Sintering and contact formation of glass containing silver pastes


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Abstract

The silver paste composition for the front side has a strong influence on the firing behaviour, contact formation and resulting efficiency of the solar cell. It is state of the art that the paste glass is needed for etching the ARC silicon nitride during firing and also plays a major role for the transport of silver to the silicon surface. However, the kinetics of the silver transport is still under discussion. A main challenge to understand the underlying mechanisms is the analysis of the microstructure evolution of the paste during firing in the high speed PV firing cycle. In this work PV high speed firing conditions were simulated by usage of a simple laboratory furnace. The microstructural evolution of a model paste was observed and correlated to obtained contact resistances. Moreover, systematic variations of the paste glass were investigated. The overall contact formation kinetics can be divided into two independent but strongly interacting single kinetic phenomena: (i) the reaction kinetics at the wafer surface and (ii) the phase transport kinetics of the silver paste. The reaction kinetic at the wafer surface is composed by three important single reactions: silver solution and precipitation in the amorphous interface layer, interface layer growth, and silicon etching. The phase transport kinetics of the metallization paste determines the quantity of glass that is mixed with the etching products in the interface layer and is dominated by the densification rate of the silver powder and the viscous flow of the paste glass. The paste glass has crucial influence for both kinetics (i) and (ii). In this study the paste glass chemistry has a dominating impact compared to the glass rheology. By an appropriate choice of the raw materials regarding the sinter behaviour and targeted selection of the powder properties substantial control over the paste contacting performance is possible.

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Keywords: Solar cell; Metallization; Silver; Glass; Sinter kinetic; Efficiency

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1. Introduction

Metallization is a key process step in the fabrication of crystalline silicon solar cells. It is well known, that the composition of the metallization paste has a strong influence on the firing behaviour, contact formation and resulting efficiency of the cell. Despite the number of established cell designs and concepts, many cell manufacturers prefer the metallization by screen printing and firing of thick film pastes. Commonly, metallization pastes consist of silver powders with minor glass additions dispersed in an organic binder. Different theories concerning the contact formation are published [1-4]. Consensus exists about etching of the anti reflection coating (ARC) silicon nitride during firing by the paste glass and the transport of silver to the silicon surface. However, under discussion are differences in detailed diffusion mechanisms and kinetics of the silver transport. Hong and co-workers state that a certain amount of silver is oxidized and dissolved by the liquid glass phase formed by the added glass powder [2,3]. Subsequently, the silver is reduced directly on the crystalline silicon surface to give electrical Schottky contacts by reactions like

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\begin{align*}
6 \text{Ag}_2\text{O}_{(\text{glass})} + \text{Si}_3\text{N}_4(\text{wafer}) & \rightarrow 12 \text{Ag} + 3 \text{SiO}_2(\text{glass}) + 2 \text{N}_2, \\
2 \text{Ag}_2\text{O}_{(\text{glass})} + \text{Si}(\text{wafer}) & \rightarrow 4 \text{Ag} + \text{SiO}_2(\text{glass}), \text{ and/or} \\
2 \text{PbO}_{(\text{glass})} + \text{Si}(\text{wafer}) & \rightarrow 2 \text{Pb} + \text{SiO}_2(\text{glass}).
\end{align*}
\]

The characterization of already applied electrical contacted solar cells after back etching of the metallization in conjunction with theoretical simulations gives a detailed insight on the formation of silver crystallites on the surface on mono-crystalline wafers [5,6]. However, the evaluation of the microstructure of the silver paste in conjunction with the contact formation is not regarded. Hilali and co-workers [7] have shown that size and number of silver particles at the glass/silicon interface are crucial factors for the contact resistance. Other published research data on detailed mechanisms refer often to very specific application environments or experiments performed under thick film conditions (temperature dwell time of several minutes) [1-4,8,9]. Thus, the experiments deliver limited information for firing conditions, which are typical for solar cells.

Of course, the emitter donation is important for a low contact resistance as well. Depth profile characterisation of the phosphorus donation by secondary ion mass spectroscopy (SIMS) discovered a depth of standard emitters of up to 100 to 200 nm (higher than \(10^{20}\) phosphorus atoms per cm\(^2\)) below the silicon surface [10]. These emitter layers have a sheet resistivity of approximately 60 Ω/sq, which is sufficient for contacting the circuit path. To enhance the charge gain of the cells, a narrow donation depth < 100 nm is useful to reduce recombination losses. This will result in a sheet resistivity higher than 90 Ω/sq. Thus, contacting the emitter layers within 100 nm is necessary to maintain the lower sheet resistivity of 60 Ω/sq. However, due to the fast etching progress such narrow contact layer are not achieved, yet.

