

Impact of silver powder grain size and inorganic additives on the performance of front-side pastes

Stefan Körner, Kathrin Reinhardt, Uwe Partsch & Markus Eberstein, Fraunhofer IKTS, Dresden, Germany

ABSTRACT

This paper presents the results of a study of the influence of silver powder particle size and inorganic additives on sintering and electrical performance of a PV front-side metallization paste. Three different silver powder grain sizes were used in sample front-side pastes. Also examined is the effect of using four different inorganic additives determined by their redox potential. Solar cells produced using the sample pastes were electrically characterized, and selective etch-backs and FESEM investigations were performed to correlate electrical performance with the glassy interface between the metallization and the silicon wafer. In the absence of additives, the highest efficiencies were obtained with the medium silver grain size. If the inorganic species has an oxidizing nature, the mass transport of silver in the glass phase can be enhanced. However, the etch process at the wafer surface is also improved by a greater quantity of silver oxide in the flowing glass. It is shown that if the oxidizing capacity of the additive is too powerful, the electrical performance is negatively influenced. Moreover, the impact of additives is highly dependent on the silver particle size.

Introduction

The metallization step is one of the key processes in the manufacturing of crystalline solar cells: glass-containing silver pastes are usually screen printed and fired in a rapid thermal process (RTP). During the firing step, the glass dissolves the silver and flows viscously onto the silicon wafer. The silver-containing glass melt reacts with the silicon nitride layer (anti-reflective coating – ARC), which is thereby removed; during the temperature peak and cooling ramp, the silver precipitates at the interface [1–3]. It was recently reported [4] that the overall contact formation kinetics of a front-side silver metallization can be divided into two independent but strongly interacting single kinetic phenomena: 1) the phase transport kinetics and mass transport of silver in the silver paste; and 2) the reaction kinetics at the wafer surface. The phase transport kinetics are determined by the sintering behaviour of the silver powder, the glass chemistry and its viscosity, and the silver oxidation and dissolution in the glass phase. The reaction kinetics at the wafer surface are determined by the etching process of the silicon nitride and the P-doped silicon, as well as by the formation of silver precipitations during thermal treatment. Both these processes are

dependent on the oxygen partial pressure [5,6]; one way of changing the oxygen partial pressure at the interface is to use a paste containing an inorganic additive.

“One way of changing the oxygen partial pressure at the interface is to use a paste containing an inorganic additive.”

This paper reports the investigation of the influence of silver particle size and inorganic additives on the sintering and electrical performance of the metallization paste. In particular, three different silver powder grain sizes were used to examine the phase transport kinetics, and four different inorganic compounds varying in their redox behaviour were chosen to affect the reaction kinetics at the interface. Three of the compounds have an oxidizing influence, and one of them exhibits a reducing characteristic. Given the redox potential and the related oxygen partial pressure in the interface region during firing, the silver dissolution (and thus the silver mass transport) in the glass should be influenced: the

amorphous interlayer should therefore contain different quantities of silver precipitations. To examine this concept, the electrical performance of the solar cells was studied.

Experimental

For the study, sample pastes without additives were first formulated using three silver powders (Technic Inc.) which differ in particle size distribution (Table 1) and will be referred to as coarse, medium and fine. The pastes contain 95 vol% silver powder and 5 vol% glass frit. A lead-oxide- and bismuth-oxide-free frit with a particle size of $d_{50} = 1.5\mu\text{m}$ was employed as the glass frit.

Next, sample pastes were formulated with $(95-x)$ vol% silver, 5 vol% glass and x vol% inorganic additive. The inorganic additives included in the pastes were utilized as received from the supplier; Table 2 shows the redox behaviour of each additive. In order that the additives would be activated before and during silver densification, they were chosen for their thermal decomposition property in the

	Coarse	Medium	Fine
PSD [μm]	1.3–3.2	0.6–1.9	0.4–1.0

Table 1. Particle size distribution (PSD) of silver powders used.

Additive	Redox behaviour
A	oxidation ++
B	oxidation +
C	reduction +++
D	oxidation +++

Table 2. Additives used, categorized according to their redox behaviour.

temperature range 200–600°C. This property should have a significant effect on the oxygen partial pressure in the paste: the silver dissolution, the penetration of the ARC, and the possible etching process of the wafer surface during RTP should therefore be influenced.

