Research Article

Grown Low-Temperature Microcrystalline Silicon Thin Film by VHF PECVD for Thin Films Solar Cell

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Hydrogenated microcrystalline silicon thin films can be used to fabricate stable thin film solar cell, which were deposited by very high frequency plasma-enhanced chemical vapor deposition at low temperatures ($\sim 200^\circ\text{C}$). It has been found that the obtained film presented excellent structural and electrical properties, such as high growth rate and good crystallinity. With the decreasing of silane concentration, the optical gap and the dark conductivity increased, whereas the activation energy decreased. A reasonable explanation was presented to elucidate these phenomena. In addition, we fabricated p-i-n structure solar cells using the optimum microcrystalline silicon thin films, and preliminary efficiency of 4.6% was obtained for $1\ \mu\text{m}$ thick microcrystalline silicon thin film solar cells with open-circuits voltage of 0.773 V and short-circuits current density of $12.28\ \text{mA}/\text{cm}^2$. Future scope for performance improvement lies mainly in further increasing the short-circuit current.

1. Introduction

Hydrogenated microcrystalline silicon ($\mu\text{c-Si:H}$) is an interesting material as an absorber layer for solar cells. The low absorption coefficient for light with $k > 700\ \text{nm}$ ($\alpha = 10^2 - 10^3\ \text{cm}^{-1}$) of this material requires thick layers ($1 - 3\ \mu\text{m}$) to collect the radiation efficiently [1]. Therefore, high deposition rates are necessary to make this material a good candidate for industrial production [2]. In this regard, many studies based on plasma-enhanced chemical vapor deposition (PECVD) have been made to improve the growth rate and the film quality, especially for the crystallinity [3, 4]. The very high frequency (VHF) PECVD technique is one of the most acceptable approaches to grow device quality $\mu\text{c-Si}$ thin films within a short fabrication time, owing to efficient gas dissociation and lower ion energy than radio frequency (RF) plasma [5, 6]. The thin film solar cells with high efficiencies have already been made using this technique [7, 8]. However, the optimization of the devices requires a deeper investigation of the material properties in different excitation frequency.

In our previous work, we reported that the $\mu\text{c-Si:H}$ thin films could be deposited with the optimum crystallization at 250°C at the rate of $\sim 3.54\ \text{nm}/\text{min}$ by using RF-PECVD of

SiH_4 diluted with Ar and H_2 [9]. Thus, the enhancement of the growth rate without degrading crystallinity is one of the major challenges.

In this study, we focused our research on the application of 81.3 MHz VHF PECVD to improve the material properties. The effects of experimental parameters on microstructure and optoelectronic properties of the intrinsic $\mu\text{c-Si:H}$ thin films were studied. And the results on preliminary $\mu\text{c-Si:H}$ thin film solar cells were also presented.

2. Experimental

The $\mu\text{c-Si:H}$ thin films were deposited on c-Si and glass substrate in a capacitively coupled parallel plate reactor using a plasma excitation frequency of 81.36 MHz. The electrode configuration consists of a 15 cm diameter powered electrode and a $14 \times 10\ \text{cm}$ substrate carrier support as the grounded electrode. The electrode distance is constant with 4 cm.

The effect of the silane concentration on the microcrystalline silicon films has been studied by varying the silane concentration ($R = [\text{SiH}_4]/([\text{SiH}_4] + [\text{H}_2])$) from 4 to 13%. For all samples the deposition temperature and total pressure were kept constant at 200°C and 0.45 Torr, respectively. The

FIGURE 1: Schematic view of $\mu\text{c-Si:H}$ thin film solar cell.

input VHF-power density was modulated to an appropriate value as 0.64 W/cm^2 for the $\mu\text{c-Si:H}$ thin films.

The microstructures of the samples were characterized by Raman spectroscopy and X-ray diffraction (XRD). Raman signals were detected by a Jobin Yvon Horiba HR800 spectrometer with an excitation light source of wavelength of 532 nm. The XRD measurements were performed on a Rigaku D/Max-III C X-ray diffractometer in a standard θ - 2θ configuration using Cu $K\alpha$ radiation (0.15406 nm). The optical properties of the thin films were measured at room temperature over a wavelength range of 400–2500 nm using an ultraviolet-visible-near-infrared spectrophotometer (Shimadzu UV-3600). The dark conductivity was measured using a Keithley 6517A electrometer with coplanar configuration by vacuum evaporation Al electrodes on the films.

