H surface of $0.95 < \beta_{\text{Si}} < 1$. SiH_3 is only lost by diffusion to and reaction at the *a*-Si:H surface and the values of β_{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 β_{SiH_3} is independent of the substrate temperature with an averaged value of β_{SiH_3} of 0.30 ± 0.03 . On the basis of these observations, the growth process of *a*-Si:H has been addressed.

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APPENDIX: DETERMINATION OF THE KINETIC GAS TEMPERATURE

The kinetic gas temperature T_{gas} has been determined from the Doppler broadening of the $\text{Si } 4s^3p_2 \leftarrow 3p^2\ ^3P_1$ atomic transition. The measured absorption profile is a convolution of the Gaussian Doppler profile and the Lorentzian linewidth profile of the laser and is consequently fitted to a Voigt 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_{gas} ,⁷⁷ 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.⁷⁸ To this end, the laser light intensity in the cavity has been chosen sufficiently low (laser pulse energy in the cavity is $E < 1 \times 10^{-8} \text{ J/pulse}$, as calculated from the measured laser pulse energy before the cavity and the transmission of the first cavity mirror).

The values of T_{gas} are shown in Fig. 11 as a function of the substrate temperature T_{sub} . The dependence of T_{gas} on

FIG. 11. The kinetic gas temperature T_{gas} , as determined from the Doppler broadening of the Si $4s\ ^3P_2 \leftarrow 3p^2\ ^3P_1$ transition at 250.69 nm (inset) as a function of the substrate temperature T_{sub} . The dashed line shows a fit through the measurements obtained for a SiH_4 flow of 0.5 SCCS, yielding $T_{\text{gas}} = (1850 \pm 80)$ 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 different pressures. These additional measurements show an average temperature of $T_{\text{gas}} = (1500 \pm 200)$ K.

T_{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_{gas} . The horizontal fit through the data points shows that T_{gas} is independent of T_{sub} with a T_{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 β_{SiH_3} and β_{Si} . These measurements yield an (averaged) value for T_{gas} of (1500 ± 200) K that is independent of the pressure. A T_{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.^{49,69} Therefore, a T_{gas} of (1500 ± 200) K that is independent of T_{sub} is assumed for the measurements of β throughout the paper.

¹A. von Keudell, T. Schwarz-Selinger, M. Meier, and W. Jacob, Appl. Phys. Lett. **76**, 676 (2000).

²P. R. McCurdy, K. H. A. Bogart, N. F. Dalleska, and E. R. Fisher, Rev. Sci. Instrum. **68**, 1684 (1997).

³P. Ho, W. G. Breiland, and R. J. Buss, J. Chem. Phys. **91**, 2627 (1989).

⁴W. M. M. Kessels, P. R. McCurdy, K. L. Williams, G. R. Barker, V. A. Ventura, and E. R. Fisher, J. Phys. Chem. B **106**, 2680 (2002).

⁵J. C. Rey, L. Y. Cheng, J. P. McVittie, and K. C. Saraswat, J. Vac. Sci. Technol. A **9**, 1083 (1990).

⁶A. Matsuda, K. Nomoto, Y. Takeuchi, A. Suzuki, A. Yuuki, and J. Perrin, Surf. Sci. **227**, 50 (1990).

⁷J. Perrin, Y. Takeda, N. Hirano, Y. Takeuchi, and A. Matsuda, Surf. Sci. **210**, 114 (1989).

⁸W. M. M. Kessels, M. C. M. van de Sanden, R. J. Severens, and D. C. Schram, J. Appl. Phys. **87**, 3313 (2000).

⁹A. von Keudell, T. Schwarz-Selinger, W. Jacob, and A. Stevens, J. Nucl. Mater. **290**, 231 (2001).

¹⁰D. A. Doughty, J. R. Doyle, G. H. Lin, and A. Gallagher, J. Appl. Phys. **67**, 6220 (1990).

¹¹A. Nuruddin, J. R. Doyle, and J. R. Abelson, J. Appl. Phys. **76**, 3123 (1994).

¹²J. Perrin, M. Shiratani, P. Kae-Nune, H. Videlot, J. Jolly, and J. Guillon, J. Vac. Sci. Technol. A **16**, 278 (1998).

¹³J. M. Jasinski, J. Phys. Chem. **97**, 7385 (1993).

¹⁴P. Kae-Nune, J. Perrin, J. Jolly, and J. Guillon, Surf. Sci. Lett. **360**, L495 (1996).

¹⁵A. Tserepi, W. Schwarzenbach, J. Derouard, and N. Sadeghi, J. Vac. Sci. Technol. A **15**, 3120 (1997).

¹⁶M. Hertl and J. Jolly, J. Phys. D **33**, 381 (2000).

¹⁷P. Chabert, G. Cunge, J. P. Booth, and J. Perrin, Appl. Phys. Lett. **79**, 916 (2001).

¹⁸S. Gomez, P. G. Steen, and W. G. Graham, Appl. Phys. Lett. **81**, 19 (2002).

