Temperature dependence of the surface reactivity of SiH$_3$ radicals and the surface silicon hydride composition during amorphous silicon growth

W.M.M. Kessels *, J.P.M. Hoefnagels, P.J. van den Oever, Y. Barrell, M.C.M. van de Sanden

Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received 18 June 2003; accepted for publication 22 October 2003

Abstract

For hydrogenated amorphous silicon (a-Si:H) film growth governed by SiH$_3$ plasma radicals, the surface reaction probability $\beta$ of SiH$_3$ and the silicon hydride (–SiH$_x$) composition of the a-Si:H surface have been investigated by time-resolved cavity ringdown and attenuated total reflection infrared spectroscopy, respectively. The surface hydride composition is found to change with substrate temperature from –SiH$_3$-rich at low temperatures to ≈SiH-rich at higher temperatures. The surface reaction probability $\beta$, ranging from 0.20 to over 0.40 and with a mean value of $\beta = 0.30 \pm 0.03$, does not show any indication of temperature dependence and is therefore not affected by the change in surface hydride composition. It is discussed that these observations can be explained by a-Si:H film growth that is governed by H abstraction from the surface by SiH$_3$ in an Eley-Rideal mechanism followed by the adsorption of SiH$_3$ at the dangling bond created.

Keywords: Amorphous surfaces; Infrared absorption spectroscopy; Laser methods; Plasma processing; Silicon; Sticking; Surface chemical reaction

Understanding of the growth kinetics of thin films is a major effort in materials science. Especially when the films are synthesized by gas phase activation of molecules such as in plasma enhanced chemical vapor deposition, the situation is rather complex due to the large variety of plasma species and broad range of possible surface reactions. For hydrogenated amorphous silicon (a-Si:H) film growth by SiH$_4$ plasmas however, it is generally assumed that the growth process of high-quality films is dominated by SiH$_3$ radicals [1–3]. The growth process of a-Si:H is therefore described by surface reactions of SiH$_3$ [4], but only recently the proposed surface reactions have risen above the level of speculations due to the availability of ab initio calculations and molecular dynamics (MD) simulations. The objective of this letter is to obtain more insight into the surface reactions of SiH$_3$ radicals that rule a-Si:H growth.
from experimental investigations of the SiH$_3$ surface reactivity and the chemical nature of the a-Si:H surface during growth.

The SiH$_3$ surface reactivity, expressed in terms of the surface reaction probability $\beta$ [5], has been addressed in several studies. However, the reported $\beta$-values of SiH$_3$ are either determined for one single substrate temperature only [6,7] or are derived from the conformality of particular deposition profiles and are therefore indirect [5,8,9]. In this letter, we report on direct measurements of $\beta$ of SiH$_3$ during regular deposition conditions and for different substrate temperatures. Furthermore, we consider the temperature dependence of the sticking probability $s$ of SiH$_3$, with sticking being one of the possible SiH$_3$ reactions that can take place at the surface (with $s \leq \beta$). The results will be related to the a-Si:H surface composition in terms of the surface silicon hydrides (–SiH$_x$). The observations will be used to discuss the surface reactions of SiH$_3$ as proposed on the basis of density-functional-theory (DFT) calculations and MD simulations in literature.

The experiments have been carried out in a remote SiH$_4$ plasma created by the expanding thermal plasma method [10]. The deposition process using this method is characterized by three aspects which are beneficial for the present study: (i) under regular plasma conditions, a-Si:H growth is governed almost completely by SiH$_3$ radicals [3,11]; (ii) the growth process is not affected by ion bombardment because of the low self-bias (<2 V) [12]; and (iii) surface reactions by H radicals are expected to be of minor importance because the H flux to the a-Si:H surface is much smaller than the SiH$_3$ flux [11].

The surface composition of the a-Si:H has been deduced from in situ attenuated total reflection infrared spectroscopy experiments, similar to those described in [13]. The experiments involve the deposition of a-Si:H films on a GaAs internal reflection element while surface specificity has been obtained by ion-induced desorption of the surface hydrogen. The spectra measured in the Si–H stretching region reveal narrow absorption lines which reflect the –SiH$_x$ presence at the surface and which are identified on the basis of crystalline silicon literature. Fig. 1 gives the –SiH$_x$ surface composition of a-Si:H for three substrate temperatures: the a-Si:H surface at 100 °C contains mainly trihydrides (–SiH$_3$) and is balanced by dihydrides (≈SiH$_2$) whereas at 250 °C the –SiH$_3$ hydrides have disappeared and the monohydrides (≈SiH) have become dominant. At 400 °C the surface contains only ≈SiH hydrides. These results obtained for SiH$_3$ governed growth conditions are in good agreement with a previous study in an inductively coupled plasma [14], which revealed that the –SiH$_x$ surface composition is governed by thermally activated decomposition reactions. These reactions convert the surface hydrides from –SiH$_3$ to ≈SiH$_2$ to ≈SiH for increasing temperature.

