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Influence of emitter properties on contact formation to p⁺ silicon

Susanne Fritz^a, Stefanie Riegel^a, Sebastian Gloger^a, Dietmar Kohler^a,
Markus König^b, Matthias Hörtheis^b, Giso Hahn^a

^aUniversity of Konstanz, Department of Physics, P.O. Box X916, 78457 Konstanz, Germany

^bHeraeus Precious Metals GmbH & Co. KG, Heraeusstr. 12 - 14, 63450 Hanau, Germany

Abstract

In this study we investigate the influence of the B surface concentration $N_{surface}$ on the contact formation of Ag and Ag/Al thick film pastes to p⁺-type Si. From literature it is known, that for contacting POCl₃ emitters a high P surface concentration is necessary for a reasonable contact resistance [1,2]. This work aims to examine if the same holds for B emitters. For this purpose, three emitters with different B surface concentrations are realized and contacted with pure Ag and Al containing Ag (Ag/Al) thick film pastes: a BBr₃ emitter (I: $N_{surface} \sim 3E19 \text{ cm}^{-3}$, $R_{sh} = 50 \text{ } \Omega/\square$), and two alternative emitters without BBr₃ diffusion (IIa: $N_{surface} \sim 1E20 \text{ cm}^{-3}$, $R_{sh} = 55 \text{ } \Omega/\square$; IIb: $N_{surface} \sim 1E19 \text{ cm}^{-3}$, $R_{sh} = 330 \text{ } \Omega/\square$). The specific contact resistance ρ_c is determined using the Transfer Length Method (TLM). With Ag/Al paste $\rho_c = 9.95 \text{ m}\Omega\text{cm}^2$ on emitter IIa and $\rho_c = 37.6 \text{ m}\Omega\text{cm}^2$ on IIb could be determined. For the same emitter type a higher $N_{surface}$ therefore results in a lower ρ_c . This cannot be observed for different types of emitters as $\rho_c = 4.8 \text{ m}\Omega\text{cm}^2$ was measured on emitter I. For a pure Ag paste the same trend can be observed but with ρ_c being at least a factor of four higher, as expected [3-5]. Electron microscopy analysis reveals that for pure Ag pastes no direct contacts between Ag crystals on the Si surface and the Ag bulk exist. In contrast, for the Ag/Al pastes a direct connection between the Ag/Al particle in contact with the silicon surface and the Ag finger can be found. We propose that the low contact resistance for Ag/Al pastes may be due to direct contacts of Ag/Al spots to the Ag bulk.

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1. Introduction

During the last years a lot of work has been carried out on understanding the process of contacting n-type emitters (e.g. [1,2]). In contrast, the mechanism of contact formation to p⁺ Si is not well understood up to now. It has been shown, that adding Al to an Ag thick film paste reduces the specific contact resistance ρ_c [3-5]. To contact POCl₃ emitters, a high P surface concentration ($N_{surface} \sim 1E20 \text{ cm}^{-3}$), is

necessary [1,2], while for B emitters the influence of the surface concentration has not been investigated yet.

In this work, the influence of the B surface concentration of the p-type emitter on the contact formation is examined. Therefore, three emitters differing in B surface concentration $N_{surface}$, depth d and B-glass layer formation are realized. The wafers are contacted with three different pastes: two experimental pastes - a pure Ag paste (paste Ag) and an Ag/Al paste with the same glass system (AgAl) - as well as a commercially available Ag/Al paste with a different glass system (AgAlref).

2. Experimental

For the experiment n-type Czochralski (Cz) wafers with a resistivity of $\sim 4 \Omega\text{cm}$ are used. After texturisation in an alkaline bath the different emitters are formed: I) emitter type I ($N_{surface} \sim 3\text{E}19 \text{ cm}^{-3}$, $R_{sh}=50 \Omega/\square$, $d=0.7 \mu\text{m}$), IIa) emitter type II ($N_{surface} \sim 1\text{E}20 \text{ cm}^{-3}$, $R_{sh}=55 \Omega/\square$, $d=0.47 \mu\text{m}$), IIb) emitter type II ($N_{surface} \sim 1\text{E}19 \text{ cm}^{-3}$, $R_{sh}=330 \Omega/\square$, $d=0.47 \mu\text{m}$) - emitter type I is a BBr_3 emitter, for type II the emitter is diffused from a B containing glass. $N_{surface}$ and d are determined by an electrochemical capacitance voltage (ECV) measurement. The corresponding emitter profiles are shown in Fig. 1. The emitters IIa and IIb show up to a depth of $\approx 0.3 \mu\text{m}$ almost parallel profiles. The ECV profile of emitter I reveals a deeper emitter and B depletion at the surface.

