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Research on the boron contamination at the p/i interface of microcrystalline silicon solar cells deposited in a single PECVD chamber*

Zhang Xiao-Dan(张晓丹)†, Sun Fu-He(孙福和), Wei Chang-Chun(魏长春), Sun Jian(孙 建), Zhang De-Kun(张德坤), Geng Xin-Hua(耿新华), Xiong Shao-Zhen(熊绍珍), and Zhao Ying(赵 颖)

Institute of Photo-Electronics, Thin Film Devices and Technique of Nankai University, Key Laboratory of Photo-Electronics, Thin Film Devices and Technique of Tianjin, Key Laboratory of Photo-Electronic Information Science and Technology (Nankai University), Ministry of Education, Tianjin 300071, *China*

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This paper studies boron contamination at the interface between the p and i layers of μc-Si:H solar cells deposited in a single-chamber PECVD system. The boron depth profile in the i layer was measured by Secondary Ion Mass Spectroscopy. It is found that the mixed-phase μc-Si:H materials with 40% crystalline volume fraction is easy to be affected by the residual boron in the reactor. The experimental results showed that a 500-nm thick μc-Si:H covering layer or a 30-seconds of hydrogen plasma treatment can effectively reduce the boron contamination at the p/i interface. However, from viewpoint of cost reduction, the hydrogen plasma treatment is desirable for solar cell manufacture because the substrate is not moved during the hydrogen plasma treatment.

Keywords: boron contamination, single chamber, microcrystalline silicon, solar cells
PACC: 8115H, 7360F

1. Introduction

High efficiency silicon thin film p-i-n solar cells require high collection efficiency in the whole range of solar spectrum. However, μc-Si:H solar cells prepared in single-chamber systems usually show poor short wavelength response because of the residual boron doping in the i layer. The residual boron doping (and/or boron diffusion from the p layer) lowers the electrical field and increases carrier recombination at the p/i interface, which reduces the blue light response and overall conversion efficiency. Although multiple chamber deposition systems can be used to solve the cross contamination problem, the capital cost of a multi-chamber system is much higher than a single-chamber system. In addition, single-chamber systems normally have a mechanical simplicity, which becomes a favorable factor for reducing the maintenance downtime of manufacturing lines. Therefore, single-chamber deposition systems not only have been widely used for a-Si:H solar cells production but also expected to be used in high efficiency μc-Si:H solar cell depositions. Technically, one would expect that for μc-Si:H solar cell deposition in a single-chamber system, the boron contamination deteriorates the solar cell performance more drastically than a-Si:H solar cells because of the highly diluted and reactive plasmas used for μc-Si:H deposition.

Over the years, people have developed many ways to resolve the cross-contamination problems in single-chamber systems. High vacuum pumping, CO_2 plasma treatment, reactive NF_3 gas flush, a short vapor flush with H_2O, and NH_3 gas flush are normally used after the p-layer deposition to reduce the residual boron contamination in single chamber systems for a-Si:H solar cell deposition.[1−5] These methods can partly reduce or eliminate the sources of residual boron in the reactor, which possibly include diborane

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†Corresponding author. E-mail: xdzhang@nankai.edu.cn

gas molecules, adsorb boron atoms, and high-boron-content, chemical vapor deposited a-Si:H:B film that adhered to the electrodes and walls of the reactor. These boron containing materials can be released at the beginning of the i-layer deposition by the H_2+SiH_4 plasma, resulting in an undesirably high level of boron in the i-layer near the p/i interface. Because of the sensitivity of μc-Si:H to impurities, the development of single-chamber deposition for μc-Si:H solar cells is a challenging task. The fist attempt in this new field was presented by Li *et al.*[6] Recently, Kaneka showed a success in using single-chamber system for high efficiency μc-Si:H depositions without the details about the method of contamination reduction.[7]

In this paper, we studied the effect of boron contamination on the properties of μc-Si:H thin films with different crystalline volume fraction (X_c).[8] We measured the boron incorporation in μc-Si:H films by means of secondary ion mass spectroscopy (SIMS). The influence of boron contaminations on the material structures was characterised by using x-ray diffraction (XRD) and Raman measurements. Various samples made with different chamber histories and pretreatments were studied. From the experimental results, we suggest an effective hydrogen plasma treatment to reduce the boron contamination. This method can restore the short wavelength response for μc-Si:H solar cells made in a single-chamber system.

