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Doped Microcrystalline Silicon Layers for Solar Cells by 13.56 MHz Plasma-enhanced Chemical Vapour Deposition

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Abstract

Doped hydrogenated microcrystalline silicon thin films play a critical role in multi-junction thin-film silicon solar cells, because their crystallinity has a large influence on the properties of intrinsic microcrystalline silicon absorber layers grown on them. The doping efficiency of the doped layers depends strongly on their crystallinity and hence a high-crystallinity doped layer is desired. In this study, highly crystalline doped microcrystalline silicon films are formed on 300 mm × 400 mm glass substrates using a conventional parallel-plate PECVD reactor operated at 13.56 MHz. Raman spectroscopy is used to analyse the crystallinity of the films. The conductivity of the films is measured using the co-planar electrode method. The effects of the deposition parameters on the Raman crystallinity and conductivity of the doped films are investigated. The RF power is found to play a key role for achieving a high crystallinity in the doped layers, whereby a high crystallinity can only be obtained within a narrow RF power range. The influence of the RF power on the lateral thickness uniformity of the deposited films is also examined. It is found that the RF power has a strong influence on the lateral uniformity of the deposited films, with intermediate power giving the best thickness uniformity.

Keywords: Silicon thin-film solar cells; doped microcrystalline silicon; thin films; crystallinity

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1. Introduction

Doped hydrogenated microcrystalline silicon (μc-Si:H) thin films play a critical role in multi-junction thin-film silicon solar cells. Boron-doped p-type μc-Si:H thin films have attracted attention due to their good electrical and optical properties [1-3]. They have high electrical conductivity, high transparency, and a high stability against light-induced degradation compared to hydrogenated amorphous silicon (a-Si:H) films. They have achieved wide application in p-i-n devices, where they are used as the window layer in thin-film solar cells and p-n heterojunction solar cells. The highly conductive p-type μc-Si:H thin film, in combination with a transparent conductive oxide (TCO), enables to reduce the series resistance of p-i-n solar cells. P-type μc-Si:H thin films have been used to replace p-type silicon carbide layers as the window layers in a-Si:H thin-film solar cells due to their higher transparency [4]. One of the major applications of p-type μc-Si:H thin films is as the window layer of the microcrystalline silicon bottom cell of amorphous silicon/microcrystalline silicon thin-film tandem solar cells ("micromorph" cells) [5-7]. In this application, the crystallinity of the doped layers is a key factor that can impact on not only the doping result of the doped layer but also on the intrinsic layer subsequently grown on it [7].

In this paper, we study the effects of RF power and pressure on the Raman crystallinity (i.e., on the crystallinity of the silicon film based on Raman measurements) and the conductivity of the doped silicon films. We also investigate the influence of the process parameters on the thickness uniformity of the doped layers, which is important for application in thin-film solar cells.

2. Experimental details

2.1. Thin film preparation

The doped microcrystalline silicon thin films were deposited onto 30×40 cm^2 soda-lime glass substrates in a vacuum chamber (base pressure < 1×10^{-6} Torr) which is one of several process chambers of a commercial cluster tool system. A schematic of the PECVD process chamber is shown in Fig. 1. The gas flow configuration is such that the gas is fed in from one side of the chamber and pumped out at the opposite side. The thin films are grown using a conventional 13.56-MHz parallel-plate PECVD technique. The substrate is attached to the upper electrode, using a grounded metallic carrier. In all our depositions, the substrate temperature was kept constant at 200°C. The deposition pressure was varied from 0.8 to 1.8 Torr and the RF power from 30 to 80 W. The $SiH_4/(SiH_4 + H_2)$ flow rate ratio was kept constant at 2% in all depositions. Hydrogen-diluted diborane gas (2% B_2H_6 in H_2) and phosphine gas (2% PH_3 in H_2) were used as the dopant gases. The $B_2H_6/(SiH_4 + B_2H_6)$ gas flow ratio was kept constant at 0.1%, while the $PH_3/(SiH_4 + PH_3)$ gas flow ratio was kept constant at 0.4%.