The surface reaction probability $\beta$ of SiH$_3$ has been determined by time-resolved cavity ringdown measurements monitoring the decrease in SiH$_3$ density at a distance of 5 mm from the substrate after a minor periodic modulation of the SiH$_3$ density. The experimental procedure is described.

---

Fig. 1. Surface hydride (–SiH$_x$) composition of the a-Si:H as obtained by attenuated total reflection infrared spectroscopy for substrate temperatures of (a) 100 °C, (b) 250 °C, and (c) 400 °C.
in which it is also demonstrated that SiH₃ is not reactive in the gas phase. Information on α is therefore obtained by measuring the SiH₃ loss time to the surface at different pressures, as shown in Fig. 2 for substrate temperatures between 50 and 450 °C. The loss time of SiH₃ can be expressed by

\[ \tau_{\text{SiH}_3} = \frac{A_0}{D} + \frac{4l_0}{v_{\text{th}}} \frac{1 - \beta/2}{\beta} \]

with \( D \) the diffusion coefficient and \( v_{\text{th}} \) the thermal velocity of SiH₃ and \( A_0 \) and \( l_0 \) geometrical factors [6]. The increase of \( \tau \) with pressure is therefore due to slower diffusion at higher pressures (lower \( D \)) while \( \beta \) can be deduced from the extrapolated loss time at zero pressure which reflects the “free-fall” limit of the SiH₃ radicals [15]. The SiH₃ thermal velocity \( v_{\text{th}} \) has been calculated from the gas temperature (1500 ± 200 K, independent of the substrate temperature) obtained from Doppler linewidth studies of Si radicals in the plasma, while \( l_0 \) has been deduced from the slope of the linear fits of the data in Fig. 2.

The resulting values for \( \beta \) of SiH₃ are shown in Fig. 3. The surface reaction probability \( \beta \) ranges from 0.20 to over 0.40 with a mean value of \( \beta = 0.30 \pm 0.03 \) and without any indication of temperature dependence for the temperature range and conditions studied. The \( \beta \) values show also good agreement with those obtained previously by indirect means under SiH₃ dominated conditions [9] and with the \( \beta \) value at 300 °C determined in a radiofrequency plasma using time-resolved mass spectrometry [6]. The temperature independence of \( \beta \) is consistent with the results obtained by the aforementioned indirect investigations based on the conformality of deposition profiles [5]. Furthermore, the temperature independence is also in accordance with the results from MD simulations (discussed below) that revealed \( \beta = 0.18 \) [16].

Direct experimental determination of the sticking probability \( s \) of SiH₃ (with \( s \leq \beta \)) is unfeasible in the present experiment but information on the temperature dependence of \( s \) can be obtained from the Si growth flux as shown in Fig. 4 [5,9]. The growth flux, which can be expressed by

\[ \Gamma_{\text{Si}} = \frac{1}{4} n v_{\text{th}} \frac{s}{1 - \beta/2} \]

for SiH₃ governed growth, shows no clear dependence on the substrate temperature while also the density \( n \) of SiH₃ in front of the substrate and \( v_{\text{th}} \) are independent of substrate temperature. As a consequence, also \( s \) of SiH₃ is substrate temperature independent. This temperature dependence of both \( \beta \) and \( s \), which might simply indicate that \( s = \beta \), puts strict constraints on the surface reactions of SiH₃, particularly because the surface –SiHₓ composition changes drastically. We will use this information to obtain more insight into the dominant surface reactions of SiH₃. Although
several surface reactions have been proposed in the literature, we will limit ourselves to three reactions for which evidence exists from both DFT calculations and MD simulations.

