

Metallization: The technology with highest efficiency gain potential for c-Si cells

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ABSTRACT

This paper summarizes the status and potential of screen-printing technology, and describes the results and thoughts of ISC Konstanz relating to the present and future of metallization technology. A microstructural investigation of contact formation and the possible electrical transport mechanism from the emitter into the metal finger is briefly discussed. In addition, the simulation results using Silvaco, which model the drop in V_{oc} due to so-called *metal-induced recombination*, are presented. Several options for reducing this recombination in order to improve solar cell efficiency are then proposed.

Introduction

In the last few years, efficiencies of 20% have been achieved with industrial-standard screen-printed passivated emitter and rear cell (PERC), passivated emitter and rear totally diffused (PERT) and interdigitated back contact (IBC) solar cells; even higher efficiencies have been demonstrated by some companies (e.g. TRINA, Solar World, LG electronics, Motech, ISC Konstanz with BiSoN and ZEBRA).

PERC p-type, and in particular PERT and IBC n-type, solar cells are almost perfect devices before undergoing screen-printing metallization. Implied open-circuit voltages (V_{oc} s) of more than 700mV are achievable, before a screen-printing firing step is performed. During this step, recombination takes place underneath the metal fingers, causing one of the major losses in the finished device; in some cases, the resulting V_{oc} is reduced to a value of around 650mV, which is detrimental. If the V_{oc} could be kept at the same level as that before metallization, the efficiency could be increased by about 1.5% abs. This can be achieved by the use of (for example):

- Softer non-fire-through pastes, in combination with laser contact opening
- Evaporated contacts
- Plating (on the top as well)
- Passivated contacts

These and many other topics – for example replacing Ag by Cu, making plating more robust,

understanding the mechanism behind screen printing, and industrially interconnecting cells with conductive adhesives – have been discussed at metallization workshops organized in the last two years by ISC Konstanz [1]. ISC Konstanz's results and opinions regarding the present and future of metallization technology are presented in this paper.

Status of standard metallization

“Soccer is so popular, because it's a simple game.” These words of wisdom could also loosely apply to the relationship of screen printing to solar cell metallization. Although there have been many efforts to replace screen printing in the past 10 years, this has never happened: the technique remains by far the predominant way

of establishing local metal contacts on crystalline solar cells.

“Amazing progress has been made in the field of paste development.”

Apart from the convenience and the long-term experience in the PV industry of using screen printing, amazing progress has been made in the field of paste development. The workhorse and symbol for the technique's remarkable evolution are the silver pastes for front-side metallization. Excellent contact formation, for sheet resistances above $90\Omega/\text{sq.}$ and surface concentrations of $10^{20}/\text{cm}^3$, of phosphorus-doped emitters can be obtained with commercial fire-through silver pastes

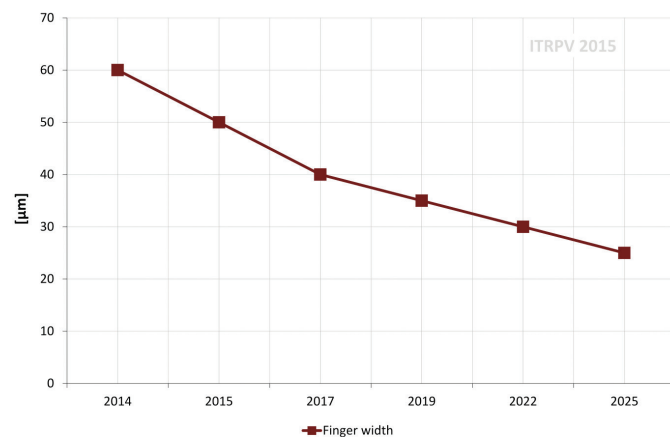


Figure 1. Predicted trend of finger width in screen printing, according to the ITRPV roadmap [2].

