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What makes a high-performing screen-printed Ag contact? Realities and idealities from microscopical insight

S. Olibet[1], D. Rudolph[1], E. Cabrera[1], J. Hoornstra[2], A. Carr[2], A. Weeber[2], Y. Fu[3], R. Kopecek[1]
[1]ISC Konstanz, Germany, [2]ECN Petten, Netherlands, [3]KTH Stockholm, Sweden

Abstract

High-performing screen-printed and co-fired Ag contacts feature Ag-crystallites grown into Si. Our experiments show that the commonly observed benefit of ultra-fast firing may be the enhancement of direct or close contact formation of these Ag-crystallites to the bulk of the Ag-finger. While so far these Ag-crystallites grown into Si are needed for low contact resistivity, they lead to contact induced recombination losses as exemplarily shown by model pastes etching deeply into the emitter. Advances such as high-performing emitters being able to be contacted by newest generation Ag-pastes lead to standard c-Si solar cells being fully limited by the Al back metallization besides the bulk quality. But for advanced high-efficiency concepts like PERC and n-type cells, contact induced recombination becomes the main efficiency limiting factor. Based on our large microscopic contact database together with resulting solar cell data, we intend to quantify these losses and give guidelines for process optimization within current industrial cost-efficient process limits, i.e. using screen-printing and cost-effective emitters. Finally, the ideal contact should avoid any metal grown into Si. By temperature-dependent contact resistivity measurements, current conduction mechanisms can be identified. We apply such measurements to two different microscopic current conduction path systems.

1. Introduction

Simple Ag-pastes with glass-frit consisting of PbO, SiO_2 and B_2O_3 only were fabricated within Hipersol for firing process modeling comparison purpose [1]. Within a large firing parameter variation experiment with these pastes, we find the firing condition dependence to be very similar to the one observed with commercial Ag-pastes. By SEM and EDX after selective contact etch-back we search the microscopic reason for this observed firing profile dependence.

Furthermore, with these simple Hipersol model pastes the trade-off between microscopic contact formation and contact induced recombination is very pronounced. At their example, we generally discuss this trade-off within current state of the art homogeneous emitter and Ag-pastes and outline its modeling.

The ideal contact should avoid the Ag-crystallites grown into Si that are characteristic for state-of-the-art screen-printed Ag-contacts, and is a MIS-like contact for diffused emitters. The dominating current conduction paths can in principle be distinguished by temperature-dependent contact resistivity measurements. We present the results of such measurements within two different current conduction path systems.

2. Experimental

Screen-printed Ag-pastes with 5 different glass frits consisting of PbO, SiO_2 and B_2O_3 only, with varying SiO_2/PbO and B_2O_3/PbO ratio, also zero for either or, were used to fabricate standard monocrystalline Si solar cells with full-surface screen-printed Al back-side metallization. Solar cells with these Ag-pastes as well as their reference cells with commercial Ag-paste contacts feature 50 Ω/sq emitters. Solar cell results given are averages over at least 4 solar cells. Fast-firing profiles are acquired by a data logger riding 1 m behind the solar cell through the belt furnace. By taking SEM micrographs after selective contact etch-back, different contact components can be studied [2]. At least 4 SEM micrographs of the same sample are taken. EDX spectra for elemental composition analysis are averaged over at least 3 areas of 375 μm^2 each. Temperature-dependent contact resistivities are measured by the transfer length method [3]. Very reliable data with excellent linear fits could be acquired.

3. Results and Discussions

3.1 Influence of firing belt-speed on glass homogeneity and its relation to contact resistivity

Figure 1 shows the fast-firing peak-temperature and belt-speed dependent microstructure by SEM including EDX analysis after selective contact etch-back compared to the resulting solar cell series resistance. Starting with a high-temperature short-time firing profile, either the peak-temperature or the belt-speed is lowered. Results shown are with Hipersol Ag-paste containing PbO and B_2O_3 as glass frit components only. While the absolute values differ, trends and relations are the same with the other four Hipersol model Ag-pastes.

