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Observation of the contact formation of PV frontside pastes by in-situ contact resistance measurement

Kathrin Reinhardt[a], Ulrike Schmidt[b], Stefan Körner[a], Robert Jurk[a], Uwe Partsch[a],
Markus Eberstein[a]*

[a]*Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Winterbergstraße 28, 01277 Dresden, Germany*
[b]*Fraunhofer IKTS; now with: Dresden University of Technology TUD, Helmholtzstraße 18, 01069, Dresden, Germany*

Abstract

A large number of solar cell front side contacts is still produced by printing and firing of glass containing silver pastes. The role of the glass frit in the short firing cycles is not fully understood so far. To overcome this, an in-situ contact resistance measurement method was introduced. This examination method allows a time correlation of phase transport and reaction related phenomena and can be used as a basis for specific operations in the paste development. Thereby, the in-situ contact resistance curves of glass-containing silver metallization could be assigned to microstructural phenomena such glass melting, silver solution, ARC etching and silver precipitation. The results of the correlations between electrical characteristics and the formed microstructures confirmed the decisive importance of the glass phase in the silver metallization for contact formation processes.

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Keywords: front side pastes, glass frit, photovoltaic cells, contact formation, in-situ contact resistance

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* Corresponding author. Tel.: +49-351-2553-7518; fax: +49-351-2554-265.
E-mail address: markus.eberstein@ikts.fraunhofer.de

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1. Introduction

Thick film conductor pastes are commonly used as metallization to manufacture crystalline silicon solar cells. These glass containing silver pastes are usually screen printed and fired in a rapid thermal process (RTP). During thermal treatment the glass dissolves silver and wets the silicon wafer at the paste/wafer interface. An etch process opens the silicon nitride layer (ARC) and during the temperature peak and cooling slope silver precipitates at the interface [1,2,3] (see Fig. 1). The silver mass transport and viscous flow of the glass is crucial for the contact formation [4].

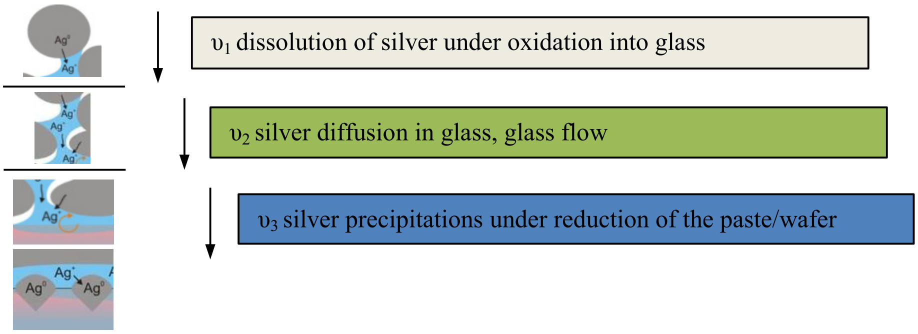

Fig.1. Phase transport kinetics in the sintering paste microstructure [4]

The electrical resistance of materials is determined by their atomic structure and microstructure. Changes in the microstructure have a direct effect on the electrical resistance. As a result, the measurement of the contact resistance during the firing step – called in-situ resistance measurement – has a high potential to examine the ongoing sintering and reaction processes [5]. However, existing equipment for in-situ resistance measurement allows only investigations at low heating rates of 10 K/min. To achieve significant resistance curves for microstructure formation during the RTP at about 1000 K/min a new measurement setup was developed and tested on the example of common PbO containing front side pastes.

2. Experimental

For the preparation of silver model pastes the raw materials (silver and PbO containing glass powder, which is typical in PV application) were mixed in appropriate ratios with respect to their volume fractions (95:5) with an organic binder, which is ethyl cellulose (5 wt%) dissolved in terpineol and dibutyl phthalate. The homogenization of the paste was performed on a three-roll mill (Exakt 120 E). The deposition on multi crystalline wafer (68 Ω/sq emitter, 1x1 inch) were done by screen printing. The test layout for the in-situ contact resistance measurements are five 2x1.5 mm² lines with a pitch of 2 mm between them. Firing happens at different peak temperatures in an infrared belt furnace (BTU, PVD-600) and during this in-situ contact resistance characterizations were measured at a home-build set up. Therefore, a data logger of type Q18, Datapaq Ltd. was used for the realization of a quasi-4-point probes method. An adapter for the data logger was developed. At this stage, the experimental setup allows not a normalization for the measured values, so absolute resistances are given. For discussion of the contact formation the curve shape is the point of interest and are discussed in detail. Next to this the efficiencies of the solar cells were measured also at a home-build set up. As a measure for silver mass transport during firing, paste/silicon interface microstructures were visualized by selective etch back of the silver metallization with nitric acid (65 %, 80 °C, 7 min). Subsequently the remaining glass layer was investigated with FESEM (Carl Zeiss NVision40).

