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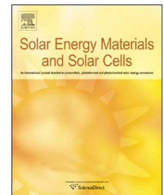

# Improved metal adhesion with galvanic nickel plating to silicon solar cells

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ABSTRACT

Nickel galvanic displacement (NiGD) plating to silicon surfaces allows for the deposition of self-limiting sub-micron nickel layers. This paper reports the use of NiGD plating as an adhesion-promoting seed layer for light-induced plated nickel and copper (LIP-NiCu) contacts on chemically-etched silicon surfaces. The improved adhesion, which is attributed to surface roughening caused by the oxidation and subsequent etching of silicon in the fluoride-containing electrolyte, is quantified by stylus-based scratch measurements and shown to increase with the duration of sintering at 350 °C. The width-normalised cut-off force for NiGD layers, sintered for 10 min, was approximated by a normal distribution with a mean of 114 ± 32 N/mm. Unsintered NiGD and sintered LIP-only control samples, plated onto similar chemically-etched silicon surfaces, were insufficiently adherent to be measured. The poor adhesion of the unsintered NiGD contacts was attributed to the formation of voids and an oxide-rich interface layer during the galvanic displacement process. Although sintering at 350 °C appeared to reduce the thickness of the interfacial oxide and eliminate the voids, the oxide was not totally removed and contributed to the measured contact resistance of sintered NiGD-treated contacts of ~ 15 mΩ cm$^2$ being more than an order of magnitude higher than laser-ablated LIP-NiCu contacts on a similar *n*-type emitter surface. Adhesion priming layers formed using NiGD were used to metallise selective-emitter cells patterned using aerosol jet etching and having planarised contact regions. Although the LIP-NiCu contact grid was strongly adherent, the average area-normalised series resistance ($R_s$) was 0.96 ± 0.18 Ω cm$^2$, the majority of which is attributed to high contact resistance arising from a residual interfacial oxide.

## 1. Introduction

Silver consumption remains the highest non-silicon cost for commercial screen-printed silicon solar cells [1]. As such, the cost of producing PV devices can be reduced through the use of cheaper metallisation materials, such as nickel and copper, which can be plated to exposed silicon regions of the cell [2–8]. However, the transition to more widespread use of plated contacts has been slower than expected due to the continued improvement of commercially-available screen-printing technology [9–11] and difficulties in achieving adequate plated metal adhesion strength. The use of soldered busbars for module interconnection is projected to continue for the foreseeable future [1], despite the development of low-temperature busbar-less configurations [12–15]. Consequently, it is desirable for plated contacts to withstand standard soldering and encapsulation practices.

A solution for enabling strong adhesion of plated contacts to silicon is through the use of picosecond lasers for the ablation of dielectric layers [4,5,7,16–21]. Picosecond laser ablation results in laser-induced periodic (nanoscale) surface structures which may form due to the interference between the incident laser beam and surface plasmon-polariton waves, or alternatively as proposed by Gurevich & Gurevich, hydrodynamic instabilities in the melt layer [22]. The roughened surface can provide numerous nucleation sites to anchor the plated metal and consequently, through this anchoring, adhesion of the plated metal to the silicon may be improved. Surface roughness has also been demonstrated to be critical for enabling strong plated metal adhesion to smoother, chemically-etched silicon surfaces [23–25].

This paper describes the development of nickel galvanic displacement (NiGD) plating [26] for the deposition of adhesion-promoting seed layers without requiring prior laser or chemical roughening of planar or alkaline-textured silicon surfaces. The NiGD process enables a reduction of one processing step compared to the chemical roughening procedures described in Ref [25]. Avoiding laser damage when creating openings in the dielectric can also reduce recombination in those regions. The deposition of nickel onto the silicon surface during NiGD plating is driven by localised redox reactions involving the

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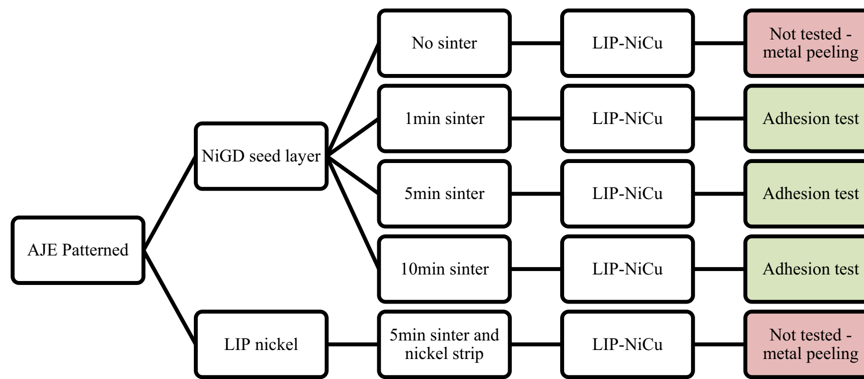


**Fig. 1.** Process flow for finger adhesion measurements for samples which were: (a) patterned using AJE and metallised using a NiGD seed layer; and (b) patterned using AJE and metallised using a LIP Ni seed layer. All sintering steps were conducted at 350 °C under $N_2$ ambient. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

oxidation of silicon to enable nickel reduction. The nickel-loaded, alkaline NiGD electrolyte does not contain reducing agents and is ideally driven only by the redox reactions occurring at the surface [27–29]. Yao et al. used NiGD plating to deposit sub-micron nickel layers in a self-limiting process. Although they commented on the improvement of plated metal adhesion that resulted [30,31], this improvement was not quantified in order to establish the real benefit. Furthermore, the study concluded that plating equipment refinements were required to improve temperature control, illumination directionality and ensure single-sided, dry-back plating in order to achieve reliable results.

