Cavity ring down detection of SiH3 in a remote SiH4 plasma and comparison with model calculations and mass spectrometry


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I. INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) produced by plasma decomposition of SiH₄ is a widely used material with its major applications in thin film solar cells and thin film transistors. For optimization of the deposition process and the a-Si:H film properties, detailed knowledge on the elementary plasma and surface reactions is essential. Therefore numerous studies on the plasma composition have been carried out, mainly in radio frequency (rf) parallel plate reactors. From this consideration, the plasma processes and the contribution of the different plasma species to film growth are also investigated in the so-called expanding thermal plasma (ETP). This technique distinguishes itself mainly by the fact that it is capable of depositing good quality a-Si:H at much higher rates (up to 10 nm/s) than by conventional techniques.¹,² Apart from the fact that this technique has potential for cost-effective solar cell production, it also enables investigation and verification of film growth mechanisms under more "extreme" conditions. These conditions are rather well defined (as will be shown below) due to the fact that the remote nature of the technique allows for independent parameter control and variation.

Up to now, the SiH₃ dissociation process and species contributing to film growth in the expanding thermal plasma have been studied by several diagnostics, such as Langmuir probes, ion and threshold ionization mass spectrometry, optical emission spectroscopy, and surface reaction probability measurements.³⁻⁵ These studies have revealed that under "optimized" conditions, the SiH₄ is primarily dissociated by H emanating from the Ar–H₂ operated plasma source because electron-induced ionization and dissociation of SiH₄ are insignificant due to the low electron temperature (0.1–0.3 eV).³⁻⁵ Furthermore, it has been shown that the contribution of positive ions SiₙH₄⁺ (with n up to 10) to film growth is about 6%.⁴,⁵ The contribution of radicals other than SiH₃ is expected to be rather small because the contribution of SiH₃ is estimated at ~90% from threshold ionization mass spectrometry (TIMS) measurements performed at the position of the substrate.⁷

Although mass spectrometry yields directly information relevant for deposition plasmas because it measures the species very close to the wall, it cannot be applied easily and nonintrusively at several positions in the plasma. Spatially resolved measurements at several positions are useful for the investigation of the generation and loss processes of species in the plasma. For this reason, SiH₃ has recently also been detected by cavity ring down spectroscopy (CRDS) in the ETP setup.⁸,⁹ In this absorption technique, the A→A₁ transition at 217 nm of a SiH₃ plasma used for high rate deposition of hydrogenated amorphous silicon. The obtained densities of SiH₃ and its axial and radial distribution in the cylindrical deposition reactor are compared with simulations by a two-dimensional axisymmetric fluid dynamics model. The model, in which only three basic chemical reactions are taken into account, shows fairly good agreement with the experimental results and the plasma and surface processes as well as transport phenomena in the plasma are discussed. Furthermore, the SiH₃ density determined by cavity ring down spectroscopy is in good agreement with the SiH₃ density as obtained by threshold ionization mass spectrometry. © 2001 American Vacuum Society [DOI: 10.1116/1.1339015]
\[ \tau_\lambda = \frac{dc}{(1 - R_\lambda + A_\lambda)} \]

with \( c \) the speed of light. For an axisymmetric density profile \( n(r) \) with radial coordinate \( r \), the absorption at a lateral position \( y \) depends on the cross section \( \sigma_\lambda \) of the absorbing species and its line-integrated number density over the absorption path length \( 2l \):

\[ A_\lambda(y) = \sigma_\lambda \int_{-l}^{l} n(r)dr = \sigma_\lambda \int_{-l}^{l} n(\sqrt{x^2 + y^2})dx, \]

with \( l = \sqrt{R^2 - y^2} \) and \( R \) the radius of the setup. By comparing the decay time for the cavity with absorbing species with the decay time for the ‘‘empty’’ cavity, the absorption and the (line-integrated) density of the absorbing species can be calculated.

In addition to the measurements described in Refs. 8 and 9, in this article the absorption by SiH\(_3\) measured at several axial positions is presented as a function of the SiH\(_4\) flow. Furthermore, measurements at different lateral positions are also given, enabling a calculation of the spatially resolved SiH\(_3\) density by means of Abel inversion. In Ref. 8, a homogeneous SiH\(_3\) density has been assumed over a path length of 30 cm.

