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Nanocrystalline silicon films prepared by laser-induced crystallization*

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The excimer laser-induced crystallization technique has been used to investigate the preparation of nanocrystalline silicon (nc-Si) from amorphous silicon (α-Si) thin films on silicon or glass substrates. The α-Si films without hydrogen grown by pulsed-laser deposition are chosen as precursor to avoid the problem of hydrogen effluence during annealing. Analyses have been performed by scanning electron microscopy, atomic force microscopy, Raman scattering spectroscopy and high-resolution transmission–electron microscopy. Experimental results show that silicon nanocrystals can be formed through laser annealing. The growth characters of nc-Si are strongly dependent on the laser energy density. It is shown that the volume of the molten silicon predominates essentially the grain size of nc-Si, and the surface tension of the crystallized silicon is responsible for the mechanism of nc-Si growth.

Keywords: laser annealing, crystallization, nanocrystalline silicon
PACC: 6170A, 6150C, 6146

1. Introduction

Following a report of efficient photoluminescence from porous silicon,[1] materials composed of silicon nanocrystals (nc-Si) have attracted considerable interest due to their potential applications in Si-based optoelectronic devices. Many methods have been proposed to prepare nc-Si thin films, such as pulsed-laser ablation, plasma-enhanced chemical vapour deposition and radio frequency magnetron sputtering and so on.[2−4] Laser annealing of amorphous semiconductor films has received much attention since its emergence in 1970s for the distinctive features of rapid crystallization and selected area processing.[5,6] Initially, this rapid crystallization technique is used mainly to realize the transformation of amorphous materials to polycrystalline or to remove the damages accompanying the ion implantation.[7−9] Recently, it has been exploited as a means of fabricating nc-Si from α-Si films.[10,11] The intense visible light emission at room temperature from this low-dimensional Si structure has been successfully observed. The properties of the nc-Si films depend dramatically on their preparation process. The surface roughness, the nanocrystallite size and the fraction of the crystallinity is related to the laser energy density, substrate property and hydrogen content in the films. Therefore, the understanding of the growth process and the nature of the material itself is important for improving and optimizing these materials.

In this paper, the process of nc-Si preparation from amorphous silicon (α-Si) thin films by the excimer laser-induced crystallization (ELC) technique is presented, In this process, in order to eliminating the influence of hydrogen content in the α-Si films on the quality of nc-Si, the α-Si films is deposited on silicon or glass substrates by a pulsed-laser deposition (PLD) process, which can fabricate pure amorphous silicon films without hydrogen contents. The details of the formation and structure of resulting nc-Si films are presented. The relationship between the growth characters of nc-Si and the laser energy density is studied.

2. Experiment

The laser-annealing experiments are carried out on α-Si films at room temperature. All the α-Si films are deposited on Si (100) or glass substrates in a typ-

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ical PLD system. The pressure in the chamber is initially evacuated to less than 1.3×10^{-5} Pa and remains about 1.3×10^{-3} Pa by filling Ar as a buffer gas during the deposition. A XeCl excimer pulsed laser, with a full width at half maximum of 20 ns and a wavelength of 308 nm, is used as the ablation source. The laser beam is operated at 5 Hz and is incident on the silicon target at an off-normal angle of 45°. The typical deposition conditions are as follows: laser focused area is 2 mm^2, laser energy density is 2.5 J/cm^2, target-substrate distance is 3cm and the thickness of the deposited films is about 200 nm. The as-deposited samples are cut into small rectangular specimens of 1×2 cm^2 in size and loaded into an annealing chamber, where nitrogen ambient pressure is kept at about 13 kPa. All the annealing experiments are performed using the same XeCl excimer laser.

Scanning electron microscopy (SEM) and high resolution transmission–electron microscopy (HRTEM) observations are carried out on a Hitachi S-4200 apparatus and a JEM-2010 electron microscope respectively. Atomic force microscopy (AFM) measurements are carried out using a Nanoscope 3 contact-mode scanning probe microscope. Raman scattering spectra measurements are performed in a Renishaw 2000 micro-Raman spectrometer with a He-Ne laser (632.8 nm radiation) used as the excitation source.

3. Results and discussion

The characters of the laser-ablated films are closely related to the experimental conditions, such as the chamber pressure, laser power density and target-substrate distance.[12,13] To avoid the droplet ejection from the silicon target, a moderate laser power density is adopted to ablate the silicon target in our experiment. Figure 1 shows the SEM images of α-Si thin films before and after the laser-induced crystallization. It is shown that the α-Si thin film prepared under the typical conditions is continuous and without any droplets and debris (Fig.1 (a)). After laser annealing with an energy density of 240 mJ/cm^2, an apparent change in the surface morphology takes place and many nanograins appear on the thin film surface (Fig.1 (b)). The average grain size is about 12 nm, which is much smaller than the thickness of the original film.

