

LIGHT INDUCED PLATING OF SILICON SOLAR CELL CONDUCTORS USING A NOVEL LOW ACID, HIGH SPEED COPPER ELECTROPLATING PROCESS

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ABSTRACT: The focus of this work concerns the current status of using electrochemically deposited copper as the primary front side conductor for silicon solar cells. Plated conductors consisting of nickel and copper offer many advantages over the use of screened silver paste, including cost savings, reduced shading losses, lower contact resistance and higher line conductivity. Traditionally, the drawbacks of using electroplated copper include low plating speed, the corrosive nature of the chemistry, and poor adhesion of the plated conductors. A novel copper chemistry based on a low-acidity electrolyte is introduced, which permits higher plating speeds and improved throughput when compared to sulfuric acid copper formulas. Additionally, the low corrosiveness of the chemistry makes it more compatible with different cell designs and equipment configurations. A series of experiments is presented which compares the properties and adhesion results of the new electrolyte with a commercially available sulfuric acid copper chemistry. The reliability of cells and modules fabricated using laser ablation patterning and light-induced plating of the new copper chemistry is independently verified by IEC 61215 testing. This work offers a roadmap for eliminating silver paste costs while simultaneously improving the performance and reliability of solar cells.

Keywords: silicon, wet chemical metallization, electrodeposition, cost reduction

1 INTRODUCTION

The majority of silicon solar cell production currently utilizes screen printed silver paste as the conductor grid. Screen printing is attractive due to its process simplicity and high throughput capability. However, there are several notable disadvantages of silver paste. From an efficiency standpoint, silver paste suffers from high contact resistance, relatively high line resistance when compared to the bulk metal, and power loss due to excessive shading. Also, the high firing temperatures required for silver may degrade cell efficiency and cause excess stress in the cell, further reducing yield. Finally, silver is very expensive, and represents a significant portion of the of the cell's production cost [1]. At this point, replacement of silver is necessary for further cost reductions.

Alternative approaches to conductor metallization have been proposed in the past, including screen printing of low cost metals such as copper, a two-step seed and print approach, use of evaporated metal contacts, and wet chemical metallization [2]. Most of the approaches have failed due to process complexity and cost issues. However, wet chemical metallization poses some unique advantages, and it may be both cost effective and production-ready in the near future.

2 DIRECT PLATING ON SILICON

Most technology roadmaps predict a gradual migration to electroplated front side conductors during the coming years [3]. Although various iterations of plated conductors have been proposed, currently the most promising application is the sequential direct plating on silicon (PoSi) with nickel and copper on a laser structured pattern. Figure 1 shows an example of how this process could be substituted into the standard crystalline silicon production process flow. In this example, a cell with a homogeneous emitter is patterned by laser ablation removal of the silicon nitride antireflective coating in the region of desired plating. Then the cell is plated with nickel and copper in a wet chemical plating bath, using a

conveyorized, high volume plating tool. Nickel is chosen because it forms a very good electrical contact to silicon and it is an excellent diffusion barrier, and copper because of its low cost and excellent current carrying ability.

The main driver for switching to a direct PoSi process is cost reduction, as copper is approximately 100X cheaper than silver (according to spot prices at the time of writing). However, there are additional benefits to be gained from a switch to electroplated contacts. As mentioned, nickel forms a low-resistance ohmic contact to silicon, whereas silver paste only forms sporadic point contacts (crystallites) after firing. Also, due to the self-aligned nature of wet chemical metallization, the plated conductor widths are defined by the laser ablation process, and can be less than 30 μm wide. Electrodeposited metals are also more conductive than paste, because of their dense, uniform grain structure. Finally, electroplating is a low temperature process, which induces little stress when compared to high temperature paste firing, and also allows the use of unique low temperature materials such as temperature-sensitive passivation layers and a-Si (PERC, heterojunction cells).

However, there have also been noted challenges to adoption of copper plated conductors for production processes. Copper plating is typically a time consuming process when compared to screen printing, and even silver plating. Also, there is a potential for high internal stress in the copper deposit that can cause mechanical stresses in the cell, especially when plated at high speeds. Conductors plated with nickel and copper typically suffer from poor adhesion compared to sintered silver pastes. Finally, there are concerns about copper diffusion into the emitter, which would cause poisoning and reduced cell performance. The copper chemistry introduced in this paper is based on a novel formulation which attempts to resolve these issues, and offers a better plating solution for integration into high volume manufacturing.

