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Effect of substrate temperature and pressure on properties of microcrystalline silicon films

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In this paper intrinsic microcrystalline silicon films have been prepared by very high frequency plasma enhanced chemical vapour deposition (VHF-PECVD) with different substrate temperature and pressure. The film properties were investigated by using Raman spectra, x-ray diffraction, scanning electron microscope (SEM), and optical transmittance measurements, as well as dark conductivity. Raman results indicate that increase of substrate temperature improves the microcrystallinity of the film. The crystallinity is improved when the pressure increases from 50Pa to 80Pa and the structure transits from microcrystalline to amorphous silicon for pressure higher than 80Pa. SEM reveals the effect of substrate temperature and pressure on surface morphology.

Keywords: microcrystalline silicon, VHF-PECVD, Raman spectra, SEM
PACC: 6860, 7230, 7360F, 7850G

1. Introduction

Since hydrogenated microcrystalline silicon (μc-Si:H) was prepared by Veprek and Marecek in 1968,[1] it has attracted much attention for various device applications.[2−5] For application in solar cells, microcrystalline silicon has lower light-induced degradation and larger absorption coefficient in the infrared spectral region than amorphous silicon,[6] so microcrystalline silicon will take the place of amorphous silicon in the photovoltaic market.[7] Many methods have been successfully used to prepare device grade microcrystalline silicon, such as plasma enhanced chemical vapour deposition (PECVD),[8−10] hot-wire chemical vapour deposition (HWCVD)[11] and reactive sputtering.[12,13] Now the technique widely used for preparing microcrystalline silicon is the conventional radio frequency PECVD. But the low deposition rate of PECVD hampers the industrial production of microcrystalline silicon solar cells.

In this paper we report our result for hydrogenated microcrystalline silicon films grown by VHF-PECVD. Compared with the conventional RF-PECVD, VHF-PECVD has lower electron temperature and higher electron density. The effect of substrate temperature and pressure on the properties of samples was investigated.

2. Experimental details

Two series of intrinsic silicon films were prepared by a capacitive-coupled PECVD system by using a plasma excitation frequency of 60MHz. The Electrode space from the cathode to anode was 20 mm. Silane diluted in hydrogen was fed as the source gas and the total gas flow rate was kept at 60sccm. The discharge power for the plasma was 20W. The silane concentration (SC=$SiH_4/(SiH_4+H_2)$ was 4% or 5% for different series. The SC was 4% and the pressure was 120Pa when the substrate temperature was varied from 30°C to 220°C. When the pressure was changed between 50Pa and 190Pa, the SC was 5% and the substrate temperature was fixed at 180°C.

The deposition rate was calculated from the thickness obtained from an optical transmission spectrum. The dark conductivity was measured at room temperature by using an Al coplanar contact electrode. Raman spectrum and x-ray diffraction (XRD) were used to characterize the crystallinity of the films. The surface morphology was researched by Philips Sirion

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200 Field Emission Gun Scanning Electron Microscope (FEG-SEM).

3. Result

3.1. The effect of substrate temperature

In Fig.1 the deposition rate and dark conductivity as a function of the substrate temperature is presented. The deposition rate and dark conductivity markedly depend on the substrate temperature. Increasing the temperature leads to the increase of the deposition rate from 4.2 Å/S to 6.5 Å/S. The dark conductivity is enhanced sharply from 2.96×10^{-9}S/cm to 2.39×10^{-3}S/cm when the substrate temperature increases from 30°C to 220°C. The sharp change in dark conductivity reflects the change of microstructure which is confirmed by the Raman spectra.

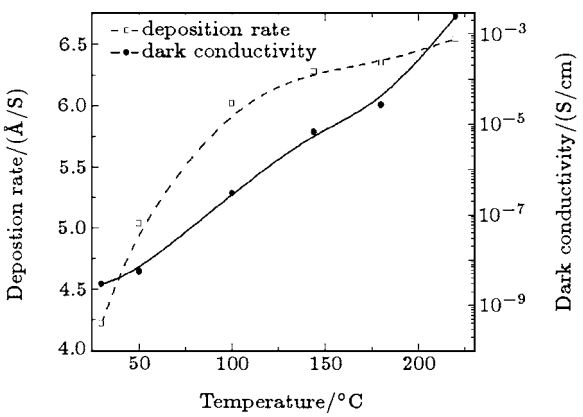


Fig.1. Deposition rate and dark conductivity for films deposited at different substrate temperature.

