

## CONTACT FORMATION ON P-DOPED SI BY SCREEN-PRINTING PURE AG PASTES FOR BIFACIAL N-TYPE SI SOLAR CELLS

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**ABSTRACT:** n-type solar cell concepts increasingly utilize emitter formation by diffusion from boron doped sources. Combining the advantage of n-type silicon material and bifacial cell architecture enables high-efficiency and versatile photovoltaics. In case of boron emitters, it was standard until now to form a metal-semiconductor contact by screen-printing Al containing Ag pastes. Instead of utilizing Al to enable Ag to form a sufficient contact with the risk in loss of  $V_{oc}$  and FF, different glass compositions for pure Ag pastes were developed to form a contact with low impact on cell efficiency. In direct comparison this method in the first try already surpasses the performance of commercial Al containing Ag pastes in direct comparison. The experimental pastes show a distinctive gain in solar cell characteristics in contrast to commercial pure Ag pastes. In this case we reached an overall efficiency of 18.6% using pure Ag pastes. Contact resistivity values thereby range below 1-2  $m\Omega cm^2$  comparable to pure Ag pastes on n-type emitters and Ag/Al pastes on p-type emitters.

**Keywords:** screen-printing; Ag paste; boron emitter; contact formation; n-type

### 1 INTRODUCTION

High-efficiency solar cells use n-type Si substrates due to the higher bulk lifetime and low susceptibility to degradation. With the use of n-type substrates, challenges from the common use of p-type emitters from, e.g.,  $BBr_3$  diffusions arise. An example is contact formation of the screen-printed metal paste to the bulk Si substrate. Considering the widespread utilization of the method in industry, different approaches to deal with the challenge and optimize the contact quality have been done. Commonly, Al containing pastes are used to successfully form a contact to the B emitter [1] with contact resistivity values below 10  $m\Omega cm$ . Yet this approach brings restrictions in firing parameters and a drop in  $V_{oc}$  and fill factor, compared to contact formation with Ag pastes on n-type emitters. Yet simply using Ag pastes on p-type emitters has so far not been successful [1-3]. B emitters lack the precipitates deemed necessary for the contact formation behavior of pure Ag pastes [4] with the standard glass composition forming shallow surface crystals [4,5]. Furthermore, B emitters usually display a surface dopant concentration below  $10^{20} cm^{-3}$ , making it even harder to form a proper contact. The advantage of pure Ag pastes, however, is the lack of the deep crystal formation behavior that Al containing pastes display. Without it,  $V_{oc}$  and fill factor values should remain unaffected following the undisturbed space-charge region.

### 2 EXPERIMENTAL

Comparison and detailed investigation of the influence, physics and results of different pastes were carried out on bifacial n-type Si solar cells and TLM (transfer length method) precursors. Fully textured bifacial cells as well as TLM test structures were one-side  $BBr_3$  diffused and afterwards obtained a selective back surface field (s-BSF) by  $POCl_3$  diffusion and selective etch-back. During diffusions PECVD (plasma enhanced chemical vapor deposition)  $SiN_x:H$  was used to shield the respective backside of the wafer from parasitic in-diffusion. All samples were then passivated by double-side thermal  $SiO_2$  and PECVD  $SiN_x:H$  stack passivation.

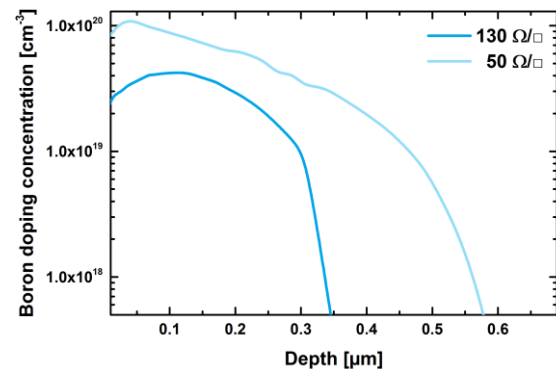
Screen-printing and contact firing were done using mesh printing contact grids on both sides and a firing belt furnace, respectively. Finally, the cells were fully characterized using a flasher setup for IV measurements, a combination tool for reflection, thermography and additional measurements, as well as a TLM measurement setup to determine contact resistance obtained from TLM samples.

Screen-printing was done with various commercially available state-of-the-art pure and Al containing Ag pastes, as well as with experimental pure Ag pastes developed in cooperation with Johnson Matthey. Latter pastes were varied in Pb and Te content as well as glass composition to optimize contact formation on p-doped layers.

