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Research on the optimum hydrogenated silicon thin films for application in solar cells*

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Hydrogenated silicon (Si:H) thin films for application in solar cells were deposited by using very high frequency plasma enhanced chemical vapour deposition (VHF PECVD) at a substrate temperature of about 170 °C. The electrical, structural, and optical properties of the films were investigated. The deposited films were then applied as i-layers for p-i-n single junction solar cells. The current–voltage ($I-V$) characteristics of the cells were measured before and after the light soaking. The results suggest that the films deposited near the transition region have an optimum properties for application in solar cells. The cell with an i-layer prepared near the transition region shows the best stable performance.

Keywords: hydrogenated silicon thin film, transition region, Si:H thin film solar cell, stability
PACC: 8155H, 6855

1. Introduction

Amorphous silicon (a-Si:H) solar cells are among the most promising thin film photovoltaic devices owing to their high performance and low fabrication costs.[1] However, illumination of this kind of solar cell results in the formation of metastable defects, which greatly decreases their efficiencies. In the last 20 years, extensive work has been done to understand the light-induced degradation and to develop materials and devices that will reduce this degradation. Among the materials studied, microcrystalline silicon (μc-Si:H) thin films have gotten much attention over their amorphous counterparts because of their higher electrical conductivity and less light induced degradation. [2,3] Intrinsic μc-Si:H thin films have been used as active layers for solar cells. [4] However, since μc-Si:H solar cells require much thicker active layers (i-layers), the low deposition rate of microcrystalline films hinders the cost effectiveness in device application. In order to resolve the problem, the intermediate materials between amorphous and microcrystalline silicon are now attracting great attention.[5,6] This kind of material is considered to be promising for active-layers in Si:H solar cells due to its high stability and high rate deposition.

Usually, Si:H films and Si:H solar cells were prepared by conventional radio frequency (13.56 MHz) plasma enhanced chemical vapour deposition (RF PECVD), which has a very low growth rate. In order to increase the growth rate, very high frequency plasma enhanced chemical vapour deposition (VHF PECVD) has been used. This method has shown great potential for its low deposition temperature and high growth rate in preparing high quality films and solar cells. [7,8]

In this paper, we report the deposition of Si:H films and Si:H thin film solar cells by VHF PECVD and the exploration of the stability of Si:H films. Our results show that the material deposited near the transition region has an optimum electronic properties, which is suitable to be applied in stable Si:H solar cells.

2. Experimental details

Intrinsic Si:H films and Si:H based p-i-n solar cells were prepared in a high vacuum multi-chamber VHF PECVD system. SiH_4 and H_2 were used as reactant gas for the deposition of Si:H films and i-layers of the solar cells. The deposition pressure, substrate temperature and plasma power density were fixed at 120 Pa, 170 °C and 20 mW/cm^2, respectively. The silane con-

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centration (SC = $SiH_4/(H_2+SiH_4)$) was changed from 4% to 20%. n-type crystalline Si wafers and glass were used as substrates for the deposition of individual intrinsic films.

The thickness of the Si:H films was about 500 nm, which was measured by a step profilemeter. The dark conductivity (σ_d) and photoconductivity (σ_{ph}) were measured with co-planar Al electrodes. Fourier transform infrared (FTIR) spectroscopy was used to characterize the hydrogen bond configuration and hydrogen content in the deposited films. Microstructure factor, R, was calculated using the equation $R = I_{SiH_2}/(I_{SiH_2} + I_{SiH})$, where I_{SiH_2} and I_{SiH} are the areas of the stretching SiH_2 and SiH peaks of the FTIR spectra, respectively. Constant photocurrent method (CPM) was used to study the absorption properties of the samples. The stability of the films against light soaking was evaluated by measuring the photoconductivity after illumination.

