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Hot-wire chemical vapor deposition and characterization of p-type nanocrystalline Si films for thin film photovoltaic applications

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ABSTRACT

P-type nanocrystalline Si (p-nc-Si) films were deposited by hot-wire chemical vapor deposition (HWCVD) system using SiH_4, B_2H_6, and H_2 as reactants. The effect of H_2 flow rate on the material properties of p-nc-Si films were investigated using Raman spectroscopy, X-ray diffractormeter, ultraviolet–visible-near infrared spectrophotometer, Fourier transform infrared spectroscopy, field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). Moreover, the electrical properties, such as carrier concentration, activation energy, dark conductivity, and Hall mobility, of p-nc-Si films were also measured. It was found that H_2 flow rate played an important role in forming of p-nc-Si, decreasing the deposition rate, and increasing the crystallinity of p-nc-Si films. FESEM and TEM micrographs also showed the enhancement of crystallinity with adding H_2 flow rate. Furthermore, the change of microstructure at various H_2 flow rates was found to affect the electrical properties of p-nc-Si films. Details of the growth mechanism in p-nc-Si films will be discussed also. Moreover, the optimum p-nc-Si film was used as window layer in n-type crystalline Si heterojunction (HJ) solar cell. After the deposition parameters were optimized, the Si HJ solar cell with the open-circuit voltage of 0.58 V, short-circuit current density of 33.46 mA/cm^2, fill factor of 64.44%, and the conversion efficiency of 12.5% could be obtained.

1. Introduction

The p-type Si (p-Si) films have attracted significant attention because of their potential use to produce low-cost and large-area electronic devices such as solar cells or thin-film transistors. For the application of window layer in solar cells, p-Si layers with good conductivity and low absorption are necessary. The p-type microcrystalline Si (p-μc-Si) films have advantages of relatively high conductivity, low activation energy, and low absorption compared to their amorphous counterpart. However, p-μc-Si films were found to produce worse cell performance due to lattice mismatch with intrinsic amorphous silicon in the case of p/i/n structure thin-film solar cells. The p-type nanocrystalline Si (p-nc-Si) films would be the alternative promising candidate as window layer because the lattice mismatch between p/i interface was expected to be less than p-μc-Si films. Moreover, as compared with p-type amorphous Si (p-a-Si) films, the p-nc-Si films possess less optical absorption and better electrical property which are suitable for photovoltaic device applications. Furthermore, the p-nc-Si films have better electronic stability than p-a-Si films because the amorphous structure of Si films suffers from the problem of Stabler-Wronski effect which leads to decrease the solar cell performance. It has been reported that the performance of solar cells can be improved using p-nc-Si films [1–3].

The growth of p-Si films is a key issue in the fabrication of Si based thin-film devices because the material and electrical properties of p-Si films play an important role in determining the device performance. The boron atoms are often used as the dopant source to deposit p-Si films. The in-situ doping process is an attractive subject because of its economic feasibility and without subsequent annealing process. Moreover, hot-wire chemical vapor deposition (HWCVD) has been receiving great interest due to its ability to deposit Si films with a high deposition rate than other techniques, such as plasma-enhanced chemical vapor deposition [4–8]. Over the past years, the deposition of Si based thin films using HWCVD has been studied extensively. The HWCVD system possesses high source gas utilization especially to generate reactive H atoms which are decomposed from H_2 gas [9,10]. During the HWCVD growth process, the reactive H atoms are easily to affect the growth mechanism and change the film properties. The reactive H radicals can effectively etch weak Si bonds from disordered or strained bonding sites in Si films, leading to a transition from an amorphous network to a crystalline network during film growth [11–13].

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In this study, p-nc-Si films were prepared by HWCVD system using SiH_4, B_2H_6, and H_2 as reactants. Raman spectroscopy, X-ray diffractometer (XRD), ultraviolet–visible-near infrared spectrophotometer, Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM) were used to investigate the effect of H_2 flow rate on the material properties of p-nc-Si films. Moreover, the electrical properties, such as carrier concentration, activation energy (E_a), dark conductivity (σ_d), and Hall mobility, of p-nc-Si films were also measured. Details of the growth mechanism in p-nc-Si films at various H_2 flow rates will be discussed. Furthermore, the optimum p-nc-Si film was applied to window layer in n-type crystalline Si (n-c-Si) heterojunction (HJ) solar cell. The solar cell characteristics were investigated also.

2. Experimental details

The p-nc-Si films were prepared using HWCVD system. Two parallel tungsten wires (diameter: 0.5 mm; length: 15 cm) were used as the catalyzers and set above the substrate at a distance of 48 mm. Before the deposition process, the chamber was pumped down to a base pressure of 2.67×10^{-4} Pa. The source gases were SiH_4, B_2H_6, and H_2 which were controlled by mass flow controllers in HWCVD system. During the p-nc-Si film deposition, the filament and substrate temperatures were kept at 1650 and 225 °C, respectively. The chamber was maintained at 10.67 Pa. The p-nc-Si films with a thickness of 550 nm were prepared at various H_2 flow rates. The detailed deposition parameters of p-nc-Si films were summarized in Table 1.

