

New Ag metallization pastes for solar energy cost reduction

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ABSTRACT

To lower the price of energy generated by crystalline silicon solar cells, either the production cost of the cells per Wp must continue to fall or the efficiencies will need to increase. Cost reductions in the metallization step have so far been achieved by improving the printability and conductivity of the silver metallization paste for the front-side contacts: as a result, the amount of silver metallization paste used has been halved in recent years. Other improvements in silver metallization paste, such as finer-line printing and reduced resistance of contacts on high ohmic emitters, have enabled an increase in average efficiency of several tenths of a per cent each year. The reductions in production cost and the increases in efficiency will continue for the next few years, but to further bring down the overall cost per Wp, there is a need for new cell types that can offer higher efficiencies and a lower cost of solar energy per Wp. Some advanced cell types already in mass production are n-type cells and metal wrap-through (MWT) cells. Each of these types of cell can be produced using robust, traditional screen-printing technology with silver metallization paste. The silver paste plays a vital role in these advanced cell designs and will be discussed in detail in this paper.

Introduction

The ultimate goal of solar energy is to be economically competitive with current sources of electricity. Although the price of crystalline silicon solar cells and the resulting modules has dropped significantly in the last few years, the cost per Wp must go down even further.

There are two ways to reduce the cost per Wp. The first is to reduce the production cost, which depends on the cost of consumables. To reduce the cost of a consumable, either the purchase price can be lowered or the amount used can be reduced. In 2012 a large part of the overall reduction in the cost of solar cells came from the fall in the purchase price of polysilicon and aluminium metallization paste. In the case of silver metallization paste, the cost reduction was the result of a steep drop of almost 20% in paste usage. By improving the conductivity and printability of the silver paste, the amount of silver needed per cell has been decreased by more than 50% [1] in three years. Even when the increase in the silver price over the last three years is taken into account, the cost per Wp of silver usage is now lower than ever.

The second way to reduce the cost per Wp is to increase the amount of Wp produced per solar cell – in other words, increase the efficiency (η). Silver metallization paste has been one of the most important facilitators of efficiency increases in recent years. The increase in efficiency arises from many small improvements: 1) an increase in short-circuit current (I_{sc}) due to a decrease in metallized area; 2) an increase in fill factor (FF) due to reduced finger-line resistance and contact resistance (R_c ;

and 3) an increase in open-circuit voltage (V_{oc}) due to reduced phosphor concentration in the emitter. All of these changes have been made possible because of improvements in the screen-printable silver paste used for front-side metallization.

Compared to the beginning of 2009, the price of silver per troy ounce has more than doubled – from ~US\$13 to a figure approaching US\$30. But, because of the enormous reduction in silver usage and the associated increase in efficiency made possible by improvements in the silver metallization paste, an actual cost reduction of 25% per Wp has been realized (Fig. 1), despite the higher price of silver.

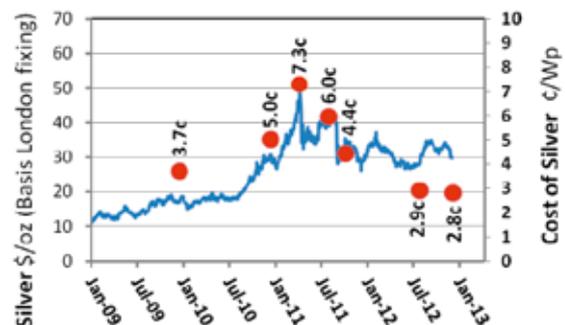


Figure 1. Price of silver per troy ounce (—) from January 2009 to January 2013 vs. the cost of silver per Wp (•) for front-side metallization.

Although silver is a precious and expensive metal, it has properties that make it unique as a contacting and conducting metal for crystalline solar cells. First, it is the metal with the lowest resistance. Second, assisted by glass frit, silver is able to grow silver crystallites on the silicon interface in a single step, by simple and reliable processing, resulting in a low-resistance electrical contact between the emitter and the bulk silver. Silver is a noble metal, which means that complex processing is not required to prevent oxidation, and, by nature, it provides the reliability needed in Si modules. Third, and finally, silver has been used for over 30 years for contacting solar cells and has proved to be reliable and robust.

