A RISK ASSESSMENT OF WET CHEMICAL METALLIZATION PROCESS CANDIDATES FOR PRODUCTION IMPLEMENTATION

Adam Letize, Donald P. Cullen
MacDermid Photovoltaics Solutions, Inc.
245 Freight St., Waterbury, Connecticut 06702, USA
Tel: 1.203.575.5600, Fax: 1.203.575.7916, aletize@macdermid.com

ABSTRACT: Silicon PV cell manufacturers are motivated to introduce new cell processing technologies in an effort to reach grid parity while still maintaining an acceptable profit. As a result, next generation cell designs are in development which utilize wet chemical metal deposition to replace silver paste as the electrical contacts and conductors. The widespread adoption of these processes is imminent, but there is uncertainty about which cell designs and associated chemical processes are the most production friendly, highest yield, and most economically viable. This study introduces proposed process sequences for standard industrial cell designs which can make use of chemical metallization technologies. Some chemical deposition processes still face technical obstacles and will require additional improvements in order to become production-ready solutions. A detailed discussion of the risks, and potential rewards that will result from overcoming these obstacles, is presented.
Keywords: Silicon, Electrodeposition, Wet Chemical Metallization, Cost Reduction

1 INTRODUCTION

The most important factor affecting the widespread adoption and installation of photovoltaic conversion systems is the specific cost per watt of the system. In order to reach grid parity, this cost must be lowered. This can be achieved either by reducing material and processing costs of the solar cell, or by increasing the cell's conversion efficiency. Although traditional screen printed silver conductor technology has seen continual improvements to increase efficiency, the cost of the metal itself is still a significant portion of the overall cost. Additionally, silver paste suffers from the constraints of screen printing and inefficient contact to the underlying doped silicon emitter. Finally, silver paste printed cells require excessive thermal processing that can induce micro-cracks, bowing, and other thermal stresses on the cell, as well as diminish the effectiveness of the passivation layer on the wafer's surface.

An alternative metallization technique for front side conductors is the use of wet process chemicals and self-aligned plating. The implementation of wet chemical metallization process schemes for the formation of conductors on silicon solar cells is advantageous for multiple reasons. Using nickel seed layers for silicon contact allows for reduced thermal processing temperatures from 800-900°C down to <400°C while achieving significantly lower contact resistance than silver paste, due to the continuous contact of Ni-Si compared to the localized 'spike' contacts made by firing paste. Additionally, a novel patterning techniques, such as inkjet resist or laser ablation, can reduce optical losses caused by shading by as much as 50%, especially when combined with high aspect-ratio plating [1]. Finally, such a process scheme would enable the replacement of silver with less expensive metals like copper in a high-throughput production scenario, leading to an increase in yield and an overall reduction of cost.

2 WET CHEMICAL METALLIZATION

The use of wet chemical metallization for electrical contact formation is well known in the electronics industry, as it figures prominently in the fabrication of printed circuit boards and semiconductors. The adaptation of these technologies to the metallization of silicon solar cells is already underway for high efficiency cell production [2]. However, the drive for reduced materials cost will cause standard cell manufacturers to begin adapting wet chemical metallization technologies in the coming years. Figure 1 compares standard screen print metallization to some new process schemes featuring electrodeposition of metal conductors.

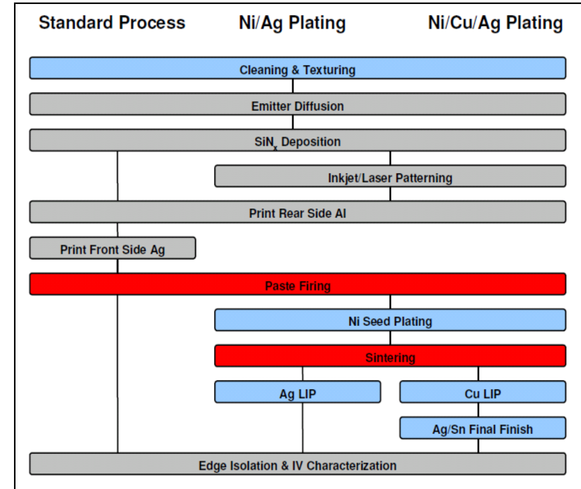

Figure 1: Production sequence of traditional screen printed Ag paste, and two new process flows utilizing wet chemical metallization.