As an organic vehicle, all the pastes include 5 wt% ethyl cellulose, which was dissolved in dibutyl phthalate and terpineol. All raw materials were mixed using a standard procedure and then homogenized on a three-roll mill (EXAKT 120E). The pastes were characterized by means of hot stage microscopy (HSM), and screen printed on multicrystalline silicon wafers (68Ω/sq. emitter, 2" × 2"): a layout with one busbar and 22 fingers was chosen. Firing takes place at different peak temperatures in an infrared belt furnace, and the efficiency and serial resistance of the resulting solar cell were measured using a custom-built set-up at Fraunhofer IKTS, Dresden.

To study the microstructure at the interface of the metallization and the silicon wafer, FESEM (field emission scanning electron microscopy) images (Carl Zeiss NVision40) were captured for investigating a correlation between paste recipe, interface microstructure and electrical data. The quantity and distribution of silver in the glassy interface was adjusted by selectively etching back the silver metallization layer using nitric acid (65%, 7 min, 70°C). An FESEM investigation was performed after each etch-back step.

Results

The sintering behaviour, as recorded by HSM, of dried paste samples having different silver grain sizes is shown in Fig. 1. With decreasing silver particle size, the sinter onset occurs at a temperature of about 275°C, compared with 350°C for the coarser paste. The paste with the coarse powder shows a maximum densification at about 600°C. After sinter onset, between 300 and 350°C, the medium powder exhibits a higher sinter rate than at higher temperatures, and above 350°C, the sinter rate is comparable with that of the coarse silver powder; the maximum densification is reached at about 550°C. The paste with the fine silver powder yields a sinter onset at the lowest temperature; moreover, the shrinkage behaviour differs from that of the other two pastes, an effect that has already been reported in the literature [7]. The maximum densification of the fine powder is not as high as that of the other two pastes.

Fig. 2 shows the efficiencies and

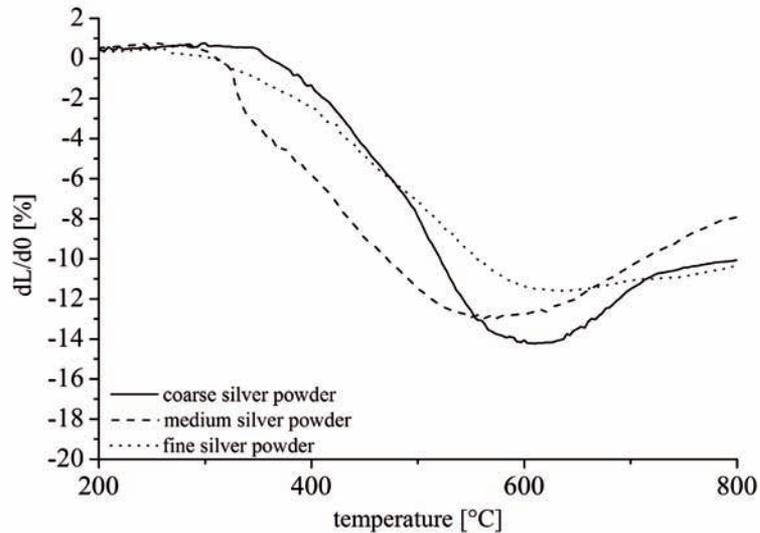


Figure 1. Sintering behaviour of pastes with different grain sizes as a function of temperature at a heating rate of 10Kmin⁻¹, recorded by HSM and normalized to 55% green density.

