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Film growth precursors in a remote SiH_4 plasma used for high-rate deposition of hydrogenated amorphous silicon

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The SiH_4 dissociation products and their contribution to hydrogenated amorphous silicon (*a*-Si:H) film growth have been investigated in a remote Ar–H_2–SiH_4 plasma which is capable of depositing device-quality *a*-Si:H at 10 nm/s. SiH_3 radicals have been detected by means of threshold ionization mass spectrometry for different fractions of H_2 in the Ar–H_2-operated plasma source. It is shown that at high-H_2 flows, SiH_4 dissociation is dominated by hydrogen abstraction and that SiH_3 contributes dominantly to film growth. At low-H_2 flows, a significant amount of very reactive silane radicals, $SiH_x (x \leqslant 2)$, is produced, as concluded from threshold ionization mass spectrometry on SiH_2 and optical emission spectroscopy on excited SiH and Si. These radicals are created by dissociative recombination reactions of silane ions with electrons and they, or their products after reacting with SiH_4, make a large contribution to film growth at low-H_2 flows. This is corroborated by the overall surface reaction probability which decreases from ~0.5 to ~0.3 with increasing H_2 fraction. The film properties improve with increasing H_2 flow and device-quality *a*-Si:H is obtained at high H_2 fractions where SiH_3 dominates film growth. Furthermore, it is shown that at high-H_2 flows the contribution of SiH_3 is independent of the SiH_4 flow while the deposition rate varies over one order of magnitude. © *2000 American Vacuum Society.* [S0734-2101(00)08005-2]

I. INTRODUCTION

The increasing demand for clean energy sources has initiated a lot of research on hydrogenated amorphous-silicon (*a*-Si:H) and its application in thin-film solar cells. To increase their competitiveness with conventional energy sources, the work in this field is mainly focused on increasing the solar cells' (stable) efficiency, the application of new low-cost materials, and the improvement of the production processes, which should all be compatible with large-area deposition and a high throughput. In this respect, one of the central questions is whether it is possible to deposit *a*-Si:H suitable for the application in thin solar cells at high growth rates (preferably$>$1 nm/s). Several investigations have already addressed this question,[1–10] and recently it was shown that device-quality *a*-Si:H can be obtained even at a rate of 10 nm/s with the expanding thermal plasma.[11,12] This technique combines a high-pressure thermal plasma source with a low-pressure deposition chamber and is, therefore, a real remote plasma. The *a*-Si:H obtained has some remarkable properties, such as an enhanced hole drift mobility, and the good film quality is confirmed by the results on the first, not yet optimized, solar cells which contained intrinsic *a*-Si:H deposited at a rate of 7 nm/s.[11,12]

To have insight into the conditions under which good-quality *a*-Si:H can be obtained at high-deposition rates and what are the limitations, the reactions in the plasma and at the film surface are studied for the expanding thermal plasma. It yields a better understanding of the deposition process of *a*-Si:H and the resulting film properties, which enables further process and film quality optimization. This knowledge is also of importance for other (low-deposition rate) SiH_4 plasmas, and it can yield insight into how to increase the growth rate in these plasmas while maintaining good film quality.

This article, which is part of a project aiming at a good understanding of the plasma processes and film growth in the expanding thermal plasma, deals with the plasma chemistry which has already been addressed globally in previous work.[13] Here, the dissociation reactions of SiH_4 are considered in more detail and information on the contribution of the specific reaction products to film growth is obtained from applying several plasma diagnostics. This is done for different plasma conditions and the results are related to the obtained film properties, which are presented in detail in another article.[14] It is focused on the silane radicals ($SiH_x, x \leqslant 3$) because an extensive investigation of the ion chemistry showed that the contribution of $Si_nH_m^+$ ions is less than 10%, in terms of Si atoms deposited, for all conditions.[15,16] The contribution of the different radicals is expected to have important implications for the film quality because the film properties are strongly dependent on the plasma parameters while the contribution of the ions remains about constant. The radicals are studied by a combination of diagnostics, such as threshold ionization mass spectrometry, optical emission spectroscopy, and aperture–well experiments, which have been applied to two parameter studies: the variation of the plasma source operation by changing the H_2 flow in the source and the variation of the downstream SiH_4 density.

II. EXPERIMENT

A. Deposition setup and plasma source operation

The deposition setup is depicted schematically in Fig. 1 and it consists of a cascaded arc plasma source and a depo-

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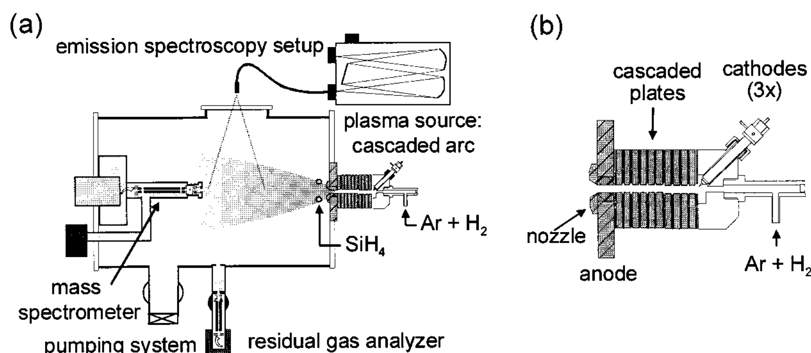

FIG. 1. (a) Schematic of the expanding thermal plasma and plasma diagnostics. The mass spectrometer is located at the usual position of the substrate holder. (b) The cascaded arc plasma source.

sition chamber. In the latter, SiH_4 is injected where it is dissociated by the reactive species emanating from the Ar–H_2-operated plasma source. The deposition setup and cascaded arc are described in detail in Refs. 16 and 17, respectively, and the conditions for the plasmas studied in this article are listed in Table I. Here, only the characteristics of the plasma emanating from the plasma source will be described briefly for its different operation conditions and some striking differences between the expanding thermal plasma and conventional deposition plasmas will be given.

The cascaded arc is a thermal plasma source and it is operated on a mixture of Ar and H_2, at high pressure and high gas flows [expressed in standard cubic centimeters per second (sccs)]. In the source, there is typically an electron density $n_e = \sim 10^{22}\,\mathrm{m}^{-3}$ and an electron and heavy-particle temperature $T_e = T_h = \sim 1$ eV.[17] The pressure in the deposition chamber is kept low (~0.20 mbar) by means of roots blowers with a high pumping capacity. Therefore, the plasma expands from the cascaded arc into the deposition chamber. Operated on pure Ar, the downstream plasma has a high electron density and relatively low electron temperature: both Thomson-scattering experiments as well as Langmuir-probe measurements have revealed $n_e = \sim 10^{19}\,\mathrm{m}^{-3}$ and $T_e = \sim 0.3$ eV for the presented conditions.[16,18] The dissociation of SiH_4 by electron processes is, therefore, negligible in comparison with dissociation reactions by reactive ionic and atomic particles. When the source is operated on pure Ar this is mainly by Ar^+.

When H_2 is admixed to the Ar in the arc, n_e in the downstream region is drastically reduced (a factor of 40 going from 0 to 10 sccs H_2) due to associative charge transfer reactions between Ar^+ and H_2 followed by dissociative recombination with electrons.[13,16,19,20] T_e decreases to 0.1–0.2 eV (Refs. 16 and 20) and the dominant ion in the downstream region changes to H^+.[16] Furthermore, the H_2 in the cascaded arc is effectively dissociated due to the high gas temperature (~1 eV) in the plasma source.[21] Consequently, for a considerable fraction of H_2, the cascaded arc acts predominantly as an atomic hydrogen source.

For different H_2 fractions, the total ion flow emanating from the arc has been determined by radial Langmuir-probe measurements just after the arc exit. It revealed an ion fluence of almost 3 sccs for a pure Ar plasma and 0.07 sccs for a plasma with 10 sccs H_2.[13,16] The amount of H in the downstream region has been quantified by means of two-photon-absorption laser-induced fluorescence (TALIF) under similar conditions in a different reactor.[22] The determination of the total fluence of H available for SiH_4 dissociation from these measurements is more complicated. Although it is expected that the H_2 in the cascaded arc is nearly fully dissociated, it has been shown that a significant amount of H is lost by recombination in the nozzle of the plasma source and by fast radial escape of H from the shock. The forward flow of H has been estimated at roughly 1–2 sccs for an injected H_2 flow of 10 sccs.[22]

Apart from the fact that SiH_4 is not dissociated by electrons, other important differences with conventional plasma deposition techniques are the low energy that ions gain in the plasma sheath (~1–2 eV) and the relatively high gas temperature [1000–1500 K (Refs. 23 and 24)]. The low ion energy is a consequence of the low T_e and it saves the deposited films from severe ion bombardment (additional ion energy can be obtained by applying an external rf bias on the substrate). The high gas temperature is due to the fact that the plasma is thermal in origin.