The measured SiH\(_3\) density and its radial distribution in the cylinder-symmetric deposition chamber are furthermore compared to those obtained by two-dimensional axisymmetric model calculations. These calculations have been performed using the commercial computational fluid dynamics software PHOENICS-CVD. In the model, only the (supposedly) basic gas phase and surface chemical processes are taken into account. It is assumed that H is the only reactive species emanating from the Ar–H\(_2\) operated plasma source and that reaction (1) is the only SiH\(_4\) dissociation process. No ion and electron processes are taken into account, reducing it basically to a hot, reactive gas model. As concluded from previous studies, this is fairly reasonable, especially as far as the production of SiH\(_3\) is concerned. From this simplified model, better insight into the processes and into the transport phenomena in the reactor can be gained. The simulations, combined with the experimental results on the radial profile of the SiH\(_3\) density, are furthermore helpful for the comparison of SiH\(_3\) densities obtained by CRDS with those obtained by TIMS at the position of the substrate holder. It will be demonstrated that the densities show good agreement.

II. DEPOSITION SYSTEM AND OPTICAL SETUP

A cross-sectional side and front view of the expanding thermal plasma is given in Fig. 1. The setup consists of a cascaded arc plasma source and a downstream deposition chamber. In the cascaded arc a thermal Ar–H\(_2\) plasma is created at a pressure of \(~400\) mbar using an Ar flow of 55 sccs and a H\(_2\) flow of 10 sccs. The arc is current controlled at 45 A and the arc voltage is \(~140\) V. The plasma expands supersonically into the low-pressure deposition chamber (0.2 mbar) leading to a stationary shock at approximately 5 cm from the arc exit. At this distance, pure SiH\(_4\) is added to the plasma by means of an injection ring with a diameter of 7.5 cm. For the experiments reported here, the SiH\(_4\) flow is varied between 0 and 25 sccs. At 35 cm from the arc exit, a substrate holder with a diameter of 10 cm is positioned that is pumped by means of a 450 l/s turbopump reaching a base pressure of \(~10\) \(^{-6}\) mbar.

For the CRDS measurements, a stable optical cavity is created by two plano-concave mirrors (\(~97\)% reflectivity around 217 nm, \(~100\) cm radius of curvature, 2.5 cm diameter) at a distance of 108 cm apart. The mirrors are mounted on flexible bellows and a very small Ar flow is used to protect them against deposition. The lateral and axial position can be set by means of a sliding vacuum seal. The measurements reported here have been performed at a position of 0.6, 3.6, and 11 cm from the substrate (see cross-sectional side view Fig. 1). For an axial position of 3.6 cm, lateral measurements have been performed from 0 to 11 cm from the axis (see cross-sectional front view Fig. 1). Laser radiation from a Nd:YAG pumped dye laser (Spectra-Physics DCR-11/Sirah PrecisionScan-D) is introduced in the cavity. Operated on Coumarine 440 and frequency doubled with a BBO crystal, the dye laser delivers radiation with a tunable wavelength between 214 and 227 nm, an estimated bandwidth of \(~0.2\) cm\(^{-1}\), and a typical pulse energy of \(10\) \(\mu\)J. A wavelength scan is given in Refs. 8 and 9, but in this study the laser wavelength has been kept at 217 nm. The output intensity behind the exit mirror is measured through a narrow bandpass filter (10 nm) with a photomultiplier (Hamamatsu R928) and a digital 500 Ms/s, 100 MHz oscilloscope (Tektronix TDS340a). For all measurements, an average over 64 laser shots is taken and from the resulting
transient signal the ring down time $\tau$ is determined from a weighted least-squares fit of the logarithm of the transient data. In the measurements described here, $\tau$ is first determined for an Ar–H$_2$ plasma, which did not show any absorption, and then for the Ar–H$_2$–SiH$_4$ plasma containing SiH$_3$. Furthermore, no absorption due to SiH$_4$ has been observed in agreement with the literature (onset absorption at $\sim$170 nm).$^{11}$

III. MODEL

Two-dimensional axisymmetric simulations of the stationary gas flows, transport phenomena, and gas phase and surface reactions in the downstream deposition reactor have been carried out with the commercial computational fluid dynamics software PHOENICS-CVD.$^{13}$ A description of the modeling of the transport phenomena and chemical reactions of multicomponent gas mixtures and the applied numerical methods can be found in Refs. 14 and 15. First a description of the reactor and the processes taken into account in the model will be presented as well as the simplifications and assumptions used. Second, some typical gas flow phenomena in the reactor as calculated by the model will be illustrated.

