

## N-TYPE BI-FACIAL SOLAR CELLS WITH BORON EMITTERS FROM DOPED PECVD LAYERS

A. Frey, J. Engelhardt, S. Fritz, S. Gloger, G. Hahn, B. Terheiden  
 Department of Physics, University of Konstanz, 78457 Konstanz, Germany

Author for correspondence: alexander.frey@uni-konstanz.de Tel.: +49 7531 882081, Fax: +49 7531 883895

Co-authors: josh.engelhardt@uni-konstanz.de, susanne.fritz@uni-konstanz.de, sebastian.gloger@uni-konstanz.de, giso.hahn@uni-konstanz.de, barbara.terheiden@uni-konstanz.de

**ABSTRACT:** This work is mainly focused on an alternative method for emitter formation by means of boron diffusion from a boron-doped plasma-enhanced chemical vapor deposition (PECVD) doping source. With this approach only *one* high temperature process is necessary for emitter *and* BSF/FSF formation (co-diffusion), without depletion of surface doping concentration. This enables time and cost-efficient fabrication of solar cells with high conversion efficiencies, as shown in this work, on large area (156.25 cm<sup>2</sup>) bi-facial devices with conversion efficiencies up to 19.7% measured with white back sheet. Furthermore, the contact formation with screen-printing of silver/aluminum (Ag/Al) pastes and its emitter shunting behavior due to Ag/Al spikes, varying with the firing conditions in a belt furnace, are of major interest. Low contact resistance values below 4 mΩcm<sup>2</sup> can be realized with screen-printed Ag/Al contacts on 55-70 Ω/sq PECVD boron emitters. In addition, Ag/Al spikes with a depth of around 1-3 μm could be detected with SEM measurements.

**Keywords:** n-type, bi-facial, boron, PECVD, screen printing

### 1 INTRODUCTION

n-type silicon as base material for solar cell production is known for its favorable electrical properties compared to p-type silicon. One reason is the lower sensitivity of n-type silicon to common metal impurities like iron and copper due to the lower capture cross sections for holes (minority carriers in n-type Si) and accordingly the lower recombination rates at these defect sites [1]. Another advantage is the absence of boron-oxygen related defects which result in a strong degradation of the cell performance under illumination (LID) for typical p-type silicon solar cells [2], if the solar cell is not regenerated [3].

With the use of n-type silicon as base material new challenges arise such as the formation of boron emitters and its appropriate passivation and contact formation. A common method for emitter formation is thermal diffusion of boron atoms into the silicon substrate from a boron tribromide (BBr<sub>3</sub>) or boron trichloride (BCl<sub>3</sub>) diffusion source [4]. With these methods at least two high temperature steps are necessary for emitter and back/front surface field (BSF/FSF) formation. High temperature treatments are known for their detrimental influence especially on Czochralski-grown (Cz) silicon with high oxygen content and therefore should be avoided [5]. Another drawback of a typical BBr<sub>3</sub> based boron emitter profile is the depletion of the surface doping concentration originating from an oxidation step during emitter formation. This may lead to disadvantages in terms of passivation quality and contact formation.

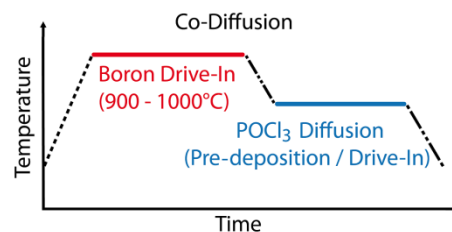
This work shows an alternative method for emitter formation by means of boron diffusion from a boron-doped plasma-enhanced chemical vapor deposition (PECVD) doping source [6-9]. With this approach only *one* high temperature process is necessary for emitter *and* BSF/FSF formation (co-diffusion), without depletion of surface doping concentration. This enables time and cost-efficient fabrication of solar cells with high conversion efficiencies on large area (156.25 cm<sup>2</sup>) bi-facial devices.