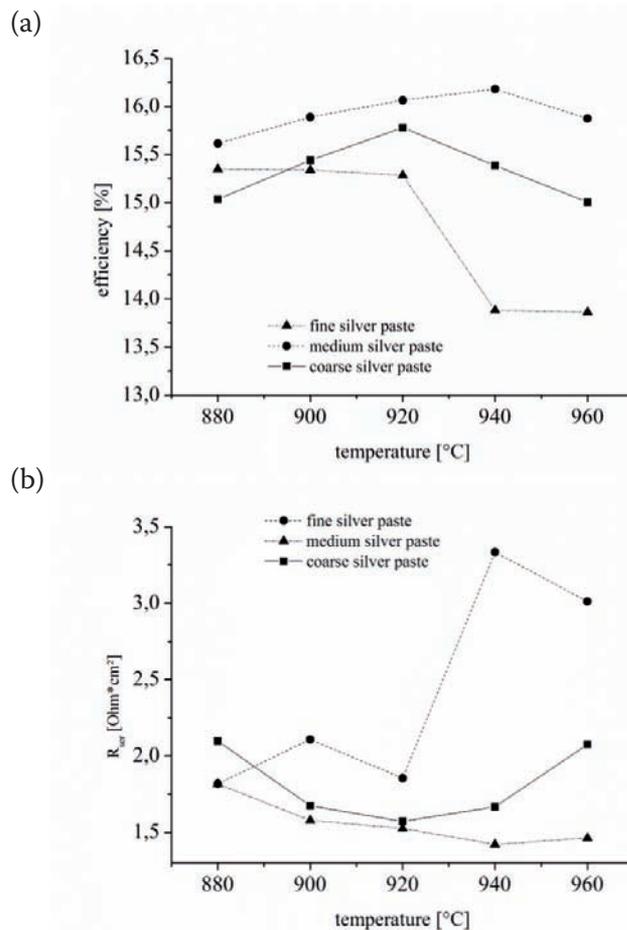


Figure 2. Dependency of efficiency (a) and serial resistance (b) of the three pastes on peak firing temperature.

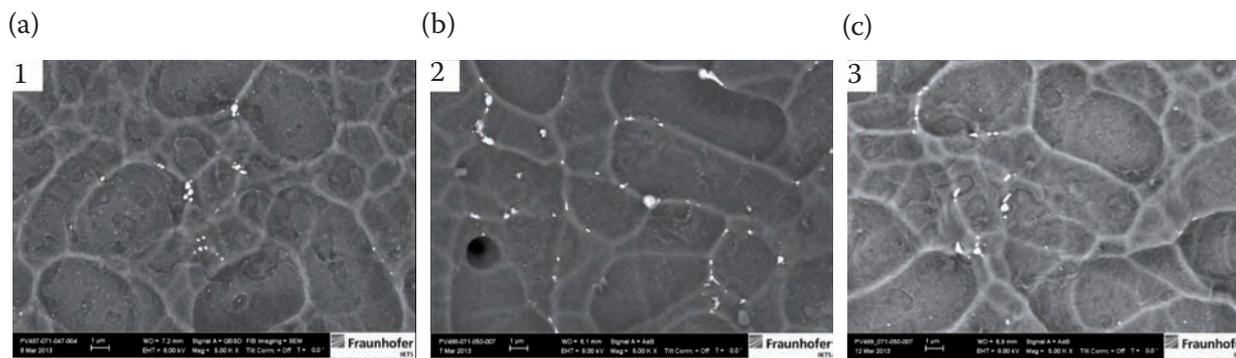


Figure 3. Wafer surface, showing the glassy interfaces after selective etch-back of the silver metallization using nitric acid: (a) paste with coarse silver powder; (b) paste with medium silver powder; (c) paste with fine silver powder.

serial resistances of the solar cells obtained with the three pastes as a function of the peak temperature during firing. The sample paste with the medium silver powder demonstrates the most stable and highest efficiency in the complete process window, reaching above 16%; in contrast, the serial resistance is the lowest of the three in the full peak firing temperature range.

“The sample paste with the medium silver powder demonstrates the most stable and highest efficiency in the complete process window.”

The coarse silver paste shows a clear maximum efficiency at 920°C, but this is somewhat lower than the efficiencies obtained for the medium powder. The serial resistance of the coarse silver paste also reaches a clear minimum at 920°C, which is close to that of the medium silver paste.

The fine silver paste exhibits a narrow process window between 880 and 920°C; efficiencies above 15% can be achieved in this temperature range, whereas at higher temperatures the efficiency decreases dramatically. From the EHM measurements, the electrical characteristics show good correlation with the sintering behaviour. The efficiencies and serial resistances obtained from the fine silver powder at lower temperatures are similar to those of the coarse silver paste, and at higher peak firing temperatures both these characteristics deteriorated. The medium powder, however, demonstrates a different behaviour.

Fig. 3 shows the glassy interface after selective etch-back of the silver metallization fingers. Both of the

wafer surfaces 1 (Fig. 3(a)) and 2 (Fig. 3(b)) are glazed with a thin, almost homogeneous glass film. In principle, two types of silver precipitations occur at the interface in the frame of this study. The first type is referred to as *colloids*, which are very small in size ($\ll 1\mu\text{m}$) and statistically spread over the whole wafer surface. The second type is referred to as *nuggets* – these

are somewhat bigger (0.5–1 μm) and located at the silicon texture edges. At the same firing peak temperature, the amount and type of silver precipitation varies with the silver particle size used.