Improvements in 'standard' solar cells

The most straightforward methods for improving efficiency are:

- increase voltage and current by reducing the doping level of the emitter;
- increase current by reducing the metallized surface;
- increase fill factor by reducing the finger-line and contact resistances.

By reducing the doping concentration in the emitter, band-to-band and Auger recombination will be reduced as a result of a higher minority-carrier concentration. Shockley-Read-Hall recombination will also be reduced because of a decrease in the 'dead layer'. A drawback of reducing the doping level is that two resistances increase: 1) the resistance due to lateral conductivity [2] increases because of an increase in sheet resistance, and 2) the contact resistance increases because of an increase in the depletion area between the silver and the silicon [3,4]. Predictions made in the ITRPV report [5] of the increase in sheet resistance for the coming years are shown in Fig. 2.

To limit the impact of increased sheet resistance on the FF , the finger-line spacing has to be reduced. But if the widths of the finger lines are not decreased in equal proportions, the

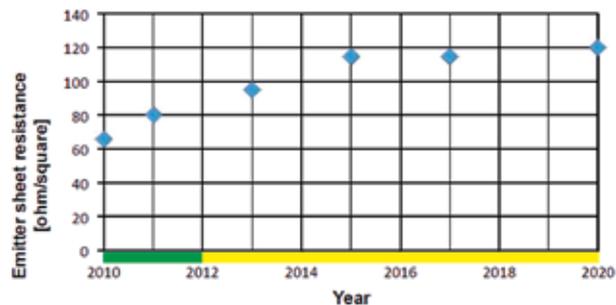


Figure 2. Predictions of the changes in sheet resistance from 2012 to 2020.

covered metal area is increased, thus lowering the current. By changing the paste composition, it has been possible to reduce the width of the finger lines from $130\mu\text{m}$ to less than $60\mu\text{m}$ (Fig. 3) while keeping the aspect ratio the same or even higher. This allows the finger-line spacing to be reduced by 50% (depending on the finger-line width and exact number of finger lines), effectively lowering the impact of the emitter resistance while keeping the covered area constant, or even decreasing it (Fig. 4). As an example, for 60 fingers of $130\mu\text{m}$ at $65\Omega/\text{sq}$, a calculation using the formula from Meier [4] yields a power loss of $0.357\text{mW}/\text{cm}^2$ due to emitter resistance. For an identical emitter with 120 fingers of $60\mu\text{m}$, a power loss of $0.092\text{mW}/\text{cm}^2$ can be calculated.

To fully benefit from the increase in sheet resistance, however, a low contact resistance is required. Decreasing the doping concentration in the n-type emitter leads to an increase in minimal potential contact resistance. Reducing the doping concentration from 5×10^{20} to 1×10^{20} results in a twentyfold increase in contact resistance for silver (which has a Schottky barrier height Φ_b close to $0.6\text{--}0.8\text{eV}$) [6]. However, the contact resistance which can be obtained at that concentration is still low enough to obtain high-efficiency solar cells. In other words, there are no theoretical limits for using silver as a contact material for high-efficiency solar cells.

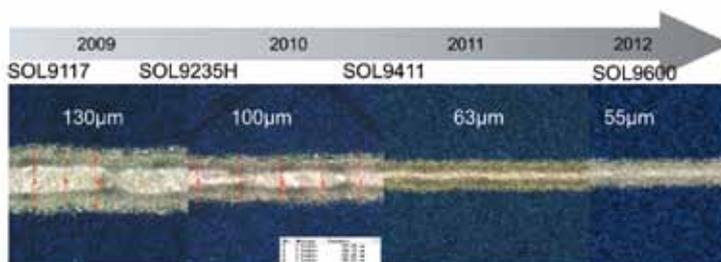


Figure 3. Reduction in line widths over the period 2009–2012.

