CONTACT FORMATION ON BORON DOPED SILICON SUBSTRATES FROM PASSIVATING PECV-DEPOSITED DIELECTRIC DOPING LAYERS WITH ANTI-REFLECTIVE PROPERTIES BY SCREEN-PRINTING AG PASTES FOR HIGH-EFFICIENCY N-TYPE SILICON SOLAR CELLS

Josh Engelhardt*, Alexander Frey, Susanne Fritz, Gabriel Micard, Stefanie Riegel, Giso Hahn and Barbara Terheiden
University of Konstanz, Department of Physics, Box 676, 78457 Konstanz, Germany
*Author of correspondence: josh.engelhardt@uni-konstanz.de, +49-7531-88-2080

ABSTRACT: n-type silicon solar cell designs for high-efficiency commonly incorporate boron emitter formation. PECV-deposited boron diffusion sources are an alternative to primarily used boron gas diffusion sources. CVD layers are multi-functional allowing for diffusion of boron, surface passivation and contact formation by one single layer. In this case, these BSG layers are applied in a co-diffused cell design for screen-printed contacts. Reaching iV_{OC} values of over 660 mV as ARC layers, BSG layers are shown to be capable to support the contact formation of commercial Ag pastes to boron emitters at standard firing conditions. An analysis of the contact resistivity as well as the contact formation by SEM is conducted to verify the high quality of the screen-printed contact.
Keywords: boron, contact, diffusion, PECVD, screen-printing

1 INTRODUCTION

High-efficiency solar cells use n-type silicon substrates due to the higher bulk lifetime and lower susceptibility to degradation. Furthermore, a larger amount of processing steps is generally needed to fabricate such type of solar cell. Expensive boron emitter formation as well as complex metallization techniques and cell structures are used to achieve the necessary efficiency to be cost-efficient.

In the last years, alternative process steps have been developed to simplify process steps. One of these were PECV(plasma-enhanced chemical vapor)-deposited doped layers (i.e. boron silicate glasses, BSG) enabling co-diffusion of emitter and FSF (front surface field) or BSF (back surface field) diffusion in one single step without additional masking steps [1-4].

The same layer could also be used as a passivation layer and thereby render a commonly used and costly Al_2O_3/SiN_x-stack obsolete. The passivation quality has to survive the high-temperature co-diffusion step. If applied to the front or the back (e.g. for bifaciality) it also has to have anti-reflective, non-absorbent properties. Furthermore, it has to allow for any form of cost-effective metal contact formation, such as screen-printing. Therefore, such BSG layers are multi-purpose layers [3].

2 EXPERIMENTAL

The deposition of dielectric doping layers was performed using an ICP(inductively coupled plasma)-PECVD tool with a single deposition chamber. Beside silane, carbon dioxide and diborane diluted in hydrogen were used as reactive gases forming a comparably carbon-free BSG (SiO_x:B) layer. The n-type silicon substrates were KOH etched and standard industrially cleaned before deposition of doping layers with different thicknesses. The following diffusions were carried out in a tube diffusion furnace using a co-diffusion step comprising of a high temperature drive-in similar to standard boron diffusions and a subsequent low temperature step for a $POCl_3$ diffusion of a FSF/BSF. Symmetrical boron emitter samples for saturation current density j_0 and implied open circuit voltage iV_{OC} measurements were processed alongside on FZ-Si substrates and passivated by either the remaining SiO_x:B doping layer or a fired Al_2O_3/SiN_x-stack deposited after the doping layer removal.

The emitter profile and passivation parameters were measured using electrochemical capacitance-voltage measurement (ECV), four-point probe and a Sinton Lifetime Tester (QSSPC) setup. The optical properties of the doping layers were determined by ellipsometry.