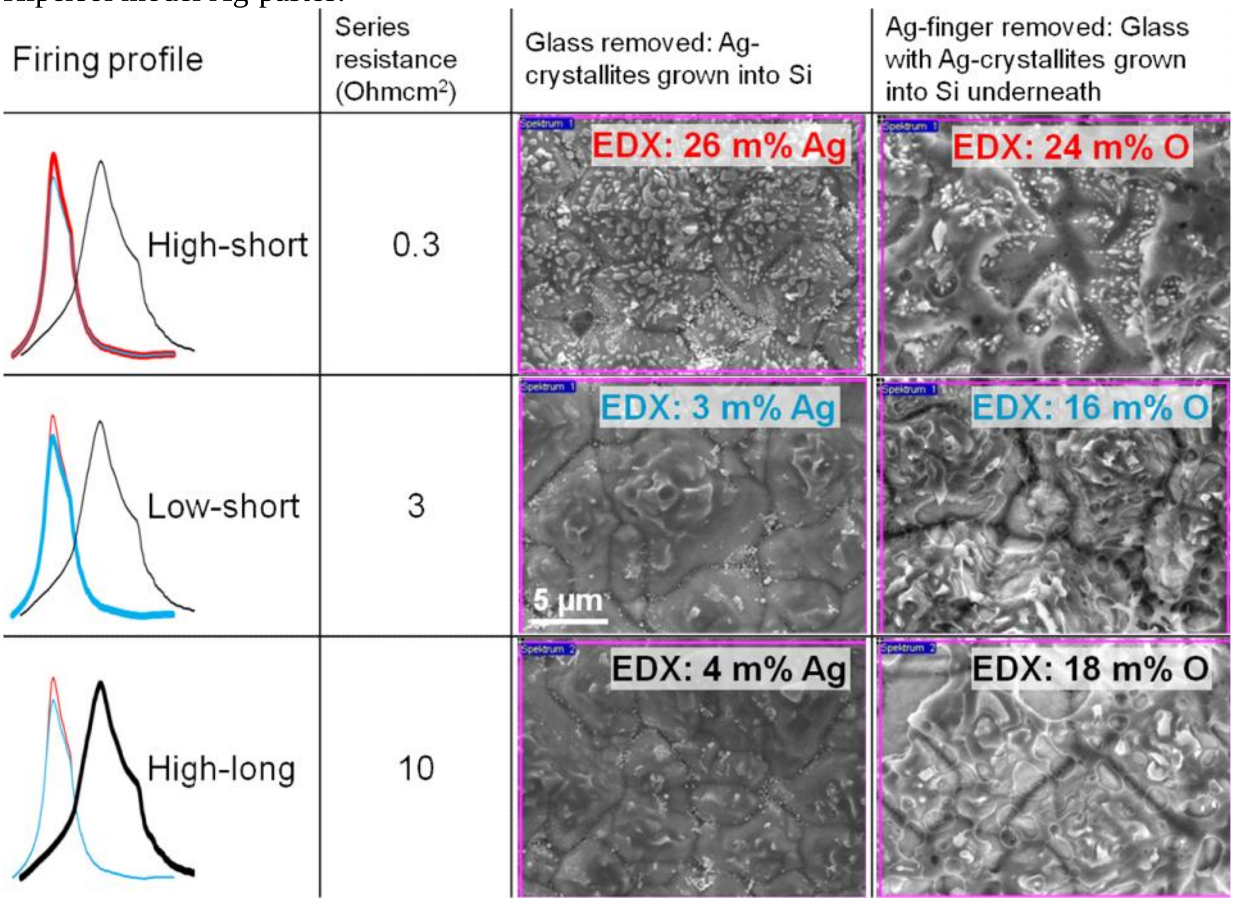

Figure 1. Firing dependent solar cell series resistances and SEM top views of EDX analyzed contact compositions after selective contact etch-back.