TABLE I. Setup conditions of the expanding thermal plasma for high-rate deposition of a-Si:H.

Ar flow	55 sccs
H_2 flow	0–15 sccs
Arc current	45 A
Arc voltage	70–140 V
Arc pressure	~400 mbar
SiH_4 flow	1–20 sccs
Downstream pressure	0.18–0.20 mbar

B. Threshold ionization mass spectrometry

The substrate holder has been replaced by a mass spectrometer (see Fig. 1) to analyze the flux of radicals towards the substrate. The mass spectrometer, with a similar geometry as the substrate holder, is a modified version (PSM Upgrade) of the Hiden Analytical EPIC 300, which suffered from detection of plasma photons because its detector was in direct line of sight with the plasma source.[16] In the upgrade, the detector is blocked from photons from the source by adding a Bessel-box type of energy analyzer. Gas extraction

takes place by a knife-edged extraction orifice with a diameter and thickness of 50 μm. This leads to an effusive flow of the plasma species in the mass spectrometer, which is differentially pumped by a 56 l/s turbopump. During plasma operation with a typical pressure of 0.20 mbar, the pressure in the mass spectrometer is within the range $7\times10^{-7}-10^{-6}$ mbar. The ionizer region with the filament is located at about 24 mm from the extraction orifice. The linear filament is made of thoriated iridium and yields a high electron emission current I_e at relatively low temperatures: I_e is actively controlled at 50 μA, corresponding with a filament temperature of about 1800 K. Behind the ionizer the Bessel box is located, which is followed by the mass filter (with rf-driven pre- and postfilter) and channeltron (DeTech 415).

To distinguish ionization of radicals in the mass spectrometer from dissociative ionization of SiH_4 the threshold ionization or appearance potential method has been used. This method is described in detail in the literature.[25,26] Briefly, the energy of the electrons emitted by the filament is scanned in the vicinity of the ionization potential of the radical of interest, while monitoring the intensity at its mass-over-charge ratio. At electron energies E higher than the ionization potential E_i of the radical but lower than the potential for dissociative ionization of the parent molecule into the specific ionic channel (appearance potential E_a), the measured intensity $I(E)$ is a measure for the radical density n in the plasma:

$$I(E)=\alpha I_e\sigma(E)n, \quad \text{with } E_i<E<E_a, \tag{1}$$

with $\sigma(E)$ the cross section for ionization and α a geometry and mass-dependent proportionality constant. The measured radical intensity is corrected for the contribution by pyrolysis, i.e., thermal decomposition, of SiH_4 on the filament by subtracting the signal at $E<E_a$ obtained for the "plasma off" condition. Herein, differences in the SiH_4 signal at $E\gg E_a$ during "plasma on" and "plasma off" (due to SiH_4 consumption and/or gas temperature effects) are taken into account.[27]

Quantification of the radical density takes place by linking the radical intensity to the measured intensity of the parent SiH_4 molecule at $E\gg E_a$.[25,26] The latter can directly be related to the known partial pressure of SiH_4 during "plasma off." In this method, besides the difference in cross sections for electron-induced ionization of the radical and parent molecule (at the appropriate electron energies), also the difference in surface reactivity should be taken into account. SiH_4 is not reactive and will lead to a residual partial pressure in the mass spectrometer, whereas silane radicals are rather reactive[28] and are easily lost on their way to and in the ionizer. Therefore, practically only SiH_x radicals in the beam of the effusive flux that reaches the ionizer without wall collisions (determined by the acceptance angle) contribute to the SiH_x intensity (beam component), whereas the measured intensity for SiH_4 has both a beam and residual density component. This difference can be taken into account by a correction factor C that can be estimated from the density n_{beam} of SiH_4 in the beam originating directly from the extraction orifice and the density n_{res} of residual SiH_4 at the position of the ionizer:

$$C=\frac{n_{beam}+n_{res}}{n_{beam}}. \tag{2}$$

For a SiH_4 density n and a thermal velocity v in front of the extraction orifice with area A, these densities in the ionizer at a position l from the extraction orifice are given by[29]

$$n_{beam}=\frac{nA}{4\pi l^2} \quad \text{and} \quad n_{res}=\frac{\frac{1}{4}nvA}{S}, \tag{3}$$

where S is the pumping speed for SiH_4 at the position of the ionizer. For the present setup, this yields $C\approx35$ when using $S=56$ l/s. This high value of C means that the residual SiH_4 density in the ionizer is much higher than the density of SiH_4 in the beam directly originating from the extraction orifice. The residual gas density in the ionizer can be reduced by applying double partial pumping as done by Kae-Nune *et al.*[26] Furthermore, our case differs from the one described by Singh, Coburn, and Graves[30] by the fact that for silane radicals the surface loss probability is much higher than for the radicals studied in their work.

In this procedure it is important that the emission current I_e is independent of electron energy E. This requires that I_e is controlled at rather low currents because at higher currents space charge can easily build up around the filament for low-E values, as described by the Child–Langmuir law. This can cause I_e to deviate considerably from the demanded I_e and to depend on E. This effect has experimentally been investigated yielding that for $I_e=50\,\mu$A the influence of space charge is negligible down to $E=5$ eV.

Furthermore, space-charge effects, as well as the thermal energy distribution of emitted electrons, the potential drop along the filament, and contact and surface potentials of the electrodes, lead also to an electron energy which is not purely monoenergetic. This causes an apparent onset of the signal below the ionization potential and troubles the determination of the ionization potential and/or calibration of the electron energy scale. For the Hiden system the half width at half maximum value is estimated to be within 0.5 eV. The electron energy scale has been calibrated by means of the ionization potential of noble gases and applying the commonly used linear extrapolation method.[31] This revealed that the electron energies are ~1.4 eV lower than indicated by the energy scale.

C. Emission spectroscopy

Emission spectroscopy has been applied to monitor the emission by excited SiH and Si radicals. For SiH the $A^2\Delta-X^2\Pi$ electronic transition band at around 414 nm has been analyzed and for Si I the $4s^1P^0-3p^{21}S$ transition at 390.6 nm. The emission spectroscopy setup is a modified version of the one described in Ref. 32, which dealt with measurements under less relevant plasma conditions in terms of resulting *a*-Si:H quality. By means of a high-grade fused-

silica fiber (Oriel 77532), the total (i.e., nonlocal) emission by the plasma in the region from the substrate to ~20 cm upstream has been collected and focused on a Czerny–Turner monochromator (Jobin–Yvon HR 640) with a focal length of 640 mm and a dispersion of 1 nm/mm. The entrance slit used is 250 μm and a charge-coupled-device camera (SBIG ST-6 Optohead), recording a wavelength range of ~11 nm, has been used as the detector.

Emission by Ar in a pure Ar plasma is used as a reference to correct for reduced transmission due to deposition on the spectroscopic window. Furthermore, the integration time is chosen such that the correction for this reduced transmission is rather constant for the different plasma conditions. Moreover, the reactor is cleaned by means of an Ar–CF_4 plasma after every measurement.

Only nonlocal and relative measurements of the emission intensity have been performed, and from fitting simulations of the SiH emission spectrum to the experimental data the vibrational and rotational temperatures of the excited radical have been extracted. This technique, explored by Perrin and Delafosse,[33] is applied by using an improved version of the program described in Ref. 32.

D. Other diagnostics

The other diagnostics will be presented only briefly as they are described extensively in previous articles. The depletion or net consumption of SiH_4 for the different plasma conditions has been determined by a residual gas analyzer (Balzers Prisma QMS 200) located at the side of the deposition chamber. The difference in the measured signal I due to SiH_4 (at $m/e=28-32$) when the plasma is on and off can be attributed completely to the consumption of SiH_4.[13] The equivalent flow of SiH_4 that is consumed by the plasma $\Phi_{SiH_4,cons}$, is calculated by multiplying the fraction of SiH_4 that is consumed with the initial SiH_4 flow Φ_{SiH_4}:

$$\Phi_{SiH_4,cons}=\left(\frac{I_{off}-I_{on}}{I_{off}}\right)\Phi_{SiH_4}. \quad (4)$$

The overall surface reaction probability of the species contributing to growth has been determined from so-called ''aperture–well'' experiments.[28,34] This technique uses a well, created by two substrates, in which reactive particles from the plasma entering through a small slit in the upper substrate are trapped. From the distribution of amount of film deposited on both substrates an overall surface reaction probability β_0 can be calculated, which depends on the relative fluxes of the reactive species entering the well and their particular surface reaction probability β. More information can be found in Ref. 28.

