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Reduction of the boron cross-contamination for plasma deposition of p–i–n devices in a single-chamber large area radio-frequency reactor

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Abstract

In this article, a new treatment to reduce boron contamination of the interface between the p- and i- layer is presented. An ammonia flush, performed at 10 Pa for 1 min, after deposition of the p-layer considerably reduces the boron contamination at the p–i interface of amorphous silicon p–i–n solar cells prepared in a single-chamber reactor. This treatment avoids the need to move the substrate out of the reactor during the full deposition process of a solar cell, thereby reducing costs. The measurement of boron contamination depth profile in the i-layer was done by Secondary Ion Mass Spectroscopy and the effectiveness of the treatment was supported by quantum efficiency and I–V measurements of solar cells.

Keywords: Amorphous silicon; Solar cells; Boron contamination; Plasma processing and deposition

1. Introduction

Plasma-enhanced chemical vapor deposition (PECVD) of photovoltaic p–i–n solar cells in a single-chamber plasma reactor offers advantages of time and cost compared to multi-chamber processes which use separate reactors for production of the p-, i- and n-layers. The p-layer is a boron-doped silicon thin film deposited by plasma in a gas mixture containing silane and a boron source gas. In a single-chamber PECVD reactor, the silane plasma subsequently used to deposit the undoped silicon intrinsic film (i-layer) leads to the recycling of impurities [1]. Indeed, at the initial phase of this new PECVD step, the reactor walls, the pumping ducts and the coated substrate itself can release freshly deposited boron-containing molecular species which participate in the plasma chemistry during deposition of the i-layer. Boron contaminates the i-layer at the p–i interface and thereby weakens the strength of the critical electric field in the i-layer close to the p–i interface. This provokes a less efficient carrier separation just in this zone and leads to a reduced collection efficiency in the solar cell, resulting in a deterioration of the final solar cell performance [2]. Therefore, for mass production of solar cells in a single-chamber reactor, it would be advantageous if some treatment applied between the deposition of the p- and i-layers could reduce the boron contamination at the interface and thus maintain cell performance. The fall of boron concentration at the p–i interface should be as sharp as possible so that the transition between the p-layer and i-layer is abrupt. Various treatments with encouraging results have already been studied [3,4]. Recently, a new treatment using a water vapor flush has been introduced, allowing the deposition of cells with high performance (due to reduced boron cross-contamination); such a water flush surprisingly does not aggravate the light induced degradation [2]. Based on this preceding study, we examine in the present paper the effect of an

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ammonia flush on the boron contamination. One advantage of ammonia is that it is already established in standard industrial installations. We will compare the performances of cells prepared with no treatment, with the water vapor flush treatment, and with the new ammonia flush treatment.

2. Experimental details

The experimental apparatus is a modified version of the industrial KAI-S Plasma Box TM reactor commercialized by Unaxis Displays. It is a parallel plate capacitively coupled reactor, 47 cm wide × 57 cm long, with a 2.4 cm gap between the RF electrode and ground electrode. A loadlock chamber was used to introduce substrates into the reactor without breaking vacuum. Sequences of p–i layers were deposited on silicon wafers laid on a glass substrate 47 cm × 37 cm × 1 mm to test the ammonia flush treatment between the p- and i- layers. Trimethylboron (TMB), $B(CH_3)_3$, instead of diborane, B_2H_6, was used as the boron source gas because of its superior thermal stability in the hot reactor thereby causing less boron contamination [5]. The gas parameters used for the p-layer were: flow rates 70/60/1/50 sccm of $SiH_4/CH_4/TMB/H_2$ at 40 Pa; for the i-layer: flow rates 160/40 sccm of SiH_4/H_2 at 50 Pa. The excitation frequency was 40.68 MHz at 60 W RF power for an i-layer deposition rate of approximately 0.3 nm/s at a substrate temperature of 200 °C. The effectiveness of the treatment was evaluated by means of Secondary Ion Mass Spectroscopy (SIMS), tracing the boron and oxygen concentration depth profiles across the p–i interface, deposited on c-Si wafers [2]. The SIMS measurement of boron was performed using an $O^+{}_2$ ion beam, and the corresponding profile of oxygen was performed using a Cs^+ ion beam.