Clearly, high(-temperature)/short(-time) firing results in most Ag-crystallites grown into Si. Despite the similarly few Ag-crystallites formed when applying the low-short and the high-long firing profile, the series resistance measured on the resulting cells differs. This can be explained by looking closer at the glass layer coverage that is notably different: it is very inhomogeneous with high-short firing, less inhomogeneous with low-short and rather homogeneous with high-long firing. Note that the total amount of glass is considerably higher when high-short firing is applied. Thus, with a very similar amount of Ag grown into Si the contact resistivity differs because the glass layer thickness homogeneity dictates if some of these Ag-crystallites get into close contact with the Ag-finger and thus enable efficient current conduction.

The benefit of ultra-fast firing may thus in general be this inhomogeneous glass-layer formation – and not the absolute amount of glass on the Si surface – enabling glass-free pyramid tips and thus direct contacts between Ag-crystallites grown into Si and the bulk of the Ag-finger to form.

3.2 Trade-off between microscopic contact formation and contact induced recombination

As a result of the many directly contacted Ag-crystallites formed when high-temperature / short-time firing our simple Hipersol model pastes, same low series resistance as with commercial pastes are reached. However, the commercial reference Ag-paste solar cell efficiency is with 17.5% considerably higher. Our simple Hipersol model pastes lead to significantly reduced Vocs and PFFs, as summarized in Fig. 2 together with SEM micrographs of the Si surfaces after full contact etching. Again, only results from binary PbO/B_2O_3 glass frit are shown as trends with firing are very similar for all 5 pastes.

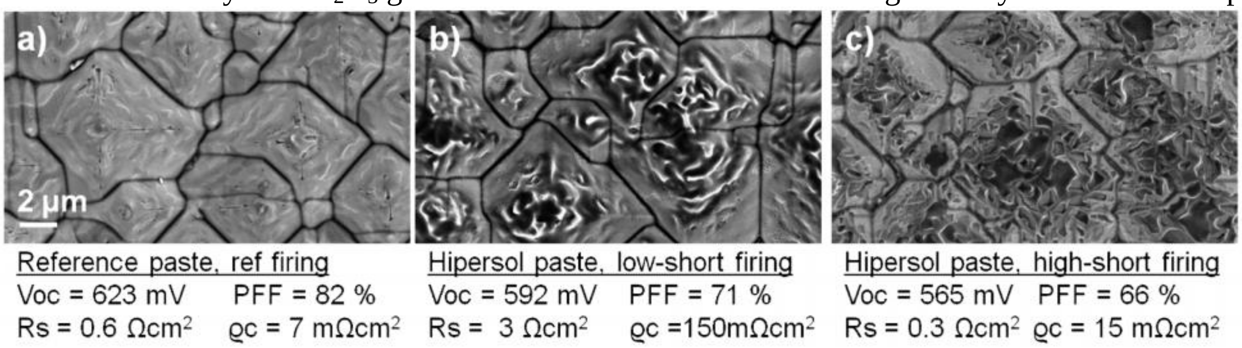

Figure 2. Solar cell parameters resulting from the contact microstructures shown by SEM after full contact etch, exposing the Si surface and imprints of etched-away Ag-crystallites.

With Hipersol model paste, one notices the etched-away pyramid tips, already at low firing temperature where Ag-crystallite formation does not yet take place. At high firing-temperature, in addition, imprints of deeply etched-in Ag crystallites are observed. Note that our Hipersol Ag-pastes feature Ag, Pb, O and Si contents within industrial Ag-paste averages. Too aggressive Si etching of commercial Ag-pastes is probably hindered by glass additives like Al, Zn and Mg. Basically, an inversely selective emitter forms with Hipersol model pastes, as exemplarily shown in Fig. 3:

a) Commercial reference paste: The highly doped 50 Ohm/sq emitter successfully shields contact recombination. Voc is limited to 623 mV by the high emitter recombination in the open area. PFF is with 82% very high.
b) Hipersol paste, low-temperature firing: The glass-etching of the Si surface leaves the emitter lightly doped under the contact. Lacking thus field-effect passivation, surface recombination at this unpassivated lightly doped emitter under the contact is very high and Voc thus reduced down to 592 mV and PFF to 71%.
c) Hipersol paste, high-temperature firing: Same situation as b) with additional penetration of Ag-crystallites deep into the remaining emitter and the space charge region. Voc is reduced to 565 mV and PFF to 66% by even higher recombination at the Ag-surface contacting the very lightly doped emitter region up to full local penetration of the contact through the emitter into the base. Note that these cells still have shunt resistances of 4 $k\Omega cm^2$, and thus not macroscopic shunting in the classical sense is responsible for the observed PFF-loss.