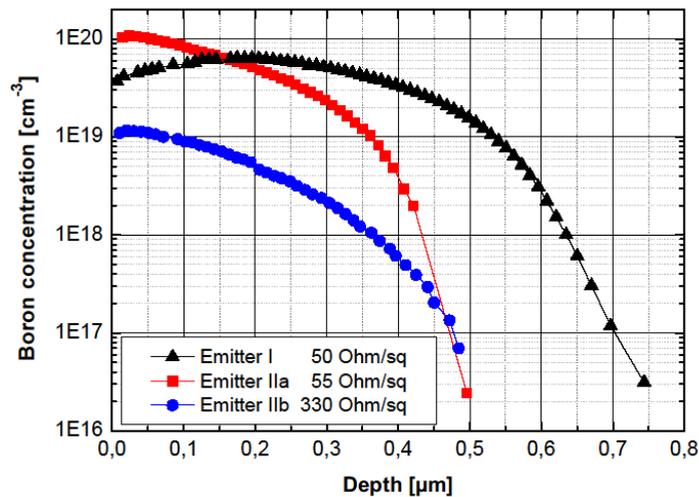


Fig. 1. ECV profiles of emitters I, IIa and IIb. The profiles of the emitters IIa and IIb are almost parallel up to a depth of $\approx 0.3 \mu\text{m}$. Emitter I is deeper and shows B depletion at the surface.

After emitter formation a $\sim 75 \text{ nm}$ thick plasma enhanced chemical vapour deposition (PECVD) $\text{SiN}_x\text{:H}$ layer is deposited. Contact formation of the three different pastes is realized by screen printing a TLM test structure and firing under standard conditions in a belt furnace (peak temperature $\sim 800^\circ\text{C}$). Contact resistance analysis is done by TLM measurements. For subsequent scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis of the contact area, contacts are etched back in *aqua regia* (HNO_3+HCl , 1:3) to remove only the bulk Ag or in *hydrofluoric acid* (HF (5%)) to remove the glass layer as well.

3. Results

In Fig. 2 the specific contact resistance ρ_c of the different samples is shown. The error bars indicate the standard deviation of the measurement of different TLM structures on the same wafer. The errors for paste Ag on emitter I are too small to be visible.

In the case of the 50 Ω/\square emitter (I) ρ_c can be reduced from 22.3 $\text{m}\Omega\text{cm}^2$ (paste Ag) to 4.8 $\text{m}\Omega\text{cm}^2$ (AgAl) and 6.3 $\text{m}\Omega\text{cm}^2$ (AgAlref) by adding Al to the paste. The same trend can be observed for emitters IIa and IIb. Within the limits of accuracy of the measurement, values for ρ_c of the pastes AgAl and AgAlref are comparable for all emitters. The reduction of ρ_c by adding Al to an Ag thick film paste has been observed by other authors as well [3-5].

The influence of N_{surface} can be seen by comparing ρ_c for the two type II emitters. For paste AgAl and emitter IIa ($N_{\text{surface}} \sim 1\text{E}20 \text{ cm}^{-3}$) $\rho_c = 10.0 \text{ m}\Omega\text{cm}^2$ can be determined, while for emitter IIb ($N_{\text{surface}} \sim 1\text{E}19 \text{ cm}^{-3}$) $\rho_c = 37.6 \text{ m}\Omega\text{cm}^2$ is measured. The same tendency can be found for the other pastes: for the same emitter type a higher N_{surface} results in a lower contact resistance. This is in accordance with the results for n-type emitters [1,2]. However, the observed relationship between N_{surface} and contact resistance does not hold for different types of emitters. Although emitter I shows a lower surface concentration ($N_{\text{surface}} \sim 3\text{E}19 \text{ cm}^{-3}$) than emitter IIa, the measured ρ_c are reduced by a factor of two for both pastes containing Al and by more than one order of magnitude for paste Ag. The detrimental effect of the B depletion at the surface of emitter I therefore seems to be negligible. The emitter depth in contrast may play an important role for the contact resistance, as emitter I is at $N_{\text{surface}} \sim 1\text{E}19 \text{ cm}^{-3}$ about 200 nm deeper than emitter IIa. Additionally, the different types of emitter formation possibly cause different defects at the emitter surface, and may influence contact formation.

