EMITTERS GROWN BY RAPID VAPOUR-PHASE DIRECT DOPING FOR HIGH EFFICIENCY SOLAR CELLS

Stefan Lindekugel¹, Thomas Rachow², Nena Milenkovic¹, Armin Richter¹, Jan Benick¹, Stefan Janz¹, Stefan Reber³

¹Fraunhofer Institute for Solar Energy Systems

Heidenhofstraße 2, D-79110 Freiburg, Germany

Phone: +49 761 4588 5270, fax: +49 761 4588 9250

E-mail: Stefan.Lindekugel@ise.fraunhofer.de

² now with Robert Bosch GmbH

³ now with NexWafe GmbH

ABSTRACT: In this paper we present results about excellent p-type emitters using a rapid vapour-phase direct doping (RVD) process. The main differences between the RVD process and standard BBr₃ tube furnace emitters like single sided processing, short process durations and higher degree of freedom in doping profile design are discussed in detail. Lifetime samples featuring a simple RVD emitter on one side have been processed and resulted in an emitter saturation current of less than 16 fA/cm². Solar cells with the high efficiency TOPCon structure implementing this RVD emitter have been fabricated. They show open-circuit voltages of up to 687 mV, short circuit currents of up to 41.8 mA/cm², fill factors of up to 81 % and a maximum efficiency of 23.3 %. Keywords: Emitter, Rapid Vapour-Phase Direct Doping, Epitaxy

1 INTRODUCTION

Today's most common emitter formation process is solid phase diffusion of phosphorus or boron from doped silicate glass (PSG and BSG). For realizing a p-type diffusion in solar cells silicate glass is typically grown in a tube furnace using BBr₃ as precursor. This process although very well understood has some restrictions like a limited control of the dopant concentration due to a set concentration in the BSG, the double sided nature of the process and the necessity of post process wet chemical silicate glass etching.

With emitters grown by rapid vapour-phase direct doping (RVD) some of those limitations can be avoided and even additional features can be enabled. RVD is a silicate glass less process where the dopants diffuse directly from the precursor gas into the wafer surface. With directly grown emitters as presented in this paper the process only takes a few minutes and still leads to excellent solar cell performance. Due to the tools designed and built at Fraunhofer ISE we are able to provide an inline capable process where there is no need for a rear side masking in order to get a single sided emitter. As the RVD process is a direct gas phase diffusion there is no silicate glass formation and therefore no need for a post process wet chemical etching. The shape of the doping profile can be designed rather freely as for the directly doped emitter the doping concentration can be varied with the gas flow as for examples shown in [1]. And finally this process is in principle transferrable to a high throughput inline reactor as shown in [2].

First tests applying our RVD emitter in n-type PERL solar cells resulted in a maximum efficiency of 21.7 % with an open-circuit voltage of 675 mV, a short-circuit current of 40.8 mA/cm^2 and a fill factor of 78.7 % as presented in [3]. Based on those promising results a new high efficiency solar cell batch has been processed and results are presented in this paper.

1.1 Rapid Vapour-Phase Direct Doping (RVD)

As presented in [1] the rapid vapour-phase direct doping (RVD) method features three kinds of reactants: silicon, boron (B_2H_6) and hydrogen (H_2).

The dopants diffuse directly from the vapour phase into the silicon wafer. Due to the high temperature process and the hydrogen atmosphere native oxide is etched away insitu in the process. With no oxide left on the wafer surface and since no additional oxygen is provided no silicate glass is formed. As not a grown glass layer but the gas directly is the doping source the doping concentration can easily be controlled over a wide range by changing the flow rate of the source gas. Experiments showing the effects of the B_2H_6 flow and doping time on the doping concentration as well as the dependence of the junction depth and the doping time have been presented in [1].

2 EXPERIMENTAL PROCEDURE

The experimental focus of this paper lies on the RVD emitter. The RVD emitter incorporates all the advantages mentioned before. For this paper test samples featuring RVD emitter with different diffusion durations have been prepared and characterised with Electrochemical Capacitance-Voltage (ECV), saturation current density (J_0) and effective minority carrier lifetimes (τ_{eff}) measurements. Whereby the ECV profiles were measured with a Wafer Profiler CVP21(WEP), and the J_0 and the τ_{eff} values were extracted from measurements using the QuasiSteady State PhotoConductance (QSSPC) method (WCT120, *Sinton instruments*).

