

Preprint 39th EUPVSEC & 8th WCPEC Conference, 26-30 Sep, 2022, Milan

MODEL FOR CONTACT FORMATION OF NOVEL TeO₂ CONTAINING Pb-FREE SILVER PASTE ON N⁺ AND P⁺ DOPED CRYSTALLINE SILICONFabian Geml^{1,*}, Benjamin Gapp¹, Simon Johnson^{2,+}, Patricia Sutton², Angela Goode², Jonathan Booth², Heiko Plagwitz¹, Giso Hahn¹¹University of Konstanz, Department of Physics, 78457 Konstanz, Germany

*fabian.geml@uni-konstanz.de, Tel: +49 7531 884995

²Johnson Matthey Technology Centre, Sonning Common, Reading, RG4 9NH, UK⁺Now with Fenzi AGT Netherlands BV, 6222 NZ Maastricht, The Netherlands

ABSTRACT: Silver (Ag) pastes are widely used in the global market for most solar cell architectures. In particular, lead (Pb) is no longer wanted in productions for environmental reasons. In this work, a model for the contact formation between Pb-free, tellurium (Te) oxide containing screen-printable Ag pastes and silicon is presented. It is shown that Te plays a key role in this model. Te is not only an important part in etching the surface passivation layers with TeO₂ dissolving the dielectric layer, but also for a formation of the contacts with Te forming a compound consisting of Ag₂Te. Using EDX mapping, precise contact regions can be examined and interpreted for contact formation. The used paste is a novel developed commercial paste which is on a par with other pastes used in industry concerning the resulting contact properties. This is also demonstrated in this work by the very low contact resistances of less than 1 mΩcm² over a wide range of fire peak temperatures. It is additionally shown that good resistances can be achieved on both n- and p-doped regions.

Keywords: Silver, Screen printing, Metallization

1 INTRODUCTION

Most Si solar cell concepts are relying on contacting n⁺-doped Si surfaces with Ag [1, 2]. The Ag paste, which is mostly screen-printed, is then fired to etch through the passivation layers and form the contact [3, 4]. The global Ag paste market is moving from the former standard of PbO-based paste system towards lead-free formulations, e.g. Bi₂O₃/TeO₂ based systems [5]. Therefore, it is essential to understand how metals such as Bi and Te affect contact formation in order to optimize paste formulations. In this work, we present results leading to a new model. Therefore, instead of usual commercial pastes with glass frits, a novel developed Ag paste consisting of no glass frits but milled crystalline metal oxides such as TeO₂ is used.

2 EXPERIMENTAL

During sample preparation, the monocrystalline n/p-type Czochralski (Cz) Si substrate (4-5 Ωcm) is etched and cleaned. Samples are textured using a KOH-based alkaline solution with alcohol-based additives. Emitters are formed within a diffusion step in classic POCl₃ or BBBr₃ tube furnace diffusions, respectively, aiming for an emitter sheet resistance of 75 Ω/sq. Afterwards, the samples are etched in diluted HF and then coated with PECVD SiN_x:H for surface passivation. In a subsequent step, all samples are screen-printed with the same Ag paste in TLM (transfer length method) and grid structures. All samples are (co-)fired in a belt furnace at various peak temperatures. The samples are first analyzed by applying TLM measurements and afterwards investigated by SEM (scanning electron microscopy) / TEM (transmission electron microscopy). For the latter, small lamellas are cut by FIB (focused ion beam) and also analyzed by mapped EDX (energy dispersive X-ray spectroscopy).

3 RESULTS AND DISCUSSION

The contact formation model is shown in Fig. 1. First,

the Ag paste consisting of Ag powder and crystalline mixed oxides (Si oxides as well as metal oxides) is screen-printed on a SiN_x:H passivated n⁺-emitter. The SiN_x:H is here denoted as a stoichiometric version in order to give a suggestion for reaction equations. (A)

During firing the paste reaches a partly molten state where the mixed oxides including TeO₂ move to the interface with the passivation layer and start etching this layer. (B)

A Si-rich glass layer is formed in the liquid phase. The TeO₂, which is partly responsible for the etching process, forms atomic Te according to the reaction equation $3\text{TeO}_2 + \text{Si}_3\text{N}_4 \rightarrow 3\text{Te} + 3\text{SiO}_2 + 2\text{N}_2(\text{g})$. (C)

While Ag alloys with the Si, the Te moves away from the interface and reduces the Ag atoms present in the liquid phase, mostly as ions. In the process, it forms Ag₂Te. (D)

In the final state, Ag nanoparticles are present in the liquid phase, which form precipitates in the glass during solidification and may contribute to the current flow via tunneling or when connected to the silver bulk [6]. (E)

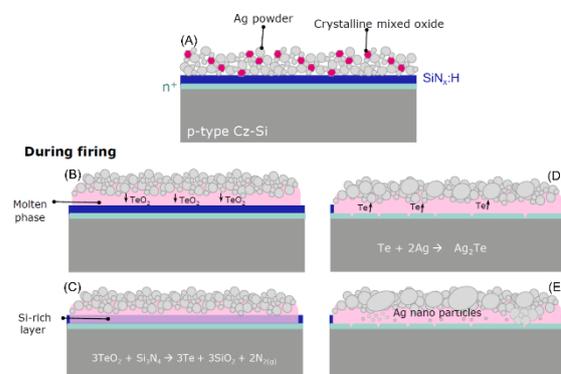


Figure 1: Schematic model of contact formation with a PbO-free paste based on TeO₂.

