Growth characteristics of amorphous-layer-free nanocrystalline silicon films fabricated by very high frequency PECVD at 250 °C*

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Amorphous-layer-free nanocrystalline silicon films were prepared by a very high frequency plasma enhanced chemical vapor deposition (PECVD) technique using hydrogen-diluted SiH_4 at 250 °C. The dependence of the crystallinity of the film on the hydrogen dilution ratio and the film thickness was investigated. Raman spectra show that the thickness of the initial amorphous incubation layer on silicon oxide gradually decreases with increasing hydrogen dilution ratio. High-resolution transmission electron microscopy reveals that the initial amorphous incubation layer can be completely eliminated at a hydrogen dilution ratio of 98%, which is lower than that needed for the growth of amorphous-layer-free nanocrystalline silicon using an excitation frequency of 13.56 MHz. More studies on the microstructure evolution of the initial amorphous incubation layer with hydrogen dilution ratios were performed using Fourier-transform infrared spectroscopy. It is suggested that the high hydrogen dilution, as well as the higher plasma excitation frequency, plays an important role in the formation of amorphous-layer-free nanocrystalline silicon films.

Keywords: nanocrystalline silicon, amorphous incubation layer, plasma enhanced chemical vapor deposition

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1. Introduction

In the past decades, nano- and microcrystalline silicon have received much attention owing to their potential applications in solar cells, memory devices, and display devices.[1−3] Among the different approaches to obtain nanocrystalline silicon (nc-Si) films, plasma enhanced chemical vapor deposition (PECVD) has attracted the most attention due to its low-cost and highly controllable method for film growth, which is especially suitable for large-scale film deposition.[4,5] So far, many experiments have shown that deposition parameters, especially the hydrogen dilution level, play an important role in the formation of nc-Si films.[6−9] It has been demonstrated that the heavy hydrogen dilution of silane is effective in promoting the phase transition from amorphous to crystalline.[6−9] In fact this transition depends not only on the hydrogen dilution level but also on the film thickness. nc-Si grown on the insulator surface generally contains an initial amorphous layer, the so-called "amorphous incubation layer".[10−13] It has been demonstrated that a large incubation layer and the nonuniformity of the crystalline structure in the growth direction will result in a low short-circuit current and deteriorate the performance of the device.[14] Therefore, it is essential to reduce the thickness of the amorphous incubation layer as much as possible. However, compared with the thick film, only a few previous studies have been done on the structure properties of ultrathin Si films, especially those fabricated by very high frequency PECVD (VHF-PECVD).[13,15,16]

In this work, amorphous-layer-free nc-Si films were prepared from hydrogen-diluted SiH_4 at 250 °C in a VHF–PECVD (40.68 MHz) system. Raman spectra show that the thickness of the initial amorphous incubation layer on silicon oxide gradually decreases with increasing hydrogen dilution ratio. High-resolution transmission electron microscopy reveals that the initial amorphous incubation layer can be completely eliminated at a hydrogen dilution ratio of

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98%, which is lower than that needed for the growth of amorphous-layer-free nc-Si by using an excitation frequency of 13.56 MHz. Moreover, the growth rate of the amorphous-layer-free nc-Si is much higher than that fabricated at 13.56 MHz. Combined with the analysis of Fourier-transform infrared spectra, it is suggested that the high hydrogen dilution, as well as the higher plasma excitation frequency, plays an important role in the formation of amorphous-layer-free nc-Si films.

2. Experiment

In each growth process, nc-Si films were deposited simultaneously on a glass substrate and an Si wafer from hydrogen-diluted SiH_4 at 250 °C in a VHF–PECVD (40.68 MHz) system, respectively. It should be noted that the Si substrate is covered with a silicon-oxide layer with a thickness of about 2 nm, which is measured by an ellipsometer. The hydrogen dilution ratio (R_H), defined as $R_H = [H_2]/([H_2] + [SiH_4])$, was varied from 87% to 99%. The radio frequency (RF) power was 30 W and the pressure in the chamber remained at 60 Pa. The structure characteristics of the films were evaluated by Raman scattering spectroscopy, whose excitation source was an Ar^+ laser ($\lambda = 488$ nm). The structure features of the films were characterized by high-resolution transmission electron microscopy (HRTEM) on a JEM-4000EX microscope. A Fourier transform infrared (FTIR) spectroscope was employed to record the bonding configurations of the samples.