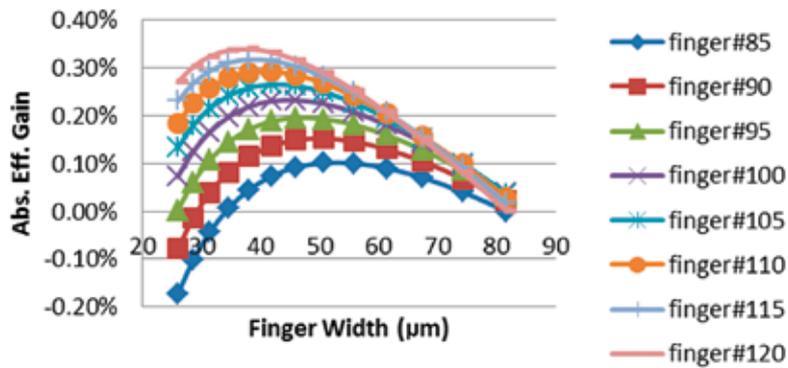


Figure 4. Expected impact of line width (change in open area) and number of finger lines (changes in $R_{emitter}$ and R_s) on efficiency (for a sheet resistance of $100\Omega/sq.$ and a finger height of $15\mu m$).

The limits for using silver are more practical in nature and relate to how many crystallites can be formed (since crystallites will act as resistors in parallel) while maintaining low recombination currents. By changing the paste chemistry, it is possible to grow a much higher density of silver crystallites, especially on lightly doped surfaces (Fig. 5).

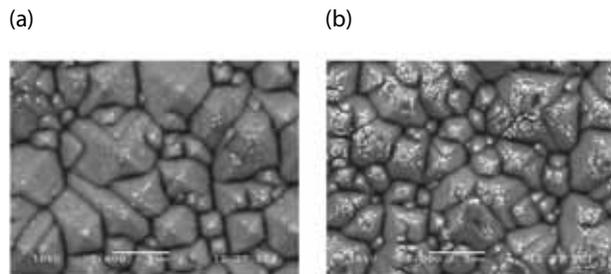
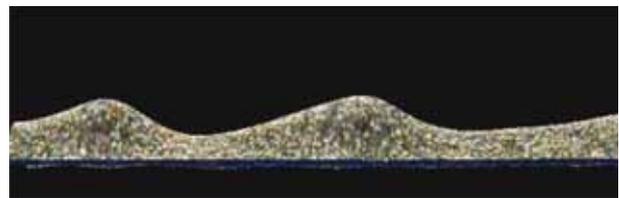


Figure 5. Crystal formation on a high ohmic emitter: (a) with old-generation paste, and (b) with current-generation paste.

Since any conductor can be seen as a large number of resistors in series, the conductivity of a silver finger line is dominated by the areas having the highest local resistance. These areas are the parts with small cross sections, whether caused by a low finger-line height or by a constriction, or by both. By improving the finger-line uniformity, the impact that these high-resistance constrictions have on the total conductivity can be reduced. Whereas in older-generation pastes the highest points could be several times as high as the lowest points, in current-generation pastes (depending on processing) this difference is much smaller (Fig. 6). Because of improvements in printability, resulting in more uniform lines, either a higher FF can be obtained with the same amount of silver paste (i.e. efficiency gain), or the amount of silver paste can be reduced without impacting on FF (i.e. cost reduction).

(a)



(b)



Figure 6. (a) Older-generation paste with high tops and deep valleys; (b) current-generation paste with a more uniform height.

The overall conductivity of silver finger lines is determined by the 'bulk' conductivity (conductivity of the fired silver paste independent of the line dimensions), or, in other words, how well the finger lines sinter. The sintering is influenced not only by the firing temperature, but also by the size distribution and shape of the silver particles. Over the years, the 'bulk' resistance of the fired silver has been gradually improved.

