

SIMULTANEOUS BORON EMITTER DIFFUSION AND CRYSTALLIZATION OF TOPCON LAYERS VIA RAPID VAPOUR-PHASE DIRECT DOPING

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ABSTRACT: The alternative boron emitter diffusion process rapid vapour phase direct doping (B-RVD) is applied to *n*-type silicon wafers with tunnel oxide passivated contact (TOPCon) rear sides. A variation of the B-RVD process parameters led to an increase of the emitter depth and less pronounced increase of the surface concentration with increasing process temperature, time and B₂H₆ concentration. For the first time, a simultaneous crystallization of the phosphorus doped amorphous silicon a-Si(n) layer in the TOPCon layer during the B-RVD process is investigated. For this, the B-RVD process with the lowest tested process temperature of 900 °C and with the lowest determined emitter saturation current density J_{0e} of 13 fA/cm² and the highest bulk lifetime of > 6500 μs was chosen. The transformation of a-Si(n) to poly-Si within this combined process is demonstrated. Directly after the RVD process, TOPCon layers are already very well passivating the surfaces. An additional hydrogenation step leads to further improvement. On a solar cell precursor fabricated with simultaneous a-Si(n) crystallization on the rear side and B-RVD emitter diffusion on the front side promising results with an iV_{OC} of ≥ 700 mV and an implied fill factor (*iFF*) of 84.7 % were measured.

Keywords: Boron Diffusion, Passivating Contact, Annealing

1 INTRODUCTION

Rapid vapour-phase direct doping (RVD) is an alternative emitter formation process without formation of a silicate glass. Instead, diffusion takes place directly from the gas phase using dopant precursors like B₂H₆ or PH₃ in hydrogen atmosphere [1–3]. The resulting emitter profile depends on the dopant concentration in the gas phase that can be adjusted during the process leading to higher flexibility compared to conventional diffusion. In contrast to a conventional diffusion process with the formation of a silicate glass, where the concentration of the dopant source cannot be easily changed and the glass remains on the surface. For example, with RVD an in-situ dopant-free drive-in step is feasible simply by switching to an inert atmosphere. Combining boron emitters formed by RVD (B-RVD) at ≥ 980 °C with the tunnel oxide passivated contact (TOPCon) rear side structure [4] fabricated after emitter diffusion, solar cell efficiencies up to 24 % were already demonstrated [2].

TOPCon consists of an ultra-thin interfacial oxide (SiO_x) on which an amorphous silicon (a-Si) layer is deposited [4]. After deposition, a high-temperature annealing step is necessary (leading to crystallization of the a-Si layer to a poly-Si layer, dopant diffusion and – depending on layer and process conditions – also pinhole formation in the tunnel oxide). This process is typically done in inert atmosphere at temperatures in the range of 800 – 1050 °C.

As both, the RVD process and the crystallization of the TOPCon layer take place at elevated temperatures, the whole process sequence could be simplified by combining the two processes. A schema of the final structure with simultaneous emitter diffusion and TOPCon crystallization is depicted in Figure 1. Hence, it could be possible to skip one high temperature process in the process sequence. In this case TOPCon layers have to be deposited prior to the B-RVD process and the crystallization has to take place during the B-RVD

process. Such a simultaneous process was already applied for *p*-type cells with TOPCon crystallization during POCl₃ diffusion [5]. However, the process took place at 900 °C and below and boron diffusion requires higher temperatures.

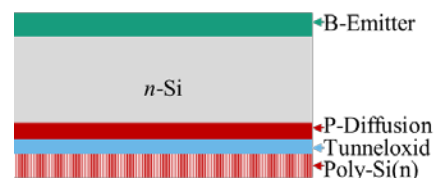


Figure 1: Schema of a cell precursor with simultaneously diffused emitter on the front side and crystallized TOPCon layer (tunnel oxide plus crystallized poly-Si(n)) on the rear side via RVD.

To combine the B-RVD process with the TOPCon crystallization, either a reduction of the RVD process temperature or an adaption of the TOPCon layers to withstand higher crystallization temperatures than studied in previous contributions have to be realized.