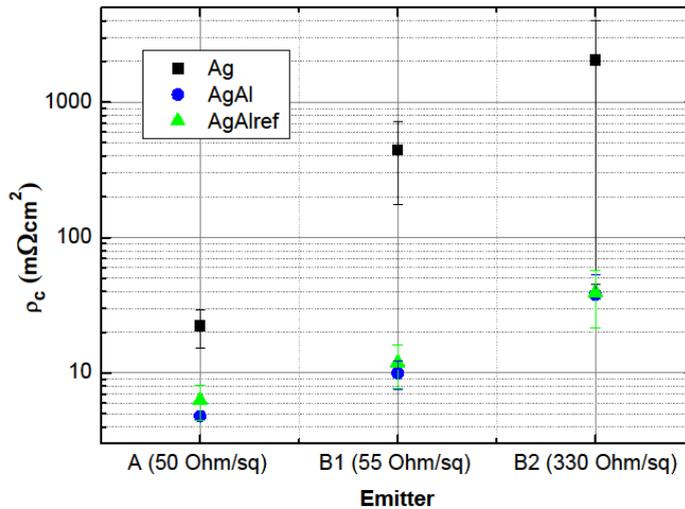


Fig. 2. Specific contact resistance ρ_c determined by TLM measurements for the three different emitters and the different Ag thick film pastes. The error bars indicate the standard deviation of different TLM measurements on the same sample.

To gain further insight into the process of contact formation for Ag as well as for Ag/Al thick film pastes, the contacts are etched back in either *aqua regia* or HF (5%). Then the contact area is analysed by SEM and EDX.

The analysis of the contact area of paste Ag reveals Ag crystals on the silicon surface. On emitters I and IIa large Ag crystals can be found on top of the pyramids and smaller ones in the valleys (Fig. 3, left). The crystals on top of the pyramids stick out of the silicon surface. For emitter IIb regions with large Ag crystals are rare and contain fewer crystals (Fig. 3, right). Additionally some of the contact spots are empty, as the crystals were removed in the HF solution. The low coverage with Ag crystals may explain the high ρ_c of the emitter IIb samples. After etching of the bulk Ag with *aqua regia* no bare Si surface can be found for all emitters. The glass frit is covering the Ag crystals on the Si surface.

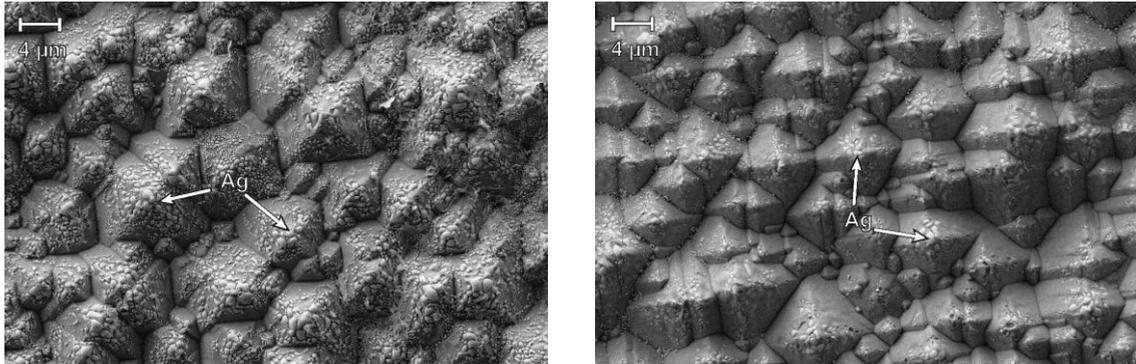


Fig. 3. Top view SEM micrographs of etched back contacts (HF) of paste Ag. Left: emitter I. Large Ag crystals on top of the silicon pyramids, smaller ones in the valleys. Right: emitter IIb. Fewer Ag crystals on top of the pyramids.

