



4th International Conference on Silicon Photovoltaics, SiliconPV 2014

Boron emitters from doped PECVD layers for n-type crystalline silicon solar cells with LCO

Josh Engelhardt^{a,*}, Alexander Frey^a, Lisa Mahlstaedt^a, Sebastian Gloger^a, Giso Hahn^a, Barbara Terheiden^a

^aUniversity of Konstanz, Department of Physics, P.O. Box 676, D-78457 Konstanz, Germany

Abstract

The intensified research into n type silicon solar cells over the last few years let the application of boron doped emitters in suitable cell concepts become the preferred method to form the necessary p n junction. In this study an alternative process to fabricate a boron doped emitter via diffusion from a PECV deposited doping source is presented and optimized for n type crystalline silicon solar cell concepts. Doping profiles with a high surface concentration in combination with low emitter saturation current density values are achieved for improved contact and passivation characteristics. The boron emitter profile is compatible with various contacting techniques i.e. screen printing and vapour deposited Al, allowing for low resistant contacting with Ag/Al pastes or sputtered Al. The comparably low emitter saturation current density j_{0E} of 44 fA/cm² allows for a V_{OC} of 666 mV, and thereby a cell efficiency of 19.7% is demonstrated on a large area (156.25 cm²) solar cell.

© 2014 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Peer-review under responsibility of the scientific committee of the SiliconPV 2014 conference

Keywords: PECVD; boron; LCO; ablation; co-diffusion; n-type

1. Introduction

N type silicon substrates are commonly known for their low sensitivity to metal impurities such as iron, resulting in lower recombination losses and higher charge carrier lifetimes [1]. Furthermore, the reduction of susceptibility to

* Corresponding author. Tel: +49-7531-88-2080; fax: +49-7531-88-3895.
E-Mail address: josh.engelhardt@uni-konstanz.de

degradation due to boron oxide complex formation is an advantage for the usage of n type Si substrates in solar cell technology. The necessary boron doped emitter is commonly diffused from liquid sources like BBr_3 . Despite reaching low emitter saturation current densities j_{0E} and suitable emitter doping profiles, there are certain disadvantages connected to this method for emitter formation, like e.g. pile down of surface concentration due to oxidation [2]. The alternative process of PECV(plasma enhanced chemical vapour) deposited doping sources allows for high surface doping concentrations, a variation in shape of the doping profile and low j_{0E} values. It allows for different contact methods to be applied and cell concepts with large passivated areas. Using PECVD layers as doping sources allows to form a B doped and a P doped region, applying only one high temperature step, i.e. a co diffusion process. While PECVD emitter sources are currently investigated by many groups [3 6], the necessary properties for an application in high efficient solar cells is not yet demonstrated. A further reduction of j_{0E} and an improved contact quality will lead to the desired cell efficiencies for respective cell designs.

2. Experimental

To form the boron doped emitter on the rear side of the solar cell, a boron doped (containing) source layer is deposited by a PECVD reactor (Oxford Plasma Lab 100). A PECVD $\text{SiN}_x\text{:H}$ layer is used to protect this boron doped source layer from contamination and overcompensation by phosphorous during the co diffusion step. We optimized the deposition process and diffusion parameters to achieve different sheet resistances in the range of 50 90 Ω/\square . The co diffusion is performed in a diffusion furnace in a two step process similar to the one reported in [3,4]. First, the boron doped emitter is formed in a drive in step from the source layer in a temperature range of 900 1000°C. Secondly, the phosphorous doped front surface field (FSF) is formed at a lower temperature typical for phosphorous diffusions. During the following cleaning steps the capping and source layer as well as a potential boron rich layer (BRL) is removed.

Czochralski (Cz) grown silicon samples with a boron emitter on one side and a phosphorous FSF on the other are used to determine the sheet resistance by the four point probe (4PP) technique and the dopant profiles by electro chemical capacitance voltage (ECV) measurement. The samples for the determination of j_{0E} are symmetric float zone silicon samples (n type; 200 Ωcm) with a boron emitter on both sides, and they are passivated using annealed atomic layer deposited Al_2O_3 and/or a stack of Al_2O_3 and PECVD $\text{SiN}_x\text{:H}$ fired in a belt furnace. The j_{0E} measurements are carried out by transient photoconductance decay (PCD) using a Sinton lifetime tester.

The back junction mono facial solar cells have a selective phosphorous FSF and a shallow boron emitter. The front side of the cell is passivated with a $\text{SiN}_x\text{:H}/\text{SiO}_2$ stack and the rear side with an $\text{Al}_2\text{O}_3/\text{SiN}_x\text{:H}$ stack. After firing the front side screen printed Ag contacts, the rear side passivation layer is locally ablated using a picosecond laser before being homogeneously sputtered/evaporated with Al.

