The a-Si:H growth mechanism

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The a-Si:H growth mechanism: Temperature study of the SiH₃ surface reactivity and the surface silicon hydride composition during film growth

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ABSTRACT

We report on two experimental studies carried out to reveal insight into the interaction of SiH₃ radicals with the a-Si:H surface as assumed essential in the a-Si:H growth mechanism. The surface reaction probability β of SiH₃ on the a-Si:H has been investigated by spectroscopic means as a function of the substrate temperature (50 - 450 °C) using the time-resolved cavity ringdown technique. The silicon hydrides –SiH_x on the a-Si:H surface during deposition have been studied by the combination of *in situ* attenuated total reflection infrared spectroscopy and argon ion-induced desorption of surface hydrogen. For SiH₃ dominated plasma conditions, it is found that the surface reactivity of SiH₃ is independent of the substrate temperature with $\beta = 0.30 \pm 0.03$ whereas the silicon hydride composition on the a-Si:H surface changes drastically for increasing substrate temperature (from –SiH₃ to =SiH₂ to ≡SiH). The implications of these observations for the a-Si:H growth mechanism are addressed.

INTRODUCTION

Although the efforts on constructing a growth model for a-Si:H have been fruitful and have contributed greatly to the understanding of the a-Si:H deposition process, there are several issues in the growth mechanism of a-Si:H that are still not completely unraveled [1]. The interaction of SiH₃ radicals with the a-Si:H surface under different surface conditions (as *e.g.*, determined by the substrate temperature) is one particular unresolved issue. Although recently several SiH₃ surface reactions have been proposed on the basis of *ab initio* calculations and simulations such as density-functional theory (DFT) calculations and molecular dynamics (MD) simulations [2,3,4,5,6], there is still insufficient experimental data. Therefore we have carried out dedicated experiments using the expanding thermal plasma (ETP) technique [7] which is well-suited for these kind of studies:

- the conditions in an Ar-H₂-SiH₄ plasma can be chosen such that a-Si:H film growth is approximately for 90% due to SiH₃ radicals as revealed from cavity ringdown spectroscopy and threshold ionization mass spectrometry [8,9];
- ion bombardment does not play a role because the low electron temperature in the plasma leads to a very low self-bias during deposition (<2 V) [10];
- surface reactions by atomic hydrogen H from the plasma are of very minor importance as there are clear indications that the H flux towards the a-Si:H is much lower than the SiH₃ flux [11].

In this paper, we will address the surface reactivity of SiH₃ and the silicon hydride composition of the a-Si:H surface as a function of the substrate temperature.

SURFACE REACTION PROBABILITY OF SiH_3 ON THE a-Si:H SURFACE

The surface reactivity of SiH_3 has been determined by using time-resolved cavity ringdown spectroscopy as described in Ref. [12]. Briefly, the decrease in SiH_3 density at a distance of 5 mm from the substrate is monitored after a minor periodic modulation of the SiH_3 density by a rf power pulse. From the time-constant associated with the decrease, *i.e.*, the loss time of SiH_3 , the surface reaction probability β can be determined because it is shown that SiH_3 is not reactive in the gas phase [12]. Figure 1 shows the loss time of SiH_3 as a function of the reactor pressure for different substrate temperatures. The loss time increases with pressure because SiH_3 diffusion to the substrate is slower at higher pressures. At zero pressure however, the SiH_3 loss time is unaffected by diffusion (“free-fall limit”) and reflects directly the surface reactivity of the SiH_3 . The (extrapolated) loss time at zero pressure is therefore used to calculate the values of β for the different substrate temperatures. In this calculation, necessary information about the diffusion geometry is derived from the slope of the lines in Fig. 1 and a (constant) gas temperature of 1500 ± 200 K is used as derived from Doppler linewidth measurements of the (low-density) Si radicals present in the plasma [13].

Figure 2 shows the values of β as obtained for the different substrate temperatures. The figure reveals that β of SiH_3 is not significantly influenced by the substrate temperature. This is in good agreement with previous investigations which used a very indirect method (*i.e.*, not directly monitoring the SiH_3 radical itself) and for which it was not completely clear whether the β values derived could (solely) be attributed to SiH_3 radicals [14]. Furthermore, the average value of $\beta = 0.30 \pm 0.03$ is in agreement with most of the values reported in the literature as listed in Table I [15]. This indicates that the β value of SiH_3 is for the largest part a “radical property” although some influence of the conditions and type of plasma used on β cannot be excluded. Moreover, we find a very good agreement with previous studies of β of SiH_3 done in the same ETP setup using an indirect method under similar plasma conditions [15]. Furthermore, we have also found that the Si growth flux (*i.e.*, product of deposition rate and Si atomic density in the film) is independent of the substrate temperature in the range 50 - 450 °C. This implies that the sticking probability s ($\leq \beta$) is temperature independent [15].

