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Low temperature deposition of boron-doped microcrystalline Si:H thin film and its application in silicon based thin film solar cells

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Boron-doped hydrogenated microcrystalline silicon thin films (p-μc-Si:H) have been deposited by RF-PECVD method at different temperature, and the temperature dependence of growth kinetics and opto-electronic properties of p-μc-Si:H thin films have been studied. Both the deposition rate and the dark-conductivity of the p-μc-Si:H thin films drop down when the substrate temperature decreases. XRD and Raman measurements are used to characterize the micro-structure of p-μc-Si:H thin films prepared at different substrate temperature. Grain size of p-μc-Si:H thin films with different thickness as a function of substrate temperature has been investigated. Amorphous silicon thin film solar cells with *p–i–n* structures were fabricated on deposited boron doped μc-Si:H layers. The best cells performance is obtained for p-layers processed at 90 °C.

1. Introduction

Nowadays, the sunlight enters into the amorphous silicon solar cells through p-layer for both *n–i–p* structure and *p–i–n* structure. Due to the reason that the mobility of photo-generate holes is smaller than that of electrons, it makes for the collection of holes when sunlight incident from p-layer. As the window layer, p-type materials need to have larger optical band gap, lower light-absorption coefficient and thickness. On the one hand, more sunlight can pass through the p-layer and enter into the intrinsic layer to generate more charge carriers. On the other hand, the recombination between the minority carrier of p-layer and holes collected from intrinsic layer can be reduced. Thus, the output current of solar cells can be improved. In addition, the built-in electric filed between p-layer and n-layer can be enhanced and the transport and collection of photo-carriers therefore the stability of solar cells can be improved efficiently. Moreover, the p-type materials need to have larger conductivity so that the series resistance can be reduced and the ohm contact can be formed between p-layer and the TCO. Several kinds of p-type materials have been developed including p-type a-Si:H, p-type a-SiC:H, p-type μc-Si:H, and so on.

As the window layer of solar cells, p-type a-SiC:H had once enhanced the open circuit voltage (Voc) and efficiency (Eff) of solar cells. When carbon atoms are doped into the amorphous silicon, the optical band gap of p-type materials can be increased [1]. In 1980, the p-a-SiC:H was incorporated into a-Si:H solar cells by Tawada, and the Voc was increased from 0.8 to 0.9 V [2]. However, p-a-SiC:H had itself disadvantage: the dark-conductivity and the optical band gap were restricted reciprocally, due to the incorporate of carbon atoms, furthermore, the defect state density of the material was large [3].

The electrical property of p-μc-Si:H had been studied extensively [4,5]. Compared with p-a-Si:H, they have greater doping efficiency, higher electrical conductivity, higher mobility, lower light-absorption coefficient, and they have received more and more attention for the photovoltaic applications. Low activation energy can contribute to the enhancement of built-in potential while high conductivity can reduce series resistance.

Several deposition techniques have been established to prepare p-μc-Si:H thin films, including ion beam mixing [6], plasma-enhanced chemical vapor deposition (PECVD), and hot-wire chemical vapor deposition (HWCVD) [7–9], among which PECVD appears to be a promising deposition method for large-area thin film technology and has been employed for industrial applications, while HWCVD has itself advantage: enhancing the deposition rate largely and keeping the quality of the thin films.

In this paper, fabrication of p-μc-Si:H thin films using RF-PECVD at different substrate temperature is described and the influence of substrate temperature on the micro-structure and optoelectronic properties of p-μc-Si:H thin films is investigated. Also, the photovoltaic characteristic of *p–i–n* structure solar cells incorporated

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with p-μc-Si:H thin film that deposited at low temperature are studied.

2. Experimental

A serial of p-μc-Si:H thin films are deposited on 7059 glass substrate by RF (13.56 MHz) plasma-enhanced chemical vapor deposition at different substrate temperature. Silane (SiH_4), hydrogen (H_2) and 0.5% diborane (B_2H_6) are used as the source gases. The hydrogen dilution rate ($R = SiH_4/(SiH_4 + H_2)$) is 0.5%, and the B_2H_6 concentration in silane is 0.5% in gas phase. The gas pressure and power density are kept at 180 Pa and 350 mW/cm^2. The substrate temperature is varied from 60 to 200 °C, and p-μc-Si:H films with different thickness are prepared for different measurement by adjusting the deposition time. The *p–i–n* structures solar cells consisted of specular glass/SnO_2/p-μc-Si:H/i-a-Si:H/n-μc-Si:H/Al are fabricated in a multi-chamber PECVD system. The deposition conditions of each layer are summarized in Table 1.

The thickness of films was measured using a surface profiler (AMBIOS XP-2), thereafter the deposition rate can be obtained. The micro-structure of the p-μc-Si:H films was characterized by X-ray diffractometer (XRD, Philips PANalytical X'Pert, CuKα), then the average crystallite size D of μc-Si:H can be estimated according to Debye–Scherrer formula [10]:

$$D = K\lambda/\beta\cos\theta$$

where K (≈1) is a constant, λ (=0.154187 nm) is the wavelength of X-ray, β is the full width of half maximum (FWHM) of the diffraction peak, and the θ is the diffraction angle. Raman scattering is performed to characterize the structure of p-μc-Si:H films. The 514 nm laser line is used for the excitation. AFM measurement is also used to characterize the surface morphology of p-μc-Si:H films. The electrical conductivity of the films is measured using an Al coplanar contact electrode by Keithley 6430 Source/measure unit at room temperature. The light *J–V* characteristics of solar cells are measured under AM1.5 solar simulator at 25 °C.