III. RESULTS

A. H_2 flow series

In this section, the dissociation of SiH_4 is considered for different operating regimes of the cascaded arc as presented in Sec. II A. The SiH_4 flow is kept fixed at 10 sccs. The net consumed SiH_4 flow is given in Fig. 2 as a function of the H_2 flow in the cascaded arc. For zero H_2 flow, the SiH_4 consumption is very large (~60%). This can be attributed to ion-induced reactions as mainly Ar^+ emanates from the plasma source. For increasing the H_2 admixture the SiH_4 consumption first decreases due to decreasing ion fluence while for H_2 flows >3 sccs the reactions with H take over. From that point, the SiH_4 consumption increases slightly due to an increasing H flow from the arc. Apparently, the consumption of SiH_4 for the H-dominated region is lower than for the ion-dominated region. In Fig. 2, also the corresponding deposition rate for a substrate temperature of 400 °C is given. From the fact that the deposition rate (when corrected for the Si atomic film density) scales very well with the consumption of SiH_4, it can be concluded that the consumed SiH_4 is mostly converted into a-Si:H and not into polysilanes, as also corroborated by the small fraction of Si_2H_6 and Si_3H_8 observed.[13,16]

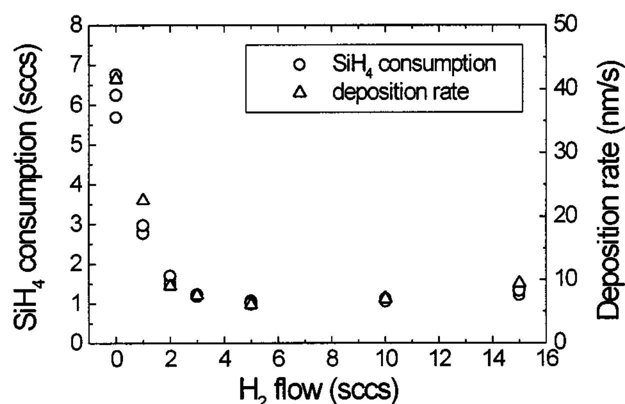

FIG. 2. Consumption of SiH_4 expressed in equivalent flow as a function of H_2 admixture in the cascaded arc. The SiH_4 flow is 10 sccs. The corresponding deposition rate for a substrate temperature of 400 °C is given on the right axis.

At high-H_2 flows, it is expected that mainly SiH_3 will be created as the reaction of H with SiH_4 leads to hydrogen abstraction of SiH_4:

$$H+SiH_4\rightarrow SiH_3+H_2. \quad (5)$$

The rate of this reaction is given by $1.8\times10^{-16}\times\exp(-1925/T)$ $m^3\,s^{-1}$ for a gas temperature T (in K) in the range 290–660 K, while at higher temperatures rates higher than predicted from this relation have been proposed.[35] Therefore, SiH_3 has been measured by threshold ionization mass spectrometry. An electron energy scan at $m/e=31$ corresponding with the SiH_3^+ ion is given in Fig. 3. The used integration time per step in E is 1.5 s. At low values of E a hump due to direct ionization of SiH_3 can clearly be seen, while at higher energies the signal due to dissociative ionization of SiH_4 comes up. The depicted electron energy scale is not rescaled, and the too high ionization and appearance potential of SiH_3 and SiH_4 are in fair agreement with the shift of +1.4 eV obtained from the calibration procedure. For high E, the signal for ''plasma on'' is normalized to the one

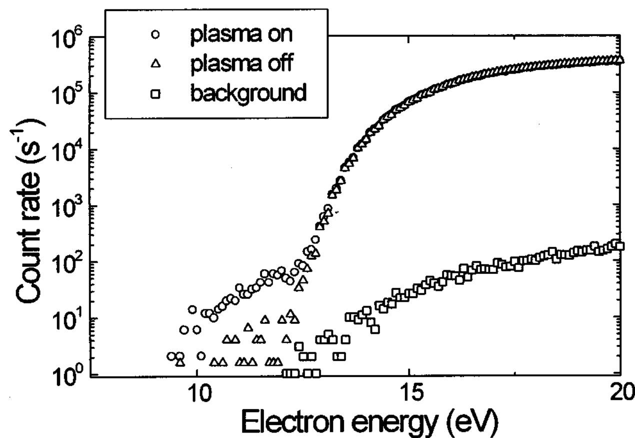

FIG. 3. Electron energy scan at $m/e=31$ for determination of the SiH_3 density. The values for ''plasma off'' are normalized to those of ''plasma on'' at high electron energies. Both the H_2 and SiH_4 flows are 10 sccs. The background signal, obtained with SiH_4 flow=0 sccs, is due to an (unknown) contaminant in the mass spectrometer.

for ''plasma off'' such that the signal for ''plasma off'' due to pyrolysis (at $E<E_a$) can be subtracted directly from the radical signal.

The densities of SiH_3 obtained for different H_2 flows in the arc are given in Fig. 4(a). A complication arises from the fact that the gas extraction orifice becomes easily clogged due to the high-deposition rate. This is (partly) circumvented by monitoring a reference signal, but especially the SiH_3 measurements at very low H_2 flows, with deposition rates up to 60 nm/s, were cumbersome. The absolute values of the SiH_3 densities have been estimated by the method described in Sec. II B. The partial ionization cross sections of SiH_4 have been taken from Ref. 36. Information about ionization cross sections for SiH_x radicals has been only recently available from work by Tarnovsky, Deutsch, and Becker who determined ionization cross sections for SiD_x radicals.[37] The latter cross sections for SiD_3 and SiD_2 radicals at $E=10$ eV are, respectively, a factor of ~4 smaller and ~2 larger than those estimated by Kae-Nune *et al.*[26] from ionization cross sections of CD_x radicals.[38,39] We note that the absolute scale of the SiH_3 density in Fig. 4(a) has a considerable uncertainty, mainly due to the uncertainty of S (and, consequently, C) for SiH_4 at the position of the ionizer.

The SiH_3 density shows a steep decrease going from zero to a small H_2 flow, followed by a gradual increase for higher flows. The latter is in agreement with an increasing flow of H from the cascaded arc. For the interpretation of the SiH_3 density at low-H_2 flows, it is important to realize that at these flows much more SiH_4 is consumed. The SiH_3 density at 0 sccs H_2 is about equal to the one at 15 sccs H_2, yet the net consumed SiH_4 flow is at least a factor of 4 higher. It is, therefore, better to consider the contribution of SiH_3 to film growth. Determination of the absolute value of the contribution from the densities[26] in Fig. 4(a) is, however, cumbersome. First, there are uncertainties in the absolute density itself. Second, estimations on the thermal velocity v and sticking probability s of SiH_3 are required, where especially s

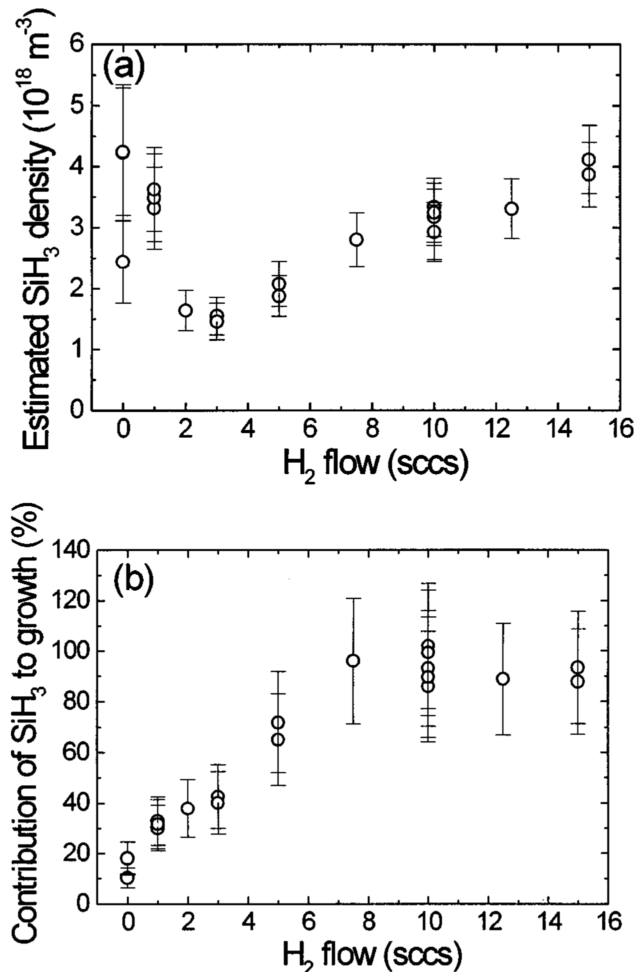

FIG. 4. (a) SiH_3 density obtained from threshold ionization mass spectrometry and (b) contribution of SiH_3 to a-Si:H film growth as a function of H_2 flow (SiH_4 flow is 10 sccs).