Figure 1. Measured loss times of SiH_3 as a function of the reactor pressure for different substrate temperatures.

Figure 2. Surface reaction probability β of SiH_3 as a function of the substrate temperature.

Table I: Overview of the surface reaction probabilities β reported for the SiH_3 radical as obtained under different experimental conditions and by several techniques (RT = room temperature).

	β (substrate temperature)	Experimental conditions	Technique applied	Ref.
indirect techniques	0.10 ± 0.01 (RT) $- 0.21 \pm 0.01$ (350 °C)	Hg photo-CVD, SiH_4 with Hg	grid	[16]
	0.26 ± 0.02 (240 °C)	rf triode, SiH_4	grid	[17]
	0.26 ± 0.05 (RT – 480 °C)	rf triode, SiH_4	grid and trench	[14]
	0.29 0.33 0.37 (20 – 250 °C)	dc triode, SiH_4 dc anode, SiH_4 rf diode, SiH_4	aperture-well assembly	[18]
	0.18 (RT)	rf diode, H_2 - SiH_4 (63%)	infrared laser absorption	[19,20]
	0.28 ± 0.05 (200 °C)	hollow cathode (CVD-like), SiH_4	macroscopic trench	[21]
	0.25 ± 0.06 (250 °C - 325 °C) 0.33 ± 0.05 (400 °C)	ETP plasma, Ar-H_2 - SiH_4	aperture-well assembly	[15]
direct techniques	0.05 ± 0.01 (RT)	microwave, He-Cl_2 - SiH_4 (6%)	mass spectrometry	[22]
	0.28 ± 0.03 (300 °C)	rf diode (afterglow), SiH_4	appearance potential mass spectrometry	[23]
	0.15 (RT)	rf diode, He-SiH_4 (50%)	infrared laser absorption	[24]
	0.03 (RT)	in afterglow		
	0.30 ± 0.03 (50 - 450 °C)	ETP plasma, Ar-H_2 - SiH_4	cavity ringdown spectroscopy	present work
	0.18 (RT)	-	molecular dynamics	[2]

COMPOSITION OF THE SILICON HYDRIDES ON THE a-Si:H SURFACE

The composition of the silicon hydrides $-\text{SiH}_x$ on the a-Si:H surface during deposition has been investigated by means of very sensitive *in situ* infrared absorption spectroscopy measurements using the attenuated total reflection (ATR) technique. Films of a-Si:H have been deposited on a GaAs ATR crystal for three substrate temperatures (100, 250, 400 °C) and surface specificity has been obtained by ion-induced desorption of the surface hydrides by means of exposing the film to a gentle Ar plasma for 10 s [25]. By comparing the infrared spectra before and after this desorption step, information is obtained about the surface hydrides removed from the a-Si:H surface and consequently about the surface hydrides initially present on the a-Si:H.

The results depicted in Fig. 3 show the relative composition of the $-\text{SiH}_x$ species on the a-Si:H surface for the three substrate temperatures. Conclusions about the hydrogen coverage of the surface cannot easily be deduced from the measurements [26] although the data indicate that the surface contains a considerable amount of hydrogen. The results are in good agreement with previous investigations for ICP plasma deposited a-Si:H films which revealed that the dominant silicon hydrides on the surface change from $-\text{SiH}_3$ to $=\text{SiH}_2$ to $\equiv\text{SiH}$ for increasing substrate temperature [26]. A very striking result is however that this drastic change of the a-Si:H surface as a function of substrate temperature does not affect the surface reaction probability β of SiH_3 .

Figure 3. Relative surface hydride ($-\text{SiH}_x$) composition of a-Si:H as obtained by *in situ* attenuated total reflection infrared spectroscopy for substrate temperatures of (a) 100 °C, (b) 250 °C, and (c) 400 °C.

DISCUSSION ON THE IMPLICATIONS FOR THE a-Si:H GROWTH MODEL

The experimental observations discussed above have direct consequences for the a-Si:H growth mechanism in terms of the SiH_3 surface reactions. We will discuss on these consequences by briefly considering some of the SiH_3 surface reactions reported in the literature.

