Light Induced Plating of Silicon Solar Cells Using Boric Acid-Free Nickel Chemistry

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Abstract — **A novel boric acid-free nickel plating chemistry has been developed to plate nickel onto silicon solar cells. This bath enables light induced plating (LIP) of nickel without the use of external rectification. The resulting deposit is low stress and has been shown to be an effective barrier to copper diffusion. Solar cells plated using this nickel bath demonstrate electrical, adhesion and reliability results similar to silver paste controls. In addition, these plated cells have lower contact resistance and higher metal conductivity than silver paste controls using similarly diffused wafers . The advantages of a boric acid-free nickel bath will be reviewed in detail.**

I. Introduction

Nickel-copper plated front contacts have been investigated by multiple research organizations and solar cell manufacturers over the last few years. [1-6] In addition to reduced cost, plated contacts may offer optical and electrical performance advantages. [1-7] Successful implementation of plated contacts into mainstream manufacturing requires both excellent performance of plated cells and commercial availability of plating chemistry and equipment that can be easily integrated into a solar cell manufacturing line. Metal plating is already established in high volume manufacturing in many industries, so the challenge is to adapt the chemistry and equipment to work with silicon solar cells. In addition, it is important to ensure that restricted chemicals are not included in the plating chemistries used. In 2010, boric acid, which is a component in commercially available nickel plating chemistries, was added to the candidate list of Substances of Very High Concern (SVHC) as part of REACH (European Union regulation concerning the Registration, Evaluation, Authorisation and restriction of Chemicals). Although boric acid chemistries can still be used, there are additional restrictions and requirements placed on the users.

This paper will discuss the formulation of a boric acid-free nickel plating bath that can be used to deposit nickel on silicon solar cells. Properties of the resulting nickel film will be discussed. In addition, performance of solar cells plated from this bath will be presented and compared to solar cells plated using boric acid containing nickel plating baths.

II. Plating Nickel on Solar Cells

Nickel plating has been around since the 1800s. In 1916, Professor Oliver P. Watts formulated an electrolyte that combined nickel sulfate, nickel chloride, and boric acid. [8] This formulation is the foundation of modern nickel electroplating. In 1950, Barrett reported commercial use of a nickel sulfamate bath in the US. [9] Nickel deposits from the sulfamate nickel plating bath are known to have a lower internal stress than those from a Watts bath; however, the sulfamate nickel bath costs more to make than the Watts nickel bath.[9] Both of these plating chemistries contain boric acid.

Watts and sulfamate nickel plating baths have been used to plate nickel on silicon solar cells. The nickel layer serves two purposes: 1) a source of nickel in order to form a nickel silicide (NiSi) ohmic contact and 2) a diffusion barrier for copper. In order to form this NiSi ohmic contact on a silicon solar cell, the ARC layer, typically silicon nitride (SiNx), must be removed in order to expose a clean silicon surface for nickel plating. Two of the more common approaches used for patterning the ARC layer are 1) masking & wet chemical etching and 2) laser ablation [10]. Table 1 lists two possible process flows that can be used to form plated contacts starting from the front side ARC patterning step. Once the ARC layer is removed, nickel can be deposited on the exposed silicon. The nickel silicide layer is formed by annealing, either after the deposition of the nickel layer, or after subsequent deposition of a copper layer over the nickel as illustrated in Table 1. For either approach, the nickel deposit must be uniform and low stress in order to function as a copper barrier and maintain good adhesion to the silicon surface. Many different factors can impact the quality of the nickel deposit such as the patterning process, cleaning steps prior to plating, equipment used, and plating chemistry.

Solar cells have been plated using direct electroplating and light induced plating (LIP) with and without rectification [5]. Direct electroplating requires that the areas to be plated, such as the bus bar and grid lines, are directly contacted to the rectifier which can be difficult to do with such fragile substrates. LIP takes advantage of electrons generated when

the solar cell is illuminated so the electrical connection can be made to the backside of the solar cell loosening the requirements for the contact design and it can be performed with or without rectification. It is important to formulate the plating bath chemistry to be compatible with the method of deposition whether it is direct electroplating or LIP.