is not accurately known within a factor of 2. Therefore, another method is proposed which is, in our opinion, more reliable. However, not generally applicable: as the increase of the H_2 flow from 10 to 15 sccs leads only to more H from the arc (the ion flow slightly decreases[16]), it is plausible that the *increase* in SiH_4 consumption and a-Si:H deposition rate between 10 and 15 sccs (see Fig. 2) is completely due to a higher SiH_3 density. Linking the increase in deposition rate to the increase in SiH_3 signal, a direct relation between the SiH_3 signal and the deposition rate is obtained, from which the contribution of SiH_3 to film growth, as given in Fig. 4(b), can be calculated. The absolute value of the presented contribution relies, of course, fully on the above assumption with respect to the increase in deposition rate between 10 and 15 sccs H_2. However, as will be shown below, this assumption is also plausible on the basis of the other results with respect to the plasma chemistry and the surface reaction probability. It is, therefore, expected that the presented values of the absolute contribution are much more accurate than estimations on the basis of the SiH_3 density. We note however, that both methods yield the same relative dependence of the contribution of SiH_3 to film growth, while the absolute

values of the contributions in Fig. 4(b) are not in contradiction with those calculated from the SiH_3 densities in Fig. 4(a) when reasonable values for v and s of SiH_3 are applied. In Fig. 4(b) there is still some uncertainty in the exact contribution, mainly due to the fact that the deposition rate and SiH_3 density have been determined in different experiments, but it is clear that the contribution of SiH_3 increases with H_2 flow and saturates at higher H_2 flows (where it dominates film growth with a contribution of around 90%).

Figure 4(b) shows that at low-H_2 flows, other species than SiH_3 contribute significantly to film growth. As mentioned above, at these flows SiH_4 dissociation is governed by reactions induced by positive ions emanating from the plasma source. Ar^+ and H^+ can undergo dissociative charge transfer with SiH_4 leading to silane ions SiH_n^+ ($n \leqslant 3$, SiH_4^+ is unstable[40]):

$$Ar^+(H^+) + SiH_4 \rightarrow SiH_n^+ + pH_2 + qH + Ar \quad (n \leqslant 3). \quad (6)$$

The reported reaction rates $k_{ch.ex.}$ for Ar^+ are in the order of $10^{-16}\,m^3\,s^{-1}$ and at thermal energies mainly SiH_3^+ is created.[40] For H^+ only a rate for the reaction leading to SiH_3^+ has been proposed, which is equal to $5\times10^{-15}\,m^3\,s^{-1}$.[40] Silane ions initiate cationic cluster $Si_nH_m^+$ formation by sequential ion–molecule reactions with SiH_4.[15,16,41]

$$Si_nH_m^+ + SiH_4 \rightarrow Si_{n+1}H_p^+ + qH_2, \quad (7)$$

with rates $k_{ion-mol}$ estimated at $\sim10^{-16}\,m^3\,s^{-1}$. It has been shown that the contribution of the positive ions to film growth is less than 10% in terms of Si atoms deposited.[16] The previously used assumption that $s=1$ for these ions has recently been justified by molecular dynamics studies which yielded $s>0.85$ for all types of hydrogenated Si surfaces.[42] Remarkable is that the contribution of the ions is rather independent of the H_2 flow admixed in the arc, while the ion fluence from the arc is heavily dependent on this H_2 flow.[16] This can be understood from dissociative recombination reactions of silane ions with electrons:

$$SiH_n^+ + e \rightarrow SiH_m + pH + qH_2 \quad (n \leqslant 2), \quad (8)$$

with reaction rates k_{rec} in the order of $10^{-13}T_e^{-1/2}\,m^3\,s^{-1}$ (T_e in eV).[40] These reactions compete with the ion–molecule reactions (7), but as long as the product of the reaction rate for dissociative recombination and the electron density is much larger than the product of the reaction rate for ion–molecule reactions and the SiH_4 density, i.e., $k_{rec}n_e \gg k_{ion-mol}n_{SiH_4}$, dissociative recombination will prevail. This is certainly the case at low-H_2 flows where n_e is high[16] and dissociative recombination occurs almost instantaneously after reaction (6), leading to a significant production of radicals like SiH_2, SiH, and Si. The rather constant contribution of the cationic clusters is explained by the fact that the ion–molecule reactions can only get important when n_e is significantly reduced by reaction (8). For a SiH_4 density of $\sim10^{20}\,m^{-3}$ this is expected to occur at $n_e \approx 10^{17}\,m^{-3}$, which is roughly equal to the value of n_e at higher H_2 flows.

From reaction (6) and (8), the relatively high SiH_3 density at low-H_2 flows can also be understood. In both reactions, H

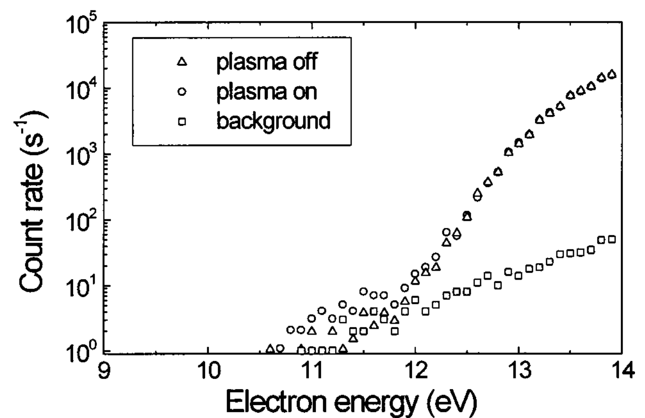

FIG. 5. Electron energy scan at $m/e=30$ for detection of SiH_2. The values for ''plasma off'' are normalized to those of ''plasma on'' at high electron energies. The H_2 flow is 0 sccs and the SiH_4 flow is 10 sccs. The background signal, obtained with SiH_4 flow=0 sccs, is due to a contaminant in the mass spectrometer.

can be generated which can subsequently react with SiH_4 creating SiH_3 [reaction (5)]. This can lead to a considerable density of SiH_3 under conditions where the SiH_4 consumption is high, and it explains the initial decrease of the SiH_3 density at low-H_2 flows. Another possible reaction that can generate SiH_3 from the reaction products of reaction (6) is

$$SiH_2^+ + SiH_4 \rightarrow SiH_3^+ + SiH_3. \quad (9)$$

On the basis of the aforementioned reasoning, this reaction with a rate of $\sim10^{-15}\,m^3\,s^{-1}$ (Ref. 40) will become as important as dissociative recombination when n_e is reduced to $\sim10^{18}\,m^{-3}$.

In order to measure the radicals created in reaction (8), threshold ionization mass spectrometry has been applied. SiH_2 radicals could only be detected for $H_2=0$ sccs, where the SiH_2 production is also expected to be at maximum. As shown in Fig. 5, the radical signal is rather weak (estimation of the SiH_2 density on the basis of the procedure described in Sec. II B yields $\sim10^{18}\,m^{-3}$ at 0 sccs H_2) and the SiH_2 density in front of the substrate holder is apparently too low for the measurements at nonzero H_2 flows. It should be noted that detection of SiH_2 is more complicated than the detection of SiH_3. First, SiH_2 has a higher surface reaction probability than SiH_3,[28] which can lead to a higher loss of SiH_2 during extraction from the plasma. Second, the difference between the ionization potential of SiH_2 and the appearance potential of $SiH_2{}^+$ from SiH_4 is smaller,[26] while at $m/e=30$ a strong residual signal due to contamination in the mass spectrometer appears at slightly lower electron energies than the appearance potential (see Fig. 5). This residual signal, which is not related to the SiH_4 flow, is measured in pure Ar. Although its origin is still unclear, NO^+ created by ionization of NO is a likely candidate. This radical, possibly created at the hot filament from residual N_2 and O_2, has an ionization potential around 10 eV.[43]

The presence of contamination together with a relatively low density in front of the mass spectrometer are probably

also the reasons why SiH and Si radicals could not be detected. The low radical densities can be due to a small production rate or to a large loss rate, e.g., by fast reactions with SiH_4 as will be addressed in Sec. IV. Furthermore, for the present setup the detection limit of the radicals is rather high due to the interfering high residual gas density in the mass spectrometer, as discussed in Sec. II B.