In this contribution first results of a variation of the RVD process parameters (temperature, time and B₂H₆ concentration) mainly with the aim to reduce the thermal budget are presented. Emitter properties and bulk lifetimes are analysed. One process is chosen for investigation of the simultaneous TOPCon crystallization and B-RVD emitter formation process. This is investigated with respect to i) stability of the TOPCon layer against in-diffusion of boron, ii) passivation of the TOPCon layer after the RVD process and additional hydrogenation and iii) implied open-circuit voltage of the passivated final cell precursor.

2 EXPERIMENTAL PROCEDURE

For all experiments *n*-type FZ wafers (1 Ωcm, 200 μm thick, shiny-etched) were used. Some samples were directly diffused after a cleaning step (RCA procedure) using the B-RVD process in the tool RTCVD160 designed for epitaxial growth [6]. A scheme of the chamber of this tool is depicted in Figure 2. The process gas flows between two rows of silicon samples standing on quartz carriers (not depicted). Due to the temperature profile in this tool, only one position per row can be used for homogeneous diffusion processes. As the rear side of the samples is in contact with the quartz carrier (separated by Si-dummies), the process is not symmetric.

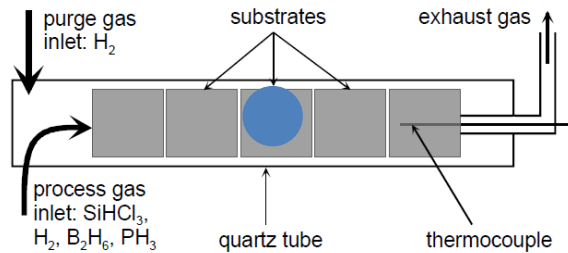


Figure 2: Principle of the diffusion chamber in the tool RTCVD160, adapted from [6]. Only one row of samples is visible, the second one is parallel to the first one and the process gases flow between the two rows. Due to the temperature profile, only one position per row can be used (marked in blue).

Emitter profiles were measured by electrochemical capacitance voltage profiling (ECV) for different diffusion temperatures, times and B_2H_6 concentrations in hydrogen atmosphere. The resulting bulk lifetimes of some wafers were measured with a Sinton WCT-120 quasi-steady-state photoconductance (QSSPC) lifetime tester after etch back of the emitter using KOH and passivation by AlO_x .

One process was chosen for simultaneous emitter diffusion and crystallization of the phosphorus doped a-Si(n) layer in the TOPCon layer. For this experiment, FZ wafers were first thermally oxidized to prevent additional bulk defect recombination [7,8]. Samples with TOPCon layers (50 nm a-Si(n) deposited by PECVD on a 1.6 nm thick thermally grown tunnel oxide (TO)) on the rear side (RS) and on both sides (BS) were prepared. Symmetrically processed samples obtained an additional SiO_2 layer on both sides deposited by PECVD to prevent boron diffusion into the TOPCon layer. Then the samples were processed in the RTCVD160 either in pure hydrogen atmosphere or with added B_2H_6 .

The resulting doping profiles were measured by ECV, the layer thickness and crystallinity of the poly-Si layer in the TOPCon layer by ellipsometry, the effective lifetime (τ_{eff}) and implied open-circuit voltage (iV_{OC}) by calibrated photoluminescence imaging (PLI) and QSSPC. The lifetime measurements were performed directly after the high temperature processing and after additional hydrogenation of the TOPCon layer and emitter passivation via AlO_x deposited by atomic layer deposition (ALD). The process flow for the different samples is depicted in Figure 3.

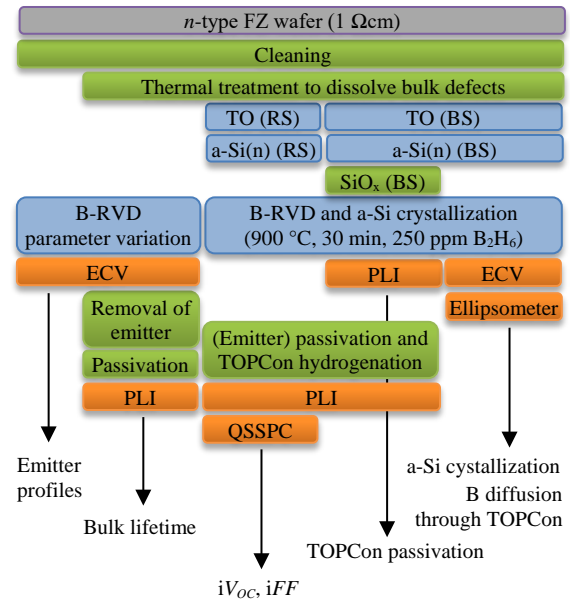


Figure 3: Process flow of samples described in this contribution.

