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Single-chamber processes for a-Si:H solar cell deposition

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ABSTRACT

For deposition of a-Si:H p-i-n solar cells, a single-chamber plasma enhanced chemical vapor deposition process at the frequency of 13.56 MHz is developed. A 40×40 cm² deposition chamber, which represents typical industry reactors equipped with showerhead electrodes is employed. Various methods are applied to reduce the boron-cross contamination from the boron-doped p-layer into the intrinsic layer, which is considered to reduce solar cell efficiency by losses especially in the short wavelength range. Three different device configurations and four different chamber treatment methods are studied, aimed to reach stable device efficiencies comparable to multi-chamber systems at minimum chamber treatment effort and treatment time. An ex-situ CO₂-plasma treatment applied after deposition of the p-doped layer is found to be effective to reduce boron-cross contamination. However, this CO₂-treatment is a time-consuming process step for production. We found a less time consuming treatment: by a chamber evacuation to 9×10^{-7} mbar subsequent to p-layer deposition. Initial and stable efficiencies of 10.2% and 7.7%, respectively, were obtained. This latter treatment results in a sharp drop of the boron concentration from $\sim 5 \times 10^{20}$ cm⁻³ in the p-doped layer to $\sim 10^{17}$ cm⁻³ in the intrinsic layer. For comparison of different reactor geometries and their influence on the cross-contamination we used a small-area (10 \times 10 cm²) lab-type reactor.

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1. Introduction

Single-chamber processes for thin-film a-Si:H solar cell production can be economically preferable compared to multichamber deposition processes since there is considerable saving in capital. However, a major drawback of single-chamber processes is the cross-contamination of doping atoms [1–11]. In particular, during the p-layer deposition for p-i-n solar cells, boron doped material covers the counter electrode and the reactor walls. During the subsequent i-layer deposition, boron may be etched from the chamber wall by hydrogen and may be incorporated into the i-layer, i.e. boron recycling takes place [1]. To produce state-of-the-art solar cells this boron contamination needs to be avoided or reduced to a tolerable level. Encouraging efforts for the application of single-chamber processes have been reported with CO₂-plasma (ex-situ) chamber treatment at the p/i-interface [2-4]. However, this treatment method requires a long treatment time due to the required transfer of the substrate out of the process chamber. In-situ chamber treatments with the substrate remaining in the chamber during deposition of all

* Corresponding author. E-mail address: t.merdzhanova@fz-juelich.de (T. Merdzhanova). silicon layers may save much treatment time. Indeed, the application of an in-situ H_2O - or NH_3 -flush at the p/i-interface was reported to result in a rather short treatment time, a low boron concentration in the intrinsic layer and high efficiency of the a-Si:H solar cell [5,6]. Some other in-situ treatments, however, like an H_2 -plasma flush and an O_2 -plasma at the p/i-interface [7,8] lead to a high boron concentration in the i-layer and reduced solar cell efficiency.

The aim of the present work is to develop a single-chamber process for industry relevant reactors with a size 40×40 cm² for deposition of a-Si:H solar cell with high stabilized efficiencies. We study different process chamber treatment methods in order to reduce the boron-cross contamination in the i-layer and the treatment duration as well as to increase treatment effectiveness. Also the influence of the device configuration e.g. by the insertion of additional layers between i-layer and p-layer on the boron cross-contamination near the p/i-interface and the stabilized solar cell performance are investigated.

2. Experimental details

The thin-film a-Si:H p-i-n solar cells were prepared using plasma-enhanced chemical vapor deposition (PECVD) system. An