Although the reaction pathway proposed is not counter to the fact that SiH_2 has only been detected for 0 sccs H_2 and that SiH and Si could not be observed at all, optical emission spectroscopy has been applied to find more confirmation. The $A^2\Delta-X^2\Pi$ electronic transition band of SiH at ~414 nm and the Si I $4s^1P^0-3p^{21}S$ transition at 390.6 nm, represented, respectively, by SiH* and Si*, have been studied. Unlike conventional plasmas, T_e in the downstream region is too low for the creation of these electronically excited species by electron-induced excitation or dissociation to be significant. Accordingly, Si* and SiH* are mainly created by dissociative recombination of SiH_n^+ with electrons [reaction (8)], where enough energy is available for electronic excitation of the produced silane radicals. Therefore, it is believed that the emission of these excited species is an indication of the occurrence of reaction (8). Because of their fast radiative decay [radiative lifetime τ for Si I $4s^1P^0$ and SiH $A^2\Delta$ is, respectively, 4.1 and 534 ns (Ref. 44)], their emission is expected to be proportional to the number of recombination events. On the basis of this, the emission intensity per unit of time displayed in Fig. 6(a), reveals that more dissociative recombination takes place at low-H_2 flows when more ions emanate from the arc. The fact that both the SiH* and Si* emissions show the same dependence validates the assumption that a fixed percentage (i.e., independent of H_2 flow) of the reaction products in reaction (8) are SiH* and Si*. In Fig. 6(b), the emission intensity is corrected for the total amount of SiH_4 consumed showing that reactions (6) and (8) are relatively more important at low-H_2 flows, in agreement with the reaction pathway proposed.

The assumption that the emission by SiH* and Si* displays in fact the recombination of silane ions can roughly be validated by relating the emission intensity to the ion fluence from the arc. From stationary rate equations for reactions (6), (7), and (8) a local radiative decay rate for the excited species can be calculated:

$$\frac{n_{SiH_x^*}}{\tau}=\frac{n_{Ar^+/H^+}\, n_{SiH_4}k_{ch.ex.}}{n_e k_{rec}+n_{SiH_4}k_{ion-mol}}n_e k_{rec}, \tag{10}$$

where $n_{SiH_x^*}$ is the density of the excited species and n_{Ar^+/H^+} the density of Ar^+ and H^+ from the arc. At low H_2 flows the ion–molecule reactions (second term in the denominator) can be neglected compared to dissociative recombination which leads to a radiative decay rate linear in the Ar^+/H^+ ion density. Assuming a similar global behavior, it is expected that at low-H_2 flows the total radiative decay rate is linear in the ion fluence from the arc. This is indeed true for the emission intensity per unit of time (integrated over a large part of the downstream region), as can be seen in Fig. 7, where the slope of the fit in the double-log plot is almost equal to 1 (0.90).

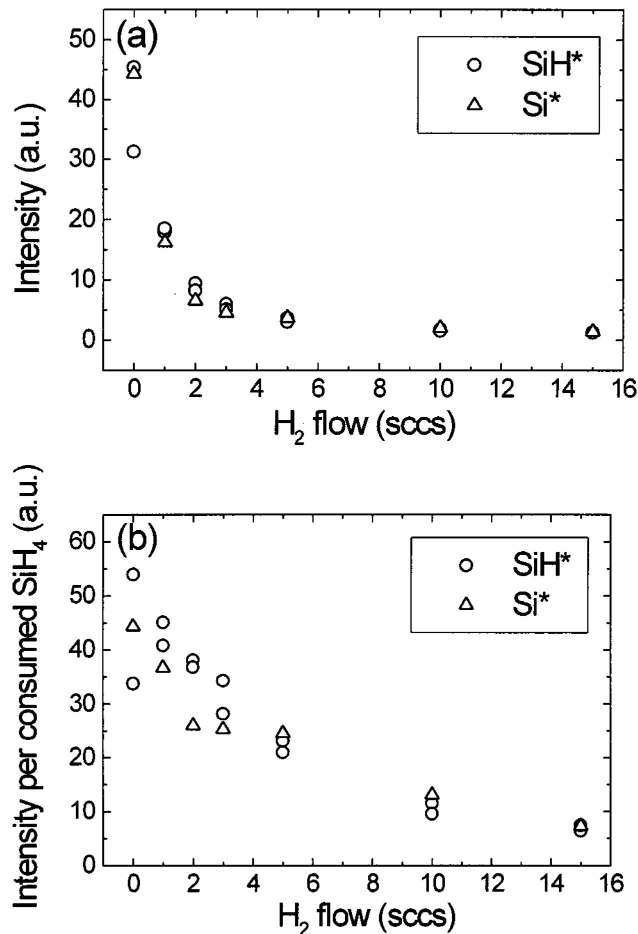

FIG. 6. (a) Emission intensity of SiH*($A^2\Delta-X^2\Pi$) and Si*($4s^1P^0-3p^{21}S$) per unit of time. The SiH_4 flow is 10 sccs. (b) Emission intensity divided by SiH_4 consumption (in arbitrary units).

The rotational and vibrational temperatures of the excited SiH radical are shown in Fig. 8 and do not show a clear dependence on the H_2 flow. This implies an excitation mechanism that is independent of the H_2 flow. The vibrational temperature is around 3000 K and the rotational temperature is between 1400 and 1500 K. The gas temperatures in the expanding thermal plasma are in the range 1000–1500 K.[23,24]

The increasing contribution of SiH_3 and the decreasing production of $SiH_x(x\leq 2)$ radicals for increasing H_2 flow are expected to affect the overall surface reaction probability β_0, which depends on the relative contribution of the different species and their surface reaction probability β. For SiH_3 the reported values of β are within the range 0.1–0.3, while for $SiH_x(x\leq 2)$, values in the range 0.6–1 have been reported.[28] This explains the decrease of β_0 with increasing H_2 flow, as shown in Fig. 9. Values of β_0 estimated on the basis of the presented contributions of SiH_3 and $Si_nH_m^+$ and the production of $SiH_x(x\leq 2)$ radicals are also given in Fig. 9. These values are obtained by the procedure described in

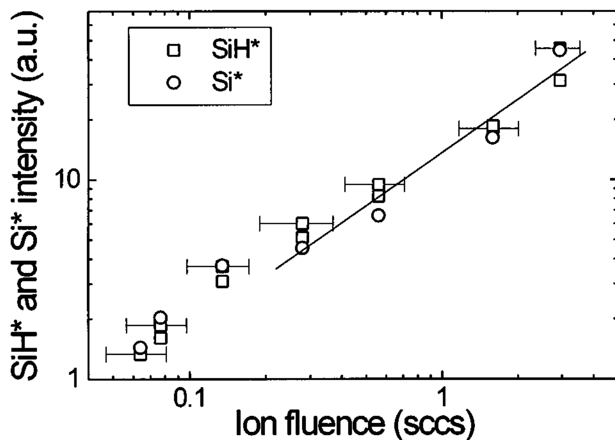

FIG. 7. Emission intensity of SiH* and Si* from Fig. 6(a) as a function of the ion fluence emanating from the arc. The line is a fit to the data points for H_2<5 sccs, where the ion–molecule reactions can be neglected compared to dissociative recombination reactions.

Ref. 28 using $s=\beta=0.28$ for SiH_3, $s=\beta=1$ for $Si_nH_m^+$, and $s=\beta=0.6$ for $SiH_x(x\leqslant 2)$, independent of the H_2 flow. The values from this simplified estimation show fairly good agreement. The rather low β, which needs to be assumed for $SiH_x(x\leqslant 2)$, can possibly be explained by the fact that these radicals are very reactive with SiH_4 and can have reacted to polysilane radicals (with possibly a lower β) before reaching the substrate (see Sec. IV).

