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Influence of the deposition parameters on the transition region of hydrogenated silicon films growth*

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Hydrogenated microcrystalline and amorphous silicon thin films were prepared by very high frequency plasma-enhanced chemical vapour deposition (VHF PECVD) by using a mixture of silane and hydrogen as source gas. The influence of deposition parameters on the transition region of hydrogenated silicon films growth was investigated by varying the silane concentration (SC), plasma power (P_w), working pressure (P), and substrate temperature (T_s). Results suggest that SC and T_s are the most critical factors that affect the film structure transition from microcrystalline to amorphous phase. A narrow region in the range of SC and T_s, in which the rapid phase transition takes place, was identified. It was found that at lower P or higher P_w, the transition region is shifted to larger SC. In addition, the dark conductivity and photoconductivity decrease with SC and show sharp changes in the transition region. It proposed that the transition process and the transition region are determined by the competition between the etching effect of atomic hydrogen and the growth of amorphous phase.

Keywords: microcrystalline silicon, amorphous silicon, transition region, VHF PECVD
PACC: 8115G, 8155H, 6855

1. Introduction

Microcrystalline silicon (μc-Si:H) thin films are of great interest for their potential applications in large-area thin film devices, such as solar cells,[1] thin film transistors,[2] and sensors.[3] Several deposition techniques have been developed to prepare μc-Si:H thin films, e.g., radio-frequency plasma-enhanced chemical vapour deposition (RF PECVD),[4,5] VHF PECVD,[6] hot wire chemical vapour deposition (HWCVD),[7,8] electron cyclotron resonance plasma chemical vapour deposition (ECR-CVD),[9] and radio-frequency magnetron sputtering.[10] Among these techniques, VHF PECVD appears to be an optimal deposition method for its high deposition rate in preparation of high quality films.[11,12]

Microcrystalline silicon thin films used as absorber layers in solar cells have showed significant advantages.[13,14] Compared with amorphous silicon (a-Si:H) solar cells, μc-Si:H solar cells are more stable against the light induced degradation.[15] In addition, the absorption coefficient of μc-Si:H is much larger than that of a-Si:H in the infrared spectral region. So, a μc-Si:H solar cell can be combined with a a-Si:H cell to form the so-called "micromorph" tandem solar cells, which have appeared to be very efficient and stable.[16]

Studies indicated that the optimum μc-Si:H used for solar cells is not obtained with the largest grain size and the highest crystalline content.[17] In fact, μc-Si:H solar cells with their i-layers prepared near the transition region showed the best cell performance.[14] Thus, the transition films from microcrystalline to amorphous silicon attract considerable attention.[18−20] It was reported that the deposition parameters, such as the substrate temperature, hydrogen dilution,[21] and the plasma power,[22] could influence the transition process. Some properties of films prepared under the

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deposition conditions near the transition region were also studied.[23,24] However, to the best of our knowledge, there was little information about the combinatorial effects of the deposition parameters studied by VHF PECVD. Particularly, the mechanism about the transition process was scarcely concerned, although three growth models for μc-Si:H, i.e. the "surface diffusion model", "etching model" and "chemical annealing model",[25] were proposed.

In this paper, the influence of deposition parameters on the transition from μc-Si:H to a-Si:H growth was studied. Series of samples were deposited under a variation of SC, T_s, P, and P_w. The changes in the structural properties, which indicate the transition from highly crystalline to amorphous growth, were investigated by Raman scattering and x-ray diffraction measurements. Electrical properties have been analysed by the dark conductivity and photoconductivity measurements.

2. Experiment

Intrinsic Si:H films were prepared on 2 cm× 10 cm glass substrates by VHF PECVD at 60MHz frequency in an ultra-high vacuum deposition chamber. The distance between the cathode and the anode was fixed at 2.0 cm. A mixture of silane (SiH_4) and hydrogen (H_2) with a total flow rate of 60 sccm (standard cubic centimeter per minute) was used as the source gas. Series of samples have been prepared by changing deposition parameters and the detailed deposition conditions are listed in Table 1.

Table 1. Si:H films deposition conditions.

Series number	SC/%	T_s/°C	Pressure/Pa	Power/W
1	1–7	170	120	20
2	4	110–260	120	20
3	4	200	60–180	20
4	1–7	170	50	20
5	4	170	120	15–35

The thickness of the films was measured by optical transmission spectra, and all of the samples have a similar thickness of about 1000 nm. Raman scattering and x-ray diffraction (XRD) measurements were used to investigate the structural properties of the samples. The dark conductivity (σ_d) and photoconductivity (σ_{ph}) were measured with a Keithley 617 electrometer at room temperature in a coplanar electrode configuration, with σ_{ph} determined under the white light (100mW/cm^2).