2. Experimental details

The μc-Si:H films were deposited by using a capacitively coupled ultrahigh vacuum (UHV) parallel plate single-chamber system with a base vacuum of 10^{-6} Pa. The reactor is equipped with a load lock system for transportation of the substrates. The details of this set-up were reported in our previous paper.[9] In this study, the distance between the cathode and substrate was fixed at 2.1 cm for all layers. The excitation frequency of electrical source was 60 MHz. The pressure and flow rates were independently controlled by a downstream throttle valve controller and upstream mass flow controllers, respectively.

The films were deposited on Eagle 2000 glass substrate. The thickness of all samples was about 500 nm. A chemical etching process was used to enhance the texture of ZnO films made by sputtering (from IPV). The ZnO coated glass substrates were used for the fabrication of single-junction μc-Si:H solar cells. The electrical properties of μc-Si:H samples were measured with a co-planar Al electrode configuration. The length of Al electrode was about 1.6 cm and the distance between the two Al electrodes was about 0.055 cm. The structural properties of μc-Si:H samples were characterised with XRD (type: PAN algtical X'PertPRO) and Raman (type: MKI Renishaw 2000) measurements. The boron concentration at p/i interface was measured by using SIMS (IMS-4F). The solar cell performance was characterised with current versus voltage (I–V) measurements under an AM1.5 solar simulator at 25 °C.

3. Results and discussion

Figure 1 shows Raman spectra of the three samples. The Raman signal collected in the micro-Raman experiment is equal to the integral, taken over the excited volume, of the depth distribution of each phase.[10] The excited volume depends on the penetration depth of the laser light used. The penetration depth of 514-nm light is in the order of 100 nm for a-Si:H and 300 nm for μc-Si:H, whereas with 633-nm light it reaches about 1 μm for both materials. Even though for the measurements were on the μc-Si:H-layer side, the Raman measurements with the 633-nm laser reveal the structural properties of whole sample thickness, including p/i interface region. These three curves showed a mixed-phase signature with a broad peak at ~480 cm^{-1} and small narrow peak at 515 cm^{-1} for sample C prepared at 7% silane concentration, medium crystalline volume fraction (X_c) with a large sharp peak at 518 cm^{-1} for sample B prepared at 6.5% silane concentration, and high X_c with a large sharp peak at 516 cm^{-1} for sample A prepared at 5%

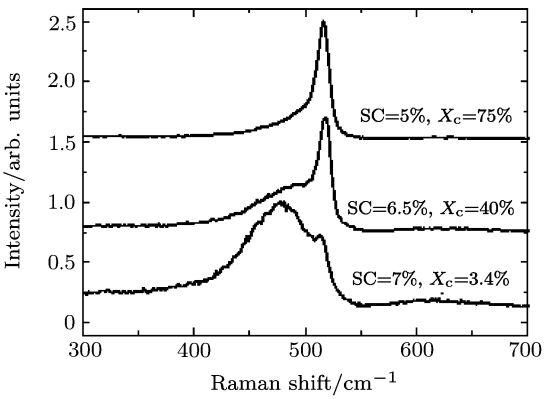


Fig.1. Typical Raman scattering spectra of p/i structures made at different hydrogen dilution ratios (SC=SiH_4/(H_2+SiH_4).

silane concentration. It is evident that the structure of materials changed from mix-phase to high X_c with increasing hydrogen dilution. The de-convolution of the Raman spectra showed that the X_c was around 70% for sample C, around 40% for sample B, and around 3% for sample A.

Figure 2(a) shows the XRD results of samples prepared at different silane concentrations measured by GI-XRD. All of the three samples show three different peaks at 28.385, 47.285, and 56.105, which corresponds to the diffraction from the ⟨111⟩, ⟨220⟩ and ⟨311⟩ crystal orientations, respectively. In order to learn more information about the material structures, different XRD measurement modes (θ/θ XRD) were used to investigate the structural differences in the three samples. The detailed results are shown in Fig.2(b), where the intensity of ⟨220⟩ crystalline orientation decreased with the increase of silane concentration and it disappeared at 7% of silane concentration. Figures 2(a) and 2(b) show different results for the same series of sample by using different XRD measurement modes. In fact, the fundamental theory for GI-XRD is that the detector receives the information from all diffractions of different planes related to silicon materials when each little angle (0°–3°) is fixed.

