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Optical emission spectroscopy study on deposition process of microcrystalline silicon

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This paper reports that the optical emission spectroscopy (OES) is used to monitor the plasma during the deposition process of hydrogenated microcrystalline silicon films in a very high frequency plasma enhanced chemical vapour deposition system. The OES intensities (SiH^*, H^*_α and H^*_β) are investigated by varying the deposition parameters. The result shows that the discharge power, silane concentrations and substrate temperature affect the OES intensities. When the discharge power at silane concentration of 4% increases, the OES intensities increase first and then are constant, the intensities increase with the discharge power monotonously at silane concentration of 6%. The SiH^* intensity increases with silane concentration, while the intensities of H^*_α and H^*_β increase first and then decrease. When the substrate temperature increases, the SiH^* intensity decreases and the intensities of H^*_α and H^*_β are constant. The correlation between the intensity ratio of $I_{H^*_\alpha}/I_{SiH^*}$ and the crystalline volume fraction (X_c) of films is confirmed.

Keywords: microcrystalline silicon, VHF-PECVD, optical emission spectroscopy

PACC: 6860, 7230, 7850G

1. Introduction

Hydrogenated microcrystalline silicon has attracted great attention recently for application in solar cells due to its better stability and higher absorption coefficient than amorphous silicon in the infrared spectral region.[1−3] The conventional technique of preparing microcrystalline silicon films is the radio frequency plasma enhanced chemical vapour deposition (RF-PECVD) from source gas. Microcrystalline silicon solar cells require a thick active layer for the low absorption coefficient in the visible spectral region. Whereas the deposition rate of microcrystalline silicon prepared by RF-PECVD is low. The very high frequency plasma enhanced chemical vapour deposition (VHF-PECVD) technique has been developed to improve the deposition rate for its good compatibility for RF-PECVD.[4−6] Although the deposition process of VHF-PECVD has been studied extensively[7], the mechanism is still unclear and needed to be studied. Optical emission spectroscopy (OES) is a method capable of providing information of the excited species in the plasma.[8]

In this paper, we used OES to investigate the growth of hydrogenated microcrystalline silicon films in a VHF-PECVD system. We report the relation between OES and deposition parameters such as the discharge power, silane concentrations and substrate temperature. The correlation between the intensity ratio of $I_{H^*_\alpha}/I_{SiH^*}$ and the microstructure of films is also discussed.

2. Experimental

Microcrystalline silicon films were grown on the glass substrate by a VHF-PECVD system using a frequency of 60 MHz. SiH_4 diluted in H_2 was fed as the source gas and the total gas flow rate was kept at 60 sccm. The gas pressure was fixed at 120 Pa. The discharge power was modulated from 10 W to 45 W at silane concentration ($SC=100\%\times SiH_4/(SiH_4+H_2)$) of 4% and 6%. The SC was changed from 2% to 8% at the discharge power of 20 W and 10 W. The substrate temperature was increased from 30 °C to 220 °C.

The PR650 Spectra Colorimeter with a spectral range of 380–780 nm was used to collect the OES from the plasma during the deposition process. To achieve a stable measuring result PR650 began to record the data after the plasma glowed for 120 sec-

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onds. The measuring point was near the substrate surface because the plasma near the substrate determines the film's structure. Raman spectroscopy was used to study the structure of films and the intensity ratio $(I_{520\,\mathrm{cm}^{-1}} + I_{500\,\mathrm{cm}^{-1}})/(I_{520\,\mathrm{cm}^{-1}} + I_{500\,\mathrm{cm}^{-1}} + I_{480\,\mathrm{cm}^{-1}})$ was used to evaluate the crystalline volume fraction of films. The Raman scattering was performed from the film side using Renishaw MKI 2000 ($\lambda = 632.8\,\mathrm{nm}$ He–Ne laser).

3. Results and discussion

3.1. Effect of discharge power

Figures 1(a) and 1(b) show the OES of the plasma with different discharge power at SC of 4% and 6%.