The effect of improved pastes

To illustrate improvements in contacting, two groups of solar cells were made on wafers with an average sheet resistance of $75\Omega/sq.$: one using an 'old' reference paste and the other using the new SOL9610A paste (Table 1).

Paste	I_{sc} [A]	V_{oc} [mV]	FF [%]	η [%]	R_s [m Ω]	R_{sh} [Ω]	R_c [Ω]	Line width [μm]	Paste usage [g]
Reference	8.726	626.4	77.20	17.34	3.3	190	0.304	70.8	0.110
SOL9610A	8.706	625.8	78.44	17.56	2.6	202	0.217	76.3	0.122

Table 1. Comparison of an 'old' reference paste and SOL9610A

By improving the contacting mechanism, R_c has been decreased from 0.304 to 0.217 Ω , resulting in a lowering of the series resistance (R_s) by over 20%. A small lowering of I_{sc} and V_{oc} (which is due to a slight increase in finger-line width) is countered by an increase in FF of 1.6% relative, resulting in an effective increase in efficiency of 0.22% absolute. By optimizing the finger-line width, this improvement could potentially be increased by another 0.05% absolute.

Further increases in sheet resistance will increase the blue response of the solar cell as a result of a reduction in recombination, leading to a gain in both I_{sc} and V_{oc} . However, a downside of this decrease in doping level is that the Fermi level (E_f) is lowered, effectively increasing the depletion zone of the Schottky contact [4]. For a 'classic' silver paste, this increase in contact resistance will result in a catastrophic failure in contacting, ending up with an FF below 70%. But with the improved contacting system of SOL9610A, it is possible to contact even sheet resistances greater than 100 Ω .

In a direct comparison on high-ohmic monocrystalline wafers (Table 2), finger lines of equal width were printed, resulting in comparable values for I_{sc} and V_{oc} ; the main difference is in the FF obtained. The line resistance of the finger lines (and thus the grid resistance – R_{grid}) printed with SOL9610A was expected to be slightly lower than that with the reference paste: although the line widths and deposited masses are comparable for both pastes, there is a difference in the line dimensions. For the reference, the minimum and maximum line heights were 4 μm and 20 μm ; in the case of SOL9610A, the values were 5 μm and 15 μm , indicating that the overall uniformity had been improved, resulting in a lower line resistance. The actual difference of ~40% in R_{grid} is due to very high R_c for the reference, thereby reducing the current's flow through the emitter at locations of high line resistance.

The main reason for the good FF of SOL9610A, however, is the improved contact because of, for example, an increase in the number of silver crystallites grown on the silver-silicon interface. As a result of this improved contact it was possible to obtain high voltages and current because of the low surface doping, leading to efficiencies over 19%. When the doping concentration of the emitter (and therefore the recombination in the emitter) decreases, the interaction between emitter, anti-reflective coating (ARC) and silver paste becomes more critical for lightly doped homogeneous emitters, and the chemistry of the paste is the key to obtaining low-ohmic contacts.

Advanced screen printing for standard cells

When thinner finger lines are used, the screen for screen printing becomes limiting in both line height and line uniformity (Fig. 7). One method for overcoming this limitation is the introduction of a second print step for the front-side pattern. Two different process flows are now possible: 'double print' (or 'print on print') and 'dual print'.

Double print

With double print, in a first print step only the finger lines are deposited. In a second print step a full pattern is deposited, with the finger lines exactly on top of the first print. The busbars are printed only once, resulting in finger lines with a very high aspect ratio and relatively few busbars (in order to conserve silver usage). In the second print, constrictions and other high-resistance regions are 'repaired', as more paste is deposited in the valleys of the finger line than on the peaks. For the first and second prints, specialized pastes may be used

Paste	I_{sc} [A]	V_{oc} [mV]	FF [%]	η [%]	R_s [m Ω]	R_{sh} [Ω]	R_c [Ω]	R_{grid} [Ω]	Line width [μm]	Paste usage [g]
Reference	9.188	632.2	62.43	15.18	15.9	90	8.0	136	66	0.159
SOL9610A	9.183	634.2	78.05	19.03	4.0	106	1.4	97.6	67	0.152

Table 2. Comparison of a 'classic' reference paste and SOL9610A for $R_{sheet} = 104\Omega/\text{sq}$.