3. Results and discussion

Figure 1 shows the Raman spectra of the films grown with various hydrogen dilution ratios at the same deposition period of 10 minutes.

When the hydrogen dilution ratios are lower than 93%, the Raman bands peak at around 480 cm^{-1}, which corresponds to the transverse optical phonon mode of amorphous Si. As the R_H increases to 96%, the Raman peak rapidly shifts to 515 cm^{-1}, which originates from the transverse optical phonon mode of crystalline Si. These results indicate that the microstructure of the films experiences a phase transition from amorphous to crystalline when the R_H increases from 93% to 96%. The Raman peak is also found to gradually shift to 520 cm^{-1} with a further increase in R_H up to 99%. These results imply that the crystallinity, as well as the average size of the crystalline grains, increases with an increase in the hydrogen dilution ratio. The crystalline fraction and the thickness of the corresponding films are plotted as R_H, as is shown in Fig. 2. For nc-Si films, the crystalline fraction X_c was evaluated from the Raman spectrum by using $X_c = (I_c + I_m)/(I_c + I_m + I_a)$, where I_c, I_m, and I_a are the integrated intensities of the crystalline Gaussian peak at around 520 cm^{-1}, the intermediate Gaussian peak at around 510 cm^{-1}, and the amorphous Gaussian peak at around 480 cm^{-1}, respectively.[15] One can see that the films are amorphous when the R_H is lower than 93%. However, as the R_H is enhanced to 96%, the crystalline fraction X_c rapidly increases to 51%. At $R_H = 99\%$, the crystalline fraction can reach up to 71%. From Fig. 2,

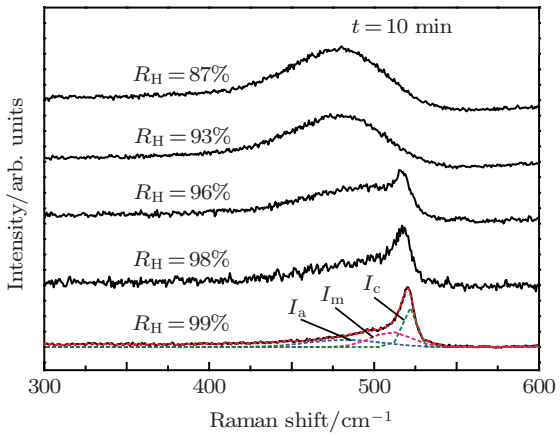


Fig. 1. (colour online) Raman spectra of the films grown with different hydrogen dilution ratios, R_H, at a fixed deposition time of 10 minutes. Three Gaussian line profiles (dashed lines) are fitted to a Raman spectrum of the film grown with $R_H = 99\%$.

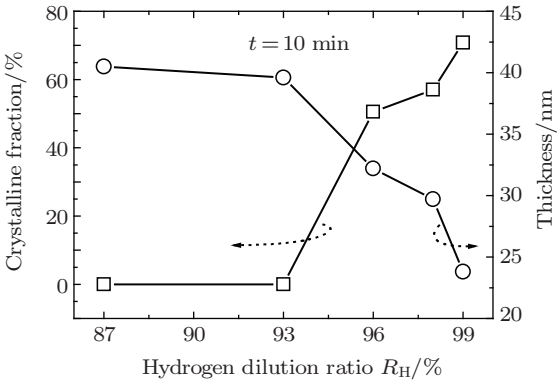


Fig. 2. Crystalline fraction and thickness as a function of hydrogen dilution ratio, R_H, for the films deposited at a fixed deposition time of 10 minutes.

it is found that the film thickness monotonously decreases from 41 nm to 24 nm as the R_H increases from 87% to 99%. These results show that the increase in hydrogen dilution level not only results in a phase transition from amorphous to crystalline but also decreases the film thickness.

