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Experimental evidence of direct contact formation for the current transport in silver thick film metallized silicon emitters

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Great advances have been achieved in the development of silver pastes. The use of smaller silver particles, higher silver content, and, thus, less glass frit allow modern silver pastes to contact high resistive emitters without the necessity of a selective emitter or subsequent plating. To identify the microscopic key reasons behind the improvement of silver paste, it is essential to understand the current transport mechanism from the silicon emitter into the bulk of the silver finger. Two current transport theories predominate: i) The current flows through the Ag crystallites grown into the Si emitter, which are separated by a thin glass layer or possibly in direct contact with the silver finger. ii) The current is transported by means of multistep tunneling into the silver finger across nano-Ag colloids in the glass layer, which are formed at optimal firing conditions; the formation of Ag crystallites into the Si surface is synonymous with over-firing. In this study, we contact Si solar cell emitters with different silver pastes on textured and flat silicon surfaces. A sequential selective silver-glass etching process is employed to expose and isolate the different contact components for current transport. The surface configurations after the etching sequences are observed with scanning electron microscopy. Liquid conductive silver is then applied to each sample and the contact resistivity is measured to determine the dominant microscopic conduction path system. We observe glass-free emitter areas at the tops of the pyramidal-textured Si that lead to the formation of direct contacts between the Ag crystallites grown into the Si emitter and the bulk of the silver finger. We present experimental evidence that the major current flow into the silver finger is through these direct contacts. © 2011 American Institute of Physics. [doi:10.1063/1.3665718]

I. INTRODUCTION

Screen printing is still the most widely spread metallization technology in the photovoltaic industry, due to its high degree of industrialization and due to the lack of market-ready, cost-effective alternatives. The subsequent co-firing step is crucial for achieving good solar cell performance; therefore, the firing temperature profile must be optimized for each silver paste-emitter profile combination and with respect to the rear-side contact, where each paste has its emitter contacting limit. Even though a reduced emitter doping concentration impairs the contact formation when using screen printing technology, with the improvement of the composition of silver pastes, it is possible to contact emitters with high sheet resistances up to currently 100 Ω/sq and, thus, to reach higher efficiencies through increased short-circuit currents and open-circuit voltages.¹

The ingredients of a current commercial silver paste are silver particles, glass frit, solvents, and binders. The glass frit is essential for the contact formation because, during firing, it etches the SiN_x layer and allows for the formation of Ag crystallites in the silicon emitter and nano-Ag colloids in the glass layer, which form the front-side solar cell contact.

However, the glass frit is also responsible for increasing the contact resistance, due to the poorly conducting glass layer that it forms on the silicon surface.² Varying the glass frit content in the silver paste influences the opening of the SiN_x layer, the size and density of Ag crystallites formed, and the contact resistance.^{2,3} The optimum glass frit content opens sufficiently the SiN_x layer to result in the formation of many small Ag crystallites grown into the silicon emitter together with a thin glass layer containing many nano-Ag colloids, resulting in good contact and, thus, in low contact resistance.

The firing step is critical for the contact formation. Underfiring results in an insufficient SiN_x opening, while overfiring leads to an increased isolating glass layer thickness.^{2,4} A short dwell time decreases the contact resistance, due to the formation of a thinner glass layer.⁵ Finally, during the firing step, on top of the Ag crystallites and the glass layer—containing nano-Ag colloids, the metal particles in the bulk of the silver finger are sintered and need to ensure a good conductivity along the finger to the busbar.

In this study, we investigate the reasons for the successful development of silver pastes, which are now capable of contacting high resistive emitters. We attempt to resolve the two current transport theories predominating in literature:⁶ i) The current flows through the Ag crystallites grown into the Si emitter, which are separated by a thin glass layer or possibly in direct contact with the silver finger.^{2,7} ii) The current is

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transported by means of multistep tunneling into the silver finger across nano-Ag colloids in the glass layer, which are formed as the result of optimal firing conditions; the formation of Ag-crystallites into the Si surface is synonymous with over-firing.^{8,9} For our investigations, we perform microscopic observations after sequential etch-back of the metallization from different silver thick film pastes. To evaluate the relative importance of the possible current transport paths from the silicon emitter into the bulk of the silver finger, we apply liquid conductive silver to the different stages of the etched-back contacts and measure the contact resistivity.