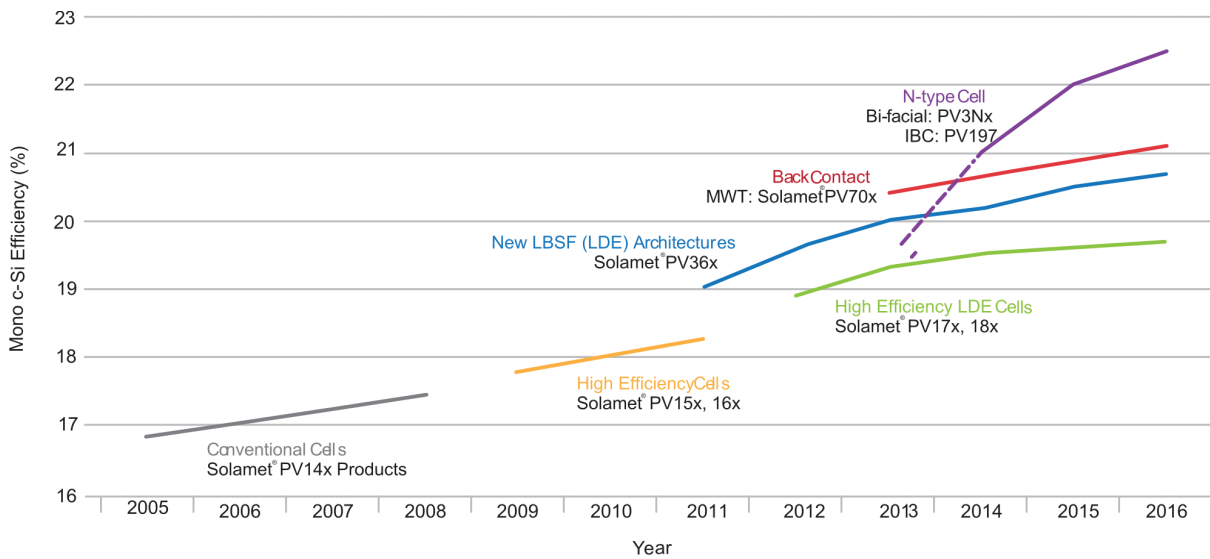


Figure 2. DuPont Solamet roadmap [3].

from various paste manufacturers.

At the same time, a reduced line resistance, mainly because of the high solid content of the metal paste, and an improved printability at a high aspect ratio, have opened the way for fine-line printing in the range of 30µm-wide apertures. In combination with the employment of finer mesh materials for the screens and innovative emulsion materials, a successful implementation was possible. As a consequence, the consumption of Ag paste was reduced, resulting in material costs savings of almost 70–100%. And this trend of narrower finger widths continues: as indicated in Fig. 1, according to the ITRPV roadmap [2], the finger width is expected to decrease further, to 25µm, in the next decade.

As an additional benefit of the thinner lines, the shadowing losses have also decreased. Increasing the number of busbars on the wafer to four or five and simultaneously minimizing their widths have also helped to reduce losses and to adapt to the improved power output of the devices. The enormous flexibility and demonstrated potential for cost reduction have so far curbed (at least for standard solar cells) any efforts to switch to another metallization approach. Fig. 2 illustrates – for example – how the paste supplier DuPont has customized its paste technology to different solar cell concepts over the last 10 years and contributed continuously

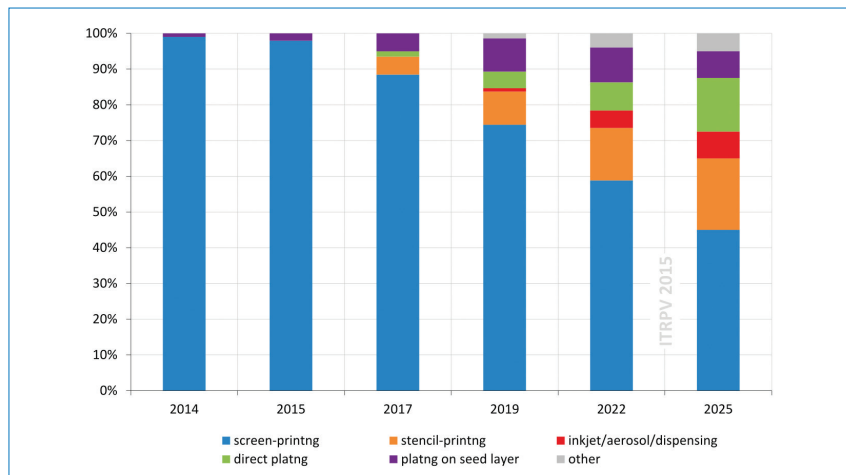


Figure 3. Trend of different metallization technologies, predicted by the ITRPV roadmap [2].

evolving products for improving device performance levels. This example is representative of the ongoing evolution of the entire solar cell industry in the last few years.

Potential of screen printing

Again, on a football theme, the German writer Ernst Probst once wrote: “The most important thing in football is the opponent. Nobody likes him but without him you cannot start.” This is also true for the free-market economy, and especially for the field of solar cell metallization; without the competition of other metallization schemes, screen printing would not

be where it is today. There are several other metallization techniques, such as seed and plate, inkjet printing, laser transfer printing, aerosol printing, flexographic printing and dispensing [4–8]. Most of these were developed by research institutes and never found their way into commercial production; some made it to production but failed, and others are still in development and might one day replace screen printing in solar cell metallization.

Because of its dominant status, screen printing is the benchmark process for the industrial application of metallization: the simple maintenance, low breakage rate (<0.15%) and inline throughput of 3,200 wafers/hour