As mentioned above, the reactor has been assumed to be axisymmetric (see Fig. 2). Consequently, the outlet toward the pumping system has been assumed to be located along the complete side of the reactor for one axial position. The total area of the outlet has been set equal to its actual value. Another important simplification is that the supersonic region is left out of the model. The model starts 5 cm from the arc exit at the position of the SiH$_4$ injection ring. For all species one uniform inlet area has been assumed, which has been set equal to the estimated beam area at that position (supersonic expansion under 45°). Therefore only subsonic flows have been taken into account, while the inlet conditions (as defined below) have been taken from experimental data in the region of the shock. Although this is a good approximation because the conditions before the shock are not influenced by the conditions downstream, it causes some deviations in the radial, subsonic outer region of the shock, because this region is not taken into account in the model (see Fig. 2). For the calculation domain, a nonuniform cylindrical grid has been used with 25 grid points in the radial and 40 grid points in the axial direction. The grid is locally refined near the inlet, the substrate, the outlet, and the reactor walls. Grid independence of the results has been checked by using a 50×80 grid for some representative situations. The differences were smaller than 5%.

In the model, only five species (Ar, H$_2$, H, SiH$_3$, and SiH$_4$) are considered, while no electrons and ions have been taken into account. This is a fairly good approximation for the experimental conditions described, i.e., with significant H$_2$ dilution, as concluded from previous experimental investigations of the plasma.$^{3,5,7,9}$ At the inlet, Ar, H$_2$, H, and SiH$_4$ are introduced in the reactor with an axial velocity of 800–850 m/s and a quadratic profile in radial direction. At the inlet a single gas temperature equal to 3000 K has been assumed for the mixture. These values for the velocity and temperature are derived from laser-induced fluorescence (LIF) measurements on Ar.$^{16}$ The Ar flow is 55 sccs, while the H and H$_2$ flow at the inlet are calculated from the initial H$_2$ flow of 10 sccs and the H$_2$ dissociation degree $a$. The inlet pressure is set at ~0.23 mbar,$^{17,18}$ and varies slightly with the actual total gas flow. At the outlet, the flow has a radial velocity of typically 16 m/s as determined by the pumping capacity. All walls are isothermal and maintained at a temperature of 500 K, except for the substrate holder, which is set at 700 K. This is approximately equal to the typical temperature during deposition (400 °C)$^{1,2}$

The only gas phase reaction taken into account is reaction (1), in which SiH$_3$ is produced by hydrogen abstraction of SiH$_4$. Based on the results of Goumri et al.$^{19}$ for temperatures $T$ in the range of 290–660 K, the rate of this reaction has been set at $1.8 \times 10^{-16} \exp(-1925/T)$ m$^3$s$^{-1}$ for the complete temperature interval in the model.

For H and SiH$_3$ surface reactions have been implemented. H can recombine at the walls by the reaction

$$H(g) + H(s) \rightarrow H_2(g),$$

with recombination coefficient $\gamma$. It has been assumed that $\gamma$ is independent of the wall temperature and for the simulations with only Ar–H$_2$, $\gamma$ has been set equal to 0.2, the value proposed for stainless steel.$^{20}$ For simulations with SiH$_4$ in which all walls are covered with a-Si:H, $\gamma$ is set equal to 1.$^{20}$ SiH$_3$ can get lost at the surface by deposition while simultaneously splitting off gaseous H$_2$

$$SiH_3(g) \rightarrow a-Si:H(s) + H_2(g).$$

For this reaction, a sticking probability $s$ of SiH$_3$ equal to the surface reaction probability $\beta$ has been assumed, i.e., $s = \beta$. Recombination of SiH$_3$ with H at the surface forming gaseous SiH$_4$,$^{21-23}$ is not included in the calculations described, but it has been determined that this has negligible implications for the calculated SiH$_3$ and SiH$_4$ density when the SiH$_3$ consumption is small. In the presented calculations $\beta$ is taken to be 0.3 and assumed to be surface temperature independent.$^6$ Reactions (1) and (5) imply that for every Si atom deposited 1.5 gaseous H$_2$ molecules are generated. In reality, for the heated substrate holder almost two gaseous H$_2$ molecules are generated per Si deposited and for the relatively cold walls approximately 1 gaseous H$_2$ molecule.$^7$

