Progress in cost reduction in silver pastes for crystalline silicon cells

Mark Thirsk, Linx Consulting LLC, Mendon, Massachusetts, USA

ABSTRACT
Silver paste is a key component of the design of nearly all silicon wafer solar cells manufactured in 2011. The high cost of the precious metal in the paste formulation means that silver paste is also the second-highest component of the total cost of materials. This article reviews the silver paste supply chain and the challenges in silver paste formulation and manufacture, and discusses some of the approaches for reducing or removing entirely the use of silver in crystalline silicon cell manufacture.

Introduction
Silver pastes have been the mainstay of crystalline silicon solar cell interconnection for the past 40 years. The unique benefits in making reliable, low-resistance connection to crystalline silicon, as well as forming low-resistance grids and busbars, make silver an excellent technical solution for solar cell manufacture. Unfortunately, the nature of silver as a noble metal gives its value in global markets significant volatility that is unconnected to local PV market conditions. In the past two or three years this has meant that the percentage of the bill of materials (BOM) for solar cells which relates to silver paste has increased dramatically as silver bullion prices have climbed.

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Solar cell manufacturers have identified the reduction of the silver paste contribution to the BOM as a key requirement for lowering the overall price of solar modules. While significant progress has been made in optimizing both silver paste formulations and printing processes to reduce overall cost, significant challenges remain if cost targets are to be met.

Current trends in silver paste
Silver paste is used as a high-conductivity metal on both the front and the back of many solar cell designs in production today. The functionality of paste differs somewhat on the front and back sides of the cell, and thus the formulation of the paste changes. All pastes are based on silver particles that are delivered with functional components in a solvent or oil-based carrier.

For front-side applications, glass frit is combined in the paste to facilitate an aggressive etching process during firing to make contact through the antireflective coating layer with the underlying silicon. The fired paste must make a low-resistance contact with the underlying silicon through the etched antireflective coating, for high-conductivity grid lines to carry current away from the cell. Different doping levels and antireflective coating materials lead to optimized formulations for each cell type.

For back-side pastes, the glass frit content can be reduced since no etching property is required, but the back-side busbar geometry is often larger than on the front and must make good electrical contact with the aluminium paste that forms the back-surface field. In the past, back-side pastes often contained significant quantities of aluminium powder, but this is less common today.

Generally about 0.2g of silver paste is used on the front side, whereas 0.05g is used on the back. In addition, approximately 1.2 to 1.5g of aluminium paste may be used to form a back-surface field. Functionality of the paste is driven by the silver particle size and its distribution and morphology, by the composition and chemistry of the glass frit, and by processing conditions. Front-side silver pastes are commonly optimized for various levels of doping and different antireflective coating materials, and even for n-type and p-type silicon.

Environmental concerns have also driven a reduction of lead and cadmium content in the glass frit. While the removal of these elements initially led to some compromises in functionality, more recent formulations appear to have addressed these concerns.

The problem with silver paste
The supply chain for silver pastes has one significant problem to overcome. The base material for the manufacture of any silver paste is electronic-grade silver, a material that is both extremely valuable and prone to price variations on global markets on a day-to-day basis.

As has been well documented, the cost of silver spiked in May 2011 at almost 300% above the price of January 2009, before falling again to between $30 and $35 per ounce today. The usual product pricing schemes for precious metal products rely on passing the market cost of the precious metal content to the next owner at the time of sale.

The value added in the creation of the product by the supplier is often a small and fixed part of the final selling price. The total paste price volatility leaves little room for cost reduction efforts on the part of the paste supplier and user.

Companies who manufacture products using precious metals must find business structures that can cope with the significant working capital demands and market risks of holding silver metal during the manufacturing process. These concerns imply that large well-capitalized companies with experience in handling precious metals are often advantaged in the supply of paste.

Technology trends
The 2011 International Technology Roadmap for PV calls for a reduction of 50% in the cost per watt of consumables from 2010 to 2020. As part of this cost reduction the roadmap envisages reducing the silver consumption per cell from 0.3g per cell in 2010 to 0.025g per cell in 2020 – an order of magnitude reduction in one decade. This can only be achieved through a significant redesign of silicon cell architecture, removing much of the silver on the front and back sides of the cell.

Although other high-conductivity metals exist, the direct replacement of silver in screen-printing paste formulation is not straightforward. The most obvious replacement – copper – does not make satisfactory paste. Copper is not a precious metal and brings with it oxidation problems, as well as being incompatible with a functioning silicon diode. The lack of a
simple replacement for silver is driving silver reduction efforts in cell-making technology.

**Paste reformulation** that maintains good ohmic contact with the underlying silicon, and high conductivity of the fired grid lines and busbars, is critical. Reduced silver content pastes have been formulated by all major suppliers in the last 12 months; these pastes can reduce the amount of silver in front-side printing by as much as 20% while maintaining other functional properties.

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**Double printing** attempts to overcome one of the limitations of the screen-printing process, namely the difficulty of producing structures with a high aspect ratio. Since the paste is liquid at the time of printing and can slump after screen snap-off, in addition to its reduction in thickness upon firing, it has proved difficult to formulate standard pastes that can print a thickness-to-width ratio greater than 0.3. Hot-melt pastes printed at high temperature and using a wax-based carrier to achieve high aspect ratios have met with only limited success. Significant efforts in the last two years to develop processes that lay down a second paste print on top of the first have been successful in both reducing finger width and increasing aspect ratio. Matching of pastes for the first and second prints has allowed optimized contact resistance and finger conductivity while offering overall paste consumption reductions. However, the penalty of adding high-precision alignment for the second print, and the extra drying capacity required in the screen-printing line, offset some of the overall advantages of double printing.

