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Material properties and growth process of microcrystalline silicon with growth rates in excess of 1 nm/s

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ABSTRACT

The expanding thermal plasma (ETP) has been used to deposit microcrystalline silicon ($\mu\text{c-Si:H}$) with rates up to 2.7 nm/s. Typical material properties of well crystallised material are crystallite sizes of 20 nm, photo- and dark conductivity of 2×10^{-5} and 2×10^{-7} S/cm respectively, and an activation energy of 600 meV. The radical densities of SiH_3 , SiH , and Si present in the gas phase have been quantified. In conditions where $\mu\text{c-Si:H}$ is deposited the atomic hydrogen flux towards the surface is of the same magnitude or higher as the flux of deposited radicals. Furthermore, the abundance of radicals such as SiH and Si is large and may contribute several tens of percent to the deposition rate.

INTRODUCTION

The deposition of $\mu\text{c-Si:H}$ is often achieved by diluting silane in hydrogen. Issues in the research on this material include the growth mechanism, and especially the role of atomic hydrogen in it, and obtaining high growth rates [1,2,3]. Since microcrystalline silicon has a lower absorption coefficient than a-Si:H in the visible part of the spectrum, the layers have to be thicker (several microns) when implemented in a solar cell. Higher growth rates than that currently achieved are therefore required.

Two techniques to deposit $\mu\text{c-Si:H}$ are radio frequent plasma enhanced chemical vapour deposition (RF-PECVD) and hot wire or catalytic chemical vapour deposition (HW- or Cat-CVD). In RF-PECVD electrons gain energy in an oscillating electric field and dissociate the silane and hydrogen by electron impact. Under conditions for $\mu\text{c-Si:H}$ deposition ions are an abundant species [4]. In HW-CVD the radicals are created by dissociation of silane and hydrogen at a hot, typically 2000 K, tungsten filament. The radicals may react in the gas phase or at the surface leading to the growth of a silicon containing film.

Since several years we deposit a-Si:H with an expanding thermal plasma and study its growth process. The thermal plasma is created at pressures of 0.5 bar in a mixture of argon and hydrogen and under these conditions the plasma is a source of atomic hydrogen. This plasma expands into a low-pressure (20 Pa) vessel in which silane is injected. The atomic hydrogen reacts with the silane and creates silane radicals by hydrogen abstraction. The expanding plasma transports the radicals to the substrate 35 cm further downstream. Under a-Si:H deposition conditions SiH_3 is the most important radical while growth rates of 7 nm/s are obtained [5].

In this paper we will demonstrate that we can deposit $\mu\text{c-Si:H}$ silicon at rates up to 2.7 nm/s using the expanding thermal plasma. Different radicals present during the deposition are measured and their densities quantified and the relation with the obtained material structure is outlined. The observations for our technique will be generalised for RF-PECVD and HW-CVD.

EXPERIMENTAL DETAILS

Cavity ring down spectroscopy is used to determine the densities of the SiH₃, SiH and Si radicals at a distance of 3.6 cm in front of the substrate. In Table I the used transitions and their wavelengths are given. In all these cases a tuneable dye laser with a pulsed Nd-YAG pump laser was used to obtain the required wavelength. For a more elaborate discussion on the principle and discussion of cavity ringdown spectroscopy we refer to [5].

Table I. Electronic transition of the different radicals and the corresponding wavelength.

Radical	Transition	Wavelength (nm)
SiH ₃	$\tilde{A}^2A_1 \leftarrow X^2A_1$	247.00
SiH	$A^2\Delta \leftarrow X^2\Pi [Q_1(11.5)]$	413.46
Si	$4s^3P_2^0 \leftarrow 3p^2^3P_1$	250.69

In-situ single wavelength (623.8 nm) ellipsometry is used to determine the growth rate and optical properties. The material structure is studied by both X-ray diffraction (XRD), using the Cu-K α line, and Raman spectroscopy using a diode laser with a wavelength of 785 nm.

RESULTS

The results presented here are obtained with a flow of 55 sccs argon, 30 sccs hydrogen and a variable flow of silane unless stated otherwise. This series has as advantage that the cascaded arc is always working under the same conditions and therefore producing the same amount of atomic hydrogen. The substrate temperature is kept at 250°C. Under similar conditions with 10 sccs H₂ and 10 sccs SiH₄ a-Si:H is deposited with the ETP [5].

SiH_x radical densities

In figure 1(a) the radical densities of SiH₃, SiH and Si are plotted as function of the silane flow. SiH₃ is the most abundant Si containing radical and increases with the silane flow. The SiH₂ densities have not been measured yet. The SiH density increases slightly as function of the silane flow and is at least a decade lower than the SiH₃ density. The Si density decreases with silane flow and is about a factor 10 lower than the SiH₃ density at the lowest silane flow. Both Si and SiH densities remain rather constant although the silane flow changes about a factor of ten. Based on etch experiments of μ c-Si:H the flux of atomic hydrogen towards the surface in absence of silane is in the order of $1 \times 10^{21} \text{ m}^{-2} \text{ s}^{-1}$, corresponding to densities of $1.5 \times 10^{18} \text{ m}^{-3}$. This density is indicated in the figure at zero silane flow. This density will decrease with increasing silane flow due to the creation of SiH_x radicals and H₂ by atomic H.