Table 1: Example ARC Patterning & Plating Flows

Laser Ablation	Mask & Wet Etch
Open ARC with Laser	Deposit Mask
Clean	Open ARC with Wet Etch
Nickel & Copper Plate	Clean
Anneal to form NiSi	Nickel Plate
Clean	Strip Resist
Tin Plate	**Anneal to form NiSi**
	Clean
	Nickel, Copper, & Tin Plate

III. Boric acid-free Nickel Plating Bath

A boric acid-free nickel plating bath was formulated in response to the restrictions being placed on boric acid as part of REACH. There are numerous advantages of this boric acid-free plating bath. In order to demonstrate these advantages, a lab scale study comparing this boric acid-free nickel chemistry with three boric acid containing nickel plating chemistries was performed. The pH, internal stress, and conductivity of the plating baths were monitored over a 5 week period. Table 2 lists the plating baths compared and summarizes the results. The boric acid plating baths tested fall into 3 different categories: 1) Watt's nickel (nickel sulfate / nickel chloride), 2) Nickel sulfamate, and 3) Technic proprietary formulation (Ni A) which is similar to the boric acid-free nickel bath but contains boric acid.

Table 2: Comparison of Nickel Plating Baths

	Watts Nickel	Nickel Sulfamate	Ni A w/ Boric Acid	Boric acid-free Ni A
Contains Boric Acid	Yes	Yes	Yes	No
pH target	4.0	4.0	4.0	2.0
Internal Stress over 5 weeks (MPa)	-20 (comp) to 20 (tensile)	-50 (comp) to 40 (tensile)	-15 (comp) to 15 (tensile)	-15 (comp) to 15 (tensile
LIP w/o rectificatio n	No	No	Yes	Yes
Technic Product Names	*Watts Ni Semi bright*	*Technisol Ni 2420*	*N/A*	*Technisol Nickel D2428*

As shown in Table 2, the operating pH of the boric acid-free nickel plating bath is 2.0 versus a pH of 4.0 for the boric acid containing plating baths. In addition, the operating pH of the boric acid-free plating bath is very stable over time. Figure 1 compares the pH monitored over 5 weeks for the four baths tested. The red arrow indicates when the pH was adjusted based on a drift of ± 0.10 from the operating pH. The boric acid-free Ni plating bath required only one adjustment over the 5 weeks; whereas all the other plating baths required 2 or more adjustments. In addition, the pH excursions for Ni A with boric acid and the Watts Ni bath were larger than any excursion for the boric acid-free nickel.

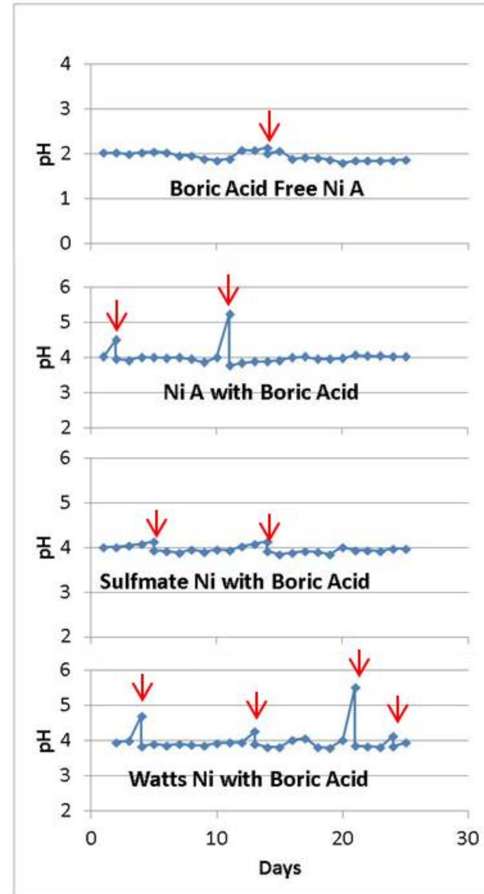


Fig. 1: pH monitoring over 5 weeks for nickel plating baths. Red arrow indicates pH adjustment when pH drifted ±0.10 from target.

In addition to the boric acid-free nickel bath having a stable pH over time, this bath has been formulated to plate nickel on silicon solar cells using LIP with or without rectification. Both the Watts and sulfamate plating baths are commonly used in other industries for nickel plating but are not specifically formulated for LIP plating on solar cells. Initially, the sulfamate nickel plating bath was used to plate nickel on a silicon solar cells using LIP without rectification; i.e. the backside of the solar cell is connected directly to the

anode and the plating current is generated by illuminating the solar cell. This approach was not successful, with very little nickel plating observed unless rectification was used with the LIP; i.e. the backside of the solar cell is connected to the rectifier (DC power supply) and current is applied while illuminating the solar cell.