Figure 3 presents the Raman spectra of the samples deposited at a period of 60 minutes. It is clear that all the Raman peaks are located at around 520 cm^{-1}, which is almost independent of the R_H. However, the shape of the Raman peak turns out to be more symmetric with increasing R_H. The crystalline fraction and the thickness of the corresponding samples as a function of R_H are also plotted in Fig. 4. As the R_H increases from 87% to 99%, the crystalline fraction increases from 54% to 89%, while the film thickness decreases from 366 nm to 164 nm. Comparing Fig. 2 with Fig. 4, it can be found that film thickness plays an important role in the crystallization of the film. The crystallization of the films does not occur directly on the substrate at relatively low hydrogen dilution ratios. An amorphous incubation layer exists on the amorphous substrate at the initial growth stage of the nc-Si films. The thickness of the initial amorphous incubation layer on silicon oxide gradually decreases with increasing hydrogen dilution ratio.

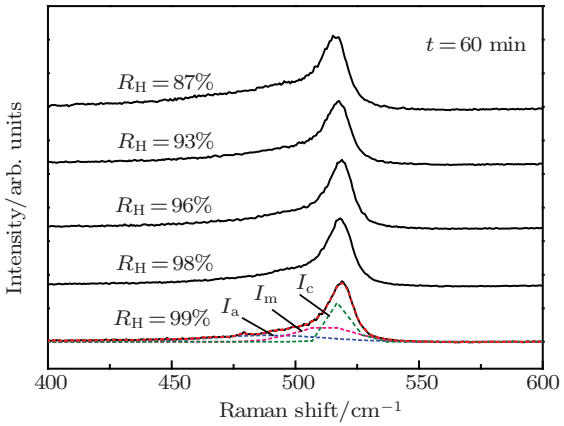


Fig. 3. (colour online) Raman spectra of the films grown with different hydrogen dilution ratios, R_H, at a fixed deposition period of 60 minutes. Three Gaussian line profiles (dashed lines) are fitted to a Raman spectrum of the film grown with R_H = 99%.

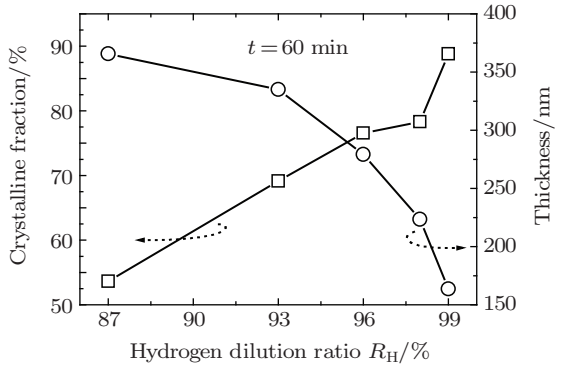


Fig. 4. Crystalline fraction and thickness as a function of hydrogen dilution ratio, R_H, for the films deposited at a fixed deposition time of 60 minutes.

To further investigate the growth behavior and the microstructural evolution of the nc-Si films, cross-sectional transmission electron microscopy (TEM) analyses were performed. Figure 5 shows the cross-sectional TEM bright field images of the films deposited at R_H = 98%. From Fig. 5(a), it is clear that some fastigiated structures grow directly on the silicon-oxide layer. The HRTEM image shown in Fig. 5(b) reveals that the fastigiated structures are composed of nanocrystals with different preferential growth directions, while the HRTEM image of Fig. 5(c) further shows that the crystallites with a diameter of about 6 nm to 10 nm are directly formed on the silicon-oxide layer. This clearly demonstrates that the initial amorphous layer can be eliminated when the hydrogen dilution ratio increases to 98%, which is completely different from those observed in the films grown at 13.56 MHz. In a conventional parallel plate radio frequency glow-discharge (13.56 MHz) system, an initial amorphous incubation layer with a thickness of more than 10 nm generally exists on the amorphous