3. Results and discussion

3.1. Structural properties

Figure 1 shows the Raman spectra of films deposited at various SC under the condition of T_s=170°C, P_w=20W, and P=120Pa (series 1). The transition from microcrystalline to amorphous growth induced by increasing SC is clearly shown in the figure. In a Raman spectrum, the peak at about 520cm^{-1} is due to the transverse optic (TO) mode of crystalline silicon. The peak at about 510cm^{-1} is attributed to the crystallites with diameters less than 10nm or a silicon Wurzite phase[26,27] and can also be included in the crystalline fraction. The broad band centred at about 480 cm^{-1} is attributed to the amorphous silicon phase. For samples deposited at SC values below 4%, each Raman spectrum reveals a predominant peak at about 520 cm^{-1}, which corresponds to the microcrystalline phase. When SC increases, the peak at about 520 cm^{-1} decreases. When SC increases to 4%, both amorphous (480 cm^{-1}) and crystalline phase (520 cm^{-1}) are observed. When SC increases to 7%, the material is predominantly amorphous. This phenomenon demonstrates the shift of μc-Si:H to a-Si:H growth. An abrupt change in the structure, which indicates the abrupt transition from microcrystalline to amorphous growth, is observed in the SC range between 4% and 5%. This analysis is confirmed by the XRD measurements performed. Figure 2 illustrates the structural analysis made by XRD measurements. A continuously increasing amorphous phase with increasing SC can be observed obviously. In the spectra for samples deposited at SC $<$ 4%, diffraction peaks corresponding to the (111), (220) and (311) planes appear with a preferential orientation of (111). The intensities of these peaks decrease as SC increases, which suggests the decrease of microcrystalline phase and the increase of amorphous phase. For samples prepared at SC $>$ 4%, the XRD spectra show the amorphous phase. In addition, the average grain size of Si (111), determined by using the Debye–Sherrer formula, decreases with the increase of SC. The growth transition in the SC regime between 4% and 5% is also clearly observed in these XRD spectra. The results are in good agreement with the Raman spectra.

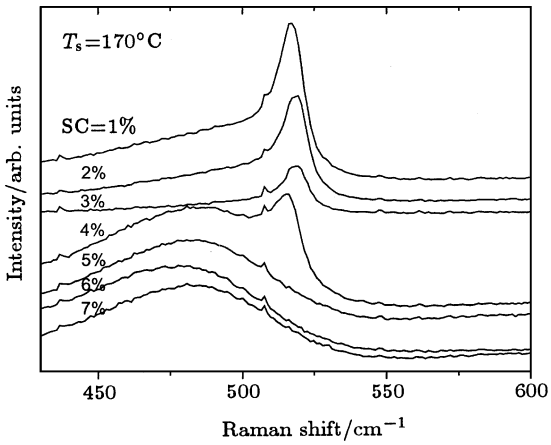


Fig.1. Raman spectra of silicon films deposited at various silane concentration.

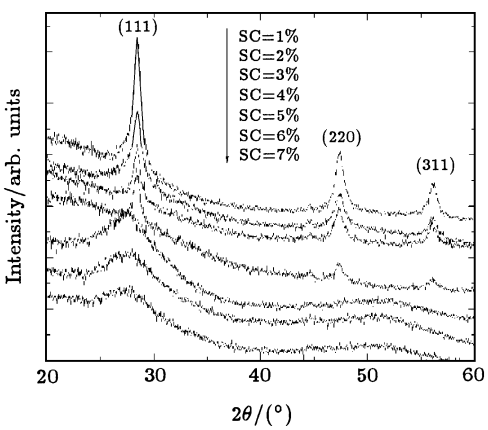


Fig.2. XRD patterns of silicon films deposited at various silane concentration.

The substrate temperature is found to be another critical deposition parameter to determine the transition from μc-Si:H to a-Si:H growth in our experiments. To determine the dependence of the growth on the substrate temperature, a series of experiments were performed at a plasma power P_w of 20W, P=120Pa, and SC=4% (series 2). Raman scattering measurements have been applied to obtain evidence on the structural changes of the films. Figure 3 shows the Raman spectra of the films deposited. An increase of microcrystalline phase can be observed as T_s increases from 110°C to 260°C. The film prepared at 110°C shows mainly a broad band centred at 480 cm^{-1}, which is the characteristic of TO mode of a-Si:H. For films deposited at T_s higher than 170°C, only a sharp peak at about 520 cm^{-1} is observed, which represents that the films are mainly microcrystalline. For the film prepared at 140°C, both a small peak at about 520 cm^{-1} and a broad band centred at 480 cm^{-1} are observed. From the figure, the abrupt transition from microcrystalline to amorphous silicon growth taking place in the range of 170 °C–110°C is observed.