2.1 Pattern formation

In order to utilize self-aligned metal deposition processes, a pattern must first be formed by selectively removing the silicon nitride passivation coating on the cell's front side. This can be achieved by various methods, including application of a resist material by inkjet and wet chemical etching, or laser ablation. Laser ablation is an especially attractive option, as the recent development of pico- and femto-second lasers has essentially eliminated the melting phenomenon that can potentially damage the emitter [3].

The proposed pattern formation techniques mentioned above have several advantages. Both techniques are off-contact approaches, which will improve process yield over traditional screen printing by reducing breakage, and will allow for the use of thinner silicon wafers. Also, these processes permit the structuring of ultra-fine fingers less than 50 µm wide (Figure 2). The ability to form narrower fingers reduces the shading losses experienced by traditional cells, which in turn can lead to more closely-spaced fingers, better electron capture, and higher I_{sc}. The improvement in light absorption alone can lead to an efficiency gain of 0.4-0.5% absolute.

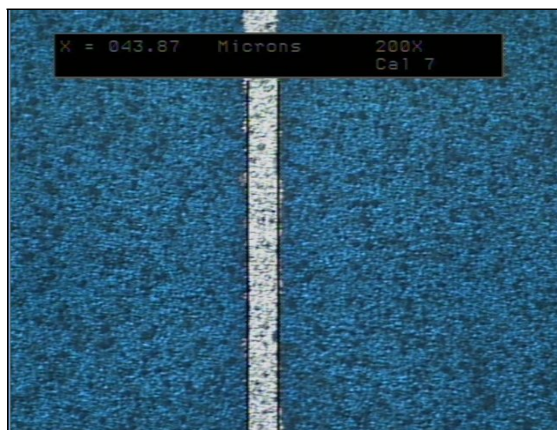

Figure 2: Narrow finger formed by inkjet resist and wet etching of the SiN_x coating.

2.2 Nickel as a silicon contact layer

Plated nickel as a seed metallization layer on silicon is also advantageous as a substitute for paste. Printed silver paste only forms localized, discontinuous contact to the silicon substrate during a high temperature firing process (figure 3). In contrast, a plated nickel seed layer forms a continuous electrical contact with the silicon which has a lower contact resistance than silver and doesn't require high temperature firing [4]. A low-temperature (as low as 250-300°C) annealing process forms a nickel silicide layer that further reduces contact resistance. Nickel plated seed layers can also achieve low contact resistance on shallow-doped homogeneous emitters, permitting the production of cells with higher V_{oc} and thus better efficiency. Finally, if copper is utilized as the primary plated conductor, nickel is an excellent barrier layer that prevents diffusion of copper into the space charge region of the solar cell, which is an industry concern [5].

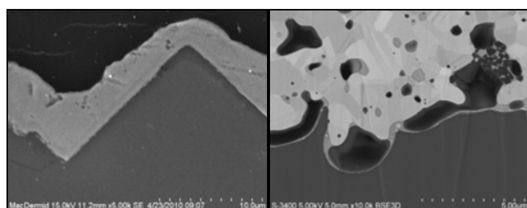

Figure 3: Cross-sectional comparison of continuous contact from Ni seed plating of Si (left) and discontinuous, porous contact from silver paste (right).

2.3 Full conductor metallization

Once a low-resistance metal-silicon contact is formed using nickel, the grid structure is grown using either silver or copper. This serves to reduce the metal line resistance, which also reduces overall series resistance in the cell. Silver can be plated at deposition rates in excess of 2.0 µm/minute using either a traditional electrodeposition technique, or alternately a light induced plating (LIP) method can be applied. A high aspect-ratio, electroplated silver layer exhibits higher bulk conductivity at lower plating thickness due to the deposit's continuity and morphology, whereas a fired silver paste suffers from conductivity loss because of the porous nature of silver flakes. Also, the implementation of an optimized grid pattern consisting of narrower, more closely-spaced lines reduces the total quantity of metal necessary for the front side conductor, which further reduces material cost.

