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Fabrication of high growth rate solar-cell-quality μc-Si:H thin films by VHF-PECVD*

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Several series of Si:H films were fabricated by the very high frequency plasma enhanced chemical vapour deposition (VHF-PECVD) at different substrate temperatures (T_s) and silane concentration (SC=[SiH_4]/[SiH_4+H_2]%). The results of Raman spectroscopy showed structural evolution of the Si:H films with the variation of T_s and SC. The results of x-ray diffraction (XRD) measurements indicated that T_s also influences the crystal orientation of the Si:H films. The modulation effect of T_s on crystalline volume fraction (X_c) is more evident for the high SC, which shows different trend compared to low SC. In addition, the growth rate of the films also showed a regular change with the variation of SC and T_s. Different samples in the series showed a similar increase in dark conductivity and a decrease in photosensitivity with increasing T_s and decreasing SC. Device-quality microcrystalline silicon materials were deposited at a high growth rate, characterized by relatively low dark conductivity and relatively high photosensitivity in a certain crystalline range. The microcrystalline silicon solar cell with a conversion efficiency of 4.55% has been prepared by VHF-PECVD.

Keywords: VHF-PECVD, device-quality microcrystalline silicon, Raman spectroscopy, XRD
PACC: 8115H, 7360F, 7830

1. Introduction

Hydrogenated microcrystalline silicon (μc-Si:H) has attracted much attention because it is a material with a variety of applications such as solar cells, image sensors and thin film transistors (TFTs).[1–3] The thin film solar cell made from μc-Si:H film has shown almost no light-induced degradation, in contrast to the hydrogenated amorphous silicon (a-Si:H) film.[4] Currently, it is observed that the best cell performance has been achieved with silicon materials prepared near the transition zone to the amorphous growth range.[5] It is very important to find the transition zone for the fabrication of high-efficiency solar cells. Although there are many studies about the structural change of Si:H films with the variation of the substrate temperature (T_s) and the silane concentration (SC=[SiH_4]/[SiH_4+H_2]%), they are almost all focused on a large range.[6–8] For example, T_s varied from 250 to 500°C, which is too high to be suitable for the application of solar cell.[9]

In this paper we perform a study on several series of μc-Si:H films prepared at different T_s and SC under a small range of deposition conditions to obtain a series of hydrogenated microcrystalline silicon materials for solar cells. In addition, to overcome the drawback of conventional plasma-enhanced chemical vapour deposition (PECVD), the VHF-PECVD technique is applied. Aside from the high deposition rate, it can also improve the grain size of films.

2. Experimental details

All samples with a thickness of about 1000nm were prepared using 60MHz PECVD at various T_s and

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SC. To overcome the bottleneck of μc-Si:H as an absorber layer, generally having low deposition rate, relatively higher pressure (of about 120Pa) was applied. All samples were grown on Corning 7059 glass, which had been treated by HF (5%).

The Raman scattering experiment was performed using a 632.8nm He–Ne laser. Here, the crystalline volume fraction (X_c) was used to describe the crystallinity of the films.[10] In addition, x-ray diffraction (XRD, Rigaku D/MAX 2500) using Cu$K\alpha$ radiation with wavelength of 0.15405nm was also applied for the characterization of the structural variation of the films. Dark-and photo-conductivity measurements were performed at room temperature using an Al co-planar contact electrode.

3. Results and discussion

Raman spectroscopy is also a powerful tool to investigate the structural properties of silicon-based films.[11–14] Figure 1 shows the Raman spectra of Si:H films deposited at different T_s but a fixed SC=5%. The film prepared at lower T_s (140°C) shows a broad peak near 480cm^{-1} which is the characteristic of the transverse optical (TO) mode of a-Si:H. In fact, the peak of the TO mode of the crystalline silicon (c-Si) centres at 520cm^{-1}. For the film prepared at 170°C there appears a small 'shoulder' in higher wavenumber except for the peak at 480cm^{-1}. With increasing T_s, the 'protrusion' becomes the 'shoulder' and ultimately evolves into a sharp peak at 516cm^{-1} (T_s=250°C). The shift of TO peak position to lower wavenumber, as compared to c-Si (520cm^{-1}), is attributed to the crystallite size effect and stress within the film.[15]

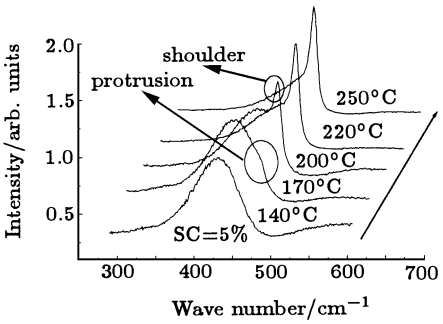


Fig.1. Raman spectra of silicon films prepared at different substrate temperatures for SC=5%.