Furthermore, the contact formation by screen-printing of silver/aluminum (Ag/Al) pastes [10-13] and the emitter shunting behavior due to Ag/Al spikes, varying with the firing conditions in a belt furnace, are of major

interest because they are not yet completely understood. Therefore, the specific contact resistance values for screen-printed contacts on PECVD boron emitters with differing sheet resistances are investigated on test-structures using the transfer length method (TLM) for several firing conditions. The shunting behavior of screen-printed contacts is investigated by lock-in thermography (LIT) and scanning electron microscopy (SEM) measurements to get a deeper understanding of the firing conditions necessary for fabrication of highly efficient n-type bi-facial solar cells.

### 2 EXPERIMENTAL

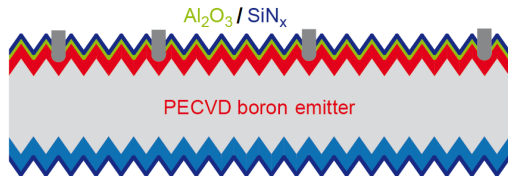
Emitter formation by means of boron diffusion from a boron-doped PECVD doping source [6-9] is described in the following. First a boron-doped PECVD layer is deposited on one side of the n-type silicon substrate. To protect the boron doping source from overcompensation by phosphorus in the following co-diffusion step, the doping source is capped by a silicon nitride layer (SiN<sub>x</sub>). The co-diffusion temperature profile is depicted in Fig. 1.



**Figure 1:** Process sequence of the co-diffusion for emitter and BSF/FSF formation in one high temperature step. The boron drive-in is obtained at temperatures in the range of 900-1000°C whereas the FSF/BSF formation is obtained after cooling down to lower temperatures.

First the boron emitter is formed by diffusion of boron atoms from the doping source into the silicon substrate. This drive-in step is conducted at high temperatures in the range of 900-1000°C. After cooling down to lower temperatures the phosphorus FSF/BSF is

formed during a standard  $\text{POCl}_3$  diffusion. The capping and doping layers are removed in the following cleaning steps. The resulting boron emitter does not suffer from surface depletion such as e.g. emitters from  $\text{BBr}_3$  diffusions and ensures high surface doping concentrations  $N_{\text{surf}} > 7 \cdot 10^{19} \text{ cm}^{-3}$  and low emitter saturation current densities  $j_{0e} < 60 \text{ fA/cm}^2$ , leading to high implied  $V_{\text{OC}}$  values above 680 mV as already shown in [6].

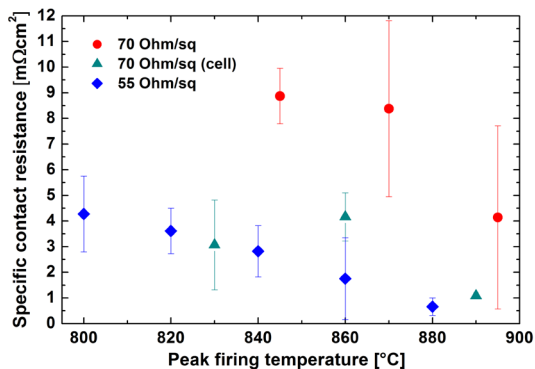


**Figure 2:** Cross section of TLM test structures for investigation of the specific contact resistance for screen-printed Ag/Al contacts on PECVD boron emitters.

Contact formation using screen-printing of commercially available Ag/Al pastes is of major interest for the production of bi-facial solar cells. Therefore, test structures using a TLM grid structure according to Fig. 2 are fabricated for different PECVD boron emitters with sheet resistivities in the range of  $R_{\text{sh}} = 55\text{-}70 \text{ } \Omega/\text{sq}$ . The contact formation is realized in an infrared (IR) belt furnace for peak firing temperatures in the range of 820-920°C (set point).