In a further improvement, copper can be used as the plated conductor. The substitution of copper for silver can reduce the metal cost significantly, as copper has a comparable bulk conductivity of 59.6 MS/m versus 63.0 MS/m for silver. As of August 2011, the cost of copper at $9 USD/kg represents more than a 99% cost reduction compared to silver, at $1300 USD/kg. Figure 4 shows the capability of plating a thick, high-aspect ratio copper deposit on a narrow nickel seed layer.

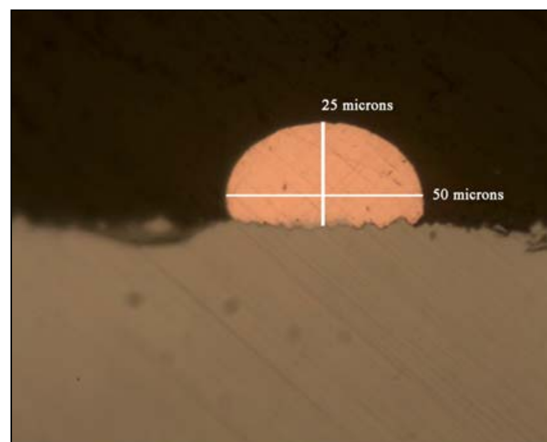

Figure 4: Cu finger with high aspect-ratio formed by electrodeposition.

3 APPLICATIONS OF WET CHEMICAL METALLIZATION PROCESSES

The deployment of wet chemical metallization processes by the solar cell industry is seen as a stepwise, evolutionary transition. Initially, chemical metallization will be used only as a form of repairing traditional paste cells with electrical deficiencies. Next, cell manufacturers will begin to reduce the quantity of paste printed on each cell, and grow the bulk of the conductor using LIP metallization. Finally, cell makers will eliminate screen printing on the front side altogether, and will instead use a fully metallized conductor process, in order to realize the greatest cost reduction and efficiency gain. Figure 5 demonstrates the proposed sequence of transitions for plating front side conductors on solar cells.

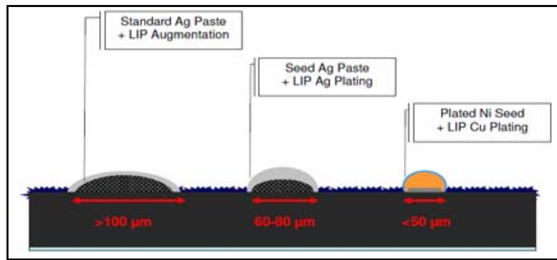

Figure 5: Schematic image of the stepwise integration of wet chemical metallization into solar cell production.

3.1 Paste augmentation

Wet chemical metallization of solar cells was first introduced in production as a method of improving, or 'augmenting' the electrical properties of traditional screen printed cells. In this process, a layer of silver is plated, typically in a LIP mode, directly on top of printed and fired silver paste. The plated silver can improve the cell efficiency by reducing series resistance in 3 ways. First, the growth of more silver metal on top of the paste will reduce the resistance of the cell grid. Second, the silver plating chemistry works to 'fill in' the pores of the paste, thus improving the bulk conductivity of the paste itself. Finally, LIP Ag can help form a more continuous, lower-resistance contact to the underlying silicon, which also serves to reduce series resistance. For this reason, paste augmentation is especially useful for cells with high series resistances resulting from sub-optimal firing and poor Ag-Si contact.

