Reduction of the phosphorus contamination for plasma deposition of p–i–n microcrystalline silicon solar cells in a single chamber*

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(Received 29 November 2009; revised manuscript received 20 January 2010)

This paper investigates several pretreatment techniques used to reduce the phosphorus contamination between solar cells. They include hydrogen plasma pretreatment, deposition of a p-type doped layer, i-a-Si:H or μc-Si:H covering layer between solar cells. Their effectiveness for the pretreatment is evaluated by means of phosphorus concentration in films, the dark conductivity of p-layer properties and cell performance.

Keywords: phosphorus contamination, single chamber, microcrystalline silicon, solar cells
PACC: 8115H, 8630J, 7360F

1. Introduction

The hydrogenated microcrystalline silicon solar cells are of great importance because of their potential stability. At present, most of the μc-Si:H solar cell deposition occurs in a multi-chamber reactor deposition system.[1−4] Plasma-enhanced chemical vapour deposition (PECVD) of p–i–n solar cells in a single plasma reactor offers the advantage of a low cost in comparison with multi-chamber processes which use separate reactors for production of the p-, i- and n-layers.[5] But in a single chamber PECVD reactor, phosphorus contamination from the reactor walls can release freshly deposited phosphorus-containing molecular species which degrades the performance of the solar cells. Therefore, for mass production of solar cells in a single chamber reactor, it would be practical if some contamination treatment techniques, applied between the two solar cells deposition process, could reduce the phosphorus contamination and so maintain the solar cell performance.

In this work, several techniques used to reduce the phosphorus contamination were investigated. Their effectiveness was evaluated by means of the improvement of p-layer properties and cell performance. We measured the phosphorus concentration in μc-Si:H films by means of secondary ion mass spectroscopy (SIMS). The experimental results showed that the deposition of a p-layer, hydrogen plasma treatment or deposition of an a-Si:H or μc-Si:H covering layer after the n-layer of the last cell could effectively reduce the phosphorus contamination.

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^{-5} Pa. The reactor is equipped with a load-lock system for transportation of the substrates. The details of this setup were reported in our previous paper.[6] The excitation frequency of electrical source was 75 MHz. The pressure and flow rates were independently controlled by a downstream throttle valve controller and upstream mass flow controllers, respec-

*Project supported by Hi-Tech Research and Development Program of China (Grant Nos. 2007AA05Z436 and 2009AA050602), Science and Technology Support Project of Tianjin of China (Grant No. 08ZCKFGX03500), National Basic Research Program of China (Grant Nos. 2006CB202602 and 2006CB202603), National Natural Science Foundation of China (Grant No. 60976051), International Cooperation Project between China–Greece Government (Grant Nos. 2006DFA62390 and 2009DFA62580), and Program for New Century Excellent Talents in University of China (Grant No. NCET-08-0295).
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tively.

The films were deposited on Eagle 2000 glass substrates. The Asahi 'U' type glass substrates were used for the fabrication of single-junction μc-Si:H solar cells. The structure is glass/SnO_2/p-μc-Si:H/i-μc-Si:H/n-a-Si:H/Al. The electrical properties of μc-Si:H samples were measured with a co-planar Al electrode configuration. The length of Al electrode was about 1.60 cm and the distance between the two Al electrodes was about 0.045 cm. The structural properties of μc-Si:H samples were characterised with Raman (LabRAM HR 800) measurements. The phosphorus concentration was measured by using Secondary Ion Mass Spectroscopy (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. The integrated intensity ratio (X_c)[7]

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

was determined by deconvolution of the spectra into three signal peaks at approximately 480, 510 and 520 cm^{-1}. Where the peak centred at around 520 cm^{-1} corresponds to the crystalline phase, whereas the peak centred at around 510 cm^{-1} peak, attributed to the defective part of the crystalline phase, is usually included in the crystalline part, the peak centred at 480 cm^{-1} corresponds to the amorphous phase.