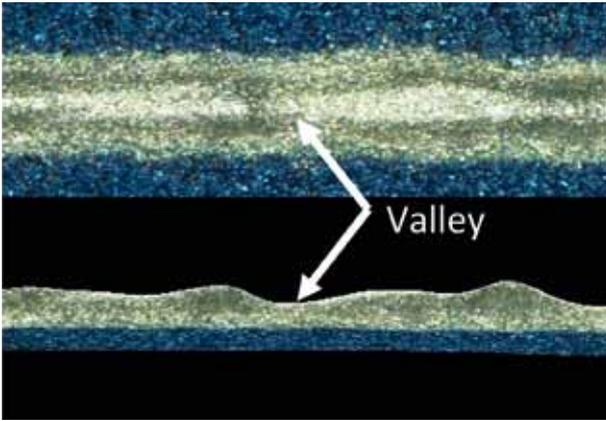


Figure 7. A 'valley' in a finger due to wire mesh, resulting in an increase in resistance.

which are optimized for either low contact resistance (first print) or improved conductivity and passivation (second print).

Dual print

With dual print, the finger lines are deposited in a single print step, while the busbars are printed in a separate step, which could be either before or after the deposition of the

finger lines. The advantages of this over a single print are that optimized pastes and screens can be used for the two different steps, to ensure a low lay-down of paste for the busbars and a high aspect ratio for the finger lines. Other screen types, such as stencil screens, can be used in one or both steps.

Comparison of single versus double print

Two-step print processes have been accepted by industry and are currently being used in large-scale production. Both ISFH [7] and ECN [8,9] have shown that with these process flows, higher efficiencies are obtainable and reductions in paste consumption are feasible.

One of the major advantages of double printing is that by printing the finger lines twice, more paste is deposited in the valleys than on the peaks during the second lay-down. The resulting finger lines consequently have a more uniform height, allowing a lower lay-down while keeping the same line resistance. Moreover, because the resulting finger lines will have a higher aspect ratio, a narrower screen opening can be used, creating either a larger non-covered area and an increase in I_{sc} or a greater number of finger lines, resulting in a comparable I_{sc} and a higher FF .

In a direct comparison between the single printing of SOL9610A and a dedicated double-print paste (SL80-8012) (Fig. 8 and Table 3), the differences are clear. Even when

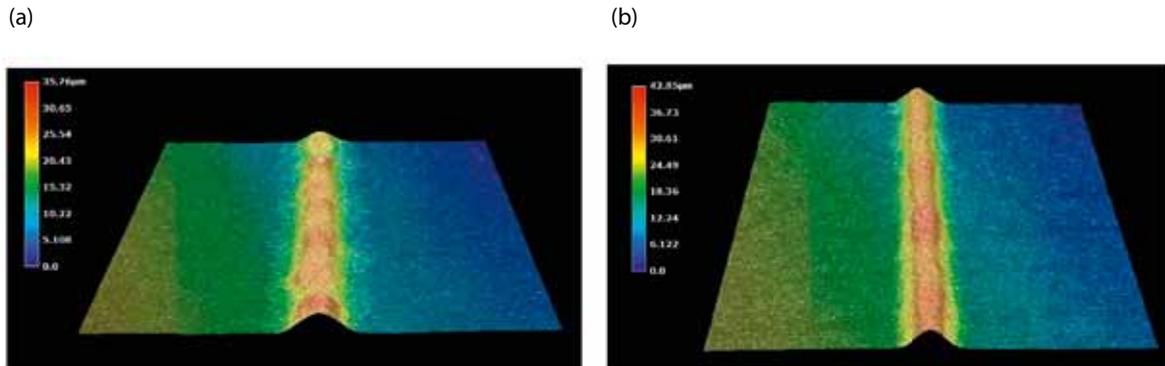


Figure 8. Fingers obtained by (a) single print of SOL9610A, 72µm wide, 20.7µm high; and (b) double print of SL80-8012, 62µm wide, 26.3µm high.