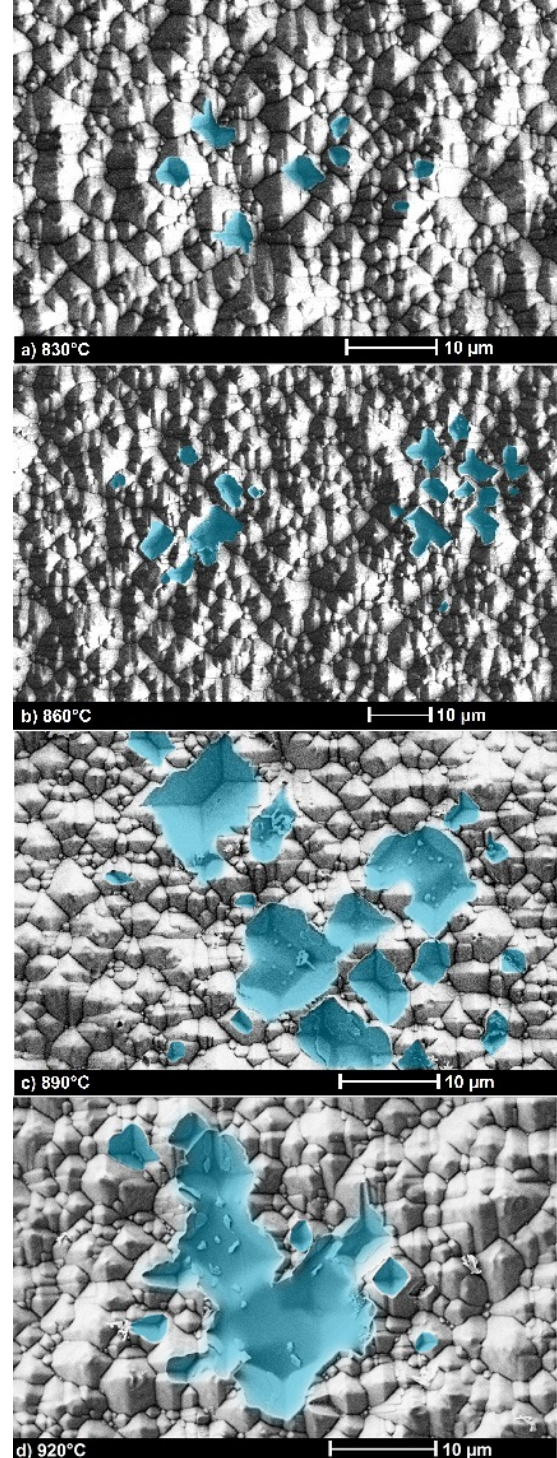
### 3 CONTACT FORMATION RESULTS

Fig. 3 shows the specific contact resistance values obtained from the TLM measurements as function of the peak firing temperature for the different sheet resistivities in the range of  $R_{\text{sh}} = 55\text{-}70 \text{ } \Omega/\text{sq}$ . 70  $\Omega/\text{sq}$  (cell) means TLM measurements on a finished solar cell. The contact resistance decreases with increasing peak firing temperature. Nevertheless low values below  $4 \text{ m}\Omega\text{cm}^2$  can be realized with screen-printed Ag/Al contacts on 55-70  $\Omega/\text{sq}$  PECVD boron emitters even for low temperatures.



**Figure 3:** Specific contact resistance for screen-printed contacts with commercially available Ag/Al paste on PECVD boron emitter. 70  $\Omega/\text{sq}$  (cell) means measurements on a finished solar cell.

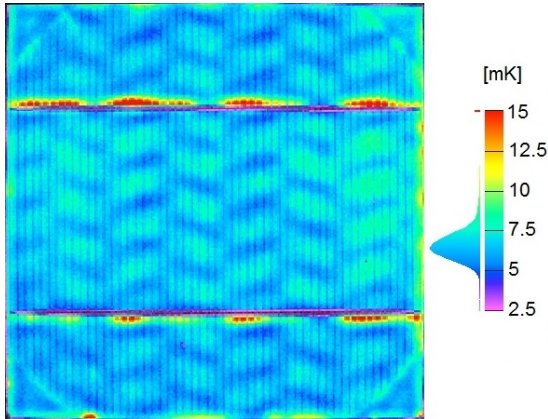
However, a low contact resistance is not the only requirement for an appropriate screen-printed contact. In particular, when using Al containing pastes shunting problems due to Ag/Al spike formation may occur when the firing process is not controlled carefully.