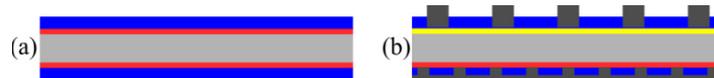


Fig. 1. (a) Symmetric j_{0E} sample with boron doped emitter (red) and passivation layer(s) (blue); (b) mono-facial solar cell with FSF (yellow) and rear boron emitter (red).

3. Results and discussion

3.1. Emitter formation and characterization

The possibility to reach high surface doping concentrations of boron emitters can be advantageous for contact formation and the rear side design in solar cell fabrication. This requires to omit an oxidation step after diffusion, which would decrease the doping concentration near the wafer surface (pile down effect), as used e.g. in BBr_3 diffusion processes. Using a stack of PECVD layers as doping source and capping layer, the possibility of the pile down effect is significantly reduced.

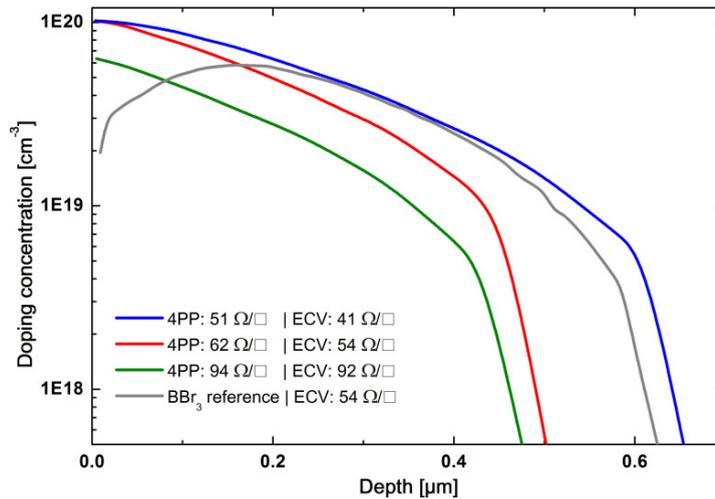


Fig. 2. Boron emitter profiles determined by ECV measurements. Sheet resistance values measured with 4PP and ECV.

Table 1. j_{0E} measured by transient PCD, sheet resistance & surface doping concentration according to Fig. 2.

Sheet resistance (4PP) [Ω/\square]	Sheet resistance (ECV) [Ω/\square]	Surface doping concentration [cm^{-3}]	j_{0E} [fA/cm^2]	Implied V_{OC} (j_{0E}) [mV]
51	41	1.0E20	61	680
62	54	1.0E20	44	688
94	92	7.7E19	37	692

In comparison to the BBr_3 diffused emitter, all our PECVD source emitters show a higher surface concentration ($N_{A,\text{surf}} > 7 \cdot 10^{19} \text{ cm}^{-3}$) due to the absence of depletion by an oxidation step. The shape and depth of the profiles are otherwise similar. In particular for screen printing purposes a deeper emitter profile is advantageous to avoid shunting. Shallow emitters on the other hand are preferred for contacting methods like sputtering or vapour deposition.

The high surface doping concentration has a minor influence on j_{0E} in comparison to BBr_3 emitters [2], but is low enough to result in no significant restrictions on cell level. Compared to similarly diffused emitters [3–6], our j_{0E} values are lower due to a reduction in surface recombination despite the high surface concentration. An important influence is the complete removal or prevention of a potentially highly recombination active BRL. Without a BRL, the implied V_{OC} reaches values of about 690 mV, allowing for cell efficiencies of above 21%.

During diffusion the wafer is exposed to rapid changes in temperature while unloading from the diffusion furnace. These changes can cause dislocations and other recombination active damages within the Si substrate [7], and result in a decrease of j_{0E} and consequently V_{OC} . Causal for the damage is the mechanical stress, which is low for a standard diffusion due to symmetry of the BSG growing on all sides of the Si wafer during the diffusion process. In the case of a co diffusion this symmetry in dopant layer thickness is broken. The PECVD layers present on one side of the wafer can bend it due to the difference in thermal expansion coefficients, resulting in higher mechanical stress and recombination active defects.

By controlling the cooling/heating rate and/or the thermal distribution along the Si substrate surface, the influence of mechanical stress can be reduced significantly. We chose to lower the unloading temperatures to achieve a more controlled heating and cooling of the wafer, preventing the thermal shock, which occurs at commonly used unloading procedures. The measured bulk lifetimes are comparatively higher after diffusion with 200 K lower unloading temperatures. The relative lifetime difference is in the range of 0.5–1.0 ms on a level of 2

3 ms, depending on the substrate quality.