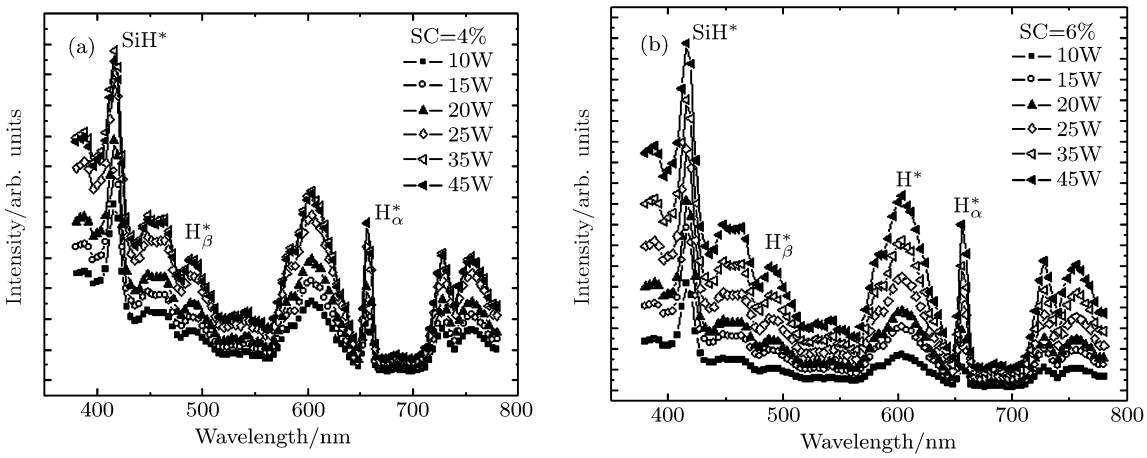


Fig.1. OES with different discharge power (a) at SC of 4% and (b) at SC of 6%.

As that shown in the Fig.1(a), we focus on the species such as SiH* (414 nm), H^*_α (656 nm) and H^*_β (486 nm). Figure 2(a) shows the variation of OES intensities as a function of the discharge power at SC of 4%.

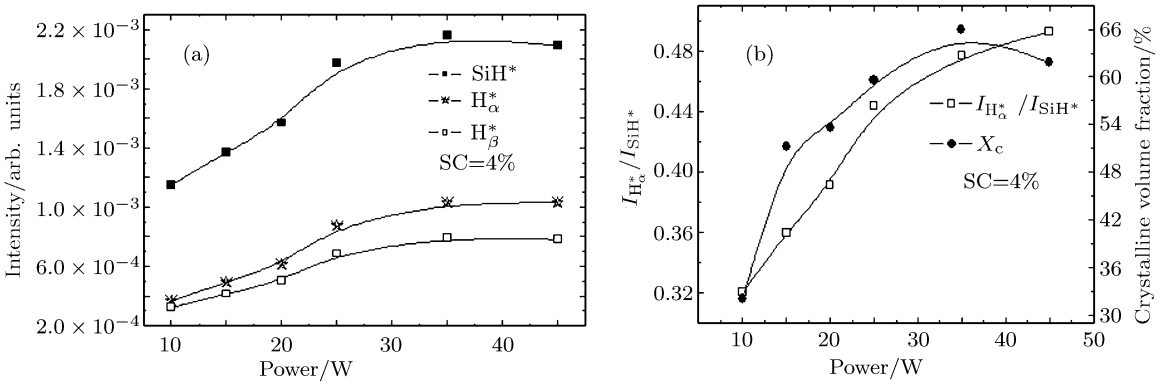


Fig.2. (a) OES intensity of SiH*, H^*_α and H_{β^*} versus the discharge power at SC of 4%. (b) $I_{H^*_\alpha}/I_{SiH^*}$ and X_c as a function of the discharge power at SC of 4%.

The intensities of SiH*, H^*_α and H^*_β increase with the discharge power and the maximal values appear at 35 W. The intensities seem to be constant for the discharge power higher than 35 W. The intensity ratio of $I_{H^*_\alpha}/I_{SiH^*}$ affects the structure of the growing film.[9,10] To investigate the relation between $I_{H^*_\alpha}/I_{SiH^*}$ and the structure of films, Raman spectroscopy was used to study the films. The variation of $I_{H^*_\alpha}/I_{SiH^*}$ and crystalline volume fraction evaluated from Raman spectra as a function of the discharge power is shown in Fig.2(b). When the discharge power increases from 10 W to 35 W, $I_{H^*_\alpha}/I_{SiH^*}$ is enhanced from 0.32 to 0.48 and X_c is enhanced from 32% to the maximal value of 66%. At 45 W, $I_{H^*_\alpha}/I_{SiH^*}$ is 0.49 and

X_c is reduced to 62%.