3 RESULTS

3.1 B-RVD emitters

Emitter profiles were measured after processes with a variation of temperature, time and B_2H_6 concentration in the hydrogen atmosphere. Profiles and corresponding sheet resistance (R_{SH}) values are depicted in Figure 4.

The emitter profiles are between 100 nm and 400 nm deep and the depth increases with time and temperature as expected for a diffusion process. For increasing B_2H_6 concentration, there seems to be a saturation of the incorporated boron atoms for a B_2H_6 concentration above 750 ppm. Most applied process parameters lead to boron surface concentrations between $3 \times 10^{19} \text{ cm}^{-3}$ and $6 \times 10^{19} \text{ cm}^{-3}$ with a minor increase with increasing process temperature and time. This behaviour is most probably influenced by an autodoping effect in the applied tool. Only a higher B_2H_6 concentration leads to an increase of the surface concentration to $> 10^{20} \text{ cm}^{-3}$.

For a solar cell electrical properties like the bulk lifetime and the recombination at the front side given in the emitter saturation current density J_{0e} are important quantities. However, bulk lifetimes of all passivated samples depicted in Figure 4 were low after the processes and resulting J_{0e} values could not be evaluated. Low lifetimes were most probably caused by activation of intrinsic defects in the FZ material [7,8]. The activation can be prevented by applying a thermal pre-treatment. This was done in subsequent experiments. However, to simulate J_{0e} values and compare the different profiles the program EDNA [9] was used (depicted in Figure 4). J_{0e} values increase with increasing process temperature and partly with increasing time and B_2H_6 concentration. The best process regarding low J_{0e} values seems to be the one with the lowest process temperature of 900 °C.

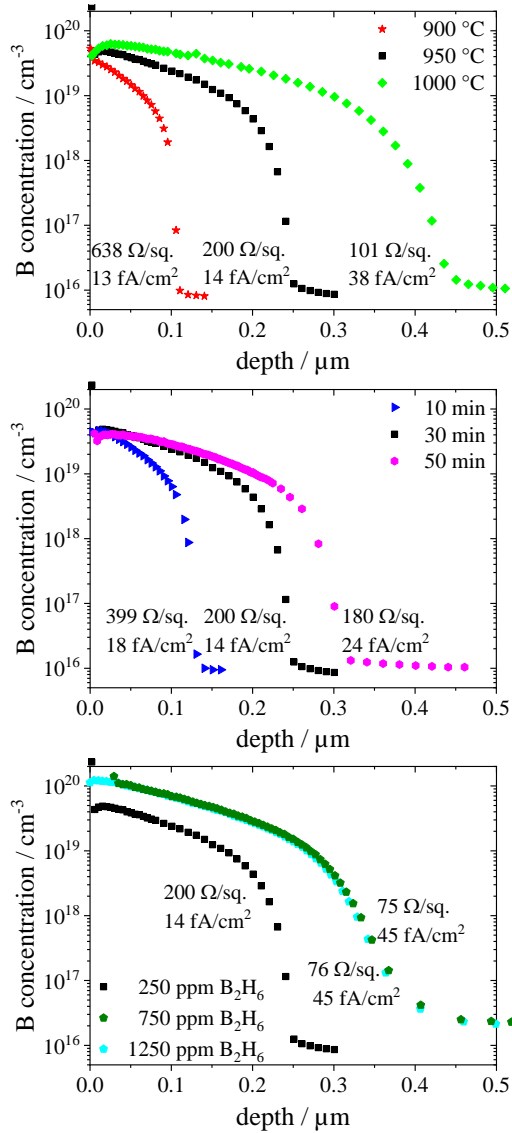


Figure 4: Boron profiles after RVD processes dependant on process temperature (top), process time (middle) and doping gas concentration (bottom) measured by ECV. If not mentioned otherwise, process parameters are $T = 950\text{ }^{\circ}\text{C}$ for 30 min and a dopant gas concentration of 250 ppm B_2H_6 . For each profile the sheet resistance (R_{SH}) given in $\Omega/\text{sq.}$ was calculated and the emitter saturation current densities (J_{0e}) given in fA/cm^2 were simulated using the software EDNA [9] assuming an adapted surface recombination velocity for the specific surface concentrations passivated with AlO_x deposited by thermal ALD according to [10].