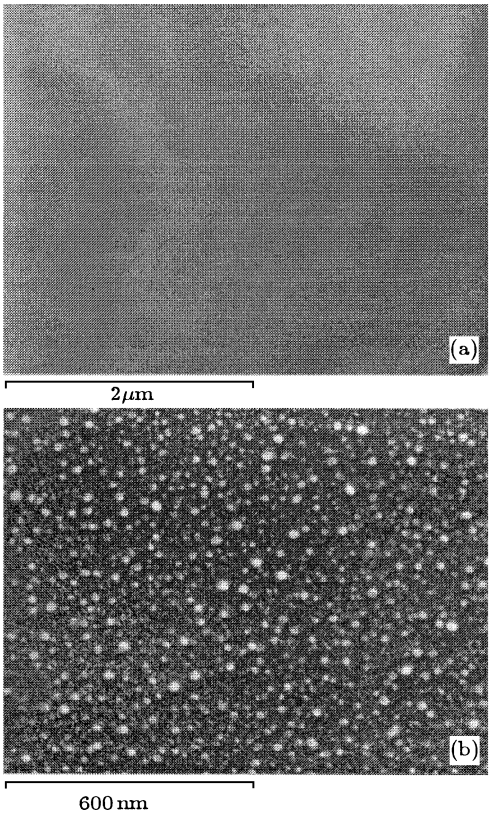


Fig.1. SEM images of α-Si thin films before (a) and after (b) crystallization.

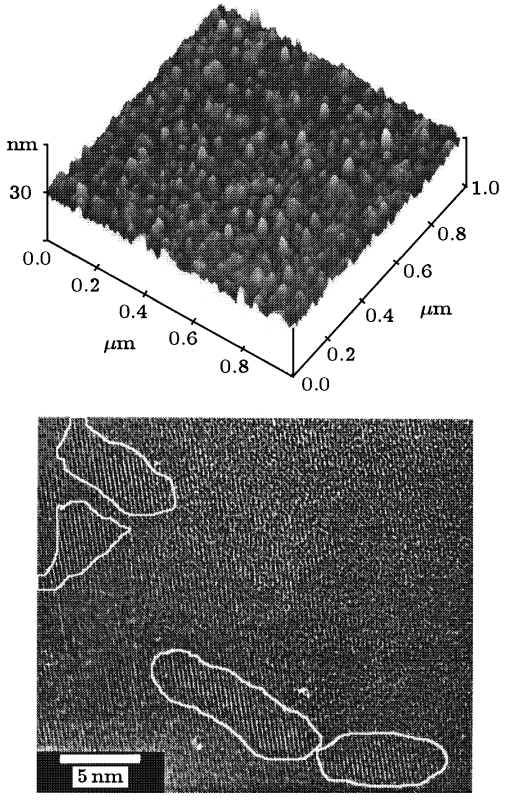


Fig.2. AFM and HRTEM images of the sample irradiated at the laser energy density of 240 mJ/cm^2.

The corresponding AFM and HRTEM images of the annealed sample are presented in Fig.2. The AFM image displays that most nanograins with some smaller ones around are in hill-like appearance and some of them in the surface of the film can be found simultaneously. This result is consistent with that of the HRTEM, which shows that the grains in the thin film are nc-Si in different sizes.

Figure 3 provides the typical Raman spectra for the as-deposited, crystallized α-Si thin films on glass substrates. It can be seen that curve a has a broad spectrum peaked at $480\,\mathrm{cm}^{-1}$, which is the characteristic spectrum of the α-Si. The bands at 514 and $517\,\mathrm{cm}^{-1}$ in curves b and c show the existence of nanocrystalline silicon grains. Additionally, in curve c lies another band at about $295\,\mathrm{cm}^{-1}$, which is related to the scattering on the LA modes in nc-Si.[14] From the different positions of characteristic peaks for nc-Si grains, it can be concluded that the higher the laser energy density, the larger the grain size of the annealed samples.

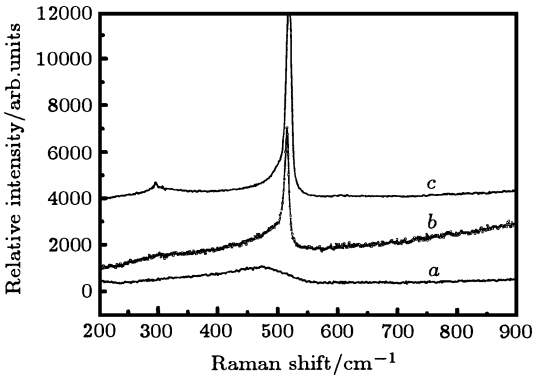


Fig.3. Raman spectra for the as-deposited a and annealed samples b and c at the laser energy densities of 240, $303\,\mathrm{mJ/cm}^2$ respectively.