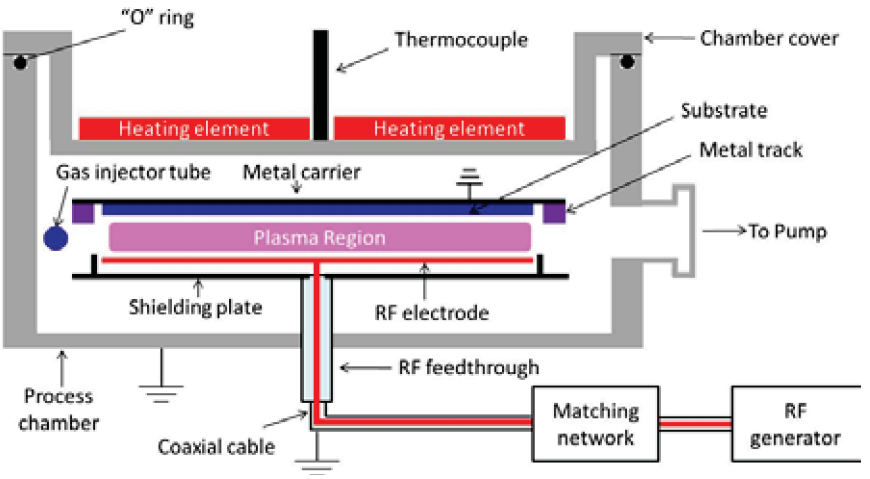

Fig. 1. Schematic of PECVD process chamber.

2.2. Characterisation

A confocal micro-Raman spectrometer (Renishaw, inVia Raman microscope) with a green (514 nm) Ar laser was used for measuring the crystallinity of the doped thin films. The crystallinity was determined through curve deconvolution of the measured Raman spectra. The Raman spectra were deconvoluted into three peaks at 520, 510 and 480 cm^{-1}, corresponding to the crystalline silicon phase, a defective crystalline silicon phase, and an amorphous silicon phase, respectively. The crystallinity X_c was determined via

$$X_c = (I_{520} + I_{510})/(I_{520} + I_{510} + I_{480}) , \quad (1)$$

where I_{520}, I_{510} and I_{480} are the integrated areas of the three deconvoluted peaks.

The dark conductivity of the thin films was measured at room temperature in a co-planar electrode configuration, in which two parallel aluminium electrodes (each 20 mm × 3 mm) with a 1 mm gap in between are evaporated onto the thin films. A source meter is used to apply a dc voltage between the two electrodes and to measure the current generated. The dark conductivity σ_d can be determined by

$$\sigma_d = Iw/(Vld) , \quad (2)$$

where I is the measured current, V the applied voltage, d the thickness of the thin film, w the width of the gap between the two electrodes, and l the length of the electrodes.

3. Results and discussion

3.1. Raman crystallinity and electrical properties

RF power and deposition pressure are the two most critical process parameters in the PECVD process with respect to the properties of the deposited silicon thin films. In this paper, one of the main objectives

was to investigate how the RF power and deposition pressure affect the Raman crystallinity of the doped silicon films. We performed three sets of experiments for p-type doped films and one set of experiments for n-type doped films. In the experiments for the p-type doped films, the films were prepared at three different pressures (0.8, 1.2 and 1.8 Torr), whereby the RF power was varied. The deposition time was fixed at 20 minutes in each experiment. The p-type films all have a thickness of about 35 nm. The Raman crystallinity of the p-type doped films prepared under the above-mentioned conditions are shown in Fig. 2(a). The n-type films were deposited at 1.5 Torr and the results are shown in Fig. 2(b). In Fig. 2, the lines connecting the data points serve as guides to the eye. It can be seen in Fig. 2(a) that a high Raman crystallinity (> 50%) of the p-type doped films can, for a given pressure, only be obtained within a very narrow RF power range. It can also be seen that the RF power window that gives high crystallinity shifts towards higher RF power with increasing deposition pressure. A similar power window can be found in Fig. 2(b) for n-type doped films.

Figure 3 displays the conductivity of the prepared n-type films versus the RF power. It can be seen that highly conductive n-type films can only be achieved within a narrow RF power range, a trend similar to that observed for their Raman crystallinity (see Fig. 2(b)). The films with high crystallinity have high conductivity, implying that the highly crystalline silicon thin films have a higher doping efficiency than their amorphous counterparts.

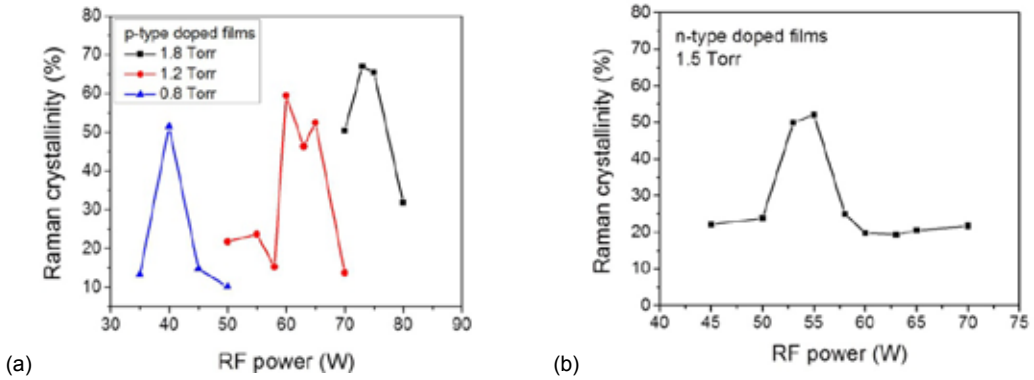

Fig. 2. Influence of RF power on the crystallinity of (a) p-type μc-Si:H films and (b) n-type μc-Si:H films.