The growth rate as function of silane flow is plotted in figure 1(b). The high growth rates obtained are evident. Silane flow rates lower than 0.7 sccs result in μ c-Si:H. The growth rate $r_{d,i}$ due to species i with density n_i in the gasphase is:

$$r_{d,i} = \frac{1}{4\rho} \frac{s_i}{1 - \beta_i / 2} n_i c \quad (1)$$

Where ρ is the atomic density of the deposited network ($5 \times 10^{28} \text{ m}^{-3}$), s_i the sticking

Figure 1. (a) Radical densities of SiH₃, SiH, and Si as obtained with cavity ring down spectroscopy at a distance of 3.6 cm in front of the substrate as function of silane flow, (b) growth rate as function of the silane flow together with the estimates for the contribution of the different radicals to the film growth.

coefficient of species i , β_i its surface reaction probability and c its mean thermal velocity in our plasma (≈ 700 m/s, for silane radicals). If figure 1(b) we plotted the contributions of different radicals. Here we assumed for SiH₃ $s=0.09$ and $\beta=0.26$, for SiH $s=\beta=0.95$, and for Si $s=\beta=1$. Etching by atomic hydrogen is not taken into account. At the lowest silane flows the large contribution to the growth rate by Si and SiH is evident.

The typical SiH₄ depletion, as is measured with mass spectrometry, is 60% and is constant up to at least a silane flow of 1.4 sccs. This demonstrates that the amount of silane is the limiting factor and not the amount of atomic H from the plasma source. For the following it is important to notice that with increasing silane flow the ratio atomic H-flux over SiH_x-growth flux will decrease although exact quantification is not yet possible and that also the composition of the SiH_x radical flux changes.

Material properties

The change in material structure with changing silane flow is evident in many material properties. As an example, we present the hydrogen content in figure 2. At the lowest silane flows the hydrogen content is low and peaks at higher flows. Such behaviour has also been reported for material deposited with conventional RF plasmas [2].

Figure 2. The hydrogen content in the films as is determined from the 640 cm⁻¹ IR-absorption.

From the IR absorption spectra the narrow peaks in the 2000-2100 cm⁻¹ wavenumber region associated with SiH and SiH₂ on c-Si surfaces are observed for the samples deposited with silane flows below 0.7 sccs. Above this value the ‘amorphous’ 2000 and 2100 cm⁻¹ peaks are observed.

The change in structure is also evidenced in Raman spectra, see figure 3. The Raman spectrum of the sample deposited with 0.5 sccs silane is dominated by the c-Si peak near 520 cm⁻¹, demonstrating a microcrystalline

structure. XRD measurements indicate a preferential (111) orientation and a typical

Figure 3. Raman spectra for two samples deposited at (a) 0.5 sccs silane and (b) 1.4 sccs. crystallite size of 20 nm as is determined from Scherrer's formula. The sample deposited at 1.4 sccs silane shows a broad peak around 480 cm⁻¹ (figure 3(b)),

indicating an amorphous structure. The sample deposited at 0.7 sccs still has a clear crystalline contribution with also a clear amorphous peak.

The refractive index at a photon energy of 2 eV is typically around the 3.10 whereas the extinction coefficient is 0.040, corresponding to an absorption coefficient of 5×10^3 cm⁻¹. These low values indicate a porous material. Using Bruggeman for c-Si with voids and a refractive index in the IR of typically 3.0 we estimate a void fraction of about 20%. The Tauc bandgap is typically 1.90 eV.

The dark and photoconductivity of the microcrystalline samples (silane flow <0.6 sccs) are typically 2×10^{-7} S/cm and 2×10^{-5} S/cm as is measured with coplanar electrode geometry. The activation energy is typically 600 meV. The dual beam photoconductivity method yields defect densities of $0.5-1 \times 10^{17}$ cm⁻³.

DISCUSSION: Comparison with a-Si:H deposition

The advantage of the expanding thermal plasma is that the primary chemistry under the conditions studied is mostly driven by reactions of atomic hydrogen with silane. Our standard conditions for the deposition of amorphous silicon are 10 sccs H₂ and 10 sccs SiH₄. The main reaction is believed to be the hydrogen abstraction reaction:

Under these conditions about 10% of the silane is depleted as is known from mass spectrometry measurements [6]. It is also known from H/D exchange experiments that almost all the atomic hydrogen is used in the creation of silane radicals [7]. In our microcrystalline conditions we used a three times larger hydrogen flow resulting in a three times larger atomic hydrogen flow from the arc as we conclude from the etch rates as function of hydrogen flow (not shown). Furthermore the silane flow is typically 20 times lower. This explains the high depletion since we have a surplus of atomic hydrogen with respect to the injected silane (0.5 sccs). Based on a crude estimate we expect at least 3 sccs H emerging from the arc. So after

complete reaction (2) with silane still 2.5 sccs H could be available. This surplus of atomic hydrogen may result in secondary abstraction reactions with SiH_3 leading eventually to Si. It should be noticed that enough atomic hydrogen is available to achieve this. Although we think that hydrogen is lost more effectively in transport than the silane radicals due its larger diffusion coefficient and effective recombination at the walls of the vessel we still expect a surplus of atomic hydrogen at the growing surface [8].

