

MICROSCOPIC THICK FILM CONTACT FORMATION MECHANISM TO P(P+) SI AND INFLUENCE OF THE METAL CONTACT ON THE SI SUBSTRATE – LESSONS LEARNED FROM THE KONSENS PROJECT

Stefanie Riegel¹, Susanne Fritz¹, Katharina Dressler¹, Axel Herguth¹, Markus König², Matthias Hörteis², Giso Hahn¹

¹University of Konstanz, Department of Physics, 78457 Konstanz, Germany

²Heraeus Deutschland GmbH & Co. KG, Heraeusstr. 12 - 14, 63450 Hanau, Germany

Author for Correspondence: Stefanie.Riegel@uni-konstanz.de

ABSTRACT: The German research project KONSENS investigated the contact formation of screen-printed contacts to crystalline silicon. Special focus was set on contact formation to boron emitters using Al containing Ag thick film pastes and on the formation of local Al contacts. The contact resistances to B emitters using Al containing Ag thick film pastes show dependence on surface topography, i.e. the surface texture. Regarding paste composition, we found that contact formation may be influenced by the amount of Al, as well as by the amount of glass frit. The SiN_x:H layer serves as a mask during contact formation preserving the Si surface structure above the contact points. A small hole within the SiN_x:H layer allows for material exchange and thereby facilitates contact formation. This means that the contact spots show the same surface morphology as the Si. Additionally, we find that the contact spots are crystalline and consist mainly of Ag. The pn-junction can be smeared out at points of direct metal-silicon contact. Our data suggest that the Al from the Ag thick film paste does not lead to local Al doping underneath the contact spots. Our findings can be explained by a model for contact formation of Al containing Ag thick film pastes to B emitters. The formation of Al rear contacts is influenced by the Al particle size in the Al thick film paste. Smaller Al particles allow for a more homogenous full area Al BSF. On PERC rear structures smaller Al particles in the Al thick film paste result in a thicker local Al BSF and less maximum spread distance of diffused Si in the Al thick film paste. **Keywords:** metallization, screen printing, contact formation, boron emitter, PERC structure, local BSF

1 INTRODUCTION

Most Si solar cells are contacted by screen-printing and fast-firing of thick film metallization pastes. For novel cell concepts including B emitters or PERC(passivated emitter and rear cell)-type structures, the contact formation process is still neither fully understood nor completely optimized.

The German research project KONSENS investigated the contact formation of screen-printed contacts to B emitters using Al containing Ag thick film pastes and the formation of local Al contacts. The investigations on Al containing Ag thick film pastes are carried out with respect to two topics: a) the influence of the Si substrate (e.g. surface texture) and emitter type (e.g. doping element and diffusion source), and b) the influence of paste composition, i.e. Al content, content of glass frit. These investigations allow for a deeper understanding of contact formation and contact structure. With regard to Al thick film pastes for local contacts to p-type silicon, the influence of Al particle size on (local) BSF (back surface field) formation and Si diffusion into the Al thick film paste is investigated.

2 EXPERIMENTAL

2.1. Al containing Ag thick film pastes

For the investigations on Al containing Ag thick film pastes, textured Si substrates with different B emitters are used. SiN_x:H is PECV(plasma-enhanced chemical vapor)-deposited and the Ag thick film paste provided by *Heraeus* is screen-printed and fired in an IR belt furnace using standard firing conditions (peak T_{wafers}≈800°C). The resulting contacts are investigated with regard to contact resistance by TLM (transfer length method) and structural information is gained by means of SEM (scanning electron microscopy), TEM (transmission electron microscopy), EDX (energy dispersive x-ray spectroscopy) and XRD (x-ray diffraction) measurements. The influence of the contact on the

pn-junction is investigated by EBIC (electron beam induced current) measurements.

2.2. Al thick film pastes

For the investigations on Al thick film paste, four Al thick film pastes prepared at University of Konstanz are applied on bare Si wafers and on Si wafers with locally opened PECVD SiN_x:H layers. The thick film pastes consist of Al powder of different particle size distribution, glass frit, binder and solvent and differ only in the Al particle size distribution. The d90 values (90% of the Al particles have a diameter smaller than this value) of the Al particle diameters are given in Table 1. The Al thick film pastes are screen-printed, dried and fired in a standard firing step (peak T_{set}=840°C). Contacts are characterized by ECV (electrochemical capacitance voltage), optical and electron microscope measurements.

Table 1: Al particle diameter of the Al powders used for the different Al thick film pastes (d90 values).