This work aims to gain additional knowledge about the effects of the paste composition on the firing behaviour, contact formation and resulting efficiencies of the solar cells. To investigate the time and temperature dependent development of the silver microstructure, experimental simulation of the PV firing was performed by interrupted firings in a laboratory furnace. The resulting microstructures were evaluated in terms of phase composition, distribution and contact resistance. The impact of glass additives on the overall shrinkage behaviour of silver powders was studied on pressed powder compacts. Systematic variations in powder mixtures of the silver particle size, glass content and glass composition were carried out and the electrical performance of the resulting solar cells is discussed.
2. Experimental

2.1. Microstructure of the paste-silicon-interface

For the evaluation of the silver paste microstructure in dependence on firing temperature and time, a model paste consisting of 95 vol.% silver (d_{50} = 1.5 μm) and 5 vol.% lead oxide glass were dispersed in an organic vehicle to form a paste. This paste was printed on 60 Ω/sq standard multi crystalline silicon wafers, 2 x 2 inch, to form test structures fitting the requirements to measure the contact resistivity after firing. For simulation of the rapid thermal processing in an infrared radiation furnace, the wafers were taken to a laboratory furnace, which could be set in temperature between 400 °C and 850 °C. The temperature was observed using a thermo couple placed directly next to the wafer. Upon putting a wafer into the furnace, the temperature drops for a short time but increases with high velocity. The firing time is measured starting from the point where the temperature reached the initial value. The wafers then remained for 0, 5, 10, 45 s in the furnace and finally removed quickly. Subsequently, cross sections of the resulting silver-film/silicon interface were prepared using the focused ion beam method and analyzed by SEM (FESEM, Zeiss, Oberkochen). The contact resistance of the wafers were measured by the four point method (home-built measuring setup of Fraunhofer IKTS, Dresden).

2.2. Shrinkage of glass containing silver powders

The determination of the shrinkage behaviour of the pure powders was investigated on cylindrical compacts of fine silver powder (d_{50} approximately 2 μm) and coarse silver powder (d_{50} approximately 6 μm) containing different fractions of lead oxide glass (0, 5, 10, and 20 vol.%). The cylindrical samples with a height and a diameter of 2 mm were manufactured by unidirectional pressing using 64 MPa. These compacts were characterized in their green density (geometry and mass) and subsequently their sinter shrinkage was monitored in a Hot Stage Microscope (HSM, Leica, Wetzlar) with a constant heating rate of 10 K/min in air. Glass viscosity was estimated by evaluation of the silhouettes of glass powder compacts in the HSM: Sinter onset, sinter offset, ball point and hemisphere point.

2.3. Influence of the glass composition on the paste contacting

For the preparation of the pastes the raw materials (silver and glass powder) were mixed in appropriate ratios with respect to their volume fractions (95:5) by using dibutylphthalat and terpineol as solvents and ethyl cellulose as the organic binder. First mixing of the materials was performed in a flat glass beaker using a spatula according to an internal standard procedure. Afterwards the final homogenization of the paste was performed on three-roll mill (Exakt 50). While the silver powder (grade 519, Technic Inc.) was used as received, the glass frits were ground in an attrition mill in order to produce comparable particle size distributions (d_{50} = 1.5 μm). The glass viscosity was determined by complementary methods. T_g was determined by a horizontal dilatometer (Netzsch 404 E, ΔT_g ≈ ± 3 K). Bending beam viscometry was utilized for the range log η = 12.3 to 9 Pa s (Bähr VIS 401, Δlogη ≈ ± 0.15). In the higher temperature range heating microscopy was performed to determine characteristic viscosity fixed points of the glass powder. The efficiency of the solar cells obtained from metallized wafers with the model pastes were acquired by a home-built measuring setup of Fraunhofer IKTS, Dresden.
3. Results and Discussion

3.1. Microstructure of the paste-silicon-interface

Fig. 1 (left) depicts the microstructure of the model paste on a silicon wafer at a temperature of 450 °C after 45 s, consisting of silver (I), glass particles (II), pores (III), and the silicon surface (IV). At this temperature, sintering necks have formed between the silver particles and groups of silver particles start to fit tightly to the silicon surface and the glass particles, e.g. in the picture centre. The glass particle shows sharp edges indicating no softening at this temperature. It acts as a rigid inclusion hindering the overall shrinkage of the paste powder. A closer look to the glass particle/silver interfaces discovers dark grey shadows, assumingly originated by diffusion of silver, even at this low temperature. In Fig. 1 (right) the microstructure at 500 °C 0 s is shown. Sintering of the silver particles has continued and the glass particles start to soften, preferably in the silver contaminated regions. Simultaneously, glass flows to the silicon surface and starts the interfacial wetting process. Small bubbles in the interface indicate an etching according to equations (1) to (3) has begun. Only 45 s later (Fig. 2 left), a thoroughly connected layer starts to form between the silver/glass film and the silicon surface. Upon further temperature/time