If we compare the relative abundance of SiH and Si under microcrystalline conditions with those of a-Si:H conditions [5], it is concluded that these radicals are much more important than in a-Si:H growth conditions. For comparison the SiH_3 radical contributes to about 90% of the growth in a-Si:H, SiH about 2% and Si only 0.2%.

We conclude that the main difference of conditions in which we deposit microcrystalline silicon with conditions in which we deposit a-Si:H is the larger production of atomic H than the amount of injected silane molecules. This leads to on the one hand an efficient use of the silane and still a considerable flux of atomic hydrogen to the growing surface. However due to the surplus of atomic hydrogen additional abstraction reactions, leading to more reactive radicals as SiH_x ($x < 3$), are also important.

Comparison with HWCVD and PECVD

We will try to make a short comparison of the growth process and material properties as obtained with the expanding thermal plasma as described here and of the hot wire and RF PECVD technique.

Microcrystalline silicon is deposited by the expanding thermal plasma, HW-CVD and RF-PECVD by using a high dilution of silane in hydrogen, while under lower dilution amorphous silicon is deposited. Also the concentrations of silane in hydrogen in these techniques are comparable, typically a few percent. The silane gas consumption is in general higher than under amorphous silicon conditions, as may be seen from the comparison of the obtained growth rates per injected silane flow. The general tendency in all these techniques will be an increase of atomic hydrogen production with increasing dilution, irrespectible of the type of silicon radicals already created, and often this is used to conclude that atomic hydrogen is necessary for the formation of crystallites. So we observe many similarities between the different techniques.

For the gasphase the following general picture arises. With increasing dilution (=decreasing silane flow) the atomic hydrogen production increases. This will have several consequences. Firstly, besides the normally active dissociation process of silane (electron dissociation of silane in RF and catalytic/thermal dissociation in HW) the hydrogen abstraction reactions like (2) will become increasingly more important. This might result in the production of more reactive radicals, as e.g. Si, of course depending on the mean free path. Secondly the flux of atomic hydrogen to the substrate will increase.

Thus there appear two possible causes for the change of material structure from a-Si:H into $\mu\text{c-Si:H}$ with increasing H_2 dilution. The first is the increasing importance of SiH_x radicals with $x < 3$, which becomes significant for the lower silane flows. The second is the increasing flux of atomic hydrogen towards the growing surface. This latter species is normally held responsible for the crystallisation process.

Apparently there are two limiting conditions in which $\mu\text{c-Si:H}$ is formed. The first condition the main silicon containing radical is SiH_3 and there is enough atomic H present at the surface to induce crystallisation. The second condition is the case in which all the silane is stripped of H in the gas phase to yield Si and there is still enough atomic hydrogen to

result in microcrystalline silicon. Hamers *et al.* [4] have reported measurements on the surface reaction probability. In their results on RF-PECVD it was observed that the surface reaction probability of the radicals under conditions of microcrystalline formation are low and around 0.2. This is an example of the first extreme. Indeed the dilution is close to the dilution needed to obtain polymorphous or amorphous silicon. In that same paper HW was studied which yielded higher surface reaction probabilities (up to 0.56) with increasing dilution. This might be an example of the second condition, where most of the silane is stripped to Si.

The different methods to deposit $\mu\text{c-Si:H}$ appear to be governed by the same reaction mechanisms. On one hand a high atomic hydrogen production, resulting in efficient silane source gas utilisation, and on the other hand both an increase of the atomic hydrogen flux toward the surface and, depending on the pressure, more abstraction reactions in the gas phase leading to more reactive radicals.

CONCLUSIONS

The expanding thermal plasma is used to deposit $\mu\text{c-Si:H}$ with growth rates upped 2.7 nm/s. The material is characterised extensively. The sizes of the crystallites is typically 20 nm and the photo- and dark conductivity 5×10^{-5} and 5×10^{-7} S/cm with an activation energy of 0.6 eV. We have measured the different growth precursors that are present during the deposition of $\mu\text{c-Si:H}$ using an expanding thermal plasma. The main conclusions are that the atomic hydrogen flux towards the surface is abundant in conditions where micro-crystalline silicon is formed and that the radicals SiH_x ($x < 3$) are relatively more abundant than in conditions where a-Si:H is deposited. The latter is due to successive abstraction reactions of silane radicals by atomic H.

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