Solar cells were deposited in another KAI-S reactor, where the plasma con ditions were optimized for solar cell peformance as described in Ref. [2]. The deposition temperature of the a-Si:H layers and cells was 200° C keeping the pressure at 30 Pa and applying a RF power level of 60 W. The total feed gas flow was 150 sccm for the intrinsic layer deposition. To reduce powder formation the silane was diluted by hydrogen to a silane concentration of 70% during the i-layer deposition. Under these i-layer preparation conditions, deposition rates of 0.33 nm/s have been obtained. In this single-chamber reactor, 0.3 μm thick p–i–n a-Si:H solar cells were deposited on glass/TCO substrates (Type Asahi U, based on SnO_2:F). To obtain the full potential for high-efficiency a-Si:H solar cells, a buffer layer was inserted between the p- and the i-layer [2]. It should be noted that this buffer alone has usually already a beneficial effect on the boron cross contamination in the i-layer. Sputtered ITO and aluminium were used as a back contact. The boron contamination in the i-layer close to the p-layer was indirectly evaluated by performing voltage-dependent quantum efficiency measurements as well as by monitoring the global cell performance, in particular the cell fill factor [2]. The I–V characteristics were measured under AM 1.5 illumination using a Wacom WXS 140S-10 sun simulator. The cells were light-soaked for over 1200 h under the light of a high-pressure sulfur lamp at 50 °C. The spectrum of this microwave-powered sulfur lamp is close to the AM 1.5 spectrum and is adjusted to 100 mW/cm^2.

3. Results and discussion

3.1. SIMS analysis

Fig. 1 shows the SIMS boron profile for a p–i–p–i sandwich structure. The effect of an ammonia flush treatment between the p- and i-layer depositions is compared with the effect of no treatment. We observe a more abrupt transition of the boron concentration at the p–i interface in the case of the ammonia flush treatment, showing a reduced boron cross-contamination compared with no treatment. Water vapor treatment gives similar, intermediate results [2].

Fig. 2 compares the SIMS oxygen profiles of p–i–p–i structures treated with a water vapor flush and an ammonia flush. Clearly, one advantage of the ammonia treatment compared to the water vapor treatment is that ammonia does not introduce oxygen contamination into the reactor [2,6]. This might be important for microcrystalline silicon solar cells. The variation in the level of oxygen concentration in Fig. 2b is due to the difference in base pressure (atmospheric contamination) between the different gas lines used for p- and i-layer depositions.

3.2. Solar cell performance

Fig. 3a and b show the I–V characteristics for one cell prepared with ammonia flush treatment (1 min flush and pumping times) and one cell prepared with the water vapor flush treatment (5 min. flush and pumping times), before and after light-induced degradation. The changes in the characteristic for ammonia with 5 min flush and pumping times were insignificant and are omitted from the figure for

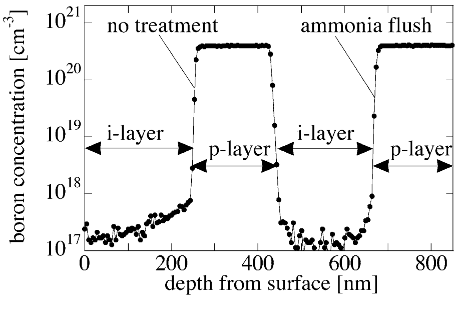

Fig. 1. SIMS profile of the oxygen concentration of p–i–p–i sandwich structures: (a) with water vapor flush treatments; and (b) with ammonia flush treatments. In all cases, the flush durations and the pumping durations were 1 min. The pressures during the flush are shown on the figures.

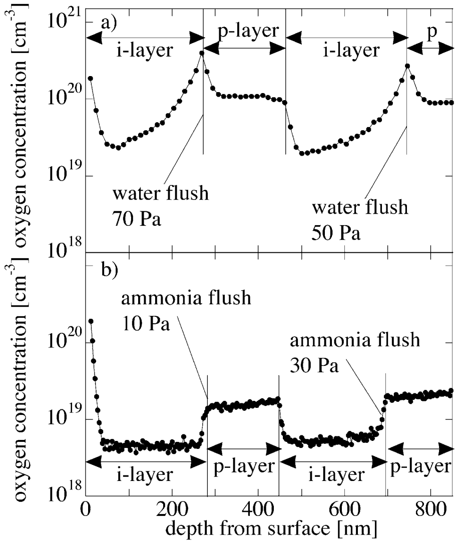

Fig. 2. SIMS profile of the oxygen concentration of p–i–p–i sandwich structures: (a) with water vapor flush treatments; and (b) with ammonia flush treatments. In all cases, the flush durations and the pumping durations were 1 min. The pressures during the flush are shown on the figures.

clarity. Ammonia-treated cells are comparable to the cells prepared with the water vapor flush except for a reduction in V_{oc} of 20 mV for the initial conditions. After light-induced degradation (Fig. 3b), the characteristics of the cells treated with the ammonia and water vapor flush are very similar, with fill factor 63.7%. Their performance is markedly superior to light-soaked cells prepared with no flush treatment in Ref. [2] (fill factor 61.1%).

