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## Improvement of hydrogenated amorphous silicon properties with increasing contribution of SiH<sub>3</sub> to film growth

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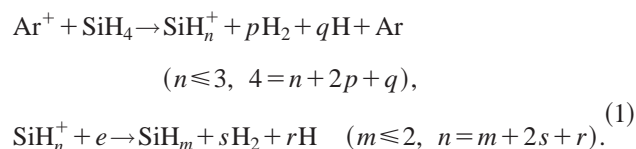
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From cavity ring down spectroscopy and threshold ionization mass spectrometry measurements in a remote Ar–H<sub>2</sub>–SiH<sub>4</sub> plasma it is clearly demonstrated that the properties of hydrogenated amorphous silicon (*a*-Si:H) strongly improve with increasing contribution of SiH<sub>3</sub> to film growth. The measurements corroborate the proposed dissociation reactions of SiH<sub>4</sub> for different plasma settings and it is shown that film growth is by far dominated by SiH<sub>3</sub> under conditions for which solar grade quality *a*-Si:H at deposition rates up to 10 nm/s has previously been reported. © 2001 American Vacuum Society. [DOI: 10.1116/1.1365131]

For hydrogenated amorphous silicon (*a*-Si:H) deposited by means of plasma decomposition of SiH<sub>4</sub>, it is commonly accepted that the high quality of the films is directly related to a dominant contribution of SiH<sub>3</sub> to film growth.<sup>1,2</sup> This is mainly attributed to the relatively low sticking probability of SiH<sub>3</sub> and its high surface mobility on an almost fully hydrogenated *a*-Si:H surface. To obtain more evidence for the aforementioned relationship, also under the less studied, but technologically very interesting conditions of high rate deposition, the contribution of SiH<sub>3</sub> to film growth is investigated for the expanding thermal plasma (ETP) and related to the film properties obtained. With this remote deposition technique solar grade *a*-Si:H can be obtained at deposition rates up to 10 nm/s,<sup>3,4</sup> and, as will be shown in this article, under conditions where film growth is by far dominated by SiH<sub>3</sub>.

The ETP technique is based on dissociation of SiH<sub>4</sub> in a low pressure deposition chamber by means of an Ar–H<sub>2</sub> plasma generated in a high pressure cascaded arc plasma source.<sup>5,6</sup> Recently, it was shown that the film properties obtained by this technique depend strongly on the amount of H<sub>2</sub> admixed in the cascaded arc.<sup>3,7</sup> Figure 1 shows that the deposition rate decreases drastically when a small H<sub>2</sub> flow is admixed, whereas the film quality, here only illustrated by the photoconductivity, improves significantly. This behavior has been attributed to the dissociation processes of SiH<sub>4</sub> and the radicals generated. Due to the low electron temperature in the downstream deposition chamber,<sup>5,6</sup> SiH<sub>4</sub> dissociation is governed by reactions with reactive ionic and atomic particles emanating from the cascaded arc. At very low H<sub>2</sub> flows these are mainly Ar<sup>+</sup>,<sup>6</sup> which leads to dissociative charge

exchange with SiH<sub>4</sub> followed by (fast) dissociative recombination with electrons:



Initially, this leads dominantly to SiH<sub>*m*</sub> (*m* ≤ 2) radicals which are highly reactive, both with the *a*-Si:H surface as with SiH<sub>4</sub> (leading to reactive polysilane radicals).<sup>5,8</sup> When increasing the H<sub>2</sub> flow, the amount of ions from the cascaded arc decreases considerably and mainly H emanates from the arc as reactive species. Therefore the reaction<sup>5,8</sup>



takes over at high H<sub>2</sub> flows. The improvement of the film properties with increasing H<sub>2</sub> flow has therefore been attributed to the transition from a high contribution of very reactive (poly)silane radicals to a dominant contribution of SiH<sub>3</sub> to film growth. Furthermore, the drastic decrease in deposition rate at low H<sub>2</sub> flows can be understood from the fast diminishing importance of the efficient ion-induced reactions, while the gradual increase at higher H<sub>2</sub> flows can be attributed to an increasing H flow from the cascaded arc. Ion–molecule reactions also play a role, but the contribution of Si<sub>*n*</sub>H<sub>*m*</sub><sup>+</sup> ions to film growth is small (<10%) and almost independent of the H<sub>2</sub> flow.<sup>6</sup> It is therefore not responsible for the observed trend in film quality. The above mentioned reaction pathway has been proposed on the basis of several plasma diagnostic investigations reported previously.<sup>5,6,8</sup> In this article clear evidence will be presented by direct SiH<sub>3</sub> measurements using cavity ring down spectroscopy (CRDS) and threshold ionization mass spectrometry (TIMS).