3.2 Seed paste and conductor metallization

The next logical use of wet chemical metallization is printing/firing of a thin seed layer of paste, and then plating of the bulk metal conductor using wet chemical process [6]. In this method, cell manufacturers can continue to use known patterning techniques, and the strong adhesive bond of fired silver paste is maintained. The manufacturer can normally print much narrower lines, however, because higher paste thickness is no longer required. Utilization of LIP plating to build the conductor results in a less expensive, more conductive grid, while at the same time reducing shading on the cell's surface. In a further step to reduce cell material costs, the plated silver can be replaced with nickel, copper, and a thin solderable finish such as tin or silver.

3.3 Full metallization

The final transition in the adoption of wet chemical metallization is the complete replacement of paste and the associated screen printing technologies. As described earlier, the nickel-silicon contact has several distinct advantages over paste, and can be used in combination with patterning processes that form very narrow fingers. The bulk conductor can be formed using LIP Ag, or a Ni/Cu/Ag stack, like in the seed paste process flow.

Figure 6 represents a theoretical simulation of the potential efficiency gain that can be realized by transitioning to the previously mentioned metallization processes. The properties of standard industrial silver paste are taken from [7] and the equations and calculations for efficiency were derived from [8]. The simulation is for a two bus bar cell design with a sheet resistance of 70 Ω/□ and standard aluminum BSF. A silver paste contact resistance of 10 mΩ*cm^2 and bulk resistance of 5.0 μΩ*cm was used, compared to 1.0 mΩ*cm^2 and 2.5 μΩ*cm for fully plated conductors. An aspect ratio of 0.1 for printed Ag was assumed, and a maximum plated conductor thickness of 25 μm, due to process time limitations. The graph demonstrates that as manufacturers move to narrower finger grids, the use of plated conductors not only becomes attractive, but also becomes increasingly necessary.

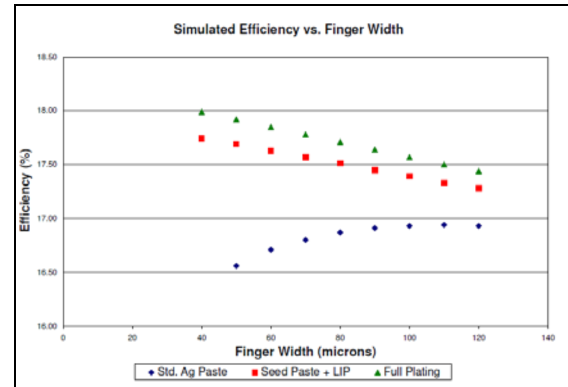

Figure 6: Simulated efficiency comparison of the three different conductor technologies with narrowing finger widths.

4 TECHNICAL CHALLENGES

The implementation of a new process technology carries with it some inherent obstacles and risks. In the case of replacing silver paste with plated conductors, some of these factors are already known. Table I lists the primary challenges associated with implementing wet chemical metallization, and the proposed method of resolving these issues.

Table I: Technical risks and proposed solutions for implementing plated metal conductors.

Technical Risks	Proposed Solutions
Shunting of shallow emitters	Optimized barrier layer Sintering process control
"Ghost plating" on ARC	Adjust ARC for minimized porosity
Adhesion of metals to seed paste	Paste/chemical bath compatibility
Adhesion of metals to Si surface	Proper silicide formation Low stress metal deposition, silicide Novel silicon texturing chemistry
Solderability of plated conductors	New thermal profiles for plated metals

As it relates to electrical performance of the new cell technology, shunting of the emitter during nickel annealing, and background, or "ghost" plating are the principal concerns. Shunts are of special importance, because the industry is continuously moving towards shallower emitters, which are more susceptible to diode

shunts. This problem is analogous to firing silver paste, and can be addressed in the same manner. Optimization of the sintering profile, and use of process control measures for both the nickel seed layer and the sintering step will minimize deleterious effects caused to the emitter during sintering. The risk of background plating has been addressed elsewhere [9]. Exhibiting proper precautions during post-diffusion cleaning and ARC deposition has greatly reduced the incidence of ghost plating.

