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High-rate a-Si:H and µc-Si:H film growth studied by advanced plasma and in situ film diagnostics

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ABSTRACT

Plasma and in situ film studies have been applied to the expanding thermal plasma to obtain basic insight into the deposition of a-Si:H and µc-Si:H at high rates (> 10 Å/s). A study of the density of plasma radicals (Si, SiH, SiH₃) and of the radicals’ surface reactivity has revealed that SiH₃ is the most important radical for the growth of both materials. In situ attenuated total reflection infrared spectroscopy and spectroscopic ellipsometry have revealed a thick interface layer and consequently long incubation time for the materials deposited at a high deposition rate.

INTRODUCTION

High-rate deposition and the Expanding Thermal Plasma

Photovoltaics can become a much more competitive energy source through achieving ‘economy-of-scale’. This can only be obtained when the throughput of solar cell production lines is considerably increased while keeping the investment in equipment relatively low. Industry is therefore focused on increasing the deposition rate of the a-Si:H and µc-Si:H material for silicon-based thin film solar cells.

A possible candidate for achieving high-rate deposition at the industrial scale is the “Expanding Thermal Plasma” (ETP, Fig. 1) developed at the Eindhoven University of Technology [1]. The features of this remote plasma technique are very high deposition rates (10-100 Å/s) and a low ion bombardment that can be increased and regulated by an external rf bias. The technique consists of a cascaded arc plasma source which is operated at high gas flows and high pressure (300 Torr). This leads to very effective dissociation/ionization of the gas and consequently a plasma with very high reactivity emanates from the source into the low-pressure (0.15 Torr) reactor. When operated on Ar-H₂ mixtures (for Si-based films), the plasma source creates a downstream afterglow plasma in which electrons and ions play a minor role and the source basically acts as a high flux H source. The primary dissociation channel of the SiH₄ injected into this downstream plasma are consequent reactions with H. Ar species play a negligible role in the downstream plasma and Ar is only injected to ensure a good plasma source operation (although this is not strictly necessary).

Optimum quality a-Si:H is obtained when SiH₄ is abundant with respect to the H density. This is achieved for a H₂/SiH₄ flow ratio of ~1 (this corresponds to a

Figure 1. The Expanding Thermal Plasma (ETP)
equivalent “H/SiH4 flow” ratio of ~0.1). Films of μc-Si:H are obtained for cases where the H2/SiH4 flow ratio is >50 (equivalent “H/SiH4 flow” ratio of >5).

Besides being an interesting candidate for high-rate deposition of Si films at the industrial scale, the ETP technique can also contribute to gaining more generic insight into the possibilities and limitations of high-rate deposition. In this paper we will therefore briefly report on the status of our investigations of the plasma and film growth processes for both the a-Si:H and μc-Si:H material. However, first the material properties will briefly be addressed.

**Material properties of high-rate deposited a-Si:H and μc-Si:H**

The fact that low-defect density a-Si:H can be obtained by the ETP at deposition rates up to 100 Å/s has already been addressed extensively in previous publications [1]. At the moment, the efforts concerning a-Si:H are mainly focused on the integration of the material in solar cells [2]. A very important issue in this respect seems to be the relatively high substrate temperature (~400 °C) that is required to obtain good quality a-Si:H at the highest rates.

The fact that also μc-Si:H can be deposited at high rates has only been reported recently [3]. Films with crystallite fractions up to 70% and crystallite sizes of 200-300 Å have been obtained at deposition rates between 10 and 30 Å/s for a substrate temperature of 250 °C. The dark and photoconductivity are typically $10^{-7} \Omega^{-1} \text{cm}^{-1}$ and $10^{-5} \Omega^{-1} \text{cm}^{-1}$ respectively; the activation energy is ~600 meV and the $E_g$ optical band gap ~2.0 eV. Densification of the material seems to be an important issue for the μc-Si:H because it seems to have a relatively high fraction of voids.

**EXPERIMENTAL DETAILS OF PLASMA AND IN SITU FILM DIAGNOSTICS**

The density of SiH4 radicals has been obtained by the highly-sensitive absorption technique cavity ring down spectroscopy (CRDS, Fig. 2). The measurements have been performed at a distance of 3.6 cm from the substrate holder. The technique and the spectral details of the detected radicals Si, SiH and SiH3 have been described in Ref. 4 and the measurements for the a-Si:H conditions have now been extended to the μc-Si:H conditions. Entirely new time-resolved CRDS measurements have also been applied to determine the gas phase and surface loss rates of the radicals. In particular, the surface reaction probability $\beta$ is a very important parameter because it yields direct information on the importance of the radicals for the film growth process. In time-resolved CRDS measurements the decay of the radical density is monitored after stopping its production (e.g., by switching the plasma off) and the decay time $\tau$ gives information on how fast the radical is lost in the gas phase and/or on the surface. Here we have monitored the decay of the radical density after a minor periodic disturbance of this density. Consequently information on $\beta$ is obtained during the deposition process itself, which is different from the commonly applied technique of switching the plasma off completely.