Glass/SnO_2/ZnO was used as substrates for the solar cells, where the n-layers were thermally stable phosphorus-doped nanocrystalline silicon (nc-Si:H) and the p-layers were boron-doped microcrystalline silicon (μc-Si:H) prepared by VHF PECVD. The solar cells were light-soaked under one sun light at about 50 °C for stability studies. The current-voltage ($I-V$) characteristics of the cells were measured before and after the light soaking.

3. Results and discussion

3.1. Raman spectroscopic analysis

Raman spectra of the deposited Si:H films are shown in Fig.1. The peak at about 520 cm^{-1} is due to the transverse optical (TO) mode of crystalline silicon. The peak at around 480 cm^{-1} is related to the TO mode of a-Si:H. From the figure, we can observe that the sample deposited at SC = 4% shows both amorphous ($\sim$ 480 cm^{-1}) and crystalline ($\sim$ 520 cm^{-1}) phases. When SC > 4%, the films are in the amorphous phase characterized by the band centred at about 480 cm^{-1}. This phenomenon demonstrates the transition of μc-Si:H to a-Si:H growth as SC increases. It is known that the peak at 480 cm^{-1} is sensitive to the short-range order of the amorphous silicon network. The change in the band line-width is associated with the change in Si bond angle, while the shift in the peak position is related to the change in bond length.[9,10] As shown in the figure, the peak position of the a-Si:H does not shift with the increase of SC and the full-width at half maximum (FWHM) of the band at 480 cm^{-1} is found to be almost constant. Thus, the increase of SC does not change the Si-Si short-range order in the a-Si:H films. For further investigating the effect of SC on the structure of the a-Si:H films, we studied the medium range order (MRO) of the a-Si:H samples. The Raman spectra of a-Si:H were deconvoluted with four Gaussians peaks as follows. Figure 2 shows the deconvoluted spectrum of the sample deposited at SC = 20%. In the figure, the peak at about 150 cm^{-1} to the transverse acoustic (TA) mode, the peak at about 300 cm^{-1} to the longitudinal acoustic (LA) mode, the peak at about 410 cm^{-1} to the Si-Si longitudinal optical (LO) mode, and the peak at about 480 cm^{-1} to the TO mode.[11] The change in the medium range order was estimated from the ratio of the integrated intensities, I_{TA}/I_{TO}.[11]

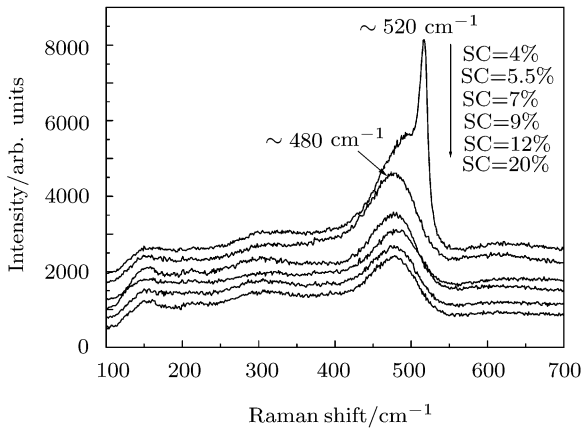


Fig.1. Raman spectra of Si:H films deposited at various silane concentration.

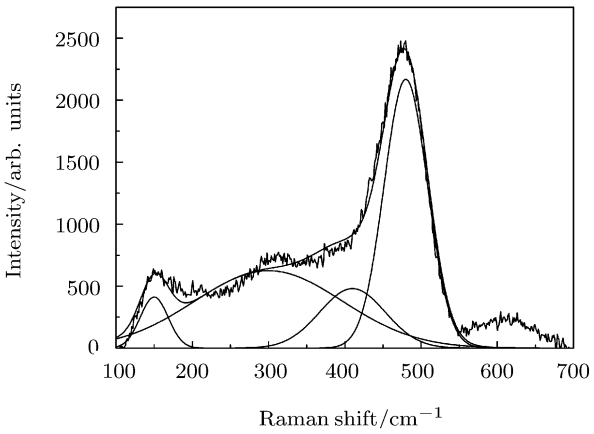


Fig.2. The deconvoluted spectrum of the sample deposited at SC = 20%.

