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Microcrystalline-silicon thin films prepared by chemical transport deposition

Yuki Tomita, Masao Isomura *

Department of Electrical and Electronic Engineering, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan

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ABSTRACT

We have investigated on the production of microcrystalline-silicon (μc-Si) films from solid Si sources by the chemical transport deposition, and could obtain photo-sensitive μc-Si films. The crystallinity and photo-sensitivity of μc-Si films are improved by increasing hydrogen pressure and the highest photo-sensitivity of 50 times is obtained at 200 Pa. The high density of atomic hydrogen probably causes the defect passivation in the high-pressure conditions. The distance between the Si target and the substrate is also important to improve the film properties, and a shorter distance is effective for higher deposition rate, crystallinity and photo-sensitivity.

1. Introduction

Microcrystalline-silicon (μc-Si) has great potential for low-cost and high-efficiency thin film solar cells. The μc-Si thin films have sensitivity in the wavelength from 300 to 1000 nm, and can be deposited at low temperatures. The application of μc-Si thin films for multi-junction solar cells has attracted much attention [1,2]. For the preparation of μc-Si films, several deposition techniques have been employed. In these methods, the plasma CVD has been mainly used for μc-Si with highly diluted silane with hydrogen [3]. In this report, we study the preparation of μc-Si thin films from solid Si sources by chemical transport deposition with hydrogen radicals [4]. This method does not require unsafe gases, such as silane, and is expected to realize safer and lower cost processes with larger area sizes. We also attempted the electronic doping of μc-Si from solid sources.

2. Experimental

Chemical transport deposition is performed in hydrogen atmosphere by a solid Si target placed on a cathode electrode. The target is exposed to high-density hydrogen plasma by applying RF electric power to the cathode electrode. Si-H$_x$ radicals are formed via chemical reactions with the Si target and atomic hydrogen radicals, and transported to substrates. Then, Si films are deposited with hydrogen desorption reactions on the substrate surface. The μc-Si thin films were prepared on glass substrates (corning #7059) and the film thickness was kept around 300 nm. The distances between the Si target and the substrate were 100 and 200 mm. The RF power was 180 W and the hydrogen gas flow rate was 100 ccm. The hydrogen pressure was varied from 20 to 200 Pa and from 20 to 50 Pa for the distance of 100 and 200 mm, respectively. The substrate temperature was fixed at 200 °C. For electronic doping from solid sources, three Al blocks of 5 mm diameters were placed on the 4 in. Si target. The crystallinity of μc-Si was evaluated by Raman spectroscopy, and the optical-absorption coefficients were calculated by transmission and reflection spectra. The electric characteristic was evaluated by photo and dark conductivities. The content of aluminum (Al) was evaluated by X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

3.1. Deposition rate

Fig. 1(a) and (b) show the deposition rate of μc-Si thin films as a function of hydrogen pressure when the distance between the Si target and the substrate was 100 and 200 mm, respectively. In the case of 100 mm, the deposition rate is drastically increased up to 50 Pa, decreased from 50 to 100 Pa, and then stabilized above 100 Pa. The atomic hydrogen radicals are generated more by increasing the pressure, and probably cause more Si-H$_x$ radicals below 50 Pa. But the shortened mean free path disturbs the transition of Si-H$_x$ radicals to the substrate above 50 Pa. On the other hand, in the case of 200 mm, the deposition rate is monotonically decreased with the increase in the pressure from 20 to 50 Pa and μc-Si films were not formed above 50 Pa. The influence of the mean free path is more stressed for a longer

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* Corresponding author. Tel.: +81 463 58 1211; fax: +81 463 59 4014.
E-mail address: isomura@keyaki.cc.u-tokai.ac.jp (M. Isomura).

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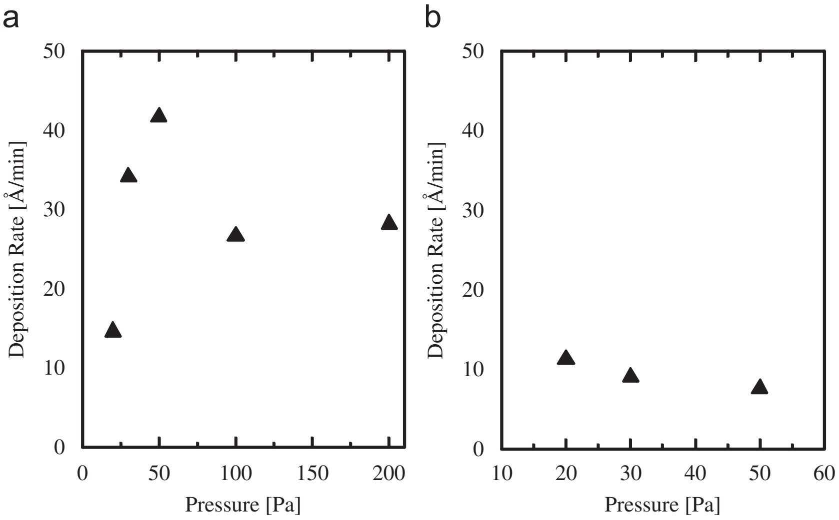

Fig. 1. The deposition rate of μc-Si thin films as a function of hydrogen pressures. The distances between the Si target and the substrates are 100 mm (a) and 200 mm (b).

distance. μc-Si films were not formed below 10 Pa in both the 100 and 200 mm cases, due to insufficient atomic hydrogen radical density.