**Figure 2.** Plasma and in situ film diagnostics
Information on the film growth process is obtained from the combination of the *in situ* film diagnostics attenuated total reflection infrared spectroscopy (ATR-FTIR) and spectroscopic ellipsometry (SE). ATR-FTIR has been applied by using ZnSe or Si ATR crystals such that the sensitivity is enhanced by 30 reflections of the infrared beam at the top surface. It therefore reveals accurate depth information on the SiH bonds in the films. SE has been applied to obtain information on interface/surface layer formation, evolution of the surface roughness, etc. The SE data have therefore been analyzed in a simple 2-layer model by a procedure similar to the ones described in Refs. 5 and 6. The dispersion model proposed by Jellison and Modine [7] has been used and the optical functions for both materials are considerably different: for µc-Si:H $\varepsilon_1$ has a maximum at a higher photon energy while also the optical band gap deduced from $\varepsilon_2$ is higher than for a-Si:H. The interface/surface layer has been modeled as a 50/50 vol.% mixture of the bulk material and voids.

**RESULTS**

**Radical densities**

The density of the radicals Si, SiH, and SiH$_3$ are given for different H$_2$/SiH$_4$ flow ratios in Fig. 3. The figure shows that the SiH$_3$ radical has the highest density in the plasma both for the a-Si:H (low ratio) and µc-Si:H (high ratio) conditions. The high density of SiH$_3$ suggests that SiH$_3$ is most probably the dominant radical for the formation of the films whereas the decreasing SiH$_3$ density with increasing H$_2$/SiH$_4$ flow ratio correlates with the lower deposition rate of µc-Si:H. The SiH density shows a slight increase when going to the µc-Si:H conditions but the Si density increases by a factor of ~100. This indicates that Si is relatively much more important for µc-Si:H film growth than for a-Si:H film growth.

Atomic hydrogen H is another radical which can be very important for a-Si:H and especially µc-Si:H film growth. No direct density information is available yet for the Si-depositing plasmas but model calculations have revealed that the flux of H to the surface during a-Si:H film growth is ~50 times lower than the flux of SiH$_3$ [5]. For the µc-Si:H conditions, it is expected that H plays a very significant role because the flow of H from the plasma source is higher and less H is consumed in the SiH$_4$ dissociation process.

![Figure 3. Density of SiH$_4$ radicals for a-Si:H (low H$_2$/SiH$_4$ flow ratio) and µc-Si:H conditions (low H$_2$/SiH$_4$ flow ratio).](image)

![Figure 4. Decay and time-constants $\tau$ of Si and SiH$_3$ after a temporal increase of their density by a minor disturbance to the plasma.](image)
Radicals’ surface reactivity

Before conclusions can be drawn on the importance of the radicals for the deposition process, information is also required on their surface reaction probability $\beta$. Values of $\beta$ have been deduced from time-resolved CRDS measurements that were performed under steady-state deposition conditions, i.e., the values of $\beta$ are really valid during the actual deposition process. So far, we have only applied this technique to the a-Si:H conditions. A typical time-resolved measurement of the Si and SiH$_3$ density decay is given in Fig. 4.

First, from the variation of the decay time $\tau$ with the partial SiH$_4$ pressure, it has been deduced that Si is very reactive with gaseous SiH$_4$ [reaction rate $=(1.4\pm0.2)\times10^{-16}$ m$^3$s$^{-1}$] while SiH$_3$ does not react in the gas phase. This fact alone largely explains why the decay of Si in Fig. 4 is much faster than the decay of SiH$_3$. Subsequently, from total pressure series, $\beta$ values for Si and SiH$_3$ have been obtained, yielding $0.9<\beta\leq1$ and $\beta=0.30\pm0.05$, respectively. Information on $\beta$ of SiH has recently been obtained by another technique, both for a-Si:H and $\mu$-c-Si:H. These measurements revealed $\beta=0.96\pm0.04$ for both materials [9].