3.2. Cell results and LCO

The mono facial solar cells (156.25 cm² cell area) are rear side contacted by local laser opening/ablation (LCO) and then homogeneously sputtered with aluminum (Al). The varied parameters are the laser wavelength, the opening structure (dot grid, dashed lines and lines) and the opened/metallized rear side area.

Table 2. Cell results for mono-facial solar cells: LCO ($\lambda = 532$ nm) and sputtered Al.

LCO structure	Metallized area [%]	V _{OC} [mV]	FF [%]
Dots	1	666	77.4
Dots	3	662	77.7
Dashed lines	3	662	75.7
Lines	3	656	75.7

LCO in combination with sputtered Al allows for smaller metal contact areas than screen printing. As shown in Table 2 the metallized area is only in the range of 1–3%. The commonly used laser contact opening pattern are parallel lines (see Fig. 3c) resulting in a V_{OC} value of 656 mV due to the comparatively high metallized area necessary for a sufficiently low series resistance. The V_{OC} value can be increased using a dashed lines structure similar to those used in PERC cell fabrication. The series resistance decreases due to the smaller distance between contacts, while the laser treated area increases. Yet the optimal balance between maximal passivated surface area and fill factor is a dot grid using a close packed circles structure. The contact distance is even smaller, while the laser treated area is maximized for the same metallized area in comparison with the lines and dashed lines pattern. The only structural variable left then is the percentage of metallized rear side area. According to Table 2 a reduction of the area for a given dot grid leads to a higher V_{OC} value due to an increase in passivated cell area and a smaller area that is actively treated by laser light. The decrease from 3% metallized area with the dashed lines and the lines pattern to 1% for the dot grid increases the V_{OC} to 666 mV and the FF to 77.4%. The optimal laser contact opening spacing then depends solely on the conductivity of the rear side emitter and the passivation quality. So far the best solar cell with this cell concept reached 19.7% cell efficiency.

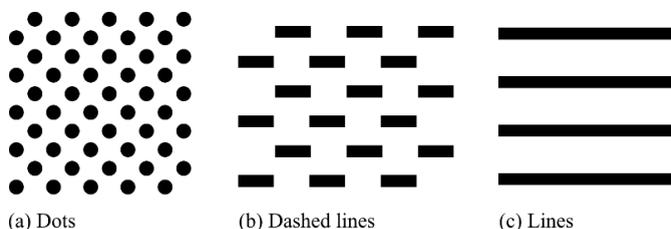


Fig. 3. LCO patterns: (a) close-packed dot grid; (b) dashed lines grid (PERC); (c) parallel lines.

Considering the dielectric layer stack used in this case and the surface doping concentration of the boron emitter, a 532 nm picosecond laser was determined to be optimal for LCO [8]. The ablation of the dielectric layer stack should not compromise the electrical properties, like e.g. the performance of the emitter. Due to the high doping concentration, the free carrier absorption is increased on the substrate surface. Such an increase results in different non linear absorption channels [9] and a higher absorption rate near the surface [10] for ultra short laser pulses. Therefore, the wavelength and pulse length of the laser source decreases the ablation threshold (energy necessary for complete removal of dielectric layer(s)) below the pulse energy threshold for critical laser damage to relevant solar cell regions (e.g. the space charge region). The ablation process is in this case considered to be damage free in the sense that it does not influence any relevant parameters for the efficiency of the solar cell. The main types of point defects caused by laser damage [11] are formed on the surface and are located in rear side areas later contacted by

Al. Neither the passivation nor the quality of the Al contact are measurably affected by the possible increase of recombination at these surface regions due to laser damage. Even the increase of laser treated cell area (larger than contact/metallized area due to Gaussian laser pulse profile) using a dot grid instead of a line pattern, does not measurably influence the cell performance. Fig. 4 depicts the emitter underneath the laser treated area covered by the Al layer. Considering that no laser damage can be detected, a shallow emitter with a high surface doping concentration for a low contact resistance with Al was chosen for the back junction solar cell design. The higher sheet resistance allows for a low recombination loss in the emitter and therefore a better passivation quality.

Due to the suitability of the optimized emitter and mono facial design for a high efficiency solar cell concept, it will be applied to Bridgman grown n type substrates in future investigations.