In the case of the coarse silver paste, the interface layer contains many silver colloids which are spread over the whole surface (Fig. 3(a)). In contrast, the interface of the medium

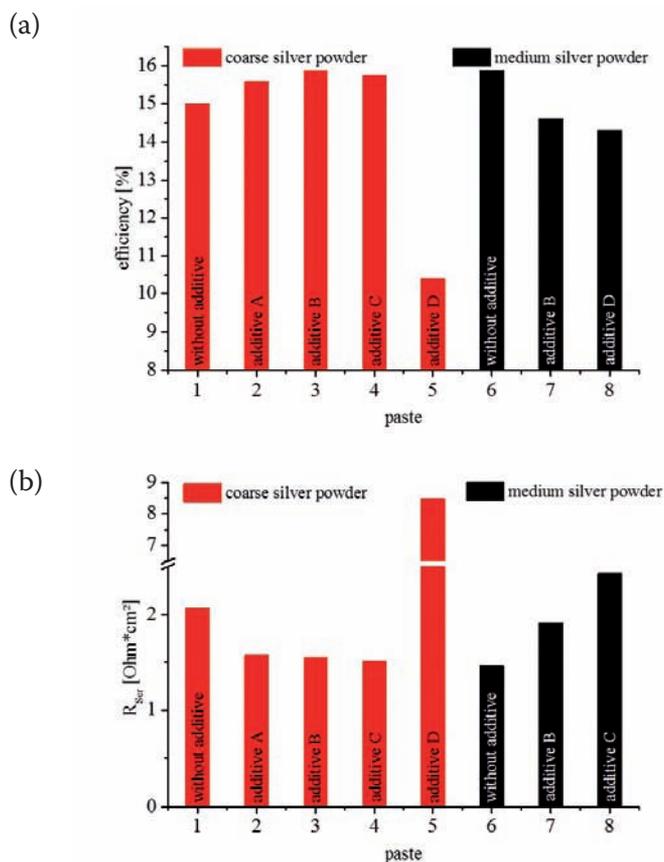


Figure 4. Efficiency (a) and serial resistance (b) of pastes with inorganic additives at a peak firing temperature of 960°C.

silver powder paste shows fewer silver colloids spread over the wafer surface in the glass phase (Fig. 3(b)). Furthermore, they are not as big as those for the coarse silver paste; however, there are more nuggets at the texture edges of the silicon. Again in good correlation with HSM and efficiency, the fine silver powder (Fig. 3(c)) exhibits almost the same type, amount and distribution of silver precipitation in the thin glass film as the coarse silver paste. For the highest peak firing temperature, the amount of silver dissolved in the glass frit should therefore be approximately the same.

In terms of the electrical characteristics and the appearance of the interface, the results of the fine and coarse silver powders are similar. With this in mind, the inorganic additives are put in the pastes with coarse and medium silver powders only.

The influence of the different additives on cell performance as a function of the silver powder particle size used is shown in Fig. 4. In the case of the coarse silver powder paste (red bars), an improvement in cell performance for all additives except the last one can be seen. The two oxidizing additives A and B show an improvement in cell performance of

0.6 and 0.9% in comparison with the reference case without additive. With the reducing additive C, a gain of 0.8% is obtained, yielding an efficiency of 15.8%. This result is in the range of the best efficiency reached with the medium silver powder without additive. By contrast, the strongest oxidizing additive D results in a decrease in efficiency of about 4.5%. Different reasons are assumed for this deterioration and will be discussed later.

The two most effective additives were introduced into the medium silver paste. Fig. 4 shows the influence of the inorganic additives B and C on the efficiency at 960°C peak firing temperature (black bars). A decrease in efficiency is obtained for both additives: additive B lowers the cell performance by about 1.3%, while additive C decreases the efficiency by about 1.5%.

Fig. 5 compares the glassy layers on the wafer surfaces after selective etch-back of the coarse silver metallization. A significant change in silver precipitations at the interface compared with Fig. 3(a) is evident. With oxidizing additive A Fig. 5(a), the glassy layer becomes more inhomogeneous than in the case of the reference state: the silver precipitations differ in quantity and type. The

colloids are much smaller than for the pastes without additives, while the nuggets at the texture edges have increased in size and number.