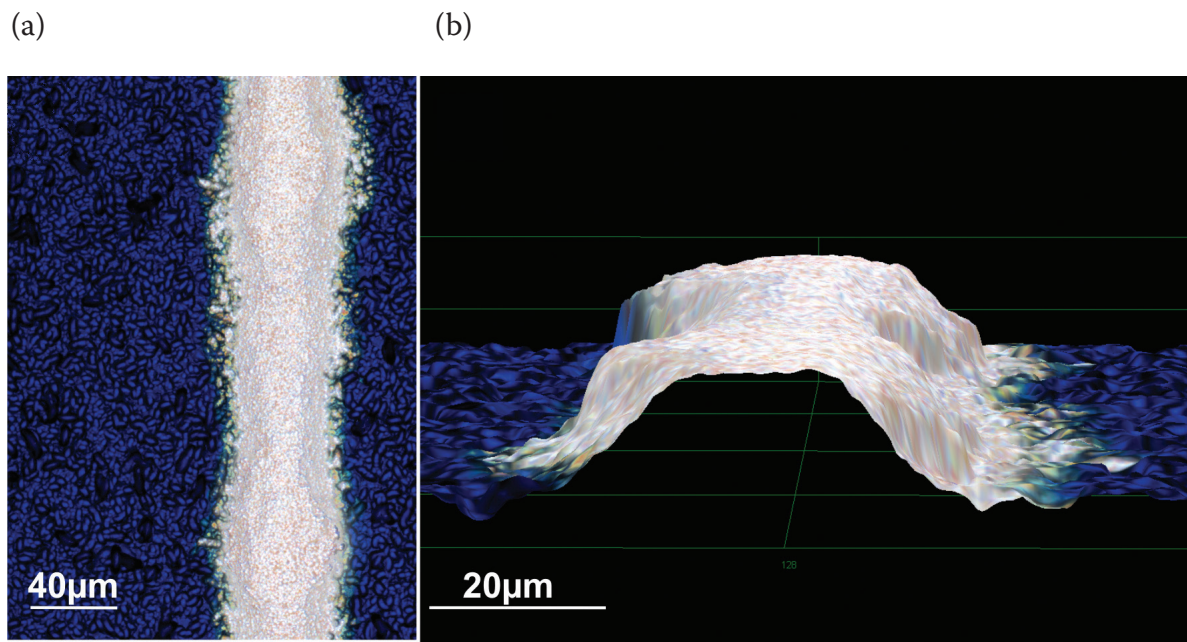


Figure 4. Ag finger, screen printed using the double-printing technique: (a) top view; (b) 3D image. (Images taken by laser scanning microscopy.)

collectively make up the standard to be beaten. To evaluate future potential, two questions are of significance: is the technology still compatible with cell concepts of the future, or even beneficial, and can it be implemented at competitive costs compared with alternative techniques? On the one hand, the convenience of a solution (such as the one represented by screen printing) that incorporates in one step the contact formation through a dielectric layer and good adhesion is attractive. On the other hand, the high-temperature steps required for sintering that are mainly used at present may cause problems and limitations for high-efficiency solar cells.

The improvements described above for silver fine-line pastes are a key benefit. Another is the enormous set of parameters that can be covered by this method with the use of various metal pastes. There have been many niche products in the past that were tailored to special requirements and trends, such as via pastes for metal wrap-through (MWT) applications or non-fire-through silver pastes that helped to avoid recombination losses. The simple combination of different materials, such as aluminium and silver, by spatially resolved patterns represents a platform for further adaptations. The competition of different paste suppliers guarantees further innovation in this field. A technique that could draw on these advantages, without the claim of a radical technological U-turn, is stencil printing; the roadmap shown in Fig. 3

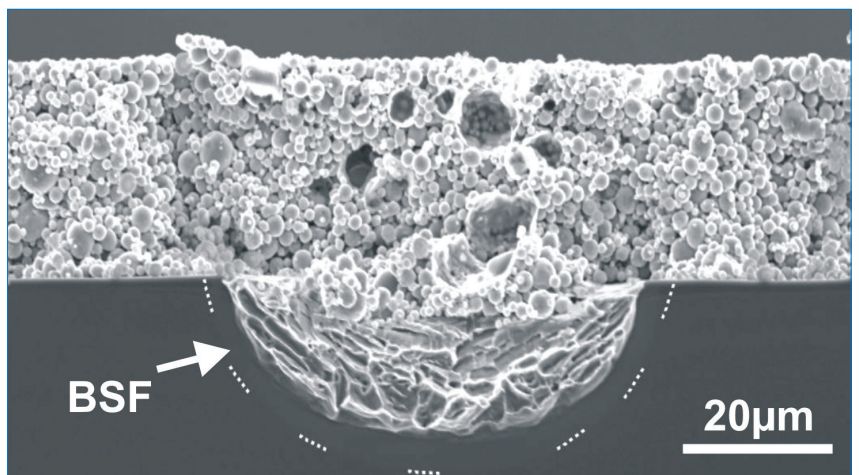


Figure 5. SEM cross-sectional view of the Al BSF of a locally opened passivated rear-side solar cell [12].

predicts that this metallization method represents the best opportunities for growth in the future. Thick-film paste technology, however, is still expected to dominate the market over the next 10 years.

Some representative thick-film pastes are discussed next, to illustrate the wide range that is available.

“Silver is currently the chief material used for fine-line fire-through metallization of passivated phosphorus emitters.”

Ag pastes

As already mentioned, silver is currently the chief material used for fine-line fire-through metallization of passivated phosphorus emitters and probably will remain so during the next few years. Improvements to glass additives have reduced the performance losses caused by the metallization. Research into the mechanisms for contact formation will make it possible to contact even more lightly doped emitters than those currently used in production, which is discussed in the next section. Fig. 4 shows a screen-printed Ag finger line manufactured by the double-printing technique.

