Current and future metallization challenges and solutions for crystalline cell manufacturing

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This paper first appeared in the third print edition of *Photovoltaics International* journal.

ABSTRACT

In any solar cell process, the metallization step is critical as it often sets conditions and limitations for the other process steps. The main metallization technique used today in Si solar cell production is screen-printing of metallic pastes; namely, Ag pastes for the front side, Al pastes for most of the rear side, and Ag or Ag-Al pastes for the solder pads at the rear. While these techniques are clearly robust and convenient, they have limitations. Therefore, alternatives are being investigated. A technique that is presently finding its way into production is two-step metallization with Ag plating. Another more radical approach is to avoid printing altogether, instead using some kind of ablation followed by plating. For the rear, the full Al-BSF is being replaced by dielectric passivation and local Al-alloyed contacts. Back-contacted cells are increasingly being introduced in production, and they pose very specific challenges to metallization. For the sustainability of Si photovoltaics, it is crucial that the future metallization solutions only make use of abundantly available and non-toxic materials.

Introduction

Thick-film metallization by means of screen-printing is the contacting technique employed by more than 85% of photovoltaic solar cell manufacturers. The majority of solar cells produced worldwide are fabricated using silver thick-film contacts on the front and aluminum thick-film contacts on the rear side. In addition, solder pads on the rear are formed using Ag and Ag-Al pastes. A process simplification in the front and rear contact formation was enabled by the development of the silicon nitride firing-through process of the front side Ag paste and the formation of the back surface field (BSF) by an Al paste during the same firing step. This has elevated screen-printing to be classed as one of the key process steps in silicon solar cell manufacturing.

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The demand towards high-efficiency and low-cost solar cells has increased the research effort on thick-film contact formation processes and pastes in the past decade. Nevertheless, further reduction of the price/Wp requires processes on larger and thinner wafers with higher throughputs. In this framework, novel cell concepts, such as metal wrap-through (MWT), emitter wrap-through (EWT), back contact (BC) and silicon heterojunction (SHJ) have been developed. Finally, material availability for future gigawatt production drives the contact development towards alternative metallization techniques adapted from microelectronics and modified for the needs of the solar cell industry.

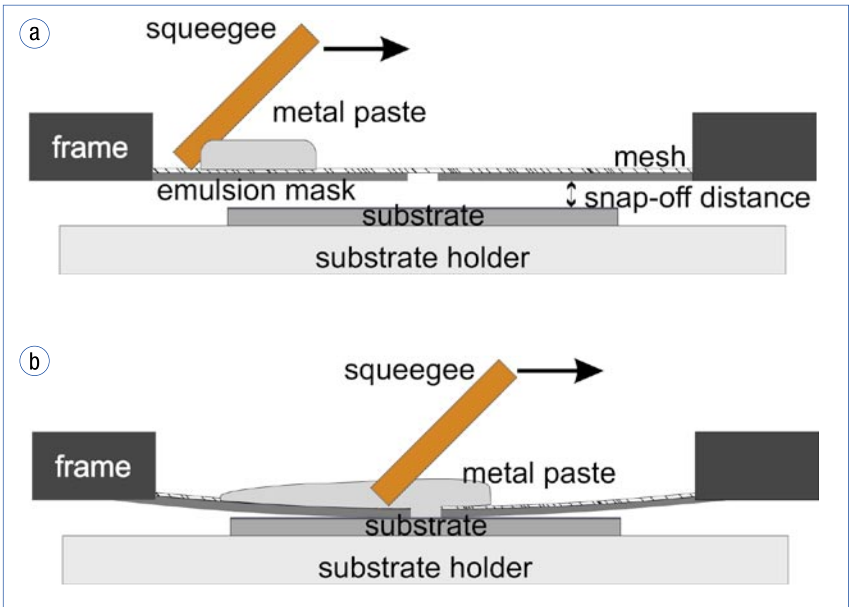

Figure 1. Schematic illustration showing (a) non-contact screen-printing, and (b) in-contact screen-printing of a metal paste.