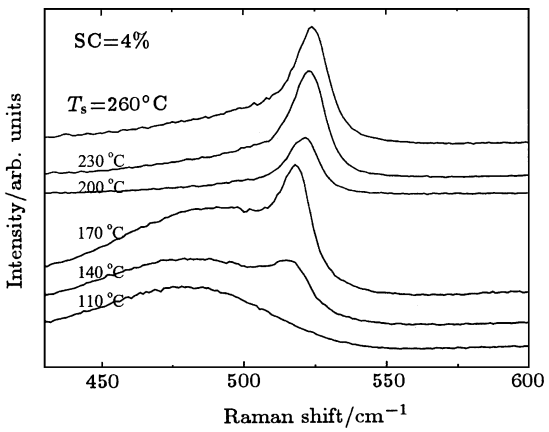


Fig.3. Raman spectra of silicon films deposited at various substrate temperature.

The influence of the working pressure on the transition from microcrystalline to amorphous silicon growth was also investigated. Figure 4 shows the Raman spectra of films prepared at P ranging from 60Pa to 180Pa with SC=4%, T_s=200°C and P_w=20 W (series 3). A sharp peak at about 520 cm^{-1} for each sample of this series is observed. The transition from microcrystalline to amorphous phase cannot be clearly identified from these Raman spectra. However, as the working pressure increases, the intensity of the crystalline peak decreases, which indicates the increase of amorphous phase with the increase of P. It was reported that the density of the low-energy hydrogen ion impinging on the substrate increases with the decrease of pressure.[28] This effect may result in the more microcrystalline phase growth at lower pressure. For further understanding the influence of the pressure, structural properties of two series of samples deposited with various SC at 120Pa and 50Pa were compared. Figure 5 shows some of the Raman spectra of samples deposited at 50Pa, with T_s=170°C, and P_w=20W (series 4). The Raman spectra of samples deposited at 120Pa are shown in Fig.1. The influence of the working pressure on the transition region is observed: under high-pressure condition (P=120Pa), the transition starts at 4% of SC (Fig.1); while under low-pressure condition (P=50Pa), the transition starts at 6% of SC (Fig.5). The result suggests that the transition region is shifted to larger SC at lower pressure.

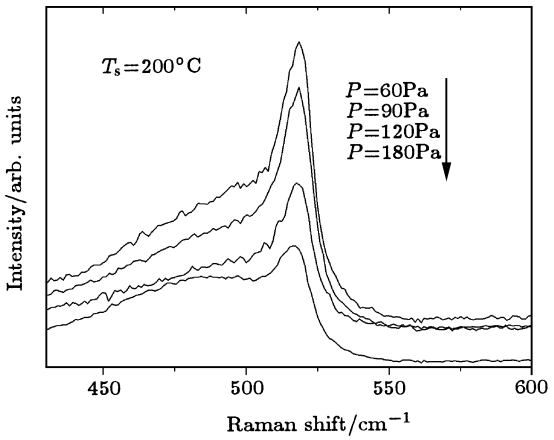


Fig.4. Raman spectra of silicon films deposited at various working pressure.

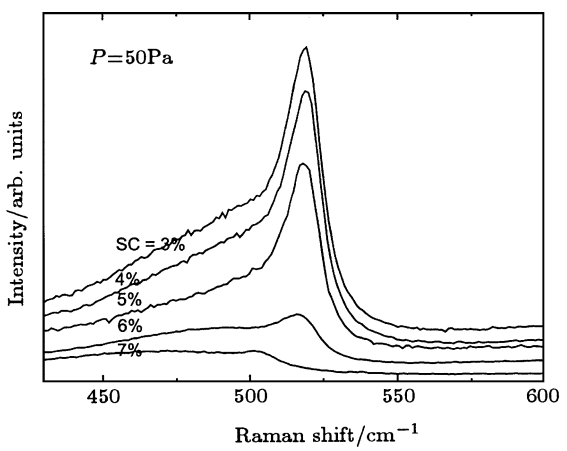


Fig.5. Raman spectra of silicon films deposited with various silane concentration at 50Pa.