Al pastes

Al pastes are a cheap and simple solution for rear-side metallization. Modifications have improved the V_{oc} of standard solar cells [9] in the past. A focus of the development is the tuning of the pastes to the new requirements of a passivated rear side with local contacts [10]. Good adhesion on the dielectric layer and the formation of a passivating back-surface field (BSF) at the contact areas are features of these pastes.

The scanning electron microscope (SEM) cross section in Fig. 5 gives an impression of the dimensions of such a local contact established during the sintering of the Al paste matrix. The interaction of the paste and the silicon is restricted to the area where Al was in direct contact with the silicon. Al paste, however, cannot be easily interconnected with solder contact strings. Applications proposing a treatment with, for example, an adhesion layer could be one solution for economizing expensive silver paste that is still being used for the solder pads [11].

AgAl pastes

Rear-side pad pastes, formerly a mixture of Ag and Al, have been improved in the past by gradually reducing the Ag content in order to cut the costs, while meeting the challenge of avoiding a negative effect on conductivity and solderability. Silver paste with a very small content of Al is still the main candidate for screen-printed contacts on p^+ emitters with low contact resistivity but high recombination because of Al spiking [13].

Cu pastes

A shortage of silver in the future, and the consequential increase in the price, could motivate the use of alternative materials for solar cell metallization. The potential for cost reduction was witnessed in the replacement of silver as the sintered metal. Copper pastes are already the focus of research efforts and could be a substitute for silver, at least for printing non-contacting bus bars [14,15].

The main problems of copper are its high diffusivity into silicon, with a detrimental effect on the minority-carrier lifetime, and its strong

oxidation in ambient air/oxygen, leading to soldering problems. Unless these issues are addressed or avoided, copper pastes will not be a viable candidate for replacing silver pastes.

Microstructure of screen-printed contacts

The contacts on the n-type emitters of industrial crystalline silicon solar cells are mainly formed by firing silver-based, screen-printable, thick-film pastes through passivating silicon nitride anti-reflection coatings, to contact the textured Si surface. The resulting contact resistivities, however, are orders of magnitude higher than the theoretically expected n-type Si emitter/Ag contact resistivities. The contact resistivity is directly related to the solar cell efficiency through the series resistance and thus the fill factor. Emitters with phosphorus surface concentrations well above the P solubility limit in Si are currently necessary in order to achieve acceptable contact quality.