Combining the information on the surface reactivity with the one on the radical densities in Fig. 3, shows that SiH$_3$ is indeed the most important radical for a-Si:H film growth. This is most probably also the case for $\mu$-Si:H film growth because the $\beta$ values of the radicals will not change drastically when going from a-Si:H to $\mu$-c-Si:H conditions. Furthermore, it shows that the contribution of Si to $\mu$-c-Si:H film growth is much higher than for a-Si:H: the contribution of Si to $\mu$-c-Si:H film growth reaches a level of a few percent.

Hydrogen bonding configuration and interface layer

ATR-FTIR has been applied to monitor the hydrogen bonding configuration as a function of the film thickness. In Fig. 5(a) the absorbance due to SiH and SiH$_2$ in the film (extracted from the SiH$_x$ stretching region at around 2000-2100 cm$^{-1}$) is given for an a-Si:H and $\mu$-c-Si:H film, both deposited at 250 ºC. Several observations can be made: Firstly, for both types of films the SiH$_2$ absorbance is larger than the SiH absorbance showing that most hydrogen in the film is bonded as SiH$_2$ (taking the difference in absorption cross-sections into account). For a-Si:H, this is already well-known and therefore the a-Si:H is usually deposited at temperatures of ~400 ºC [1]. Furthermore, Fig. 5(a) indicates that the a-Si:H contains more hydrogen than the $\mu$-c-Si:H. Elastic recoil detection (ERD) on the other hand has not revealed a considerable difference in hydrogen concentration (for both materials ~20 at.% at 250 ºC). Such a discrepancy between infrared spectroscopy and ERD results has been observed before [10] and it indicates a considerable amount of non-bonded hydrogen in the $\mu$-c-Si:H. Finally, the absorbance values do not increase linearly with increasing film thickness. This can be partially explained by the fact that the film thickness on the horizontal scale is deduced from the deposition rate that has been assumed homogeneous over the film. A slightly lower deposition rate at initial film growth might therefore explain the non-linearity of the SiH$_2$ absorbance. The SiH absorbance, however, shows more non-linearity and even shows an incubation time effect.

The presence of an interface layer and incubation time is also observed when looking at the shift in the absorption peak positions as shown in Fig. 5(b). For both materials, it takes a thickness of about 500 Å before the peaks have reached their “bulk position”.

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Figure 5. (a) Infrared absorbance of SiH and SiH$_2$ bonding mode vs. film thickness for the a-Si:H and µc-Si:H films as obtained by in situ attenuated total reflection infrared spectroscopy. (b) Corresponding relative shift in peak position of the SiH and SiH$_2$ peaks vs. film thickness.

The peak widths of SiH and SiH$_2$ do not show a trend with film thickness. However, for the µc-Si:H the SiH peak width is broader than for the a-Si:H (90 cm$^{-1}$ and 70 cm$^{-1}$, respectively) while the SiH$_2$ peak is narrower (40 cm$^{-1}$ instead of 65 cm$^{-1}$).

Interface layer and surface roughness

More information on the interface layer has been obtained from spectroscopic ellipsometry SE [5,6]. Figure 6 shows our first SE results as obtained for a-Si:H and µc-Si:H films. Both materials clearly show an incubation time before bulk film growth takes place. Initially, an interface layer is formed whose thickness suddenly decreases after coalescence of the nucleation sites occurs. Thereafter, the thickness of the interface/surface layer again increases considerably for the µc-Si:H film which may indicate the formation of the crystallites [6]. Figure 6 also shows that the interface layer is relatively thick for the high-rate deposited films. For comparison, an interface layer thickness of only 20 Å has been observed for a-Si:H deposited by rf PECVD at a rate of 0.35 Å/s [6]. The thick interface layer might demonstrate an important issue for the imple-
mentation of Si-based films deposited at high-rate in solar cells. A possibly related aspect is that the final surface roughness of the films is relatively high: the surface roughness is almost a factor 10 higher than for the low-rate deposited rf PECVD material [6]. It is also important to note is that a-Si:H deposited at relatively low rates (2.7 Å/s) by the ETP technique (under conditions that are also dominated by SiH3 radicals [11]) have revealed almost no interface layer and a normal surface roughness.

CONCLUSIONS

It is shown that the combination of several plasma and in situ film diagnostics applied to the same deposition setup is very powerful for gaining insight into the growth process of a-Si:H and µc-Si:H at high deposition rates. The investigations have revealed that both a-Si:H and µc-Si:H growth are governed by the same radical (SiH3) although the importance of SiH and Si increases for the µc-Si:H conditions. The first in situ infrared spectroscopy and spectroscopic ellipsometry data have indicated the formation of a relatively thick surface/interface layer for the high-rate deposited films which can be an important issue for the incorporation of the material into solar cells.

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