The deposition rate of p-nc-Si films was calculated from the film thickness measured by a surface profilometer (model: P-10, KLA-Tencor Inc.). The material properties of p-nc-Si films were measured using Raman spectroscopy (model: Nanofinder 30, Tokyo Instruments Inc.), XRD (model: MXP-III, Bruker Inc.), ultraviolet–visible-near infrared spectrophotometer (model: UV-3101PC, Shimadzu), and FTIR (model: DA8.3, Bomem Inc.). The XRD analyses were performed in a grazing-incidence configuration using a standard Cu Kα source (0.15405 nm). For the FTIR measurements, the detector was used to measure the infrared transmission in the wavenumber range from 40 to 4000 cm^{-1} with a resolution of 1 cm^{-1}. The surface morphology and cross-sectional structure of p-nc-Si films were analyzed by FESEM (model: JSM-6700F, JEOL Inc.) and TEM (model: JEM-1200EX, JEOL Inc.). The operating voltages of SEM and TEM were 3 kV and 200 kV, respectively. The TEM specimens were prepared by both mechanical thinning and ion milling processes. Two pieces of the samples were glued face-to-face with an epoxy adhesive (Epoxy Bond 110, Allied High Tech Products Inc.) and sandwiched between silicon sheets to obtain a cross-sectional structure. After thinning by mechanical disk grinder and polishing by diamond lapping film, the cross-sectional TEM specimen (thinning to about 100 μm thickness) was adhered to a supporting grid and then ion milled by precision ion polishing system (model:691, Gatan Inc.). During this thinning process, the ion milling was terminated until a very small perforation at the cross-sectional interface of specimen was obtained. The thickness around the perforation is lower than 100 nm where permitting of microstructure observation in TEM. The carrier concentration and Hall mobility of p-nc-Si films were measured by the van der Pauw–Hall measurement. For the measurement of σ_d, two coplanar strips of Al electrodes were deposited using thermal evaporation. A metal box, a hot plate and a picoampere meter were set to measure the σ_d. The E_a of σ_d was estimated from Arrhenius plot in the temperature ranged between 50 and 160 °C. Furthermore, the optimum p-nc-Si film was used as window layer in n-c-Si HJ solar cell. The solar cell characteristics such as short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and conversion efficiency (η) were measured at 100 mW/cm^2 (AM 1.5) using a solar simulator (model: class A 91160A, Newport-Oriel Instruments Inc.).

Table 1
Deposition parameters of p-nc-Si films by HWCVD.

Parameter	Value
Substrate temperature	225 (°C)
Filament temperature	1650 (°C)
Deposition pressure	10.67 (Pa)
Gas flow rate	
SiH_4	1 (sccm)
B_2H_6	5 (sccm)
H_2	0–150 (sccm)

3. Results and discussion

The deposition rates of p-nc-Si films as a function of H_2 flow rate was shown in Fig. 1. The deposition rate of p-nc-Si film with the H_2 flow rate equal to 0 sccm was 0.248 nm/s, and as the H_2 flow rate increased, a lower deposition rate was measured. The content of H atoms in mixture gases was increased with increasing the H_2 flow rate. Moreover, the H_2 was easily decomposed to reactive H atoms in HWCVD system. The growth of p-nc-Si films would be etched by the H atoms, and then, the deposition rate was decreased.

Fig. 2 shows the variation in Raman spectra of p-nc-Si films at various H_2 flow rates. The inset of Fig. 2 shows the Raman spectrum of p-nc-Si film prepared at H_2 flow rate of 150 sccm which was deconvoluted with three Gaussian peaks that were centered at 480 cm^{-1} (amorphous phase), 510 cm^{-1} (crystalline phase with a grain size smaller than 10 nm) and 520 cm^{-1} (crystalline phase with a grain size larger than 10 nm), respectively [14,15]. As could be seen from Fig. 2, the peaks in Raman spectra shifted from 480 to 520 cm^{-1} with increasing H_2 flow rate from 0 to 150 sccm. Moreover, the peak intensity at 520 cm^{-1} enhanced as the H_2 flow rate increased and possessed a wide region of peak at 480 cm^{-1}, suggesting the evolution of Si nanocrystalline phase embedded into the amorphous state with increasing H_2 flow rate.

The effect of H_2 flow rate on XRD patterns of p-nc-Si films was shown in Fig. 3. At the H_2 flow rate of 0 sccm, the diffraction pattern showed one weak peak at $2\theta = 28.4°$ which was corresponding to (111) plane of crystalline Si structure. The crystallinity of this film was very low and close to amorphous structure. With increasing H_2 flow rate from 25 to 150 sccm, three diffraction peaks at $2\theta = 28.4°$, 47.3° and 56.1° which were corresponding to (111), (220) and (311) planes of crystalline Si structure, respectively, could be observed. Notably, the diffraction peaks became stronger with increasing the H_2 flow rate. The H atoms could effectively etch the Si–H and Si–H_2 weak bonds from disordered or strained bonding sites during film growth, and hence, leading to enhance the crystallinity of p-nc-Si films.

Fig. 4 shows the variations of grain size (from XRD patterns) and crystalline fraction (from Raman spectra) as a function of H_2 flow rate. The grain size is determined using the Debye–Scherrer formula

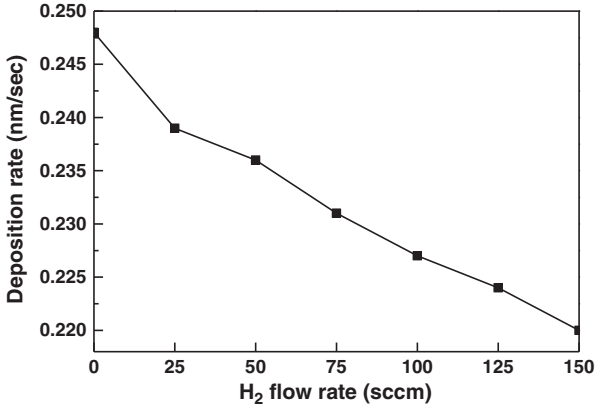

Fig. 1. Deposition rates of p-nc-Si films as a function of H_2 flow rate.