During the development of the boric acid-free nickel plating bath, the goal was to achieve a nickel deposit using LIP without rectification. A conductivity metric was identified to predict when a nickel plating solution is capable of LIP plating without rectification. This conductivity metric was used during the formulation of the boric acid-free nickel as a quick test to identify when the formulation was ready for LIP plating without rectification. The plating solutions in Table 2 were tested using the conductivity metric and the results are shown in Figure 2. The Ni A bath with and without boric acid has a conductivity that enables LIP plating without rectification; however, the Watts Ni and sulfamate formulations do not. In order to confirm these results, laser ablated solar cells were plated for 7 mins in plating equipment designed to immerse the front side of the solar cell in the plating solution and maintain a dry backside. The front side of the cell was illuminated and the dry backside was connected to the anode. Figure 3 compares the top down SEM images of grid lines plated using LIP without rectification in both the boric acid-free nickel bath and the sulfamate nickel bath. Figure 3a shows that nickel plating from the boric acid-free Ni bath did occur on the grid lines; i.e. the area in between the dotted white lines. Very little nickel plated from the sulfamate plating bath as shown in Figure 3b. In order to get a thicker layer, the time or light intensity would need to be increased. However, this demonstrates that the boric acid-free nickel bath is more conductive than the sulfamate nickel bath and is capable of plating nickel on the solar cell without the use of external rectification. Although LIP plating without rectification is possible with this plating chemistry, it may not be the preferred method of plating in high volume manufacturing. This, however, does demonstrate the unique properties of this boric acid-free nickel plating bath.

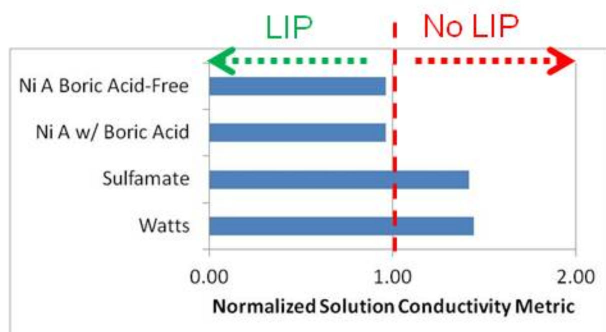
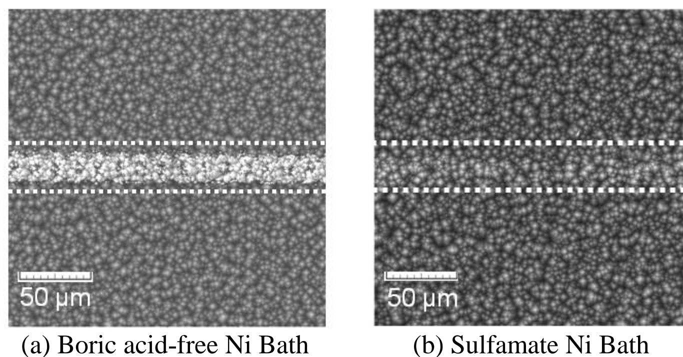


Fig. 2: Results from study used to predict if plating chemistry is capable of LIP without rectification.

In addition, the internal stress of the nickel deposited from each bath was measured using stress tabs from the Deposit Stress Analyzer System, Specialty Testing & Development Co. once a week over the 5 week period. As shown in Table 2, the Ni A baths with and without boric acid have the lowest max internal stress over the 5 week period. It is interesting to note that the max stress for the Watts nickel bath in this study was measured to be ~20 MPa which is much lower than the 185 MPa reported in literature. [11]



(a) Boric acid-free Ni Bath (b) Sulfamate Ni Bath

Fig. 3: Top down SEM images of grid lines plated using LIP without rectification for two different nickel plating chemistries. (1000 X, dotted lines added to highlight location of grid line)

A 50 week bath study of the internal stress in the nickel deposited from the boric acid-free chemistry was also performed using the same method of measurement. Figure 4 shows the results of these measurements. The initial data point from the fresh bath shows a highly compressive value which requires further investigation. However, within one week of operation, the internal stress is measured to be 20 MPa compressive. The maximum tensile stress observed over this time period is 60 MPa. The green line in Figure 4 is the maximum expected internal stress of 55 MPa for nickel deposited from a sulfamate bath as reported in literature [11]. The majority of data points measured from the boric acid-free nickel fall below this line. For comparison, the red line in Figure 4 shows the maximum internal stress expected for a deposit from a Watts nickel bath from literature [11]. A nickel deposit with a low internal stress is expected to have better adhesion performance than a highly stressed film.