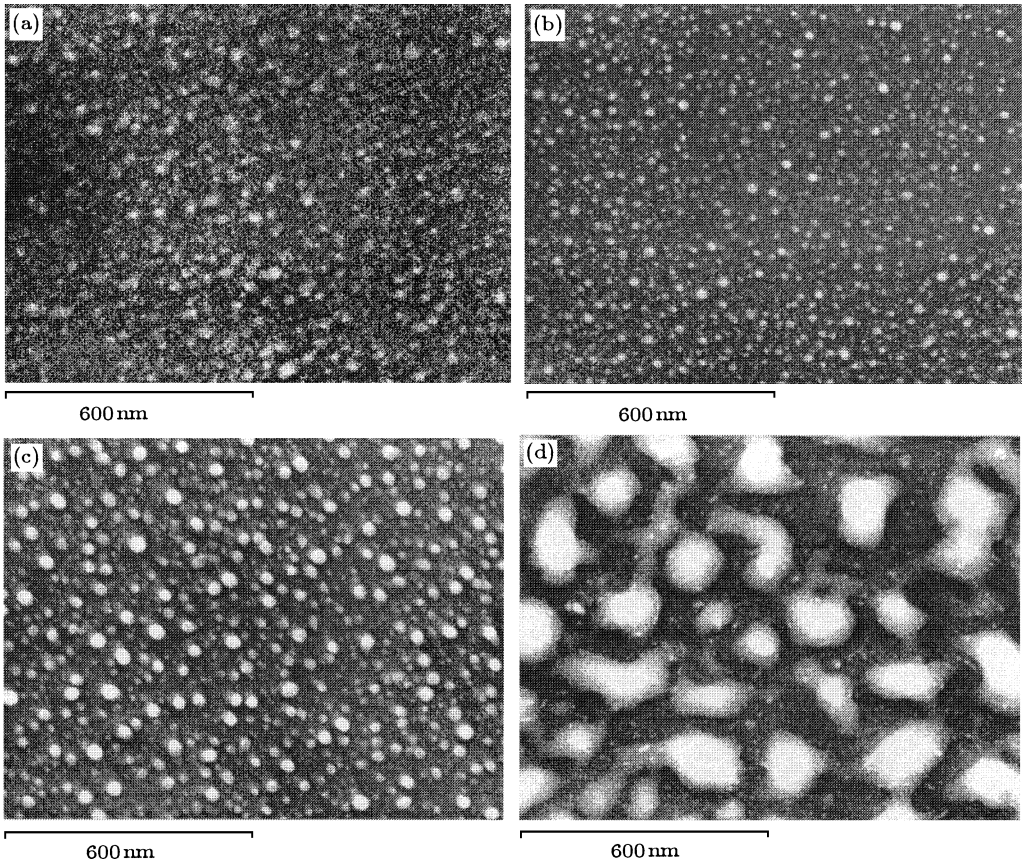


Fig.4. SEM images of the samples irradiated at the laser energy densities of (a) $202\,\mathrm{mJ/cm}^2$ and (b) $240\,\mathrm{mJ/cm}^2$, (c) $303\,\mathrm{mJ/cm}^2$, (d) $480\,\mathrm{mJ/cm}^2$.

It is well accepted that the size of the crystallite in laser-crystallized films is extremely sensitive to the energy density of the laser beam.[15] The critical energy density for the crystallization process is the full-melt threshold (FMT), at which the film just melts through its entire thickness. When the energy density is well below FMT, the growth characters of the nc-Si grains can be attributed to the difference between

the adhesion force of the crystallized silicon attracting the molten silicon and the agglomeration force of the molten silicon. According to Shih *et al*,[16] when the laser melts the top portion of the α-Si films, nucleation would occur at the interface of liquid-solid silicon, fine grains would grow up as the liquid silicon accumulates on their surface due to the fact that crystalline silicon has a better thermal conductivity and the adhesion force between the molten silicon and nc-Si is greater than the agglomeration force of the molten silicon. The grain size would depend on the amount of molten silicon. Figure 4 presents our SEM images of the annealed samples at different laser energy densities. It can be seen that the grain sizes of nc-Si become larger with increasing the laser energy density when it is well below the FMT, as shown in Figs.4(a)–4(c). At a laser energy density of 480 mJ/cm^2 (Fig.4 (d)), the substrate under the c-Si grains is exposed, indicating that the whole α-Si film has melted completely. Actually, Increasing laser energy density results in more molten α-Si, which makes it possible that more liquid silicon accumulates on to nc-Si surface to make grains larger in the cooling down period. All the results support the fact that the volume of molten silicon essentially predominates the grain size of nc-Si and the surface tension is responsible for the mechanism of nc-Si growth.

4. Conclusion

XeCl (308 nm) excimer laser crystallization of α-Si films prepared by PLD has been performed in our experiments, and all the films display an apparent change on their surface morphology after crystallization. The experimental results given by HRTEM, SEM, AFM and Raman scattering have shown that the size of laser-annealed silicon nanocrystallites can be successfully controlled by varying the laser energy density. The mechanism causing the nc-Si growth is the molten silicon atoms attached to the nanocrystalline nucleus due to their surface tension. The grain size of nc-Si is related to the volume of the molten α-Si induced by absorbing laser energy.

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