In order to investigate the influence of the power, we deposited Si:H films with P_w ranging from 15W to 35W (series 5). Figure 6 shows the Raman spectra of these samples. In the range of the power studied, purely amorphous phase was not observed; each of the spectra shows a peak at 520 cm^{-1}, which indicates that these films are mainly microcrystalline. The transition region cannot be clearly identified. However, when P_w increases, the intensity of the crystalline peak increases, which indicates that the transition region will be shifted to larger SC if higher P_w is applied. We give our explanation as following: increases of P_w results in an increase of atomic hydrogen amount as well as the enhancement of SiH_4 decomposition. However, in the parameter range of study, while the decomposition of hydrogen is not saturated, most of the SiH_4 has been decomposed. Therefore, increases of power will result in an increase of the ratio of atomic hydrogen to film precursors, which leads to the more microcrystalline phase in the films. So, at higher P_w, larger SC is needed to obtain the transition films, i.e. the transition region will be shifted to larger SC.

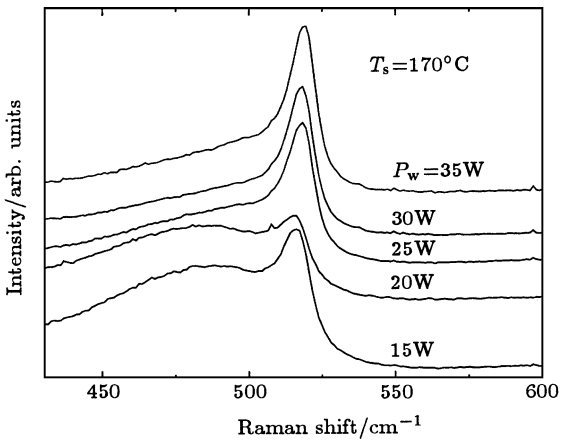


Fig.6. Raman spectra of silicon films deposited at various plasma power.

Based on the "surface diffusion model" and the "etching model" for the growth mechanism of Si:H films,[25] and our experimental results discussed above, we propose that the transition process and the transition region are determined by the competition between the etching effect and the growth of amorphous phase. Samples of series 1, which were deposited with various SC, were chosen for the discussion. In the whole regime of SC, the amount of atomic hydrogen from the plasma decreases with the increase of SC, which leads to a decrease of surface coverage by the bonded hydrogen and also a decrease of the local heating by hydrogen-recombination reactions on the growth surface.[25] Hence, the surface diffusion length of the film precursors (e.g. SiH_3) decreases. In addition, the amount of the film precursors increases with the increase of SC. In result, when SC increases, more and more film precursors have no time to find the stable sites and they quickly bond with the dangling bonds in the growing surface, which leads to the increase of amorphous phase. Furthermore, atomic hydrogen has an effect to break the weak Si–Si bonds in the amorphous network and remove the weakly bonded Si atom.[25] This effect is also weakened with the increase of SC, which results in more amorphous phase in the films. The increase of the amorphous phase with SC discussed above can be considered as the decrease of the etching effect and the enhancement of the growth of amorphous phase. In general, the film structure changes from microcrystalline to amorphous phase on continues increase of SC. In particular, a significantly sharp phase transformation happens to take

place at 4% < SC < 5%.

A question is that why the microcrystalline phase decreases abruptly in the narrow transition region. Why does not the transition process take place gradually in a broader range? We suggest that the change of the competition is non-linear in the whole SC range, which results in the transition region. Figure 7 is a schematic diagram to describe the transition process. The range of SC is divided into three regions. In the first region (SC < 4%), along with the increase of SC, the ratio of atomic hydrogen to film precursors decreases, which leads to the decrease of etching effect and the enhancement of amorphous phase growth. However, the change in the competition is relatively small and the samples deposited in this region have large crystallinities and are predominately microcrystalline. This region is named as the microcrystalline growth region. When SC increases to a certain threshold value (~4%), the ratio of atomic hydrogen to film precursors and the μc-Si:H nucleation, which is triggered in presence of atomic H in the plasma,[29] reaches to a critical point. Thus, along with the increase of SC in the range of 4% < SC < 5%, the etching effect of atomic hydrogen decreases while the growth of a-Si:H increases remarkably. The network of the films deposited in this region is in an intermediate state composed of a random of microcrystals, voids and amorphous tissues, which can be easily perturbed by changing the dose of atomic H treatment.[30] This narrow region is named as the transition region. After SC exceeds another threshold value (5%), although the competition changes further with the increase of SC, the change is much less than that in the transition region. The films deposited are predominantly amorphous. This region is named as the amorphous growth region. The effects of other deposition parameters, such as T_s, P_w, and P, can be explained by the similar analysis. The individual effect of each parameter on the ratio of atomic hydrogen to film precursors and the transition process is influenced by each other.