The Raman spectra of films deposited at different substrate temperature are shown in Fig.2. At the substrate temperature of 30°C, the film shows a broad peak near 480 cm^{-1} which is the characteristic of vibrational transverse optical mode of amorphous silicon, so the film is purely amorphous. Along with the increase of the substrate temperature the peak near 480 cm^{-1} decreases and the peak near 520 cm^{-1} increases. At 100°C, there are two peaks in the Raman spectra which means that the films is near the transition from amorphous to microcrystalline silicon. As the substrate temperatures are higher than 140 °C, the peak near 480 cm^{-1} disappears and the peak near 520 $cm^{-1}$is dominant. At the same time, the position of peak shifts from 516.66cm^{-1} (100°C) to 519cm^{-1} (220°C), which is caused by crystallite size effect and stress within the material.[14,15]

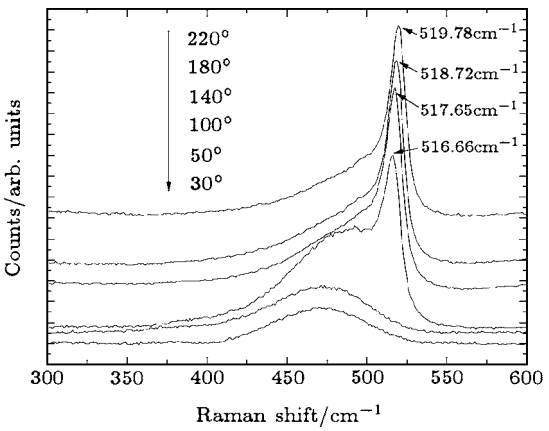


Fig.2. Raman spectra for films deposited at different substrate temperature.

Figure 3 shows the x-ray diffraction pattern of films prepared at different substrate temperature. For the microcrystalline silicon films used in this study, there are three orientations (111), (220) and (311). Along with the decrease of the substrate temperature from 220°C to 140°C, the intensity of three peaks decreases. The silicon film prepared at 30°C has no diffraction peaks, namely the film is purely amorphous.

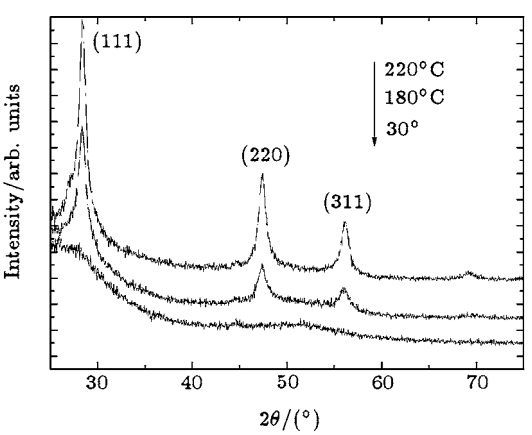


Fig.3. X-ray diffraction data for films deposited at different substrate temperature.

Figure 4 shows the surface morphology of the film prepared at 30°C. Figure 5 shows the surface morphology of the film prepared at 180°C. Although both samples are composed of small grains, the boundaries between the grains are not clear at the substrate temperature of 30°C. After increasing the substrate temperature to 180°C, the clear grain boundaries appear and the number of grains decreases.

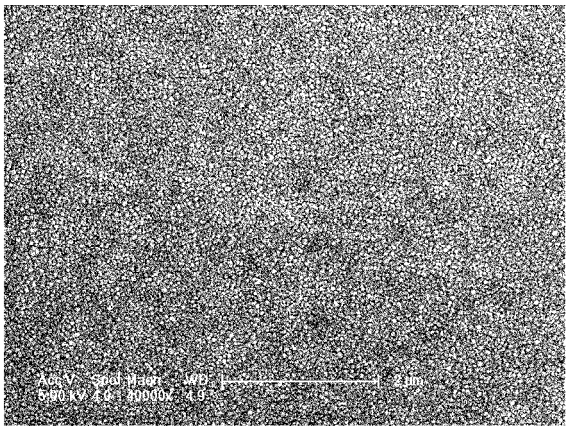


Fig.4. SEM image of the film deposited at the substrate temperature of 30°C.