B. SiH_4 flow series

The influence of the partial pressure of SiH_4 on the plasma processes has been studied by varying the SiH_4 flow while keeping the plasma source conditions fixed. The H_2 flow in the arc is set at 10 sccs because for this condition mainly H emanates from the source and the best a-Si:H film properties have been obtained.

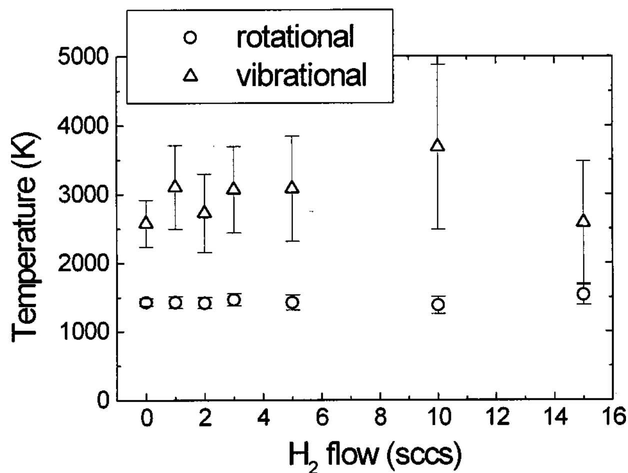

FIG. 8. Vibrational and rotational temperatures of SiH* obtained from the fit to the experimental spectrum of the $A^2\Delta-X^2\Pi$ transition. The SiH_4 flow is 10 sccs.

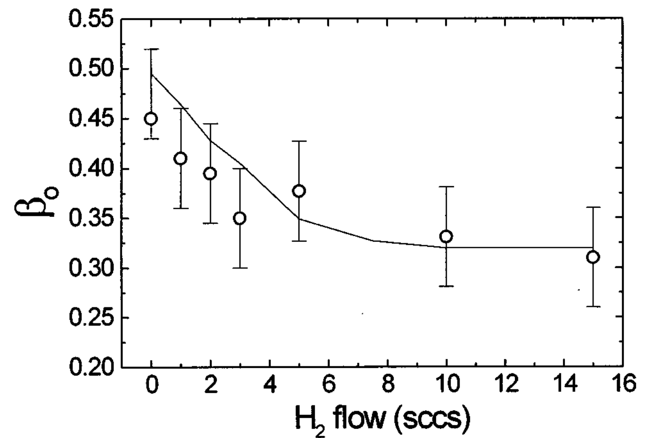

FIG. 9. Overall surface reaction probability β_0 as determined from aperture–well experiments for 10 sccs SiH_4 and varying H_2 flows. The line represents estimations of β_0 on the basis of the contributions of the different species to film growth. Further explanation is given in the text.

The consumed SiH_4 flow and corresponding deposition rate are given in Fig. 10. The SiH_4 consumption increases with SiH_4 flow and it can roughly be divided into two regions. Up to ~3 sccs the increase is steeper than at higher flows where the SiH_4 consumption increases only gradually with SiH_4 flow. It means that at low-SiH_4 flows a larger fraction of the SiH_4 is consumed than at higher flows. This behavior suggests that the amount of H available for SiH_4 dissociation is the limiting factor, whereas the total flow of SiH_4 consumed at high-SiH_4 flows is about equal to the forward flow of H as estimated from the TALIF measurements (see Sec. II A). It corroborates that a considerable amount of H from the cascaded arc is lost before it can dissociate SiH_4.[22]

In Fig. 11(a) the SiH_3 density is given, showing the same dependence on the SiH_4 flow as the SiH_4 consumption. Consequently, the contribution of SiH_3 to film growth, as shown in Fig. 11(b) and calculated by the method described in Sec. III A, is fairly constant for the different SiH_4 flows. This means that SiH_3 dominates film growth independent of the SiH_4 flow and for deposition rates ranging from 1 to 10 nm/s.

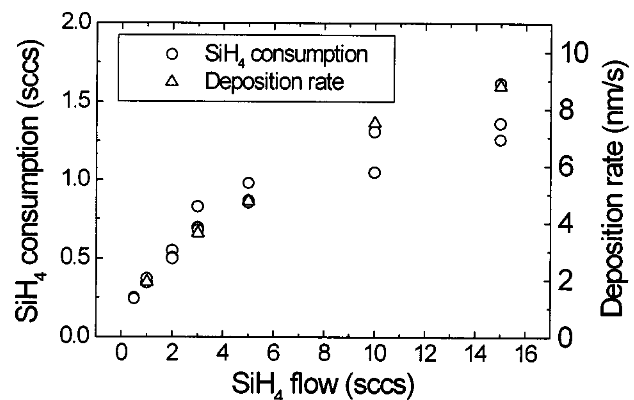

FIG. 10. Consumption of SiH_4 expressed in equivalent flow for constant H_2 flow (10 sccs) in the arc. The corresponding deposition rate for a substrate temperature of 400 °C is given on the right axis.

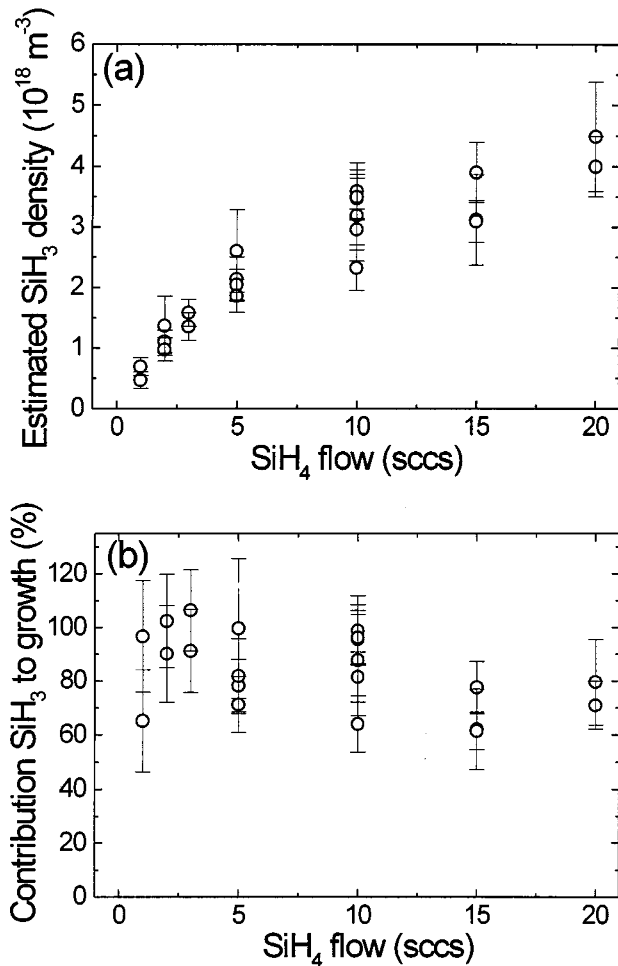

FIG. 11. (a) SiH_3 density obtained from threshold ionization mass spectrometry and (b) contribution of SiH_3 to a-Si:H film growth as a function of SiH_4 flow (H_2 flow is 10 sccs).

The rather constant contribution of SiH_3 has implications for reactions that affect the SiH_3 density. Hydrogen abstraction by H from SiH_3:

$$H + SiH_3 \rightarrow SiH_2 + H_2, \tag{11}$$

has a considerable reaction rate at 300 K ($2 \times 10^{-17}\, m^3\, s^{-1}$ [45]) in comparison with reaction (5), and the rate for the disproportion reaction between two SiH_3 radicals:

$$SiH_3 + SiH_3 \rightarrow SiH_2 + SiH_4, \tag{12}$$

is even higher [$\sim 10^{-16}\, m^3\, s^{-1}$ at 300 K (Refs. 40 and 45)]. These reactions lead to SiH_2 production, and especially reaction (12) can become very important at high-SiH_4 flows as it is quadratically dependent on the SiH_3 density. These reactions are apparently not very important, as they would lead to an increasing contribution of SiH_2, or its reaction products (polysilane radicals) with SiH_4, to film growth at the expense of the contribution of SiH_3. This is not obvious in Fig. 11(b).