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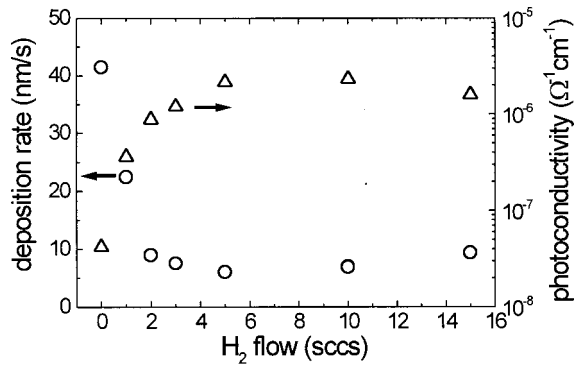


FIG. 1. Deposition rate and AM1.5 photoconductivity ( $100 \text{ mW/cm}^2$ ) for  $a\text{-Si:H}$  films deposited at a substrate temperature of  $400^\circ\text{C}$  and with an Ar and  $\text{SiH}_4$  flow of 55 and 10 sccs, respectively, an arc current of 45 A, and a chamber pressure of 0.20 mbar. The  $\text{H}_2$  flow in the Ar- $\text{H}_2$  operated cascaded arc plasma source is varied.

The CRDS and TIMS measurements have been performed under experimental conditions identical to those in Fig. 1. With CRDS, the line-of-sight integrated absorption by  $\text{SiH}_3$  has been measured for an axial position of 0.6 cm from the substrate holder. This was done by probing the  $\text{SiH}_3 \tilde{A}^2A_1 \leftarrow \tilde{X}^2A_1$  transition which has a broad absorption band ranging from  $\sim 200\text{--}260 \text{ nm}$  due to the predissociative nature of the upper state.<sup>9</sup> In Fig. 2, the parts of the absorption spectrum measured with CRDS are given for two different conditions and compared with the spectrum reported by Lightfoot *et al.*<sup>9</sup> The experimental setup and procedure for the CRDS measurements are presented in detail in Ref. 10. The line-integrated density of  $\text{SiH}_3$  is calculated from the absorption cross section estimated for 215 nm ( $2.4 \times 10^{-21} \text{ m}^2$ ),<sup>9</sup> while the local axial value of the density is estimated from Abel inverted lateral absorption profiles yielding the radial distribution of  $\text{SiH}_3$ .<sup>11</sup> The TIMS measurements have been performed with a Hiden analytical mass spectrometer at the position of the substrate.<sup>8</sup>

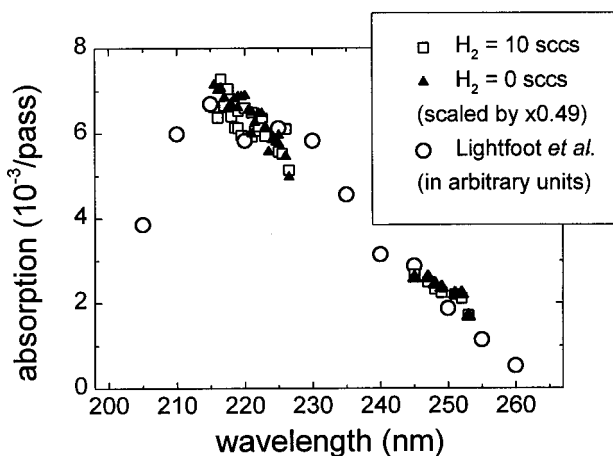


FIG. 2. Parts of the  $\text{SiH}_3$  absorption spectrum as measured by cavity ring down spectroscopy for a  $\text{H}_2$  flow of 0 and 10 sccs. The absorption values for 0 sccs  $\text{H}_2$  are multiplied by a factor of 0.49 and the spectrum reported by Lightfoot *et al.* (Ref. 8) is given in arbitrary units.