### 3 RESULTS AND DISCUSSION

#### 3.1 Emitter properties

The  $BBr_3$  emitter with a sheet resistance  $R_{sheet}$  of 50  $\Omega/\square$  used in this study was originally developed for optimized contact formation with Al containing Ag pastes (Fig. 1).



**Figure 1:** Profiles of the two B emitters used for bifacial solar cells and TLM test structures

In contrast, TLM studies with pure Ag pastes showed no difference in contact resistivity values on samples with different boron emitter profiles. Therefore, to show

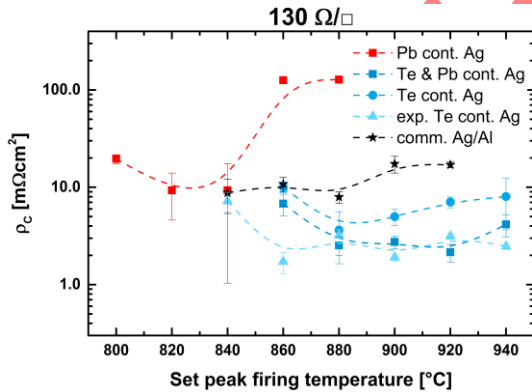
the advantage of Ag pastes on the highest level possible, we choose the emitter best suited for Al containing pastes (Tab. I) and a high ohmic emitter to show the restrictions of Ag/Al pastes. Similar emitter profiles are common to newer diffusion sources, such as CVD BSG (borosilicate glass) sources [6] also capable to be contacted with pure Ag pastes. Thereby, an emitter saturation current density of  $<40 \text{ fA/cm}^2$  on Float-Zone (FZ) n-type Si substrates can be reached, if passivated with  $\text{Al}_2\text{O}_3$ . Yet on the Czochralski (Cz) Si substrate passivated by  $\text{SiO}_2/\text{SiN}_x\text{:H}$  and used here for solar cell and TLM samples, the implied  $V_{OC}$  value remains 657 mV or 678 mV for the low and high ohmic emitters, respectively.

**Table I:** General B emitter characteristics and  $iV_{OC}$  values for  $\text{SiO}_2/\text{SiN}_x\text{:H}$ -stack passivation

$R_{Sheet}$	$50 \Omega/\square$	$130 \Omega/\square$
$N_{Surface}$	$8.0 \cdot 10^{19} \text{ cm}^{-3}$	$2.3 \cdot 10^{19} \text{ cm}^{-3}$
$N_{Max}$	$1.1 \cdot 10^{20} \text{ cm}^{-3}$	$4.2 \cdot 10^{19} \text{ cm}^{-3}$
Depth	600 nm	370 nm
$j_{0E, Al_2O_3} (FZ, n)$	$<40 \text{ fA/cm}^2$	$<30 \text{ fA/cm}^2$
$iV_{OC, SiO_2/SiN_x} (Cz, n)$	657 mV	678 mV

### 3.2 Contact investigations

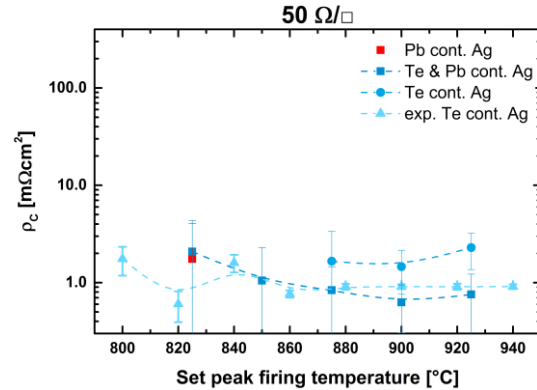
Ag/Al pastes are commonly used for contacting B doped Si by screen-printed contact finger grids. Due to the high solubility of Al in Si, contact formation of metal to semiconductor is facilitated [7]. With increasing firing temperature the specific contact resistance  $\rho_c$  decreases for Ag/Al pastes on low ohmic emitters. Yet below  $1\text{--}2 \text{ m}\Omega\text{cm}^2$ , shunting of the space-charge region (SCR) in solar cells commonly occurs. On high ohmic emitters (Fig. 2) the resistance never drops so low and instead increases for higher temperatures again.