State-of-the-art

Screen-printing (see Figure 1) is established in high throughput solar cell manufacturing as a reliable metallization technology. The front side grid is printed in one step while the rear side is contacted by a full area-covering Al paste and a following Ag/Al contact pad, both of which are applied by screen-printing. The applied screen-printing pastes are soft-baked in a conveyor belt furnace. The contact formation is performed in a high temperature process using a firing furnace. In industrial applications, screen-printing lines can reach throughputs of 1500-2000 wafers/hour, with a typical line width of 100 to 150µm.

The printing process consists of three single steps, illustrated in Figure 1. In the first step, the screen is covered with paste by moving a squeegee over the surface of the screen-printing mask in the filling phase. Secondly, the squeegee moves over the screen, again applying an additional vertical force that presses the screen on the wafer and the paste through the meshes of the mask. In the last step the mask is lifted, creating distance to the solar cell's surface, which is known as the snap-off distance. The printing process is determined by the following parameters: printing speed (squeegee speed), squeegee pressure and snap-off distance. The screen-printing quality is determined by the printing parameters, the screen-printing paste and the screen quality.

Silver paste is the most commonly used material for front side metallization of silicon solar cells. Although a large variety of silver pastes is commercially available, the composition is rather similar. The pastes consist of silver particles, solvents, glass frit and binding agents.

Ultimately, the goal of the contact formation is a good adhesion, a high aspect ratio, a high line conductivity and a low Ohmic resistance between the contact and the highly-doped emitter layer. The shape of the silver particles can vary between flakes and spheres and are in the order of 1-10μm in size. The trade-off in the choice of the particles' shape and size is either the density being too high or the formation of agglomeration. The latter leads to clogging of the screen and could be avoided by providing sufficient large screen openings (where the opening is approximately five times larger than the particle size). Other compromises are decided upon by defining the viscosity and the relaxation time, which is the paste's or another system's need to return from low viscosity back to high viscosity.

The lead-oxide silicate glass frit is responsible for adhesion, contact formation and line conductivity. It provides the penetration through the SiN_x layer, assists silver crystallization and reduces the melting point of silver.

Contact formation is performed using an inline firing belt furnace with different heat zones. In first heat zone the solvents are evaporated at maximum temperatures of 300°C. The temperature is ramped up to 500°C in the second heat zone, at which point the organic binders in the paste are burned. In the next heat zone, the contact is formed by applying fast temperature ramping between 800 and 900°C. The high temperature is applied for up to five seconds and subsequently cooled down to room temperature.

Aluminum-containing pastes are most often used for the rear side contact. By firing the paste into the silicon at high temperatures – a step that is performed simultaneously with the front side contact – a BSF is formed. A thickness of approximately 20μm of aluminum is required for the BSF formation to take place correctly.

Two-step metal process

As an alternative to the state-of-the art metallization technologies, an interesting concept is the two-step metal process. This process is based on the idea of first applying a thin metal seed layer to create a good Ohmic contact between the metal and the semiconductor and subsequently applying a thick highly conductive metal layer. In this way, the amount of freedom of optimization of both the properties of the solar cell contacts and the underlying emitter is enlarged. The thin seed layer is optimized to contact a lowly-doped emitter, with a surface dopant concentration of $1x10^{19}cm^{-3}$. This seed layer can be, for example, a silicide that has good electrical and mechanical properties. Decreasing the doping level of the emitter, compared to a profile suited to be contacted by screen-printing, will most importantly result in enhanced surface passivation and will lead to higher energy conversion efficiencies.

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The second metal layer needs to be optimized to be highly conductive, so the natural choice for this material is silver or copper. For front contacted solar cells it is important that a narrow seed layer is deposited and that the subsequently applied thick metal layer will not cause too much widening of the contacts compared to the width of the seed layer, such that a low degree of shadowing underneath the contacts can be achieved.

Metallization based on silver

A first implementation of the two-layer concept for front side metallization is based on fine line printing in combination with (light-induced) silver plating. Using this kind of process most resembles the traditional screen-printing of silver. There are several techniques under investigation for application of the thin seed layer by printing means. Advanced screen-printing, inkjet printing, pad printing, aerosol jetting and sintering of metal powder will be discussed later.