Figure 3 shows the value of I_{TA}/I_{TO} as a function of SC, which was calculated from the deconvoluted spectra. As shown in the figure, the value of I_{TA}/I_{TO} increases with SC, which indicates the increase in disorder on the medium range. This change in structure is related to the growth mechanism of a-Si:H. In hydrogen-diluted deposition, the ratio of atomic hydrogen to film precursors determines the structure of the Si matrix. With SC increasing, the ratio decreases, leading to a decrease of surface coverage by the bonded hydrogen, which results in the decrease of the surface diffusion length of the film precursors (e.g. SiH_3).[12] In addition, the amount of the film precursors increases with the increase of SC. As a result, more and more film precursors have no time to find the stable sites and they quickly bond with the dangling bonds on the growing surface, which leads to the increase of the disorder in amorphous network. We define the regime of SC $\leq$ 4% as the microcrystalline growth region, the regime of 4% $<$ SC $\leq$ 5.5% as the transition region, and the regime of 5.5% $<$ SC $\leq$ 12% as the region near the transition region. As seen in Fig.3, the films deposited near the transition region have an improved lattice structure.

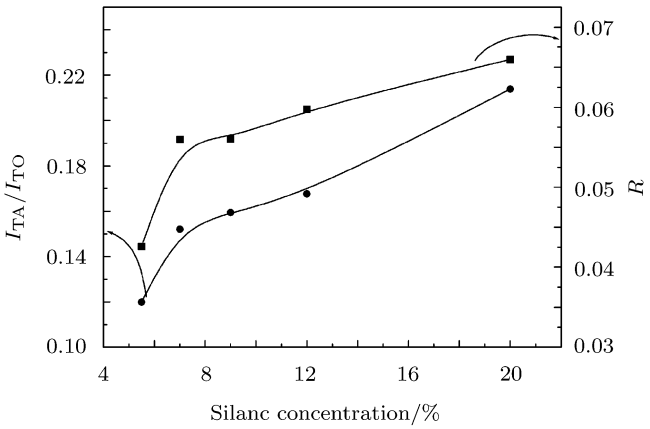


Fig.3. Ratio of the intensity of the TA band to that of the TO band. I_{TA}/I_{TO}, and microstructure factor, R, as a function of silane concentration.

3.2. Optical absorption spectra

The optical absorption properties of the samples were studied by constant photocurrent method (CPM). Figure 4 shows the measured optical absorption spectra. From the figure, we can observe that in the low energy regime ($<$ 1.9 eV), the μc-Si:H film (deposited at SC = 4%) shows a higher absorption coefficient than the sample deposited in the a-Si:H growth region. In this regime, the sample deposited at SC = 9% shows a medial absorption coefficient. While, in the high energy regime ($>$ 1.9 eV), the a-Si:H films show much higher absorption coefficients than the sample deposited in the μc-Si:H growth region. The samples deposited at SC = 9% and SC = 20% show almost the same absorption coefficient in the high-energy regime.

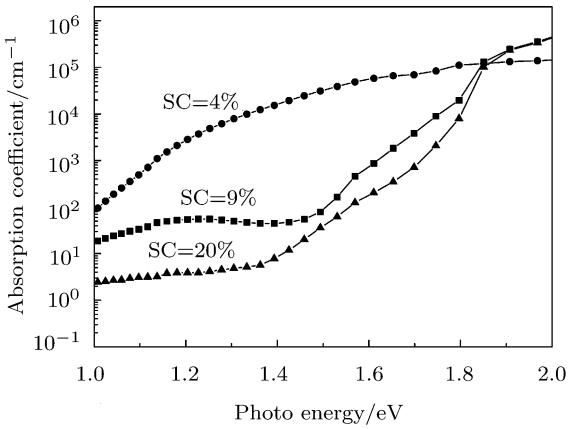


Fig.4. Optical absorption spectra of samples deposited at SC = 4%, 9% and 20%.