Figure 3 shows the variation of SiH*, H^*_α, H^*_β intensities and $I_{H^*_\alpha}/I_{SiH^*}$ as a function of the discharge power at SC of 6%. The OES intensities increase with the discharge power monotonously and no trend to be constant appear. $I_{H^*_\alpha}/I_{SiH^*}$ shows the similar change as the OES intensities.

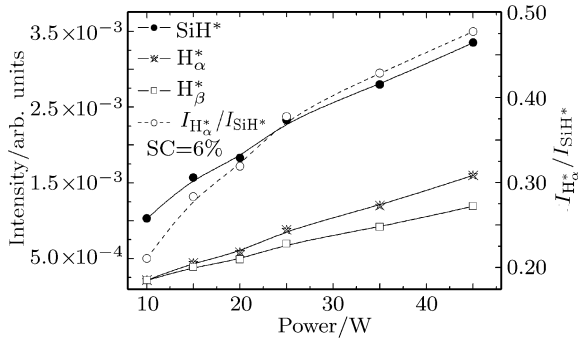


Fig.3. OES intensity and $I_{H^*_\alpha}/I_{SiH^*}$ as a function of the discharge power at SC of 6%.

The dissociation rate of SiH_4 increases with the discharge power, which leads to an enhancement of OES intensities. At SC of 4%, the dissociation rate is stable at the high discharge power and OES intensities tend to be constant with the increase of discharge power in the range of 10 W to 45 W. But increasing SC to 6% will need higher power to obtain the trend. H^*_α and SiH* are the excited states of atomic hydrogen and SiH, so $I_{H^*_\alpha}/I_{SiH^*}$ provides the information for the corresponding ratio of atomic hydrogen to film precursors. The atomic hydrogen density increases with the discharge power and the atomic hydrogen can etch weak Si–Si bonds to form strong Si–Si bonds (crystalline mode),[11] so $I_{H^*_\alpha}/I_{SiH^*}$ and X_c increases with the discharge power. When the discharge power is increased to 35 W at SC of 4%, the etching rate of the atomic hydrogen and the growing rate of films are nearly equal. For the discharge power higher than 35 W $I_{H^*_\alpha}/I_{SiH^*}$ increases continually and the etching is dominant, but microcrystalline silicon is hard to be etched. So X_c tends to be constant in general although $I_{H^*_\alpha}/I_{SiH^*}$ increased to 0.49.

3.2. Effect of silane concentration

Figure 4(a) shows the effect of SC on OES intensities at the discharge power of 20 W. The SiH* intensity increases monotonically with SC. The intensities of H^*_α and H^*_β increase when SC is increased from 2% to 4%. For SC higher than 4% the intensities of H^*_α and H^*_β decrease a little and are constant in general. The correlation between $I_{H^*_\alpha}/I_{SiH^*}$ and X_c is shown in Fig.4(b). Both $I_{H^*_\alpha}/I_{SiH^*}$ and X_c are reduced with the increase of SC from 2% to 8%. $I_{H^*_\alpha}/I_{SiH^*}$ is 0.49 and X_c is 74% at SC of 2%. After SC enhanced to 6% $I_{H^*_\alpha}/I_{SiH^*}$ is 0.32 and X_c is 39% which that suggests that the film is still microcrystalline. Continually increasing SC to 7%, $I_{H^*_\alpha}/I_{SiH^*}$ is reduced to 0.29 and X_c is zero which means that the film is amorphous.