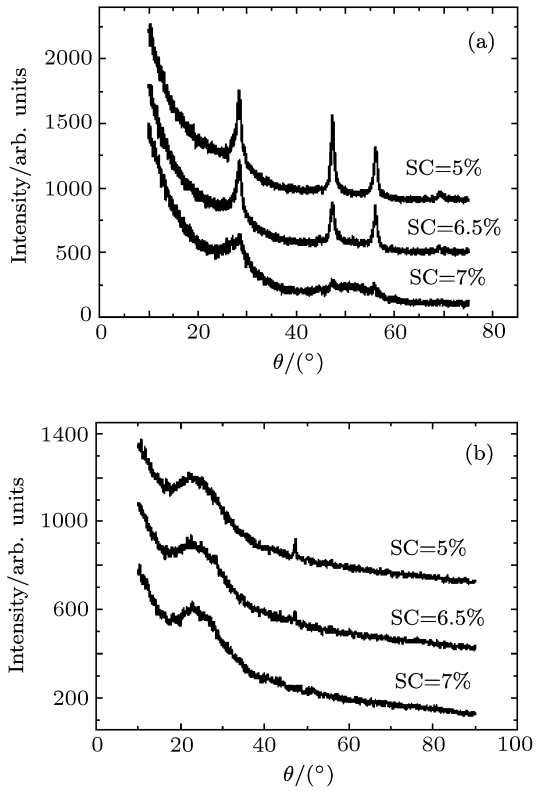


Fig.2. (a) Glancing incidence XRD (GI-XRD), (b) θ/θ XRD measurement results of samples prepared at different silane concentrations.

As for silicon material, the intensity of (111) crystal plane is the strongest. All samples show the highest intensity of ⟨111⟩ crystalline orientation peak in this experiment. However, the principle of θ/θ XRD measurement mode was that the detector receives the information only from the diffractions of the planes parallel to the surface of sample. Combining the above experimental results, we conclude that the ⟨220⟩ crystal orientation was the strongest orientation parallel to the growth orientation of sample. Therefore, different XRD measurement modes reveal the different structural information of samples. The θ/θ XRD measurement mode reflects the change of preferential orientation of samples. According to the results of Matsui *et al* the short circuit current (J_{sc}) density of μc-Si:H solar cells depends on the preferential crystalline orientation of the intrinsic layer.[11] The reason is that the high intensity of the ⟨220⟩ peak results in a high texture on the material surface, which is important for the absorption of long-wavelength light in μc-Si:H solar cells.

Figure 3 shows the SIMS boron profiles of samples A, B and C. The samples have a p/i structure, where the p layer thickness was the same as that in an actual solar cell. Our main interest in the SIMS analysis is the variation of the boron concentration profile at the p/i interface. In Fig.3, the boron concentration of the p layer is about 1×10^{21} at.cm^{-3} for sample C and 3×10^{20} at.cm^{-3} for samples A and B. The curves of the boron concentrations in the p layers are not very smooth because the substrate is Eagle 2000 glass. The boron concentration decreases almost three magnitudes (from the dashed line) from 10^{20} at.cm^{-3} down to 10^{17} at.cm^{-3} through the whole intrinsic layer. The shallow continuous decrease of boron concentration

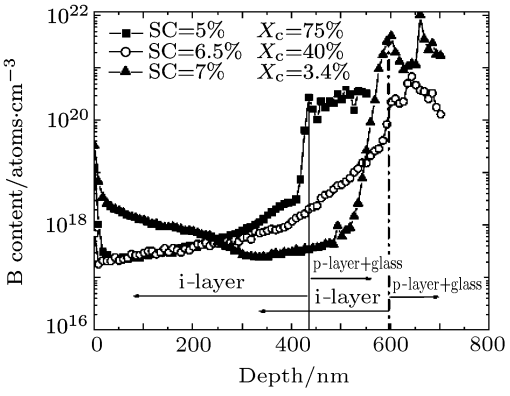


Fig.3. Boron profiles of sample A (SC=5%), B (SC=6.5%), and C (SC=7%) deposited on Eagle 2000 glass substrate.