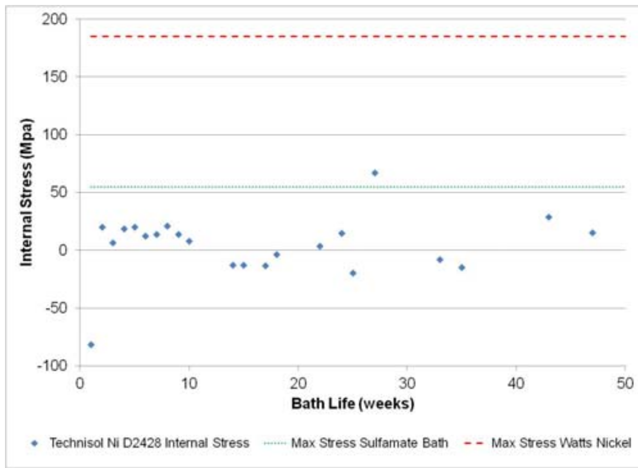


Fig. 4: Internal stress of nickel films deposited from a boric acid-free nickel plating bath over a 50 week bath life study.

IV. SOLAR CELL RESULTS

156 x 156 mm semi-fabricated (no metalized front grid) and fully processed silver paste control cells have been acquired by two different research organizations in order to test both process flows listed in Table 1. One set of cells, purchased from Energy Research Center of the Netherlands (ECN), were p-type mono-silicon textured cells with an 80 ohm/sq emitter, silicon nitride ARC layer, and fired Al/Ag backside. At Technic, these cells were patterned with a mask & wet etch process and plated and will be referred to as wet etch cells. The other set of cells, purchased from Fraunhofer ISE, were p-type Cz silicon, 1.5-4.0 ohm-cm, textured with a 90 ohm/sq emitter, silicon nitride ARC layer, and fired Al/Ag backside. A UV picoseconds laser ablation process was used by Fraunhofer ISE to pattern the front grid[12]. These cells were plated at Technic and will be referred to as laser ablated cells. Nickel plating was performed using the boric acid-free chemistry. Copper was plated over the nickel using a Technic low stress copper chemistry. For adhesion and reliability testing, a tin layer was deposited over the copper layer using a Technic tin chemistry specifically developed to be compatible with LIP.

Laser ablated, plated samples were IV tested using a Sinton FCT-400. 5 laser ablated, plated samples and 5 silver paste control samples from the same batch of cells were measured. Table 3 shows the results. The plated cells perform the same if not slightly better than the silver paste controls. The series resistance (R_s) is lower for the plated cells even though the plated metal lines on these cells are thinner; i.e. less volume of metal.

Table 3: IV Properties for Ag Paste Control vs. Laser ablated, plated cells

	% Eff	% FF	R_s (Ω-cm^2)	Grid W (um)	Grid Thk (um)
Ag Paste	18.96 ± 0.05	79.59 ± 0.19	0.56 ± 0.02	41.5 ± 9.0	20.2 ± 6.0
Technic Plate	19.08 ± 0.05	80.04 ± 0.21	0.46 ± 0.04	45.7 ± 5.9	13.8 ± 3.5

The contact and line resistivity was measured using the ContactSpot technique [13]. Figure 5 compares the effective contact resistivity of the silver paste control with cells plated from the boric acid-free Ni A bath and the sulfamate nickel bath. The plated cells have a median contact resistivity that is approximately half that of the silver paste controls. In addition, Table 4 shows that the plated lines are more than double the conductivity of the silver paste controls with a line resistivity very close to that of pure copper[13]. A larger sample size is needed to confirm if samples plated in the boric acid-free nickel are consistently lower in contact and line resistivity than samples plated in the sulfamate nickel bath. This study emphasizes that plated lines are more conductive and have a better contact resistance than silver paste controls.