**Figure 2:** Contact resistance measurements from TLM test structures of different pastes dependent on the set peak firing temperature on a  $130 \Omega/\square$  B emitter

Old generation pure Ag pastes containing Pb were verified to contact at least at low set peak temperatures in contrast to older publications and at a comparable level to commercial modern pastes. Yet, the latter pure Ag pastes contact in a broader firing range and at higher temperatures as well. Adding Te, used to supplement or even substitute Pb, shifts the minimum contact resistance value to higher temperatures and outweighs the influence of Pb on contact formation behavior. By optimization of the glass composition in the experimental only Te containing paste (no Pb), the window broadens further and  $\rho_c$  values of below  $2 \text{ m}\Omega\text{cm}^2$  can be reached. With

this paste, levels only double the average value for the same paste on a far lower  $R_{Sheet}$  B emitter of  $50 \Omega/\square$  can be reached (see Fig. 3).



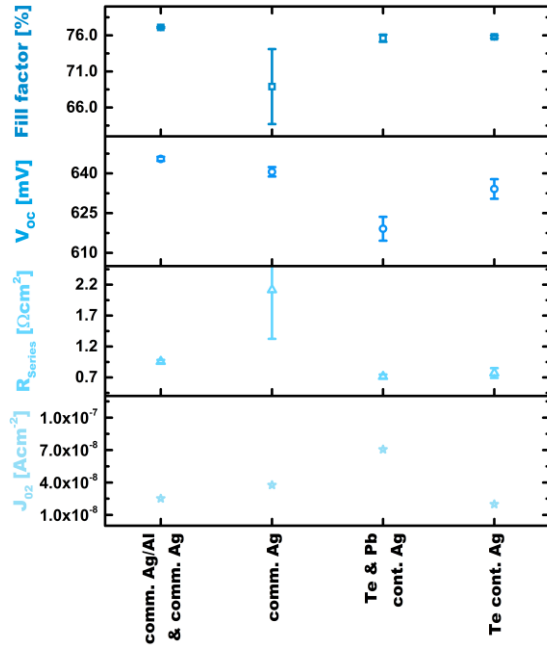
**Figure 3:** Contact resistance measurements from TLM test structures of different pastes dependent on the set peak firing temperature on a  $50 \Omega/\square$  B emitter

Considering the firing temperature range, the overall behavior of the pastes on a low ohmic emitter is similar to Fig. 2. It also ranges in the same resistivity range as Ag/Al do. Even the old generation Pb based Ag paste reaches a measureable resistivity value, but only for a single low temperature. Pure Ag pastes, independently of their composition, apparently do vary less with  $R_{Sheet}$  as Ag/Al pastes do. Limiting influence for the Ag/Al pastes thereby might be either the depth (area of contact with spikes) or the surface doping concentration. Since pure Ag pastes do not penetrate the space-charge-region, they do not suffer from these limiting influences and further display higher contact crystal densities. The self-limiting nature of Ag paste contact formation by glass layer growth at higher temperatures also diminishes the possibility of ‘spiking’.