Before running simulations with SiH$_4$, first the value of the dissociation degree $\alpha$ of the H$_2$ emanating from the arc
has to be set. On the value of $\alpha$ it can be decided from simulations with only Ar and H$_2$ by comparing the calculated H density with the one determined by two-photon-absorption LIF (TALIF) in an Ar–H$_2$ plasma.$^{24}$ The calculated H densities for $\alpha=2\%$ and $\alpha=5\%$ are given in Fig. 3. The H densities obtained for $\alpha=2\%$ show good agreement with the experimental ones, especially at small $z$ values. The difference for larger $z$ values can possibly be attributed to the different reactor geometry (e.g., the chamber diameter is 32 cm instead of 50 cm) and the absence of a substrate holder in the reactor wherein the TALIF measurements were performed. Concerning the radial H densities, the behavior of the experimental and simulated densities show very good agreement, i.e., flat profiles in the center of the reactor. In the following sections, results of simulations with both $\alpha=2\%$ and $\alpha=5\%$ will be presented, because a better agreement with the experimental data is obtained for values of $\alpha$ slightly larger than $2\%$. Small differences in $\alpha$ for the two setups might be caused by the aforementioned differences in reactor geometry as well as by the slightly different cascaded arc plasma source and its operating conditions during the TALIF measurements. The latter were performed with an Ar flow of 50 sccs, a H$_2$ flow of 8.3 sccs, and an arc current of 40 A.

In Fig. 4 results of a simulation with typical standard conditions, i.e., with 10 sccs SiH$_4$ and a substrate temperature of 700 K, are given. The presented pressure, axial, and radial velocity fields, and streamlines yield insight into the gas flows in the reactor. The pressure at the inlet (0.23 mbar) and in front of the substrate holder (0.22 mbar) is slightly higher than the global pressure of 0.20 mbar in the rest of the reactor. The slightly higher pressure in front of the substrate holder that extends $\sim 5$ cm upstream indicates a flow stagnation zone. This can also be seen from the velocity contour plots. The axial velocity decreases from $\sim 850$ m/s at the inlet to zero just in front of the substrate holder, where it is partly converted into radial velocity. At the corner of the substrate holder, a radial velocity up to $\sim 100$ m/s is generated. The radial velocity iso-lines and streamlines also indicate a recirculation zone with a flow velocity less than 25 m/s. Furthermore, the radial velocity is $\sim 16$ m/s at the outlet of the reactor toward the pumps. These observations and values are typical for all conditions considered in this work and they are not seriously influenced by the chemical reactions taking place.

IV. RESULTS AND DISCUSSION

A. Cavity ring down measurements

1. Lateral scan and radial density profile

Before addressing the absorption by SiH$_3$ and its local density for different SiH$_4$ flows, first information on the radial distribution of SiH$_3$ has to be obtained. Therefore the absorption has been measured for different lateral positions $y$ at an axial position of 3.6 cm from the substrate holder. Unfortunately, due to practical limitations, lateral measurements could only be performed at this axial position and for lateral positions ranging from 0 to 11 cm. At 3.6 cm from the substrate holder, it is not expected that the SiH$_3$ density is affected by the substrate holder due to surface loss of SiH$_3$. The typical gradient length$^{25}$ of the SiH$_3$ density toward the surface is smaller than 3 cm as calculated from its diffusivity$^{26}$ and surface reaction probability.$^6$ The SiH$_3$ density, however, can be affected slightly by the stagnation of the plasma beam in front of the substrate holder (see Sec. IV B).

In Fig. 5, the absorption $A_A(y)$ at $\lambda=217$ nm is given as a function of $y$ for a SiH$_4$ flow of 10 sccs. The data have been averaged over ten separate measurements and the error bars have been calculated from the standard deviation. For an axisymmetric density profile, the density $n(r)$ of SiH$_3$ at radial position $r$ can be calculated from $A_A(y)$ by the Abel inversion of Eq. (3)$^{27}$

![Fig. 3. Experimental axial H density as determined by two-photon laser-induced fluorescence in an Ar–H$_2$ plasma (Ref. 24), compared to the calculated H densities for two values of the H$_2$ dissociation degree $\alpha$. The experimental values are obtained in a reactor with a somewhat different geometry and cascaded arc and for slightly different plasma conditions (50 sccs Ar, 8.3 sccs H$_2$, and 40 A arc current). The model starts at 5 cm from the arc outlet situated at $z=\sim 5$ cm.](image1)

![Fig. 4. Calculated iso-lines for the (a) static pressure, (b) axial, and (c) radial velocity, as well as for the (d) streamlines for a condition typically used for a-Si:H deposition. The pressure is given in mbar; the velocity in m/s.](image2)
file, although in the interpretation of the deduced radial SiH3 is believed that it gives a reasonable description of the pro-
fectly and that it is certainly not unique. Nevertheless, it be taken into account that it does not describe the data points
ited part of the profile. Concerning the fit in Fig. 5, it should
that only a few data points are available and only for a lim-
the radius of the setup $y=R=25$ cm. For presentation purposes, at $y<0$ the same values are given as for $y>0$. Furthermore, the lateral absorption profile as calculated from the simulated SiH3 density (i.e., product of line-integrated density and absorption cross section) with $\alpha=5\%$ is given for the same axial position (see Sec. IV B).