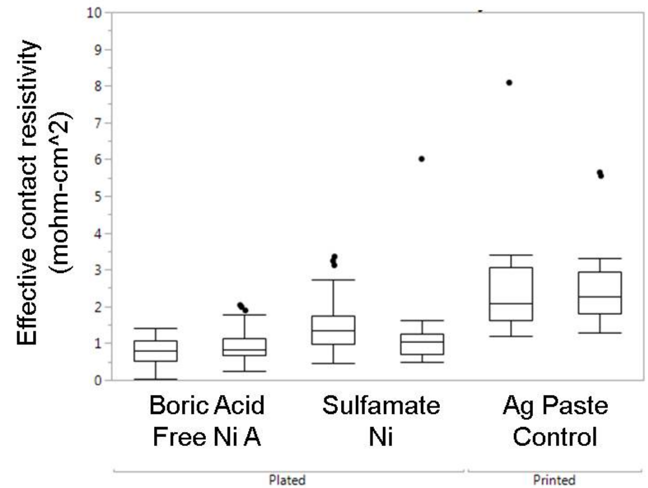


Fig. 5: Comparison of effective contact resistivity for plated contacts versus silver paste control.

Table 4: Comparison of line resistivity for plated cells versus silver paste control

	Line Resistivity (ohm-m)
Ag Paste Control	$5.0 \pm 0.4 \times 10^{-8}$
Plated from Ni A w/o boric acid	$1.9 \pm 0.1 \times 10^{-8}$
Plated from Sulfamate Ni	$2.2 \pm 0.1 \times 10^{-8}$
Pure Copper [13]	1.72×10^{-8}

The contact resistance and adhesion of plated cells is significantly impacted by the quality of the silicon / nickel

interface. Figure 6 shows a SEM cross-section of a wet etch cell after nickel and copper plating imaged at Massachusetts Institute of Technology (MIT). This image shows that the interface between the silicon and the nickel is clean and uniform. The surface preparation of the silicon surface and the nickel plating process play a critical role in this resulting clean interface.

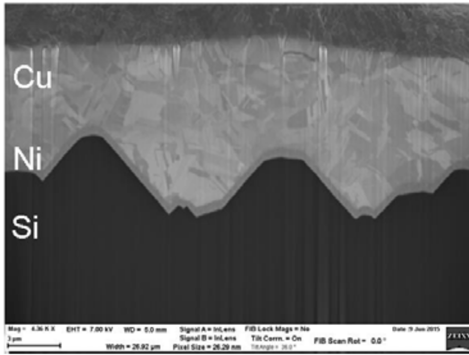


Fig. 6: SEM cross section of a Ni/Cu plated grid line.

Wet etch samples plated with Ni/Cu/Sn were peel tested at MIT [15] to determine the adhesion of the plated samples compared to silver paste controls. Ribbon similar to what is used in industry was first hand soldered onto the busbars of both the plated and silver paste cells. A 180° pull angle was used with a pulling speed of 200 mm/min using the ADMET eXpert 5600 Series Universal Testing System. This force tester gage has a load limit of 2.2 lbf (9.786 N) ~ 4.893 N/mm. The samples were secured to a vacuum plate for peel testing and the force required to pull the ribbon away from the cell was measured. The adhesion strength is the force per unit width of the ribbon. Figure 7 shows the maximum adhesion values for 10 plated samples compared to 5 silver paste control samples. The maximum adhesion values for the plated samples range from 3 to 4.5 N/mm. The silver paste control samples range from 2 to 3.5 N/m. The adhesion performance of the plated cells are as good as or better than the silver paste controls [15]. Previous work showed that the nickel film functioned as a barrier to copper diffusion based on dry heat annealing studies [16].

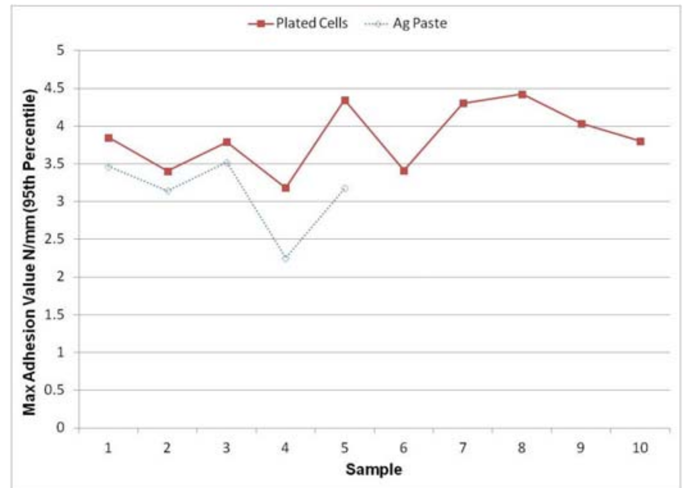


Fig. 7: Peel test results comparing the maximum adhesion value of plated cells versus silver paste cells