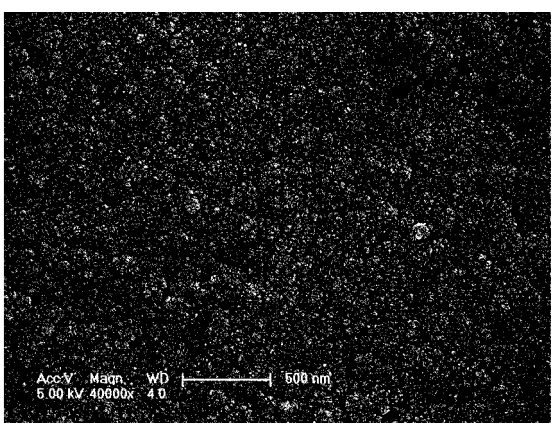


Fig.5. SEM image of the film deposited at the substrate temperature of 180°C.

3.2. The effect of gas pressure

Figure 6 depicts the variations of deposition rate and photosensitivity of films as a function of the gas pressure. Along with the increase of the pressure the deposition rate increases monotonously from 5.08Å/s to 8.9Å/s. The dark conductivity at 50Pa is 9.72×10^{-8}S/cm. When the pressure is increased to 80Pa, the dark conductivity is increased to 2.7×10^{-7}S/cm. When the pressure is continually increased from 120Pa to 190Pa, the dark conductivity is reduced from 2.46×10^{-7}S/cm to 1.3×10^{-9}S/cm.

The Raman spectra of films prepared at different pressure are shown in Fig.7. There are two peaks near 480 cm^{-1} and 520m^{-1} in the Raman spectra at 50Pa, so the film is mixed by microcrystalline silicon and amorphous silicon. When the pressure is enhanced to 80Pa, the peak near 520 cm^{-1} is dominant indicating the film is microcrystalline. When the pressure is continually increased, the peak near 480 cm^{-1} increases whereas the peak near 520 cm^{-1} decreases. At 150Pa, there are two peaks but the peak near 480cm^{-1} is dominant. At 190Pa, the peak near 520cm^{-1} disappears and the film is purely amorphous. The x-ray diffraction pattern also reflects the change (Fig.8).

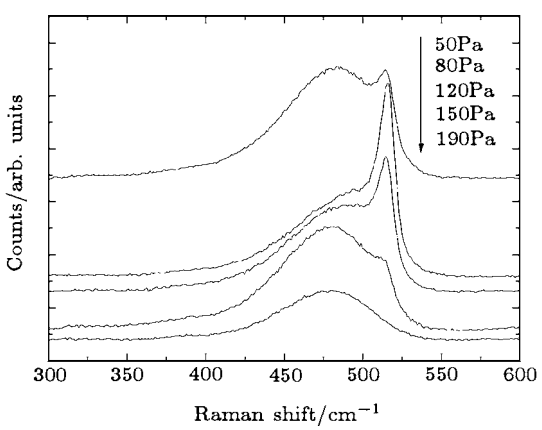


Fig.7. Raman spectra for films deposited at different pressure.

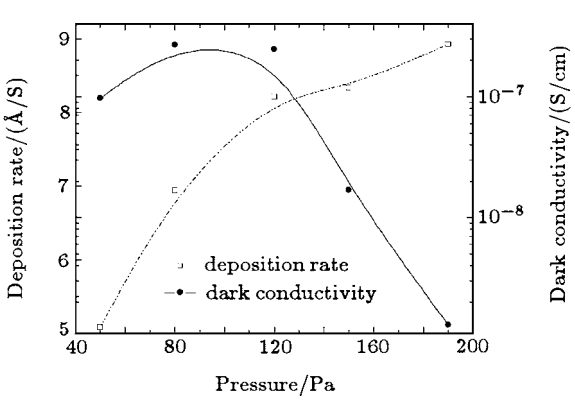


Fig.6. Deposition rate and dark conductivity for films deposited at different pressure.

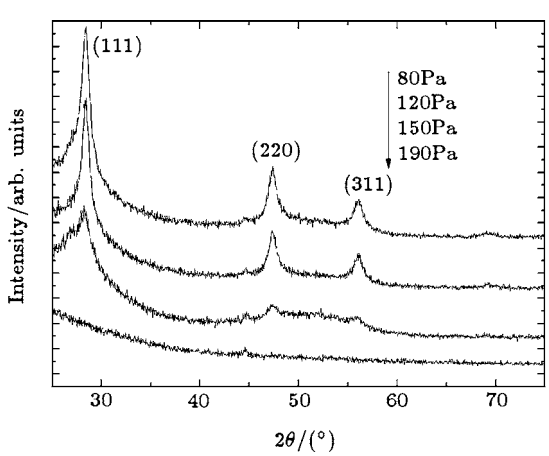


Fig.8. X-ray diffraction data for films deposited at different pressure.