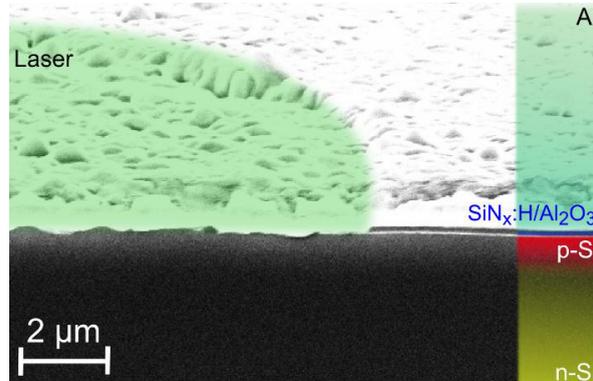


Fig. 4. Scanning electron microscopy image depicting the cross-section of LCO on the rear side of the solar cell. On top of the silicon substrate (yellow) the shallow boron doped emitter (red) is visible. In the laser treated area (lime) the passivation stack ($\text{SiN}_x\text{:H/Al}_2\text{O}_3$; blue) is ablated before sputtering Al (green).

4. Conclusion

We demonstrated emitters from a PECVD source with a sheet resistance range of $50\text{--}90\ \Omega/\square$ and j_{0E} values below $61\ \text{fA}/\text{cm}^2$, resulting in an implied V_{OC} value above 680 mV. The application to mono facial n type solar cells resulted in a V_{OC} of 666 mV and a cell efficiency of 19.7% using LCO (532 nm) and sputtered Al on large area n type Cz Si substrates. For LCO a dot grid pattern was found to be ideal to increase V_{OC} and FF due to an increase in passivated cell area and decreased series resistance. The ablation process is in this case considered to be damage free, even using a dot grid pattern.

Acknowledgements

The financial support from the BMU projects FKZ 0325581 and FKZ 0325449A via a subcontract granted by SolarWorld Innovations GmbH is gratefully acknowledged. We like to thank Dr. Bianca Gründig Wendrock for providing wafer samples, Dr. Bernd Bitnar and Dr. Phedon Palinginis for guiding and accompanying the cell development activities.

References

- [1] Macdonald D, Geerligs LJ. Recombination activity of interstitial iron and other transition metal point defects in p- and n-type crystalline silicon. *Appl Phys Lett* 2004; 85(18):4061-3.
- [2] Schiele Y, Fahr S, Joos S, Hahn G, Terheiden B. Study on boron emitter formation by BBr_3 diffusion for n-type Si solar cell applications, In: *Proc 28th EUPVSEC, Paris 2013*. p. 1242-7.
- [3] Wehmeier N, Schrapf G, Wagner H, Lim B, Harder N-P, Altermatt PP. Boron-doped PECVD silicon oxides as diffusion sources for simplified high-efficiency solar cell fabrication. In: *Proc 28th EUPVSEC, Paris 2013*. p. 1980-4.
- [4] Keding R, Rothhardt P, Roters C, Fallisch A, Hohage S, Hofmann M, Woehl R, Borchert D, Biro D. Silicon doping performed by different sources aiming co-diffusion. In: *Proc 27th EUPVSEC, Frankfurt 2012*. p. 1906-11

- [5] Cabal R, Jourdan J, Grange B, Veschetti Y, Heslinga D. Investigation of the potential of boron doped oxide deposited by PECVD Application to advanced solar cells fabrication processes. In: Proc 24th EUPVSEC, Hamburg 2009. p. 1605-8
- [6] Babics M, Cortés-Juan F, Ponce-Alcántara S, Cubera O, Sánchez G. Optimization and development of a new IBC process with only one diffusion step. In: Proc 27th EUPVSEC, Frankfurt 2012. p. 1700-3.
- [7] Morizane K, Gleim PS. Thermal Stress and Plastic Deformation of Thin Silicon Slices. *J Appl Phys* 1969; 40(10):4104-7.
- [8] Engelhardt J, Ohl S, Hahn G, Terheiden B. Correlation of Stress in Silicon Nitride Layers with their Complete Removal by Laser Ablation. *En Proc* 2013; 38:707-12.
- [9] Choi TY, Grigoropoulos CP. Plasma and ablation dynamics in ultrafast laser processing of crystalline silicon. *J Appl Phys* 2002; 92(9):4918-25.
- [10] Stuart BC, Feit MD, Herman S, Rubenchik AM, Shore BW, Perry MD. Nanosecond-to-femtosecond laser-induced breakdown in dielectrics. *Phys Rev B* 1996; 53(4):1749-61.
- [11] Arora VK, Dawar AL. Laser-induced damage studies in silicon and silicon-based photodetectors. *Applied Optics* 1996; 35(36):7061-5.