The missing fraction of film growth in Fig. 11(b) takes place by positive ions and radicals other than SiH_3. As addressed in Refs. 15 and 16, the contribution of ions is almost

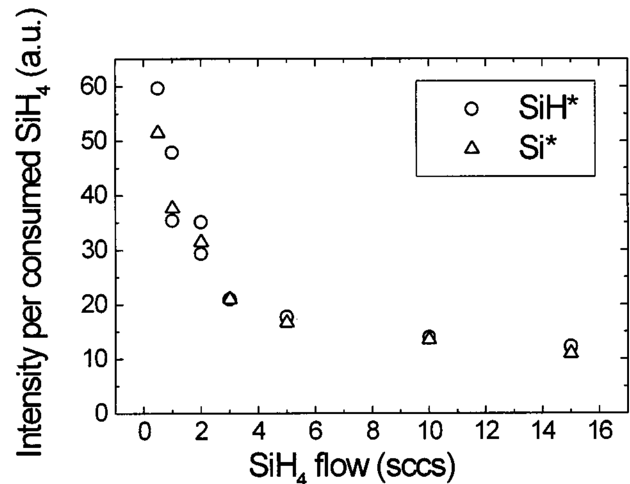

FIG. 12. Emission intensity of $SiH^*(A^2\Delta - X^2\Pi)$ and $Si^*(4s^1P^0 - 3p^{21}S)$ per unit of time and divided by SiH_4 consumption (in arbitrary units). H_2 flow is fixed at 10 sccs.

independent of the SiH_4 flow and less than 7%, while the average number of Si atoms per ion increases with SiH_4 flow. The ion size has implications for the products created by dissociative recombination of the ions. Although less frequent, recombination will still take place under this condition with relatively low n_e and it is expected that the rate for dissociative recombination of the ions with electrons does not heavily depend on the size of the ions.[16,40] At low-SiH_4 flows there are relatively more silane ions SiH_n^+ and their recombination leads to $SiH_x (x \leq 2)$ radicals (and, thus, to SiH^* and Si^*) while the recombination of the cationic clusters at larger SiH_4 flows most probably leads to larger neutral fragments. It is, therefore, expected that the emission of SiH^* and Si^* is relatively stronger at low-SiH_4 flows. This is indeed the case, as can be seen in Fig. 12, and it provides more evidence for the reaction pathway for cationic cluster formation proposed in Ref. 15. Furthermore, the rotational and vibrational temperatures of the excited SiH radical (not shown) do not show a clear dependence on the SiH_4 flow and are, respectively, about 1500 and 3000 K, as in Fig. 8.

IV. DISCUSSION

From the combination of the results obtained by the different diagnostics, the dissociation mechanisms of SiH_4 in the expanding thermal plasma are fairly well understood. For the H_2 flow series, it is convincingly shown that the contribution of SiH_3 increases with H_2 flow and becomes constant for H_2 flows $>$ 7.5 sccs. This is independent of the assumption used to determine the absolute contribution to film growth. The latter assumption, which leads to the conclusion that SiH_3 dominates the deposition process for high-H_2 flows with an estimated absolute contribution of around 90%, seems, however, very plausible and is corroborated by the value of the overall surface probability β_0 of $\sim$0.3 at high-H_2 flows. The absolute SiH_3 density in Fig. 4(a) can fully account for the presented contribution of SiH_3 to film growth, but the calculation of the contribution of SiH_3 on the

basis of this density leaves too much freedom in the absolute value due to uncertainties in the absolute density of SiH_3 itself (mainly due to the factor C) as well as in v and s. It is therefore, expected that the presented method is much more accurate, although the estimation of the exact contribution is, of course, very sensitive on the accuracy and reproducibility of the deposition rate and SiH_3 signal.

At lower H_2 flows, it is shown that there needs to be a significant contribution of radicals other than SiH_3 as the contribution of positive ions does not compensate for the lower contribution of SiH_3. Figure 6(b) suggests that the production of $SiH_x(x\leqslant 2)$ from dissociative recombination is about a factor of 6 larger at $H_2=0$ sccs than at $H_2=10$ sccs. This roughly compensates the decrease in contribution of SiH_3, as shown in Fig. 4(b), but it is premature to conclude that $SiH_x(x\leqslant 2)$ radicals govern film growth at low-H_2 flows. First of all, the emission intensity in Fig. 6 is not collected in the whole deposition chamber, making it difficult to speculate about how many more recombination events there are at low-H_2 flows. Second, in the determination of the contribution of SiH_3 it is assumed that β and s of SiH_3 are independent of the H_2 flow. It can, however, not be excluded that β and s are somewhat higher at low-H_2 flows due to a higher reactivity of the a-Si:H surface. For example, the higher contribution of $SiH_x(x\leqslant 2)$ radicals can lead to more surface dangling bonds. This would also contribute to the increase of β_0 in Fig. 9. But, most important is that the emission intensity is only an indication of the recombination of silane ions. It does not reveal information on the specific species created, and finally contributing to film growth. As mentioned before, the radicals produced in reaction (8) have a rather high reactivity with SiH_4 and can be converted into other species before reaching the substrate. Contrary to SiH_3, which is not very reactive with SiH_4 [reaction rate $<4\times10^{-20}\,m^3\,s^{-1}$ at 300 K (Ref. 45)], reaction rates in the order 10^{-16}–$10^{-17}\,m^3\,s^{-1}$ [at $\sim$0.2 mbar and 300 K (Refs. 40, 46, and 47)] have been proposed for SiH_2, SiH, and Si. This means that for a typical SiH_4 density of $\sim10^{20}\,m^{-3}$, the radicals have reacted with SiH_4 within 50–500 μs, and this is shorter than the transport time of the radicals to the substrate ($\sim$500–1000 μs). This shows that the influence of the radicals created from reaction (8) cannot be derived simply from Fig. 6 and that additional, more extensive investigations are required.

Although still some questions remain unanswered, a correlation between the reaction products of SiH_4 dissociation and the a-Si:H film quality can already be made. This will be discussed only briefly, as it will be addressed more extensively in another article, where also the film properties for the different plasma conditions are given.[14] As mentioned earlier, a considerable H_2 flow in the arc is necessary to obtain good film properties (the optimum film quality is obtained with 10 sccs H_2 and 10 sccs SiH_4 flow), which shows the importance of the contribution of SiH_3 to film growth. The optoelectronic film properties depend strongly on the H_2 flow while the structural film properties only become inferior at very low-H_2 flows (<2 sccs). Under these conditions, a-Si:H is obtained that contains a considerable void fraction. This can be understood from a significant contribution of radicals with a very high β and is also in line with the higher surface roughness of the films as determined by *in situ* ellipsometry.[48] That film growth dominated by SiH_3 does not automatically lead to good film quality can be seen from the deterioration of the film properties for decreasing SiH_4 flow. Under these conditions, the contribution of SiH_3 to film growth is about constant, while both structural and optoelectronic properties are inferior at low-SiH_4 flows (<3 sccs). This is less understood, but it can possibly be attributed to the fact that at low-SiH_4 flows the reaction products from dissociative recombination are smaller. Their impact on the film quality could be different from the impact of larger neutral fragments created by recombination of cationic clusters at larger SiH_4 flows. For example, the small Si and SiH radicals can penetrate the subsurface region[49] and introduce dangling bonds in the film, which can degrade the film properties.

V. CONCLUSIONS

The dissociation of SiH_4 in the expanding thermal plasma used for high-rate deposition of device-quality a-Si:H has been investigated by different plasma diagnostics. The density of SiH_3 has been determined by threshold ionization mass spectrometry and the contribution of SiH_3 to a-Si:H film growth has been determined without using estimates on the SiH_3 thermal velocity and sticking probability. It is shown that at high-H_2 flows SiH_4 dissociation mainly takes place by hydrogen abstraction by H emanating from the Ar–H_2-operated plasma source. Under these conditions, film growth is dominated by SiH_3 (estimated contribution $\sim$90%) and the best a-Si:H film quality is obtained.

The contribution of SiH_3 decreases with decreasing H_2 flow and at low-H_2 flows the dissociation of SiH_4 is dominated by reactions with ions from the plasma source. As confirmed by optical emission spectroscopy on excited Si and SiH, this causes strong dissociative recombination of silane ions, producing a considerable amount of very reactive radicals, such as SiH_2, SiH, and Si. The contribution of these radicals and/or their reaction products is expected to cause the inferior a-Si:H film properties obtained at low-H_2 flows. This is corroborated by the decrease in overall surface reaction probability for increasing H_2 flow, while the overall surface reaction probability of $\sim$0.3 at high-H_2 flows corresponds to film growth dominated by SiH_3.

