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Boron doping effects on microcrystalline silicon film roughness studied by spectroscopic ellipsometry



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ABSTRACT

Microcrystalline silicon thin films were prepared in the p-type chamber using radio frequency plasma enhanced chemical vapor deposition. The surface roughness evolution of microcrystalline silicon thin films was investigated with spectroscopic ellipsometry (SE). The differences between the real-time SE and *ex-situ* SE have been studied. The effects of boron doping on the surface roughness have been analyzed using real-time SE. For the intrinsic microcrystalline silicon thin films, with an increase in the deposition time, the surface roughness exhibited the following behavior: (a) quickly increased, (b) gradually increased, (c) slightly increased. In the case of boron-doped microcrystalline silicon thin films, the surface roughness showed different behavior: (a) slightly increased, (b) quickly increased, (c) rapidly dropped, (d) increased again. Based on the KPZ model. In contrast, boron-doped silicon thin films behavior cannot be described by the KPZ model. Boron catalysis effects promote the reaction radical BH_x aggregation, and result in shadowing. Boron doping changed the film growth process.

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1. Introduction

Recently, hydrogenated micro/nanocrystalline silicon films has been a subject of scientific and technological interest due to their potential applications in optoelectronic devices, such as single electron transistors, solar cells and thin film transistors [1]. These films possess many desirable properties, such as high conductivity, high transport factor, low activation energy, good photo thermal stability, high photo-absorption coefficient, and are easy to dope [2–4]. Boron-doped microcrystalline silicon (μ c-Si:H) thin films are used for the window layer of p-i-n junction solar cells due to their high conductivity and high transparency [5–7]. The quality of boron-doped µc-Si:H film plays a key role in the performance of solar cells, due to the window layer, doping layer and the seed of the intrinsic absorbing layer. High quality boron-doped µc-Si:H films have high crystalline volume fraction, thin amorphous incubation layer, high surface roughness, and so on. Its optical and structural properties have been widely studied. Recently, Sucheta Juneja et al. [1] systematically studied the influence of diborane

 (B_2H_6) doping on the microstructural and optoelectronic properties of p-type nc-Si:H thin films. Ke Tao [8] and Teng Ge [9] studied the influence of substrate temperature on the p-µc-Si:H and intrinsic µc-Si:H structure and properties, respectively. Jinjoo Park et al. [10] studied the effects of thermal annealing on optical and electrical properties of boron doped a-SiO_x:H thin films. The surface roughness of µc-Si:H film strongly correlates with the growth mechanism. For the µc-Si:H films, the process parameters, such as the substrate temperature, silane concentration and boron doping concentration have important effects on the surface roughness.

Surface roughness can be characterized with atomic force microscopy (AFM) and spectroscopic ellipsometry (SE). There are also many *ex-situ* measuremental techniques, including X-ray diffraction, AFM, and Raman spectroscopy to investigate the μ c-Si:H grain growth process. SE possesses fast, non-destructive and precise optical characteristics. SE mainly analyzes the change of incident light and reflected light polarization state. Spectroscopic techniques have been widely used in measuring film thickness and optical parameters [11–14]. It is an effective method to characterize optical and structural properties of amorphous silicon (a-Si:H) films and μ c-Si:H films. Kumar et al. [15] studied a-Si:H and μ c-Si:H films obtained by glow discharge deposition using SE. Gu et al. [16,17]



analyzed the growth of the μ c-Si:H films deposited with very high frequency plasma-enhanced chemical vapor deposition (VHF-PECVD) method using *ex-situ* SE. Joohyun Kohd et al. [18] studied the effect of different boron dopant source gases on the nucleation and growth of p-type μ c-Si:H films using real-time SE. However, the differences between using the real-time SE and *ex-situ* SE to study μ c-Si:H film have not been reported yet. This paper studied these differences. During the low temperature deposition of μ c-Si:H films, there is a certain relation between the surface roughness and the growth mechanism. Toyama et al. [5] studied the surface roughness of boron-doped and undoped μ c-Si:H films using AFM. The effects of boron doping on the surface roughness have not been studied using real-time monitoring methods. Real-time SE not only can obtain the surface roughness, but can also help analyze the growth mechanism.