from the p/i interface through the whole layer is certainly unfavorable for solar cell performance. A steep and abrupt step-like decrease is desirable at the beginning of the i layer deposition. Sample C with a mixed-phase structure has a more abrupt transition in the boron concentration profile at the p/i interface than A and B, which shows a reduced boron cross-contamination. From the above results, we conclude that the effect of boron on the properties of μc-Si:H will play an important role. The boron contamination at the p/i interface would lower electric field and lead to lower blue response in a solar cell. This effect has been previously suggested as a working hypothesis[12] and has also been proved by experiments. Here, it is also noted that sample A with a high X_c shows a less boron contamination than sample B because the boron decreases rather abruptly at the p/i interface. In addition, the structural properties of sample A also show a more compact structure than sample B because of its relatively lower current (in Table 1). The reason for this phenomenon needs to study further.

In order to reduce the boron contamination, various techniques were investigated. Their effectiveness was evaluated by SIMS measurements. For the purpose of p-i-n solar cell fabrication, the boron contamination in the i-layer should not exceed 10^{17} atom/cm^3. The experiment has proved[13] that the boron contamination is trapped in the reactor with a much longer time than the plasma processing time of a solar cell. To solve the problem, one needs some procedure to reduce the release time of residual boron before the i-layer deposition to maintain a high throughput.

Table 1. Characteristics of p/i structures with different SCs and different treatment methods.

sample (p+i)	i layer condition	dark/photo current/mA
A	SC=5% no treatment	0.163/0.167
B	SC=6.5% no treatment	0.91/0.98
C	SC=7% no treatment	0.057/0.060
B[1]	SC=6.5% (a-Si:H, 10 min)	1.61/1.68
B[2]	SC=6.5% (μc-Si:H, 20 min)	0.018/0.019
B[3]	SC=6.5% (H plasma 20 s)	0.51/0.55
B[4]	SC=6.5% (H plasma 30 s)	0.078/0.084
B[5]	SC=6.5% (H plasma 60 s)	0.26/0.28

In the first called 'burial' method, an a-Si:H covering layer was found to give an i-layer with sufficiently low contamination impurity. The details are shown in Fig.4. The boron concentration in the p layer is about 3×10^{20} at.cm^{-3}. For the no treatment sample B, a decrease of boron concentration by a factor of 10^3 to the lowest boron contamination is attained for the i layer thicker than 600 nm. The application of a-Si:H covering layer attains a stabilized boron concentration of $\sim 1\times10^{17}$ cm^{-3} after 350 nm in the intrinsic layer, which is at least half of transition region in the sample with no treatment. In summary, we found that an a-Si:H covering layer (about 500 nm) seems to be an effective method to reduce the boron cross-contamination. However, the boron concentration decreases in the a-Si:H layer not very abrupt. A certain thickness is required.

In the next step, the influence of a μc-Si:H layer to cover the boron-doped p layer was examined. The SIMS-profiles in Fig.4 also show the p/i interface with an μc-Si:H covering layer of $\sim$500 nm on the chamber after deposition of the p layer. The maximum boron concentration of p layer is $\sim3\times10^{20}$ cm^{-3}. The boron concentration gradient at the interface is about 30 at.cm^{-3}/nm, which is quite steep. The decay of boron concentration down to 2×10^{17} cm^{-3} shows a step-like boron profile at the p/i interface. Therefore, a μc-Si:H covering layer with a thickness of $\sim$500 nm can be considered as a suitable chamber treatment method to reduce boron contamination.

Compared the a-Si:H and μc-Si:H covering layers, although their thicknesses are similar, their effect of reducing boron contamination is different. One explanation could be that the a-Si:H deposition only covers the B-contained coatings in the chamber; while the μc-Si:H deposition not only covers the B-contained

coatings in the chamber but also etches away the B-contained materials because high density atomic hydrogen in the high hydrogen diluted and high powered plasma.

