Effect of Light on Electroless Nickel Deposition for Solar Cell Applications

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Abstract

In c-Si solar cell front contact metallization, nickel-copper electroplating scheme is found to be economical compared to other available techniques. In this metallization process, nickel seed layer deposition is looking simple but very important step in terms of its grain size, minimum thickness reaching the continuity of the film and its uniformity. Thin, uniform and continuous nickel seed layer helps in reducing the metal-semiconductor contact resistance as well as prevent junction shunting during silicide formation at the metal-semiconductor interface. Although, there are different process parameters affecting the morphology of the nickel film in electroless chemical bath deposition, but due to the photovoltaic effect of the p-n junction of the solar cell, the ambient light affects the nickel deposition process. The effect of light on electroless nickel (EN) deposition has been studied in this work. For this purpose the experiments have been performed in different lighting conditions like: dark, ambient, varying intensity UV-VIS light. Also, the nickel depositions have been done for different periods of time from very small period like 30s to longer periods like: 1 min, 2 min, 3 min and 4 min to see the effect at the initial stage of depositions as well as for prolonged deposition. Alkaline bath (pH ~7.5) was selected for EN-deposition and other experimental conditions were kept same for all the experiments. EN- deposition under dark is found to be the most suitable for nickel-copper metallization process and it is having some built-in benefits which have been mentioned in this work.

Keywords: Photo-irradiation effect, electroless nickel deposition, Ni-Cu metallization, c-Si, solar cell

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1. Introduction

Metallization is the second most expensive component in c-Si solar cell fabrication after silicon wafer and it significantly affects the solar cell performance [1]. Particularly, the front contact metallization is even more important in conventional n-type emitter c-Si solar cells as compared to rear side due to its lower contact area and requirement of least metal-semiconductor contact resistance with high line conductivity and better cell efficiency. In commercially available screen printed c-Si solar cells, front contact area is ~6-8 % of cell area for ~80 μm finger width which results in shading loss. Though, recent improvements in screen printing metallization technique have reduced the front contact shading loss below 5% without reducing the fill factor. But requirement of good metal line conductivity and limited potential to increase the aspect ratio put limitations on further reduction in shading loss [2]. Also, metallization cost is a matter of concerns in today’s competitive environment among different solar cell technologies. A variety of metallization techniques are available with varying performance, cost and reliability but economical as well as reliable metallization scheme is the present need of PV industry [3]. Low cost electroplated contacts (e.g. nickel-copper) are emerging as a potential solution to higher metallization cost as well as establishing a way for further improvement in cell performance which has reached to its stagnant point in present metallization context [2].

In Ni-Cu two step metallization, first nickel is deposited on n-type silicon emitter by EN-deposition, serving as a seed layer for further copper-electroplating and as a barrier layer for unwanted Cu-diffusion into the junction region. It is found that nickel seed layer of ~200 nm is sufficient as a diffusion barrier for copper [4]. After Ni seed layer formation, it is conventionally copper electroplated to increase the metal line conductivity. The EN deposition is an autocatalytic thermo-chemical process and does not require any external potential. The substrate is simply immersed into the Ni bath containing source of nickel ions, suitable reducing agent and heat to supply activation energy. Before Cu-electroplating, the nickel seed layer on silicon is essentially annealed at high temperatures (e.g. at 410ºC for 1 min) under inert environment to form nickel silicide (preferably NiSi) at the metal-semiconductor interface and in turn to get a low resistance ohmic contact with silicon emitter [5].

The role of nickel seed layer and silicide formation at the metal-semiconductor interface is very crucial in reduction of metal-semiconductor contact resistance as well as prevention of junction shunting [6]. So, uniform, continuous and thin seed layer formation is must for further silicidation and Cu-electroplating processes to get better cell performance. In EN-deposition, there are many parameters affecting the deposition rate as well as the quality of film like: pH, bath composition, plating temperature, plating period etc. Therefore, optimization of bath parameters is very important to make a good quality seed layer. Apart from this, it is observed that the conventional electroless nickel deposition is performed in ambient light conditions and not employing any specific ambient lighting condition. But for nickel deposition on n-type emitter of a solar cell, the ambient light can significantly affect the nickel deposition due to photovoltaic effect of the solar cell. In the present work, the effect of light on EN-deposition is investigated for the solar cell application. Under different light conditions, the experiments of EN-deposition are performed keeping rest of the process parameters constant so that the effect of light on EN-deposition could be seen in a good contrast and considered as a useful parameter in electroless nickel deposition.

**Nomenclature**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ARC</td>
<td>anti-reflective coating</td>
</tr>
<tr>
<td>DI</td>
<td>de-ionized</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray</td>
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<tr>
<td>EN</td>
<td>electroless nickel</td>
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<tr>
<td>FEG</td>
<td>field emission gun</td>
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<tr>
<td>NiSi</td>
<td>nickel mono-silicide</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
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<tr>
<td>Si$_3$N$_4$</td>
<td>silicon nitride</td>
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<tr>
<td>UV-VIS</td>
<td>ultra violet-visible</td>
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2. Experimental methods

EN-deposition was carried out on ~4 cm² n-type emitter to get the average properties of deposition as compared to conventional finger pattern in c-Si solar cells. Specimen preparation before EN-deposition, optimized nickel bath composition, setup used for nickel deposition under various UV-VIS light intensities, process steps for nickel deposition and techniques used for post-deposition nickel film characterization are discussed in detail from the next paragraph.