The p-i-n structure of $\mu\text{c-Si:H}$ thin film solar cells consisted of a 50 nm thick p-type layer, a $1 \mu\text{m}$ thick intrinsic layer, and a 100 nm thick n-type layer. The schematic structure view of the $\mu\text{c-Si:H}$ thin film solar cell was shown in Figure 1. The I - V characteristics of the solar cells, that is, power conversion efficiency, open-circuit voltage (V_{oc}), fill factor (FF), and short-circuit current density (J_{sc}), were measured under AM1.5 illumination at 25°C .

3. Results and Discussion

3.1. Intrinsic $\mu\text{c-Si:H}$ Thin Film

3.1.1. Microstructures and Morphologies. Figure 2 showed the growth rate of the $\mu\text{c-Si:H}$ thin films as a function of the silane concentration at different plasma frequency. In all cases, it could be found that the growth rate decreases with the decreasing of the silane concentration. In addition, the growth rate increased significantly as the plasma excitation frequency increased from 13.56 to 81.3 MHz by a factor of about 3, owing to efficient gas dissociation.

Figure 3 demonstrated XRD patterns of the $\mu\text{c-Si:H}$ thin films deposited at various silane concentrations. The absence of any characteristic peak for thin film deposited at the silane concentration of 13% suggested that the structure of the film was mostly amorphous. The peaks located at about 28.38° , 47.38° , and 55.98° can be seen for the samples at silane concentration lower than 13%, corresponding to the diffractions from Si(111), Si(220), and Si(311) planes, respectively.

FIGURE 2: Growth rate as a function of silane concentration for the $\mu\text{c-Si:H}$ thin films.

FIGURE 3: XRD patterns of the $\mu\text{c-Si:H}$ thin films deposited at silane concentration from 4 to 13%.

Also, it can be found that the peak intensity increased and the full width at half maximum reduced with decreasing the silane concentration, indicating an enhancement in the film crystallinity [10]. The average grain size was calculated by Debye-Scherrer formula from the width of (111) peak and the obtained data were summarized in Table 1. It was shown that the grain size increased from 11.4 to 45.6 nm with decreasing the silane concentration from 13 to 4%. It is reported that hydrogen is supposed to enhance the surface diffusion of adsorbed precursors, preferentially etch off the disordered phase, and assist Si-Si bonding reconstruction within a subsurface layer [11, 12]. As expected, H_2 dilution is a very sensitive method to realize crystallization of the amorphous Si thin films.

Micro-Raman spectra of the $\mu\text{c-Si:H}$ thin films deposited at various silane concentrations were shown in Figure 4. The Raman spectra can be decomposed into three Gaussian photon bands: transverse optical mode at 520 cm^{-1} from crystalline Si, band at 510 cm^{-1} from grain boundaries, and

TABLE 1: The results of Raman and XRD analysis for the $\mu\text{c-Si:H}$ thin films deposited at various silane concentrations. $d_{\text{X-ray}}$ is the grain size; X_c is the crystalline volume fraction.

R (%)	13	9	6	5	4
$d_{\text{X-ray}}$ (nm)	0	11.4	21.6	32.3	45.6
X_c (%)	12.4	35.5	59.4	61.5	74.1

FIGURE 4: Raman spectra of the $\mu\text{c-Si:H}$ thin films deposited at silane concentration from 4 to 13%. Inset is experimental and Gaussian fitted Raman spectra of $\mu\text{c-Si:H}$ thin films deposited at the silane concentration of 9%.

band at 480 cm^{-1} from the amorphous phases. Accordingly, the crystalline volume fraction X_c can be determined by $X_c = (I_{510} + I_{520}) / (I_{480} + I_{510} + I_{520})$, where I_{520} , I_{510} , and I_{480} represent integrated intensity of Gaussian peak near 520, 510, and 480 cm^{-1} , respectively [13, 14]. Both the contributions of amorphous and crystalline Si could be clearly observed for all samples. The inset of Figure 4 showed experimental and Gaussian fitted Raman spectra of the thin film deposited at the silane concentration of 9%. The results of Raman analyses were shown in Table 1. The calculated results of all thin films showed that the crystalline volume fraction increased from 12.4% to 74.1% with the silane concentration varying from 13 to 4%. These results were consistent with the XRD results.

3.1.2. Optical Band Gap and Absorption Spectra. The absorption spectra were measured by the spectrophotometer. It is well known that the optical band gap (E_g) is related with the absorption coefficient by the following equation:

$$(\alpha h\nu)^{1/\gamma} \sim (h\nu - E_g), \quad (1)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, and γ is a constant. In the electron approximation, $\gamma = 1/2$, $3/2$, and 2 for allowed direct transition, forbidden direct transition, and indirect transition, respectively. For the Si films $\gamma = 2$, and the optical band gap can be calculated from Tauc's formula, by the following equation:

$$(\alpha h\nu)^{1/2} = B(h\nu - E_g), \quad (2)$$

FIGURE 5: Absorption coefficient (α) and optical band gap of the $\mu\text{c-Si:H}$ thin films deposited at silane concentration from 4 to 13%.