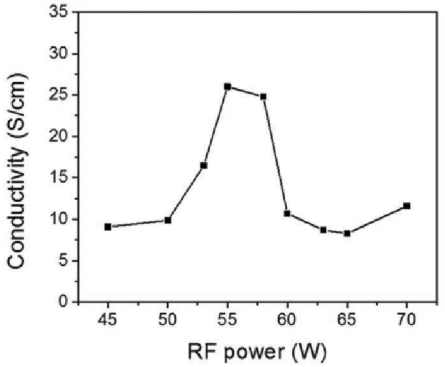

Fig. 3. Dark conductivity of n-type μc-Si:H thin films versus the RF power.

3.2. Thickness uniformity study

The thickness uniformity of the thin films is critical for the fabrication of high-quality thin-film solar modules. Two types of gas flow configuration are commonly used in industry: The first uses gas injection on one side of the chamber and gas extraction on the opposite side, giving a one-directional gas flow configuration between the parallel-plate electrodes [8, 9]. The other method uses a showerhead electrode, whereby gas extraction occurs via one or more ports [9-11]. In both configurations, a gas flow velocity gradient and a pressure gradient are unavoidable. A lot of modelling and experimental work has been done to improve the uniformity of the SiH_4 plasma [9-14]. The literature results show that a gas shower-head definitely helps in achieving a more uniform film thickness over a very large area. However, the systems without a gas showerhead still find their applications in cases where cost matters a lot and where a very large area and/or a very high thickness uniformity are not crucial. Thus, finding suitable process conditions that give relatively uniform film thickness using such simple systems is of relevance for the thin-film PV industry.

The system used in the present study has a one-directional gas flow configuration. The gas is injected into the chamber on one side and is extracted at the opposite side. The influence of the RF power on the thickness uniformity of the Si thin films is investigated experimentally. To study the thickness uniformity, the thickness is measured at twenty five positions over the whole sample area. The locations of the measured points are shown in Fig. 4. The positions at the corners are 3 cm away from the two adjacent edges. It is found that the silicon films are much thicker on the side where the gas is injected. This is a fundamental issue of this reactor design. For practical applications, to find a process which can produce a uniform thickness over an area as large as possible, it makes sense to ignore a several cm wide region along the edge of the substrate that faces the gas injector. Therefore, our uniformity analysis is performed for two areas. Area 1, which is the entire sample area, and area 2, which excludes a 6 cm wide stripe along the gas injector facing edge of the substrate. The two areas are shown in Fig. 4, together with the locations of the film thickness measurements.

The thickness data are collected from the samples made at 0.8 Torr and RF power in the 30-50 W range. In this study, the standard deviation uniformity SDU [15] was used to assess the film thickness non-uniformity. The results of these thickness uniformity measurements are shown in Fig. 5. One can see that the uniformity is best for intermediate RF powers (~40 W), reaching a SDU value of below 8% for the smaller area (area 2).

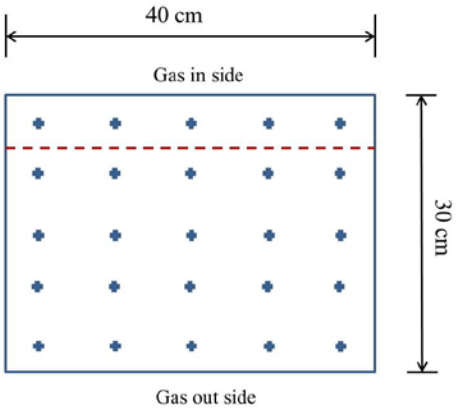

Fig. 4. Locations of silicon film thickness measurements on the 30 cm × 40 cm glass substrate.

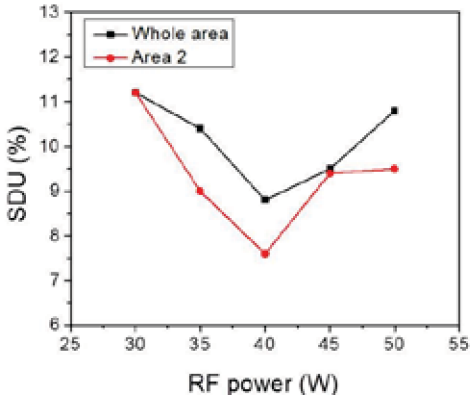

Fig. 5. Silicon film thickness non-uniformity versus RF power, for two sample areas.