¹⁹J. P. Booth and N. Sadeghi, J. Appl. Phys. **70**, 611 (1991).

²⁰M. Shiratani, H. Kawasaki, T. Fukuzawa, Y. Watanabe, Y. Yamamoto, S. Suganuma, M. Hori, and T. Goto, J. Phys. D **31**, 776 (1998).

²¹S. Takashima, M. Hori, T. Goto, A. Kono, and K. Yoneda, J. Appl. Phys. **90**, 5497 (2001).

²²K. Sasaki, Y. Kawai, C. Xuzuki, and K. Kadota, J. Appl. Phys. **82**, 5938 (1997).

²³I. M. Rusinov and A. B. Blagoev, Vacuum **58**, 256 (2000).

²⁴R. M. Robertson and M. J. Rossi, J. Chem. Phys. **91**, 5037 (1989).

²⁵J. P. M. Hoefnagels, A. A. E. Stevens, M. G. H. Boogaarts, W. M. M. Kessels, and M. C. M. van de Sanden, Chem. Phys. Lett. **360**, 189 (2002).

²⁶Cavity-Ringdown Spectroscopy: An Ultratrace-Absorption Measurement Technique, edited by K. W. Busch and M. A. Busch (American Chemical Society, Washington, D.C., 1999).

²⁷D. B. Atkinson and J. W. Hudgens, J. Phys. Chem. A **101**, 3901 (1997), and references therein.

²⁸J. R. Abelson, Appl. Phys. A: Solids Surf. **56**, 493 (1993).

²⁹W. M. M. Kessels, A. H. M. Smets, D. C. Marra, E. S. Aydil, D. C. Schram, and M. C. M. van de Sanden, Thin Solid Films **383**, 154 (2001).

³⁰A. Gallagher, Mater. Res. Soc. Symp. Proc. **70**, 3 (1986).

³¹A. Matsuda and K. Tanaka, J. Appl. Phys. **60**, 2351 (1986).

³²R. Robertson, D. Hils, H. Chatham, and A. Gallagher, Appl. Phys. Lett. **43**, 544 (1983).

³³N. Itabashi, N. Nishikawa, M. Magane, S. Naito, T. Goto, A. Matsuda, C. Yamada, and E. Hirota, Jpn. J. Appl. Phys., Part 2 **29**, L505 (1990).

³⁴P. Kae-Nune, J. Perrin, J. Guillon, and J. Jolly, Plasma Sources Sci. Technol. **4**, 250 (1995).

³⁵W. M. M. Kessels, M. G. H. Boogaarts, J. P. M. Hoefnagels, M. C. M. van de Sanden, and D. C. Schram, J. Vac. Sci. Technol. A **19**, 1027 (2001).

³⁶W. M. M. Kessels, M. C. M. van de Sanden, and D. C. Schram, J. Vac. Sci. Technol. A **18**, 5 (2000).

³⁷M. J. McCaughey and M. J. Kushner, Appl. Phys. Lett. **54**, 1642 (1989).

³⁸G. J. Nienhuis, W. J. Goedheer, E. A. G. Hamers, W. G. J. H. M. van Sark, and J. Bezemer, J. Appl. Phys. **82**, 2060 (1997).

³⁹G. J. Nienhuis and W. J. Goedheer, Plasma Sources Sci. Technol. **8**, 295 (1999).

⁴⁰S. P. Walch, S. Ramalingam, E. S. Aydil, and D. Maroudas, Chem. Phys. Lett. **329**, 304 (2000).

⁴¹S. Ramalingam, D. Maroudas, E. S. Aydil, and S. P. Walch, Surf. Sci. Lett. **418**, L8 (1998).

⁴²D. R. Bowler and C. M. Goringe, Surf. Sci. Lett. **360**, L489 (1996).

⁴³A. Gupta, H. Yang, and G. N. Parsons, Surf. Sci. **496**, 307 (2002).

⁴⁴R. Dewarrrat and J. Robertson, Appl. Phys. Lett. **82**, 883 (2003).

⁴⁵S. Ramalingam, D. Maroudas, and E. S. Aydil, J. Appl. Phys. **84**, 3895 (1998).

⁴⁶S. Ramalingam, D. Maroudas, and E. S. Aydil, J. Appl. Phys. **86**, 2872 (1999).

⁴⁷S. Ramalingam, D. Maroudas, and E. S. Aydil, J. Appl. Phys. **86**, 5497 (1999).

⁴⁸S. Ramalingam, S. Sriraman, E. S. Aydil, and D. Maroudas, Appl. Phys. Lett. **78**, 2685 (2001).

⁴⁹W. M. M. Kessels, J. P. M. Hoefnagels, M. G. H. Boogaarts, D. C. Schram, and M. C. M. van de Sanden, J. Appl. Phys. **89**, 2065 (2001).

⁵⁰H. L. Duan, G. A. Zaharias, and S. F. Bent, Curr. Opin. Solid State Mater. Sci. **6**, 471 (2002).