Fig. 2 shows an EDX cross section of a Si pyramid. A single Ag crystallite sticks into the Si bulk. We see that SiN_x:H is removed in the vicinity of this contact point, which suggests the etching of the passivation layer. The

constituents of the glassy paste components can be found moving towards the “troughs” between pyramids during firing.

The glass, identifiable mainly by the high oxygen concentration, also shows a corresponding proportion of Bi. Te is also present in the glass but accumulates more strongly in some places.

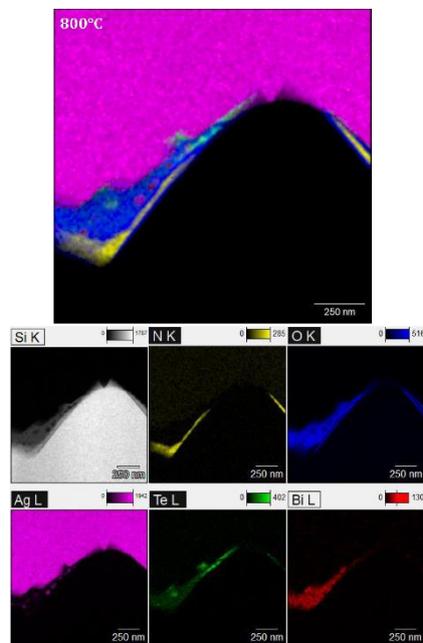


Figure 2: EDX mapped cross section of a Si pyramid with Ag crystallite at the top, combined on the top, for each element respectively on the bottom.

Fig. 3 shows an EDX cross-section of a Si pyramid trough with Ag crystallite at the top. Bi moves to the pyramid trough and to the wafer surface. Te moves upward and the alloying of Te with Ag is also visible. Within the glass layer, some thicker and thinner Ag spots are visible, which seem to intersperse the entire glass.

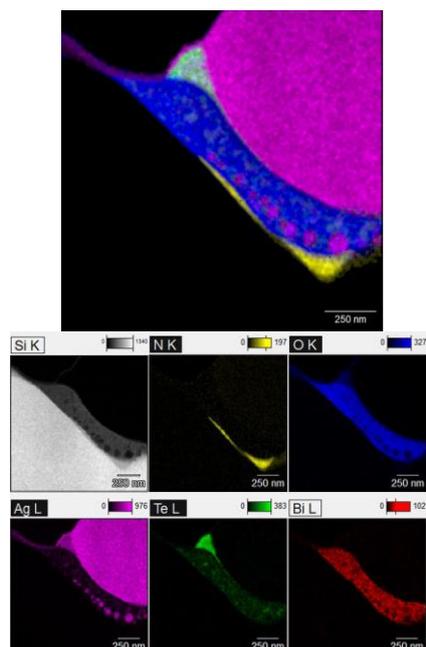


Figure 3: EDX mapped cross section of a Si pyramid

trough with Ag crystallite at the top, combined on the top, for each element respectively on the bottom.

In addition, Fig. 4 and Fig. 5 show EDX cross-sections of a Si pyramid with Ag crystallite at the top which are connected to the Ag paste bulk via an Ag_2Te phase. The formation of an Ag- and Te-rich metallic region (green region in the center) is clearly seen, which suggests the formation of Ag_2Te alloy as described in our model. The nitrogen signal is negligible in this area, which supports the hypothesis that the TeO_2 in the paste plays an important role in etching the $SiN_x:H$ passivation layer, reacting to Te and then forming Ag_2Te .

Again, it is clear that Bi is incorporated in the glass regions in addition to O and Si. Te can also be detected here. Additionally, in Fig. 5 Bi-containing glass is detected in the region of the Ag_2Te . Occasionally, Ag and Te containing particles (Ag and Ag_2Te) can be detected in the glass which may explain a possible additional current path via tunneling/hopping apart from direct contact of Ag crystallizes with the Ag paste matrix.