**Figure 4:** SEM images of samples etched with a sequence of HF and nitrohydrochloric acid. The measurement is performed on busbars of bi-facial solar cells. The area density of Ag/Al spikes depends strongly on firing temperature.

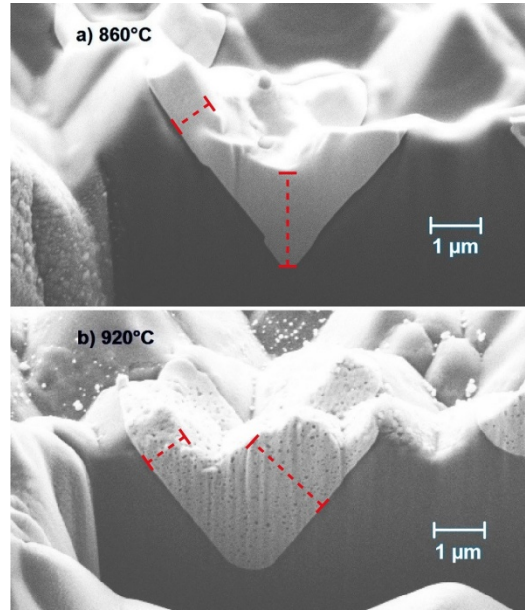
Fig. 4 shows SEM images after removal of the Ag/Al paste and contact spots with an etching sequence of HF and nitrohydrochloric acid. It is clearly visible, that the area density of the Ag/Al spikes (visible as inverted pyramids marked in blue), increases with increasing firing temperature. This coincides with the decreasing contact resistance for increasing firing temperatures due to the larger contact area with increasing area density of the Ag/Al spikes. At temperatures above 860°C massive Ag/Al spikes, with a depth up to several  $\mu\text{m}$  [10] appear, which easily short circuit the emitter with a typical depth of around 500–700 nm.

This leads to detrimental low shunt resistance values for the solar cells. The shunt locations can be visualized by lock-in thermography (LIT). Fig. 5 shows a dark LIT measurement in reverse bias (-0.6 V) for a bi-facial solar cell with firing temperature of 920°C. Strong thermal signals above 15 mK occur at the busbars due to shunts related to Ag/Al spiking. The shunt resistance of this cell is below  $500 \Omega\text{cm}^2$ , which is detrimental for cell performance.



**Figure 5:** Dark reverse lock-in thermography (LIT) measurement on a bi-facial solar cell with firing temperature of 920°C. At  $V_{OC}$  conditions strong shunt signals above 15 mK occur at the busbars due to shunts related to Ag/Al spiking. The shunt resistance of this cell is below  $500 \Omega\text{cm}^2$ .

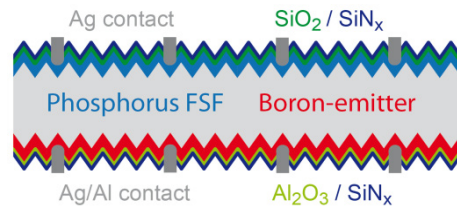
To determine the depth of the Ag/Al spikes, cross sections of the contact spots were prepared by focused ion beam (FIB) for peak firing temperatures of 860°C and 920°C as shown in Fig. 6. The SEM analysis [11] reveals contact depths in the range of 1-3  $\mu\text{m}$ . Only a small difference in contact depth for 860°C and 920°C is visible for the investigated samples, which leads to the assumption that, even for lower temperatures, the Ag/Al spikes might be deep enough to short circuit the emitter. Therefore, a compromise in the firing conditions between appropriate contact formation in terms of low contact resistance and low amount of Ag/Al spikes has to be made. This can be achieved, as shown in the following on bi-facial solar cells, for low firing temperatures in the range of 780-840°C. The correlation between contact depth and firing temperature is currently under further investigation and will be published soon.



**Figure 6:** Cross section of the contact spots by focused ion beam (FIB) for firing temperatures of 860°C and 920°C. The shown pictures are not angle corrected.