3. Results

As shown in Fig. 1, the deposition rate of p-μc-Si:H thin films decreases monotonously from 2.1 to 1.2 nm/min when the substrate temperature decreases from 200 to 60 °C. At the same time, both the dark-conductivity and photo-conductivity of those films minish from the magnitude of 10^{-1} S/cm at 200 °C to 10^{-3} S/cm at 60 °C. In addition, it can be seen from Fig. 1 that the ratio of photo-conductivity to dark-conductivity becomes large as the substrate temperature decreases. This indicates that the doping efficiency of boron in the silicon matrix decreases.

The evolution of layer crystallinity of p-μc-Si:H thin films deposited under different substrate temperature can be demonstrated with XRD spectrum. From the result of XRD given in Fig. 2, it can be seen that the X-ray diffraction signal turns weak as the substrate temperature decreases. Furthermore, the diffraction peak at (3 1 1) plane disappears when the temperature decreases to 150 °C. Indeed, the decrease of the diffraction signal at low temperature must be related to the decrease of the crystallite size. As shown in Fig. 2, the crystallite size calculated from (1 1 1) peak becomes smaller when temperature decreases.

Table 1
The deposition conditions of each layer in the fabricated a-Si:H solar cells.

Parameters	p-layer μc-Si:H	i-layer a-Si:H	n-layer μc-Si:H
Substrate temperature (°C)	60–200	270	270
Flow rate (sccm)	SiH_4:B_2H_6:H_2 = 6.4:0.64:121.6	SiH_4 = 40	SiH_4:PH_3:H_2 = 3.3:3.3:76.8
Gas pressure (Pa)	180	50	200
Power density (mW/cm^2)	350	70	140
Thickness (nm)	20	400	35

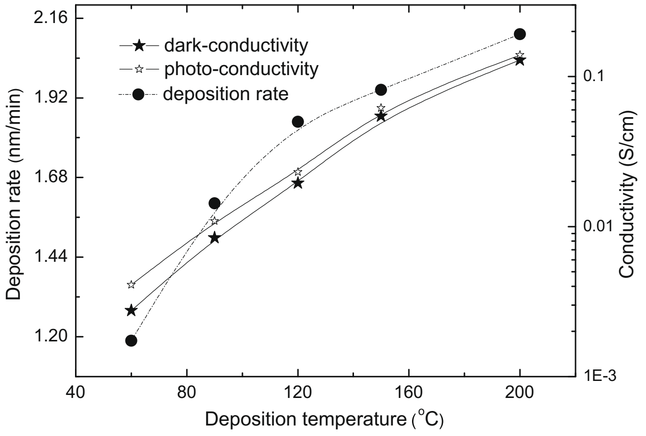

Fig. 1. The deposition rate, dark-conductivity and photo-conductivity of p-μc-Si:H thin films (about 30–40 nm thickness) deposited on glass as a function of the deposition temperature. The lines are drawn to guide the eye.

Fig. 3 displays the Raman spectra of samples of Fig. 1. There is a shoulder peak near 513 cm^{-1} in the transverse optical (TO) mode for all the samples. However, when the temperature decreases, this shoulder peak turns weak and almost disappears when the temperature is 60 °C. This indicates that the crystalline fraction originated from microcrystals decreases gradually, and the micro-structure of the thin films translates from mixed-phase (microcrystalline + amorphous) to amorphous phase. Using Gaussian 3-peaks fit, the crystalline volume fraction Xc can be estimated from the Raman spectra. In fact, Xc decreases gradually from 9.1 to 5.5% when temperature changes from 200 to 60 °C.

In Fig. 4, the surface topology of 3 × 3 μm^2 scan provided by an AFM in noncontact mode is shown for p-μc-Si:H thin films deposited on glass. The thicknesses of these films are 90, 107, 120, and 130 nm respectively, corresponding to the substrate temperature from 200 to 60 °C. It can be seen that when temperature decreases from, the density of grain in the surface drops down. Fig. 5 has shown the grain size calculated from AFM and XRD respectively, and RMS roughness of samples in Fig. 4 as a function of substrate

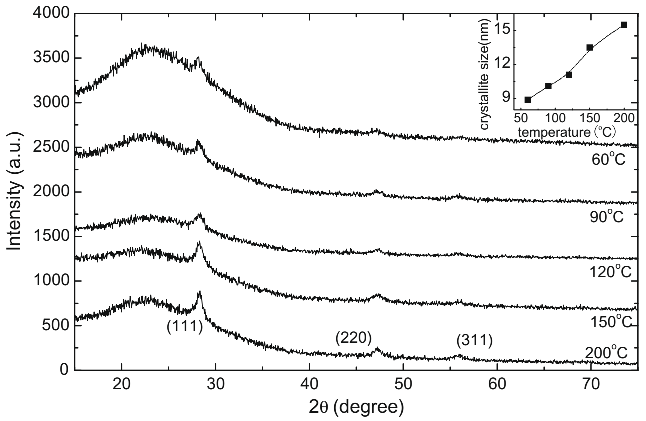

Fig. 2. The XRD measurement of p-μc-Si:H thin films (about 30–40 nm thickness) deposited on glass under different substrate temperature. The inserted graph describes the change of the average crystallite size deduced using Debye–Scherrer formula from XRD spectrum as a function of substrate temperature. The dashed line is drawn to guide the eye.