The most pressing issue that has hindered mass adoption of plated conductors on silicon solar cells is adhesion related. Thus far, an electrodeposited metal stack to the silicon surface has not shown the same mechanical adhesion that traditional fired silver pastes can obtain. This leads to downstream issues with tabbing ribbons, and questions of long-term mechanical stability. Poor metal-to-silicon adhesion may be due to a number of factors, including deposit stress and improper silicide formation. Also critical is the texture of the silicon surface. Some novel techniques used to increase the nano-roughness of the silicon under plated contacts have demonstrated great improvement of conductor adhesion. Much current research is focused on this area.

In addition to metal-to-silicon adhesion, there are also the challenges of inter-metallic adhesion and adhesion of plated conductors to a paste seed layer. Inter-metallic adhesion matters can be resolved with proper knowledge of each metal deposit's properties, and control of the metal deposition process. Adhesion of metals on seed paste can be improved by verifying compatibility of each metal's electrolyte solution, and properly matching plating chemistries with the requirements of the paste layer. Finally, the deployment of a new metal conductor grid will require re-qualification of the soldering and tabbing process when fabricating modules. Each set of metals involved in soldering require a specific thermal profile that best matches the materials involved. Conductive pastes should also be evaluated for their potential applicability to the new tabbing process.

When transitioning to a new technology, such as wet chemical metallization of solar cells, some other factors to be taken into consideration include:

- Specification and purchasing of new process equipment.
- Generation of new waste streams, and assessment of waste treatment requirements.
- Process know-how requirements and personnel training for a new technology.
- Process control and the need for inline quality assurance methods.
- Assessment of cell breakage and product yield using the new process.

These requirements are common to the implementation of any new technology, and are involved in the "growing pains" of changing any production process.

5 CONCLUSIONS

The use of wet chemical metallization techniques for the formation of conductors on silicon solar cells is near widespread implementation. Some form of the proposed process schemes will emerge because of its potential for superior electrical performance and its many economical advantages. Wet chemical metallization of conductors will be introduced in a stepwise transition of cell manufacturing methodologies, before finally supplanting silver paste as the preferred production option. The combination of custom chemical solutions, innovative equipment designs, and improved process control will help photovoltaic systems to achieve further cost reductions, and reach grid parity in the coming years.

6 REFERENCES

[1] M. Aleman, N. Bay, L. Guatero, J. Specht, D. Stuwe, R. Neubauer, D. Barucha, D. Biro, J. Rentsch, S.W. Glunz, R. Preu, Proceedings 23th European Photovoltaic Solar Energy Conference and Exhibition, Valencia, Spain, 2008.

[2] W.P. Mulligan, et al., Proceedings 19th European Photovoltaic Solar Energy Conference and Exhibition, Paris, France, 2004.

[3] G. Heinrich, M. Bahr, K. Stolberg, T. Wutherich, M. Leongardt, A. Lawerenz, *Energy Procedia* 8: 592-597 (2011)

[4] C. Boulord, A. Kaminski, Y. Veschetti, G. Poulain, D. Blanc-Pelissier, B. Grange and Mustapha Lemiti, Proceedings 25th European Photovoltaic Solar Energy Conference and Exhibition, Hamburg, Germany, 2010.

[5] J. Bartsch, A. Mondon, C. Schetter, M. Horteis, S.W. Glunz, Proceedings 2nd Workshop on Metallization, Constance, Germany, 2010.

[6] D. Pysch et al., *Progress in Photovoltaics* 17: 101-114 (2009)

[7] A.R. Burgers, *New Metallisation Patterns and Analysis of Light Trapping for Silicon Solar Cells*, Doctoral dissertation, Utrecht University, the Netherlands, 2005.

[8] C. Vazquez, L J Caballero, M A Vazquez, J Alonso, J.R. Ramos-Barrado, Proceedings 25th European Photovoltaic Solar Energy Conference and Exhibition, Valencia, Spain, 2010.

[9] S. Braun, A. Zuschlag, B. Raabe, G. Hahn, *Energy Procedia* 8: 565-570 (2011)