#### 4 SOLAR CELL RESULTS

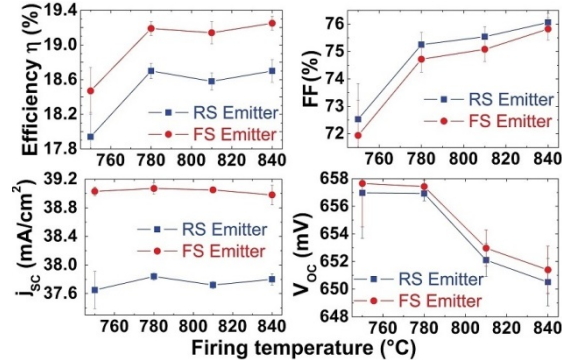
Fig. 7 shows the cross section of the bi-facial solar cells with PECVD boron emitter and selective phosphorus FSF/BSF (etch-back) [18], which are fabricated in this work under optimized firing conditions. The solar cells are alkaline textured on both sides. To investigate the cell performance with differing firing temperature, the cells were fired in a temperature range of 750-840°C. n-type Cz-grown Si wafers with a specific resistivity of  $6 \Omega\text{cm}$  have been used. The contact formation is obtained via screen-printing of Ag paste on the phosphorus FSF and Ag/Al paste on the boron emitter. To obtain a low surface recombination velocity on the boron emitter, an  $\text{Al}_2\text{O}_3/\text{SiN}_x$  stack has been used. The selective FSF/BSF is passivated by a stack of thermal  $\text{SiO}_2/\text{SiN}_x$ .



**Figure 7:** Cross section of the bi-facial solar cells with PECVD boron emitter and selective phosphorus FSF. The contact formation is obtained via screen-printing Ag paste for phosphorus FSF and Ag/Al paste for the boron emitter. To obtain sufficient passivation on the boron emitter an  $\text{Al}_2\text{O}_3/\text{SiN}_x$  stack is used.

In Fig. 8 the average cell parameters of the large area ( $156.25 \text{ cm}^2$ ) n-type bi-facial Si solar cells under low firing temperature conditions are illustrated. Best results are obtained for a bi-facial solar cell fired in the range of 780-840°C as peak firing temperature. At firing

temperature of 750°C the fillfactor (FF) drops strongly due to inappropriate contact resistance of the Ag/Al contacts. As expected, short circuit current density ( $j_{sc}$ ) is independent of the firing conditions. Open circuit voltage ( $V_{oc}$ ) is reduced with increasing firing temperature due to the degradation of the  $Al_2O_3/SiN_x$  passivation layer. For firing temperatures above 860°C (not shown in Fig. 8), cell efficiency is strongly reduced due to low shunt resistance and therefore low FF and  $V_{oc}$  values induced by Ag/Al spiking.

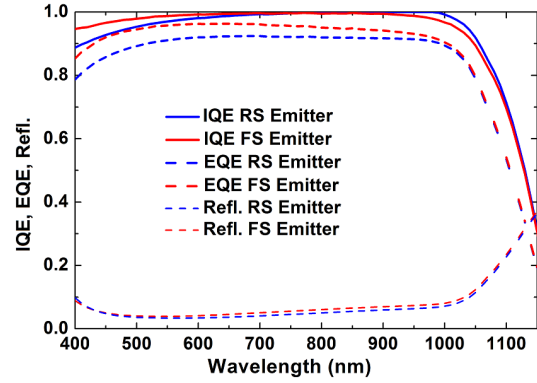


**Figure 8:** Average bi-facial cell parameters under low firing temperature conditions. Best cell results are obtained in the range of 780-840°C as peak firing temperature. The data is measured with a black back sheet.