Paste 1	Paste 2	Paste 3	Paste 4
4.2 μm	10.4 μm	13.1 μm	16.3 μm

3 RESULTS AND DISCUSSION

3.1 Al containing Ag thick film pastes

The contact resistances to B emitters using Al containing thick film pastes show a dependence on surface topography, i.e. the surface texture [1]. For these investigations alkaline-, acidic- and plasma-textured Si substrates were used and firing profiles were adapted to reach peak wafer temperatures of 800°C for each substrate structure. The lowest specific contact resistance ρ_c of ≈2.45 mΩcm² was found for plasma textured samples [1]. The reduced contact resistance for the plasma-textured surface is traced back to a higher density of Ag/Al contact spots on the Si surface [1]. Regarding paste composition, we found that contact formation may

be influenced by the amount of Al [2] as well as by the amount of glass frit in the Ag thick film paste. For both substances a higher content in the paste results in lower contact resistances. In both cases the reduced contact resistance can be traced back to a higher amount of contact spots. Though contact formation is enhanced by glass frit in the Al containing Ag thick film pastes, the glass frit is not necessary for contact formation with Al containing Ag thick film pastes to boron emitters. On bare Si samples (no PECVD SiN_x:H) contact formation with glass frit free Al containing Ag thick film pastes to boron emitters was observed [2].

The SiN_x:H layer serves as a mask during contact formation preserving the Si surface structure over the contact points except for small holes within the SiN_x:H layer, allowing for material exchange and thereby facilitating the contact formation. This means that the contact spots show the same surface morphology as the Si did before [2] including not only regular structures as pyramids but also rather chaotic structures achieved by acidic or plasma etching.

In TEM studies of the contact spots (exemplary overview see Fig 1), we find that the contact spots are crystalline (see Fig 2). This finding can be confirmed by

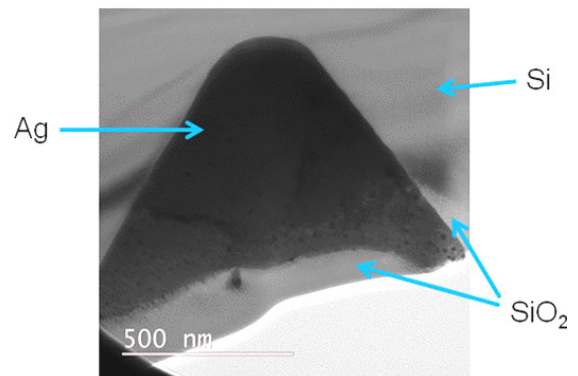


Figure 1: TEM image. Exemplary overview of Ag crystallite. High resolution images are taken from different places along the border between Ag and Si.

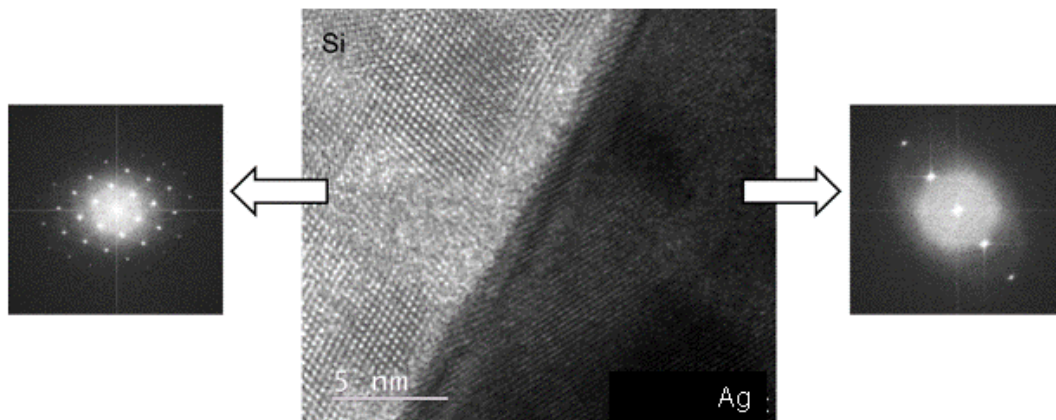


Figure 2: High resolution TEM image (middle) and fast Fourier transform of Si (left) and Ag (right) regime.