Advanced fine-line screen-printing

Advanced fine-line screen-printing is the metallization method most related to traditional screen-printing. Using hot melt ink instead of traditional paste is one way to reduce the line width of the applied fingers [1]. This type of ink is solid at room temperature and is printed at temperatures in the range of 50 to 80°C by heating the screen and the squeegee, a process that has resulted in demonstration of metal lines as narrow as 60μm. Application on the solar cell level results in increased efficiencies compared to standard screen-printing with fill factors up to 80.6% [2].

Inkjet printing

An emerging method of printing a metal seed-layer for solar cells is inkjet printing. This method has the capability to print very narrow lines and is a non-contact technology, thus ideally suited to printing on thin substrates. Most of the research carried out so far has been focused on direct printing of the complete metallization pattern; in this case, however, multiple printing is needed to obtain a sufficient thick and conductive metal layer [3,4]. A key element of this process is the development of a suitable ink as the viscosity of the ink should be sufficiently low in order to be printable.

Pad printing

Pad printing is a metallization technique based on gravure offset printing. The metallic ink is spread out on the cliché, the template with the imprinted image, after which the patterned ink is transferred to the substrate by using a silicone pad. This method allows for fine-line printing of well below 50μm, has the potential for high throughput, and is compatible with current solar cell technology since similar metal pastes can be used to apply the contact [5,6,7]. Depending on the type of pad, the method can be suited to thin and uneven wafers. A disadvantage is that the paste transfer from the template to the wafer is rather limited, giving rise to a relatively thin metal layer. Using the pad-printed line as a seed layer subsequently thickened by metal plating is a promising solution and has so far resulted in efficiencies of 17.9% on $10x10cm^2$ CZ c-Si substrates [8].

Aerosol jet printing

Another interesting method for seed layer deposition is aerosol jet printing [9]. In this case, the metal-containing ink is converted into an aerosol, a colloid with small sized metal particles suspended in a gas. In order to be able to print thin lines of metal, the aerosol is focused onto the substrate by an additional gas flow. This method allows for printing of very narrow line features down to a width of 14μm. Furthermore, it is shown that the line width is constant on uneven surfaces and is well-suited for very thin and fragile samples. Even so, the printed metal line can still be fired through a layer of silicon nitride when using slightly modified standard metal pastes. Using aerosol jet printing of a silver seed layer in combination with light-induced silver plating to thicken the layer, a solar cell efficiency of 20.3% has been reached on float zone silicon wafers [9]. Aerosol jet printing can also be combined with hot melt ink to further enhance the properties of the deposited metal lines [10]. An aerosol printer has recently been developed that can print a solar cell every 2.5 to 3 seconds [11].

Laser micro-sintering

Laser micro-sintering is a technique whereby a metal powder is distributed over the wafer area. Subsequently, the powder is locally heated by a laser [12], such that the metal powder will melt locally. As a result, a thin metal seed layer is obtained, which can have a line width of less than 30µm. During the laser sintering process, the metal also penetrates through the dielectric passivation layer. Care should be taken to avoid shunting of the solar cell, as in some cases the metal might move too deep into the silicon. Advantages of this metallization method are the reduction in thermal budget of the complete process, the applicability on thin and fragile samples, easy recycling of remaining metal powder and a reduction in contact resistance compared to printing techniques where a metal paste is used. In the case of first realized solar cell structures, a best cell efficiency of more than 14% has been reached using tungsten as the seed layer metal, where the chosen high-doping level of the emitter is the main reason for the limited performance [12].

On top of the applied seed-layer, a thick highly conductive layer can be deposited by silver plating [13,14]. This can be electroless plating, electro-plating or light-induced plating. The main advantage of light-induced plating, where the current generated by the illuminated solar cell itself is used to plate the metal, as opposed to classical electro-plating, is that the front contact grid does not have to be contacted, thus simplifying the wafer handling. In the first instance, silver is a well-suited metal to the process as no barrier layers

