The study of amorphous incubation layers during the growth of microcrystalline silicon films under different deposition conditions*

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The structural un-uniformity of μc-Si:H films prepared using a very high frequency plasma-enhanced chemical vapour deposition method has been investigated by Raman spectroscopy, spectroscopic ellipsometer and atomic force microscopy. It was found that the formation of amorphous incubation layer was caused by the back diffusion of SiH_4 and the amorphous induction of glass surface during the initial ignition process, and growth of the incubation layer can be suppressed and uniform μc-Si:H phase is generated by the application of delayed initial SiH_4 density and silane profiling methods.

Keywords: microcrystalline silicon, thin film, amorphous incubation layer

PACC: 7280N, 7830G, 8115H

1. Introduction

Microcrystalline silicon (μc-Si:H) films deposited by plasma-enhanced chemical vapour deposition (PECVD) at a low temperature is a promising material of thin film solar cells because of the low-cost and stability against light illumination.[1−3] In particular, the combination of high pressure depletion (HPD) and very-high frequency (VHF), HPD–VHF, has resulted in high deposition rates while preserving high efficiencies,[4−6] and the best efficiency of μc-Si:H solar cells of 9.1% is obtained at a rate 2.3 nm/s.[7] However, it is well proven that the structure of μc-Si:H film is un-uniformity along the growth direction, and an incubation amorphous silicon (a-Si:H) layer is generated at the interface of substrate. So, the control of the initial growth becomes more crucial, especially, under high deposition rates.

In this paper we investigate the variation of structural properties of μc-Si:H films with film thickness, prepared at different deposition rates, and the growth mechanism of the incubation layer.

2. Experiment

Intrinsic μc-Si:H films were deposited on float glass substrates by capacitively coupled VHF (75 MHz) PECVD with conventional parallel-plate electrodes using a SiH_4/H_2 gas mixture.[8−10] The SiH_4 concentration (R=[SiH_4]/([SiH_4]+[H_2])) was changed within 1.5%∼5%, and the substrate temperature was 220 °C. Series of films have been deposited, a low pressure: ∼ 350 Pa, 0.12–0.23 W/cm^2, and ∼ 66.5 Pa, 0.06 W/cm^2; at high pressure: ∼ 600 Pa, 0.75–0.85 W/cm^2. The thickness and the surface roughness of the films were measured with a spectroscopic ellipsometer (Wvase32), and scaling theory was used to study the growth process.[11] The structural properties of the samples were characterized with Raman spectroscopy and atomic force microscopy (AFM). The Raman spectra in the range 400–600 cm^{-1} have been deconvoluted into three peaks and crystallinity fractions have been estimated.

3. Results

Figure 1 shows the variation of deposition rates of μc-Si:H films with the power density at different pres-

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sures. It can be observed that with the increase of pressure and power density, deposition rate increases, and a rate above 2.0 nm/s is obtained under high pressure and high power conditions. The residence time ($\tau_{\mathrm{r-res}}$) of SiH_4 can be estimated by

$$\tau_{\mathrm{r-res}} = Fl_{\mathrm{SiH4}} p V_{\mathrm{r}} / k_{\mathrm{B}} T, \quad (1)$$

in which Fl_{SiH4} is the flow rate of SiH_4 gas, p is the pressure in the reactor, k_{B} is Boltzmann's constant, V_{r} is the volume of reactor and T is the gas temperature. So, $\tau_{\mathrm{r-res}}$ increasing with the increase of pressure means the dissociation probability of SiH_4 increases in the plasma. On the other hand, the electron density and electron temperature in the plasma increase with increasing power density, which contributes to the improvement of electron-impact dissociation of gas. As a result, the deposition rate increases with the increase of pressure and power density, due to the rise of gas utilization efficiency of SiH_4.

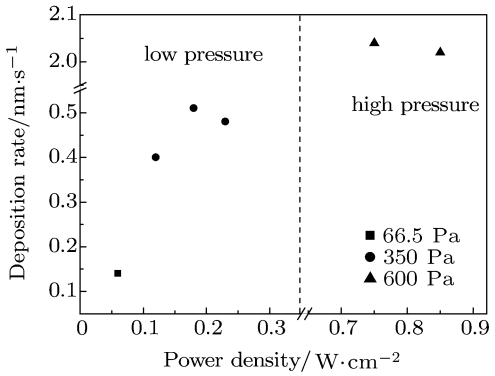


Fig. 1. Variation of deposition rate of μc-Si:H films with the power density at different pressures.