![Fig. 1. SEM images of polished cross sections of the interface model paste/Si-wafer fired at (a) 450 °C, 45 s, (b) at 500 °C, 0 s, with silver (I), glass particles (II), pores (III) and silicon (IV) areas.](image)

![Fig. 2. SEM images of polished cross sections of the interface model paste/Si-wafer fired (a) at 500 °C, 45 s, (b) at 700 °C, 5 s.](image)
increase the silver paste turns into a dense body. It is bound to the silicon wafer by the adhesive strength of an amorphous phase formed by the glass in the metallization paste together with the reaction products from the silicon etching. At 700 °C 5 s (Fig. 2, right), the amorphous layer has grown to a thickness close to 1 μm. Bright spots next to the silicon surface suggest silver precipitation from the melt within this amorphous phase. The microstructure also points at the presence of a certain amount of glass in the dense silver body. The expected transport to the silicon surface did not occur completely. Bright spots inside this amorphous areas point at crystals in the glass melt. Detailed EDX analyses of these spots suggest lead containing crystal phase as the major component. Similar crystallized areas in the amorphous silver/silicon interface glass layer were not observed.

The results of EDX analyses of both areas are shown in Fig. 3 together with the locations of the selected points. Spectrum 1 was taken from a glass inclusion inside the dense silver body and spectrum 2 was taken from the interface layer. The major signals in both spectra are located at 1.7 and 2.3 keV. The signal at 1.7 keV is coincident for lead and silicon, whereas the latter is characteristic for lead only. The obtained relative peak intensities are very similar in both spectra, whereas the signal intensity at 1.7 keV is larger in spectrum 2. This suggests a significant higher silicon concentration in the amorphous interface layer. Keeping in mind reactions (1) to (3) the obtained higher silicon concentration is expected. Silicon dioxide is formed during the etching of the silicon surface and is regarded as a strong glass network former. Thereby, the absence of crystals at the interface gives further evidence for a continuous etching on the silicon surface and the enrichment of silicon dioxide in the surrounding glassy phase during the firing cycle.

Starting from this microstructural point of view there might be two counteracting phenomena that are of great evidence for the contact formation of a glass containing silver paste on a silicon wafer. First, during sintering some silver is dissolved as silver oxide in the amorphous interface layer, transported to the silicon surface and subsequently reduced to metallic silver particles. This will result in the deliberate decreasing of the contact resistance. Second, simultaneously to the silver particle formation, the silicon
wafer is etched to form a mixture between the near paste glass parts and the etching products, mainly silicon dioxide. This leads to a growing silicon dioxide enriched glassy interface layer and an increase of the contact resistance. The corresponding effect on the total contact resistance is shown in Fig. 4, which depicts the dependence of the normalized contact resistance on the firing time at a constant temperature of 700 °C. After the first 5 seconds, corresponding to the microstructure in Fig. 2 (right) the contact resistance is decreased compared to the starting value, virtually coursed by a still thin interface layer and ongoing silver precipitation. Already 5 seconds later, at 10 seconds, the contact resistance is increased drastically to a level that does not change even after significant longer firing times. Thus, the continued silver precipitation is overlapped by an increase of the interface layer thickness.

Keeping in mind that the phosphorus donation layer at the silicon wafer surface has a thickness of approximately 200 nm only, the continued etching process will quickly eat away the highest donation volume. As a consequence, a thin layer of reduced phosphorus donation remains to form the contact at the silicon silver interface. This effect is expected to be also an important contribution to the overall contact resistance measured. Therefore, in terms of the microstructure evolution the total contact reaction kinetic is determined by three important single reactions at the wafer surface:

- Silver precipitation,
- Interface layer growth, and
- Silicon etching.

3.2. Shrinkage of glass containing silver powders

The reaction kinetic at the interface is influenced by the quantities of the substances involved. A critical point is seen in the quantity of glass taking part in the interface reaction. To gather information concerning the sinter kinetics of glass containing silver powders and the transport of glass, fine silver powder (d_{50} about 2 μm) and coarse silver powder (d_{50} about 6 μm) together with varying fractions of the lead oxide glass powder (5, 10, and 20 vol.%) were pressed to compacts. The linear sinter shrinkage of these compacts during heating is shown in Fig. 5. In case of the fine silver powder (Fig. 5, left) increasing glass contents lead to an enhanced delay in the shrinkage onsets. This means, in the first shrinkage stadium the glass acts as a classical rigid inclusion, which is confirmed by the appearance of the glass particle in Fig. 1 (left). However, at a certain point glass containing silver compacts start to shrink at a higher rate than the glass free silver compact. An evaluation of the glass viscosity gives the value of
around $10^9$ Pas, which marks the sinter onset of the pure glass [11]. The overall effect of increased glass amounts on the sinter shrinkage of the fine Ag powder is limited. In case of a coarser silver powder, the effect is similar, in principle, but here the silver powder itself starts to shrink at a higher temperature. Therefore, glass containing silver compacts show an accelerated shrinkage compared to the glass free silver compact at an earlier shrinkage state, leading to a remarkable shift of the sinter curve towards lower temperatures of up to 200 K for 20 vol.% glass.