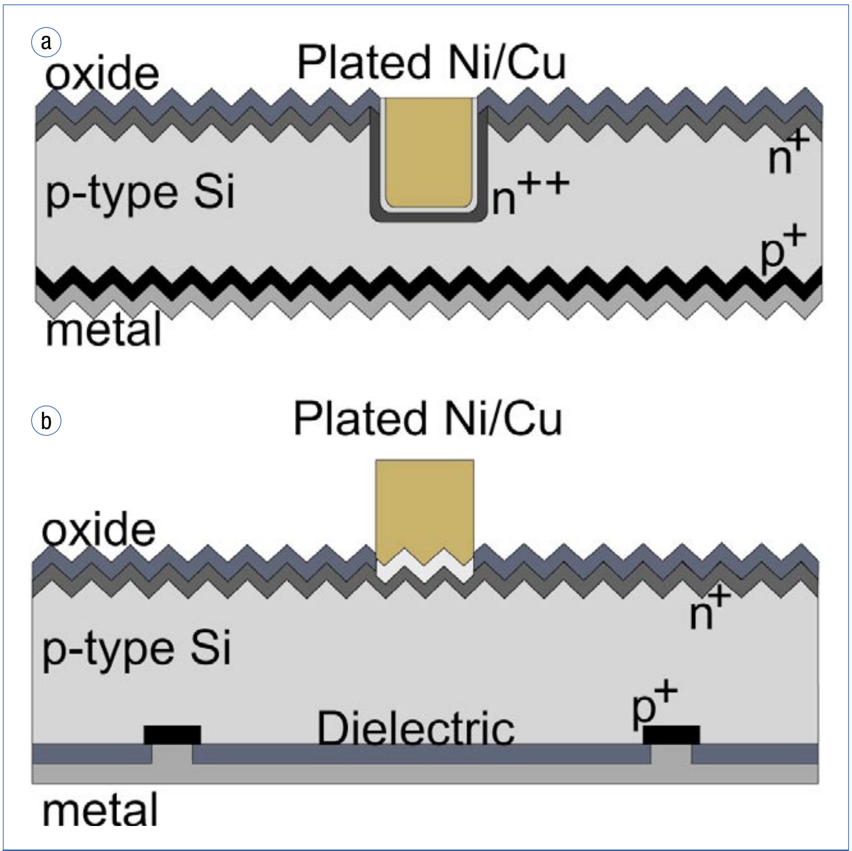

Figure 2. Illustration of different cell concepts using the two-metal-layer concept, showing (a) a buried contact solar cell, and (b) a cell with laser ablated openings in the dielectric layers in combination with a self-aligning metal plating process.