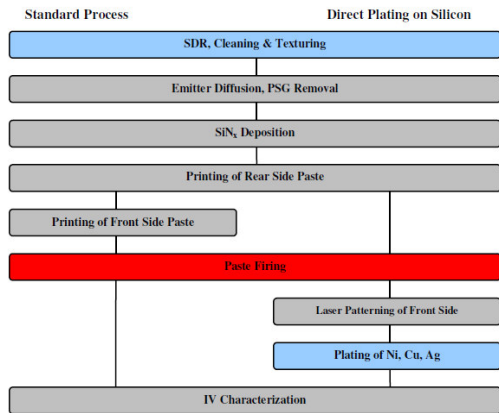


Figure 1: Standard silicon cell fabrication process flow vs. proposed PoSi process.

2.1 New electrolytic copper (EP2)

The most widely used copper electroplating chemistries are typically based on a sulfuric acid electrolyte (“acid copper”). Copper sulfate is relatively soluble, and the sulfuric-based supporting electrolyte is well buffered and highly conductive, which promotes desirable plating properties under normal operating conditions. However, there are some drawbacks to the use of traditional acid copper, specifically in photovoltaic applications. Acid copper is highly acidic and thus highly corrosive; this is thought to contribute to adhesion loss of the metallized stack due to attack on the silicon interface [4]. Second, acid copper must be plated at very high current densities (15-20 A/dm²) in order to achieve throughput metrics that make the process cost effective. When acid copper is plated at high current densities, it typically exhibits poor deposit morphology, including burning, high internal stress, and other undesirable properties that affect both the appearance and the performance of the cell.

The novel copper chemistry described here (“EP2”) is based on a different electrolyte, which appears to offer some distinct advantages. First, the EP2 chemistry contains no free acid species added, and can operate at pH levels as high as 3.0. This ensures that the chemistry is minimally corrosive towards underlying metal layers and any other exposed metals on the cell or in the plating equipment. Second, due to the unique properties of this electrolyte, it can be operated at very high current densities while still maintaining a bright, uniform plating morphology with no roughness or burning. Finally, the EP2 copper bath maintains a low internal deposit stress even when plated at high speeds (>4 μm/minute).

3 FUNCTIONAL PERFORMANCE

As mentioned, high volume manufacturing requires very high plating speeds. This is especially true in the case of copper electrodeposition. Figure 2 demonstrates the current density plating requirements for achieving a desired copper thickness in a stated period of time (assuming 100% cathodic efficiency). Plating at the high current densities required for mass production (>10 A/dm²) may adversely affect the copper deposit properties, including morphology, distribution, cathodic

efficiency, and internal stress, which ultimately will influence the efficiency, adhesion and reliability of the solar cell.

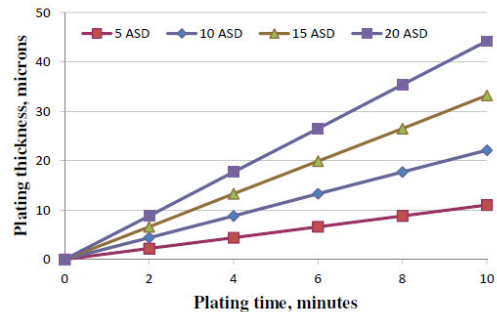


Figure 2: Copper plating thickness vs. plating time for various current densities (A/dm²), assuming 100% cathodic efficiency.

3.1 Appearance and morphology

The new EP2 copper electrolyte was first evaluated by plating a Hull cell test panel. Hull cells plating tests are designed to show the bath’s deposit appearance over a broad current density range. The results of the EP2 Hull cell test showed a uniform bright deposit from less than 1.0 A/dm² to more than 20 A/dm², with no high current density burn observed at the panel edge (figure 3).

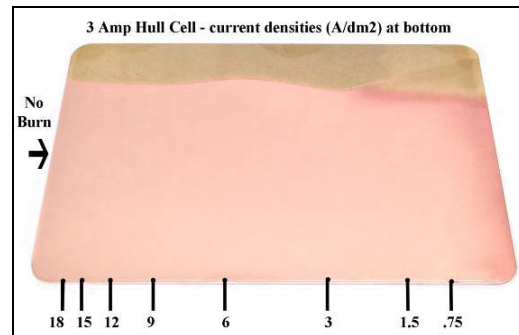


Figure 3: Brass Hull cell panel plated with the new EP2 copper electrolyte.