First of all, Matsuda *et al.* have explained their observation that the surface reaction probability β of SiH_3 is independent of the substrate temperature by the so-called physisorbed state of SiH_3 [14]. Following Gallagher [27], they proposed that SiH_3 can adsorb (physisorb) everywhere on an almost fully hydrogenated surface by forming a three-center Si–H–Si bond on surface SiH_x sites [Fig. 4(a)]. The SiH_3 in this physisorbed state subsequently diffuses over the surface until it finally sticks on a surface dangling bond [Fig. 4(a2)] or until it abstracts a H atom from the surface forming gaseous SiH_4 and a surface dangling bond [Fig. 4(a1)]. However, recent *ab initio* calculations have revealed that the three-center Si–H–Si bond is not stable [4] and therefore other surface reactions of SiH_3 with a-Si:H have been subject of investigation.

One reaction that has given particular consideration in the literature is the so-called “insertion” reaction of SiH_3 into strained Si–Si surface bonds [Fig. 4(b)]. This reaction, which does not require dangling bonds for the SiH_3 to stick at the surface, has been proposed on the basis of surface infrared studies [28] and has also been observed in DFT calculations and MD simulations [2,6]. However, it is expected that this insertion reaction is heavily substrate temperature dependent because it relies on the presence of strained Si–Si bonds on the a-Si:H surface. These strained bonds are more likely at high temperatures when the surface is composed of $\equiv\text{SiH}$ rather than at low substrate temperatures when the surface contains mainly $-\text{SiH}_3$ hydrides. Furthermore, the calculated activation energy of the insertion reaction is in the range of 0.7–0.9 eV [6] and is therefore also not compatible with the substrate temperature independent surface reaction probability β of SiH_3 .

A reaction that would be more compatible with the temperature independent β of SiH_3 is H abstraction from the surface directly by SiH_3 from the gas phase [Fig. 4(c)]. This so-called Eley-Rideal type of reaction has been observed in MD simulations and DFT calculations and the

calculated activation energy is relatively low (~ 0.09 eV) [3]. Direct H abstraction would lead to an (almost) temperature independent generation mechanism of dangling bonds on the a-Si:H surface and these dangling bonds can act as growth sites for other incoming SiH_3 radicals. The adsorption reaction of SiH_3 on top of these surface dangling bonds [Fig. 4(d)] is not expected to be temperature dependent. Therefore the combination of H abstraction and SiH_3 adsorption onto the dangling bond created can explain the temperature independent β of SiH_3 in the case that the H abstraction reaction is the rate-limiting step. In this reaction sequence, it is not required that the adsorption of the SiH_3 on the surface dangling bond takes place directly from the gas phase. Precursor-mediated sticking of SiH_3 is compatible with the observations (as long as it is not the rate-limiting step) and it might even be necessary in order to keep the dangling bond density on the a-Si:H surface sufficiently low [1]. Furthermore it has to be noted that the reaction sequence is also compatible with the changing $-\text{SiH}_x$ surface composition. Although, relatively more H atoms are present at the surface at lower temperatures, not all these H atoms will be available for H abstraction because also the incorporation rate of H into the a-Si:H is higher at low substrate temperatures (*i.e.*, the H content of a-Si:H increases when going to lower temperatures).

Figure 4. Proposed SiH_3 surface reactions: (a) physisorption with (a1) H abstraction and (a2) sticking; (b) insertion into strained Si–Si bonds; (c) direct H abstraction creating a dangling bond and SiH_4 molecule; (d) SiH_3 adsorption onto a dangling bond.

Comment to the editor: The authors realize that more views on a-Si:H growth exist (See, e.g., Ref. [5] and P. Vigneron, P.W. Peacock, and J. Robertson in these proceedings) and the different reaction mechanisms proposed in the literature can certainly not be excluded *a priori*. It remains however to be revealed how the different reactions mechanisms account for the experimental data presented in this paper. The intention of this paper is therefore to trigger discussion on the a-Si:H growth mechanism from different perspectives within the “boundary conditions” of the experimental results reported in the literature such that the a-Si:H growth mechanism will finally be resolved.