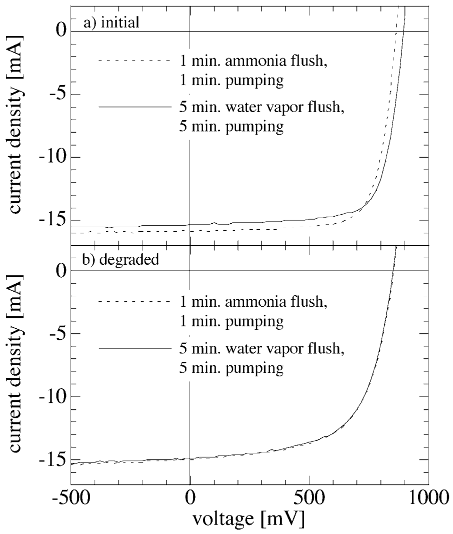

Fig 3. Effect of ammonia and water vapor flush treatments on the I–V characteristics of a-Si:H cells, about 1 cm^2 area; (a) before and (b) after light-induced degradation. The pressure during the flush was 10 Pa for both the ammonia and the water vapor treatments.

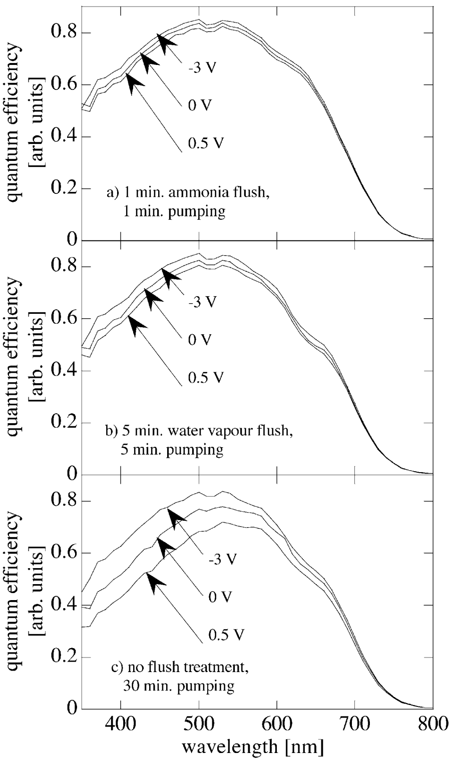

Fig 4. Effect of (a) ammonia flush, (b) water vapor flush, and (c) 30 min pumping (no treatment) on the bias-voltage-dependent quantum efficiencies before light-induced degradation. These data refer to the cells whose I–V characteristics are shown in Fig. 3a. The pressure during the flush was 10 Pa for both the ammonia and the water vapor treatments.

In Fig. 4a and b, the quantum efficiencies (before light degradation) of the cells prepared with ammonia flush and water vapor flush are shown. Quantum efficiencies in the blue region of these spectra show only a small bias-voltage dependence compared to the one in Fig. 4c for a cell prepared with no treatment between the p- and i-layers [2]. As is well known, a weak voltage dependence of the quantum efficiency in the blue region indicates a good carrier collection in the i-layer close to the p-layer, and suggests, therefore, a low boron contamination at the p–i interface. The cell with the least bias-voltage dependence, in Fig. 4a, corresponds to the solar cell prepared with the ammonia flush treatment. Again, there was no significant difference for ammonia flush and pumping times of 5 min. It may be possible to reduce the ammonia flush and pumping times below 1 min and still maintain the observed performance.

3.3. Discussion of the effect of ammonia on boron contamination

We speculate that the ammonia flush creates B–N complexes which selectively fix boron in the p-layer. The plasma chemistry of boron/ammonia has been previously investigated by infrared absorption spectroscopy [7]. Mixing ammonia and diborane gases as precursors leads to a rich variety of gas phase precursors. Solid compounds of diammoniate of diborane $[H_2B(NH_3)_2]$+$[BH_4]$ and aminoborane ($H_2B{=}NH_2$) are produced [7]. We can suppose that similar reactions occur between boron and ammonia, for example, the formation of boron nitrides B/N/H, or amines $B(NH_2)_3$ instead of boric acid $B(OH)_3$ when using water [2,8].

4. Conclusions

A new gas treatment for controlling the boron contamination at the p–i interface has been studied. This treatment consists of an ammonia flush between the deposition of the p-layer and the deposition of the i-layer, the substrate remaining in the reactor. The exposure of the reactor walls and substrate surface to the ammonia considerably reduces the boron contamination at the p–i interface because the transition between the p-layer and the i-layer is observed to be abrupt. The advantages of the ammonia treatment for the production process of amorphous silicon photovoltaic modules are: (1) a single-chamber can be used for the full solar cell deposition process; (2) the substrate can remain within the reactor during the whole deposition process; (3) the treatment time is short (1 min flush and 1 min pumping is sufficient). Moreover, since ammonia is often already installed in the gas line for other plasma processes, it would not in this case need special installation.

Performances of cells prepared with the ammonia treatment are comparable to those of the cell prepared with the water vapor treatment [2] and reach cell specifications as obtained with a standard multi-chamber process: after degradation during 1000 h at 50 °C, a V_{oc} value of 859 mV and a fill factor of 63.7%. We note that there is no worsening of the cells' degradation due to the ammonia flush. We speculate that N–H groups react with boron compounds to form stable boron amine or nitride compounds, which may be fixed in the p-layer.

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