Paste	I_{sc} [A]	V_{oc} [mV]	FF [%]	η [%]	R_s [mΩ]	R_{sh} [Ω]	R_{front} [mΩ]	Line width [µm]	Paste usage [g]
SOL9610A	8.675	627.6	76.70	17.16	4.2	23.1	38.8	72	130
SL80-8012	8.735	631.0	77.55	17.56	3.7	18.3	28.7	62	124

Table 3. Comparison of single print (SOL9610A) and double print (SL80-8012) processes.

three more finger lines are being used for a double print, the narrower finger lines (62 μm for double print versus 72 μm for single print) result in an increase in I_{sc} of 0.7%. Because of the reduced contact area (and therefore a reduction in the number of defects introduced), V_{oc} is also higher. The FF of the double print is higher than that of the single print, mainly because of the reduction in finger-line resistance (busbar-to-busbar resistance R_{front} goes down from 38.8m Ω to 28.7m Ω) owing to the more uniform finger-line height shown in Fig. 8. R_s is lower, despite the 5% reduction in silver paste usage.

N-type front-side emitter solar cells

In general, n-type wafers have higher lifetimes than traditional p-type wafers because of, for example, a lower sensitivity of the minority carriers to metal impurities [10]. As a result of this increase in lifetime and the associated increase in V_{oc} , it is possible to achieve efficiencies of 20% and above with solar cells based on n-type doped wafers.

Several different cell types based on n-type wafers are currently in production. The ones with the highest reported efficiencies are the interdigitated-back-contact (IBC) cells of Sunpower [11] and Panasonic [12], with each having reported efficiencies over 23% [13]. The production processes for these cells are completely different from those used in the conventional crystalline silicon PV industry.

The front-side emitter n-type solar cell fabrication follows a lay-out and production process that is much closer to the current production flow. The main differences lie in the diffusion, the passivating layers (also on the back side) and the metallization. Instead of an n-type emitter, a p-type emitter is now required, usually obtained by boron diffusion. The back side of the wafer contains a phosphor-diffusion-based back-surface field (BSF), and both sides are contacted using an H-pattern with two or more busbars [13–15].

To contact a p-type surface, normally an aluminium paste is used: however, for front-side n-type solar cells, this is not an option. The conductivity of aluminium finger lines is lower than that of silver ones, requiring too large a fraction of the wafer to be covered by metal. Therefore, to optimize for both contact and conductivity, aluminium-doped silver paste is commonly used.

The back side of the wafer requires a BSF to prevent recombination of minority-charge carriers on the surface. Whereas in p-type solar cells this is normally obtained in the same step as when the aluminium silicate is obtained by diffusion of some of the aluminium into the silicon, in n-type solar cells a phosphor-diffused BSF is normally used [18]. This layer is best contacted using a silver-based screen-print paste. Since the diffused BSF uses the same dopant as the emitter in the p-type solar cell, but not necessarily in the doping profile, a standard front-side paste could be used; however, an optimized paste may yield better results in terms of lower paste usage and superior performance. The paste can be

optimized for 1) the surface doping concentration, 2) the firing temperature to make it compatible with the front side, and 3) the surface texture, which can differ from the front side.

Compared to p-type solar cells, one of the drawbacks of n-type solar cells with a front-side emitter is that a silver-containing paste is required for both the front and back sides. But, by using advanced screen-print technologies such as double or dual print, the amount of silver needed on the front side has been significantly reduced in the last year. An additional effect of using a two-step printing process is that it is possible to use a contacting paste for the finger lines and a non-contacting paste for the busbars. This type of paste does not damage the silicon surface below the busbar: the recombination velocity below the busbars is not increased, which would otherwise cause a strong decrease in the dark saturation current (J_0) on the front side compared to sister cells with contacting busbars. The overall result is a reduction in silver usage and an increase in V_{oc} [12].