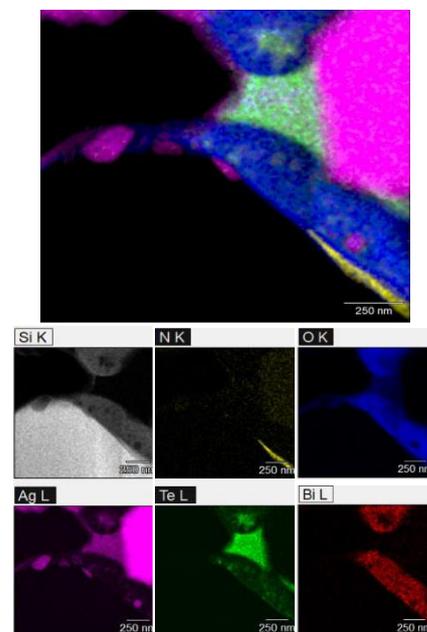


Figure 4: EDX mapped cross-section of a Si pyramid with Ag crystallite at the top, combined on the top, for each element respectively on the bottom.

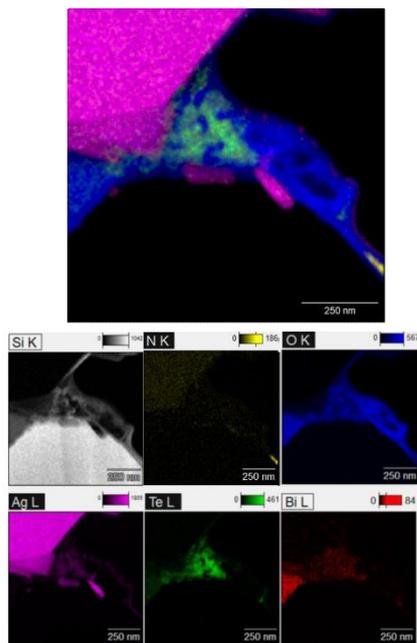


Figure 5: EDX mapped cross section of a Si pyramid trough with Ag crystallite at the top, combined on the top, for each element respectively on the bottom.

It can be shown that the Ag paste is capable of simultaneously contacting both polarities very well (POCl_3 formed n^+ -emitter and BBr_3 formed p^+ -emitter). Fig. 6 shows the specific contact resistance as a function of peak firing temperature. Values of $<1 \text{ m}\Omega\text{cm}^2$ can be achieved for a wide temperature window. Efficiencies of $>22.5\%$ could be reached at an industry partner's production line with this paste, proving the industrial applicability.

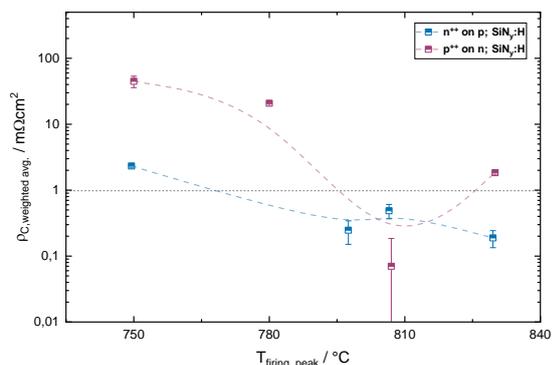


Figure 6: Contact resistivity depending on sample peak firing temperature for the same Ag paste on different emitter types.

4 CONCLUSION

In summary, Te seems to play a key role in the contacting of crystalline Si by Pb-free, Te-containing Ag pastes. It was shown that due to the presence of Si, Ag can react with Te via a redox reaction. Ag paste is capable of simultaneously contacting both n^+ and p^+ polarities with contact resistances below $1 \text{ m}\Omega\text{cm}^2$. For more details, see the invited journal publication [7].

5 ACKNOWLEDGEMENTS

Part of this work was supported by the German BMWK under contract 0324226A. The content of the publication is the responsibility of the authors.

6 REFERENCES

- [1] S. Fritz, S. Riegel, S. Gloger, D. Kohler, M. König, M. Hörtheis, G. Hahn, Energy Procedia 38 (2013) 720.
- [2] S. Fritz, M. König, S. Riegel, A. Herguth, M. Hörtheis, G. Hahn, IEEE Journal of Photovoltaics 5(1) (2015) 145.
- [3] S. Kontermann, M. Hörtheis, M. Kasemann, A. Grohe, R. Preu, E. Pink, T. Trupke, Solar Energy Materials and Solar Cells 93(9) (2009) 1630.
- [4] M.I. Jeong, S.E. Park, D.H. Kim, J.S. Lee, Y.C. Park, K.S. Ahn, C.J. Choi, Journal of the Electrochemical Society 157(10) (2010) H934.
- [5] ITRPV, International Technology Roadmap for Photovoltaics (ITRPV): Results 2021, VDMA e.V., Frankfurt 2022.
- [6] G. Schubert, F. Huster, P. Fath, Solar Energy Materials and Solar Cells 90(18-19) (2006) 3399.
- [7] F. Geml, B. Gapp, S. Johnson, P. Sutton, A.E. Goode, J. Booth, H. Plagwitz, G. Hahn, EPJ Photovolt. (2022) (submitted).