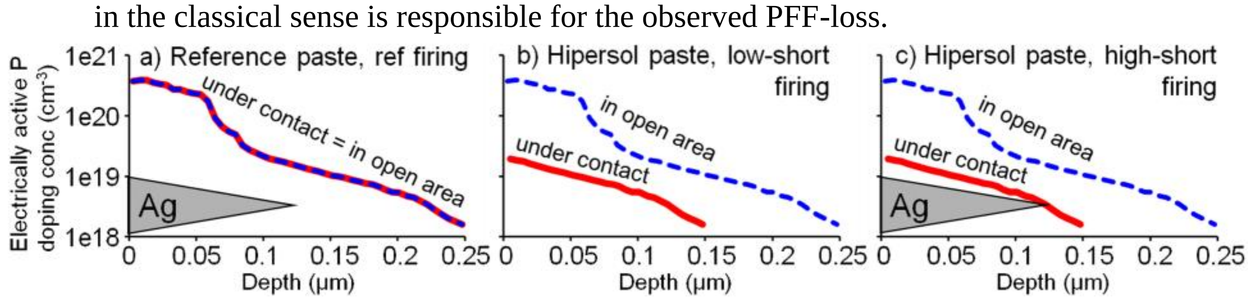

Figure 3. Emitter doping profile in the open-area and exemplarily under the contact including schematically an example of depth-relation to grown-in Ag-crystallites.

Koduvelikulathu et al. [4] model this Ag-penetration dependent Voc-loss for their n-type solar cells by lowering the whole Ag-contact finger with varying depth into their boron-doped p^+ Si-emitters. Within Hipersol, a 3D-model for the conductance through microscopically realistic contacts is set up [1] with doping and surface orientation dependent Schottky barriers calculated from ab initio [5] as input, and the influence of emitter doping profile variation and Ag-crystallite geometries on contact resistivity is studied in detail. While with old paste generations Ag-crystallite formation was critically dependent on the emitter's dead-layer, with new pastes we observe direct Ag-crystallite formation also to undoped textured Si pyramid tips [6]. Evidently with very high contact resistivity because of the current transport nature, see also Section 3.3.

Including microscopically realistic contact geometries into Koduvelikulathu's solar cell model in parallel with contact resistivity calculations by the Hipersol model, we aim to first validate these models against our experimental data base and then identify the best compromises between doping profiles, contact resistivities and contact recombination induced Voc- and PFF-losses. Finally, we are interested in getting to know by modelling the ultimate efficiency limit of homogeneous emitters within otherwise perfect solar cells but still staying within current industrial feasibility limits imposed on Ag-paste and emitter, means with screen-printed Ag-paste contacts featuring direct contacts and emitters produced by cost-effective processes.

3.3 Current-flow paths: Temperature-dependent contact resistivity measurements

c-Si solar cells with very lowest overall recombination need indirect contacts such as a doped/intrinsic a-Si:H layer stack as emitter between the c-Si and the ITO/Ag contact within Si heterojunction solar cells where Sanyo reaches 745 mV record Voc [7]. c-Si solar cells with in-diffused emitters would profit if Ag instead of growing crystallites into the Si emitter, would precipitate out into the glass, making it highly conductive such as current transport can take place directly from the emitter thorough the glass into the Ag-finger by multistep tunnelling as suggested by Li et al. [8]. Avoiding these Ag-crystallite penetration losses would substantially increase the Voc-potential of screen-printed Ag contacts. However, to our best knowledge, no high-efficiency screen-printed solar cells without Ag-crystallites grown into the Si emitter were reported so far [e.g. 9]. The discussion on whether if these grown-in Ag-crystallites are directly connected to the Ag-finger in some places or if there always is a thin glass-layer in-between is still ongoing. To shed further light on this, we measure the temperature-dependence of the contact resistivity on solar cell cut-outs featuring (i) many direct contacts, and (ii) Ag-crystallites separated from the Ag-finger bulk by a glass-layer everywhere, as identified by SEM after selective Ag-etch, see Fig. 4 (i) and (ii) and verified by conductive Ag-glue application in various contact etching states [2]. The corresponding dominant current paths are shown schematically in Fig. 4.