II. EXPERIMENTAL

Our standard solar cell process applied for this study is based on 6-inch pseudo-square *p*-type Cz Si wafers with 3–6 Ωcm base resistance. In this experiment, we investigate both pyramidal and flat surface current transport to silver pastes. We create a random pyramidal surface with alkaline etching. For the flat surfaces, we remove the saw damage from wafer production with NaOH. After, a HCl/hydrofluoric acid (HF) cleaning is followed by POCl_3 gas diffusion, HF phosphorus-glass etching, and PECVD SiN_x deposition. Subsequently, the wafers are front screen-printed with different commercial Ag pastes. The same Al paste is printed on the rear side for all cells. Finally, the co-firing step is performed in an IR-heated belt furnace.

Silver pastes of different generations and manufacturers are applied. Paste A-gen06 denotes a paste which has been on the market for several years and leads to good contacts for sheet resistances up to $\sim 60 \Omega/\text{sq}$. Pastes A-gen09 and B-gen09 denote pastes which have been commercially available since 2009 and allow the contacting of emitters with sheet resistances up to $80 \Omega/\text{sq}$. However, to make the contacting behavior of the different pastes comparable, all samples had emitter sheet resistances between 55 and $65 \Omega/\text{sq}$. Best firing conditions for each paste are identified by current-voltage (IV) and electroluminescence (EL) measurements.

Contact resistivity ρ_C [$\text{m}\Omega\text{cm}^2$] measurements are carried out by the transfer length method (TLM).¹⁰ The silver thick film contacts are analyzed with scanning electron microscopy (SEM) and energy dispersive x ray spectroscopy (EDX) after different etching sequences with aqua regia (AR) and hydrofluoric acid (HF).¹¹ Because AR is a very strong oxidizing agent,¹² one can be sure that AR does not etch the glass. Therefore, the etching sequences are selective with respect to silver and glass.

In order to determine the importance of different possible current paths from the emitter to the silver finger, liquid conductive silver is applied on the contact areas after different etching sequences, and the resulting contact resistivity was measured with TLM.

The following etching sequences are realized:

- a) no etching and initial configuration
- b) etching with AR: the Ag finger is removed and the glass and the silver beneath remains
- c) subsequent etching with AR and HF: the glass is also removed and the silver underneath the glass still remains
- d) subsequent etching with AR, HF, and AR: all silver, glass, and silver beneath the glass layer is removed and only the bare emitter remains
- e) etching with BHF: the glass is removed, the Ag-finger is lifted off, and only silver directly grown into the emitter remains

The listed contact resistivity measurements are averaged over the measurements of 12 fingers of 1 cm width on solar cell cut-outs selected from representative regions around the middle of the solar cells. For the interpretation of the results, it is assumed that the contact resistivity of the glass to the liquid conductive silver and the silver finger are equivalent.

III. RESULTS AND DISCUSSION

A. Microscopic contact formation on flat Si

Figure 1 shows SEM top views of flat $\langle 100 \rangle$ -oriented Si emitters contacted by silver paste B-gen09 after contact etching:

- After selective etching with AR to remove the bulk of the Ag finger, the inhomogeneous thick continuous glass layer on the Si surface can be observed, as shown in Fig. 1(a).
- Subsequent etching of the glass layer with HF reveals the Ag crystallites grown into the Si emitter (see Fig. 1(b)). These Ag crystallites were protected by the glass layer during the previous selective silver etching by AR.