Contrariwise, for achieving the highest solar cell performance,

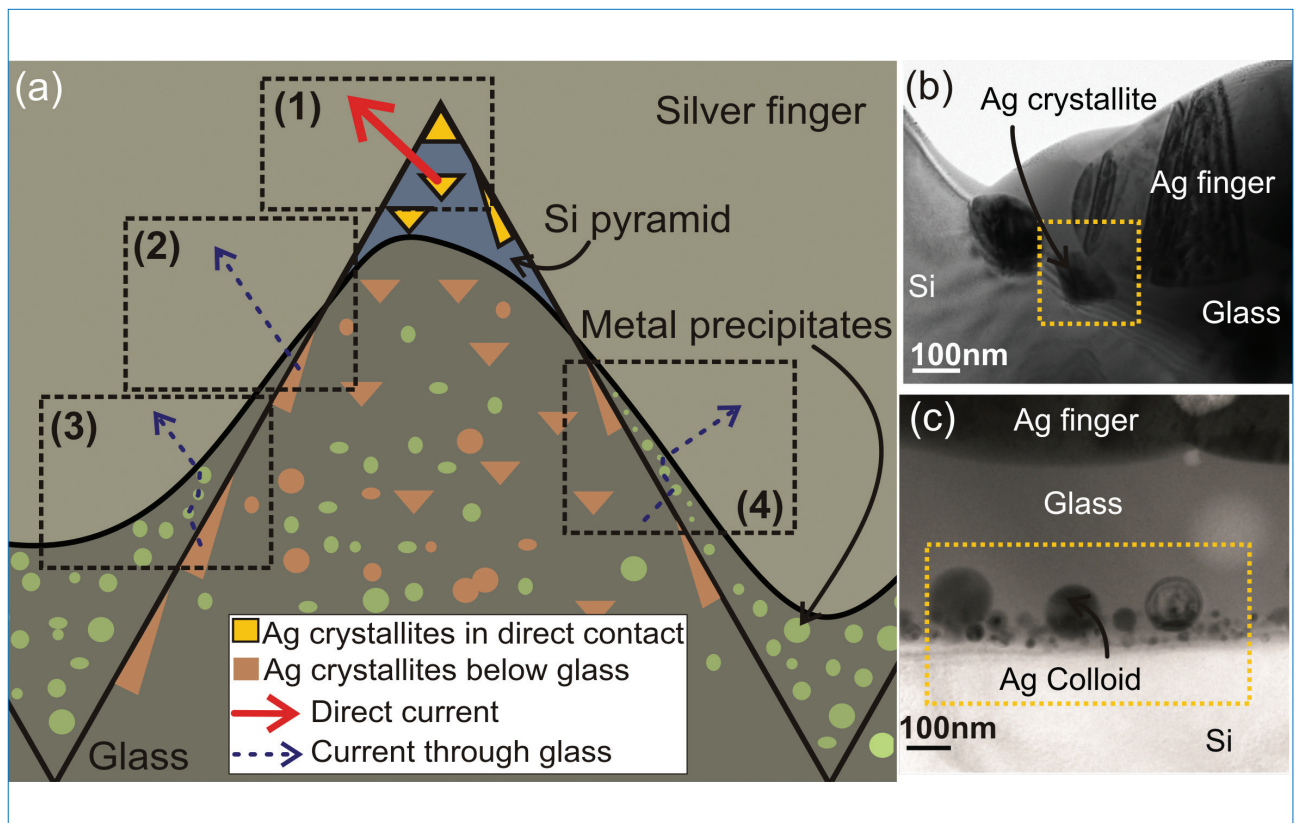


Figure 6. (a) Possible current transport mechanisms in textured Si solar cells [25]: (1) the current flows directly through Ag crystallites into the silver finger [16]; (2) the current flows through the Ag crystallites separated by a thin glass layer from the silver finger bulk [16–20]; (3) the current flows through the Ag crystallites separated from the silver finger by a glass layer, by means of the tunnelling effect due to metal precipitates in the glass [17,18] (the number of these metal precipitates can thereby enhance the conductivity of the glass); (4) the current is transported by means of multistep tunnelling from the n^+ emitter into the silver finger across nano-Ag colloids in the glass layer [21]. (b) TEM cross-sectional view of a Ag crystallite in direct contact with the silver finger. (c) TEM cross-sectional view of nano-Ag colloids in the glass layer close to the Si emitter.

emitters with low surface doping are desirable, and flat surfaces need to be contacted in the case of advanced concepts, such as the IBC solar cell; both of these requirements have the goal of minimizing recombination losses. For the fabrication of those highly efficient solar cells by the most cost-effective metallization technique available, namely screen-printing, it is therefore essential to understand, and thus accordingly improve the performance of, thick-film metallization.

Even though the continual progress in Ag paste manufacturing allows the contacting of higher-resistivity emitters without the need for a selective emitter or subsequent plating, there are still open questions: for example, how are the new pastes able to achieve better contact, and what is the dominant conduction mechanism of screen-printed Ag contacts on n^+ Si emitters? Fig. 6 illustrates the two current-transport models that are predominant in the literature [16–24], namely:

1. The current flows through the Ag crystallites grown into the Si emitter; these are separated by a thin glass layer or possibly in direct contact with the silver finger. See Fig. 6(a):(1),(2),(3), and Fig. 6(b).
2. The current is transported by means of multistep tunnelling into the silver finger across nano-Ag colloids in the glass layer; these are formed under optimal firing conditions and in locations where the formation of Ag crystallites into the Si surface is synonymous with over-firing. See Fig. 6(a):(4), and Fig. 6(c).

The most widely accepted model for explaining contact formation is that described in Schubert [17]: Ag crystallites grown into the Si are formed as a result of the redox reaction between silicon and metal oxides contained within the glass. Additional studies indicate that Ag crystallites result from the reaction between the dissolved Ag^+ and O_2 ions in the molten glass and the Si wafer, without the aid of liquid Pb formation [22] or Bi formation [23]. This reaction is strongly dependent on the ambient oxygen content during the firing process [23,24].

Microscopic investigations suggest that the largest influence on the topography-dependent contact resistance comes from the surface-sharpness-dependent glass coverage governing the number of Ag crystallites in direct contact with the

silver finger bulk [26]. Experimental evidence indicates that the major current flow into the silver finger is through Ag crystallites that are directly touching the silver finger [27]. The presence of glass-free regions, necessary for the direct connection of the Ag crystallites with the silver finger in order to achieve good-quality contact, depends on the paste composition and on the surface texture, and does not vary with the Si emitter properties [25]. Nevertheless, whether or not the Ag crystallites are in direct contact with the silver finger or in quasi-direct contact (separated from it by a very thin glass layer of less than 1nm) will continue to be up for discussion. The presence of Ag crystallites, however, is required for the transmission of the current. If it were possible to avoid the Ag crystallite formation while retaining a low specific contact resistance, an ideal

contact could be achieved, because there would be no metal penetration into the emitter, and therefore no contact-induced recombination losses; these losses are the main efficiency-limiting factor at present, as discussed in the next section.

“Contact-induced recombination losses are the main efficiency-limiting factor at present.”