The bulk lifetime was determined in a separate experiment for selected processes. After the B-RVD processes the emitters were etched back with KOH ($\geq 5\text{ }\mu\text{m}$ on both sides) and the samples were passivated with AlO_x . Assuming a good surface passivation, the measured effective lifetime (Table 1) is limited by the bulk lifetime. Lifetimes are high after the B-RVD processes, however a decrease in bulk lifetime with increasing process temperature can be observed. The reason for this is most probably an increased contamination with imurities as already stated in [2].

Table 1: Effective lifetimes τ_{eff} of B-RVD samples treated for 30 min at different temperatures. Measurements were done after etch back of the emitter and passivation with AlO_x using QSSPC (evaluated at an injection level of $1 \times 10^{15}\text{ cm}^{-3}$).

temperature / $^{\circ}\text{C}$	τ_{eff} / μs
900	6828
950	3493
1000	1406

For the first experiment with simultaneous crystallization of the a-Si layer in the TOPCon layer during the B-RVD process, the process with the lowest temperature of $900\text{ }^{\circ}\text{C}$ for 30 min was chosen as it offers a similar thermal budget as the optimum TOPCon high-temperature annealing conditions [11].

3.2 Doping profile in and below TOPCon layers

For the combined process of B-RVD on the front side and crystallization of the a-Si(n) layer in the TOPCon layer on the rear side of the samples, the crystallization was confirmed using ellipsometry measurements. Boron diffusion through the phosphorus doped poly-Si(n) layer has to be avoided to prevent the formation of a p-n junction on the rear side. In the current setup, the rear side of the wafers faces the quartz carrier. An ECV measurement on this side (green curve in Figure 5) shows a net phosphorus doping profile below the TOPCon layer as required for solar cells. But if TOPCon faces the process gas (red curve in Figure 5) boron diffuses through the TOPCon layer and overcompensates the phosphorus from the poly-Si(n). The final profile looks very similar to the one on bare silicon. In contrast to phosphorous diffusion in c-Si, there is no blocking effect [12] of the boron diffusion by the P-doped poly-Si layer. If the B-RVD process would be carried out in a setup similar to a conventional furnace with both sample sides facing the process gas, the rear side would have to be protected from boron diffusion.

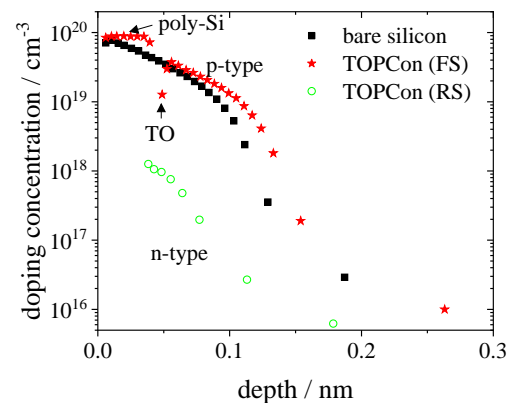


Figure 5: Doping profiles of samples with and without TOPCon layers on gas (FS) and carrier (RS) side after RVD measured by ECV. The poly-Si layer and the tunnel oxide (TO) of the TOPCon layer are indicated in the graph.

3.3 TOPCon passivation

TOPCon layers might already have high passivation qualities after annealing in H_2 atmosphere. To investigate this, symmetric samples with TOPCon layers on both sides were treated with a B-RVD process. The samples were

protected with diffusion barriers (SiO_2) on both sides prior to the process to prevent indiffusion of boron during the process into the wafer through the TOPCon layers (see section 3.2). The effective lifetime of this sample is depicted on the left side of Figure 6. The effective lifetime around $1370 \mu\text{s}$ confirms a very high passivation quality of TOPCon layers directly after the B-RVD process.

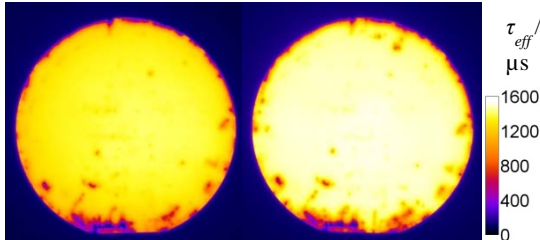


Figure 6: Effective lifetimes of a sample with TOPCon layers on both sides processed at $T = 900 \text{ }^\circ\text{C}$ for 30 min with 250 ppm B_2H_6 after RVD (left) and after an additional hydrogenation (right) measured by modulm-calibrated PLI at 1 sun.