Table I shows the results of the bi-facial solar cells with optimized PECVD boron emitter and firing temperature. The result of the best solar cell is given. RS emitter means back-junction whereas FS emitter means front-junction. The data is measured with a flasher tool with an absorbing black back sheet and a reflective white back sheet. Best results are obtained with FS emitter illumination. This indicates that the saturation current density of the boron emitter is much lower than the one of the phosphorus FSF/BSF, which is confirmed by the internal quantum efficiency (IQE) measurement shown in Fig. 9. The best cell achieved a conversion efficiency of 19.7% with an open circuit voltage of 653 mV. The measured  $V_{oc}$  values on the n-type bi-facial solar cells of above 650 mV show the high electrical quality of the boron emitters from a boron-doped PECVD doping source and are equal or even higher than  $V_{oc}$  values obtained on n-type bi-facial solar cells with boron emitters from typical  $BBr_3$ -diffusion [14-17].

**Table I:** Results of the bi-facial solar cells with optimized PECVD boron emitter and firing temperature. The data is measured with a flasher tool with an absorbing black and a reflective white back sheet.

	$V_{oc}$ (mV)	$j_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	$\eta$ (%)
<b>Black back sheet (RS emitter)</b>	652	37.9	76.3	18.8
<b>Black back sheet (FS emitter)</b>	652	38.9	76.3	19.3
<b>White back sheet (FS emitter)</b>	653	39.4	76.4	19.7



**Figure 9:** Internal quantum efficiency (IQE) measurement of the best bi-facial solar cell. IQE is higher in the case of front-junction illumination.

## 5 SUMMARY

An alternative method for boron emitter formation by means of boron diffusion from a boron-doped PECVD doping source has been demonstrated in this work. This leads to boron emitters with high electrical quality as shown in the low  $j_{sc} < 60$  fA/cm<sup>2</sup>, leading to high implied  $V_{oc}$  values above 680 mV.

Low contact resistance values below 4 m $\Omega$ cm<sup>2</sup> can be realized with screen-printed Ag/Al contacts on 55-70  $\Omega$ /sq PECVD boron emitters even for low temperatures. When using aluminum containing pastes, shunting problems due to Ag/Al spike formation may occur if the firing process is not controlled carefully. The amount and size of Ag/Al spikes increases with increasing peak firing temperature. At peak firing temperatures above 860°C massive Ag/Al spikes arise with a depth up to several  $\mu$ m which could be detected with SEM measurements. A compromise in the firing conditions has to be made between appropriate contact formation in terms of low contact resistance and low amount of Ag/Al spikes. For bifacial solar cells this has been achieved with firing temperatures in the range of 780-840°C leading to high conversion efficiencies of up to  $\eta = 19.7\%$  with reflective white background.

## 6 ACKNOWLEDGEMENTS

Part of this work was financially supported by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (FKZ 0325581) and within the project FKZ 0325449A via a subcontract granted by SolarWorld Innovations GmbH.

We thank Dr. Bianca Gründig-Wendrock for providing wafer samples, Dr. Bernd Bitnar and Dr. Phedon Palinginis for guiding and accompanying the cell development activities.

## 7 REFERENCES

- [1] D. Macdonald, L.J. Geerligs, *Recombination activity of interstitial iron and other transition metal point defects in p- and n-type crystalline silicon*, Appl. Phys. Lett. 85 (2004), 4061.

