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Plasma Deposition of p-i-n Devices using a Single PECVD Chamber: Study of the Boron Contamination

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Plasma-enhanced chemical vapour deposition (PECVD) of photovoltaic p-i-n solar cells in a single 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]. It can cause boron contamination from the reactor walls, pumping ducts or layer itself. The resulting boron contamination of the i-layer degrades the performance of the final solar cell (Fig. 1). Therefore, for mass production of solar cells in a single chamber reactor, it would be practical if some plasma treatment applied between the deposition of the p- and i-layers could reduce the boron contamination and so maintain the cell quality.

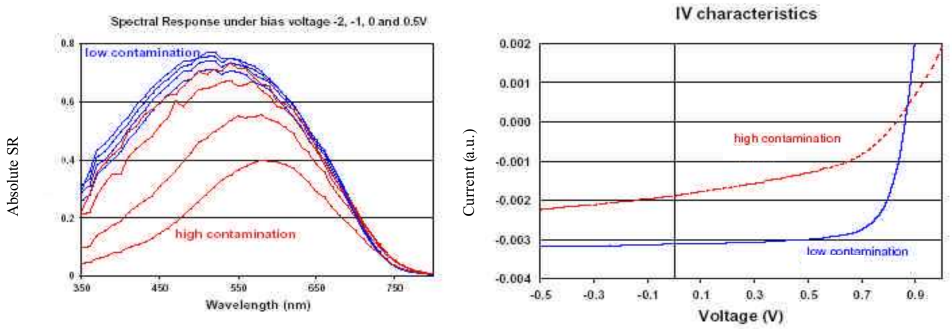

Fig. 1 : Deterioration of cell performance with boron contamination : spectral response and IV characteristics

In this work, various techniques to reduce the boron contamination were investigated. Their effectiveness was evaluated by means of Secondary Ion Mass Spectroscopy (SIMS), to study the boron concentration depth profile across the p-i interface. For the purposes of p-i-n solar cell fabrication, the boron contamination of the i-layer should not exceed 10^{17} atom/cm^3. Trimethylboron (TMB), $B(CH_3)_3$, instead of diborane, B_2H_6, was used as the boron source gas because it has superior thermal stability in the hot reactor and causes less contamination

[2]. The experimental apparatus is a modified version of the industrial KAI-S reactor commercialised by Unaxis Displays. It is a parallel plate capacitively-coupled reactor of dimensions 47 cm width × 57 cm length with 2.4 cm height between RF electrode and ground electrode. A loadlock chamber was used to introduce substrates in the reactor without breaking vacuum. Sequences of p-i layers were deposited on silicon wafers put on a glass substrate 47 cm × 37 cm × 1 mm to test different procedures between the p- and i-layers. 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 0.4 mbar; for the i-layer: flow rates 160/40 sccm of SiH_4/H_2 at 0.5 mbar. The excitation frequency was 27.12 MHz at 60 W RF power for an i-layer deposition rate of approximately 0.3 nm/s at substrate temperature of 200 °C. The procedures investigated were: pumping between p-layer deposition and i-layer deposition, gas purging, and various plasma treatments of the p-layer.

First, it was checked if physisorption or backstreaming of the TMB dopant gas was a source of contamination [2]. The substrate was exposed to a TMB gas flow in the reactor, without plasma, for 20 minutes before plasma deposition of an i-layer. This i-layer was found not to be contaminated, showing that the boron contamination is not simply due to traces of TMB gas which are desorbed from the reactor walls, pumpline, or pumps but is due to boron-containing radicals created during p-layer deposition. However, following plasma deposition of a p-layer, flushing with an inert gas (Fig. 2) or pumping for several minutes were both ineffective in preventing boron contamination of the i-layer. All-night pumping did reduce the contamination to an acceptable level (Fig. 2), which suggests that the boron source was slowly desorbed, or that the boron was slowly transformed and eventually immobilised in the p-layer.

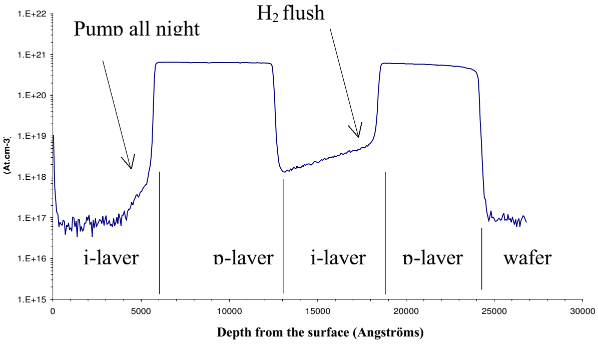

fig. 2 : Boron SIMS profile H2 flush and pump all night

The boron contamination is trapped in the reactor with a confinement time much longer than the plasma processing time of a solar cell, which means that some procedure must be found to reduce the release of boron during i-layer deposition to maintain a high throughput.