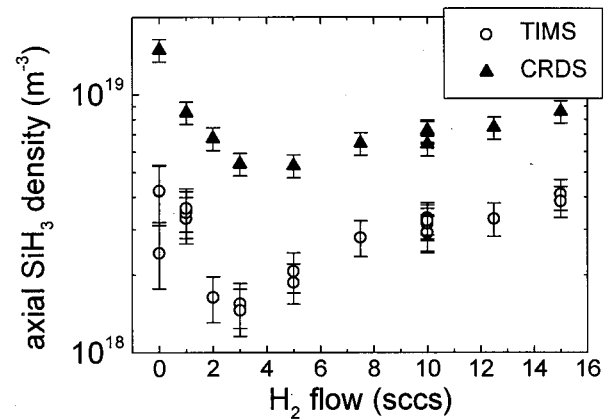


FIG. 3. The axial  $\text{SiH}_3$  density as obtained from TIMS and CRDS as a function of the  $\text{H}_2$  flow. The TIMS data refer to the position of the substrate while the CRDS data refer to a distance of 0.6 cm from the substrate.

In Fig. 3, the axial density of  $\text{SiH}_3$  as obtained by CRDS and TIMS is given as a function of the  $\text{H}_2$  flow for positions close to the substrate. For high  $\text{H}_2$  flows, both techniques yield a gradually increasing  $\text{SiH}_3$  density with increasing  $\text{H}_2$  flow as is expected from reaction (2) and from the increasing deposition rate in Fig. 1. At very low  $\text{H}_2$  flows, where  $\text{SiH}_4$  dissociation is governed by ion-induced reactions, the relatively high  $\text{SiH}_3$  density seems contradictory to the above presented reaction mechanism. This high density can, however, be understood from the very high  $\text{SiH}_4$  consumption<sup>8</sup> (up to 60%) and growth rate (see Fig. 1) at very low  $\text{H}_2$  flows. Under these conditions, a significant amount of  $\text{SiH}_3$  can be produced indirectly, for example, by H generated in reactions (1) while the relative importance of  $\text{SiH}_3$  in the deposition process remains small as illustrated below. The small discrepancy between the TIMS and CRDS data in relative behavior at low  $\text{H}_2$  flows, can most probably be attributed to experimental error in the TIMS measurements caused by clogging of the mass spectrometer's orifice due to the very high growth rate under these conditions. A significant contribution to the absorption signal by other plasma species at very low  $\text{H}_2$  flows is not expected because the measured parts of the spectrum perfectly overlap with the absorption band reported in the literature for all  $\text{H}_2$  flows (see Fig. 2). This also makes a possible influence of absorption or scattering by dust particles in the plasma, as observed in, e.g., radio-frequency (rf)  $\text{SiH}_4$  plasmas,<sup>12</sup> improbable.

Concerning the differences in absolute density, these can, among others, be attributed to the fact that the densities refer to different positions from the substrate holder. The  $\text{SiH}_3$  density in front of the substrate can decrease due to surface loss and therefore lead to a lower density in the TIMS measurements. Furthermore, for both techniques the absolute scale of the density also suffers from experimental uncertainty. For CRDS, this is mainly due to the procedure for obtaining the radial distribution of  $\text{SiH}_3$  in order to calculate the local density,<sup>12</sup> as well as due to the uncertainty in absorption cross section, which is only an approximate value (an upper limit).<sup>9</sup> The accuracy of the absolute density deter-

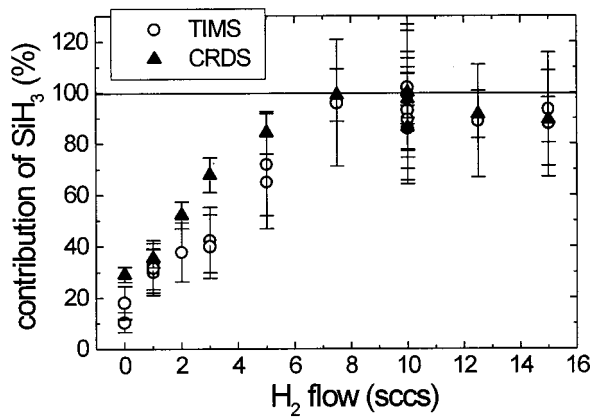


FIG. 4. The contribution of SiH<sub>3</sub> to *a*-Si:H film growth as calculated from the CRDS and TIMS measurements.

mined by TIMS is considerably limited by estimations made in the calibration procedure.<sup>8</sup> It has to be stressed that the relative values are reliable, as also indicated by the experimental error.