Initial reliability testing was performed on both wet etch and laser ablated samples. ASU fabricated single cell modules from the plated and silver paste control cells. Damp heat testing for 1000 hrs at 85°C/85% was performed at NREL and thermal cycling testing (-45°C to 85°C) was performed at Case Western Reserve University. This was a small sample set intended for an early look at reliability of the plated contacts. The plated cells used for this testing were similar in electrical performance to the silver paste controls. Table 5 shows the reliability results for laser ablated, plated cells compared to the silver paste controls. All plated cells perform similar to the Ag paste control and show less than 5% change in power post testing which is a passing result.

Table 5: Reliability results for laser ablated, plated cells in single cell modules.

Sample	Test	Δ Pmax (% rel)	Δ FF (% rel)	Δ Voc (% rel)	Δ Isc (% rel)	Δ Eff (% rel)
Control	*1000 h DH*	-0.7	-0.3	0.6	-1.0	-0.3
1	*1000 h DH*	-1.6	-0.8	0.5	-1.3	-0.8
2	*1000 h DH*	-0.9	-1.1	0.5	-0.3	-1.1
3	*1000 h DH*	-2.9	-1.9	0.3	-1.3	-1.9
4	*1000 h DH*	2.7	0.7	1.3	0.8	0.7
5	*1000 h DH*	1.5	-0.3	1.3	0.5	-0.3
Control	*200 TC*	-2.0	-1.1	0.0	-0.8	-2.2
1	*200 TC*	-2.1	-0.8	0.2	-1.3	-1.6
2	*200 TC*	-0.7	-0.4	0.0	-0.3	-0.5
3	*200 TC*	-3.2	-1.8	0.0	-1.3	-2.7
4	*200 TC*	-3.3	-4.1	0.2	0.8	-3.4

Table 6 shows the results for the wet etch cells. Unfortunately, there were not enough cells to have a silver paste control in the thermal cycling test. However, all the cells show passing results, with power changes less than 5%.

Further reliability tests are planned with a larger sample size and more silver paste controls.

Table 6: Reliability results for wet etch, plated cells in single cell modules

#	ID	Δ Pmax (% rel)	Δ FF (% rel)	Δ Voc (% rel)	Δ Isc (% rel)	Δ Eff (% rel)
Control	*1000 hr DH*	*-0.4*	*0.3*	*0.6*	*-1.3*	*0.3*
1	1000 hr DH	-2.8	-1.3	-0.3	-1.1	-1.3
2	1000 hr DH	-2.3	-1.1	0.2	-1.5	-1.1
3	1000 hr DH	-2.3	-1.4	0.0	-0.9	-1.4
4	1000 hr DH	0.0	1.0	0.8	-1.7	1.0
1	200 TC	-2.5	-1.1	-0.2	-1.1	-2.4
2	200 TC	-2.0	-0.4	0.0	-1.4	-1.9
3	200 TC	-1.6	-0.4	0.2	-1.2	-1.3
4	200 TC	-1.7	-0.3	0.2	-1.4	-1.2
5	200 TC	-3.2	-2.5	0.7	-1.2	-3.3
6	200 TC	-4.3	-2.2	-0.2	-1.8	-4.0

V. Conclusions

In conclusion, Technic has developed a boric acid-free nickel plating bath that can be used to plate nickel on silicon solar cells using LIP with or without rectification. To the best of our knowledge, there is no other boric acid-free nickel plating bath commercially available and specifically designed for LIP plating. This plating bath has a stable pH that requires little adjustment over the life of the bath. In addition, the nickel deposit produced is low stress which is important for good adhesion performance. The line and contact resistivity measured on laser ablated, plated cells is less than half that of the Ag paste controls. The cells used during this study were optimized for screen printing and not designed to take advantage of the low contact resistance and line resistivity of the plated contacts. Further studies will explore how to utilize plating to improve solar cell performance by modifying the emitter and front grid layout to bring out the true potential of plated contacts on silicon solar cells. This study also demonstrates that plated contacts have similar adhesion and reliability performance to silver paste contacts. By optimizing the plating chemistry, tooling, and solar cell design, it is expected that plated contacts can outperform silver paste contacts while saving money on materials costs.

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