This paper reframes the NiGD process as a surface priming step which improves the adhesion of LIP-NiCu contacts. The resulting plating deposit morphology and thickness using an updated NiGD plating tool was examined and the adhesion strength of NiGD/LIP-NiCu fingers was quantified using a stylus-based adhesion tester [32,33] and compared to LIP-only control groups. The optimised NiGD plating process was then applied to the metallisation of selective-emitter AJE devices featuring planarised contact grooves.

## 2. Material and methods

### 2.1. Surface and cross-sectional analyses

The samples prepared for electron microscopy analyses were alkaline-textured, 1 Ω cm, *p*-type, monocrystalline Czochralski (Cz) silicon wafers cut into squares with side lengths of 39 mm. A phosphorus emitter was formed on both sides of the wafers in a $POCl_3$ diffusion furnace, resulting in a sheet resistance of 60 Ω/□ and an electrically-active surface phosphorus concentration of $1\times10^{20}$ $cm^{-3}$. Wafer fragments were symmetrically-passivated with a $SiO_2$ (10 nm) - $SiN_x$ (65 nm) dielectric stack. Passivation of the entire rear diffused surface eliminated the possibly of LIP or corrosion-driven plating reactions and replicates the open-circuit, dry-back plating conditions established with the improved NiGD plating tool. Line openings were formed on one side of the wafer fragments using aerosol-jet etching (AJE) [34–36] to expose silicon regions ~35 µm wide. Nickel was then plated using NiGD on the exposed silicon regions in an electrolyte comprising 10% (w/v) ammonium fluoride ($NH_4F$) and 100 mM of nickel sulphate ($NiSO_4$) using a single-sided plating tool which prevented the electrolyte from contacting the rear surface of the wafer. Ammonium hydroxide ($NH_4OH$) was added to the electrolyte to adjust the pH to ~ 9. Nickel GD plating is a surface reaction and consequently no bias current/voltage was applied. Before plating, the exposed silicon regions were deglazed in 1% (w/v) hydrofluoric acid (HF) for 30 s to remove formed oxides. Nickel galvanic displacement plating was performed for 5 min at ~55 °C while illuminated by a 55 W compact fluorescent (CFL) light source [30]. The light intensity and luminosity, measured at the wafer surface using a hand held pyranometer and lux meter, were 60 W/$m^2$ and 20,000 lx, respectively.

Nickel deposits were examined using an FEI 'Nova NanoSEM 230' scanning electron microscope (SEM). The average thickness of the plated NiGD deposits was estimated using inductively-coupled plasma (ICP) spectroscopy [37]. In this process, the plated nickel was dissolved in a known volume of a dilute aqua regia solution [38] and subsequently analysed using ICP optical emission spectroscopy (OES) to determine the concentration of nickel in the aqua regia solution and therefore also the mass of nickel plated to the cell. The average thickness of the plated nickel layers was then calculated from knowledge of the total area of AJE line openings which was measured by spatially-calibrated optical microscope images.

Cross-sections of sintered NiGD contacts were milled with a focussed ion beam (FIB) and imaged using a Hitachi 'S3400' SEM and a Philips 'CM200' transmission electron microscope (TEM). TEM samples were also analysed via energy-dispersive x-ray spectroscopy (EDS) techniques to obtain an elemental analysis. All LIP-Cu samples imaged using a SEM or TEM were allowed to self-anneal in $N_2$ at 20 °C for a minimum of 30 days prior to imaging to ensure all possible grain growth was complete [39,40].

### 2.2. Adhesion measurements

Adhesion measurements were performed using 39 mm×39 mm wafer fragments laser cleaved from industrial *p*-type silicon wafers with an ~85 Ω/□ *n*-type $POCl_3$ emitter and a surface phosphorus concentration of $1\times10^{20}$ $cm^{-3}$ and a full-area screen-printed aluminium rear contact. The front surfaces were coated with a $SiO_2$ (10 nm) - $SiN_x$ (65 nm) anti-reflection coating (ARC), which had been exposed to peak temperature of 850 °C as part of the rear aluminium firing step. The ARC was patterned using AJE to form an array of 15 linear openings (width ~35 µm) spaced 1.5 mm apart.

Three categories of adhesion test samples were prepared: (a) unsintered NiGD seed layers with subsequently deposited LIP-NiCu; (b) sintered NiGD (with different sintering durations) with subsequently deposited LIP-NiCu; and (c) sintered LIP nickel seed layers with LIP NiCu [33]. All LIP of nickel and copper described in this work was conducted using a single-sided, external-bias plating tool. The process flow for the adhesion measurements is shown schematically in Fig. 1. For two groups (shown in red) the plated finger adhesion was insufficient to be measured.

The NiGD-treated samples were: (i) exposed to the NiGD solution for 5 min at 55 °C; (ii) if applicable, sintered in a rapid thermal processing (RTP) furnace at 350 °C for 1–10 min in a nitrogen gas ($N_2$) ambient; (iii) deglazed in 1% (w/v) HF; (iv) plated with MacDermaid 'Barrett SN' nickel sulphamate LIP solution for 2 min at 20 °C using a plating current of 23 mA/$cm^2$; and (v) plated with LIP copper in MacDermid 'Helios EP2 620' copper solution for 25 min at

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