**Layout changes** are a simple technique for reducing paste consumption through an optimization of the printed pattern of the grid and busbars. As cell efficiency increases, a higher density of grid fingers is necessary to carry current away from the cell. Reducing the finger width can offset the increased shadowing that results with more fingers. In current cell designs three 2mm-wide busbars are printed across the front of a cell instead of two. Inaccuracies in attaching stringers require continuous solid lines to ensure good solder joints of the stringers. With improved accuracy of stringer soldering equipment, busbar patterns can be reduced to islands or ladder-shaped structures that significantly reduce paste requirements while allowing reliable stringer connection. Even for high-efficiency cells, copper stringers can offer enough current-carrying capability to offset the need for solid busbars.

For back-side silver busbars, a reduction in paste usage has been achieved by decreasing the thickness of the print, as well as cutting down the silver content. An obvious limit to this occurs as the print thickness approaches the silver particle size used in the paste.

These techniques for reducing the amount of silver paste used and the total silver content per cell have yielded significant reductions in precious metal consumption per cell, but are nearing the practical limit of the savings they can offer. Further techniques – such as silver augmentation by plating, light-induced plating, and direct plating on silicon – offer ways of further reducing silver consumption per cell, although at the cost of increased complexity in processing and addition of new equipment. Alternative plating schemes include the following:

- **Silver augmentation**: an electroless silver deposition is plated onto a reduced-thickness paste layer after firing. The plated silver is of higher density than that of the paste and consequently has a higher conductivity. The total silver used in the grid line can then be reduced.

- **Light-induced plating**: a metal stack is plated onto the silver using a thin silver-paste seed layer that has been fired to make contact with the front side of the cell. Commonly this stack includes a nickel diffusion barrier, a thick copper conduction layer, and a tin or silver flash for silver wettability. The plated layers are deposited with either galvanic or electroless plating, whereby in the latter case no back-side contact is required. The overall result uses significantly less silver but adds process complexity and new equipment, and requires careful control of nitride integrity to avoid metal deposition in pinholes.

- **Direct plating on silicon**: to avoid the use of the thin silver seed this technology directly plates metal onto silicon. Laser ablation is required to remove nitride from the front of the cell before plating. Once the direct-plated metal, usually nickel, has been deposited, light-induced plating can be used to build up the grid and busbars. Even though this process completely eliminates silver, it does add costs to laser patterning and a further plating process.

While all of these processes have been demonstrated they are usually only applicable to the front-side metallization, and do not remove the need for silver and aluminum paste on the back side. Although significant plating capacity has been installed, there remains relatively little manufacturing that uses this technology. Many challenges have been resolved but there is still uncertainty about...
implementing plated grid and busbars in high-volume manufacturing.

Despite several metal wrap-through and emitter wrap-through designs being introduced in 2011, the most effective cell architecture change to remove silver remains the implementation of back contacts. Most designs for back-contacted cells called for aluminium metallization, deposited either as paste or by evaporation. It is possible that aluminium will require an intermetallic contact layer at the silicon interface, although successful cells have been demonstrated without such diffusion barriers. These designs have the potential to be completely manufactured without the requirement for silver, but may need high-resolution patterning processes and are several years away from implementation on a large scale. An additional innovation for back-side contact architectures is that of integrating the cell interconnect in the backsheet. This technology incorporates a copper layer into the backsheet, which is stamped to produce the lead-outs for removing power. Connection with the cells can be done by various methods, including the use of a conductive adhesive, or a solder paste that is then laser heated after module lamination.

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Conclusions

The use of silver as an interconnect metal for PV cells remains as critical as ever. The unique properties of silver as a highly conductive metal that forms stable connections to crystalline silicon means that replacing it with another single material is very difficult. A large and stable supply chain for silver paste has emerged, and optimized formulations to meet the needs of many different cell designs have been proved. The high cost of using a precious metal as an interconnect material on silicon PV wafers remains a significant problem that is only made worse by the volatility of the price of silver on the world’s metal markets. The uncertainty and risk in the cost of such a key component in the BOM is the driving force for finding replacement materials and technologies.

In 2011 most large cell producers implemented silver paste reduction programs that have yielded significant savings in the quantities of silver paste required in advanced PV modules. Many of these silver reduction schemes have reached the limit, and the next steps will include some redesign of the cell architecture or significant changes in the metallization processes.

The challenge of developing robust high-volume grid and busbar technologies remains a significant one. Both equipment makers and cell makers continue to develop alternative technologies, but in an industry where product lifetime and reliability are so critical, resistance to significant process change remains high. Major cell architecture changes that will replace the silver grids and busbars with metals such as aluminium and copper are several years off, but should be mature within the time frame identified by roadmap efforts. Whether or not these architecture changes can deliver long module lifetime and high reliability will become a significant focus for process developers, and an opportunity for all participants in the supply chain.

About the Author

Mark Thirsk is a managing partner and co-founder of Linx Consulting, which provides market-defining analysis and strategic insights across major markets in electronic materials. He has over 25 years’ experience in economic and business forecasting, strategic planning, technical marketing, product management and M&A, spanning many segments and processes in electronic materials. Mark has served on the SEMI Chemicals and Gases Manufacturers Group (CGMG) since 1999, acting as chairman between 2001 and 2003. He holds a B.Sc. (Hons.) in metallurgy and materials science from Birmingham University and an MBA from The Open Business School, and has authored multiple publications in both academic and trade publications, as well as contributing to several patents.

Enquiries

Mark Thirsk
Managing Partner
Linx Consulting LLC
PO Box 384
Mendon, MA 01756-0384
USA
Tel: +1 617 273 8837
Email: mthirsk@linx-consulting.com
Website: www.linx-consulting.com