3. Results and discussion

3.1. In-situ contact resistance – entire firing cycle

Figure 2 shows the contact resistance curve R_C (red curve) of the silver paste and the corresponding temperature profile (blue curve) during the RTP. By firing of metallized cells at stepwise increased temperatures and subsequent efficiency measurement the optimum peak temperature was determined. The plot shows that before reaching the peak temperature of 775 °C after 55 s heating, the contact resistance falls down at 620 °C (51 s) rapidly within 1.5 s to 24 ohm. The R_c-decrease is followed by a region of resistance scattering which persist in the peak temperature range. After passing the peak temperature range at 58 s the contact resistance has a minimum of about 1.5 ohm at 650 °C. During cooling from 600 °C to 350 °C R_c adjusts within 10 s at a slightly higher final value of about 9 ohm. The sharp R_C drop at 51 s can be correlated to a glass viscosity below $10^{6.6}$ Pa·s., which is the glass softening viscosity. At this viscosity the glass melt is able to flow viscously and to conduct current. The drop indicates the opening of the Si_xN_y passivation and electrical conductivity of the paste glass. The scattering of the contact resistance is assumed to be caused by continued reactions of the interface and the formation of Ag precipitates.

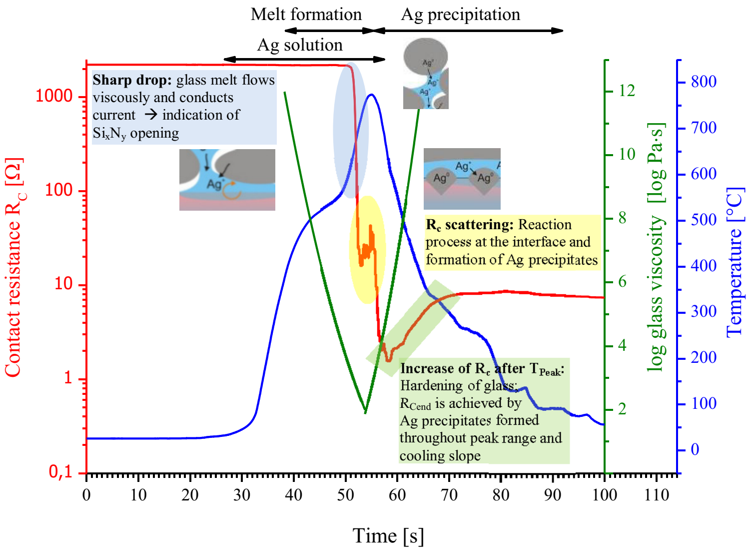

Fig.2. In-situ contact resistance curve R_C of a PbO-glass containing Ag paste

To find correlations between the R_c curve and microstructural phenomena as well as silver solution and transport processes, the contact resistance was plotted over the temperature and compared to the VFT (Vogel-Fulcher-Tammann) curve of the glass (Fig. 3). The increase of R_C after passing T_{Peak} can be easily assigned to the hardening of the glass during cooling. Thereby, the glass part on the interface conductivity vanishes and the final R_C is achieved by the Ag precipitates formed throughout the firing cycle.

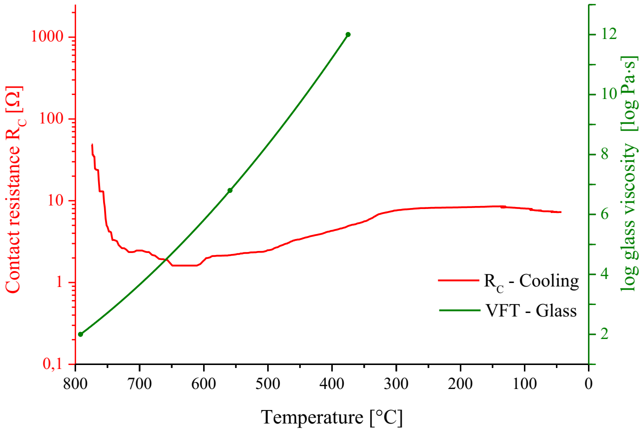

Fig.3. In-situ contact resistance curve R_C of a PbO-glass containing silver paste during cooling

3.2. In-situ contact resistance – reaction intensity and efficiency

To test how close the contact resistance scattering is correlated to reaction phenomena additional in-situ R_C experiments at firing peak temperatures of 740 °C and 805 °C were done. That means the paste was deliberately under- and overfired. In figure 4a the contact resistance curves of all three temperature profiles are plotted (green: 740 °C, red: 775 °C and purple: 805 °C). According to the height of the peak temperature different intensities of resistance scattering were measured. A high peak temperature resulted in high melting reactivity. Due to the variation of the peak temperature, the intensity of the ongoing reaction processes could be influenced and the ratio between silver solution and etching of the silicon surface can be changed. The thicker glass layer of the 805 °C probe shows a lower number of silver colloids and an increased number of large silver crystallites, compared to the optimum peak temperature of 775 °C glass layer (see Fig. 4b). This supports the hypothesis that increased firing temperature results in a more fluid and more reactive glass melt. The increased reactivity of glass effects more solution of silver, a stronger attack of silicon, more large silver precipitations and a thicker glass layer. Due to this the in-situ experiment showed stronger resistance variations, lower minimum contact resistance and a higher end R_C value in opposite to the firing peak temperature of 775 °C.