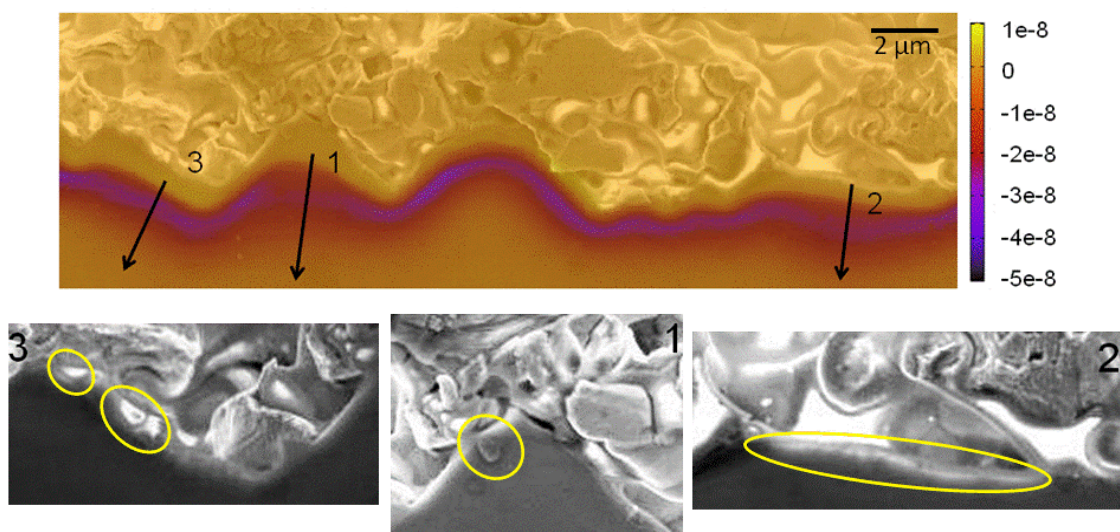


Figure 3: Top: false color image of the EBIC distribution overlaid over SEM image. Bottom: enlarged SEM images of regions 1-3. At points 1 & 2 the EBIC signal indicates a pn-junction that is smeared out. At point 3 the EBIC signal shows no influence of the metal at the Si surface. At point 1 a deep contact spot penetrates the emitter. At points 2 and 3 the metal contact is shallow and does not penetrate the emitter. In the SEM image a direct metal-Si contact is visible.

XRD measurements on contacts etched back in diluted HF [3]. The contact spots have Ag crystal structure (see Fig 2) and consist mainly of Ag. More details will be published elsewhere [3].

The pn-junction is qualitatively investigated by means of EBIC measurements on cross sections of the contact (acceleration voltage: 5 kV, penetration depth ~300 nm). The EBIC signal distribution and the corresponding SEM images are shown in Fig. 3. At point 1 a contact spot penetrates the emitter. At point 2 the metal contact is shallow enough not to penetrate the emitter. At point 3 the metal contact is shallow as well. At points 1 and 2 the EBIC signal indicates a pn-junction that is broader than next to the contact spot. At point 3 the EBIC signal shows no influence of the metal at the Si surface. This may be due to a very thin SiN_x:H layer between the metal and the Si. Additionally, our data suggests that the Al from the Ag thick film paste does not lead to local Al doping underneath the contact spots (data not shown here).

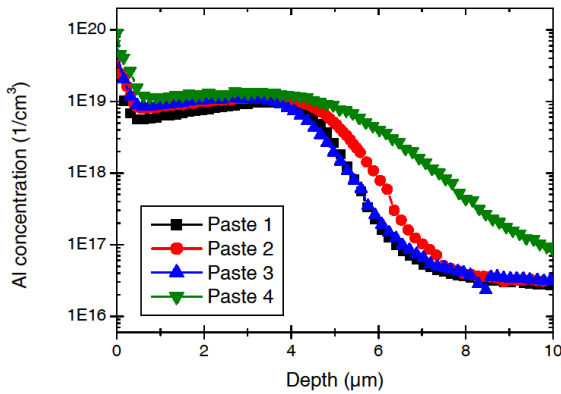


Figure 4: Doping profiles generated with the different Al thick film pastes in a standard firing step with $T_{set}=840^{\circ}\text{C}$. Profiles are measured by ECV after removing the thick film paste in diluted HCl.