In this paper, the differences between using real-time SE and *exsitu* SE to study μ c-Si:H film have been studied, and the effect of boron doping on surface roughness of μ c-Si:H film using real-time SE was reported. Based on the KPZ model [19,20], the growth mechanism is discussed.

2. Experimental details

The µc-Si:H thin films were prepared in a cluster type radio frequency PECVD system. Silane (SiH₄), hydrogen (H₂) and borane (B₂H₆) were used as source gases. B₂H₆ was 30% diluted in hydrogen. The pressure was kept at 300 Pa. Two series of samples with intrinsic and boron doped thin films were prepared. The excitation frequency was 13.56 MHz. The substrate temperature was 150 °C, the electrode gap was 2.5 cm, and the background vacuum was kept at about 4×10^{-4} Pa. The input power was set at 150 W. The silane concentration was defined as [SiH₄]/ $([H_2] + [SiH_4])$, and the value was 1%. Boron doped concentration was defined as $[B_2H_6]/[SiH_4]$, and the value was 0.5% with the total reaction gas flow of 200 sccm. The deposition time was varied from 10 min to 60 min. The glass substrate was washed by detergent, acetone, alcohol and deionized water, respectively, and then dried by nitrogen. The film thickness and surface roughness were measured with spectroscopic ellipsometer (VASE, J. A. Woollam Company). The incidence angle was fixed at 70°, with the spectral range of 200-1000 nm and 10 nm measuring step. The measured ellipsometry parameters ψ and \varDelta were analyzed using the WVASE32 software. The film crystallinity was characterized by Raman spectroscopy using a Renishaw 2000 Raman spectrometer with 632.8 nm laser excitation and 5.32 mW output power.

3. Results and discussion

Spectroscopic ellipsometry is a nondestructive method, which measures the state of polarization of the incident light and analyses the reflected light. The fundamental equation of ellipsometry is:

$$\rho = \frac{r_p}{r_s} = \tan \psi e^{i\Delta} \tag{1}$$

where ρ is the ratio of the complex Fresnel reflection coefficients. The ellipsometric parameters ψ and Δ can depict the change of polarization state of the light waves before and after reflection. The change of ψ and Δ is related to the films properties, thickness, surface roughness and so on [16]. The first crucial step of characterizing the film properties using SE is to choose the suitable model. The Bruggeman effective medium approximation (BEMA) model is an effective method to calculate the silicon films properties with a certain degree of crystallinity [21]. Hydrogenated microcrystalline silicon thin film is a complex phase material containing microcrystalline grains, grain boundaries, voids and amorphous silicon. It has been reported that its dielectric function can be depicted with the BEMA model [22]. For fitting the SE data, the µc-Si:H thin films can be regarded as a three-layer. For the μ c-Si:H thin films, there is an amorphous incubation laver in the initial growth progress. The amorphous incubation layer has a great influence on the properties of the films. An amorphous incubation laver formed during the initial growth progress was added in the fitting model. In this study, three-layer fitting model was established so that it was more close to the actual conditions. Fig. 1 shows the three-layer model, which contains the incubation layer, bulk and surface roughness layers. The surface roughness layer consists of 50% silicon film and 50% of the cavities. The film total thickness is the sum of amorphous incubation layer thickness d_i and the bulk layer thickness d_b and 0.5 times surface roughness layer thickness d_s . It is assumed that both crystalline and amorphous phases are three dimensional objects. The thickness and volume ratio of each layer were fitted with linear regression, letting the δ^2 value reach the minimum. Here, δ^2 is a reference value used to identify a better fit [15].

$$\delta^{2} = \frac{1}{N - m - 1} \sum_{i=1}^{N} \left[\left(\tan \psi_{\exp} - \tan \psi_{calcu} \right)^{2} + \left(\cos \Delta_{\exp} - \cos \Delta_{calcu} \right)^{2} \right]$$
(2)

Here, the subscripts "*exp*" and "*calcu*" express the experimental and calculated data, and N is the number of the experimental data points, while m is the number of fitting parameters. In this study, each layer thickness was obtained by ellipsonmetry data fitting. The influence of boron doping on the film growth was also analyzed by fitting the SE data.