For the pastes containing Al (paste *AgAl* and *AgAlref*) the contact area consists of small Ag crystals ($<0.5 \mu\text{m}$) on the Si surface and larger rectangular spots ($>1 \mu\text{m}$) containing both Ag and Al (Fig. 4 left), as observed by [6]. These Ag/Al contact spots retain the form of the silicon surface. Additionally, some Pb residuals can be found on the Si surface. After etching of the bulk Ag, EDX analysis shows a glass layer interrupted by spots of pure Si with the shape of the Ag/Al contact spots (Fig. 4, right). They exhibit inverted pyramids on the glass covered surface.

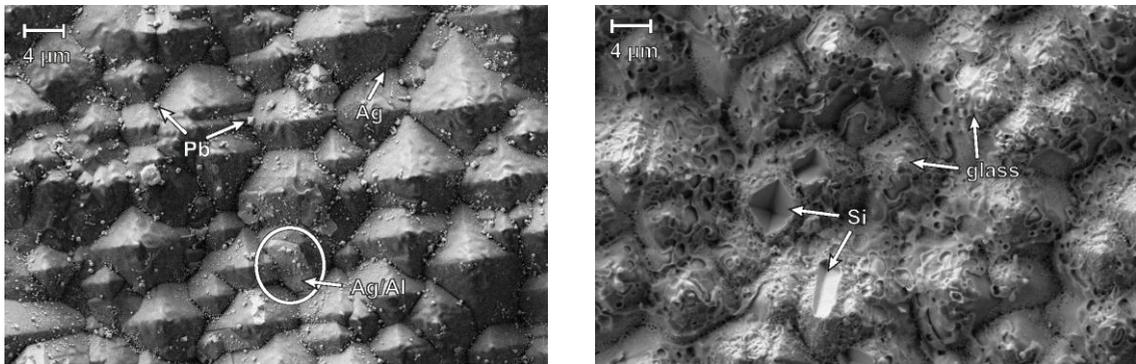


Fig. 4. Top view SEM micrographs of etched back contacts of pastes containing Al. Left: HF (5%). Rectangular spots of Ag/Al and Pb residues. Right: *aqua regia*. Rectangular spots of pure Si and glass layer.

4. Discussion and Outlook

For B emitters of the same emitter type a higher B surface concentration results in a lower ρ_c . This relationship is no longer obvious for different types of emitters. The ρ_c to emitter I is slightly lower than to emitter IIa, though $N_{\text{surface}}=3\text{E}19 \text{ cm}^{-3}$ of emitter I is significantly lower than $N_{\text{surface}}=1\text{E}20 \text{ cm}^{-3}$ of emitter IIa. Therefore other emitter related factors as for example the emitter profile or the defect concentration at the emitter surface may play a role in contact formation and have to be considered for the development of screen printing pastes. For emitter type II the surface concentration can be varied relatively simple. Thus, it is possible to further analyze the influence of the emitter profile on the contact formation. Additionally, the interaction of the emitter and the paste composition may explain the differences between the emitter types.

SEM and EDX analysis of the etched back contacts of the Al containing pastes revealed Ag/Al contact spots after etching in HF (5%) and spots of pure silicon after a treatment in *aqua regia*. Therefore it is concluded that the Ag/Al spots form a direct connection between the Si surface and the bulk Ag of the contact finger. Such direct connections could not be identified for the pure Ag paste. The reduced contact resistance found for the Ag/Al pastes may be explained by the direct current transport through these contact spots. For the Al containing pastes no obvious difference in contact structure and number of contact spots can be found. Additionally, no difference between the different emitters can be observed for these pastes. In contrast, the high ρ_c of paste Ag to emitter IIb can be explained by the observation, that less Ag contact spots can be detected on emitter IIb than on the other two emitters with higher B surface concentrations.

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