Modelling of metal-induced recombination

From experimental observations of internal quantum efficiency (IQE) measurements, for samples with various metallization fractions, one could deduce the cause of the V_{oc}

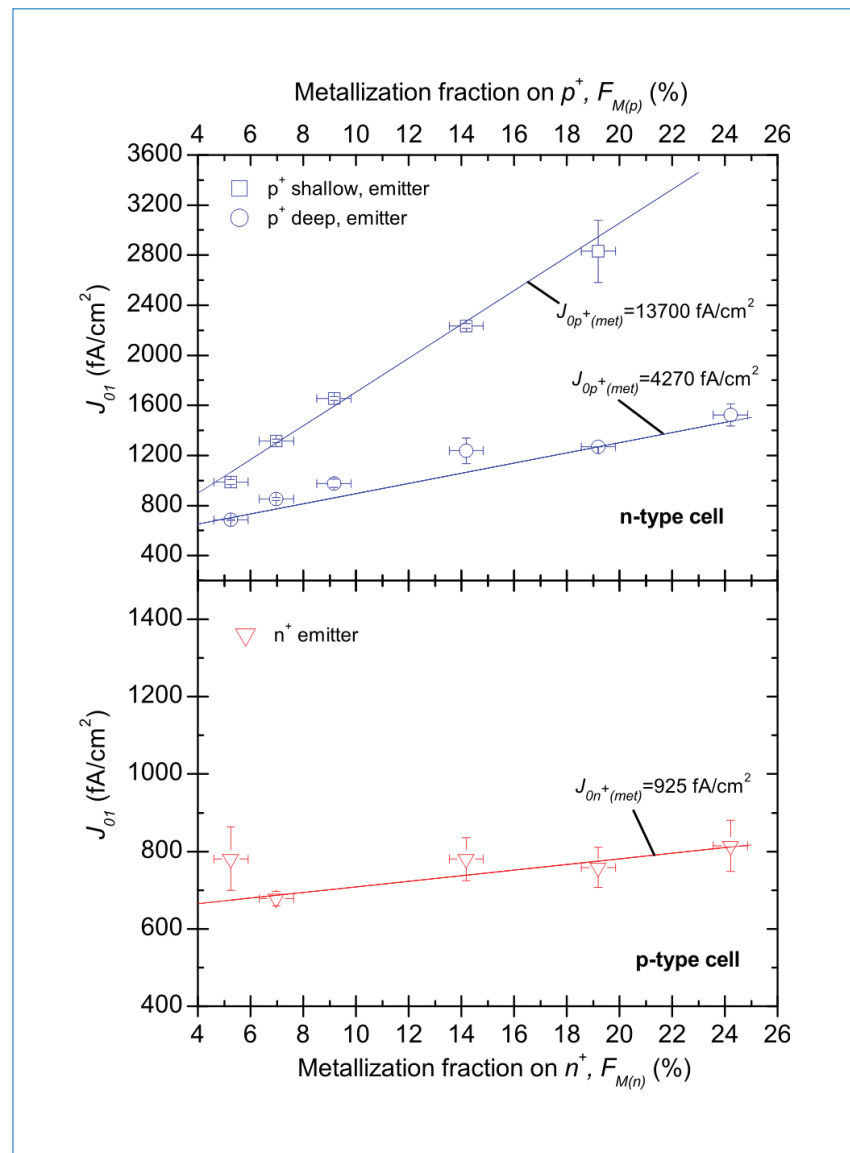


Figure 7. Modelling metallization-induced recombination losses. Experimental J_{01} for different metallization fractions on n-type and p-type cells. (Source: Edler et al. [30].)

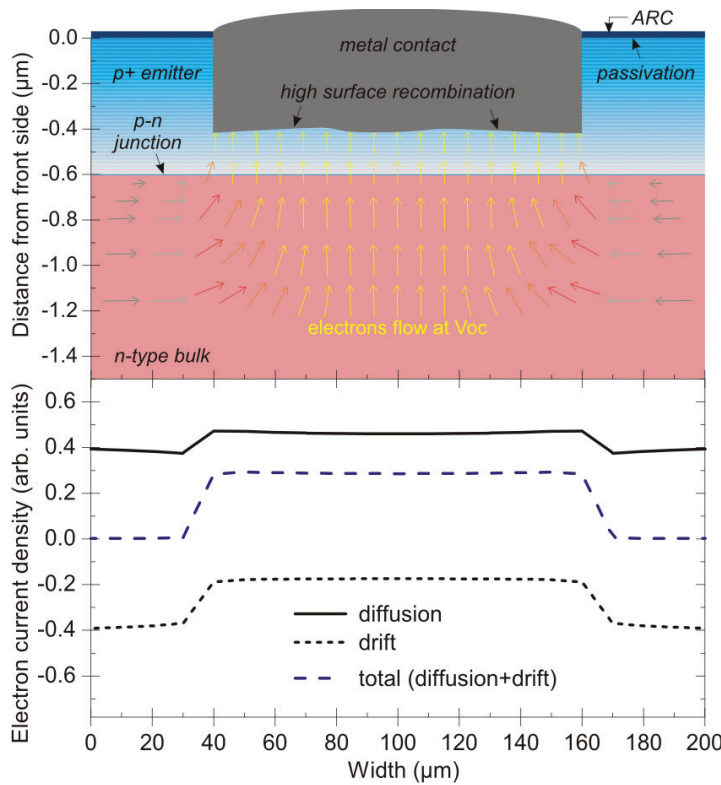


Figure 8. Electron current density map of the region under the p⁺ metal contact. Recombination currents are dominated by the diffusion currents (extracted from the ATLAS device simulation). (Source: Edler et al. [30].)