The specimens used for the experiments were laser cut semi-processed p-n junction c-Si solar cells without front side metallization. Emitter (substrate) was randomly textured and coated with silicon nitride as an anti-reflective coating (ARC). For laser cutting of bigger cells into smaller cells (2×2 cm²), CO2 laser (power 11W and wavelength 10,000 nm) was used. The schematic diagram of single junction crystalline silicon solar cell is shown in figure 1.

Since the EN-deposition has to be done on silicon emitter, the ARC coating of ~70 nm Si₃N₄ (silicon nitride) is removed by wet chemical etching process using 49% hydrofluoric acid solution {Merck, assay-49 %}. The rear side aluminum contacts of the specimen were protected from hydrofluoric acid by self-adhesive polymer sheets (cellulose-based pressure sensitive adhesive tape). After ARC removal, the samples were rinsed in DI-water and dried using nitrogen gun (N₂ purity ~ 99.999 %) and IR-lamp.

Chemical bath used for electroless nickel deposition constituted two chemicals viz. nickel chloride hexahydrate (NiCl₂.6H₂O) {Merck, assay-99 %} as a source of nickel ions and sodium hypophosphite (NaH₂PO₂.H₂O) {Merck, assay-99.5 %} as a reducing agent in DI water. For bath optimization with respect to deposition rate, uniformity and adhesion of the deposited film, three different EN-bath were studied as shown in table 1: bath 1 has higher Ni ion concentration and lower reducing agent concentration, bath 2 is the conventional Ni bath as reported in the literature [7] and bath 3 has higher reducing agent concentration as compared to conventional one (bath-2). The substrates (textured n-type Si emitter) for EN-deposition were kept horizontally upward in the nickel plating solution at 85±1°C. Bath-3 is found to be better with respect to uniformity of the nickel film as well as high deposition rate and it is used for the study of light effect on EN-deposition.

<table>
<thead>
<tr>
<th>Bath</th>
<th>NiCl₂.6H₂O (g/l)</th>
<th>NaH₂PO₂.H₂O (g/l)</th>
<th>Time of Deposition (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>20</td>
<td>5</td>
</tr>
</tbody>
</table>

There are two methods of electroless Ni deposition viz. using acidic bath or using alkaline bath. In acidic bath deposition the substrate needs to be catalytically activated e.g. using palladium chloride (PdCl₂) solution but alkaline bath doesn’t require substrate activation. Here for the experiments, alkaline method was used for EN-deposition. Nickel bath was prepared and heated in a borosilicate glass beaker maintained at constant temperature (85±1°C) and
constant pH (~7.5±0.1) during EN-deposition. For pH variation, ammonia solution (NH₄OH) {Merck, assay-30 %} was added in a very controlled manner.

The electroless nickel deposition was performed for different time periods (e.g. 60s, 120s, 180s and 240s) under different light intensities (dark, ambient light and different intensities of UV-VIS light). Low pressure mercury vapor lamp (Philips made, Max. light output-12000 lumens, type-ED28, color rendering index-70, length-8.25 inches, width-3.5 inches) was used as a source of UV-VIS light and for dark condition the bath was covered with a black box to prevent any ambient light to come in. The lamp was fixed at 26.5 cm of vertical distance from the solution level and substrate was horizontally submerged into nickel bath at a little depth of 1.2 cm so that considerable amount of light flux should reach the substrate submerged into the solution. Schematic diagram of EN-deposition for study of the effect of light is shown in figure 2.

![Schematic diagram of EN-deposition for study of the effect of light](image_url)

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**Fig. 2. Schematic of processing steps for electroless Ni deposition with varying light conditions.**

The UV-VIS light intensity was varied using autotransformer and variation was measured in terms of illuminance level using Lux-meter (Sigma Instrument, with accuracy of ±5%). To study the initial stage of nickel deposition, the nickel depositions were carried out for smaller period of time (e.g. 30s) under UV-VIS light (3500±100 Lux) and dark. After nickel deposition the samples were quickly removed from the nickel bath, properly rinsed with DI water and dried using nitrogen gun and IR lamp. The nickel deposited specimens were characterized by the Field Emission Gun-Scanning Electron Microscope (Model-JSM-7600F and Magnification-X25 to 1,000,000) equipped with an energy dispersive X-ray spectrometer (EDX).
3. Results and discussions

Variation in uniformity, continuity and surface morphology of EN-deposits have been observed by varying ambient light intensities during EN-depositions as shown in figure 3 [luminous intensity, deposition time and SEM image magnification]. So, there is significant effect of light on continuity, uniformity and surface morphology of EN-deposition because photo-generated electrons affect the deposition process.