A mono-crystalline wafer was then plated with nickel and copper contacts according to the process flow in figure 1. Plating was carried out in a light induced plating (LIP) mode using high speed horizontal equipment supplied by RENA GmbH. The copper was plated to a thickness of approximately 20 μm in 10 minutes (~10 ASD). SEM images show a very smooth, continuous deposit with excellent morphology characteristics (figure 4). There is no evidence of deposit roughness that typically may occur at high plating speeds.

3.2 Cathodic efficiency and internal deposit stress

Cathodic efficiency is a measure of how close the deposit thickness (or mass gain) is to a calculated theoretical value for a given plating experiment. The theoretical mass gain can be determined using Faraday’s Law. Any deviation from the theoretical mass gain (cathodic efficiency <100%) means that a chemical side reaction has occurred at the electrode surface during plating; most often, this involves the electrolysis of water and generation of hydrogen. This is detrimental because

hydrogen generation can cause roughness in the copper deposit, and also because a lower-than-expected efficiency means that the cells must be plated longer to reach target mass, increasing process time. Figure 5 compares the cathodic efficiency of the EP2 copper electrolyte at 20 g/L and 40 g/L copper, under normal operating conditions.

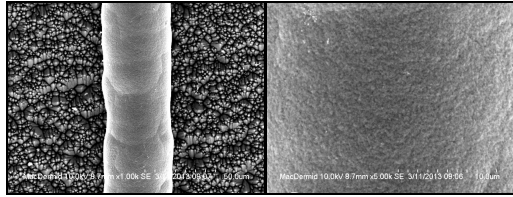


Figure 4: SEM images (1000X and 5000X magnification) of a copper finger plated at ~ 10 A/dm² by LIP.

Two different copper levels (20 and 40 g/L) can be used for bath operation, depending on the particular plating application and equipment used. In the case of light induced plating, copper concentrations must be kept low to allow for penetration of light through the plating solution. For electroplating applications not requiring light, the 40 g/L Cu operating conditions would be recommended due to its superior performance.

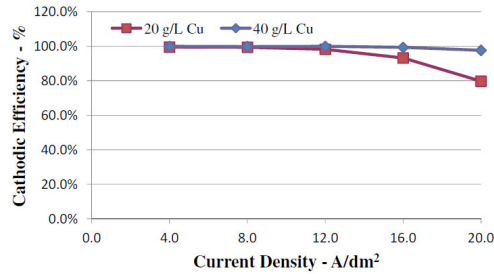


Figure 5: Cathodic efficiency vs. current density of panels plated with the EP2 electrolyte at two different copper concentrations.

Internal deposit stress testing was conducted using a custom designed plating cell and test strips from Specialty Testing & Development Co. (USA). Each test strip consists of a pair of ‘legs’ that are masked with resist on opposite sides, so that the deposit stress will cause a bend in each leg that can be quantified using a scale, and then converted to a characteristic stress of the plating deposit, taking into account the base material and plating thickness. The results for the EP2 chemistry at 20 g/L and 40 g/L copper are shown in figure 6.

4 ADHESION AND RELIABILITY

4.1 Adhesion comparison

A functional test was designed in order to compare the conductor adhesion of cells plated with the traditional sulfuric acid copper and the new low acid EP2 electrolyte. Both mono- and multi-crystalline silicon cells were fabricated using the process flow in figure 1. Cells were laser ablated using a nanosecond laser with finger contact widths of approximately 25 μ m. The

plating sequence consisted of a short cleaning of the silicon surface followed by ~ 1 μ m light induced plating of nickel, ~ 15 μ m LIP copper plating, and a thin (< 1 μ m) final finish of electroplated silver to promote solderability and prevent oxidation of the copper. The cells were not annealed during or after the wet chemical metallization process.

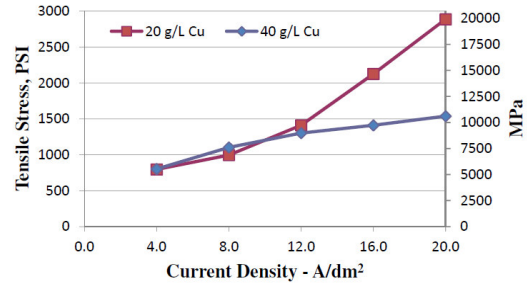


Figure 6: Internal (tensile) deposit stress of the EP2 electrolyte at two different copper concentrations.