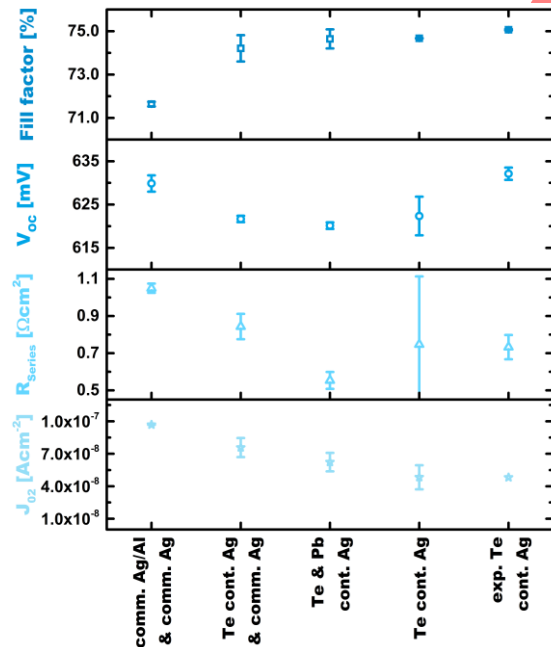
### 3.3 Solar cell results

Bifacial solar cells, processed as described before, are a straightforward and beneficial way to characterize the effect of printing the aforementioned pastes on p- and n-type Si layers. In case of the  $50 \Omega/\square$  B emitter, cells were printed with the reference group of a commercial Ag/Al paste on the B emitter and a commercial pure Ag paste on the P diffused high-low-junction. Two commercial Ag pastes, with respective lowest contact resistivity values for both sides of the cell were used as a pure Ag reference group and state-of-the-art comparison. Furthermore, a Te added old generation Pb containing pure Ag paste and a pure Te based Ag paste were printed. In direct comparison (Fig. 4) the FF is comparable on this deep and highly doped emitter except for the commercial pure Ag paste combination. The reason is an increase in series resistance on cell level despite the optimal firing temperature used for all pastes. The contact formation for the currently available pastes still lacks the optimization for B doped surfaces. Older pastes based on high Pb content perform better in contact formation, yet seem for example to in-diffuse recombination active compounds leading to a decrease in  $V_{OC}$ . The indiffusion into the SCR is also visible in a significant increase in the saturation current density of the second diode  $j_{02}$ . Standard Te based pure Ag pastes instead reach nearly the same level of Ag/Al pastes in every aspect reaching

18.6% efficiency compared to 19.1% of Ag/Al printed cells.



**Figure 4:** FF,  $V_{oc}$ ,  $R_{Series}$  and  $j_{02}$  of bifacial solar cells with a  $50 \Omega/\square$  B emitter in dependency of different screen-printing pastes. From left to right: Group 1 with comm. Ag/Al on B and comm. Ag on P layer. Group 2-4 with pure Ag paste on both layers.



**Figure 5:** FF,  $V_{oc}$ ,  $R_{Series}$  and  $J_{02}$  of bifacial solar cells with a  $130 \Omega/\square$  B emitter in dependency of different screen-printing pastes. From left to right: Group 1 & 2 with comm. Ag/Al or Te cont. pure Ag on B, respectively, and comm. Ag on P layer. Group 3-5 with pure Ag paste on both layers.

The optimal temperatures thereby range in the  $840^\circ\text{C}$  set peak firing temperature range for Ag/Al compared to  $880^\circ\text{C}$  for the Ag pastes. Considering the passivation of a

$\text{SiO}_2/\text{SiN}_x:\text{H}$  stack, H diffusion and passivation optimum ( $iV_{oc}$ ) is at the higher temperature range, preferred by pure Ag pastes. This makes pure Ag pastes interesting for inexpensive passivation layers fired commonly at higher temperatures.

Since this  $50 \Omega/\square$  B emitter is deep enough to largely prevent the majority of negative effects Ag/Al pastes have, a higher ohmic emitter was used to demonstrate the loss of Ag/Al pastes while increasing the passivation quality of the emitter. As can be seen from Tab. I, the  $130 \Omega/\square$  B emitter can reach a far higher  $iV_{oc}$  value since the doping concentration in total as well as on the surface is reduced. Lateral conductivity is still assured, given the contact resistivity values from Fig. 2. Therefore, on cell level a significant gain should be possible.

Fig. 5 shows the respective cell results on an overall efficiency level of about 18-19%. To compare the influence of the pure Ag paste on the B emitter more explicitly, the first two groups were printed with the same commercial Ag paste on the P FSF. Only the influence of the B side is visible. Ag/Al paste now drops in FF and  $V_{oc}$ . In accordance,  $R_{Series}$  and  $j_{02}$  rise as well. Since the Te containing Ag paste is not optimized, a certain degree of contaminants now reaches the SCR, resulting in a drop in  $V_{oc}$ . There is now no difference between the Pb containing and the pure Te based Ag paste in that account. Using the latter paste for both sides, only marginally improves upon the commercial Ag paste, made for a P FSF. To regain and surpass the  $V_{oc}$  value of the Ag/Al paste and improve upon the FF further, the Te based, Pb free, pure Ag paste needs to be optimized, leading to the current experimental paste with a FF increase of  $3.5\%_{abs}$  compared to commercial Ag/Al pastes.

#### 4 CONCLUSION

We showed how pure Ag pastes, old and new ones, can contact differently diffused B emitters in a wide range of diffusion and firing parameter ranges. Furthermore, TLM measurements showed a significant influence of composition, *i.e.* Te and Pb content. Bifacial solar cells, printed with experimental pure Ag pastes, result in significant improvement of FF upon the state-of-the-art presented by commercial Ag/Al pastes. Yet commercial Ag pastes cannot reach this level due to limitations stemming from the aforementioned glass composition issues. Further work has to be done, to improve passivation and overall efficiency gain for different solar cell design types to utilize the potential of pure Ag pastes on B emitters.

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