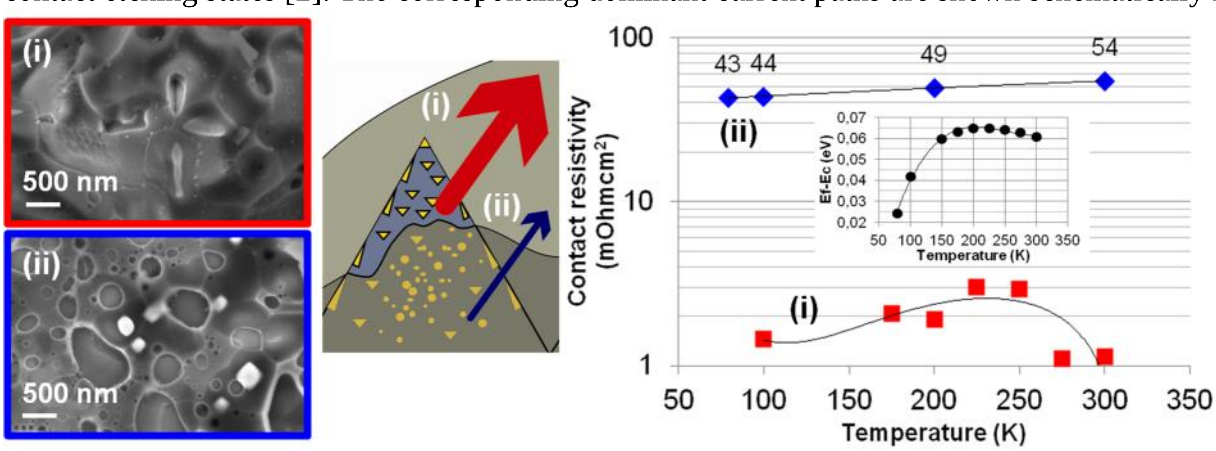

Figure 4. Temperature-dependent contact resistivity measurement on two different solar cell cut-outs featuring as visible by SEM after selective contact etch-back (i) direct Ag-crystallite/Ag-finger contacts, (ii) indirect contacts to Ag-crystallites through a separating glass layer. The schema shows the major current transport paths in these two samples.

Field-emission current based contact resistivity is almost temperature independent but continuously increasing with decreasing temperature. The contact resistivity for thermionic emission is very temperature dependent and strongly increases as the temperature decreases [3]. In accordance with FE being predominant as transport mechanism between the highly doped emitter surface and the Ag-crystallite, the direct contact resistivity (i) slightly increases towards lower temperature, see data plot in Fig. 4 but reaches a local maximum at 225 K. Interestingly, this maximum coincides with the maximum of the Fermi-level position above the conduction band for the given surface emitter doping and within the experimentally measured temperature range, see inset in data plot Fig. 4. The indirect contact resistivity (ii) – i.e. after entering the Ag-crystallite identically to (i), the current needs to be transported through the glass – decreases with decreasing temperature. So far we do not have an explanation for this behaviour.

4. Conclusions

Contact induced recombination is one of the most critical issues to be solved for high-efficiency p- and n-type monocrystalline Si solar cells. While passivated contacts would be ideal, screen-printed fire-through Ag pastes with low contact resistivities result in Ag-crystallites grown into Si. To avoid the necessity of locally highly doped regions under the contact to shield recombination within industrial cost-effective high-performing solar cell fabrication, technological guidelines from modeling based on microscopic observations can help optimize the solar cell efficiency within the trade-off between emitter-contact recombination and contact resistivity. Furthermore screen-printing pastes resulting in low contact resistivities without metal grown into Si are needed.

Acknowledgments

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