With this in mind, virtually there are two limiting cases. Using a fine silver powder and a glass with a higher viscosity, most of the glass will be trapped inside the densified silver thick film microstructure. This will increase the ohmic resistance and lower the amount of silver dissolved in the glassy phase. Subsequently the precipitation of silver in the amorphous interface layer will be reduced, what results in an increased contact resistance. Using a coarse silver powder and a lower viscous glass, opposite effects are kinetically supported, which could result in a lower contact resistivity. By an appropriate choice of the raw materials regarding the sinter behaviour and targeted selection of the powder properties (e.g. particle size distribution, manufacturing processes) substantial control over the paste contacting performance is possible.

### 3.3. Influence of the glass composition on the contact resistance

As stated above, the paste glass is mixed with the etching products at the wafer surface during firing. However, a strong influence of the paste glass chemistry on the metal precipitation behaviour could be shown in [12] in accordance with [2]. This gives evidence to the fact that the paste glass strongly determines the reaction behaviour of the liquid interface layer. The reaction kinetics described above (silver solution and precipitation, interface layer growth and silicon etching) depend on the glass chemistry, on one hand, and on the material transport kinetics driven by glass viscosity, on the other hand. For the purpose of paste optimization it is of interest, whether the influence of the glass chemistry or the glass physics, i.e. viscosity, are of main impact. We choose three lead oxide and bismuth oxide free glasses with similar basic composition but slightly varying additives. The glass viscosities in dependence on the temperature are shown in Fig. 6, left. Glass 1 (red) contains 5 mol% more network formers than glass 2 (blue), resulting in a viscosity decrease by 1-2 orders of magnitude. Glass 3 was obtained by an addition in the network forming oxides. The viscosity of the glasses 2 and 3 are regarded as similar. The
efficiencies of a front side metallization paste made from 95 vol.% silver and 5 vol.% of glass 1, 2, and 3, respectively, are plotted against the firing peak temperature on standard multi-crystalline silicon wafers in Fig. 6, right. Glass 1 having the lowest viscosity, which means highest material transport velocities for a given temperature, shows the lowest efficiency values. In contradistinction, glass 3 has the same viscosity like glass 2 but a slightly varied network former chemistry. This results in a significant higher efficiency of the manufactured solar cell. Therefore in this preliminary investigation and within the considered viscosity range the glass chemistry is dominant compared to the glass viscosity.

4. Conclusion

Due to the significant time dependences and high speed progress of the effects during the PV paste firing, results from thick film regime reported by e.g. [3,8] can only deliver limited support for optimization of paste recipes. This work aims to gain additional knowledge about the influence of the paste composition on the firing behaviour, contact formation and resulting efficiencies of the solar cells. Therefore, simulated PV high speed firing conditions and systematic variations of the paste glass were investigated.

From a microstructural point of view the overall contact formation kinetics can be divided into two independent but strongly interacting single kinetic phenomena: (i) The reaction kinetics at the wafer surface and (ii) the phase transport kinetics of the silver paste. The reaction kinetics at the wafer surface is composed by three important single reactions:

- Silver solution and precipitation in the amorphous interface layer,
- Interface layer growth, and
- Silicon etching.

The phase transport kinetics of the metallization paste determines the quantity of glass that is mixed with the etching products in the interface layer and is dominated by the densification rate of the silver powder and the viscous flow of the paste glass.

Both kinetic phenomena, namely the reaction kinetics of the interface etching and phase transformation kinetics, are influenced by the paste glass rheology and chemistry. Preliminary investigations performed on glasses having a comparable rheology but different chemistry and vice versa point at the fact that glass chemistry is the dominant property. This becomes self-evident when looking at the obvious need for fast silver dissolution, easy silver reduction, reduced etching tendency and reduced silicon dioxide solution.
By an appropriate choice of the raw materials regarding the sinter behaviour and targeted selection of the powder properties (e.g. particle size distribution, manufacturing processes) substantial control over the paste contacting performance is possible.

Acknowledgements

Financial support of the Sächsischen AufbauBank – SAB, Project #128947/2154 “SF2020” is gratefully acknowledged.

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