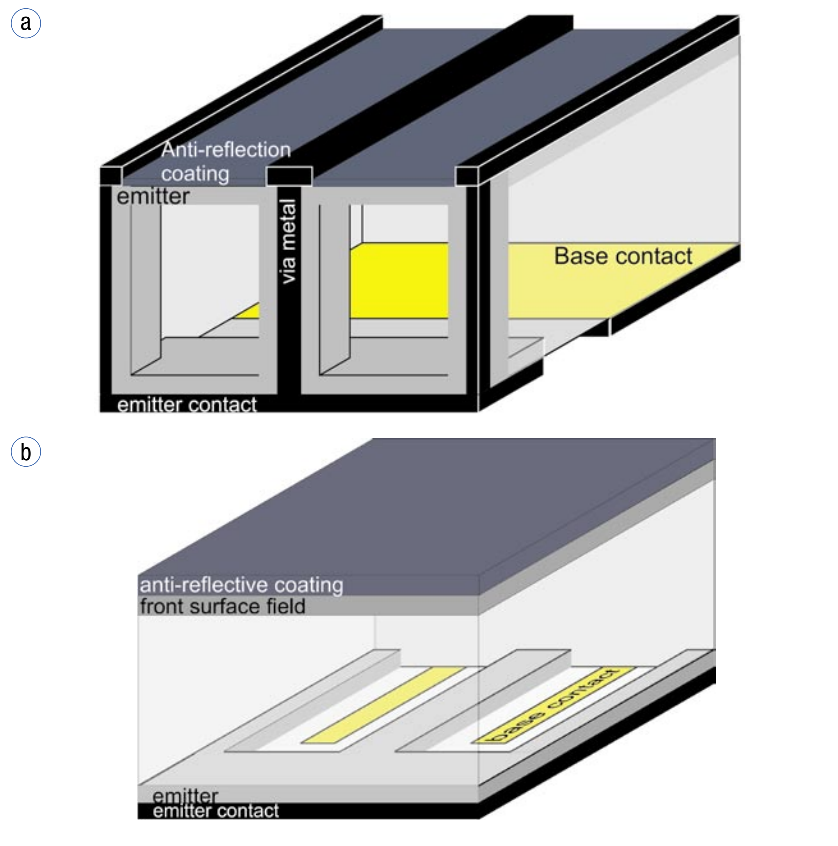

Figure 3. Schematic illustration of back-contact solar cell concepts, showing (a) a metallization wrap-through cell (MWT), and (b) a cell with interdigitated back contacts (IBC).

are needed in this case to prevent silver diffusion into the silicon. Of late, special chemical solutions, both cyanide-based and cyanide-free, are being optimized for solar cells, especially for light-induced plating where clear solutions are needed to allow for the illumination of the solar cell.

Metallization based on copper

A second more radical implementation of the two-layer concept is the application of the seed layer by electroless plating and subsequent combination with copper or silver (electro)plating (see Figure 2). It is expected that, in the near future, copper will be used more and more for silicon solar cells due to its lower cost relative to silver [15]. The metal seed layer can be converted into a silicide, which will be beneficial in terms of adhesion and can also serve as a barrier layer against copper diffusion.

A well-known concept using a layer of plated nickel and copper is the buried contact cell process [16,17,18], shown in Figure 2a. In this case, for example, 40µm-deep contact grooves are realized at the front of the cell by mechanical abrasion, which can be done by using a 15µm-thin dicing blade [19]. The contact grooves can also be made by application of a laser [16]. In this way narrow contact lines are created, which results in decreased shadow losses compared to screen-printed contacts. Since the grooves are made after surface texturing, emitter diffusion and deposition of the dielectric, a selective emitter can be made relatively easily by performing a heavy second diffusion, where the dielectric serves to protect the area outside the grooves. Nickel is electroless-plated in the grooves and on the rear of the cell. Subsequently it is sintered to create the silicide that prevents copper diffusion into the silicon and to improve the adhesion properties. Finally, a thick layer of copper is plated on top of this seed layer. Due to the narrow buried contacts, this high efficiency process allows for an industrial implementation on both mono- and multi-crystalline substrates, and has so far resulted in a large area efficiency of 17.5% [19] and 18.1% [18] on multi-crystalline 156.25cm^2 and 137cm^2 substrates, respectively. Even lower optical losses are expected for angled buried contact cells, where the groove is made under an angle in order to maximize the optical properties of this cell design [18].

A more recent application of plated nickel and copper (or silver) contacts has been triggered by the development of new laser technologies (see Figure 2b). Instead of making a deep groove, a dedicated laser process, using a picosecond laser, is used to ablate the dielectric front surface layer without creating relevant damage to the emitter [20]. After locally removing this anti-reflection coating, the nickel seed layer can be grown selectively on the bare silicon areas, while no deposition will take place on the dielectric. The nickel seed layer can then be converted into a silicide by thermal treatment. The metal contact will be finalized by electro- or light-induced plating of copper. As an alternative to laser ablation, photolithography [21] and inkjet masking [22,23] are used in combination with wet-chemical etching to locally remove the dielectric. Using a lab-scale process to show the feasibility of the electroless nickel plating and copper plating has resulted in best cell efficiencies of 21.4% on FZ-Si with a cell area of 45.75cm^2 [21].

Metallization for back-contact cells

Contact formation for back-contacted solar cells imposes specific demands on the metallization concept.

In the case of the well-known metallization wrap-through structure (MWT) (see Figure 3a), the metallization is very specific as it is the only back contact cell structure that has metal grids of the same polarity both on the front and rear surface of the cell. The interconnection of the grids through small holes in the cell is easily done by technologies like screen-printing or plating; it is expected that the new developments would be able to perform equally as well.