In a word, Raman spectroscopy reveals the structural change from amorphous to microcrystalline silicon with the increase of T_s in a small step-stage.

Figure 2 shows the x-ray diffraction spectroscopy of the above Si:H films. It is observed that there is almost no obvious diffraction peak appearing at 140°C for the SC=5% except for a small peak at the position of (111). For the sample deposited at 170°C, the (111) peak of the c-Si evidently appears and at the location of (220) also show a small peak. With the increase of T_s, the other two peaks (220) and (311) can also be seen distinctly. Furthermore, the intensity of (220) peak increases greater than that of the peaks of (111) and (311). As a result, the (220) peak shows the preferred orientation with the increase of T_s. It is evident that T_s also has a great influence on the orientation of the crystalline phase in the films.

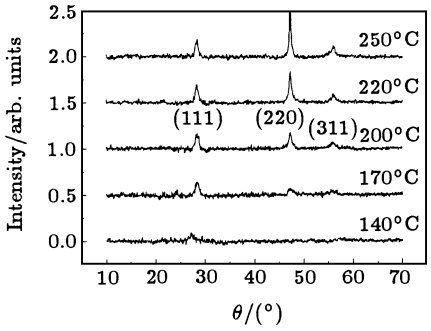


Fig.2. XRD patterns of silicon films prepared at different substrate temperatures for SC=5%.

Figure 3(a) shows the structural variation of the films prepared at different SC but fixed T_s (170°C). It can be seen that hydrogen dilution also has a great influence on the films prepared by VHF-PECVD, as we expected. Higher hydrogen dilution (low SC) is very important for obtaining the microcrystalline silicon. In fact, the microcrystalline silicon also can be fabricated under the condition of a higher SC, provided that other parameters also change appropriately, such as the increase of T_s. The details are shown in Fig.3(b). It is evident that high T_s can accelerate crystallization at a fixed SC (comparing Fig.3 (a) with 3(b)).

The X_c of the samples as a function of T_s and at various SCs is plotted in Fig.4. It is obvious that the higher X_c can be obtained at lower SC, which indicates that the hydrogen dilution is a very important factor for improving X_c. According to a previous study,[16] the materials as an active layer for μc-Si:H solar cells must have certain X_c at least higher than 30%. At the same time, it is also noticed that the variation of X_c with T_s shows different tendency for different SC. The modulation effect of T_s on X_c is more evident for higher SC samples.

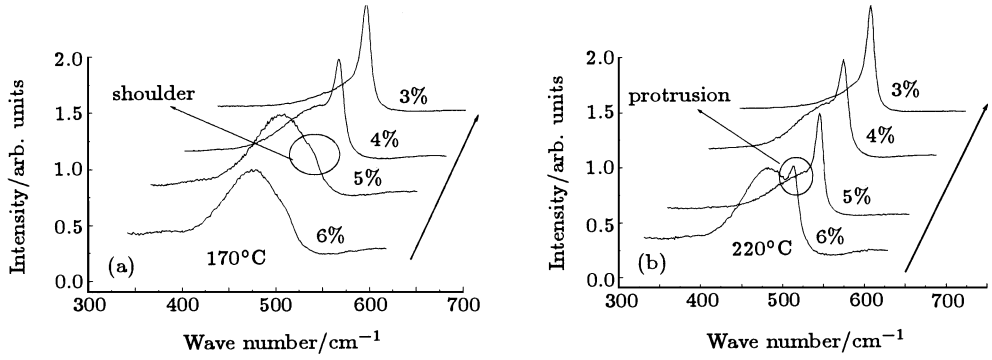


Fig.3. Raman spectra of silicon films prepared with different SC for T_s=170°C (a) and 220°C (b).