The deposition rate depends on the amount of Si-H$_x$ radicals generated by the surface reactions between the Si target and atomic hydrogen radicals. Therefore, higher deposition rates are expected by higher Si-H$_x$ radicals' generation due to the higher density of hydrogen radicals or the larger area of the surface reactions. We have not considered obtaining high deposition rates, but a sufficient deposition rate is probably achieved by designing a proper target shape and optimizing the RF power supply.

3.2. *Characteristics of μc-Si films*

Fig. 2(a) and (b) show the Raman spectra of the μc-Si thin films when the distance between the Si target and the substrate was 100 and 200 mm, respectively. The crystalline Si–Si peaks around 520 cm^{-1} gradually increase and amorphous broad signals around 480 cm^{-1} decrease, as the pressures increase. The highest crystallinity is obtained at the highest pressure in both the 100 and 200 mm cases. Probably, the higher density of atomic hydrogen radicals helps to complete the crystal growth.

Fig. 3(a) and (b) show the optical-absorption coefficients of the μc-Si films for the distances of 100 and 200 mm, respectively. The spectrum of single-crystalline Si from the literature is drawn together [5]. The absorption coefficients for 20 and 50 Pa are close to those of crystalline silicon in both distances, but those for 100 Pa show a relatively low value in the case of 100 mm. Much hydrogen atoms were probably taken into the film due to the high density of atomic hydrogen radicals. Fig. 4(a) and (b) show the photo and dark conductivity of the μc-Si films for the distances of 100 and 200 mm, respectively. The photo-sensitivities are improved from 2.0 to 50 and from 1.5 to 10 for the distances of 100 and 200 mm, respectively, with the increase in pressure. The high density of atomic hydrogen probably causes the defect passivation in the high-pressure conditions.

3.3. *Aluminum doping*

Fig. 5(a) and (b) show the Raman spectra and the optical-absorption coefficients, respectively, of Al-doped and -undoped μc-Si thin films, prepared at 50 Pa with the distance of 200 mm. The Al content roughly estimated by XPS is about 0.7 at%. The deposition rate is not affected by Al doping. Clear crystalline Si–Si peaks around 520 cm^{-1} are observed for both Al-doped and -undoped films as shown in Fig. 5(a), and the influence of Al doping is not observed in the crystallinity. The absorption coefficients of both films are close to those of crystalline silicon in the wavelength less than 700 nm, and Al doping does not have major influence on the film structure. On the other hand, the Al-doped film shows higher values, above 700 nm, which suggest that midgap states are created by Al doping. However, enhancement of conductivity is not observed. Probably, the included Al atoms are localized and do not work as acceptors in the substitutional positions.

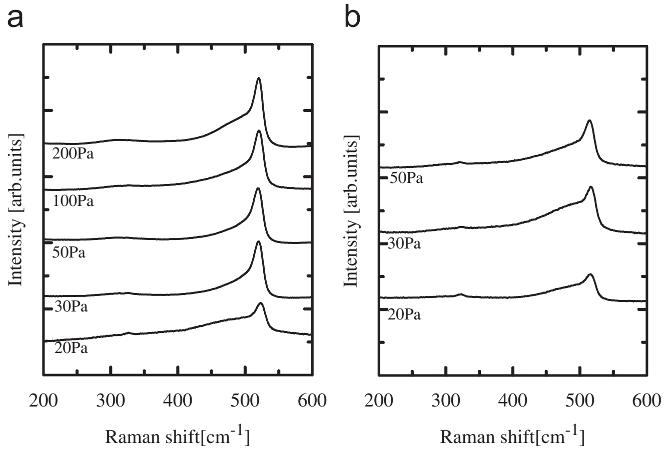

Fig. 2. The Raman spectra of μc-Si thin films prepared with several hydrogen pressures. The distances between the Si target and the substrates are 100 mm (a) and 200 mm (b).

4. Summary

1. The deposition rate of μc-Si films is increased by increasing the hydrogen pressure up to 50 Pa in the case that the distance between the target and the substrate is 100 mm, due to the