For all back-contact structures, such as that shown in Figure 3b, large-scale implementation ultimately relies on a low-cost way of contacting regions of different polarities with tight tolerances on the rear surface of the cells. Particularly for back junction concepts, this is very challenging as the concept imposes that the base-contact regions are sufficiently small to maintain a high collection probability, whereas the need for majority carriers to flow through the base towards these contact regions imposes a high density of these regions. The lateral current of majority carriers through the base of the cell also occurs at the location of the connection pads of the emitter area. These pads must have a sufficiently large area to connect electrical leads to it, but it pays to reduce their width as much as possible.

The use of photolithography throughout the processing permits for the definition and alignment of contact windows and regions without excessive shunting. It also relatively easily allows for separating the actual contact area and the real metallization coverage of the rear of the cells, keeping a large part of the metal-covered area at the rear of the cell separated from the semiconductor by use of a dielectric. However, processes with multiple aligned lithographic steps can hardly be applied in a high-throughput production line. For traditional screen-printing on the other hand, the act of forming several metal grids on a single surface with very tight tolerances of line width and spacing is extremely challenging. This is even more stressed for successive metallizations on the same surface, as the height of the deposited pattern during the first print tends to make the second print less accurate. The latter can be resolved by contactless methods that are being introduced to replace screen-printing, such as metal jetting. The conductivity of both the base and emitter metallization has to be sufficiently high to limit an increase of series resistance invoked by replacing the full coverage of the former metallization with a gridded structure. This leads to the use of highly conductive materials for both contact grids.

Whereas silver could be used for both contacts, the cost related to the abundant use of Ag would be prohibitive of its use. Plating of Cu as a relatively low cost and highly conductive material onto a layer that acts as an electrical contact and diffusion barrier for the metal into the semiconductor could resolve this problem. Plating technologies such as light-induced plating that are being investigated for conventional cells, however, will hardly be applicable when the metal is expected to be built up on both polarities at the same time. The latter will rely much more on the background knowledge that has been built up in the back-end technology of semiconductor processes on the use of formation of seed layers and subsequent electroplating.

Sustainability issues

In order to be consistent with mass production with low environmental impact, the sustainability of the selected metallization solutions has to be considered carefully. Firstly, the materials used should be available in the huge amounts required, an aspect that is closely linked with the materials' cost. A shortage of a substance on the world markets immediately results in a sharp cost increase. Al is abundantly available and therefore poses no problem. The long-term availability of Ag, on the other hand, is a subject of debate. Some studies indicate that the consumption of Ag by the photovoltaic industry will be such that the need will exceed the available resources by 2040 [24]. Others point out that the large volumes of Ag previously used in the photographic industry are now available for the photovoltaic industry. In any case, it is clear that recycling of this precious metal will become mandatory for a Terawatt industry.

The main components of the metallic screen-printing pastes, Ag and Al, are non-toxic. However, the pastes do contain non-negligible amounts of toxic substances. Cadmium was a common ingredient in the past, but has now disappeared from most commercial pastes. Lead, however, is difficult to replace. The PbO in the glass frit gives the pastes the property of firing through silicon nitride, and for replication of this property, no straightforward substitute has been found. Bi is used in some pastes, but it is more expensive and not yet considered quite as effective as Pb. It should be noted that photovoltaic panels are presently exempted from the European RoHS Legislation (Reduction of Hazardous Substance) that would otherwise exclude the use of Pb in solar cell production [25]. This is not conducive to a quick phase-out of Pb in metallization pastes.

The introduction of plating in solar cell production poses an additional environmental challenge. To be environmentally acceptable, plating solutions need to receive appropriate treatment after use, which adds to costs. Plating solutions that generate small volumes of waste per volume of deposited metal (e.g. galvanic plating) therefore have an advantage over other plating techniques.

Summary

Crystalline Si solar cells are likely to continue to dominate the photovoltaic industry over the next two decades. At the moment, screen-printing of Ag and Al pastes is the most widespread technique, albeit a technology that is reaching its limits in terms of performance and throughput. Plating is starting to find its way into the industry, initially as a means to improve the conductance of screen-printed contacts, but in the longer term as part of alternative metallization techniques that will involve totally new process sequences. For the sustainability of Si photovoltaics, it is crucial that the future solutions only make use of abundantly available and non-toxic materials.

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