$$n(r) = \frac{-1}{\sigma_a \pi} \int_{R}^{y} \frac{1}{(y^2 - r^2)^{1/2}} \frac{dA_s(y)}{dy} \, dy,$$ (6)

with $R$ the radius of the setup. For practical evaluation of Eq. (6), the lateral profile of the absorption is fitted by means of a sum of two Gaussians, both centered at $y=0$. The advantage of this method is that Gaussians are invariant to Abel inversion making the calculation straightforward. The fit is given in Fig. 5, where it has been imposed that the lateral absorption profile drops to zero at $y=R$. Other procedures for carrying out the inversion are not useful due to the fact that only a few data points are available and only for a limited part of the profile. Concerning the fit in Fig. 5, it should be taken into account that it does not describe the data points perfectly and that it is certainly not unique. Nevertheless, it is believed that it gives a reasonable description of the profile, although in the interpretation of the deduced radial SiH3 density distribution these factors should be kept in mind.

In Fig. 6, the radial profile of the SiH3 density as calculated from the fit in Fig. 5 is given. For the calculation of the density, the cross section at 217 nm has been assumed to be equal to the one reported for 215 nm. This is validated by the broad nature of the SiH3 absorption peak.8,11 In addition to a decrease in density in the outward direction due to outward diffusion and surface loss, the profile is hollow at the axis. This was actually already evident from the lateral absorption profile. The hollow profile is most probably caused by a temperature effect: A higher gas temperature at the axis in a (nearly) isobaric reactor [see Fig. 4(a)] leads to a lower SiH3 density at the axis. As already mentioned, it is not expected that the SiH3 density at a distance of 3.6 cm from the substrate is directly influenced by loss of SiH3 at the substrate holder. Model calculations presented in Sec. IV B corroborate this interpretation. Simulated radial SiH3 profiles also show a reduced density at the axis due to a higher gas temperature, albeit to a smaller extent.

Lateral absorption profiles for other SiH4 flows showed, within the experimental error, a similar dependence of the absorption on the lateral position as in Fig. 5 for 10 sccs SiH4. There might be some indications that the profile is slightly more hollow at low SiH4 flows, but within the accuracy the radial distribution of SiH3 in Fig. 6 is expected to be representative for all conditions.

2. SiH4 flow series at different axial positions

In Fig. 7, the absorption by SiH3 is given as a function of the SiH4 flow for three different axial positions, 11, 3.6, and 0.6 cm from the substrate holder. The experimental uncertainty in the measurements is less than 15%, as estimated from the reproducibility. The trend and the absolute magnitude of the absorption are roughly the same for the three positions, while the trend for increasing SiH4 flow is also similar to the one observed in the SiH3 density as determined by threshold ionization mass spectrometry (see Sec. IV C for a direct comparison). On the right ordinate of Fig. 7, also the axial ($r=0$) SiH3 density is given for the position of 3.6 cm from the substrate holder. As mentioned above, it should be kept in mind that the radial distribution, and thus the axial density, is very sensitive to the fit of the lateral profile and the errors in the absorption values. This complicates a conclusive interpretation of the exact local SiH3 density. For the other axial positions, no information on the radial distribution of SiH3 is available. However, it is expected that the scale at the right ordinate of Fig. 7 gives a rough indication
of the magnitude of the axial density at these positions. The densities are in fairly good agreement with the estimated densities in Ref. 8 where a homogeneous distribution of SiH₃ over 30 cm was assumed. More insight in the SiH₃ density at different axial positions can be obtained from the simulations, which are addressed next.

B. Model calculations

In this section, the results obtained from simulations with PHOENICS-CVD will be presented, concentrating mainly on the SiH₃ density and its spatial distribution (i.e., axial and radial density profiles). From a comparison with the experimental results, it is possible to test whether the principal processes in the expanding thermal plasma for a-Si:H deposition can be reduced to the three chemical reactions taken into account in the model. The simulations are also helpful in the interpretation and understanding of the experimental data.