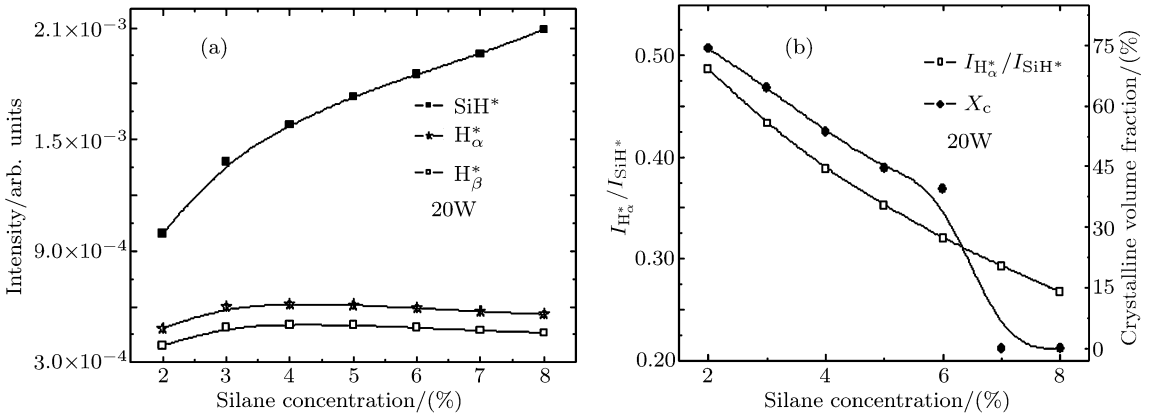


Fig.4. (a) OES intensity of SiH*, H^*_α and H^*_β versus the silane concentration at the discharge power of 20 W. (b) $I_{H^*_\alpha}/I_{SiH^*}$ and X_c versus the silane concentration at the discharge power of 20 W.

Decreasing the power leads to a reduction of the dissociation rate of the reactive gas which will decrease the OES intensities. At the discharge power of 10 W, the OES intensities are lower than that at 20 W (Fig.5). The $I_{H^*_\alpha}/I_{SiH^*}$ at 10 W is also lower than that at 20 W. At SC of 2%, $I_{H^*_\alpha}/I_{SiH^*}$ is only 0.42. When SC is increased to 3%, $I_{H^*_\alpha}/I_{SiH^*}$ is 0.31. At SC of 4%, $I_{H^*_\alpha}/I_{SiH^*}$ has been reduced to 0.27. There are two ranges for the variation of OES intensities: when SC is enhanced from 2% to 4%, the SiH*

intensity increases quickly and the intensities of H^*_α and H^*_β increase slowly; when SC is higher than 4%, the SiH^* intensity increases slowly and the intensities of H^*_α and H^*_β decrease for SC higher than 4%.

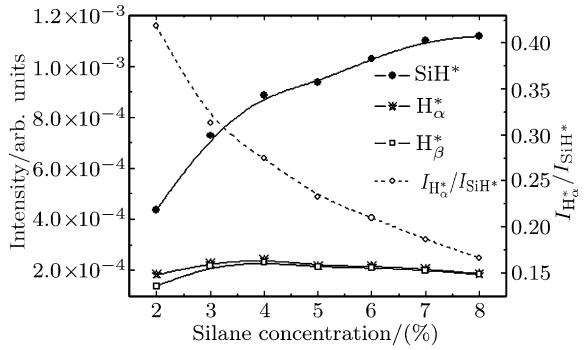


Fig.5. OES intensity and $I_{H^*_\alpha}/I_{SiH^*}$ as a function of the silane concentration at the discharge power of 10 W.

It has been known that increasing SC will induce a structural transition from microcrystalline to amorphous.[12] At high SC, the atomic hydrogen density is reduced for the annihilation reaction between the atomic hydrogen and SiH_4 which reflected in this paper as the low value of $I_{H^*_\alpha}/I_{SiH^*}$. High discharge power is favourable for the growth of microcrystalline silicon films.[13] The depletion of SiH_4 is easier to be obtained at high discharge power. Increasing the discharge power shifts the structural transition to low SC. So for SC increasing from 6% to7% at 20 W $I_{H^*_\alpha}/I_{SiH^*}$ is reduced from 0.32 to 0.29 and a structural transition takes place. Whereas when SC is enhanced from 3% to 4% at 10 W, $I_{H^*_\alpha}/I_{SiH^*}$ is reduced from 0.31 to 0.27 which suggests that the structural transition takes place at the nearby low SC.

3.3. Effect of substrate temperature

The variation of OES intensities as a function of the substrate temperature is shown in Fig.6(a).