- [2] H. Fischer, W. Pschunder, *Investigation of photon and thermal induced changes in silicon solar cells*, Proc. 10<sup>th</sup> IEEE PVSEC, Palo Alto 1973.
- [3] A. Herguth, G. Schubert, M. Kaes, G. Hahn, *Investigations on the long time behavior of the metastable boron-oxygen complex in crystalline silicon*, Progr. Photovolt.: Res. Appl. 16(2) (2008) 135-140.
- [4] Y. Schiele, S. Fahr, S. Joos, G. Hahn, B. Terheiden, *Study on boron emitter formation by BBr<sub>3</sub> diffusion for n-type Si solar cell applications*, Proc. 28<sup>th</sup> EUPVSEC, Paris 2013.
- [5] D.C. Walter, B. Lim, R. Falster, J. Binns, J. Schmidt, *Understanding lifetime degradation in Czochralski-grown n-type silicon after high-temperature processing*, Proceedings 28<sup>th</sup> EUPVSEC, Paris 2013.
- [6] J. Engelhardt, A. Frey, L. Mahlstaedt, S. Gloger, G. Hahn, B. Terheiden, *Boron emitters from doped PECVD layers for n-type crystalline solar cells with LCO*, Proc. 4<sup>th</sup> SiliconPV, 's-Hertogenbosch 2014.
- [7] N. Wehmeier, G. Schrapf, H. Wagner, B. Lim, N.-P. Harder, P.P. Altermatt, *Boron-doped PECVD silicon oxides as diffusion sources for simplified high-efficiency solar cell fabrication*, Proc. 28<sup>th</sup> EUPVSEC, Paris 2013.
- [8] R. Keding, P. Rothhardt, C. Roters, A. Fallisch, S. Hohage, M. Hofmann, R. Woehl, D. Borchert, D. Biro, *Silicon doping performed by different sources aiming co-diffusion*, Proc. 27<sup>th</sup> EUPVSEC, Frankfurt 2012.
- [9] R. Cabal, J. Jourdan, B. Grange, Y. Veschetti, D. Heslinga, *Investigation of the potential of boron doped oxide deposited by PECVD – Application to advanced solar cells fabrication processes*, Proc. 24<sup>th</sup> EUPVSEC, Hamburg 2009.
- [10] S. Riegel, F. Mutter, T. Lauermaun, B. Terheiden, G. Hahn, *Review on screen printed metallization on p-type silicon*, Energy Procedia 21 (2012) 14-23.
- [11] S. Fritz, M. König, S. Riegel, A. Herguth, M. Hörteis, G. Hahn, *Formation of Ag/Al screen-printing contacts on B emitters*, submitted to IEEE Journal of Photovoltaics (2014)
- [12] S. Fritz, S. Riegel, S. Gloger, D. Kohler, G. Hahn, *Influence of emitter properties on contact formation to p<sup>+</sup> silicon*, Energy Procedia 38 (2013) 720-724.
- [13] A. Edler, V.D. Mihailitchi, C. Comparotto, L.J. Koduvelikulathu, R. Kopecek, R. Harney, T. Bösccke, J. Lossen, *On the metallization losses of bifacial n-type silicon solar cells*, Proc. 27<sup>th</sup> EUPVSEC, Frankfurt 2012.
- [14] I.G. Romijn, B. van Aken, J. Anker, P. Barton, *Industrial cost effective n-pasha solar cells with >20% cell efficiency*, Proc. 28<sup>th</sup> EUPVSEC, Paris 2013.
- [15] S. Gonsui, S. Goda, K. Sugibuchi, N. Ishikawa, K. Honda, H. Zama, *n-type high efficiency bifacial silicon solar cell with the extremely high bifaciality of 96% in average fabricated by using conventional diffusion method*, Proc. 28<sup>th</sup> EUPVSEC, Paris 2013.
- [16] S.-W. Chiu, P.-T. Hsieh, C.-J. Huang, H.-C. Chang, C.C. Li, *Boron emitter of n-type solar cell made with BBr<sub>3</sub> and spin-coating boron sources*, Proc. 28<sup>th</sup> EUPVSEC, Paris 2013.
- [17] D.S. Saynova, I.G. Romijn, I. Cesar, M.W.P.E. Lamers, A. Gutjahr, G. Dingemans, H.C.M. Knoops, B. van de Loo, W.M.M. Kessels, O. Siarheyeva, E.H.A. Granneman, L. Gautero, D.M. Borsa, P.R. Venema, A.H.G. Vlooswijk, *Dielectric passivation schemes for high efficiency n-type solar cells*, Proc. 28<sup>th</sup> EUPVSEC, Paris 2013.
- [18] F. Book, T. Wiedenmann, S. Gloger, B. Raabe, G. Schubert, H. Plagwitz, G. Hahn, *Analysis of processing steps for industrial large area n-type solar cells with screen printed aluminum-alloyed rear emitter and selective FSF*, Proc. of the 26<sup>th</sup> EUPVSEC, Hamburg, Germany 2011.