In Fig. 8, the axial densities of Ar, H, and SiH₃ are given as a function of the axial position z for the condition with 10 sccs SiH₄. For H and SiH₃, data are given for both $\alpha = 2\%$ and $\alpha = 5\%$ as only these densities are influenced significantly by $\alpha$ within this range. In Fig. 9, the corresponding radial profiles of the gas temperature, Ar density, H density, and SiH₃ density are given for axial positions of 0.6, 3.6, and 11 cm from the substrate holder. For SiH₃, the radial density deduced from the experimental data is also presented. On the basis of these figures several comments can be made:

(i) The axial Ar density increases slightly for increasing z due to the gradually decreasing gas temperature. Just in front of the substrate holder, the Ar density shows a sharper increase due to a temperature jump (from 1500 to 700 K within 3 cm) and due to stagnation of the plasma beam (pressure increases from 0.20 to 0.22 mbar). The density of SiH₃ increases while the density of H decreases with increasing z due to, respectively, production and loss by reaction (1). The density of both reactive species decreases in front of the substrate due to surface loss. This surface loss seems to have only a small effect, however, in terms of density this effect is obscured by the temperature jump and stagnation pressure. When considering the relative densities or concentrations of the species, the effect of surface loss is much clearer. Furthermore, it is noteworthy that between the cases with $\alpha = 2\%$ and $\alpha = 5\%$ only differences in the absolute magnitude of the H and SiH₃ density are observed.

(ii) Comparing the H density with the one in Fig. 3 for the Ar–H₂ case, reveals that for $\alpha = 2\%$ the H density in front of the substrate holder has been decreased from $1.4 \times 10^{17}$ to $7 \times 10^{15}$ by admixing 10 sccs SiH₄. This shows that reaction (1) is fast enough to consume almost all H within the transit from injection ring to the substrate holder. The SiH₃ density close to the substrate holder is about a factor of 300
higher than the H density, while the difference in thermal flux is about a factor of 50. This suggests that the interaction of H with the a-Si:H surface during deposition is limited compared to the interaction of SiH₃ for the ETP technique.

(iii) For the radial profiles at different axial positions, the distribution of the Ar density is opposite the distribution of the gas temperature. This is also expected because the downstream region is nearly isobaric and Ar is largely the majority species. This means that the gas mixture properties are not significantly influenced by the chemistry occurring. Furthermore, the influence of the substrate holder, causing a homogeneous gas temperature in its vicinity, can be clearly seen.

(iv) The radial distributions of H and SiH₃ are strongly influenced by surface loss at the side walls of the reactor. The profile for the H density is much narrower than for SiH₃, which can be attributed to the higher diffusivity of H. For species with a considerable surface loss probability, a larger diffusivity causes a larger gradient length. Or, in other words, it affects densities up to a larger distance from the wall. In axial direction, this effect is not observed as the density at the axis is not determined by diffusion but by convection in the beam with a velocity of hundreds of m/s. This is true up to positions close to the substrate holder, where transport to the substrate is finally taken over by diffusion.

(v) For the radial distribution of the H density, no significant influence of the substrate holder is observed for the three axial positions. For SiH₃, a hollow profile is observed at 11 cm due to the higher gas temperature at the axis, while at 3.6 cm from the substrate holder the density is more expanded in radial direction and nearly flat in the center. The latter is probably caused by the fact that the substrate holder influences the gas temperature at this position, leading to a more homogeneous temperature and SiH₃ density. For 0.6 cm, this effect is even more pronounced.

(vi) A comparison of the simulated radial distribution of SiH₃ with the experimentally determined distribution at 3.6 cm from the substrate holder, reveals some distinct differences. The simulated profile is nearly flat in the center while the Abel inverted experimental profile is hollow. Hollow profiles are also observed in the simulated data, but only at a larger distance from the substrate holder (e.g., at 11 cm) and much less pronounced. Leaving the accuracy of the radial density profile as deduced by Abel inversion out of consideration for the moment, this might suggest that in the experiment the gas temperature at 3.6 cm is not yet influenced significantly by the substrate holder. Such a difference might be caused by a too large heat conductivity of the gas mixture in the simulations. Diffusion is, however, accurately taken into account in the simulations by the Stefan–Maxwell diffusion model. Furthermore, the heat conductivity depends on the composition of the plasma, but a slightly different composition and the presence of other minority species (radicals, ions, electrons) cannot explain the difference. To reduce the computational effort, thermal diffusion has not been included for the results presented, but it has been verified that the inclusion of this effect (on the basis of the rigid spheres approximation) leads to differences smaller than 5%. Another striking difference, which is possibly related to the difference in radial profile at r = 0, is that the simulated profile is considerably broader than the experimental radial profile (note that its width is mainly determined by the absorption at y = 11 cm in Fig. 5). In this case, the thermal conductivity can also play a role: A lower thermal conductivity would create a smaller thermal gradient length at the wall leading to a higher gas temperature in the region between the axis and the wall and therefore to a higher diffusivity of SiH₃. This higher diffusivity causes a larger gradient length for the SiH₃ density and thus a narrower profile. The radial distribution of SiH₃ is furthermore influenced by the wall temperature, whereby a higher wall temperature leads to a somewhat narrower profile (again by higher diffusivity). This effect, however, cannot account for the full difference. Another possibility is that the SiH₃ density is affected by radical–radical reactions, which are not yet taken into account in the model, for example, by

\[
\text{SiH}_3 + \text{SiH}_3 \rightarrow \text{SiH}_2 + \text{SiH}_4.
\]