The first reaction [Fig. 5(a)] is the adsorption of SiH$_3$ on a surface dangling bond [16]. This reaction has no activation energy barrier and its occurrence is generally accepted. However, its significance in a-Si:H growth (in the case that SiH$_3$ adsorbs directly from the gas phase) is usually considered to be limited because it is often assumed that the surface density of dangling bonds on a-Si:H is very low [4]. The second reaction [Fig. 5(b)] is the abstraction of an H atom by SiH$_3$ creating a surface dangling bond. Such an abstraction reaction has been considered to be important since the first growth mechanisms of a-Si:H were proposed because it leads to new sites for SiH$_3$ adsorption. Recently, evidence has been presented that this H abstraction takes place by an Eley-Rideal reaction by SiH$_3$ from the gas phase and not by “physisorbed” SiH$_3$ on the a-Si:H surface [17–19]. Although several values have been calculated [18,19], Ramalingam et al. [17] found an activation energy of 0.09 eV for H abstraction by DFT and MD simulations. This small activation energy indicates that H abstraction by SiH$_3$ is relatively weakly temperature dependent. The third reaction [Fig. 5(c)] is the insertion of SiH$_3$ into a strained Si–Si bond at the surface. This insertion reaction, proposed on the basis of experimental work [20], leads to SiH$_3$ adsorption without a surface dangling bond being involved. The insertion reaction creates a fivefold coordinated Si atom [16] and Walch et al. [21] found activation energies in the range of 0.7–0.9 eV for a Si(0 0 1)×(2×1)
surface. Furthermore, they found that insertion occurs less frequently than H abstraction, which is consistent with the higher activation energy for insertion.

We will address the consequences of the results obtained for the surface –SiH\textsubscript{x} composition and \( s \) and \( \beta \) for these three surface reactions to identify their importance in a-Si:H growth. If the insertion reaction has a similar magnitude for the activation energy for a-Si:H as for the Si(001)\((2 \times 1)\) surface (which is not necessarily the case due to the different surface structure), the relatively high activation energy implies that the occurrence of insertion is highly temperature dependent. If SiH\textsubscript{3} insertion relies also on the presence of dimer-like strained Si–Si bonds, the reaction is even more likely at high temperatures, when the surface is composed of –SiH instead of higher hydrides. As a consequence, a-Si:H film growth that is governed by SiH\textsubscript{3} insertion is expected to have a strong temperature dependence and therefore our results on \( \beta \) and \( s \) suggest that an insertion reaction as proposed in [20,21] is not very important.

The reaction in which SiH\textsubscript{3} adsorbs on a surface dangling bond has zero activation energy. This will lead to a temperature independent sticking probability \( s \) when the density of surface dangling bonds available for adsorption is temperature independent. The (nearly) temperature independent creation mechanism of dangling bonds by the Eley-Rideal reaction in Fig. 5(b) is helpful in fulfilling this condition although there is one apparent complication. On the basis of the surface –SiH\textsubscript{x} composition it is expected that more H atoms are present at the surface at low temperatures which might imply that SiH\textsubscript{3} has a higher probability to abstract H at lower temperatures. However, it should be realized that not all surface H atoms are available for H abstraction because this would lead to an exponential increase in surface sites. Moreover, the fact that at lower substrate temperatures more H atoms are incorporated into the a-Si:H [4] implies that not all surface H atoms are subject to H abstraction by SiH\textsubscript{3}. Therefore, it is plausible that the number of dangling bonds created at the surface and consequently the surface dangling bond density is not significantly temperature dependent. The combination of H abstraction by SiH\textsubscript{3} and adsorption of SiH\textsubscript{3} on the created dangling bonds can therefore explain the temperature independence of both \( \beta \) and \( s \) while it also clarifies why \( \beta \) and \( s \) are not affected by the surface –SiH\textsubscript{x} composition.

The H abstraction and SiH\textsubscript{3} adsorption reactions need to balance each other (i.e., \( s = \frac{1}{2} \beta \) when other surface recombination reactions of SiH\textsubscript{3} can be excluded) and this implies a rather high surface dangling bond density during a-Si:H growth [4] when adsorption takes place directly by SiH\textsubscript{3} from the gas phase. However, at the moment we cannot exclude that SiH\textsubscript{3} can also adsorb on other surface sites and can find dangling bonds by surface diffusion [16,22]. Such an adsorption mechanism reduces the number of surface dangling bonds but has no consequences for the above-mentioned reaction mechanism as long as the H abstraction reaction is the rate-limiting step. Furthermore, the surface mobile species can contribute to surface smoothening which is very important for a-Si:H film growth [19,22,23].

In summary, it has been made plausible that the balance between H abstraction by SiH\textsubscript{3} in an Eley-Rideal mechanism and the adsorption of SiH\textsubscript{3} on the dangling bonds created can explain the observations that \( s \) and \( \beta \) are substrate temperature independent and not affected by the temperature dependent surface –SiH\textsubscript{x} composition. These two reactions can therefore be mainly responsible for a-Si:H growth from SiH\textsubscript{3} radicals when reactions by other plasma species (SiH\textsubscript{n} \((n \leq 2)\), H, etc.) can be neglected.

**Acknowledgements**

This work has been supported by the Netherlands Foundation for Fundamental Research on Matter (FOM). The research of W.K. has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences (KNAW).

**References**