3.3. FTIR spectroscopic analysis

Light-induced degradation is associated with SiH_2 bond density in a-Si:H films, where a low SiH_2 bond density film degrades little.[13–15] In our studies, Fourier transform infrared (FTIR) spectroscopy was used to investigate the total hydrogen content and the hydrogen bond configuration in the films. Figure 5 shows the FTIR spectra of the samples. As shown in the figure, the films have major infrared absorption bands near 640 and 2000 cm^{-1} which correspond to the wagging and the stretching modes of local vibrations of mono-hydrogen (SiH) bonds, respectively.[16] An additional vibration band near 880 cm^{-1} is observed. This band is believed to correspond to the bending modes of local vibrations of SiH_2 bonds and/or $(SiH_2)_n$ complexes.[17] As SC increases, the intensity of both the wagging and the stretching mode peaks increases, indicating the increase of hydrogen content in the films. Besides, the intensity of the peak at 880 cm^{-1} increases with SC, which indicates the increase of di-hydrogen (SiH_2) bonds or $(SiH_2)_n$ content in the films.

In order to further study the hydrogen bond configuration in a-Si:H films, the absorption bands of the stretching modes were deconvoluted into two peaks at 2000 and 2080 cm^{-1}, associated with the isolated mono-hydrides (SiH) and the di-hydrides (SiH_2) or

poly-hydrides $(SiH_2)_n$, respectively. Microstructure factor, R, was calculated from $R = I_{SiH_2}/(I_{SiH_2} + I_{SiH})$, where I_{SiH_2} and I_{SiH} are the areas of the stretching SiH_2 (2080 cm^{-1}) and SiH (2000 cm^{-1}) peaks of the deconvoluted FTIR spectra respectively. The effect of SC on the microstructure factor is shown in Fig.3. With SC increasing, the microstructure factor increases, indicating the increase of SiH_2 bond density in the films. From Fig.3 and Fig.5, we conclude that the films deposited near the transition region show the low hydrogen content and SiH_2 bond density, which reflects the stability of the films.

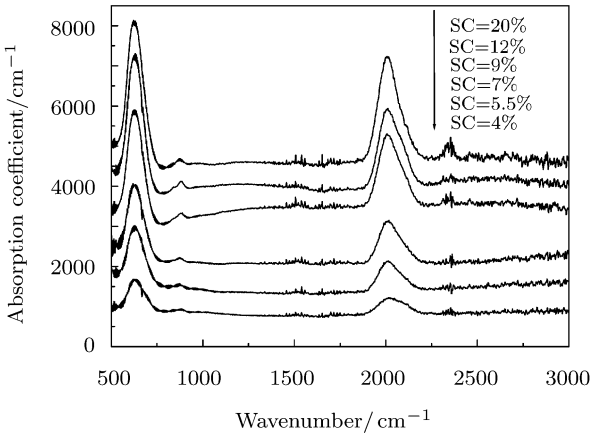


Fig.5. FTIR spectra of samples as function of silane concentration.

3.4. Electrical properties and stability

The electrical properties of the films were studied through investigation of the change in photoconductivity (σ_{ph}) and photosensitivity (σ_{ph}/σ_d). Figure 6 shows σ_{ph} and photosensitivity as functions of SC. The film deposited in microcrystalline region (SC = 4%) has a photosensitivity of about 500 and a photoconductivity of about 1.11 $\times 10^{-5}$ Scm^{-1}, which are suitable for application in μc-Si:H solar cells. With SC increasing, both the photosensitivity and σ_{ph} tend to increase initially and then decrease. The photosensitivity reaches a peak value of about 1.49 $\times 10^6$ at SC = 9%. The change in σ_{ph}, which ranges from 1.11 $\times 10^{-5}$ Scm^{-1} to 4.86 $\times 10^{-5}$ Scm^{-1}, is much less than that in photosensitivity. The result suggests that high quality Si:H film, which has a high photosensitivity and σ_{ph}, can be obtained near the transition region (SC =9%).