All contact samples were screen-printed using commercially available Ag and Ag/Al pastes and subsequently fired at different set peak firing temperatures in an IR belt furnace. The printed finger structure was a special TLM (transfer length method) pattern to determine the contact and sheet resistance. Pieces of these samples were etched in HF to remove the metal fingers and then in HCl/HNO_3 to remove the possible metal spikes in the substrate (Fig. 1). Top view images of the contacts after etching steps were recorded by SEM.
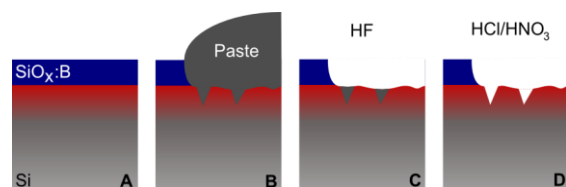

Figure 1: A: Cross section of cell front side; B: Ag/Al contact scheme; C: HF etched sample; D: HCl/HNO_3 etched sample

3 RESULTS AND DISCUSSION

3.1 Layer and emitter properties

Depending on the concentration of incorporated boron atoms, doped silicon oxide layers can be thinner than 30 nm to act as a source for a standard boron emitter with a sheet resistance R_{Sheet} of about 50 Ω/sq (Tab. 1). In case of pre-deposited doping sources by PECVD, emitter parameters such as depth and surface doping concentration ($N_{Surface}$) can be adjusted easier due to a wider parameter range of deposition and diffusion in comparison to standard boron tube diffusions (BBr_3, etc.).

Without producing a highly recombination-active boron rich layer (BRL) and avoiding a subsequent oxidation of the highly recombination-active surface, a boron emitter from PECVD doping layer diffusion can

reach $N_{Surface}$ values above $1 \cdot 10^{20}$ cm^{-3} and a depth of more than 800 nm. This allows for low contact resistance and a broader window of firing temperatures for proper contact formation. In addition, the doping layers are passivating even after the high-temperature diffusion step [3]. In comparison, j_0 values of about 80 fA·cm^{-2} and iV_{OC} values of about 660 mV (Tab. I) are the same for the remaining doping layer and a fired Al_2O_3/SiN_x-stack commonly used for boron emitter passivation. Optical properties (Tab. I) of the doping layer can also be optimized by shaping the deposition parameters. In this case, the refractive index increases from 1.45 for undoped layers to 1.7 at 633 nm due to incorporation of boron atoms in the silicon oxide. Boron atoms increase the absorption of the layer due to free carrier absorption. Yet after the drive-in step the refraction index decreases to 1.5 and the extinction coefficient decreases to values below $1 \cdot 10^{-4}$ at 400 nm due to out-diffusion of boron atoms forming the emitter and due to changes in the amorphous structure of the SiO_x:B layer while being exposed to high temperature during diffusion.

Arising from these properties of the doping layer, a solar cell concept using the doping layer for surface passivation as well as anti-reflective coating drastically reduces the necessary production steps. Therefore, we investigated the possibility to contact the boron emitter through doping layers of various thicknesses and deposition parameters by screen-printed metal paste.

Table I: SiO_x:B doping layer optical and boron emitter electrical properties. j_0 and iV_{OC} values for doping layer and Al_2O_3/SiN_x-stack passivation

SiO$_x$:B layers

Thickness	30-100 nm
n @ 633 nm	1.5
k @ 400 nm	$<1 \cdot 10^{-4}$

Boron emitter

R_{Sheet}	50 Ω/sq
$N_{Surface}$	$1 \cdot 10^{20}$ cm^{-3}
Depth	800 nm
$j_{0,SiOx:B}$	81 fA·cm^{-2}
$iV_{OC,SiOx:B}$	660 mV
$j_{0,Al2O3/SiNx}$	77 fA·cm^{-2}
$iV_{OC,Al2O3/SiNx}$	665 mV

3.2 Contact investigations

Ag/Al pastes are commonly used for contacting boron doped Si by screen-printed contact finger grids. Due to the high solubility of Al in Si, contact formation of metal to semiconductor is facilitated [5]. With increasing firing temperature, the specific contact resistance (R_C) decreases (Fig. 2).