3.2 Al thick film pastes

The four Al thick film pastes were screen printed on bare Si wafers and fired in a standard firing step to create a *full area Al BSF* as described in section 2.2. After removing the thick film paste in diluted HCl doping profiles are measured by ECV. The profiles of the pastes show similar peak doping of $(1.0 \pm 0.4) \text{E}19 \text{ cm}^{-3}$ at a depth of ~4 µm (see Fig. 4). The profiles generated with the different Al thick film pastes show a differently steep decrease. As this can be due to lateral inhomogeneities of the BSF depth, SEM measurement on wafer cross sections are done at 5-10 points per paste. Average BSF depths of 4 to 5 µm are measured with SEM. Within the observed variation range the BSF thickness is comparable for all pastes. Paste 1 (smallest particle size, $d_{90} < 4.2 \mu\text{m}$) allows for the most homogenous BSF. For larger Al particles the homogeneity of BSF thickness is comparable (see Fig. 5).

If the Al thick film pastes are printed on PERC structures, the influence of Al particle size on *local Al BSF* thickness is more pronounced than for full area BSFs. Paste 1 forms the deepest local BSF of ~3.2 µm depth in the applied process (see Fig. 6). With paste 2 and 3 a thin local BSF of ~1.5 µm is formed. For paste 4

(largest particles, $d_{90} < 16.3 \mu\text{m}$) no local BSF formation was observed.

The maximum spread distance of diffused Si from the local contact laterally into the Al thick film paste can be measured after the firing step by means of optical microscopy as the Al thick film paste is darkened by the dissolved Si (as introduced by [5]). Larger Al particles in the thick film paste tend to allow larger spread distances of diffused Si in the Al thick film paste (see Fig. 7). The only exception is paste 2. Further details on Si diffusion within the Al thick film paste depending on Al particle size and firing profile are published elsewhere [6].

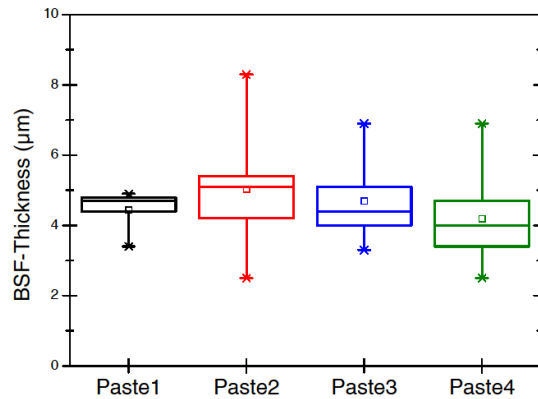


Figure 5: Thickness of *full area* BSFs generated with the different Al thick film pastes in a standard firing step with $T_{set}=840^{\circ}\text{C}$. BSF thicknesses are measured by SEM on wafer cross sections (5-10 points per paste).

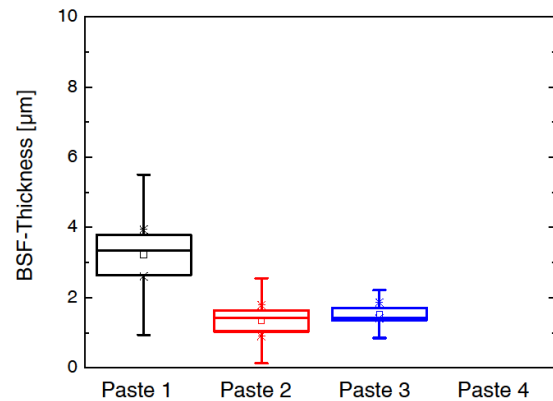


Figure 6: Thickness of *local* BSFs generated with the different Al thick film pastes in a standard firing step with $T_{set}=840^{\circ}\text{C}$. BSF thicknesses are measured by SEM on wafer cross sections. For paste 4 no local BSF could be detected.

4 CONCLUSION

4.1 Al containing Ag thick film pastes

Our findings on Al containing Ag thick film pastes can be explained by a model [3] for contact formation with Al containing Ag thick film pastes to B emitters (see Fig 8). Fig. 8.1 shows the Al containing Ag thick film pastes after drying. At temperatures $T > 600^{\circ}\text{C}$ the Al particles melt (Fig. 8.2). Ag is dissolved in Al and Al

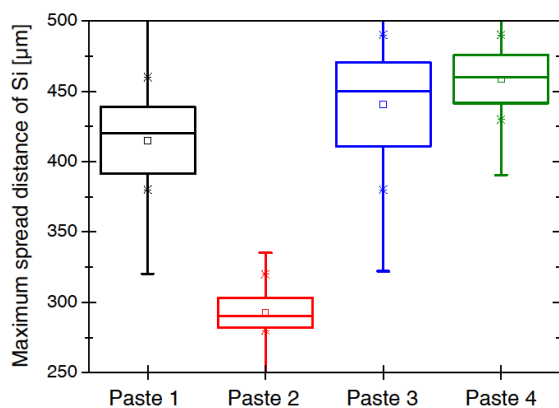


Figure 7: Si diffusion into different Al thick film pastes measured after the firing step by means of optical microscopy.