FIGURE 6: Variation of the optical band gap (E_g) of the $\mu\text{c-Si:H}$ thin films deposited at silane concentration from 4 to 13%.

where B is a constant known as the edge width parameter. Thus, the optical band gap E_g of the $\mu\text{c-Si:H}$ thin films can be obtained using the extrapolation of $(\alpha h\nu)^{1/\gamma}$ versus $h\nu$ curve [15].

As is shown in Figure 5, the absorption coefficients and the optical band gaps of the $\mu\text{c-Si:H}$ thin films had a clear dependence on the silane concentration. The absorption coefficient decreased with the silane concentration decreasing, while the corresponding optical band gap E_g increases. Figure 6 displayed optical band gap as a function of the silane concentration, where E_g estimated from (2) shows a system widening. The optical band gap increased from 1.766 to 2.175 eV when the silane concentration decreases from 13 to 4%. The results were in accordance with other reports [16], and the increase of optical band gap is due to the increasing films crystalline. Therefore, only by adjusting the silane concentration, we can tailor the band gap between 1.7 and 2.1 eV, which can be used as an absorber layer for thin film solar cell.

FIGURE 7: Dark conductivity and activation energy of the $\mu\text{c-Si:H}$ thin films deposited at silane concentration from 4 to 13%.

3.1.3. Transport Properties. It is of significance to investigate the dependence of carriers transport behavior on the silane concentration. Figure 7 presented the dark conductivity and the activation energy of $\mu\text{c-Si:H}$ thin films deposited at various silane concentrations. It could be found that the dark conductivity increased with the decreasing of the silane concentration. The reason is that the defect state decreases as the crystallinity increases. And the dominant transport mechanism is the hopping conduction for the amorphous tissue [17]. The dark conductivity increased from 1.33×10^{-3} to $1.43 \times 10^{-10} \Omega^{-1} \cdot \text{cm}^{-1}$ as the silane concentration decreased from 13 to 4%, due to enhancement in the film crystallinity. The corresponding values of conductivity activation energy obtained from temperature-dependent conductivity results (Arrhenius plot) were also shown in Figure 7. The results indicated that the activation energy decreased from 0.725 to 0.29 eV as the silane concentration decreased from 13 to 4%, which is due to the fact that E_F was located near conduction band by defect states in the distorted network at the transition between crystallites and the surrounding amorphous matrix [18].

3.2. Solar Cells. It was reported that optimum solar cells were always found close to the transition from microcrystalline to amorphous growth, with a crystallinity of about 60% [19, 20]. From the analysis carried out on the intrinsic layer, we found that samples deposited at the silane concentration of 4% present a crystallinity of about 61.5%. Thus this material seems to be the most promising material to be used to fabricate solar cell. Figure 8 presented the current-voltage characteristic of $\mu\text{c-Si:H}$ thin film solar cell. The V_{oc} of 0.773 V and FF of 0.5 were obtained. However, the J_{sc} of 12.8 mA/cm^2 was low with respect to the values, which was reported in other papers [21, 22], leading to an efficiency value of 4.6%. As we know, the value of J_{sc} is affected by the degree of light utilization, and we can use light-trapping techniques to increase the performance of microcrystalline solar cells. Also the performance of solar cells can be improved by

FIGURE 8: The current-voltage characteristic of $\mu\text{c-Si:H}$ thin film solar cell.

designing the structure of solar cells. In the future, the $\mu\text{c-Si:H}$ thin film solar cells with higher efficiency can be fabricated by optimizing the deposition parameters and designing the structure of solar cells precisely.

4. Conclusions

The $\mu\text{c-Si:H}$ thin films had been grown by VHF PECVD under different deposition conditions. In particular, we investigated the effect of the silane concentration on the microstructures and optoelectronic properties. The obtained results exhibited that the optical band gap and the dark conductivity increased with the silane concentration decreasing, while the activation energy increased, as a result of the enhancement of the crystallinity and the decrease of the defect states. As we know, optimum solar cells are always found close to the transition from microcrystalline to amorphous growth. Therefore, we fabricated $\mu\text{c-Si:H}$ thin films solar cell using this intrinsic silicon, and the V_{oc} was 0.773 V, but the efficiency was only approximately 4.6%, and the J_{sc} is a rather low value. In the future we will fabricate higher efficiency solar cells by optimizing the deposition parameters and precisely designing the structure of solar cells.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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