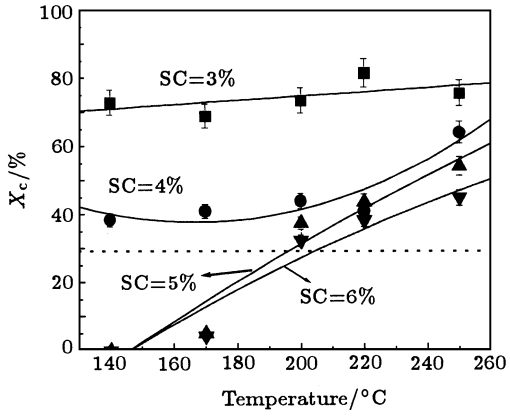


Fig.4. X_c of silicon films prepared at different T_s for various SC.

In Fig.5, the growth rates for the films deposited at an excitation frequency of 60MHz as functions of T_s for various SC are shown. It can be seen that the deposition rate increases with the decrease of T_s and the increase of SC. At SC of 3% and T_s of 250°C, we have a relatively low deposition rate of about 0.4nm/s, but it is still far higher than the deposition rate obtained by RF-PECVD. Decreasing the T_s to 140°C leads to an increase of deposition rate up to 0.6nm/s, while the film still shows microcrystalline at X_c of 70% (Fig.4).

However, it is noticed that the higher the deposition rate the lower the X_c (Figs.4 and 5). In order to obtain a high quality and low cost microcrystalline silicon film, we can increase the deposition rate under the condition of keeping a certain constant X_c.

With respect to the modulation function of T_s against X_c and growth rate, the following point might give an explanation. In fact, there are three models proposed to explain the growth of μc-Si:H. The surface diffusion model might give an explanation about these results. Namely, the surface diffusion length on the hydrogen-covered surface is enhanced because of elevating T_s, leading to an increase of crystalline volume fraction (X_c). In addition, different tendency of X_c for different SC may mean that the lower SC would lead to a larger number of hydrogen atoms. Sufficient atomic hydrogen from high hydrogen-diluted silane plasma will bring about a full surface coverage by bonded hydrogen and also produce local heating through the hydrogen-recombination reactions on the growing surface of the film. As a consequence, a higher T_s and lower SC will mean a higher X_c and lower growth rate.

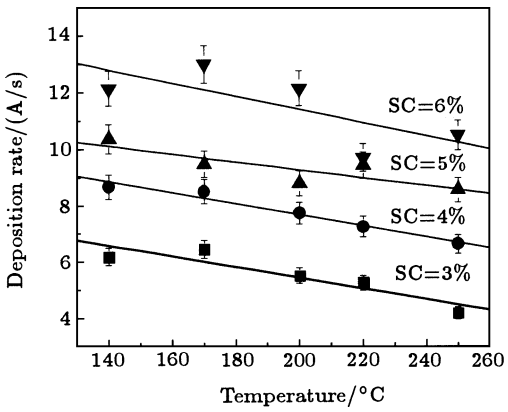


Fig.5. Deposition rate of silicon films as a function of T_s for different SC.

The investigation results of the dark conductivity measurements are shown in Fig.6(a). Dark conductivity of the samples increases with increasing T_s. In the investigated ranges of SC and T_s, the dark conductivity varies between 8.5×10^{-8} and 4.0×10^{-3} (Ωcm^{-1}). It is interesting to note that a variety of samples have a dark conductivity lower than 1.0×10^{-6} (Ωcm^{-1}) without additional treatment such as micro boron doping or gas purifying.[17,18] The activation energy (E_a) exceeds 0.5eV for dark conductivity lower than 1.0×10^{-6} (Ωcm^{-1}) in our samples.

A plot of the photosensitivity (photo/dark conductivity) is shown in Fig.6(b). Opposite to the dark

conductivity, the photosensitivity of the samples decreases with the increase of T_s and decrease of SC. The photosensitivity as a measure for the quality of solar cell absorber layers is also very important. According to the previous study by the FTJ group,[5] the photosensitivity of the sample higher than 1.0×10^3 causes the films that have undesired amorphous phase not suitable for the solar cell as absorber layers. On the other hand, using the films with a low photosensitivity produces devices with low open-circuit voltages and significant recombination losses, which also are not suitable for application as absorber layers in microcrystalline silicon solar cells. Currently, the range of photosensitivity of μc-Si:H solar cell absorber layers should be two orders. The details can be seen in Fig.6.