The Al-Ag-Si contact formation highly depends on the thickness of the dielectric layer in between. The thicker it is, the higher the peak firing temperature needs to be for the Ag/Al paste to dissolve the layer and contact the emitter. Ag/Al pastes tend to reach very low contact resistance values due to the comparatively deep and therefore large inverted-pyramidal shaped contact crystals, which are in direct contact with the Si substrate [4, 6]. Therefore, the risk of spiking and subsequent shunting of the space charge region is increased with peak firing temperature. Problematic are spikes that do not form a p$^+$ Al emitter between the n-type Si base and

the pure metal of the spike. Fig. 3 depicts the remaining pits after metal etching underneath the finger contact area. From image A (arrow) to D the pits grow in diameter as well as depth.
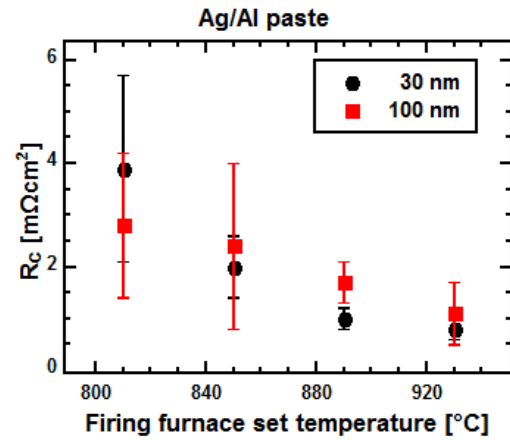

Figure 2: Specific contact resistance for Ag/Al paste in dependence on the firing furnace set peak temperature for 30 and 100 nm thick doping layers
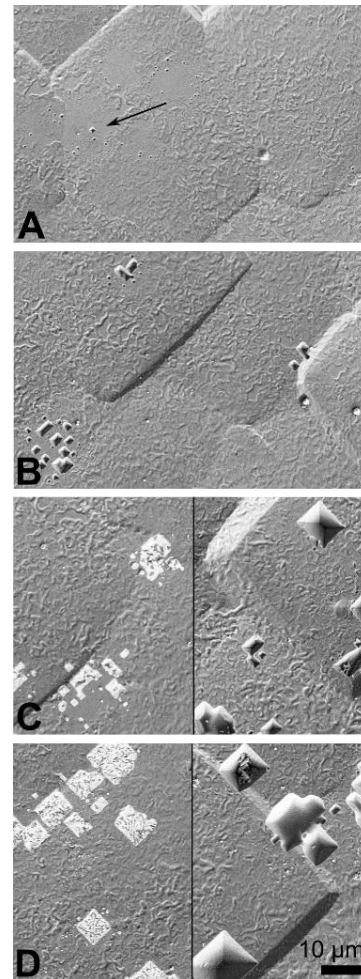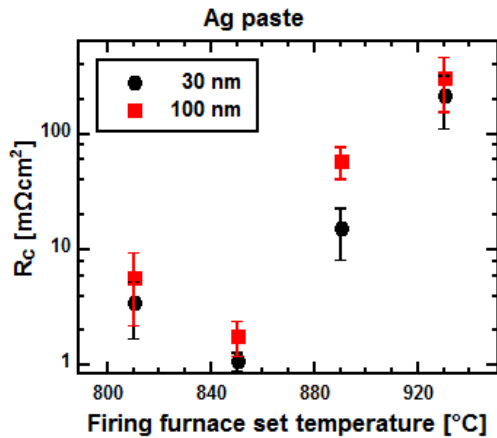

Figure 3: SEM images of areas underneath Ag/Al paste fingers after HF etch (C_{left}, D_{left}) and subsequent HCl/HNO$_3$ etch (A, B, C_{right}, D_{right}) for increasing firing furnace set peak temperatures according to Fig. 2

Ag paste

Figure 4: Specific contact resistance for Ag paste in dependence on the firing furnace set peak temperature for 30 and 100 nm thick doping layers
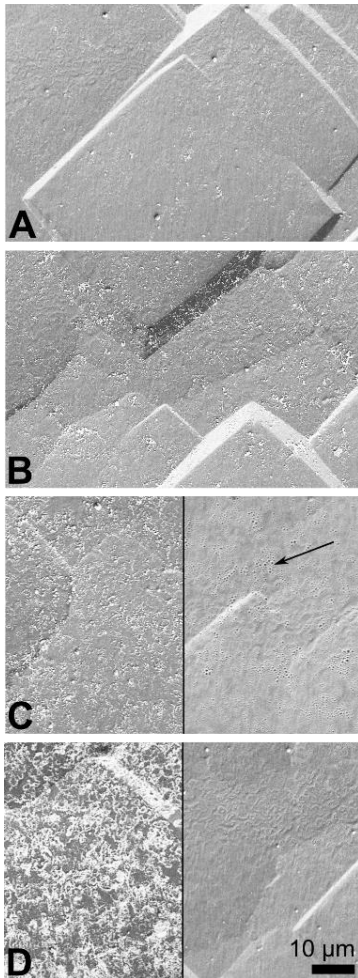
Figure 5: SEM images of areas underneath Ag paste fingers after HF etch (A, B, C_{left}, D_{left}) and subsequent HCl/HNO_3 etch (C_{right}, D_{right}) for increasing firing furnace set peak temperatures according to Fig. 4