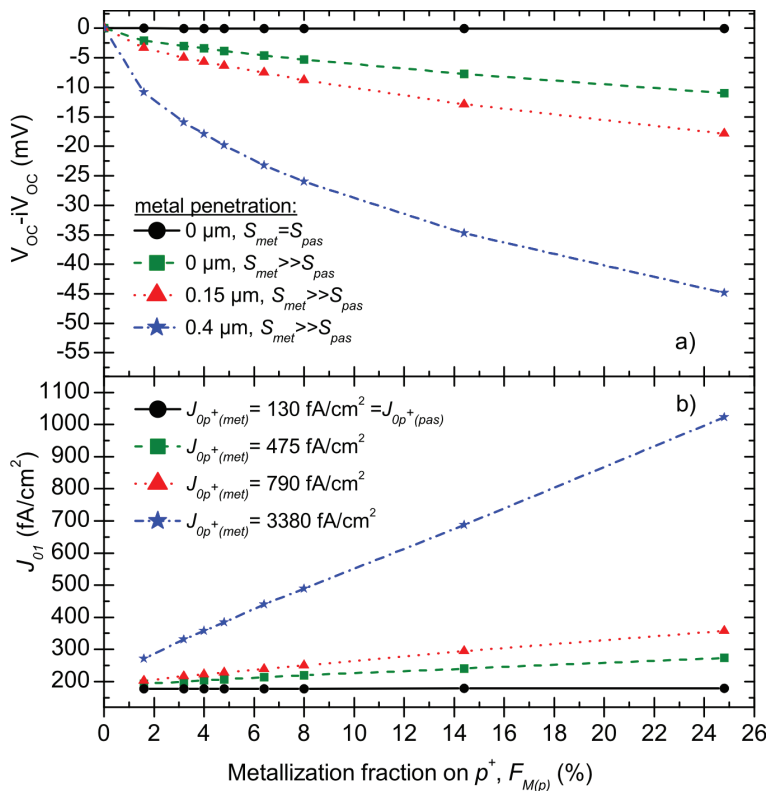


Figure 9. Simulation of the decrease in V_{oc} due to the increased J_{01} under the metal-p⁺ emitter interface, as a function of the fraction of front-side metallization and of the structural details of the p⁺ metal interface. (Source: Edler et al. [30].)

degradation as being a local effect directly beneath the metal contacts, causing an increase in recombination. Fig. 7 shows experimental dark saturation current density under the metal contacts (J_{01}) of a series of samples with different fractions of front-side metallization; the higher the J_{01} , the greater the V_{oc} losses, which reduces cell efficiency. Since J_{01} is much larger for p⁺ emitters than for n⁺ emitters, the recombination underneath the metallized regions of n-type cells limits the efficiencies more severely than it does for p-type cells.

With the use of 2D simulations, an attempt was made to capture and provide insight into the possible local effect causing V_{oc} losses after the metallization step. The ATLAS 2D device simulator tool [28] computes cell performance under V_{oc} conditions. The incorporation of microstructural details of a metal-n⁺ Si interface (p-type cell) into the simulation model classifies the role of each interface component with respect to the overall recombination under the metal contacts, and establishes a structural property correlation [29].

In order to reproduce the experimental V_{oc} , a series of simulations were performed with the assumption that the metal contact penetrates into the p⁺ emitter at various depths. The simulation model assigns a surface recombination velocity $S_{met} = 1 \times 10^7 \text{ cm/s}$ to an unpassivated ohmic contact between the metal and Si interface. The surface recombination velocity of the passivated area between the metal contacts, S_{pas} , is determined by means of a numerical fit to the experimental IQE measurements.

A highly recombinative (unpassivated) interface reduces the shielding of the diffused emitter layer and attracts minority-charge carriers (electrons) in the emitter; this phenomenon is captured in Fig. 8, which shows an ATLAS snapshot of drift and diffusion currents beneath the metal contact at V_{oc} conditions. The volume beneath the metal contact becomes depleted of electrons because of the highly recombinative interface, resulting in a leakage current across the junction due to diffusion. With increasing metal penetration, the leakage current also increases, and thus the overall dark saturation current density (J_{01}) of the cell increases.