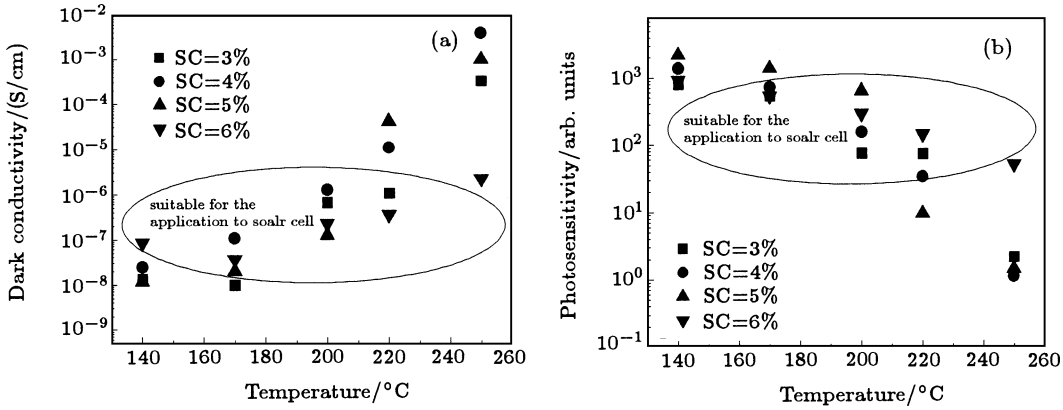


Fig.6. Dark conductivity (a) and photosensitivity (b) of silicon films prepared at different T_s for various SC.

From the above, many high-quality films can be obtained by optimization of SC and T_s. Of course, we should optimize the analysis results from X_c, dark conductivity and photosensitivity.

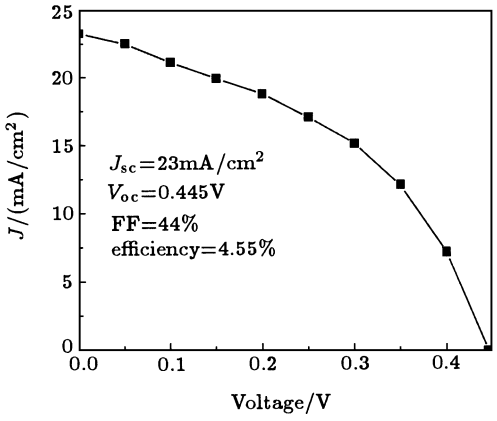


Fig.7. J–V performance of microcrystalline silicon solar cell fabricated by VHF-PECVD.

To know whether these high-quality microcrystalline silicon films are necessary for the solar cell can only be tested with the devices themselves. At first, we select the film for the application in solar cells, which is deposited at SC=4%, T_s=170°C, X_c=42%, $\sigma_d=1.08\times10^{-7}$s/cm, σ_p/σ_d=720, V_d=0.85nm/s. A microcrystalline silicon P-I-N solar cell with a conversion efficiency of 4.55% has been fabricated by VHF-PECVD. The J–V performance of the solar cell can be seen in Fig.7 (J_{sc}=23mA/cm^2, V_{oc}=0.45V, FF=44% Area=0.086cm^2). From the figure we can find that some parameters (especially the Full Factor (FF)) need be improved. It is believed that the conversion efficiency will be improved provided that other measures are taken or other optimization condition selected.

4. Conclusions

Several series of Si:H films have been fabricated by VHF-PECVD to study their structural, optical and electrical properties. Both substrate temperature (T_s) and silane concentration (SC) have decisive effect on the structural evolution of the Si:H films, which change from amorphous silicon to microcrystalline silicon, corresponding to T_s changing from low to high and SC from high to low. In addition, the results of XRD measurements also show that the orientation of the crystals in the Si:H films changes with the variation of T_s. The higher the T_s the stronger the intensity of (220) peak, which means the orientation variation of the crystals produced. The results of dark conductivity (ranging from 10^{-6} to 10^{-8}S/cm), photosensitivity (about 10^2) and X_c (>30%) indicate that a variety of

device-quality microcrystalline silicon materials with high growth rate have been prepared successfully. The microcrystalline silicon solar cell with a conversion efficiency of 4.55% has been obtained by VHF-PECVD.

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