In order to further validate the feasibility and to show the limitations of the process high efficiency TOPCon [4] solar cells with the RVD emitter have been processed. The emitter formation has been done in the rapid thermal chemical vapour deposition (RTCVD 160) set up which was designed and built at Fraunhofer ISE and is described in detail in [5,6]. In this setup the samples face the reactant atmosphere mounted in a quartz carrier system and thus building the side walls of the reaction chamber. Thereby single side processing is immanent and minimal non-reactive surfaces are given. The setup is enclosed by a quartz tube and heated optically by halogen lamps. The original idea and most common usage for the RTCVD 160 is epitaxial growth of doped silicon at atmospheric pressure in a quasi-continuous mode as the substrate wafers can be transported through the deposition zone. For the RVD emitter formation, however, the samples are solely exposed to a H₂, B₂H₆

atmosphere and no epitaxial growth is taking place.

For the emitter shown in this paper the B_2H_6 used has a concentration of 2500 ppm in hydrogen. The B_2H_6/H_2 ratio for the shown results has been set to 40 for different diffusion durations at the peak temperature. In the subsequent cool down step the B_2H_6 flow has been increased to achieve a B_2H_6/H_2 ratio of 14.8 in order to prevent out diffusion and increase the surface doping concentration of the emitter. For the samples shown in this paper the temperature was set between 900 and 1000°C during the RVD process.



Figure 1: Schematic of temperature profile for RVD emitter process.

A schematic of the temperature profile and the respective process step durations is shown in Figure 1.

For this paper only n-typ 1 Ω cm FZ wafers were processed and characterised. Before the RVD process all samples have been treated by conventional chemical cleaning and finally HF dipped and rinsed with DI water. The Al₂O₃ used for passivating the sample surfaces shown in this paper has been deposited in a PA-ALD process using an *Oxford Instruments* tool.

3 RESULTS AND DISCUSSION

3.1 ECV Measurements

The active carrier concentration has been measured by ECV. For these measurements planar samples have been processed with 7 and 10 min of diffusion time. The corresponding emitter profiles can be seen in Figure 2.



Figure 2: ECV measurements of RVD emitter diffused for 7 and 10 min.

The ECV measurement for the surface near region has been difficult. Due to the high doping gas flow during the cool down ramp ECV is not an adequate tool in this region close to the surface. Therefore the results have to be considered not totally trustworthy and the doping concentration will be shown starting from 40 nm. The two profiles of 7 and 10 min RVD duration only differ by \approx 20 nm at the depth of the p-n- junction. This corresponds to ≈ 10 % of the emitter thickness at 30 % shorter processing time.

This RVD emitter profile is comparable to a standard 90 Ω /sq tube furnace emitter diffused from BBr₃ as for example shown in [3].

Typical high efficiency emitters show a moderately doped surface and a deep doping profile. Those profiles are made in a two-step: diffusion and drive in process. One aim of further experiments would be the implementation of a high efficiency profile in a single RVD diffusion step.

3.2 J_0 measurements

Alongside the samples used for the ECV measurements wafers were processed for J_0 characterisation by QSSPC. Due to the nature of the RTCVD set up in a single process only one side is in contact to the B_2H_6/H_2 atmosphere and thereby only one side has a diffused emitter. In order to not have the emitter profile altered by a second RVD temperature load the samples for the OSSPC measurement did not undergo another RVD process but were used as non-symmetrical samples. The samples used were either planar on both sides or textured on the emitter side with a random pyramid (rp) KOH based texture and planar on the rear side. After the RVD process those samples were RCA cleaned and subsequently passivated on both sides by ALD Al₂O₃ and underwent a forming gas anneal. The RVD duration was also 7 or 10 minutes. Two 5×5 cm² samples of each kind have been processed. The values fitted from the QSSPC measurements are shown in Table 1.