Metal wrap-through (MWT)

In MWT concepts, the metal contacts from the front side are 'led' through small holes in the silicon wafer (vias) to the back side (Fig. 9). There are several advantages of this concept. First, all connectors to the module are on the back side, eliminating all width and thickness limits for the tabbing material. Because the tabbing material is on the back, it will not shadow part of the front side; moreover, it does not have to be flexible as it is no longer necessary to 'bend' the tab

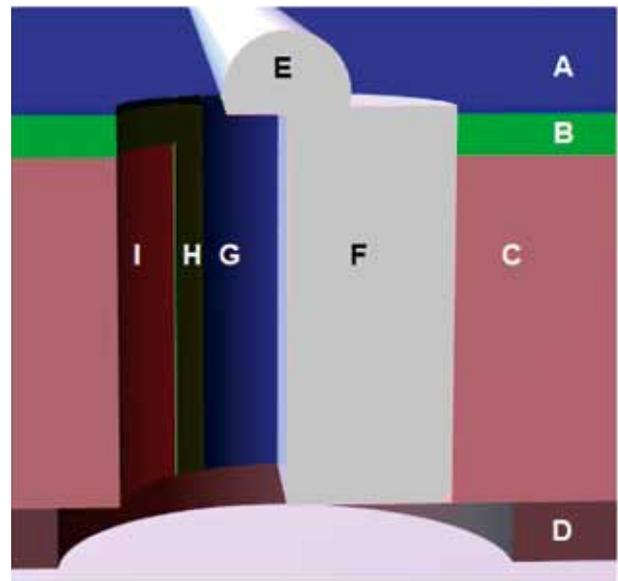


Figure 9. Cross section of an MWT via: A = ARC; B = emitter; C = bulk wafer; D = aluminium + Al-BSF; E = front-side finger; F = via plug; G = via wall, which can also be covered by emitter (H) and/or ARC (G); I = non-doped via wall.

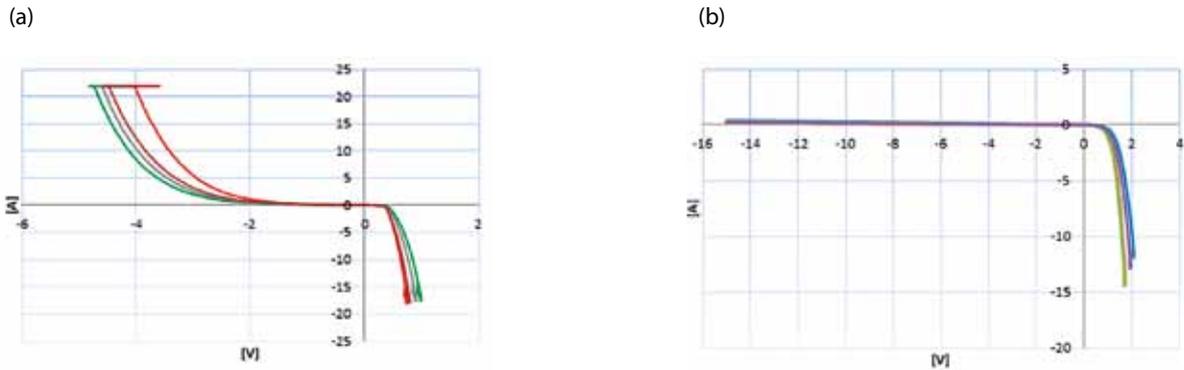


Figure 10. Reverse-current plot: (a) an unsuitable via paste; (b) a suitable via paste (HL80-7018).

around from the front side to the back. Since no busbars are required on the front side, the metallization fraction can go down by 2–3% absolute, resulting in a 2–3% increase in I_{sc} and in relative power output of the solar cell [16–18]. A cost saving is realized as a result of the reduced quantity of silver metallization paste required for front-side busbars.