3. Results and discussion

Cross contamination of μc-Si:H p-layer and i-layer by residual phosphorus is an immense challenge for device process control and optimisation in a single chamber. Dopant species previously deposited inside the reactor could be released during following depositions. For our experiment, the SIMS-profile in Fig. 1 showed phosphorus concentration of the p-doped layers deposited after n-layer in the order of 10^{19}–10^{20} cm^{-3}. In addition, the concentration of phosphorus decreased from the p-layer into the intrinsic layer down to 10^{17} cm^{-3}. The intrinsic layer I_3/p-doped layer P_3/intrinsic layer I_2/p-doped layer P_2/intrinsic layer I_1/p-doped layer P_1 were deposited in a silicon wafer. All P- and I-layers were deposited in the same condition, respectively. Each intrinsic layer/p-doped layer was deposited after n-layer. The I_1/P_1 layers were deposited after 15 hours pumping time after n_1-layer. The I_2/P_2 and I_3/P_3 layers were deposited after a few minutes pumping time after n_2- and n_3-layers. The silicon wafer was introduced into load-lock when each n-layer was deposited. The n_3-layer is heavily-doped layer. The n_2- and n_1-layers are lightly-doped layer and have the same phosphorus concentration.

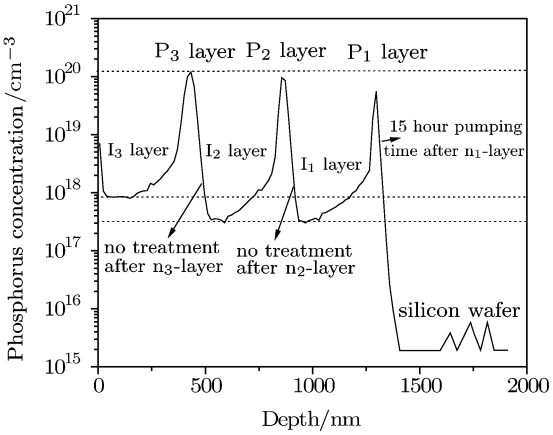


Fig. 1. Phosphorus concentration profile by SIMS measurement for p–i structures without any contamination treatment (structure: intrinsic layer I_3/p-doped layer P_3/intrinsic layer I_2/p-doped layer P_2/intrinsic layer I_1/p-doped layer P_1/silicon wafer).

The phosphorus concentration of the P_1-layer is smaller than that of P_2-layer and P_3-layer. The 15 hours pumping time reduced the contamination, which suggested that the phosphorus source was slowly desorbed. However, following plasma deposition of a p-layer, pumping for 15 hours was ineffective in preventing phosphorus contamination of the next solar cell. The phosphorus concentration of the P_3-layer deposited after the heavily-doped n_3-layer is higher than that of the P_2-layer deposited after the lightly-doped n_2-layer. The extent of μc-Si:H p-layer contamination seems to correlate with the amount of PH_3 used in the most recent n-layer. To limit phosphorus contamination, we can also develop n-layer processes with reduced PH_3 usage.

Before loading the substrate into the single reaction chamber, several pretreatment techniques were used to reduce the phosphorus contaminations: the deposition of a p-layer, hydrogen plasma treatment and deposition of an a-Si:H or μc-Si:H covering layer after n-layer of the last cell. The SIMS-profiles in Fig. 2 also showed that different treatment techniques did reduce the contamination to an acceptable level and were found to give a p-layer with phosphorus impurity in the order of 10^{17} cm^{-3} and i-layer with sufficiently low phosphorus impurity in the order of 10^{16} cm^{-3}. Contamination was reduced, but not eliminated.