Figure 2 shows the evolution of the crystallinity and the surface rms roughness of μc-Si:H films deposited at $R = 5\%$ with the increase of film thickness. The two-dimensional (2D) AFM surface morphologies with different thickness are also shown in the figure. The crystallinity increases with the increase of film thickness, and reaches saturation around a thickness of 300 nm. The rms curve can be divided into three parts: *a*, *b* and *c*. In curve *a*, the rms value increases with increasing film thickness, and reaches a maximum around 180 nm. However, the rms value decreases with increasing film thickness in curve *b*, and increases again in curve *c*. Form the AFM surface morphology for 79 nm in thickness, one can find that the microcrystalline nuclei grow preferentially in one incubation a-Si:H layer. After the thickness increases above 158 nm, the crystalline protrusions that extend above the surface enough to make contact, lead to a crystallite coalescence process with continued film growth, and coalesce to cover the surface completely. Once the crystallites have coalesced to cover the growing film surface completely, single-phase μc-Si:H growth proceeds with a resumption of surface roughening (curve *b*). When the film thickness reaches a certain value, the crystalline grains will incorporate to form large grains, and the film roughness increases again (curve *c*). Collins *et al.*[12] used real time spectroscopic ellipsometry to demonstrate the same phase transition with the accumulated film thickness also. So, tracking the evolution of the crystallinity with thickness, we can deduce the thickness of the incubation layer.

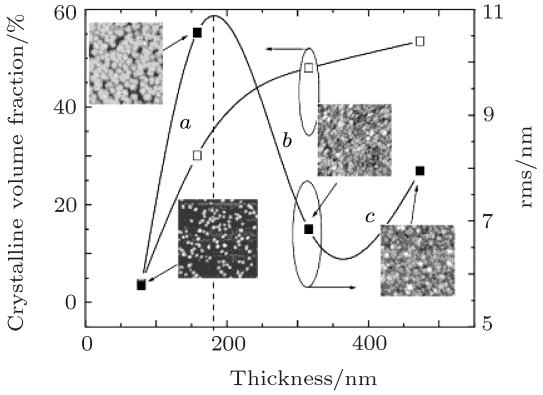


Fig. 2. Evolution of the volume fraction, the 2D AFM surface morphologies and the changing of surface rms roughness of μc-Si:H with the increase of film thickness.

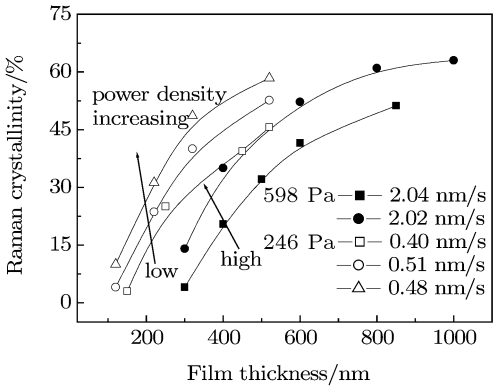


Fig. 3. The Raman crystallinity as a function of the thickness of μc-Si:H films prepared under the standard condition.

The variation of crystallinity with film thickness prepared at different deposition rates is shown in Fig. 3. Under fixed silane concentration, the thickness of incubation a-Si:H layer increases with increasing deposition rate. But, it decreases with increasing

power density under the same pressure. It was reported that the transient depletion of the SiH_4 source gas during roughly the first minute of discharge and the back diffusion of SiH_4 in the reactor would induce the formation of an incubation layer.[13,14] The occurrence of SiH_4 back diffusion could be prevented by using delayed initial SiH_4 density in the reactor, and the optimized delayed time ($t_{\rm delay}$) is given by[14]

$$t_{\rm delay} = \tau_{\rm r-res} \ln\left(\frac{Fl_{\rm SiH4}}{\pi R^2 r_{\rm d} n_{\mu\rm c}}\right), \qquad (2)$$

where $r_{\rm d}$ is the deposition rate, R is the radius of the electrode and $n_{\mu\rm c} =\sim 5\times10^{22}$ cm^{-3} is the Si atom density in the deposited silicon film.[15] According to Eq. (2), we can obtain the $t_{\rm delay}$ by the deposition rate under different deposition conditions. Figure 4 shows the variation of crystallinity of the μc-Si:H films with the film thickness after using the tailored initial silane density method. One intrusted phenomenon can be found from that the formation of incubation layer at lower deposition rates is inhibited absolutely. But, there are still a few hundred nanometers in thickness of the amorphous incubation layer under high deposition rate conditions. To explain the phenomenon, the scaling behaviour of roughening surface evolution is analysed using ellipsometer.