The uncertainty in the absolute scale of the SiH<sub>3</sub> density  $n_{\text{SiH}_3}$  close to the substrate, complicates an accurate calculation of the *absolute* value of the contribution of SiH<sub>3</sub> to film growth by the expression<sup>13</sup>

$$\text{Contribution of SiH}_3 = \frac{1}{4} n_{\text{SiH}_3} v \frac{s}{1 - \beta/2} \frac{1}{N_{\text{Si}}} \frac{1}{R_{\text{dep}}}, \quad (3)$$

where  $v$  is the thermal velocity of SiH<sub>3</sub> in front of the substrate,  $s$  and  $\beta$  the SiH<sub>3</sub> sticking and surface reaction probability, respectively,  $R_{\text{dep}}$  the deposition rate, and  $N_{\text{Si}}$  the Si atomic density in the film (dependent on plasma conditions). Moreover, the parameters in Eq. (3) are not all known with a high accuracy (especially  $v$ ,  $s$ , and  $\beta$ ) preventing precise determination of the contribution of SiH<sub>3</sub> within a factor of 2.

Therefore, here another method is used to calculate the absolute contribution of SiH<sub>3</sub>. Because at high H<sub>2</sub> flows (>5 sccs) mainly H emanates from the arc as reactive species, it is very plausible that the increase in deposition rate between 10 and 15 sccs H<sub>2</sub> in Fig. 1 is caused by an increase of the H flow (ion flow from the arc is very small and decreases with H<sub>2</sub> flow)<sup>6</sup> and consequently by an increase in the SiH<sub>3</sub> production by reaction (2). This increase in SiH<sub>3</sub> production is observed in both the TIMS and CRDS measurements, meaning that the (identical) *relative increase* in TIMS and CRDS signal can be correlated directly with the *relative increase* in deposition rate. From this relation, the absolute contribution of SiH<sub>3</sub> can be calculated with a much higher accuracy, as no information about absolute densities is required. It only needs to be assumed that  $v$ ,  $s$ , and  $\beta$  are independent of the H<sub>2</sub> flow, but these assumptions would be used when applying Eq. (3) as well. Furthermore, it is important to note that the latter method would give the same *relative* dependence of the SiH<sub>3</sub> contribution on the H<sub>2</sub> flow. The uncertainty in the contribution is now mainly determined by the reproduc-

ibility of the plasma conditions since the CRDS, TIMS, and deposition rate measurements have been performed at different times.

As shown in Fig. 4, the contribution of SiH<sub>3</sub> increases with increasing H<sub>2</sub> flow and saturates for flows larger than ~7.5 sccs. This is in perfect agreement with the proposed SiH<sub>4</sub> dissociation mechanisms. Despite the relatively high SiH<sub>3</sub> density at very low H<sub>2</sub> flows, the contribution of SiH<sub>3</sub> is relatively small because the ion-induced reactions lead initially mainly to radicals other than SiH<sub>3</sub>, whereas the contribution of SiH<sub>3</sub> to film growth increases with increasing H flow and decreasing ion flow from the cascaded arc when going to higher H<sub>2</sub> flows. Under the H dominated conditions, where the optimal film properties are obtained, the contribution of SiH<sub>3</sub> is dominant and about constant. From Fig. 4, it is estimated that film growth is approximately 90% due to SiH<sub>3</sub> with a balance by a small contribution of other (poly)silane radicals and ions. This high contribution is in very good agreement with the value for the surface reaction probability (~0.3) obtained at high H<sub>2</sub> flows<sup>8</sup> and it is higher than the reported contribution of SiH<sub>3</sub> to *a*-Si:H growth in low power rf plasmas.<sup>13,14</sup>

In summary, two diagnostic techniques have been independently applied for SiH<sub>3</sub> detection and have revealed similar results for the SiH<sub>3</sub> density and its contribution to *a*-Si:H film growth. The results corroborate the proposed reaction mechanisms in the expanding thermal plasma and a direct correlation between *a*-Si:H film quality and the contribution of SiH<sub>3</sub> to film growth is unambiguously shown. Furthermore, it is demonstrated that the previously reported plasma settings yielding solar grade *a*-Si:H at deposition rates up to 10 nm/s correspond to by far SiH<sub>3</sub> dominated film growth.

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