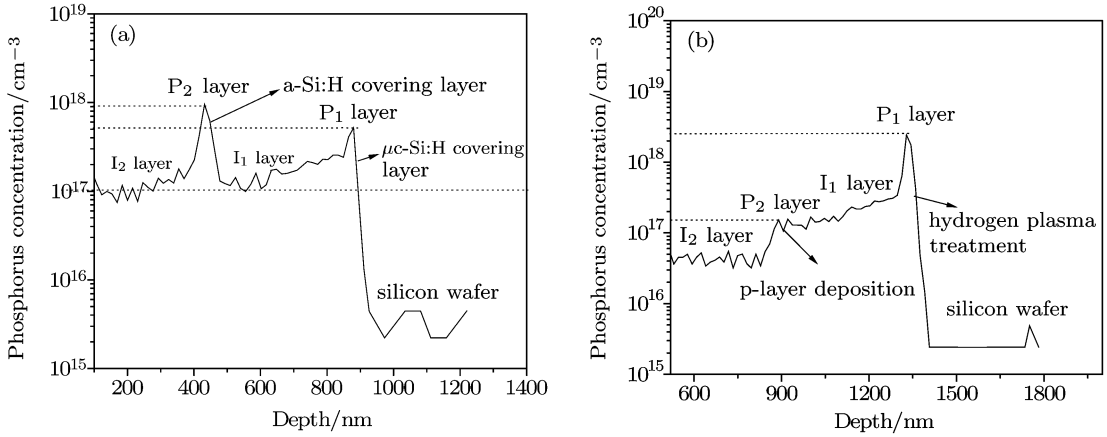


Fig. 2. Phosphorus concentration profile by SIMS measurement for a double p–i structure for (a) 'a-Si:H covering layer' (left) and 'μc-Si:H covering layer' (right) treatment, (b) 'p-layer deposition' (left) and 'hydrogen plasma (right)' treatment (structure: intrinsic layer I_2/p-doped layer P_2/intrinsic layer I_1/p-doped layer P_1/silicon wafer).

The phosphorus concentration of the P_1-layer deposited after a μc-Si:H covering layer treatment is smaller than that of the P_2-layer deposited after an a-Si:H covering layer one. The phosphorus concentration of the I_1-layer was similar to that of the I_2-layer (see Fig. 2(a)). The μc-Si:H covering layer treatment was better than the a-Si:H covering layer one. The μc-Si:H covering layer can be considered as a more suitable chamber treatment method to reduce phosphorus contamination. So we only investigate the effectiveness of a μc-Si:H covering layer for a covering layer treatment technique in the following study. The SIMS-profile in Fig. 2(b) showed phosphorus concentration of the P_2-layer deposited after a p-layer deposition in the order of 10^{17} cm^{-3} and that of the I_2-layer in the order of 10^{16} cm^{-3}, which showed that a p-layer deposition treatment is the best. The deposition of p-layer in a chamber reduces phosphorus contamination by compensation of phosphorus with boron. In addition, it etches away the phosphorus-contained materials because of high density atomic hydrogen in the high hydrogen diluted and high powered plasma. But the treatment technique could bring a large boron contamination. It is difficult to control. The hydrogen plasma treatment is not better than other techniques, which give a p-layer with sufficiently high phosphorus impurity in the order of 10^{18} cm^{-3} for the treatment technique (see Fig. 2(b)). Compared to the no contamination treatment sample (see Fig. 1), a decrease of concentration by a factor of 10^3 to the lowest contamination is attended for p-layer.

The p-layer plays role of a seed, window and doping layer for μc-Si:H p–i–n solar cell. Its properties are key factors for the crystalline growth of i-layer, and ultimately influence the characteristics of solar cell.[8] It is essential to understand the influence of the phosphorus contamination on the properties of p-layer. Figure 3 showed dark conductivities of p-layer at different treatment techniques after n-layer. There is no contamination for sample A, whereas there is no phosphorus contamination treatment after n-layer for sample B. Sample B exhibited a dark conductivity of 10^{-4} S/cm. Comparing its dark conductivity with that of sample A, we find that the reduction of its dark conductivity is attributed to phosphorus incorporation. Samples C, D and E corresponded to p-layer deposition, hydrogen plasma and μc-Si:H covering layer treatment after n-layer, respectively.

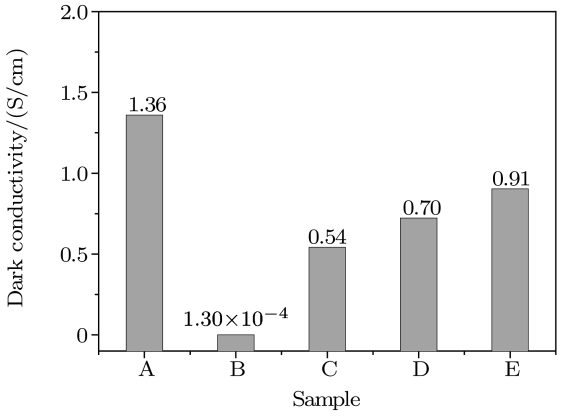


Fig. 3. Dark conductivities of p-layers prepared with different p-layer treatment time after n-layer: sample A (no phosphorus contamination); sample B (no phosphorus contamination treatment after n-layer); sample C (p-layer deposition treatment); sample D (hydrogen plasma treatment); sample E (μc-Si:H covering layer treatment).

All treatment techniques improved the dark conductivities of p-layers. The dark conductivity of sample E was similar to that of sample A, which showed

that μc-Si:H covering layer treatment was the best of all.