Figure 1 shows typical microscopic pictures of screen-printed thick film silver contacts, where Fig. 1(a) reveals a continuous glass layer underneath the bulk of the Ag finger, and Fig. 1(b) reveals, under this glass layer, a distribution of Ag crystallites as grown into the Si surface.² The density of

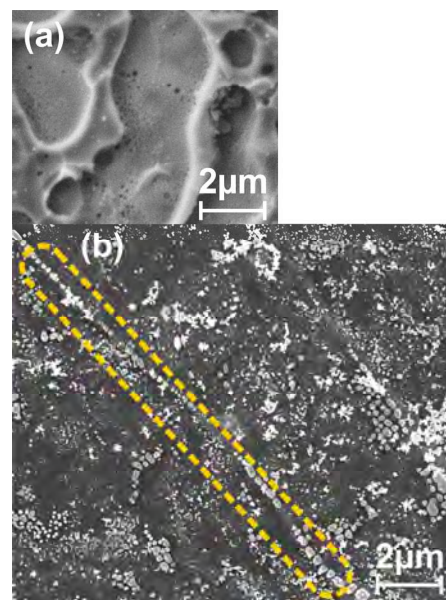


FIG. 1. (Color online) SEM top view of a flat $\langle 100 \rangle$ -oriented Si surface after selective etching of an Ag-paste B-gen09 contact. In (a), only the silver finger is selectively removed, while (b) shows the contact after additional selective glass layer etching.

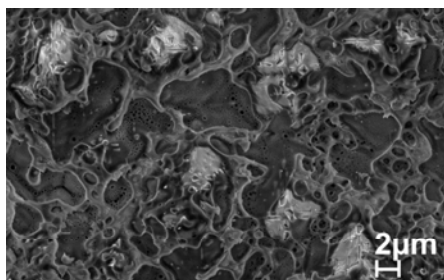


FIG. 2. SEM top view after selective silver etching of a silver paste B-gen09 contact. Pyramid tips protrude from the inhomogeneous glass layer, containing imprints of etched-away Ag crystallites as formerly grown into the Si emitter.

these Ag crystallites increases with the emitter surface doping concentration^{2,13} and depends on the firing conditions.² The sizes and shapes of the Ag crystallites are determined by the firing conditions and the Si surface orientation.^{2,4} It was recently suggested that SiP clusters or surface crystal defects in general might serve as nucleation sites for Ag crystallites on the Si surface.³ In Fig. 1(b), we observe Ag crystallites of increased density and size on a step as resulting from NaOH etching (highlighted).

B. Microscopic contact formation on pyramidal textured Si

Figure 2 shows a SEM top view of a random pyramidal textured Si surface contacted by Ag-paste B-gen09. In this figure, the silver finger has been removed by etching with AR, leaving the glass layer behind. The porous structure is the glass and the lighter features are the tips of the pyramids protruding out from the glass. Thus, the glass fills only the pyramid valleys. A closer look at the pyramid tips in Fig. 3 reveals that they contain characteristically shaped imprints. These shapes are typical for the silver crystallites grown into the $\langle 111 \rangle$ Si surface during the firing of the paste and are normally observed after etching away all silver and glass, including the silver underneath the glass layer.^{2,13} Thus, in that case, the silver crystallites are not directly connected to the Ag bulk of the finger. Our observation of imprints after solely AR etching shows that silver crystallites can also grow directly from the bulk silver into the Si surface. Figure 4 shows a sketch of the microscopically observed geometrical configuration of Si pyramids, glass, and imprints.

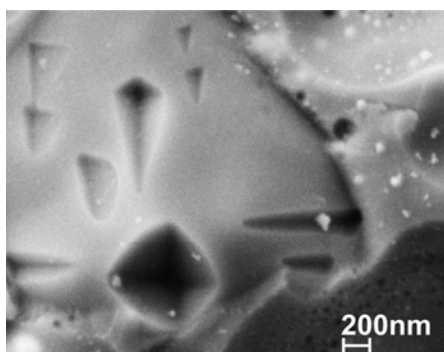


FIG. 3. Close up of Fig. 2 showing Ag crystallite imprints on the glass-free pyramid top. The glass layer covers the bottom portion of the pyramid.