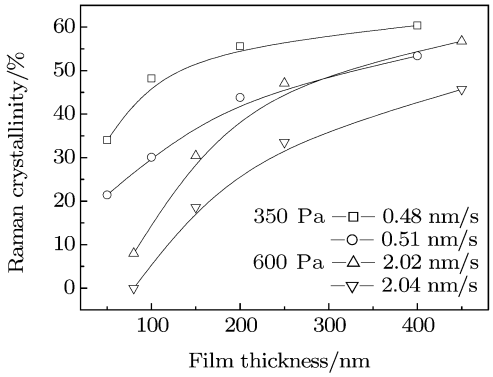


Fig. 4. Variation of crystallinity of μc-Si:H films with the thickness, for films prepared using tailored initial silane density method.

According to the KPZ model,[16] the film surface roughness $d_{\rm s}$ and film thickness d satisfy the relationship: $d_{\rm s} \sim d^{\beta}$, where β is defined as growth exponent. Different β values means different growth mechanism: $\beta = 1/2$, zero diffusion limited random growth process; $\beta = 1/3$, limited diffusion growth process; $\beta = 0$, unlimited diffusion growth process. Figure 5 shows the experimental spectroscopic parameters Ψ and Δ of μc-Si:H films deposited in different deposition time at 0.24 nm/s, and the modeled curves are also shown. The result obtained presents the excellent agreement between the model and the experimental data on the whole spectral range. With further analysis, the linear relationship of $d_{\rm s}$ and d is found in Fig. 6, and the value of β is obtained: $\beta = 0.2$.

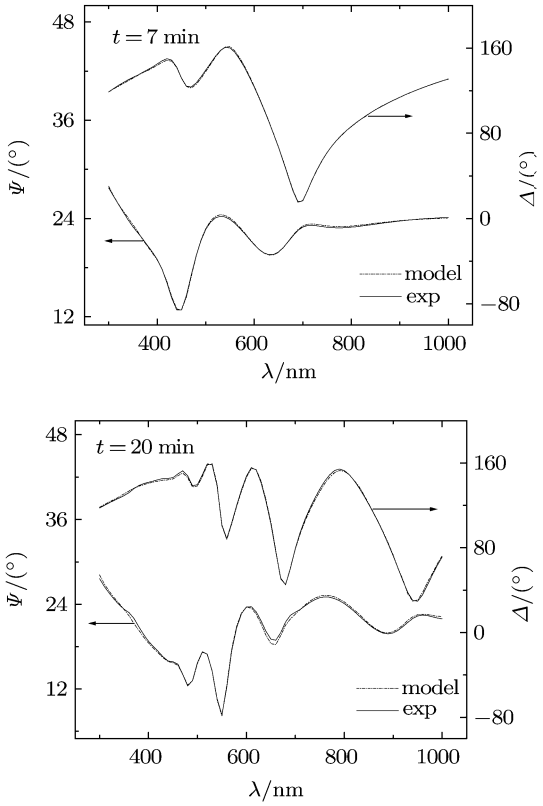


Fig. 5. Variation of experimental (solid line) and model (dash line) spectroscopic parameters Ψ and Δ of μc-Si:H films with deposition time at deposition rate 0.24 nm/s.

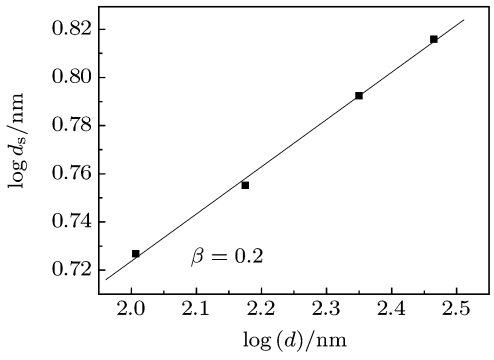


Fig. 6. The relationship between $d_{\rm s}$ and d at deposition rate 0.24 nm/s.