Typically, TOPCon layers are hydrogenated after annealing to improve the passivation quality. This was done by AlO_x deposition and FGA leading to a further improvement of the effective lifetime to around $1480 \mu\text{s}$ (right side of Figure 6). For excellent passivation qualities an additional hydrogenation process seems to be necessary. The high passivation quality confirms that TOPCon layers can be successfully annealed during the B-RVD process.

3.4 Implied open-circuit voltage

The potential of the simultaneous emitter diffusion and TOPCon crystallisation process via B-RVD for solar cells was tested with cell precursors. They obtained an emitter on the front side (B-RVD: $900 \text{ }^\circ\text{C}$, 30 min, 250 ppm B_2H_6) and a TOPCon layer on the rear side that was crystallized during the B-RVD process. These samples allow for evaluation of the implied open-circuit voltage (iV_{OC}) from PLI measurements (example in Figure 7). A high iV_{OC} of $\geq 700 \text{ mV}$ is determined in the inner part after AlO_x -based TOPCon hydrogenation. An evaluation of QSSPC measurements confirmed this iV_{OC} and shows an implied fill factor (iFF) 84.7 %. This result shows that the simultaneous process for emitter diffusion and crystallization of TOPCon layers is principally suited for the fabrication of high efficiency solar cells.

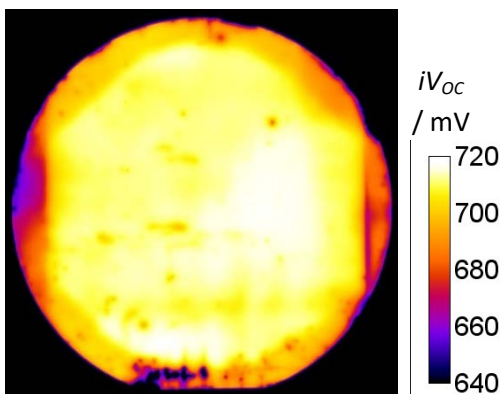


Figure 7: iV_{OC} evaluation of modulm-calibrated PLI measurement at 1 sun of a sample processed at $T = 900 \text{ }^\circ\text{C}$ for 30 min.

4 CONCLUSIONS

In this contribution, the simultaneous emitter diffusion and TOPCon crystallization process via B-RVD is demonstrated for the first time. This combined process leads to a reduction of process and handling steps and an increased flexibility of emitter profiles compared to BBr_3 diffusions.

In the first part B-RVD emitters fabricated in the lab-type tool RTCVD160 were investigated with the aim to reduce the thermal budget for a successful combination of this process with the crystallization of TOPCon layers. Emitter profiles can be tuned by adjusting process time, temperature and B_2H_6 concentration. Decreasing process temperature, time and B_2H_6 concentration lead to a reduction of the emitter depth while the surface concentration is similar for most processes around $3 \times 10^{19} \text{ cm}^{-3}$. Intrinsic emitter saturation current densities were simulated and the lowest value of 13 fA/cm^2 was obtained for the process with the lowest temperature of $900 \text{ }^\circ\text{C}$. This process also led to the highest bulk lifetime and was chosen for the first test of the combined TOPCon crystallization during the B-RVD process.

During the B-RVD process, crystallization of the TOPCon layer takes place. The TOPCon layer does not prevent diffusion of boron into the silicon which leads to an overcompensation of the phosphorus doping resulting from the n -type TOPCon layer if the layer is facing the gas stream. The passivation of TOPCon layers is already quite good after the B-RVD process with effective lifetimes of around $1370 \mu\text{s}$ measured on symmetric samples. It can be further improved to around $1480 \mu\text{s}$ by an additional hydrogenation process. Finally, a first cell precursor with passivated TOPCon rear side and B-RVD emitter was investigated. Implied open-circuit voltages of $>700 \text{ mV}$ and an implied fill factors of 84.7 % were measured. These are very promising results for future developments with further adaptations of the diffusion process and TOPCon layer properties and a solar cell batch with the application of the simultaneous emitter diffusion and TOPCon crystallization process via B-RVD has already been started.

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