Fig. 9 shows an estimate of the V_{oc} loss as a function of metallization fraction for different metal penetrations and interface conditions. The (metal contact) etching of the diffused emitter region during the

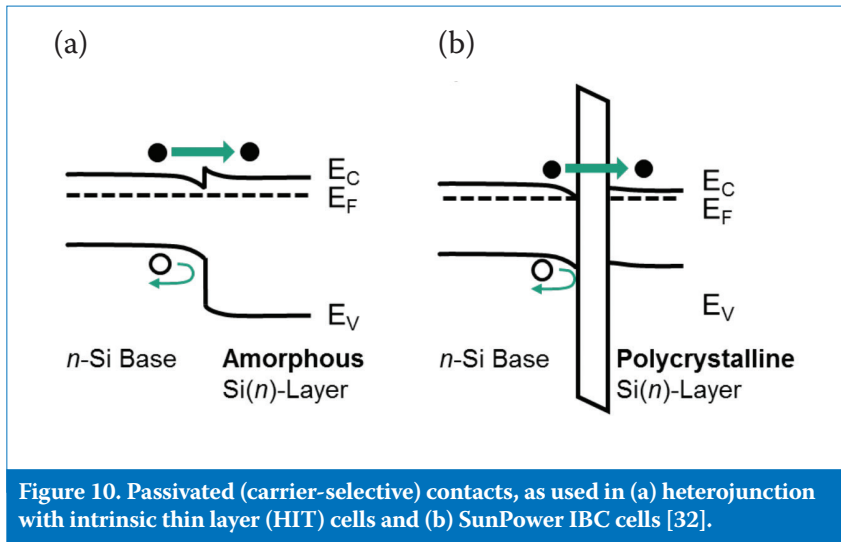


Figure 10. Passivated (carrier-selective) contacts, as used in (a) heterojunction with intrinsic thin layer (HIT) cells and (b) SunPower IBC cells [32].

firing process degrades the metal–Si interface. With increased damage to the diffused emitter, the leakage current increases and thus J_{01} increases.

Although the simulation model is a simplified representation of the actual process taking place, it does capture two important features: 1) the strong local increase in recombination, resulting in a leakage current across the junction; and 2) the reduction in the shielding effect of the diffused emitters as the metal penetrates into the Si, or the Si is etched by the glass frit. Using screen printing, a simple method to minimize the metal-induced recombination loss and the metal coverage on the emitter surface is to print floating busbars and thinner fingers; softer non-firing fingers in combination with laser ablation also demonstrate potential improvement of the cell V_{oc} [31], in addition to a reduced usage of expensive Ag. Evaporated and plated contacts also reduce the degradation of the metal–Si interface, thus offering the potential of overall lower cell J_{01} , which results in higher efficiencies.

“With further development of the metallization process, there is still significant potential for device efficiencies to reach the theoretical limit for c-Si.”

Summary and outlook

In recent years, it has mostly been screen-printing technology and the development of screen-printable metal pastes that has been responsible for the efficiency increases in the case of c-Si

solar cells. And this does not appear to be the end of it, since with further development of the metallization process, there is still significant potential for device efficiencies to reach the theoretical limit for c-Si. Similarly to c-Si being the dominant technology in the PV sector, screen-printing metallization will remain the dominant metallization technology for the next few years. Although alternative technologies, such as plating, remain of interest, they still need to prove their competitiveness in terms of robustness and cost.

What will surely also be implemented in low-cost devices in the future are passivated (or carrier-selective) contacts, similar to what Panasonic or SunPower are using to achieve the highest V_{oc} s. The Panasonic contacts, shown in Fig. 10(a), are based on amorphous Si as a passivation layer, whereas the SunPower version, shown in Fig. 10(b), uses a 1–1.5nm thin oxide and highly doped polycrystalline Si layer on top. FhG ISE also recently presented their TOPCon 4cm² solar cell, which boasts an efficiency of 25.13% and a V_{oc} of 718mV [32]. In order to be cost-effective, however, even this technology could (and may have to) be combined with low-temperature firing screen-printing pastes.

The future of metallization for c-Si solar cells is discussed in depth, and new findings presented by international scientists and industry, at the almost yearly metallization workshops organized by ISC Konstanz, other metallization specialists and various companies/organizations [1].

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Dr. Radovan Kopecek is one of the founders of ISC Konstanz. He has been working at the institute as a full-time manager and researcher since January 2007 and is currently the leader of the advanced solar cells department. He received his M.S. from Portland State University, USA, in 1995, followed by his diploma in physics from the University of Stuttgart in 1998. The dissertation topic for his Ph.D., which he completed in 2002 in Konstanz, was thin-film silicon solar cells.



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Dr. Enrique Cabrera received his Dipl.-Ing. (honours) in electrical engineering and electrical power systems from the Universidad de Santiago de Chile in 2008. In 2013 he received his Ph.D. in physics in the field of metallization of silicon solar cells at ISC Konstanz in cooperation with the University of Konstanz. He currently heads the BMBF SolarChild Project and supports R&D cooperative projects in Chile.



Dominik Rudolph studied microsystems engineering in Freiburg and received his diploma in April 2008 with a thesis topic of laser-induced metallization of silicon solar cells from an aqueous electrolyte, the research for which was carried out at Fraunhofer ISE. He joined ISC Konstanz as a scientist in 2009, where he is responsible for the metallization processes and leads the ZIM Alf project, as well as working on the EU Hercules project.



Thomas Buck studied physics at the University of Konstanz, with research for his thesis on the characterization of PEM fuel cells carried out at the Daimler Chrysler Corporation. From 2003 he worked in the field of industrial n-type solar cells at the University of Konstanz, before joining ISC Konstanz in 2008. He is engaged in metallization topics and bifacial solar cells, and is the head of the BMWi IdeAl project. R&D organization.

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