⁵¹J. Doyle, R. Robertson, G. H. Lin, M. Z. He, and A. Gallagher, J. Appl. Phys. **64**, 3215 (1998).

⁵²W. M. M. Kessels, P. J. van den Oever, J. P. M. Hoefnagels, J. Hong, I. J. Houston, and M. C. M. van de Sanden, Mater. Res. Soc. Symp. Proc. **715**, A25.6.1 (2002).

⁵³G. Olbrich, Chem. Phys. **101**, 381 (1986).

⁵⁴P. J. Chantry, J. Appl. Phys. **62**, 1141 (1987).

⁵⁵J. Perrin, O. Leroy, and M. C. Bordage, Contrib. Plasma Phys. **36**, 1 (1996).

⁵⁶W. M. M. Kessels, R. J. Severens, A. H. M. Smets, B. A. Korevaar, G. J. Adriaenssens, D. C. Schram, and M. C. M. van de Sanden, J. Appl. Phys. **89**, 2404 (2001).

⁵⁷M. C. M. van de Sanden, R. J. Severens, W. M. M. Kessels, R. F. G. Meulenbroeks, and D. C. Schram, J. Appl. Phys. **84**, 2426 (1998).

⁵⁸M. C. M. van de Sanden, W. M. M. Kessels, R. J. Severens, and D. C.

- Schram, Plasma Phys. Controlled Fusion **41**, A365 (1999).
- ⁵⁹W. M. M. Kessels, C. M. Leewis, M. C. M. van de Sanden, and D. C. Schram, J. Appl. Phys. **86**, 4029 (1999).
- ⁶⁰W. M. M. Kessels, A. Leroux, M. G. H. Boogaarts, J. P. M. Hoefnagels, M. C. M. van de Sanden, and D. C. Schram, J. Vac. Sci. Technol. A **19**, 467 (2001).
- ⁶¹W. M. M. Kessels, *et al.*, J. Vac. Sci. Technol. A **20**, 1704 (2002).
- ⁶²Technical Laboratory Automation Group, Eindhoven University of Technology, Den Dolech 2, 5600 MB Eindhoven, The Netherlands.
- ⁶³M. G. H. Boogaarts, P. J. Böcker, W. M. M. Kessels, D. C. Schram, and M. C. M. van de Sanden, Chem. Phys. Lett. **326**, 400 (2000).
- ⁶⁴A. V. Baklanov and L. N. Krasnoperov, J. Phys. Chem. **105**, 4917 (2001).
- ⁶⁵P. D. Lightfoot, R. Becerra, A. A. Jemi-Alade, and R. Lesclaux, Chem. Phys. Lett. **180**, 441 (1991).
- ⁶⁶A. A. Radzig and B. M. Smirnov, *References Data on Atoms, Molecules and Ions* (Springer, Berlin-Heidelberg, 1985).
- ⁶⁷C. Courteille, J. L. Dorier, C. Hollenstein, L. Sansonnens, and A. A. Howling, Plasma Sources Sci. Technol. **5**, 210 (1996).
- ⁶⁸S. K. Loh and J. M. Jasinski, J. Chem. Phys. **95**, 4914 (1991).
- ⁶⁹In Ref. 25, a lower T_{gas} of 700 K was assumed based on fluid dynamics simulations for different plasma conditions. In the Appendix, it is shown that T_{gas} is (1500 ± 200) K. Using this new value of T_{gas} , the value of k_{Si} , β_{Si} , and the reference data point of β_{SiH_3} at 200°C (Fig. 9) have been recalculated with respect to Ref. 25.
- ⁷⁰M. Koi, K. Tonokura, A. Tezaki, and M. Koshi, J. Phys. Chem. A **107**, 4838 (2003).
- ⁷¹The 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.
- ⁷²The value of H reflects the axial gradient of the rf-generated density profile (determined by the surface reaction probability β 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.
- ⁷³S. M. Gates, Surf. Sci. **195**, 307 (1998).
- ⁷⁴W. 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).
- ⁷⁵D. C. Marra, W. M. M. Kessels, M. C. M. van de Sanden, K. Kashefzadeh, and E. S. Aydil, Surf. Sci. **530**, 1 (2003).
- ⁷⁶A. H. M. Smets, W. M. M. Kessels, and M. C. M. van de Sanden, Mater. Res. Soc. Symp. Proc. **762**, A10.3.1 (2003).
- ⁷⁷It is noted that CRDS yields a line-integrated value of T_{gas} , whereas the spatially resolved T_{gas} is needed. Fluid dynamics calculations (Ref. 60) show, however, that the specific radial T_{gas} profile at a distance of 5 mm from the substrate is such that these two values of T_{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_{gas} is constant (Ref. 60).
- ⁷⁸J. P. M. Hoefnagels, Y. Barrell, M. C. M. van de Sanden, and W. M. M. Kessels, *Proceedings of Frontiers in Low Temperature Plasma Diagnostics V*, edited by S. de Benedictis and G. Dilecce (Istituto di Metodologie Inorganiche e dei Plasmi, Bari, Italy, 2003), pp. 255–258.