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in-line deposition system with a substrate size of $40 \times 40 \text{ cm}^2$ was fabricated by "Von Ardenne Anlagentechnik" (Germany) and contains three deposition chambers and one load lock (for details see [9]). For comparison of different reactor geometries and their influence on the cross-contamination we used a small-area $(10 \times 10 \text{ cm}^2)$ deposition system that was fabricated by Material Research Group Inc., (USA). This lab-system contains five deposition chambers. For the present work, only one deposition chamber and a load lock were used of both deposition systems. Also in both cases, for plasma excitation the RF frequency of 13.56 MHz was used. The distance between RF and grounded electrode was 1 cm. The substrate temperature ($T_{\rm S}$) was ~180 °C and ~200 °C during deposition of p-i-n solar cell at 40×40 cm² and 10×10 cm² systems, respectively. The process gas is fed into the plasma through showerhead $(40 \times 40 \text{ cm}^2)$ and longitudinal flow $(10 \times 10 \text{ cm}^2)$ electrodes. The $40 \times 40 \text{ cm}^2$ deposition reactor has a special design with well defined pumping slits around the plasma zone for direct pumping of the deposition gases, representing typical industrial reactors. High pressures of 4 mbar and discharge powers of 0.02 W/cm² were used for deposition of the a-Si:H i_1 - and i_2 -layers (p- i_1 - i_2 -n configuration). The i_1 -layer has a SiH₄/H₂ flow of \sim 41/1030 sccm, yielding to a lower deposition rate compare to i2-layer where the H2 flow was reduced to 339 sccm resulting in a deposition rate of 0.3 nm/s. Different deposition conditions were used for deposition of a-Si:H simple i-layer (p-i-n configuration) deposited in the 10×10 cm² deposition chamber with parallel plate electrodes. A low pressure of 1.3 mbar and a low discharge power of 0.01 W/cm², yielding a deposition rate of 0.2 nm/s were used. The SiH₄/H₂ flow was \sim 24/ 24 sccm. As substrates commercial Asahi U-Type transparent conductive oxide (TCO) glasses were used. For the back contact, sputtered ZnO/Ag back reflectors or thermally evaporated Ag pads $(1 \times 1 \text{ cm}^2)$ were applied. The thickness of the intrinsic layer was always \sim 300 nm and the deposition rate was \sim 0.2–0.3 nm/s.

Solar cells were prepared in three different device configurations, as shown schematically in Fig. 1. Here, (I) is a standard p–i–n configuration. In configuration p–i₁–i₂–n (II) an additional thin i₁-layer of reduced source gas silane concentration $(SC=[SiH_4]/[SiH_4]+[H_2])$ and deposition rate is placed subsequent to the p-layer deposition and in configuration p–b–i₁–i₂–n (III) a buffer b-layer is inserted between p and i₁. For the b-layer the trimethylboron (TMB) flow is gradually decreased at the p–b/i-interface, while abrupt switching off of the TMB flow was applied at p/i-interface (see Fig. 1). The CH₄ flow was kept constant during deposition of the p-and b-layers.

Four different chamber treatment methods applied at p/i- (or p-b/i-) interface for both deposition systems are described in Table 1. As indicated in Table 2, treatment A was only applied in the $40 \times 40 \text{ cm}^2$ system, while treatment C only in $10 \times 10 \text{ cm}^2$ system. The influence of the different chamber treatments and device configurations were analyzed by *I–V* characteristics, voltage-dependent quantum efficiency (QE), and light-induced degradation experiments of solar cells. A Wacom, class A solar simulator (100 mW/cm²) was used at 25 °C for the *I–V* characterization of the solar cells. QE measurements were performed at 25 °C under short-circuit conditions. Light-soaking experiments were performed under AM1.5 light at 50 °C up to 1000 h under open-circuit conditions. Secondary ion mass spectrometry (SIMS) was used to quantify the boron concentration in the i-layer.

3. Results and discussion

3.1. Influence of process chamber treatment on solar cell parameters

Fig. 2 shows the I-V characteristics and the quantum efficiency (QE) spectra of a-Si:H solar cells with device configuration type (II) (see Fig. 1b) deposited by a single-chamber process in the



Fig. 1. Schematic drawing of the solar cells with device configurations p-i-n (I), $p-i_1-i_2-n$ (II) and $p-b-i_1-i_2-n$ (III). As indicated in the lower part, the silane and TMB concentrations were varied as a function of deposition time to obtain the intrinsic i_1 - and i_2 -layers, and the buffer (b-) layer deposited between the p-doped and i_1 -layer.

Table 1

Different chamber treatments applied at p- (or b-) and i-interface.

| (A) Continuous deposition (in-situ) | (B) Chamber evacuation (in-situ) | (C) H ₂ O-flush (in-situ) | (D) CO ₂ -plasma (ex-situ) |
|--|---|--|---|
| plasma discharge kept on through p-, i- and n- layers; abrupt switching off of boron flow at p/i-interface; | plasma is turned off after p-layer; Ar flush into process gas mixture (5 min); | 12. see 1-2 in (B);3. gases pumped down; | 13. see 1-3 in (B); transfer of sample into load lock and of dummy carrier into chamber (3 min); |
| | 3. gases pumped down to $p \sim 9 \times 10^{-7}$ mbar; | 4. flush with H ₂ O vapor at $p \sim 10^{-1}$ mbar (10 s – 10 min); | 5. CO ₂ -plasma (2 min); |
| | 4. start of i-layer deposition after $T_{\rm S}$ stabilization; | 5. pump down of gases; 6. see 4 in (B); | 67. see 2-3 in (B); 8. replacement of dummy carrier in chamber by sample; 9. see 4 in (B); |

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