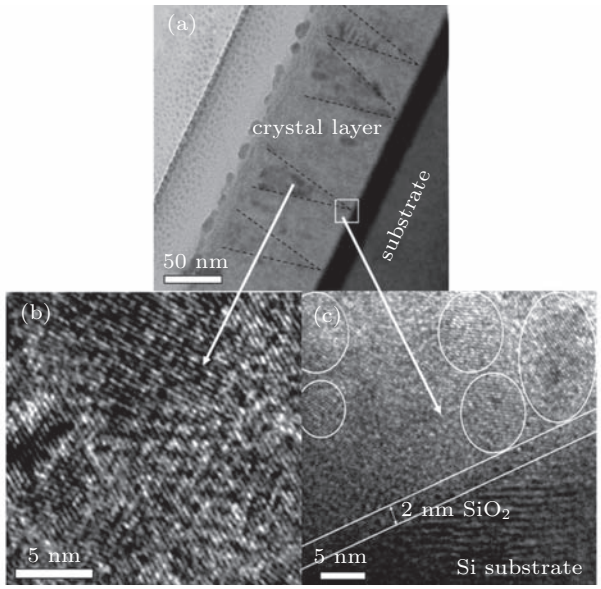


Fig. 5. (a) Cross-sectional TEM image of the film deposited at a hydrogen dilution ratio, R_H = 98%, using 40.68 MHz excitation frequencies. Panels 5(b) and 5(c) show the HRTEM images for the selected areas, respectively.

substrate, even when the hydrogen dilution ratio is up to 98%.[8] To obtain an amorphous-layer-free nc-Si, the hydrogen dilution ratio should be enhanced to 99.7%, which in turn results in a low deposition rate of 0.2 nm/min.[17,18] In our case, the nc-Si with a higher deposition rate of about 3 nm/min can be directly grown on the amorphous substrate at $R_{\rm H} = 98\%$, which strongly implies that not only the hydrogen dilution, but also the plasma excitation frequency, plays an important role in the initial growth process of the nc-Si films.

To analyze the role of hydrogen in the structure evolution of the films, FTIR was used to examine the local bonding configurations in the samples. Typical FTIR absorption spectra of the samples are shown in Fig. 6. In addition to the ~640 cm^{-1} band, there is a broad absorption band between 1900 cm^{-1} and 2150 cm^{-1} in FTIR, of which the 2000-cm^{-1} and 2090-cm^{-1} modes are assigned to the stretching modes of Si–H and Si–H_2, respectively, and the bands between 1900 cm^{-1} and 1950 cm^{-1} come from the SiH_2 complex.[9] The Si–H bonds are generally regarded to be located at compact sites, and the Si–H_2 bonds are mainly at the internal surfaces of the microvoid sites. For the SiH_2 complex, its absorption intensity is considered to be proportional to the magnitude of the internal stress embedded in the film. The SiH_2 complex acts as a pre-nucleation site on the film-growing surface.[9] By decomposing the broad band into three components centered at about 1930, 2000, and 2090 cm^{-1}, the relative absorption intensity pertaining to the SiH_2 complex at 1930 cm^{-1} can be calculated. From Fig. 7, it can be seen that the intensity pertaining to the SiH_2 complex rapidly decreases and then becomes zero with increasing hydrogen dilution ratio up to 98%. According to the FTIR spectra, the hydrogen content ($C_{\rm H}$) was also calculated.[19] The $C_{\rm H}$ was shown to decrease rapidly from 14% to 10% when the hydrogen dilution ratio increased from 87% to 93%. With a further increase in the hydrogen dilution ratio to 99%, the $C_{\rm H}$ slowly decreases down to 9%.

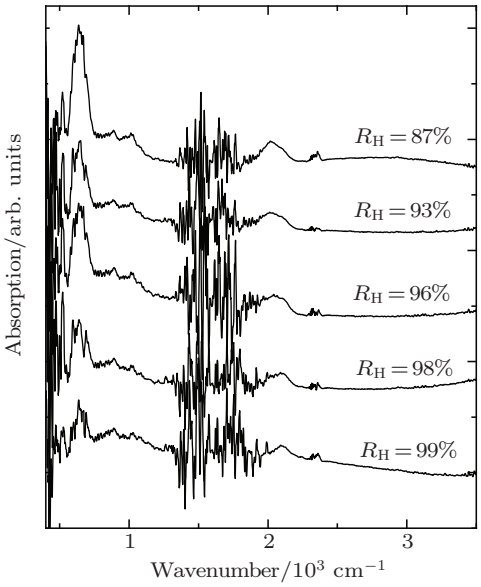


Fig. 6. FTIR spectra of the nc-Si films grown with different hydrogen dilution ratios $R_{\rm H}$.