When Si:H films are subjected to light exposure, significant changes in properties may take place. These changes in the properties of materials have a great effect on the performance of the Si:H solar cells. In our studies, the films' stability was determined by examining the degradation of the photoconductivity of the films. All Si:H films prepared were light soaked under one sun light illumination for 20 hours. The photoconductivity was measured before and after the illumination. It was found that the stability of the films decreases with SC. Figure 7 shows the degradation behaviours of photoconductivity of films deposited at SC = 4%, 9%, 20% respectively. From the figure, we can observe that the photoconductivity of the film deposited in the microcrystalline region (SC = 4%) does not decrease but increases from 1.11 $\times 10^{-5}$ Scm^{-1} to 4.79 $\times 10^{-5}$ Scm^{-1} after the light soaking. The film deposited near the transition region (SC = 9%) shows a small degradation. The degradation rate, which is defined as Deg = $(\sigma^b_{ph} - \sigma^a_{ph})/\sigma^b_{ph}$ (σ^b_{ph} and σ^a_{ph} represent the photoconductivity before and after light soaking respectively), is about 51.65%. However, the film deposited at SC = 20% is observed to have a large degradation rate of about 92.62%.

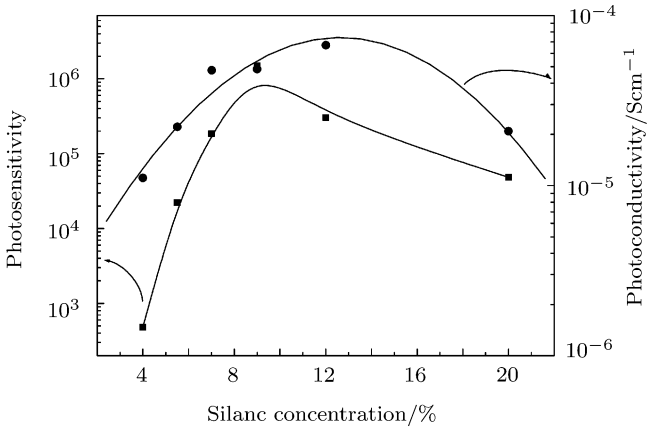


Fig.6. Photosensitivity and photoconductivity as a function of silane concentration.

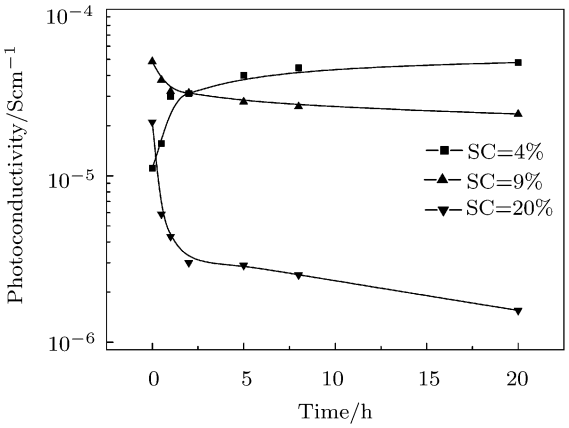


Fig.7. Dependence of the photoconductivity on illumination time of Si:H films deposited at SC =4%, 9% and 20%.

The characters of the material against light soaking suggest that moderate hydrogen dilution (SC = 9%) benefits the improvement of the stability of the material. We suggest that moderate hydrogen dilution can suppress the formation SiH_2 in the films (Fig.5), which improves the microstructure of the films. The improved microstructure of a-Si:H films leads to the enhanced stability and high quality of the films.