Ag pastes are mainly used to contact n-type (e.g. $POCl_3$ diffused) emitters [7]. The contact resistance dependence of Ag pastes is further known to have an optimum between an under-firing and an over-firing zone [8] (Fig. 4). In this case of contacting p-type Si with pure Ag paste, the specific contact resistance in the optimum drops below 2 $m\Omega cm^2$ reaching a comparatively low value uncommon for commercially available Ag pastes on boron emitters, that are normally intended for the use of contacting highly phosphorous doped Si.

SEM images (Fig. 5) support the findings of the TLM measurements. Images A to D show an increase of Ag contact crystals and a change in distribution and form. Image C even shows small etch pits (arrow) of over-fired contacts.

According to literature, Ag pastes tend not to form proper contacts to boron emitters due to lack of precipitates in form of inactive dopants or defects [9, 10] and therefore yield high contact resistance values on boron emitters [6]. In case of the samples presented here, the boron emitter is not depleted on the surface, allowing for a high $N_{Surface}$ value and therefore a higher precipitation density. Furthermore, the dielectric $SiO_x:B$ layer is not totally depleted of boron atoms being a defect region between emitter and paste. We therefore assume a facilitated contact formation of Ag to the boron emitter due to precipitates in the doped dielectric layer and in the highly doped emitter surface.

ICP-OES (optical emission spectrometry) measurements on the layer show a measureable boron content remaining after diffusion, yet electrometer measurements show a high resistivity in the $1 \cdot 10^{18}$ Ωcm range common for perfect insulators. Furthermore, the IV-curves show an ohmic behavior followed by what is assumed to be space charge limited current (SCLC) related behavior due to a large distribution of defect states within the bandgap. Therefore, it is not yet determined how exactly the layer facilitates the contact formation for Ag pastes in contrast to e.g. $SiN_x:H$ layers, which yield comparably high contact resistance values.

The boron atoms in $SiO_x:B$ doping layers after the diffusion step may not allow for sufficient conductivity through the layer but may either introduce boron atoms into the paste during etching by the glass frit or present defect states in the layer that lower the reaction energy necessary for the contact formation.

Even Ag pastes with lower glass frit content, applied commonly for contactless busbars, penetrate the doped silicon oxide and contact the boron emitter with sufficiently low contact resistance values provided the contacted area is large enough (Fig. 6).
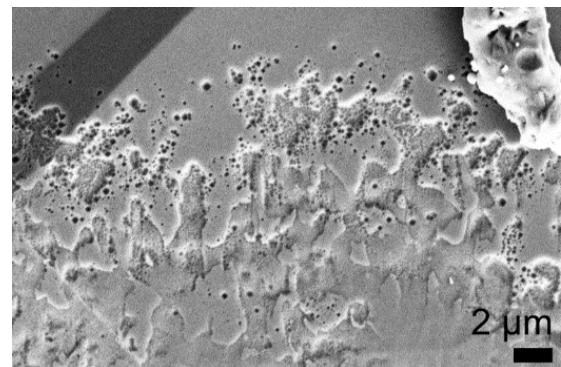
Figure 6: SEM image of an area underneath Ag paste finger for contactless busbars after HF and subsequent HCl/HNO_3 etch

4 CONCLUSIONS

In conclusion, the PECV-deposited dielectric layer proved at the same time to passivate the diffused emitter even after the high temperature drive-in step and have anti-reflective properties with a very low absorption rate. Additionally, it allows the emitter to be shaped suitable not only for screen-printing with Ag/Al, but also with pure Ag paste resulting in specific contact resistance of 2 $m\Omega cm^2$ and below.

ACKNOWLEDGEMENTS

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