In general, the effect of hydrogen dilution on the growth of nc-Si is interpreted in terms of several growth models, including the hydrogen etching model, the surface mobility model, and the chemical annealing model.[6,9,20,21] In our case, the decreased deposition rate and the improved crystalline fraction with increasing hydrogen dilution ratio indicates that hydrogen etching is important in the formation of nc-Si. It is also found that the crystalline fraction of the ultrathin films is apparently lower than that of the thick film under the same hydrogen dilution ratio. This is known to arise from the strongly interfacial stress due to the large structural mismatch presenting at the interface between the Si and SiO_2 layer. However, one can see that the thickness of the amorphous incubation layer can be gradually reduced with increasing hydrogen dilution ratio, which indicates that the strong stress existing in the amorphous incubation layer can be released with an increase in the hydrogen dilution ratio. This agrees well with the observed result that the absorption intensity of the SiH_2 complex gradually decreases with increasing hydrogen dilution ratio, as is shown in Fig. 7. It is considered that the hydrogen radicals would break or perturb the strained Si–Si bonds and form a specific SiH_2 complex on the growth zone.[9] This complex results in the structural relaxation of the amorphous island network, promoting the transformation of the nucleus structure from amorphous to nanocrystalline.[9] In addition, with increasing hydrogen dilution ratio, more and more hydrogen radicals would enhance the surface diffusion of the precursors (SiH_3) and produce local heating through hydrogen-exchanging reactions on the growing surface. This facilitates the precursors to discover energetically favorable sites, resulting in the formation of a crystalline nucleus.

In fact, the high excited frequency also plays an important role in the formation of nc-Si. In the PECVD system, the plasma density strongly relies on the excited frequency.[20] The increase in excited frequency would remarkably increase the electron den-

sity, which promotes depletion of the precursors (SiH_4 and H_2), resulting in high hydrogen atom flux to the growth surface. Therefore, the high density of hydrogen radicals would significantly enhance the hydrogen etching ability, surface-diffusion and chemical-annealing effect, thus promoting the transformation of the nucleus structure from amorphous to nanocrystalline. Undoubtedly, a hydrogen-rich environment is favored to increase the crystalline nucleation rate, which in turn reduces the thickness of the amorphous incubation layer. Therefore, it is reasonable to understand that the hydrogen dilution ratio (98%) needed for growing amorphous-layer-free nc-Si films in our work is lower than that (99.7%) needed by using the plasma excitation frequency of 13.56 MHz.[17,18]

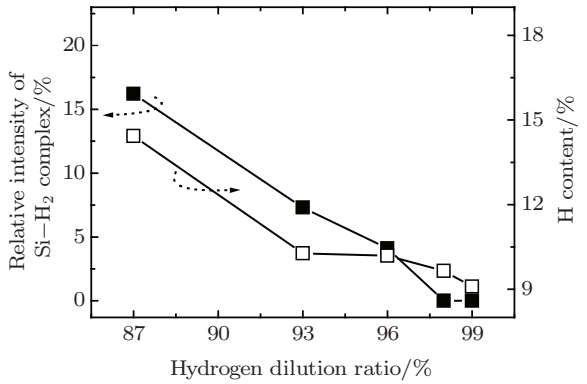


Fig. 7. The relative intensity of the Si–H_2 complex and H content as a function of hydrogen dilution ratio, R_H.

4. Conclusion

Ultrathin nc-Si films were prepared at 250 °C in VHF-PECVD. The thickness of the initial amorphous incubation layer on silicon oxide is demonstrated to gradually decrease with increasing hydrogen dilution ratio. The initial amorphous incubation layer can be completely eliminated at a hydrogen dilution ratio of 98%, which is lower than that needed for the growth of an amorphous-layer-free nc-Si by using an excitation frequency of 13.56 MHz. Moreover, the growth rate of nc-Si is much higher than that fabricated at 13.56 MHz. It is suggested that not only the hydrogen dilution, but also the plasma excitation frequency, plays an important role in the initial growth process of nc-Si films.

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