mixes with the glass. This leads to an inhomogeneous microstructure around the former Al particle. Glass frit starts etching the $\text{SiN}_x\text{:H}$. Below Al free parts of the finger, $\text{SiN}_x\text{:H}$ is removed completely (Fig. 8.3). Below inhomogeneous microstructures only small holes are etched into the $\text{SiN}_x\text{:H}$. At Al containing sites Si and Ag/Al is exchanged through small holes in the layer (Fig. 8.4). Material exchange continues and Si is consumed along the (111) faces (Fig. 8.5). During cool down Si precipitates from the mixture in small spots in the finger bulk [3]. Contact spots solidify in Ag crystal structure (Fig. 8.6).

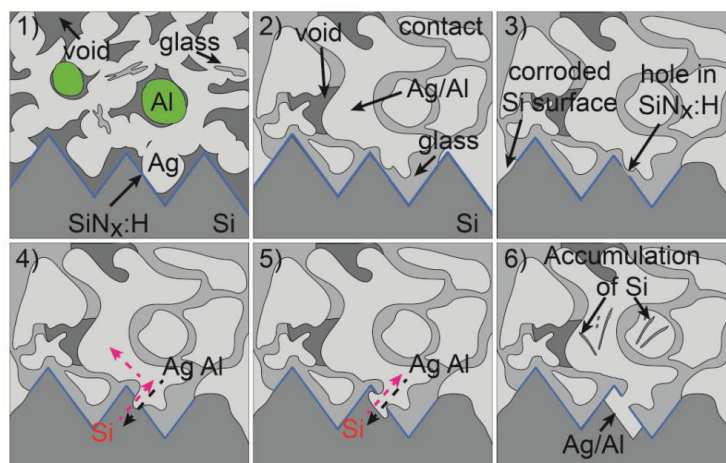


Figure 8: Schematic of the process of contact formation. 1) Ag/Al thick film paste after drying. 2) $T > 600^\circ\text{C}$: Al particles melt, react with glass and dissolve Ag. Inhomogeneous microstructure is formed around Al particles. Glass frit starts etching the $\text{SiN}_x\text{:H}$. 3) Below inhomogeneous microstructure small holes are etched into the $\text{SiN}_x\text{:H}$. Below Al-free parts, $\text{SiN}_x\text{:H}$ is removed completely. 4) At Al containing sites Si and Ag/Al is exchanged through the small hole. 5) Si is consumed along the (111) faces. 6) Cool down: Si precipitates. Contact spots solidify in Ag crystal structure.

6 REFERENCES

- [1] S. Fritz et al., Energy Procedia **67** (2015) 43-48.
- [2] S. Fritz et al., IEEE Journal of Photovoltaics **5** (2015) 145-151.
- [3] S. Fritz et al., submitted to IEEE Journal of Photovoltaics.
- [4] F.D. Heinz et al., Solar Energy Materials and Solar Cells **131** (2014) 105-109.

Our EBIC measurements give different results than the work of Heinz et al [3] who observed increased recombination only for contact spots spiking the emitter, if one traces the broader EBIC signal at the contact spots solely back to enhanced recombination. But as the EBIC signal is affected by contact formation to the sample as well as by recombination, the broadening may be due to different contact phenomena.

4.2 Al thick film pastes

The experiments presented here demonstrate, that the Al particle size in Al thick film pastes influences the formation of local as well as full area Al BSFs. For full area Al BSFs a reduced particle size of $d_{90} < 4.2 \mu\text{m}$ allows for a more homogenous BSF formation. On PERC structures smaller Al particle sizes result in an increased BSF thickness of $\approx 3.2 \mu\text{m}$. Additionally, the diffusion of Si into the Al thick film paste seems to be reduced.

5 ACKNOWLEDGEMENTS

The authors would like to thank Adnan Hammud for taking the TEM images. Part of this work was financially supported by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (FKZ 0325581) and within den KONSENS project (FKZ 0325426). The content is the responsibility of the authors.

- [5] E. Urrejola et al., Applied Physics Letters **98** (2011) 153508.

- [6] K. Dressler et al., submitted to IEEE Journal of Photovoltaics.