Although this kind of 'burial' method is an effective method to reduce the boron cross-contamination, it needs to remove the substrate into the load-lock chamber to protect the deposited p-layer otherwise the solar cell performance is degraded. In order to increase the throughput, the in-situ method reduced boron contamination is very important. So hydrogen plasma treatment was used to reduce the effect of the boron contamination. The electrical properties of samples used different treating time of hydrogen plasma can be seen in Table 1. It shows that sample B[4] like sample B[2] shows relatively low current in comparison with no treatment sample and other treated samples. As shown in Fig.4, the SIMS-profile reveals a steep p/i interface in the sample with the treatment of 30 seconds of hydrogen plasma. The boron concentration of p layer is about 2×10^{21} cm^{-3}, which is a little higher than other samples. The reason is not clear. The boron concentration profile reveals an abrupt and steep decrease by a factor of almost 10^4 down to the minimum concentration of 2×10^{17} cm^{-3} within only about 100 nm from the p/i interface. This steep step-like decrease of the boron concentration suggests that the hydrogen plasma treatment is more effective than the μc-Si:H covering layer. The boron concentration drops linearly to the level that no boron contamination exists in the intrinsic layer.

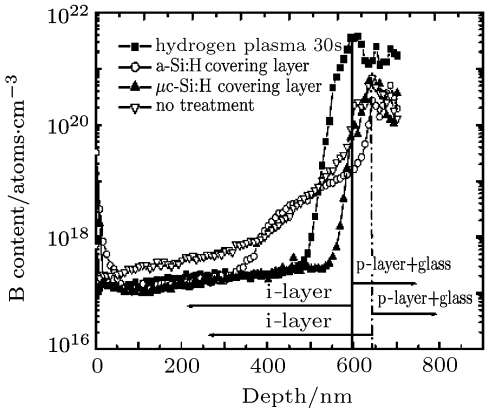


Fig.4. The SIMS profiles of the boron concentration in p/i structures prepared with different treatments before the i layer depositions.

In the summary of Fig.4, the SIMS-profiles clearly show that the most abrupt decrease of boron concentration within a distance of ∼100 nm was obtained from a μc-Si:H covering layer or a 30 s-hydrogen plasma treatment. All other treatments show an exponential boron decrease into the intrinsic layer with a transition region of over several hundreds of nanometers.

For μc-Si:H solar cells, the hydrogen plasma treatment between the p- and i-layer depositions improves the open circuit voltage (V_{oc}), the short-circuit current density (J_{sc}), and the fill factor (FF). The improvement in V_{oc}, J_{sc}, and FF indicates the improvements of the p/i interface. Through the optimization of i layer deposition parameters and the application of a 30 s-hydrogen plasma treatment, a single-junction μc-Si:H solar cell with 6.45% conversion efficiency was achieved (in Fig.5).

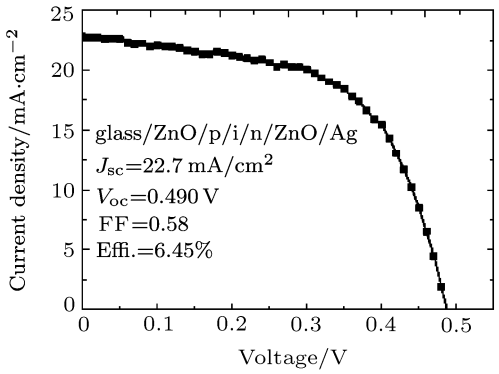


Fig.5. *I–V* curve of a single-junction μc-Si:H solar cell with an initial conversion efficiency of 6.45%.

4. Conclusions

Different methods for controlling the boron contamination at the p/i interface for the deposition of μc-Si:H solar cell in a single chamber system were studied. These treatments consist of an a-Si:H covering layer, a μc-Si:H covering layer, and a hydrogen plasma treatment between the deposition of the p and i layers. A μc-Si:H covering layer and a hydrogen plasma treatment considerably reduces the boron contamination at the p/i interface. The advantages of the hydrogen plasma treatment for the production process of μc-Si:H solar cells are: (i) the substrate can remain within the reactor during the whole deposition process; (ii) the treatment time is very short (less than 1 min). Moreover, hydrogen is already used to prepare silicon thin film, so it would not need special installation. The performance of the cells prepared with the hydrogen plasma treatment has been improved significantly.

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