For the SiH₃ densities presented, the reaction time of SiH₃ for this reaction is typically several milliseconds, meaning that reaction (7) can become very important in the recirculation zone where the diffusivity and the gas flow velocity is rather low.

(vii) An interesting question is how SiH₃ radicals from the center of the beam reach the side wall of the reactor. The radicals can either diffuse directly over the total radius of the setup or diffuse to the recirculating flow in the vortex [see Fig. 4(d)]. Here, by following the streamlines, they can be transported by convection to the region close to the wall, which they can finally reach by diffusion. On the basis of calculations of the diffusion time and the velocity of the recirculating flow, direct diffusion seems to be most important. This is in agreement with the fact that the profile of the SiH₃ density increases in width when going from 11 cm to 3.6 and 0.6 cm from the substrate holder.

(viii) In terms of (line-integrated) SiH₃ density, a better agreement with the experimental data is obtained for \(\alpha=5\%\). For this value, the line-integrated density is roughly equal to the experimental one while for \(\alpha=2\%\) it is a factor of \(~2.5\) smaller. This comparison relies strongly on the absorption cross section of SiH₃, which is quoted as an approximate value. A factor of 2.5 higher dissociation degree for H₂ in the a-Si:H deposition setup is not inconceivable on the basis of the aforementioned differences in setup and conditions. Moreover, the experimental accuracy of the TALIF measurements and the assumptions in the model are of concern. A higher rate for reaction (1) has however no influence, because the amount of H is almost fully consumed by this reaction. Furthermore, \(\alpha=5\%\) also yields better agreement in SiH₄ consumption. For 10 sccs SiH₄, the experimentally obtained SiH₄ consumption is \(~10\%–12\%\), while if all H is consumed by reaction (1) it is 10% for \(\alpha=5\%). In the simu-
absorption for of the experimental data is involved. In Fig. 5, the calculated only solid comparison that can be made as no interpretation sorptions'' with the experimental values. This is actually the ~

Eq. 6

axis at low SiH4 flows than for 10 sccs SiH4 in Fig. 5. In Fig. lateral absorption profiles show a somewhat larger dip at the is in agreement with the earlier mentioned indication that the radial distribution of SiH3 is dependent on the SiH4 flow: At low SiH4 flows a hollow profile is obtained (for 1 sccs SiH4, the density in center is reduced by ~25% of its maximum value), while at high SiH4 flows the profile is flat in the center. This is in agreement with the earlier mentioned indication that the lateral absorption profiles show a somewhat larger dip at the axis at low SiH4 flows than for 10 sccs SiH4 in Fig. 5. In Fig. 10, the calculated absorption at 11, 3.6, and 0.6 cm is given as a function of the SiH4 flow. The experimental values at 3.6 cm are given for comparison. The simulated “absorption” at 11 cm is smaller than at positions closer to the substrate holder, whereas the absorption at 3.6 and 0.6 cm are nearly identical. This behavior is in fairly good agreement with the experiments (see Fig. 7) and it shows that especially between 11 and 3.6 cm there is still a considerable production of SiH3 by reaction (1). The dependence of the absorption on the SiH4 flow is also in rough agreement, although the calculated absorption shows a steeper increase at low SiH4 flows and shows a clear saturation at high SiH4 flows. For the experiments this behavior is less apparent. In the simulations, the saturation is due to the fact that almost all H is consumed by reaction (1) at high SiH4 flows. This effect might also explain the fact that the SiH3 density in Fig. 7 and in Ref. 7, as well as the SiH4 consumption in Ref. 7, flatten off for high SiH4 flows. Apart from some other marginal phenomena (e.g., ion–molecule reactions), this means that the SiH4 consumption and SiH3 production in the ETP technique are limited by the amount of H available for the present plasma settings.