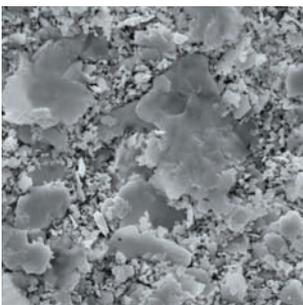
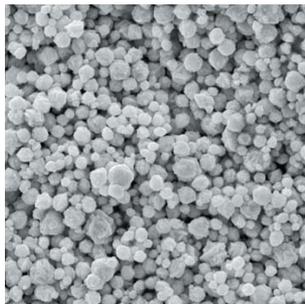
With additive B (Fig. 5(b)) the colloids have almost disappeared, but there is a greater number of silver nuggets, and their size is smaller, than for additive A. In the case of both additives, there are nuggets as large as those for the reference paste; however, there are much bigger ones adjacent to these at the grain boundaries.

Additive D is the strongest of the investigated additives with an oxidizing characteristic. This can be clearly seen at the interface between the silver metallization and the wafer surface: the glassy layer is rough and contains a lot of big silver nuggets. Not only are these nuggets to be found at the grain boundaries, but they also spread over the entire surface. In areas without nuggets, there are many colloids.

The change in the redox behaviour of the inorganic additive when additive C is used results in a complete change in appearance of the wafer surface. The glassy layer is similar to that in the no-additive and the homogenous additive B cases. With the reducing additive C, there are (as with additive A) fewer colloids than with the pure glass-

High Quality Solar Metallization Technology

Technic Engineered Powders and Flakes
The standard by which all others are measured



Technic's Engineered Powders Division is a global supplier of high quality precious metal powders and flakes specially engineered for applications in photovoltaic manufacturing.

Our customized products and commitment to ongoing research and development offer our customers the best possible technology for today's advanced solar standards.



www.technic.com

ISO 2001:2008

300 Park East Drive, Woonsocket, Rhode Island 02895 USA
Tel: 401-769-7000 Fax: 401-769-2472 info@technic-epd.com

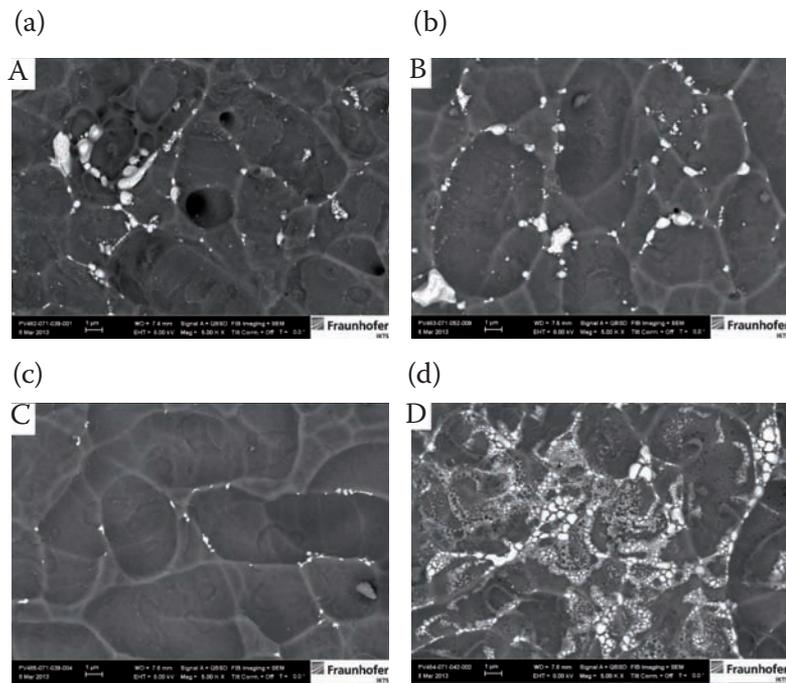


Figure 5. Wafer surface after selective etch-back of the coarse silver metallization using nitric acid. The glassy interface shown contains silver precipitations, which differ in quantity and type depending on the inorganic additive used: (a) additive A; (b) additive B; (c) additive C; (d) additive D.

containing silver powder. Nevertheless, at the grain boundaries of the silicon wafer there are more nuggets, which are rather small in size compared with those obtained with other two oxidizing species, but comparable to those for the reference state.