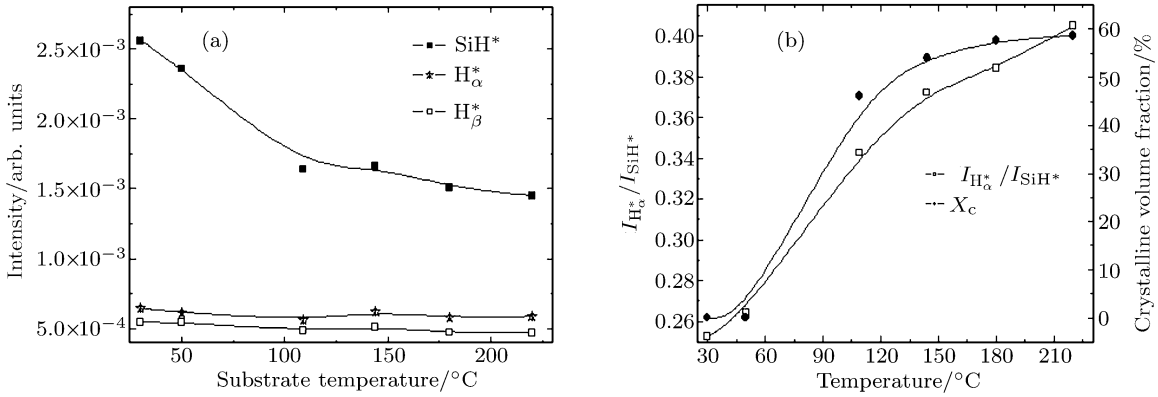


Fig.6. (a) OES intensity of SiH^*, H^*_α and H^*_β at different substrate temperatures. (b) $I_{H^*_\alpha}/I_{SiH^*}$ and X_c at different substrate temperatures.

The SiH^* intensity decreases with the substrate temperature, while the intensities of H^*_α and H^*_β are nearly unchanged. As a result, the intensity ratio of $I_{H^*_\alpha}/I_{SiH^*}$ is enhanced with the increase of the substrate temperature. Figure 6(b) shows the correlation between $I_{H^*_\alpha}/I_{SiH^*}$ and X_c at different substrate temperatures. The film is amorphous and $I_{H^*_\alpha}/I_{SiH^*}$ is low for the substrate temperature lower than 110 °C. X_c increases form 0.34 to 0.4 and $I_{H^*_\alpha}/I_{SiH^*}$ increases from 46% to 59% when the substrate temperature increases from 110 °C to 220 °C. Furthermore, the deposition rate increases from 4.2 Å/S to 6.5 Å/S although the SiH^* intensity decreases and the H^*_α and H^*_β intensities are constant.[14]

Because the pressure is fixed, the increase of substrate temperature leads to a reduction of the gas molecules' density, which causes a decrease of OES intensities. Although the gas molecules' density is reduced at the high temperature, the activity of film precursors is enhanced. Therefore the deposition rate increases with the substrate temperature. At low substrate temperature, $I_{H^*_\alpha}/I_{SiH^*}$ is low and the low atomic hydrogen density results in a low etching rate of amorphous phase, thus the growth of microcrystal is limited at low substrate temperature. Increasing the substrate temperature leads to the enhancement of $I_{H^*_\alpha}/I_{SiH^*}$ and the atomic hydrogen density. The atomic hydrogen etches the amorphous phase to form

microcrystalline phase.

4. Conclusion

The deposition process of microcrystalline silicon with VHF-PECVD was studied by the OES analysis. At SC of 4%, the OES intensities increase with the discharge power and tend to be constant for power higher than 35 W. At SC of 6%, the intensities also increase with the discharge power but they have not shown a trend to be constant. At the discharge power of 20 W, the SiH^* intensity increases with SC, while the intensities of H^*_α and H^*_β increase with SC first and then decrease slowly for SC higher than 4%. At the discharge power of 10 W, the SiH^* intensity increases quickly with SC and then the increasing rate is reduced to a stable value for SC higher than 4%, the intensities of H^*_α and H^*_β also increase with SC and then are nearly equal for SC higher than 4%. With the increase of the substrate temperature the SiH^* intensity decreases while the intensities of H^*_α and H^*_β are constant. The OES intensity ratio ($I_{H^*_\alpha}/I_{SiH^*}$) shows an effect on X_c. X_c increases with the increase of $I_{H^*_\alpha}/I_{SiH^*}$ when the discharge power, silane concentration and substrate temperature are changed.

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