The growth mechanism can be obtained by surface roughness inversion. According to the Kardar-Parisi-Zhang (KPZ) model [19], the relationship between the film surface roughness and thickness is $d_s \sim d^{\beta}$, where β is the growth index. Different β values correspond to different growth mechanisms [23]. $\beta = 1/2$, 1/3 and 0 denote the processes of zero diffusion limited random growth, finite diffusion growth and step flow growth, respectively. The surface roughness varies with the film thickness.

The Raman spectra were obtained to verify the feasibility of using elliptical polarization spectroscopy to characterize silicon thin films [24]. Fig. 2(a) shows the Raman spectroscopy data of microcrystalline silicon thin films with high X_c . Its X_c can be



Fig. 1. The three-layer model for ellipsometry data fitting.



Fig. 2. (a) Raman spectra and (b) Dielectric function spectra of microcrystalline silicon thin films.

calculated as: $X_c = (I_c + I_b)/(I_a + I_b + I_c)$, where I_a , I_b and I_c are the amorphous component at 480 cm⁻¹, intermediate tiny nanocrystalline component at 510 cm⁻¹, and integrated intensity of the regular crystalline component at 520 cm⁻¹, respectively, and X_c is 64.3%. By fitting the SE data, the information about the film thickness, surface roughness and crystallization can also be obtained. The silicon thin film pseudo-dielectric function can be obtained from SE, where $\varepsilon = \langle \varepsilon_1 \rangle + i \langle \varepsilon_2 \rangle$. In Fig. 2(b), two strong shoulders at 3.5 eV and 4.2 eV can be seen, which correspond to the crystalline structure. This is in agreement with the Raman spectra. That is to say, using SE to characterize the μ c-Si:H thin films is feasible.

Fig. 3 shows the pseudo-dielectric function of the samples measured with real-time and *ex-situ* SE. The dashed line is measured with *ex-situ* SE, and the solid line is measured with real-time SE, the surface roughness thickness can be obtained by fitting the SE data. In Fig. 3, the surface roughness is 2.59 nm and 1.96 nm, corresponding to real-time and *ex-situ* SE, respectively. In general, the $\langle \epsilon_2 \rangle$ spectra include information about the film thickness, the bulk optical constants and the surface roughness. The real-time SE amplitude of $\langle \epsilon_2 \rangle$ in the high energy part of the spectra obviously decreases, which means an increase of surface roughness. We can infer that the surface roughness measured with real-time SE is larger than that measured with *ex-situ* SE. For the real-time SE, the film is measured in almost vacuum environment, and the surface is kept in its original state. However, when the sample was transferred from vacuum to atmospheric environment, the surface was



Fig. 3. Dielectric function spectra of microcrystalline silicon thin film measuring with real-time and *ex-situ* SE.

rapidly oxidized. Some of the surface gaps will be filled with silicon dioxide, resulting in the surface roughness decline. Studying the μ c-Si:H surface roughness using real-time SE can reveal the growth mechanism.

Fig. 4 is the SE spectra of intrinsic and boron-doped μ c-Si:H thin films with different deposition time. It can be seen that there are no significant differences between intrinsic and boron-doped SE spectra at the same deposition time. The number of the SE spectra curve peaks and valleys increases with the deposition time. The change of parameters ψ and Δ reflects the film internal structure change. The structural characteristics, such as thickness *d*, surface roughness *d*_s and incubation amorphous layer thickness *d*_i can be obtained from fitting the SE spectra using the three-layer model. The surface roughness changes of intrinsic and boron doped μ c-Si:H films were analyzed.