Figure 9 and Fig.10 show the surface morphology of films prepared at 80Pa and 190Pa. As we can see, the film at 80Pa has clear grain boundaries and bigger grain size than that of the film at 190Pa.

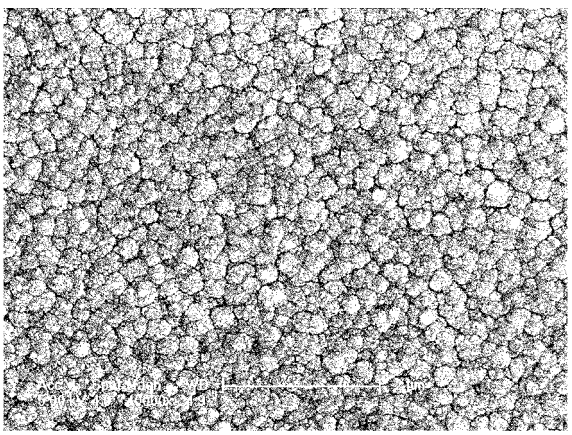


Fig.9. SEM image of the film deposited at the pressure of 80Pa.

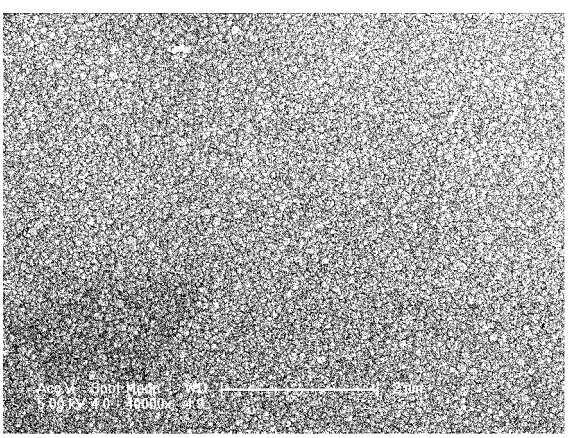


Fig.10. SEM image of the film deposited at the pressure of 190Pa.

4. Discussion

At low substrate temperature, the activity of film precursors is low and the deposition rate is limited. Along with the increase of the substrate temperature, the higher activity of film precursors leads to the higher reaction on the growing film surface. So the deposition rate is enhanced from 4.2Å/S to 6.5Å/S when the temperature is increased from 30°C to 220°C.

The surface diffusion model can be used to explain the structural transition.[16] The surface diffusion coefficient of film precursors (such as SiH_3) is correlated with the substrate temperature. At low substrate temperature the atomic hydrogen density is low and the surface diffusion coefficient is limited, it is difficult for SiH_3 radicals to diffuse enough distance to find energetically stable sites to form ordered structure. So not ordered structure is dominant and the film is amorphous at low temperature. Increasing the substrate temperature leads to the enhancement of the atomic hydrogen density. The diffusion coefficient of SiH_3 radicals is enhanced by the actions between atomic hydrogen and the growing surface, thereby the SiH_3 radicals are easier to find stable sites.

At low gas pressure, the deposition rate is limited by the low radical generation rate for the low SiH_4 density. At 50Pa, the electron temperature is too high and the bombardment on the growing film surface is severe. The result is that the growth of crystalline phase is hampered. When the pressure is higher than 80Pa, the atomic hydrogen depletes the SiH_4 and the atomic hydrogen density is high. The SiH_3 radicals on the hydrogen-covered surface can find energetically stable sites to form ordered structure. Higher gas pressure enhances the radical generation rate, so the deposition rate is increased. At the same time, high gas pressure increases the reaction between SiH_4 and the atomic hydrogen. As a result, the reduced atomic hydrogen density decreases the diffusion coefficient of SiH_3 radicals. At 190Pa, the SiH_3 radicals cannot diffuse enough distance to find energetically stable sites.

5. Conclusion

The electrical structural properties and surface morphology of films deposited at different substrate temperature and gas pressure were studied. The transition from amorphous to microcrystalline silicon was obtained by changing the substrate temperature and the gas pressure. Accompanied with an increase of dark conductivity the structure shifts from amorphous to microcrystalline silicon when the substrate temperature is increased. Along with the increase of the pressure, the dark conductivity increases to 2.7×10^{-7}S/cm at first and then decreases when the pressure is bigger than 80Pa. The structural change confirmed by Raman spectra is consistent with the change of dark conductivity.

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