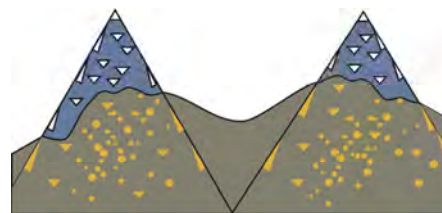


FIG. 4. (Color online) Cross-section sketch of the glass distribution: glass covered contact Ag crystallites in lower heights and imprints of etched-away Ag crystallites at the tops of the silicon pyramids.

C. Current transport mechanism investigations

The SEM top view after the etching removal of the silver finger in Fig. 5 illustrates the different components of the screen-printed Ag contact underneath the silver finger bulk:

1. Contact imprints of Ag crystallites grown into the Si emitter, which were removed together with the silver finger
2. The inhomogeneous glass layer
3. Ag crystallites grown into the Si emitter underneath the glass layer, thus separated from the silver finger by the glass layer
4. Nano-Ag colloids within the glass

Figure 5 shows that Ag crystallites grown into the Si surface and nano-Ag colloids in the glass layer coexist. Current transport from the emitter into the silver finger could take place through the Ag crystallites grown into the Si emitter separated by a thin glass layer,^{2,7} directly through the Ag crystallites grown into the glass-free pyramid tips, and via multi-step tunneling assisted by nano-Ag colloids within the glass.⁸

Table I lists the contact resistivity after the liquid-conductive silver application to the solar cell cut outs to the five different etching sequences described in Fig. 6. The following observations are made:

- a) The contact resistivity of the pyramidal textured solar cell samples is $4\text{--}8\text{ m}\Omega\text{cm}^2$. It is noteworthy that the contact resistivity on flat Si is one order of magnitude larger than on pyramidal Si, with significant differences between the pastes.

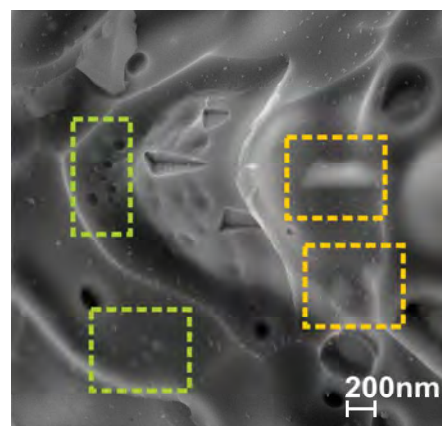


FIG. 5. (Color online) SEM top view of a Si pyramidal surface after the etching of the silver finger, illustrating the different contact components.

TABLE I. Contact resistivity measurements after the different stages of contact etching described in the caption of Fig. 6 with subsequent liquid conductive silver application.

Ag-paste	Surface	ρ_c [$\text{m}\Omega\text{cm}^2$]				
		a)	b)	c)	d)	e)
A-gen06	Pyramidal	8	20	3.5	1500	$\leq 1^a$
	Flat	200	200	25	2000	20
A-gen09	Pyramidal	6	100	3.5	1600	3.5
	Flat	150	300	10	1400	2.5
B-gen09	Pyramidal	4	700	1.5	1300	$\leq 1^a$
	Flat	50	700	3.5	1300	3.5

^aThe measured TLM data of the solar cell cut outs are reliable from values of 0.5–1.0 $\text{m}\Omega\text{cm}^2$ and above due to restrictions as given by geometry and emitter sheet resistance (i.e., doping) (Ref. 10).