![Fig. 3. SEM images (top view) showing variation in surface morphology of electroless nickel deposition due to effect of light: (L1) 2150 Lux, 60s, 5 kX; (A1) 510 Lux, 60s, 5 kX; (D1) dark, 60s, 5 kX; (L2) 1820 Lux, 120s, 5 kX; (A2) 450 Lux, 120s, 5 kX; (D2) dark, 120s, 5 kX; (L3) 1880 Lux, 180s, 5 kX; (A3) 480 Lux, 180s, 5 kX; (D3) dark, 180s, 5 kX; (L4) 1870 Lux, 240s, 2 kX; (A4) 500 Lux, 240s, 2 kX; (D4) dark, 240s, 2 kX; Other bath conditions were kept similar (bath-3, pH ~ 7.5, 85±1ºC). Light intensity (luminosity) was measured at the surface of EN-bath.](image)

The electroless nickel deposition on silicon substrate occurs in the form of nanoparticles. It is the process of nucleation and growth, initially the nuclei of nickel are formed and since it is an autocatalytic process, nickel nuclei grow and form a continuous nickel film. It can be clearly seen from the scanning electron micrographs of the nickel depositions under different light luminance as shown in figure 3. In case of dark condition, the uniformity of the nickel film is better as compared to other light conditions.

Also, in dark condition there is a better uniformity of the nickel film across the textured silicon surface. It can be seen from the cross-sectional SEM images of EN deposited samples for 120s under various lighting ambiances as shown in figure 4 [luminous intensity, deposition time and SEM image magnification].
Fig. 4. Cross-sectional SEM images of EN-deposited samples for 120s in different light conditions: (L2) 1820 Lux, 120s, 15 kX; (A2) 450 Lux, 120s, 15 kX; (D2) dark, 120s, 15 kX; keeping the rest of deposition conditions same.

The uniform, continuous and thin nickel film is having some built-in benefits like: uniform inter-diffusion and NiSi formation, reduction in contact resistance and overall metal sheet resistance, higher shunt resistance due to reduced nickel diffusion during the silicidation step and copper diffusion into junction region, lower stress level and adhesion improvement at the Si-Ni interface after annealing and finally efficient material use and induced cost reduction.

The most uniform, continuous and optimum deposition for solar cell front contact metallization using nickel-copper two step metallization is observed from 120s EN-deposition under dark condition as shown in figure 5. This is the best deposition among other deposition conditions with varying ambient light condition only and keeping rest of the process parameters constant.

Fig. 5. SEM image (top view) of uniform EN-deposition for 120s in dark ambience keeping the rest of deposition conditions same.

It is also reported that low-phosphorus content (3-5 wt. %) EN-deposits are either crystalline or consist of microcrystalline nickel, medium-phosphorus content (5-8 wt. %) deposits are either fully amorphous or mixtures of microcrystalline and amorphous phases, high-phosphorus content deposits could be fully amorphous [8]. Samples were also analyzed with respect to phosphorous content in EN-deposits using EDX data for various light luminance and deposition time.
A clear variation in phosphorous content is observed with respect to lighting conditions as shown in figure 6. For nickel deposition in dark condition, the phosphorous content in nickel film is found to be minimum (6-7%) and constant over the different deposition periods. The low phosphorous content also helps in reducing the formation of nickel phosphide during the silicidation process and in turn reducing the contact resistance.

3.1. Suggested Mechanism for variation in deposition morphology

The adverse effect of light on uniformity of nickel seed layer is proposed to be due to the suppression of nucleation process in presence of light. In EN-deposition, the very initial stage of deposition or nucleation occurs due to reduction of nickel ions by the electrons supplied by the local oxidation of silicon substrate [9]. But in presence of light, due to photovoltaic effect, the front side of the substrate (silicon emitter) becomes negatively charged, flooded with electrons which suppress the nucleation and oxidation of silicon substrate but conduct through the least resistance path (i.e. through emitter and already formed nickel nuclei thus enhancing their growth). To check this hypothesis, EN-deposition has been performed for smaller duration (i.e. 30s) under light and dark keeping all other deposition conditions same. It is found that under dark condition, the nucleation is found to be higher as shown in figure 7. Thus nucleation density decreases due to presence of light. As the time passes, growth dominates over nucleation and it is led by the reduction due to electrons supplied by the reducing agent.
Also, there is a local variation found in the deposition and growth from peak to valley of the textured substrate. It could be due to the deficient supply of the reactants in the valley region because there is diffusion limited mass transport of the reactant species and the valley region gets reduced supply due to enhanced demand from the peak region. This variation in reduced nucleation density and their enhanced growth due to the presence of light can be seen in a greater contrast for a little longer deposition like: 2-3 min.

4. Conclusion

Ambient light condition needs to be considered as an important parameter like other process parameters of the EN-deposition for solar cells because it affects the deposition process and nickel film characteristics significantly. Also, reliability and performance of the nickel-copper contact is very much dependent on the characteristics of nickel seed layer. Low phosphorous content, uniform, continuous and thin nickel seed layer deposition is desirable for better cell performance using nickel copper front contact system. Nickel deposition for ~2 min under dark ambience is found to be quite uniform from peaks to valleys of the textured emitter which is well appropriate to the nickel-copper metallization process for solar cells.

Acknowledgements

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