Figure 6 displays the thickness contour plots of the films prepared at 30, 40 and 50 W. For all three RF powers, an enhanced silicon film thickness is found near the glass sheet edge that faces the gas injector. The thickness distribution of the films prepared at 30 W and 40 W has a gradient from the gas-in side to the gas-out side, which is coincident with the pressure gradient. We also notice that, for 30 W RF power, a large area with very thin Si thickness exists near the gas-out side, giving poor thickness uniformity. When the RF power is increased to 40 W, the area with the very thin Si film disappears. If the RF power is increased to 50 W, the situation worsens again and the film thickness becomes very non-uniform. This phenomenon can be explained as follows: In silicon PECVD, the deposition depends on the absorption of the silicon-containing radicals at the growth interface and on the ion bombardment of the growth interface. The first effect is related to the pressure, the residence time of the relevant radicals and the dissociation efficiency of the precursor gas. The second effect is related to the sheath electrical field in between the growth interface and the bulk of the plasma. In PECVD, the plasma density and ion energy both increase with increasing applied RF power. When the RF power is low, most ions lose their energy through ion-neutral collisions. The sheath electrical field is also weak. Thus neutral radical transport is the dominant factor for the growing film. The experimental results reveal that the pressure is higher on the side where the gas is injected, while the pressure gradient is highest on the side where the gas is pumped out [16]. The residence time of the gas molecules is shorter in this region. If the RF power is too low (i.e., not high enough to produce a high gas dissociation rate), the deposition rate within this substrate region will be low, resulting in a very thin Si thickness in the substrate region facing the gas extraction port. When the RF power is high, the sheath electric field is strong and becomes another factor that affects the Si deposition process. Some of the ions, after colliding with neutrals, are still energetic. The strong sheath field accelerates these ions towards the substrate, lead to a strong ion bombardment and hence sputtering of the Si film. The uniformity of the sputtering effect depends on the lateral distribution of the electric field, which may be distorted locally (for example by dust or peeled-off film segments which were formed during the previous deposition runs). A locally distorted electric field would result in a non-uniform sputtering effect, which in turn would result in a poor uniformity of the Si film thickness.

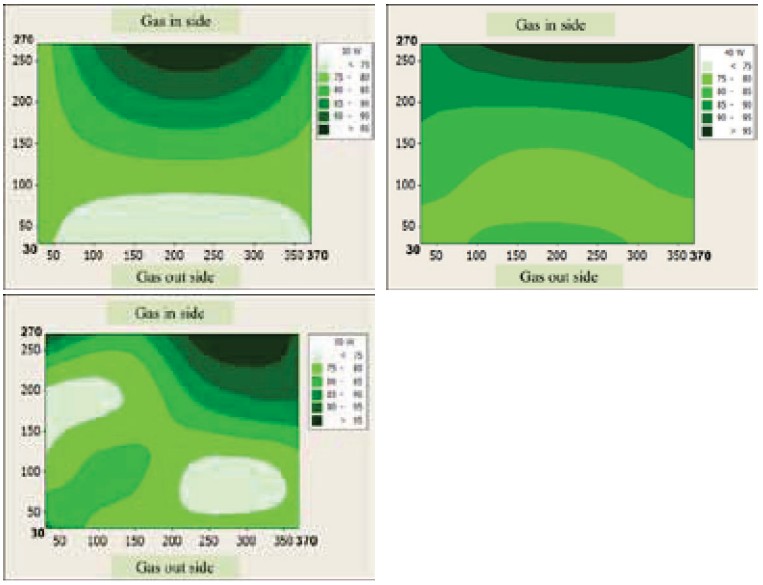

Fig. 6. Thickness contour plots over a glass sheet area of 240 mm × 340 mm (the thickness data collection zone), for the p-type μc-Si:H thin films prepared at three different RF powers (30, 40 and 50 W)

4. Conclusions

In this study, highly crystalline doped microcrystalline silicon films were formed on 300 mm × 400 mm glass substrates using a standard parallel-plate PECVD reactor operated at 13.56 MHz. The influence of RF power and pressure on the Raman crystallinity and film thickness uniformity were investigated. The RF power was found to play a key role for achieving a high crystallinity in the doped layers. Doped microcrystalline silicon films with a high crystallinity can only be obtained within a narrow RF power window. It was also found that the RF power has a strong influence on the lateral thickness uniformity of the deposited films. Despite the simple PECVD reactor design, Si films with good thickness uniformity over a large area were achieved if a suitable RF power was applied. An intermediate power gave the best thickness uniformity.

Acknowledgements

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