- b) When the silver is selectively etched and liquid conductive silver is applied for contacting, the current flows through both Ag crystallites grown into the Si surface, which are separated from the bulk silver by the glass layer and through nano-Ag colloids within the glass layer. The amount of glass detected by EDX correlates strongly with the measured contact resistivity, i.e., the largest amount of glass is detected where the contact resistivity is highest. On textured Si, the contact resistivity is increased by one or more orders of magnitude, suggesting that most of the current flows through the Ag crystallite contacts at the pyramid tops, the imprints of which were left behind after selective silver etching (see Figs. 2–5). Only where no Ag crystallite imprints can be found by SEM, i.e., with paste A-gen06 on a flat surface (for pastes A/B-gen09 imprints are found only rarely), does silver etching with subsequent liquid conductive silver application not further increase the already initially high contact resistivity.
- c) When, in addition to selective silver etching, the glass is subsequently removed, and, thus, the Ag crystallites, which were under the glass, provide points of direct contact between the emitter and the liquid conductive silver, the contact resistivity decreases for the textured surfaces to 1.5–3.5 $\text{m}\Omega\text{cm}^2$. On flat surfaces, contact resistivity values about one order of magnitude lower than the initial ones are measured when these formerly indirectly

contacted Ag crystallites are directly contacted by liquid conductive silver. In regard to the lower contact resistivity values resulting from paste B-gen09, as compared to paste A-gen06, our EDX analyses of these two as-dried Ag pastes confirm that the Ag content in the former is 5 % by weight higher than in paste A-gen06.

- d) When all silver and glass is removed, only the bare emitter with imprints remains, and, thus, liquid conductive silver application results in the same high contact resistivity of $\sim 1500 \text{ m}\Omega\text{cm}^2$ for all samples, independent of the Ag paste and surface topography. The applied liquid Ag is air dried and not sintered and shows, therefore, a larger contact resistance to the bare Si-emitter surface due to different work function levels at the abrupt interface between the dried liquid Ag and the solid Si. However, a low ohmic contact between the liquid Ag and the embedded Ag crystallites inside the Si matrix is established, because they are of the same material.
- e) Finally, when, after removing the glass layer by BHF etching, all Ag crystallites are directly contacted with liquid conductive silver, as it is expected, the lowest contact resistivity values are measured.

IV. CONCLUSION

In order to gain a better understanding of the current transport mechanisms on the front side thick film paste, solar cell metallization from current silver pastes, silver, and glass is selectively removed. SEM observations reveal that, when the bulk of the silver finger is selectively removed, some of the Ag crystallites at the top of the silicon pyramids are removed as well, because there is no glass layer at the top of some pyramids to protect these crystallites from the silver etching. In SEM pictures, these pyramid tips can be seen sticking out from the inhomogeneous thick glass layer, which is mainly concentrated in the valleys of the pyramidal structure. Thus, at the pyramid tops, direct contact between the bulk of the silver finger and the silicon exists by means of Ag crystallites grown into the emitter. The fraction of pyramid tops that are in direct contact with the bulk of the silver finger is inversely correlated with the measured contact resistivity. On flat Si emitters contacted by silver pastes of earlier generations, no such direct contacts can be observed, whereas more recent paste generations also form some sparse direct contacts to flat Si emitters. Reconnection of current paths by liquid conductive silver after sequential selective etch-back of the contact components lead us to conclude that the directly contacted Ag crystallites at the pyramid tops play a major role in the solar cell's current conduction, while less current flows through the Ag crystallites separated from the silver finger by the glass and the nano-Ag colloids contained within the glass. Specifically, we demonstrate that, with the best Ag-paste used in this study, we create direct contacts, reducing the contact resistivity by two orders of magnitude.