After plating, the wafers were spot soldered using a commercially available solder-coated copper ribbon and low-acid solder flux. The cells were then peeled at a 90° angle using an automated strength bond tester. Approximately 20-30 peel results were obtained for each cell. The following box plot shows the distribution of peel strengths (in Newtons) and the mean peel result for each combination of substrate and copper plating chemistry.

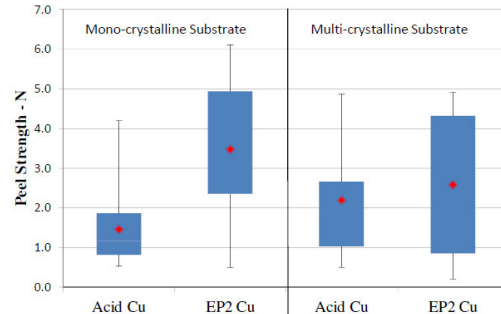


Figure 7: Peel strength adhesion comparison of sulfuric acid copper vs. the EP2 electrolyte on mono- and multi-crystalline substrates.

The results demonstrate notably higher median peel strengths for the EP2 copper versus sulfuric acid copper on the mono-crystalline substrate. On the multi-crystalline silicon substrate, the median peel strengths of the EP2 electrolyte are slightly higher, but the advantage is not statistically significant. Regardless, the EP2 plating chemistry exhibits median peel strengths greater than 2.0 N on both substrates, which is normally acceptable at most cell manufacturers.

4.2 Reliability

Cells plated with the EP2 copper electrolyte were sent to an independent test facility for IEC 61215 reliability characterization. The cells were tabbed using commercially available solder-coated ribbon and electrically conductive adhesive (ECA) paste, and built into 2X2 modules for testing. The mini-modules were subjected to 200 temperature cycles from -40°C to 85°C ,

and electrical measurements were taken in 50 cycle intervals. The results appear in figure 8. As can be seen, both groups of modules were comfortably within the IEC 61215 degradation limit of -5% power loss. The data suggests that the cells maintained the integrity of the metallized stack through thermal cycling, and also there was no diffusion of copper into the silicon, which would have led to shunting and subsequent power loss. In further testing, the reliability of EP2 copper plated cells will be evaluated after damp-heat testing and long-term accelerated aging tests.

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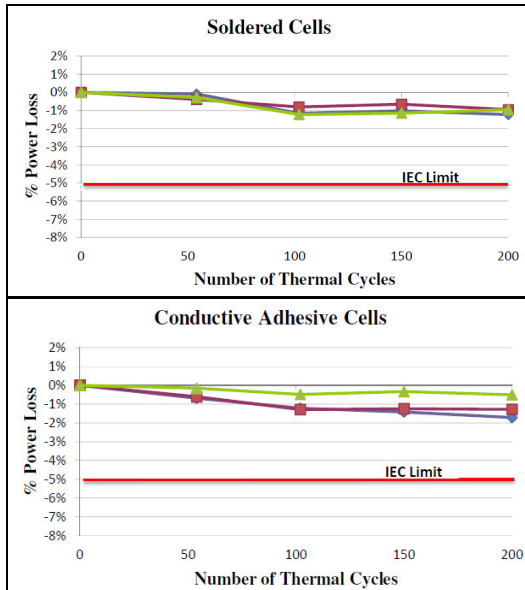


Figure 8: IEC 61215 thermal cycling reliability test showing % power loss of soldered and ECA-bonded cells.

5 CONCLUSIONS

Implementation of a copper plating process to replace screen printed silver paste has previously been limited by the adhesion of plated conductors to silicon, and by high equipment costs. Recent innovations have led to the development of a new low acid, high speed copper electrolyte that overcomes these issues. The new copper electrolyte demonstrates excellent deposit properties and improved functional performance when compared to traditional copper chemistries. Cells and modules subjected to adhesion and reliability testing showed acceptable results with the new EP2 copper chemistry. The copper plating process meets the performance and cost needs for immediate adoption in production.

6 REFERENCES

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