Fig. 5 shows the relationships between the intrinsic and borondoped µc-Si:H thin films surface roughness and deposition time. For the intrinsic µc-Si:H films, the surface roughness exhibited following behavior: quickly increased initially, then gradually increased, and then increased only slightly. The evolution of surfaces roughness can be divided into three stages. For the A₀B₀ stage, surface roughness is increasing rapidly. This is the initial nucleation process, where the nuclei atoms covered the substrate surface, resulting in the surface roughness increase [5]. During the second stage (B_0C_0 stage), surfaces roughness increases slowly. In the last stage (C_0D_0 stage), the surface roughness tends to almost a saturated state. From the B_0C_0 stage to the C_0D_0 stage, there is the grain growth process [5,25]. For the intrinsic microcrystalline silicon thin films, the surface roughness increases with the deposition time, according to the literature results [16]. In the case of boron-doped silicon thin films, the surface roughness showed different behavior: slightly increased, then quickly increased, rapidly dropped and increased again. The evolution of surfaces roughness can be divided into four stages: during the A_1B_1 stage, it increases slowly, then in the second stage (B₁C₁ stage), it increases rapidly, for the third stage $(C_1D_1 \text{ stage})$, it decreases quickly, and for the last stage (D₁E₁ stage), it increases again. Comparing the intrinsic µc-Si:H film surface roughness with boron doped films, for the primary stage (including A_0B_0 and A_1B_1 stages) it is found that the surface roughness increases. For the second stage, the increasing extent of the B_1C_1 stage is obviously larger than the B_0C_0 stage. This is due to the catalytic effect of B₂H₆ [18,26]. The boron atoms promote the film nucleation, which increases the nucleation density [18], and results in the surface roughness increase. For the C₁D₁ stage, the surface roughness declines. Due to the boron doping, the film undergoes secondary nucleation [27], and therefore the surface roughness shows an unstable oscillatory behavior [5]. For the D_1E_1 stage, the surface roughness increases again, corresponding to the



Fig. 4. SE spectra of intrinsic ((a), (c) and (e)) and boron-doped μ c-Si:H films ((b), (d) and (f)) with different deposition time, dashed lines are experimental data and solid line are fitted.



Fig. 5. The evolution of surface roughness and thickness with deposition time.

sustained grains growth [5,25].

Fig. 6 shows the log-log plots of the surface roughness ds and the film thickness *d*. Linear fitting slope corresponds to the growth index β . For the intrinsic films, the growth index β is 0.4, which is

close to 1/3, namely, the limited diffusion model. That is to say, the intrinsic film growth conforms to the KPZ growth model. From Fig. 6 (b) it can be seen that there is not linear relationship between the film thickness d and the surface roughness ds for the boron-doped microcrystalline silicon thin films. The observed behavior cannot be explained by the KPZ model. Due to the catalytic effects of boron, the surface roughness shows a decreasing phenomenon, leading to no linear relationship between d and d_s . B-containing radicals on the substrate surface at the initial stages of the microcrystalline silicon thin film growth act as catalysts to shift the attaching-detaching equilibrium of the SiH_x precursors toward the attaching direction. Boron catalysis effects promote the reaction radical BH_x aggregation, and result in shadowing. The doped boron changed the growth mechanism.

4. Conclusions

The intrinsic and boron-doped μ c-Si:H thin films were prepared using RF-PECVD. The effects of boron doping on the surface roughness have been studied using real-time SE. The study compared the differences between the real-time and *ex-situ* SE characteristics of the microcrystalline silicon thin films. The results show that the surface roughness measured with real-time SE is larger than that measured with *ex-situ* SE. Using the real-time SE can reveal the growth mechanism. For the intrinsic microcrystalline silicon thin films, the surface roughness value increased with the



Fig. 6. The relationship between the surface roughness d_s and thickness d: (a) intrinsic films (b) boron-doped films.

deposition time. Its growth index is 0.4, according to the KPZ model. For the boron-doped microcrystalline silicon films, the evolution of surface roughness can be divided into four stages. First, it increases slowly, then increases rapidly, and for the third stage it decreases quickly, while for the last stage, it increases again. There is no linear relationship between the surface roughness and thickness, so the boron-doped microcrystalline silicon thin films growth cannot be explained by the KPZ model.

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