For a fixed H_2 flow of 10 sccs in the cascaded arc, the consumption of SiH_4 has been investigated for varying SiH_4 flows. That SiH_3-dominated film growth does not guarantee good film quality is shown from the fact that the contribution of SiH_3 is independent of the SiH_4 flow, while the film properties are inferior at low-SiH_4 flows. Furthermore, it has been demonstrated that the neutral products created by dissociative recombination of positive ions are smaller at low-SiH_4 flows, as expected from the smaller size of the ions at these flows.

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[1]K. Kobayashi, M. Hayama, S. Kawamoto, and H. Miki, Jpn. J. Appl. Phys., Part 1 **26**, 202 (1987).
[2]J. Perrin, P. Roca i Cabarrocas, B. Allain, and J. M. Friedt, Jpn. J. Appl. Phys., Part 1 **88**, 2041 (1988).
[3]A. H. Mahan, J. Carapella, B. P. Nelson, R. S. Crandall, and I. Balberg, J. Appl. Phys. **69**, 6728 (1991).
[4]J.-H. Lee, S. K. Park, and C. S. Kim, Jpn. J. Appl. Phys., Part 2 **34**, L1191 (1995).
[5]M. Goto, H. Toyoda, M. Kitagawa, T. Hirao, and H. Sugai, Jpn. J. Appl. Phys., Part 1 **36**, 3714 (1997).
[6]S. Will, H. Mell, M. Poschenrieder, and W. Fuhs, J. Non-Cryst. Solids **227-230**, 29 (1998).
[7]A. Heya, K. Nakata, A. Izumi, and H. Matsumura, Mater. Res. Soc. Symp. Proc. **507**, 435 (1998).
[8]S. Morrison, J. Xi, and A. Madan, Mater. Res. Soc. Symp. Proc. **507**, 559 (1998).
[9]R. Platz, C. Hof, S. Wieder, B. Rech, D. Fisher, A. Shah, A. Payne, and S. Wagner, Mater. Res. Soc. Symp. Proc. **507**, 565 (1998).
[10]Y.-B. Park, X. Li, S.-W. Rhee, and D.-W. Park, J. Phys. D **32**, 1955 (1999).
[11]W. M. M. Kessels, A. H. M. Smets, B. A. Korevaar, G. J. Adriaenssens, M. C. M. van de Sanden, and D. C. Schram, Mater. Res. Soc. Symp. Proc. **557**, 25 (1999).
[12]B. A. Korevaar, G. J. Adriaenssens, A. H. M. Smets, W. M. M. Kessels, H.-Z. Song, M. C. M. van de Sanden, and D. C. Schram, J. Non-Cryst. Solids **266-269**, 380 (2000).
[13]M. 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); **85**, 1243 (1999).
[14]W. M. M. Kessels, R. J. Severens, A. H. M. Smets, B. A. Korevaar, M. C. M. van de Sanden, and D. C. Schram (unpublished).
[15]W. M. M. Kessels, C. M. Leewis, A. Leroux, M. C. M. van de Sanden, and D. C. Schram, J. Vac. Sci. Technol. A **17**, 1531 (1999).
[16]W. M. M. Kessels, C. M. Leewis, M. C. M. van de Sanden, and D. C. Schram, J. Appl. Phys. **86**, 4029 (1999).
[17]J. J. Beulens, M. J. de Graaf, and D. C. Schram, Plasma Sources Sci. Technol. **2**, 180 (1993).
[18]M. C. M. van de Sanden, J. M. de Regt, and D. C. Schram, Plasma Sources Sci. Technol. **3**, 501 (1994).
[19]R. F. G. Meulenbroeks, M. F. M. Steenbakkers, Z. Qing, M. C. M. van de Sanden, and D. C. Schram, Phys. Rev. E **49**, 2272 (1994).
[20]R. F. G. Meulenbroeks, R. A. H. Engeln, M. N. A. Beurskens, R. M. J. Paffen, M. C. M. van de Sanden, J. A. M. van de Mullen, and D. C. Schram, Plasma Sources Sci. Technol. **4**, 74 (1995).
[21]M. Boulos, P. Fauchais, and E. Pfender, *Thermal Plasmas: Fundamentals and Applications* (Plenum, New York, 1994), Vol. 1.
[22]S. Mazouffre, M. G. H. Boogaarts, J. A. M. van der Mullen, and D. C. Schram, Phys. Rev. Lett. **84**, 2622 (2000).
[23]G. M. W. Kroesen, D. C. Schram, A. T. M. Wilbers, and G. J. Meeusen, Contrib. Plasma Phys. **31**, 27 (1991).
[24]R. F. G. Meulenbroeks, R. A. H. Engeln, J. A. M. van der Mullen, and D. C. Schram, Phys. Rev. E **53**, 5207 (1996).
[25]H. Sugai and H. Toyoda, J. Vac. Sci. Technol. A **10**, 1193 (1992).
[26]P. Kae-Nune, J. Perrin, J. Guillon, and J. Jolly, Plasma Sources Sci. Technol. **4**, 250 (1995).
[27]Consumption of SiH_4 usually leads to a decrease of the SiH_4 signal when the plasma is turned on. This is, however, not the case for all measurements reported here. This effect, which cannot be explained by a change in SiH_4 flux into the mass spectrometer due to a change in gas temperature, has no implications for the radical measurements.
[28]W. M. M. Kessels, M. C. M. van de Sanden, R. J. Severens, and D. C. Schram, J. Appl. Phys. **87**, 3313 (2000).
[29]J. W. Coburn and E. Kay, J. Vac. Sci. Technol. **8**, 738 (1971).
[30]H. Singh, J. W. Coburn, and D. B. Graves, J. Vac. Sci. Technol. A **17**, 2447 (1999).
[31]A. J. B. Robertson, *Mass Spectrometry* (Methuen, London, U.K., 1954).
[32]G. J. Meeusen, E. A. Ershov-Pavlov, R. F. G. Meulenbroeks, M. C. M van de Sanden, and D. C. Schram, J. Appl. Phys. **71**, 4156 (1992).
[33]J. Perrin and E. Delafosse, J. Phys. D **13**, 759 (1980).
[34]D. A. Doughty, J. R. Doyle, G. H. Lin, and A. Gallagher, J. Appl. Phys. **67**, 6220 (1990).
[35]A. Goumri, W.-J. Yuan, L. Ding, Y. Shi, and P. Marshall, Chem. Phys. **177**, 233 (1993).
[36]R. Basner, M. Schmidt, V. Tarnovsky, K. Becker, and H. Deutsch, Int. J. Mass Spectrom. Ion Processes **171**, 83 (1997).
[37]V. Tarnovsky, H. Deutsch, and K. Becker, J. Chem. Phys. **105**, 6315 (1996).
[38]F. A. Baiocchi, R. C. Wetzel, and R. S. Freund, Phys. Rev. Lett. **53**, 771 (1984).
[39]This has consequences for the radical densities determined by Kae-Nune *et al.* and leads to a higher contribution of SiH_3 to film growth than presented (the ratio of the contributions of SiH_3 and SiH_2 increases by a factor of $\sim$6).
[40]J. Perrin, O. Leroy, and M. C. Bordage, Contrib. Plasma Phys. **36**, 1 (1996).
[41]A. A. Howling, L. Sansonnens, J. L.-Dorrier, and Ch. Hollenstein, J. Appl. Phys. **75**, 1340 (1994).
[42]S. Ramalingan, D. Maroudas, and E. S. Aydil (unpublished).
[43]Y. B. Kim, K. Stephan, E. Märk, and T. Märk, J. Chem. Phys. **74**, 6771 (1981).
[44]A. A. Radzig and B. M. Smirnov, *Reference Data on Atoms, Molecules and Ions* (Springer, Berlin, 1985).
[45]S. K. Loh and J. M. Jasinski, J. Chem. Phys. **95**, 4914 (1991).
[46]J. M. Jasinski, Mater. Res. Soc. Symp. Proc. **165**, 41 (1990).
[47]A. Kono, S. Hirose, and T. Goto, Jpn. J. Appl. Phys., Part 1 **38**, 4389 (1999).
[48]A. H. M. Smets, M. C. M. van de Sanden, and D. C. Schram, Thin Solid Films **343-344**, 281 (1999).
[49]S. Ramalingam, D. Maroudas, and E. S. Aydil, Appl. Phys. Lett. **72**, 578 (1998); J. Appl. Phys. **84**, 3895 (1998).