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REFERENCES

- [1] W.M.M. Kessels, A.H.M. Smets, D.C. Marra, E.S. Aydil, D.C. Schram, and M.C.M. van de Sanden, *Thin Solid Films* **383**, 154 (2001).
- [2] S. Ramalingam, D. Maroudas, and E.S. Aydil, *J. Appl. Phys.* **86**, 2872 (1999).
- [3] S. Ramalingam, D. Maroudas, E.S. Aydil, and S.P. Walch, *Surf. Sci.* **418**, L8 (1998).
- [4] A. Gupta, H. Yang, and G.N. Parsons, *Surf. Sci.* **496**, 307 (2002).
- [5] R. Dewarrat and J. Robertson, *Appl. Phys. Lett.* **82**, 883 (2003).
- [6] S. Walch, S. Ramalingam, E.S. Aydil, and D. Maroudas, *Chem. Phys. Lett.* **329**, 304 (2000).
- [7] W.M.M. Kessels, R.J. Severens, A.H.M. Smets, B.A. Korevaar, G.J. Adriaenssens, D.C. Schram, and M.C.M. van de Sanden, *J. Appl. Phys.* **89**, 2404 (2001).
- [8] W.M.M. Kessels, M.G.H. Boogaarts, J.P.M. Hoefnagels, D.C. Schram, and M.C.M. van de Sanden, *J. Vac. Sci. Technol. A* **19**, 1027 (2001).
- [9] W.M.M. Kessels, J.P.M. Hoefnagels, M.G.H. Boogaarts, D.C. Schram, and M.C.M. van de Sanden, *J. Appl. Phys.* **89**, 2065 (2001).
- [10] W.M.M. Kessels, C.M. Leewis, M.C.M. van de Sanden, and D.C. Schram, *J. Appl. Phys.* **86**, 4029 (1999).
- [11] W.M.M. Kessels, A. Leroux, M.G.H. Boogaarts, J.P.M. Hoefnagels, M.C.M. van de Sanden, and D.C. Schram, *J. Vac. Sci. Technol. A* **19**, 467 (2001).
- [12] J.P.M. Hoefnagels, A.A.E. Stevens, M.G.H. Boogaarts, W.M.M. Kessels, and M.C.M. van de Sanden, *Chem. Phys. Lett.* **360**, 189 (2002).
- [13] J.P.M. Hoefnagels, Y. Barrell, W.M.M. Kessels, and M.C.M. van de Sanden, to be published.
- [14] A. Matsuda, K. Nomoto, Y. Takeuchi, A. Suzuki, A. Yuuki, and J. Perrin, *Surf. Sci.* **27**, 50 (1990).
- [15] W.M.M. Kessels, M.C.M. van de Sanden, R.J. Severens, and D.C. Schram, *J. Appl. Phys.* **87**, 3313 (2000).
- [16] J. Perrin and T. Broekhuizen, *Appl. Phys. Lett.* **50**, 433 (1987).
- [17] J. Perrin, Y. Takeda, N. Hirano, Y. Takeuchi, and A. Matsuda, *Surf. Sci.* **210**, 114 (1989).
- [18] D.A. Doughty, J.R. Doyle, G.H. Lin, and A. Gallagher, *J. Appl. Phys.* **67**, 6220 (1990).
- [19] N. Itabashi, N. Nishikawa, M. Magane, S. Naito, T. Goto, A. Matsuda, C. Yamada, and E. Hirota, *Jpn. J. Appl. Phys.* **29**, L505 (1990).
- [20] M. Shiratani, H. Kawasaki, T. Fukuzawa, Y. Watanabe, Y. Yamamoto, S. Suganuma, M. Hori, and T. Goto, *J. Phys. D* **31**, 776 (1998).
- [21] A. Nurrudin, J.R. Doyle, and J.R. Abelson, *J. Appl. Phys.* **76**, 3123 (1994).
- [22] J.M. Jasinski, *J. Phys. Chem.* **97**, 5037 (1993).
- [23] J. Perrin, M. Shiratani, P. Kae-Nune, H. Videlot, J. Jolly and J. Guillon, *J. Vac. Sci. Technol. A* **16**, 278 (1998).
- [24] M. Shiratani, H. Kawasaki, T. Fukuzawa, Y. Watanabe, Y. Yamamoto, S. Suganuma, M. Hori, and T. Goto, *J. Phys. D* **31**, 776 (1998).
- [25] W.M.M. Kessels, D.C. Marra, M.C.M. van de Sanden, E.S. Aydil, *J. Vac. Sci. Technol. A* **20**, 781 (2002).
- [26] D.C. Marra, W.M.M. Kessels, M.C.M. van de Sanden, K. Kashefzadeh, E.S. Aydil, *Surf. Sci.* **530**, 1 (2003).
- [27] A. Gallagher, *Mater. Res. Soc. Symp. Proc.* **70**, 3 (1986).
- [28] A. Von Keudell and J.R. Abelson, *Phys. Rev. B* **59**, 5791 (1999).