Discussion

The paste with the medium silver powder demonstrates the most stable and highest efficiency (Fig. 3(b)) in the temperature range 880–960°C: this is related to the sinter kinetics of the silver powder, as seen in Fig. 1. During heating, the medium powder maintains a larger surface for a longer time, which promotes the dissolution of silver under oxidation in the glass frit. More silver can therefore be dissolved in the glass, which promotes etching of both the ARC layer and the silicon surface, as well as boosting the number of silver precipitations in the glassy interface between the silver bulk and the silicon wafer; this in turn improves the electrical contact, which is reflected in the resistance measurements. The serial resistance of the medium silver powder yields lower, and much more stable, values over the whole firing temperature range than the other two silver powders. For both coarse and fine silver powders, the contact and serial resistances are

slightly higher than those for the medium silver powders.

Since the coarse silver powder has a smaller surface than the medium powder, less silver is transported to the silicon surface. The fine silver powder may sinter at first to coarser particles and then behave similarly to the coarse silver powder. This effect was also found by Hilali et al. [7], who correlated sintering kinetics with paste performance: if the particle size is too small, cell performance decreases.

“The amount and type of silver precipitation at the wafer surface can be influenced by the use of inorganic additives.”

Fig. 5 illustrates that the amount and type of silver precipitation at the wafer surface can be influenced by the use of inorganic additives, in comparison to a pure glass-containing coarse silver paste. If the inorganic species has an oxidizing characteristic, the amount of silver located in the glassy interface is increased, which can be explained by the thermal behaviour of the

additives during RTP. During heating-up of the wafer, the additive begins to decompose, and free oxygen is produced, forming a micro-atmosphere with increased partial pressure in the paste’s microstructure. The increasing oxygen partial pressure supports the dissolution of silver as silver oxide in the glass phase. This process can start at a temperature as low as approximately 330°C [8].

Fig. 5 also shows that, with increasing oxidizing power of the additives (A, B and D), the glass layer at the wafer surface becomes more inhomogeneous. This might be due to the improved silver oxide dissolution in the paste glass, and to the related enhanced etching capability. The contact formation depends on the ratio between etching and silver precipitation at the interface. With slightly increased oxidation potential, additive A has a slightly higher serial resistance than additive B. Nevertheless, the use of an additive which oxidizes the surface too strongly (such as additive D) has a negative effect on cell performance: the reason for this is the degradation of the emitter. If the amount of silver oxide becomes too high, the etching of the surface of the wafer can be too strong, and thus the penetration can be too deep. As a consequence, the emitter becomes damaged and cell performance is decreased, which in turn results in an increasing serial resistance. The results show that, in general, inorganic additives do not work – a successful outcome depends upon an interaction between different factors, such as the grain sizes or temperatures used.

Surprisingly, the greatest improvement in cell performance can be achieved with the reducing additive C (Fig. 4). Compared with the paste without any additive, the amount of silver at the interface is almost the same. The reason for this is the unchanged oxygen partial pressure during RTP, and thus the silver dissolution in the glass frit is not affected.

If the silver particle size is reduced, the inorganic additives no longer yield an improvement in efficiency (Fig. 4 – black bars): cell performance is reduced compared with the medium silver paste. A decreased efficiency and an increased serial resistance are obtained. This is related to the optimized sintering behaviour of the medium silver paste and the supplementary effect of the additives: the additives enhance the reaction kinetics at the wafer surfaces. Because

of the aligned silver powder and glass frit, the use of additives results in an acceleration of the reaction kinetics that is too high at the interface, so that the etch depth can become too deep, and damage to the emitter can occur. Matching the size of the silver particles with the influence of the additives is therefore important.

Conclusion

The influence of silver powder particle size and inorganic additives on sintering and electrical performance of a paste was investigated; for the study, three different silver powders were mixed with 5 vol% glass. The phase transport kinetics, as well as the reaction kinetics at the interface, were found to be influenced by the silver powder grain size used. The medium silver powder provided the highest surface for the longest time, so the silver dissolution and transport onto the silicon surface was enhanced. The coarse silver powder had a smaller surface and the silver transport was not as good as for the medium grain size. This aspect correlated with the electrical performance of the solar cells obtained.

“It is important that the silver powder and the redox potential of the additives are matched.”