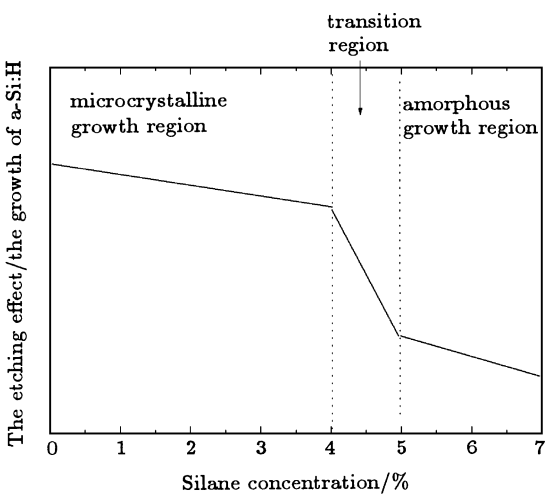


Fig.7. Schematic diagram of the deposition processes with various SC. From the left to right, films change from microcrystalline phase to amorphous phase. The slope of the line represents the competition between the etching effect of atomic hydrogen and the growth of amorphous phase.

3.2. Electrical properties

In order to investigate the electrical properties of the Si:H films prepared near the transition region, σ_d and σ_{ph} of samples deposited with various SC were characterized. Samples of series 1 were selected in our study. Figure 8 shows the behaviour of σ_d and σ_{ph} as a function of SC. Two zones can be observed in this figure. In the first zone, both σ_d and σ_{ph} decrease remarkably as SC increases from 1% to 5%. The second zone is identified for SC > 5%, where either σ_d or σ_{ph} is much smaller than that in the first zone and shows a weaker dependence on SC. The behaviour of the electrical properties in the second zone indicates that the content of the microcrystalline phase is very small. In the transition region, i.e. in the range of SC ranging from 4% to 5%, both σ_d and σ_{ph} show abrupt changes, along with the decrease of σ_d from 1.01 $\times 10^{-6}$S·cm^{-1} to 4.34 $\times$ 10^{-9}S·cm^{-1} and the decrease of σ_{ph} from 4.57 $\times$ 10^{-4}S·cm^{-1} to 6.41 $\times$ 10^{-5}S·cm^{-1}. The sample deposited near the transition region, i.e. the film deposited at SC=4%, has a photosensitivity (σ_{ph} /σ_d) of 452 and is suitable for the μc-Si:H solar cell as the absorption layer. We suggest that the change of σ_{ph} and σ_d are due to the change of the carrier mobility and/or the carrier density caused by the structural transition. In the transition region, along with the transition from μc-Si:H to a-Si:H growth, the carrier mobility as well as the carrier density changes abruptly, which leads to the abrupt change of σ_d and σ_{ph}.

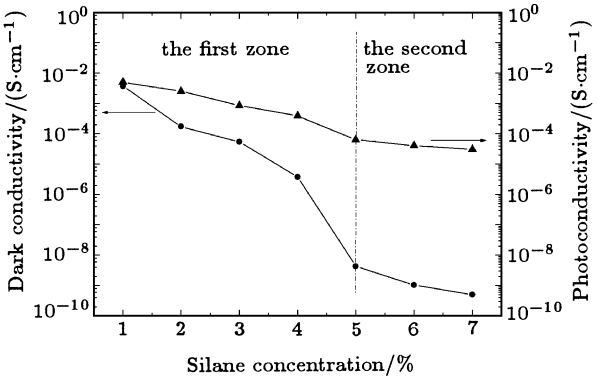


Fig.8. Dark conductivity and photoconductivity as a function of silane concentration.

4. Conclusion

Si:H films were prepared by VHF PECVD to study the transition from microcrystalline to amorphous growth. The structural and electrical properties of the samples were characterized. Results suggest that SC and T_s are the most critical deposition parameters which affect the transition process. A narrow region, in which the transition growth takes place, was observed in the range of SC and T_s. It was found that the transition region is influenced by P and P_w. At lower P or higher P_w, the transition region is shifted to larger SC. We suggest that the transition process is determined by the competition between the etching effect of atomic hydrogen and the growth of amorphous phase. The change in the competition is non-linear in the whole range of SC and T_s. In the transition region, the competition changes remarkably; while outside of the region, the change is much less obvious.

Also, we observed that the dark conductivity and photoconductivity decrease with SC and show sharp changes in the transition region.

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