The vias can be made during different stages of the solar cell fabrication. The safest option, however, is to create a via before diffusion, so that the via wall contains an n-type doping and a dielectric layer (SiN_x). Furthermore, by creating the via at this stage, the region on the back side where the connection to the module will be located will have an n-type doped surface to prevent direct electrical contact between the front-side metallization and the bulk of the wafer [19]. A drawback of this method is that the isolation around the vias on the back side has to be performed by either laser or localized etching, and this will increase the process costs or decrease the efficiency [20].

A more straightforward option is to make the vias after diffusion and wet-chemical isolation, thereby circumventing the difficulties of the previous process flow. However, the silver metallization paste which is in the via could now make direct contact with the bulk material of the wafer, both in the via and on the back side.

It is crucial that the paste used for filling the via and making contact with the module does not make electrical contact with the bulk of the wafer. The paste must also maintain a good contact with the front-side silver and have sufficiently low resistance to the back side, good adhesion to the via wall and back side, and good solderability and processing ability. Most crucial is the behaviour in reverse-bias conditions: when a high current flows under negative bias, hotspots can form in the module when it is partly shaded, resulting in module breakdown. Pastes which meet these criteria have been developed (Fig. 10).

Even with a suitable via paste, the reverse-current (I_{rev}) values can still be greater than those for standard solar cells. But, as the recombination occurs below the well-conducting

silver layer covering the via wall and back side, the actual increase in temperature is lower than for standard cells with similar values of I_{rev} , which means that a higher I_{rev} could be accepted without increased risk of module failure [21].

Conclusions

Solar energy cost reduction continues to be the focal point of the PV industry. There are several levers that affect the cost per Wp of solar modules and system installations: manufacturing yields and solar conversion efficiencies have the greatest influence on the cost per Wp of a system. The industry has benefited from the screen printing of silver metallization pastes on crystalline silicon solar cells because of its proven reliability and consistent improvement in cell efficiencies over the years.

Relative to other attempted replacements, silver metallization pastes have demonstrated the combination of good physical and chemical stability, high conductivity and good contacting behaviour. The screen-printing process helps maintain high manufacturing yields when compared with other technologies.

Investments in research and development have led to improvements in the ability of silver metallization pastes to increase cell efficiency at a lower cost per Wp: lower paste coverage, higher conductivity, and improved contacting to high-ohmic emitters are just a few achievements. The 50% reduction in paste usage has also played a part in reducing the cost per Wp.

The commercialization of new, high-efficiency cell types will also be instrumental in lowering the cost per Wp. Although these cells have different requirements in terms of the processing, conduction and contacting behaviour for the front-side contacts, suitable screen-printable silver metallization pastes are now available and improved versions are regularly released.

As a result of the continued improvement of silver metallization pastes, front-side metallization will maintain its readiness for

even higher efficiencies and lower costs per Wp, all in order to make solar energy more competitive in the near future.

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Arno Stassen joined Heraeus in 2011 as a technologist with the Photovoltaics Business Unit. He received his Ph.D. from Leiden University in the Netherlands in 2002, and worked as a researcher at the Technical University of Delft and at ETH in Zurich. Before joining Heraeus, Arno spent over five years with the photovoltaics group at ECN, the Energy Research Centre of the Netherlands, where he worked on crystalline silicon solar cells.



Dr. Weiming Zhang is currently the Vice President of Technology of the Photovoltaic Business Unit in the Thick Film Materials Division of Heraeus Materials Technology LLC. Previously, he was a worldwide technology manager and R&D manager for six years with the Thick Film Materials Division in the USA. During more than ten years with Heraeus, he has developed and commercialized many thick-film materials for various applications. He received his Ph.D. from the University of Missouri-Rolla in 1997, and has published more than 40 articles concerning photovoltaic and other metallization applications.