The variations of growth exponents with deposition rates are presented in Fig. 7. At low deposition rates under low pressure, the values of β are low, and approximately equal 0.2 with a little undulating; this suggests that deposition precursors which physically

adsorbed on the growing surface can diffuse some distances before being integrated in the film. It is very important to grow large size grains. The growth exponent β increases with increasing deposition rate under high pressure, and reaches the value of 0.5. The abnormal phenomenon is found in experiment that the value of β can exceed 0.5 at higher deposition rate and higher pressure. This indicates the deep decreasing of mobility on the surface for the precursors, thus they can be incorporated in the film immediately without diffusion; this is the so-called zero diffusion limited random growth process. One possible explanation is that under high pressure the polymerization is enhanced strongly in the plasma due to the increase of the residence time of the SiH_4 gas in the reactor. These larger silicon hydride clusters stick to the growth surface and deteriorate the surface roughness. The Monte Carlo simulation[17] of the growth model also shows that the shadowing effect of roughening surface can make the value of β higher than 0.5. The amorphous induction of glass surface will be enhanced with the reducing of the diffusion length of the precursors on the growth surface, leading to the generation of an additional incubation layer.

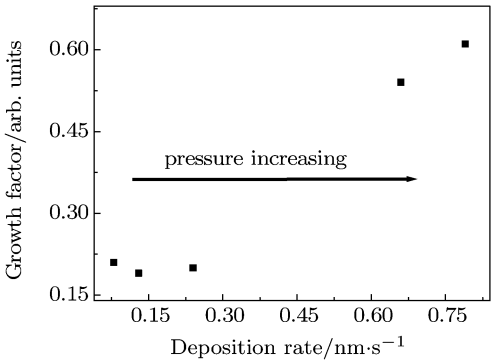


Fig. 7. The growth exponent of the μc-Si:H films versus deposition rate.

To suppress the formation of incubation a-Si:H layer under high deposition rate condition, silane profiling method is applied during the initial growth, as depicted in Fig. 8. The silane profiling is the variation of SiH_4 flow (0→3→5→8 sccm) from 67 s (calculated by using Eq. (2) at r_d = 0.58 nm/s) before to 40 s after the plasma ignition. The a and b points in the figure correspond to the changes of SiH_4 flow rate in the deposition. The evidence of the uniform growth of μc-Si:H films with thickness is shown in Fig. 9; it demonstrates again that a good control of the initial plasma condition is required.

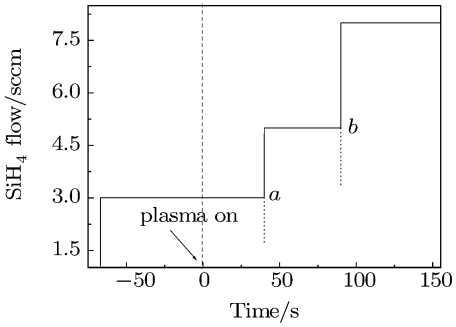


Fig. 8. Timing diagram of silane profiling schemes.

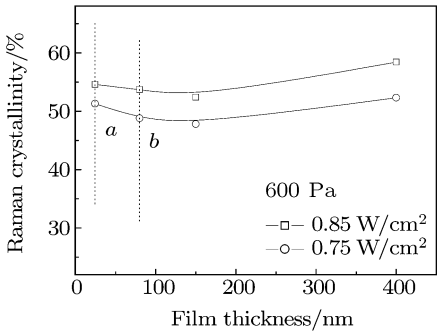


Fig. 9. The crystallinity versus film thickness for silane profiling.

4. Conclusions

The properties of incubation of a-Si:H layer is studied during the growth of μc-Si:H films under different deposition conditions. The thickness of a-Si:H layer increases with increasing deposition rate, and decreases with the increase of power density under fixed pressure. At low deposition rate, the formation of a-Si:H layer can be suppressed using delayed initial SiH_4 density method. But, at high deposition rate, due to the deeply reducing of the diffusion length for the precursors on the growth surface, silane profiling method is applied during the initial deposition process, and uniform μc-Si:H phase is generated.

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