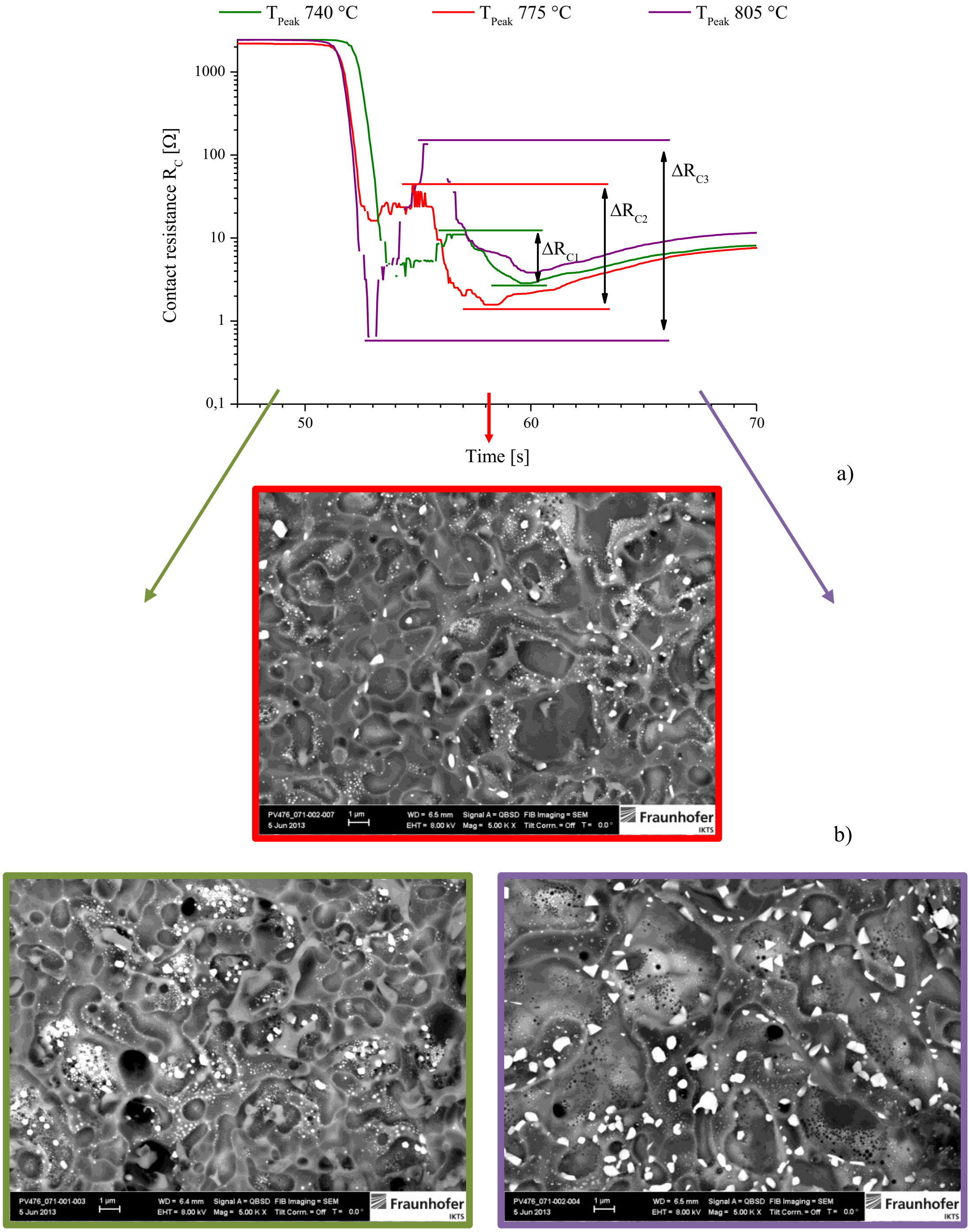

Fig.4. a) In-situ contact resistance curves R_C of a PbO-glass containing silver paste for three peak temperatures, b) FESEM images: green: T_P=740 °C, red: T_P=775 °C, violet: T_P=805 °C

4. Conclusions

The contact formation of silver front side pastes was observed by in-situ contact measurements. In the plot of the R_C characteristic points were found which could be correlated to microstructural phenomena like glass melt formation, ARC opening, reaction processes in the T_{Peak} and formation of the final R_C by hardening of the glass phase. The observations show that the contact formation can be divided into two phases:

- Melt formation and enrichment with or rather solution of silver ions at heating and peak region,
- Silver precipitations during the cooling phase.

The melting reactivity can be directly correlated to the peak temperature. This supports the hypothesis:

- Increased T_{Peak} results in a more fluid and more reactive glass melt.
- Increased reactivity of glass effects more solution of silver, a stronger attack of silicon, more large silver precipitations and a thicker glass layer

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