 Table 1: Values fitted from QSSPC measurements of samples with either 7 or 10 minutes RVD duration.

surface	RVD duration	J_0	$\stackrel{implied}{V_{oc}}$	implied FF
	[min]	[fA/cm ²]	[mV]	[%]
planar	7	16	705	82
planar	10	16	708	83
rp textured	7	21	695	81

Considering the unsymmetrical nature of the samples, single side emitter and one planar silicon surface both passivated with Al_2O_3 , 16 fA/cm² for the co-planar and 21 fA/cm² for the one side textured samples already show a high potential of the RVD processes.

As shown in Table 1 there is no difference in the J_0 for the planar samples with either 7 or 10 min RTV process. It therefore can be assumed that the J_0 for rp textured 10 min like the 7 min RVD duration lies in the range of 21 fA/cm². Therefore the J_{0e} of the RVD emitter lies both with planar and random pyramid textured surfaces in the range of standard high efficiency tube furnace emitters diffused from BBr₃.

3.3 Solar cell results

A solar cell batch using the 10 min diffused RVD emitter in a TOPCon cell design has been processed. The cell structure is shown in Figure 3. The solar cell process included a single sided random pyramid texture, the single sided RVD emitter, a full area passivated rear contact TOPCon and a Al_2O_3 front side passivation. The front side grid is defined photolithographically and consists of a stack of evaporated Ti-Pd-Ag which was thickened by electroplating. A silver layer is deposited as full area rear contact and a layer double layer of SiN_x and MgF₂ on the front side are deposited as anti reflection coating.



Figure 3: Cell structure of TOPCon architecture.

The calibrated I-V characteristics which were independently measured at Fraunhofer ISE CalLab of the best cell are shown in Table 2.The corresponding IQE, EQE and reflection properties are shown in Figure 4.

 Table 2: I-V characteristics of best TOPCon solar

 cell incorporating an RVD emitter with 10 min

 diffusion duration.

V_{oc}	J_{sc}	FF	η
[mV]	[mA/cm ²]	[%]	[%]
687	41.8	81	23.3



Figure 4: IQE, EQE and reflection measurements of the best boron RVD emitter TOPCon cell.

As one can see the V_{oc} of the best cell is with 687 mV already quite close to the implied *Voc* measured with QSSPC. It can be concluded that the TOPCon rear side passivation works almost as good as a ALD Al₂O₃. In conjunction with the 41.8 mA/cm² measured for the *Jsc* and the *FF* with 81 % this adds up to an efficiency of 23.3 %. The results proof both the very well executed solar cell process and the high potential of the RVD emitter in general as well as the excellent performance of this non-optimised highly doped, shallow emitter profile.

From the short wavelength region of the IQE shown

in Figure 4 as well as from the V_{oc} it can be seen that there is still room for optimisation. With an optimised diffusion process showing a deeper and more moderately doped emitter profile a lower Auger recombination in the emitter should be possible.

4 CONCLUSIONS

In this paper the emitter formation by rapid vapourphase direct doping (RVD) is investigated. The RVD process is per se a single sided emitter formation which does not rely on a silicate glass formation. Therefore the diffusion can easily be tuned by the gas flow of the dopant source and a subsequent silicate glass etch step is obsolete. By showing doping profiles, J_0 and minority carrier lifetime measurements as well as solar cell results featuring RVD emitter samples it has been shown that this technique has high efficiency potential.

The doping profiles of un-optimised RVD emitters are with $\approx 200 \text{ nm}$ rather shallow and a peak doping concentration of 10^{20} cm^{-3} comparatively highly doped. Nevertheless both minority carrier lifetimes with up to 340 µs and emitter saturation current with less than 16 fA/cm² already show the high potential of these process. Implementing the RVD emitter into a high efficiency TOPCon solar cell process a maximum efficiency of 23.3 % definitely shows the excellent performance of the emitter.

The spectrum of possibilities arising from the gas phase doping in terms of doping profiles, shorter processing times and process cost perspectives compared to the standard BBr₃ tube furnace processes have not yet been reviewed.

4 ACKNOWLEDGMENTS

The authors would like to express their gratitude to Harald Lautenschlager, Mira Kwiatkowska, Elke Gust, Kai Schillinger, Michaela Winterhalder, Bernd Steinhauser, Antonio Leimenstoll, Felix Schätzle and Nadine Weber at ISE for their support and input in many valuable discussions. This work was funded by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (Contract Number FKZ 0325199A).

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