Several techniques for reducing the phosphorus contamination were effective by means of the reduction of the phosphorus concentration of p-layer and improvement of p-layer electrical properties. For μc-Si:H solar cells, the optimisation of pretreatment techniques led to a short-circuit current density increment (ΔJ_{sc}) shown in Fig. 4 compared to the no treatment sample. The sample C corresponded to the treatment of deposition of p-layer. The samples D and E corresponded to treatment of hydrogen plasma and a μc-Si:H covering layer. The hydrogen plasma treatment, deposition of p-layer and a μc-Si:H covering layer were desirable. The short-circuit current density enhancement of solar cell deposited after hydrogen plasma treatment was smaller than that for other techniques, probably because of giving a p-layer with sufficiently high phosphorus impurity. The μc-Si:H covering layer was more effective than other treatments. One possible explanation is that a μc-Si:H covering layer not only covers the phosphorus-contained coatings in the chamber but also etches away the phosphorus-contained materials because of high density atomic hydrogen in the high hydrogen diluted and high powered plasma.[9] In a word, the improvement of J_{sc} indicated decrease of phosphorus contamination. In addition, quantum efficiency (QE) of solar cells gives deeper insight into the J_{sc} behaviour.[10,11] The details for the QE measurement results were reported in our previous paper.[12]

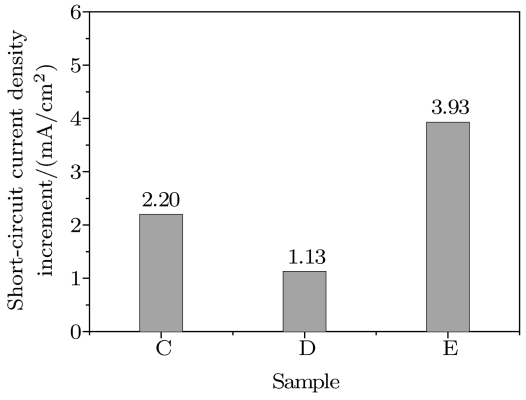


Fig. 4. Short-circuit current density increment of solar cells prepared with different treatment techniques: sample C (p-layer deposition); sample D (hydrogen plasma treatment); sample E (μc-Si:H covering layer).

Raman spectroscopy is a powerful tool for investigating the structural properties of μc-Si:H. Each device above was measured from the p-layer side and n-layer side using the wave of wavelength of 633 nm whose material up to a depth of above 500 nm contributes to the signal.[13,14] Figure 5 showed the crystallinity of them. The difference between p-layer side and n-layer side becomes smaller for treatment cells than that of sample B without treatment. It showed that the uniformity of i-layer microstructure is improved for treatment of solar cells, which partly led to the improvement of short-circuit current density.

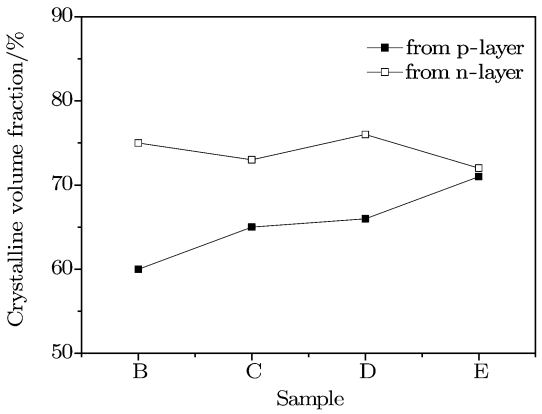


Fig. 5. Crystalline volume fraction of solar cells shown in Fig. 4 from p-layer side and n-layer side.

4. Conclusions

Several pretreatment techniques for controlling the phosphorus contamination for the deposition of μc-Si:H solar cell in a single chamber system were studied. These pretreatments consisted of hydrogen plasma pretreatment, deposition of p-type doped layer, a-Si:H or μc-Si:H covering layer between solar cells. The μc-Si:H covering layer treatment was the best. The treatments considerably reduced the phosphorus contamination and improved the short-circuit current density. The advantages of the pretreatments for the production process of μc-Si:H solar cells are: (1) it would not need substrates within the reactor during the whole treatment process after the deposition of a solar cell; (2) hydrogen, silane and diborane is already used to prepare silicon thin film, so it would not need special installation. From the industrial point of view, the treatment techniques would be preferable.

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