If the inorganic species has an oxidizing nature, the mass transport of silver in the glass phase can be enhanced. However, the etch process at the wafer surface is also improved by a greater quantity of silver oxide in the flowing glass. If the oxidizing capacity of the additive is too powerful, the electrical performance is negatively influenced. The impact of additives, however, is dependent on the silver particle size, so it is important that the silver powder and the redox potential of the additives are matched.

Acknowledgement

The authors are grateful for the financial support from the Sächsische AufbauBank for the ‘KOMET’ project (No. 1000694198).

References

- [1] Ballif, C. et al. 2003, “Silver thick-film contacts on highly doped n-type silicon emitters: Structural and electronic properties of the interface”, *Appl. Phys. Lett.*, Vol. 82, No. 12.
- [2] Schubert, G. 2006, “Thick film metallisation of crystalline silicon solar cells”, Ph.D. thesis, University of Konstanz.
- [3] Hong, K.-K. et al. 2009, “Mechanism for the formation of Ag crystallites in the Ag thick-film contacts of crystalline Si solar cells”, *Sol. Energy Mater. Sol. Cells*, Vol. 93, pp. 898–904.
- [4] Eberstein, M. et al. 2012, “Sintering and contact formation of glass containing silver pastes”, *Energy Procedia*, Vol. 27, pp. 522–530.
- [5] Cho, S.-B. et al. 2010, “Role of the ambient oxygen on the silver thick-film contact formation for crystalline silicon solar cells”, *Curr. Appl. Phys.*, Vol. 10, pp. S222–S225.
- [6] Huh, J.-Y. et al. 2011, “Effect of oxygen partial pressure on Ag crystallite formation at screen-printed Pb-free Ag contacts of Si solar cells”, *Mater. Chem. Phys.*, Vol. 131, pp. 113–119.
- [7] Hilali, M. et al. 2006, “Effect of Ag particle size in thick-film Ag paste on the electrical and physical properties of screen printed contacts and silicon solar cells”, *J. Electrochem. Soc.*, Vol. 153, No. 1, pp. A5–A11.
- [8] Heinz, M. & Stiebing, M. 2013, “Modellierung der Nanopartikelbildung in Gläsern durch Kombination von optischer Spektroskopie und Röntgenkleinwinkelstreuung”, *Proc. 87. Glastechnische Tagung*, Bremen, Germany.

About the Authors



Stefan Körner is a Ph.D. student at TU Dresden. He received his diploma in chemistry in 2012 from Chemnitz University of Technology, for which he carried out research, in cooperation with Leibniz IOM (Leipzig), on gold nanoparticles for biochemical applications. He currently works at Fraunhofer IKTS in Dresden in the thick-film technology and photovoltaics group, where he is investigating the contact formation between front-side metallization and multicrystalline silicon.



Kathrin Reinhardt is a Ph.D. student in materials science at TU Dresden. She received her diploma (FH) in chemical engineering from the University of Applied Sciences Dresden in 2006, and since then has been working in the thick-film technology and photovoltaics group at Fraunhofer IKTS. She began her Ph.D. at IKTS in 2010, on the topic of the relationships between rheological properties and deposition behaviour of highly filled suspensions.



Uwe Partsch studied electrical engineering at the Technical University of Dresden and received his Ph.D. in 2002 in the field of LTCC sensors. After working as a project and group leader in the area of LTCC integrated microsystems and multilayer ceramic fuel cells, he was appointed head of the Hybrid Microsystems department at Fraunhofer IKTS.



Markus Eberstein studied materials science with a special focus on glass at TU Berlin, and received his Ph.D. in 2001 in the field of microelectronics materials from the BAM Federal Institute for Materials Research and Testing, Berlin. He is currently the manager of the thick-film technology and photovoltaics group at Fraunhofer IKTS. The focal points of his research are structure-properties relationships of glass and ceramic thick-film materials, sintering kinetics, and dielectric and optical properties, as well as laser structuring of glass and ceramics.

Enquiries

Dr.-Ing. Markus Eberstein
Group Manager Thick Film Technology and Photovoltaics
Fraunhofer Institute for Ceramic Technologies and Systems IKTS
Winterbergstr. 28
01277 Dresden
Germany

Tel: +49 351 2553-7518

Fax: +49 351 2554-265

Email:

markus.eberstein@ikts.fraunhofer.de

Website: <http://www.ikts.fraunhofer.de>