While the existence of direct contacts between the silver finger and the Ag crystallites grown into the Si emitter was not clearly registered from contact formation of older silver pastes, numerous authors, including Ballif, Hilali, Hörteis, and Kontermann suggested that such direct contacts are

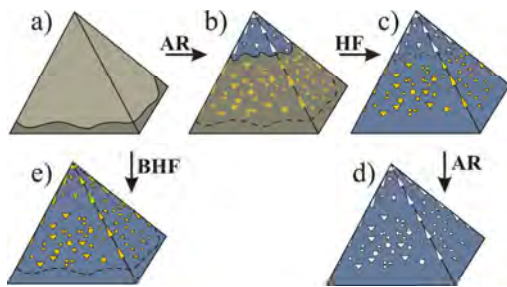


FIG. 6. (Color online) Selective etching sequences for conductive path investigations: a) Ag finger, standard solar cell configuration. b) Selective removal of Ag finger and directly connected Ag crystallites. c) Sequential selective removal of Ag finger and glass: exposure of Ag crystallites under glass. d) Removal of Ag finger, Ag crystallites, and glass: bare emitter with imprints. e) Etching of glass including lift-off of Ag finger: all Ag crystallites grown into the Si surface remain.

significant for the current transport in thick film metallized emitters.^{3,7,14,15} Now, our investigations with the investigated current commercial silver pastes show the existence of direct contacts and their preferred location at the pyramid tops. Furthermore, our current transport mechanism investigations by liquid conductive silver application after various contact etch-backs confirm that the solar cell current mainly flows through these direct contacts.

V. OUTLOOK

We would like to gain a better understanding of the Ag crystallites and nano-Ag colloid growth on different silicon surface topographies and doping densities and to investigate the role of the components of the glass layer in the current transport. Modeling of the contact formation and the current transport from the semiconductor into the metal contact will be done within the framework of the European project Hipersol.

ACKNOWLEDGMENTS

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- ¹G. Laudisio, 2nd Workshop on Metallization of Crystalline Silicon Solar Cells, Konstanz, Germany, 14 April 2010.
- ²G. Schubert, Ph.D. dissertation, University of Konstanz, 2006.
- ³M. Hörteis, Ph.D. dissertation, University of Konstanz, 2009.
- ⁴S. Kontermann, Ph.D. dissertation, University of Konstanz, 2009.
- ⁵I. B. Cooper, A. Ebong, J. S. Renshaw, R. Reedy, M. Al-Jassim, and A. Rohatgi, *IEEE Electron Device Lett.* **31**, 461 (2010).
- ⁶G. Schubert, F. Huster, and P. Fath, *Sol. Energy Mater. Sol. Cells* **90**, 3399 (2006).
- ⁷C. Ballif, D. M. Huljic, G. Willeke, and A. Hessler-Wyser, *Appl. Phys. Lett.* **82**, 1878 (2003).
- ⁸Z. G. Li, L. Liang, and L. K. Cheng, *J. Appl. Phys.* **105**, 066102 (2009).
- ⁹M.-I. Jeong, S.-E. Park, D.-H. Kim, J.-S. Lee, Y.-C. Park, K.-S. Ahn, and C.-J. Choi, *J. Electrochem. Soc.* **157**, H934 (2010).
- ¹⁰D. K. Schroder and D. L. Meier, *IEEE Trans. Electron Devices* **31**, 647 (1984).
- ¹¹– Etching with AR: HCl 32% + HNO₃ 65% 3:1, 1 [h], at room temperature
– Etching with HF after AR: HF 4%, 7 min, at room temperature
– lift-off of Ag finger with BHF: BHF 10%, agitated, as long as needed for Ag finger to fall off (~8 min), in the dark at room temperature
- ¹²A. F. Hollemann, E. Wiberg, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, 33rd ed. (Walter de Gruyter, Berlin, 1985) p. 603.
- ¹³D. Pysch and A. Mette, *Prog. Photovoltaics* **17**, 101 (2009).
- ¹⁴M. M. Hilali, K. Nakayashiki, C. Khadiolkar, R. C. Reedy, A. Rohatgi, A. Shaikh, S. Kim, and S. Sridharanb, *J. Electrochem. Soc.* **153**, A5 (2006).
- ¹⁵S. Kontermann, G. Willeke, and J. Bauer, *Appl. Phys. Lett.* **97**, 191910 (2010).