3.5. Performance of the solar cells

Since the performance of Si:H solar cells is strongly related to the properties of the intrinsic films, we applied the Si:H materials as i-layers for solar cells. All cells were light-soaked under one sun light for about 500 hours. The performance of the cells both in initial and in degraded states was measured. We find that the cell deposited at SC = 9% shows the best stable performance. The microcrystalline silicon thin film solar cell, which was deposited at SC = 4%, shows almost no degradation after the light soaking. However, its efficiency is very small, which is only about 4.5%. Figure 8 shows the initial current-voltage ($I - V$) characteristics of the cells with i-layers deposited at SC = 9% and 20%. The samples have short-circuit current densities of about 15.15 mA/cm^2 and 15.08 mA/cm^2, open-circuit voltages (V_{OC}) of about 0.86 V and 0.85 V, respectively.

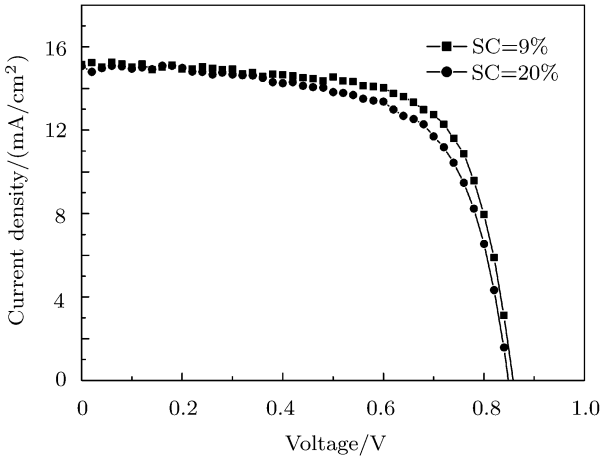


Fig.8. Initial $I-V$ characteristics of solar cells having the i-layer deposited at SC = 9% and 20%.

Figure 9 show the current–voltage ($I - V$) characteristics of the cells with i-layers deposited at SC = 9% and 20% after the light soaking. As seen in the figure, better stable performance for the cell deposited at SC = 9% is observed. The cell has an open-circuit voltage (V_{OC}) of about 0.85 V and a short-circuit current density (J_{SC}) of about 14.49 mA/cm^2 after the light soaking, whereas the cell deposited at SC = 20% has an open-circuit voltage of about 0.83 and a short-circuit current density (J_{SC}) of about 14.12 mA/cm^2 after the light soaking. The results suggest that the quality of the absorbing layer deposited at SC = 9% is high and is most suitable for the application in Si:H solar cells.

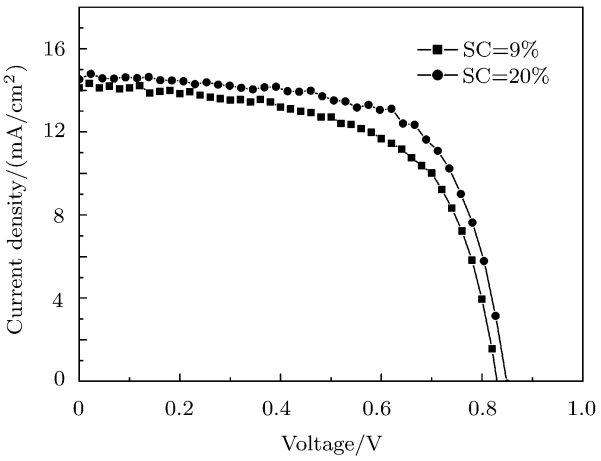


Fig.9. $I - V$ characteristics of solar cells having the i-layer deposited at SC = 9% and 20% after the light soaking.

4. Conclusion

Hydrogenated silicon (Si:H) thin films were prepared by VHF PECVD at a low substrate temperature of about 170 °C. The electrical and structural properties of the films were investigated. The films were applied as i-layers for solar cells. The stability of intrinsic films and solar cells against light soaking was studied. It was found that the Si:H films deposited near the transition region have optimum device quality and enhanced stability against light-soaking. The cell with an i-layer prepared near the transition region (SC = 9%) shows the best stable performance.

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