Two types of plasma treatment were found to give i-layers with sufficiently low contamination, although it was necessary to remove the substrate into the loadlock to protect the deposited p-layer, otherwise the solar cell performance was degraded. The first treatment was 10 minutes of plasma etch cleaning (using a SF_6, O_2 and He gas mixture) which removed the p-layer deposit from the reactor walls and eliminated almost all boron contamination (Fig. 3) of the subsequent i-layer. This may appear a trivial result, but the implication is that the boron from the p-layer of the substrate itself does not contribute to i-layer contamination. This is also the case in multi chamber processing.

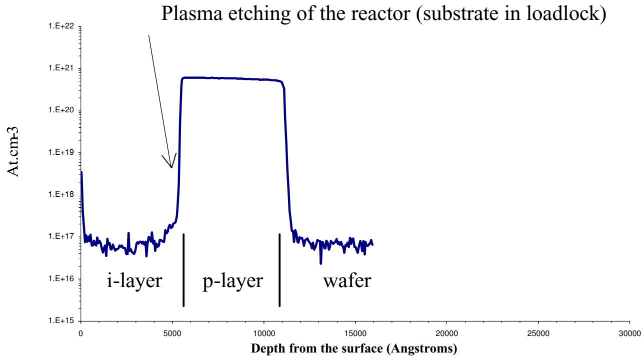

Fig. 3 : Boron SIMS profile, etch (substrate in loadlock) between p-layer and i-layer

The second strategy is to immobilise the boron in the p-layer on the reactor walls by means of an oxidising plasma: 10 minutes of plasma treatment with CO_2 [3] or O_2 (Fig.4) between the p-layer and i-layer (always with substrate in the loadlock) was observed to eliminate almost all boron contamination. Exposure to O_2 gas alone would be expected to oxidise boron in the top monolayer, but flushing with O_2 gas was in fact ineffective. Therefore, efficient oxidation requires plasma-produced radicals, and/or oxidation of sub-surface boron assisted by ion bombardment. Boron desorption by ion bombardment alone is insufficient because the same procedure using an argon or hydrogen plasma, instead of oxygen, did not reduce boron contamination of the i-layer.

Contamination was reduced, but not eliminated, by buring the boron on the reactor walls by a thin i-layer deposited while the substrate was in the loadlock. This shows that the boron source is in the reactor, not in the pumping line or pumps, because the pathlength of silane radicals out of the reactor is not more than a few cm. From the industrial point of view, however, an *in situ* plasma treatment which does not require moving the substrate to the loadlock would be preferable. It was clear that i-layer deposition at 60 W RF power, corresponding to 0.3 nm/s, caused too much plasma-induced desorption of boron from the previous p-layer. But when the RF power was reduced to 30 W to deposit at only 0.05 nm/s, the boron desorption rate was low enough to avoid excessive contamination, presumably due to the decrease in ion flux and energy in the low power plasma. Moreover, since a thin intrinsic buffer layer was sufficient to bury the boron in the p-layer from the higher power plasma, a satisfactory procedure was to initially deposit a 10 nm i-layer at 0.05 nm/s before accelerating to 0.3 nm/s. This procedure prolongs the process time by 3 minutes, and offers an alternative to removing the substrate to the loadlock. The time penalty could be minimised by finding a compromise between the RF power ramp rate and the level of contamination which can be tolerated.

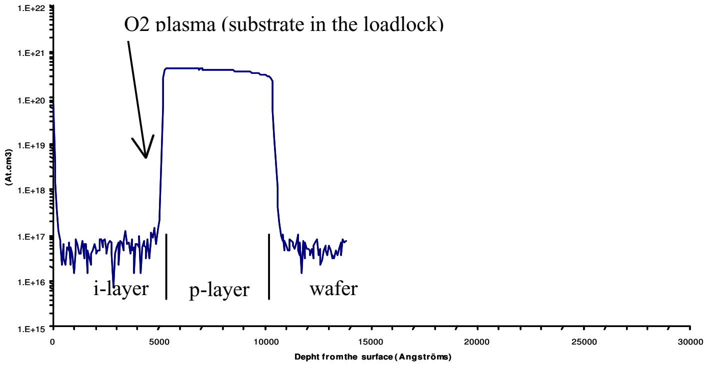

Fig. 4 :Boron SIMS profile, O_2 *plasma (substrate in loadlock) between p-layer and i-layer*

To conclude, various plasma treatments between the deposition of the p- and i-layers were investigated to avoid boron contamination during fabrication of photovoltaic solar cells in a single chamber reactor. Plasma etch cleaning and plasma oxidation are both effective provided that the substrate is removed to the loadlock during the treatment. Alternatively, the i-layer can be deposited directly after the p-layer provided that the plasma power is strongly reduced during the deposition of a shielding layer to prevent desorption of the boron from the underlying film.

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[1] P. Roca i Cabarrocas, S. Kumar, and B. Drévillon, J. Appl. Phys. **66** (1989) 3286

[2] A. Lloret, Z.Y. Wu, M.L. Thèye, I. El Zawawi, J.M. Siéfert, and B. Equer, Appl. Phys. A **55** 573 (1992).

[3] M. Kubon, N. Schultz, M. Kolter, C. Beneking, and H. Wagner, Proc.12th European Photovoltaic Solar Energy Conference, Amsterdam (1994), p. 1268