C. Comparison with mass spectrometry

Now that insight has been obtained in the radial distribution of SiH3, it is possible to make a comparison of the SiH3 densities obtained from CRDS with those obtained by TIMS. TIMS has revealed the axial (r=0) SiH3 density close to the substrate holder (mass spectrometer). For a quantitative comparison, we need to know the SiH3 density at this position from the CRDS measurements. The absorption by SiH3 at a distance of 0.6 cm from the substrate holder has been determined; however at this position no experimental information on the radial distribution is present. Two approaches can be followed to estimate the axial SiH3 density at this position. First, the axial density at 3.6 cm from the substrate holder as given in Fig. 7 can be used by assuming that the absolute magnitude of this density is not affected severely when coming closer to the substrate. This assumption seems reasonable on the basis of the simulated data in Fig. 8, where the SiH3 density decreases only slightly just in front of the substrate holder. In the second approach, the radial density profile at 3.6 cm from the substrate holder can be taken, whereby it is assumed that when coming closer to the substrate the dip in density (which is presumably due to the gas temperature) diminishes or disappears. The latter is reasonable on the basis of the fact that very close to the substrate holder, the gas temperature is dictated by the substrate holder as also shown in the simulations (albeit up to a larger distance from the substrate holder). The SiH3 density very close to the substrate holder is therefore expected to level out due to the homogeneous gas temperature. It is estimated that this leads to a rather homogeneous SiH3 density over the area of the substrate holder, which is almost a factor of 2 larger than the axial density at 3.6 cm in Fig. 7. This method is less sensitive for the actual depth of the dip in Fig. 6 obtained from the Abel inversion.

For both approaches, the axial SiH3 density from the CRDS measurements close to the substrate is given in Fig. 11 as a function of the density estimated by TIMS. The densities show a very good correlation, also in absolute magnitude. This is especially true for the first approach, whereas the expectedly more realistic second approach also gives a fairly good agreement when considering the accuracy of the calibration procedure for the TIMS measurements. In any case, a quantitative agreement within a factor of 2–3 is observed. Finally it is noted that in this comparison it is assumed that the radial distribution of SiH3 does not depend on the SiH4 flow. A somewhat more hollow profile for low SiH4
more, the axial SiH₃ density in front of the substrate holder determined by TIMS shows good agreement with the SiH₃ density obtained by CRDS and the simulated density at this position. The quantitative agreement depends again on the absorption cross section, the radial distribution of SiH₃ just in front of the mass spectrometer, as well as on the accuracy of calibration procedure of the mass spectrometry measurements. Nevertheless, an agreement within a factor of 2–3 is obtained.

All together, cavity ring down spectroscopy, mass spectrometry, and the simulations reveal identical SiH₃ densities within approximately a factor of 2–3. For the condition with 10 sccs SiH₄, a SiH₃ density of 4–8 × 10¹⁸ m⁻³ is obtained in front of the substrate holder. With reasonable assumptions for the sticking probability of SiH₃ (0.1–0.3)⁶ and its thermal velocity, this density can explain the a-Si:H deposition rate of ~7 nm/s obtained under this plasma setting.⁹ Furthermore, it should be noted that a possibly inhomogeneous radial SiH₃ density due to a spatial distribution in gas temperature is partly compensated by this temperature when the homogeneity of the deposition flux or deposition rate is considered.

The absorption determined from the line-integrated, simulated SiH₃ density shows roughly the same dependence on the SiH₄ flow as the experimental values. The calculated absorption saturates at high SiH₄ flows due to full consumption of H. An almost full consumption of H is therefore most probably also the reason why the measured SiH₃ density and SiH₄ consumption flatten off at large SiH₄ flows. It shows that the rate for H reacting with SiH₄ is fast enough to consume all H and that at high SiH₄ flows the amount of H available is the limiting factor for SiH₄ dissociation in the expanding thermal plasma.

In summary, the spatially resolved CRDS measurements and the fluid dynamics model with only the basic chemical reactions have revealed more insight into the plasma and surface reactions and the gas flow dynamics during a-Si:H deposition. The model has also proven to be very helpful in the interpretation of the experimental data while the experiments yield a test of the basic assumptions of the model. In future work, both the model and experimental information will be extended.

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The gradient length is defined as \( n / \nabla n \) with \( \nabla n \) the gradient of the density \( n \) in the direction considered. Using Milne’s boundary condition (see Ref. 26) the gradient length due to surface loss can be calculated by \( n / \nabla n = 4D(1 - \frac{1}{2} \beta) / \nu \beta \) with \( D \) the diffusion coefficient, \( \nu \) the thermal velocity, and \( \beta \) the surface reaction probability.

