FORMATION OF A LOW OHMIC CONTACT NICKEL SILICIDE LAYER ON TEXTURED SILICON WAFERS USING ELECTROLESS NICKEL PLATING

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ABSTRACT: This paper presents a low cost process for fabrication of high efficiency silicon-based solar cells from front side ARC patterning through contact line metallization. This process utilizes a screen printable etch resist to define the contact pattern and a wet etching solution to remove the exposed ARC layer. The metallization stack for the contact line pattern consists of a nickel silicide ohmic contact and a nickel and copper metal stack plated using a light induced plating (LIP) process. The nickel silicide contact is formed by annealing a thin nickel seed layer that is deposited on the silicon surface using two different alternative seed layer (ASL) processes, chemically activated and light assisted electroless plating. Through optimization of the ASL processes, a thin, uniform NiSi layer is achieved that is less than 200 nm. This thin NiSi layer should be compatible with shallow emitter silicon solar cells. An LIP process for nickel and copper over the NiSi contact areas is demonstrated.
Keywords: metallization, electrodeposition, contact

1 INTRODUCTION

Screen printing is widely used today as the metallization technique for industrial solar cells. Based on interest from PV cell manufacturers to reduce cost and minimize the limitations of their current technology platform, several options are being evaluated for better overall value. Alternative front side metallization processes for silicon solar cells have the potential to increase solar cell efficiency compared to the standard screen printed silver paste. Light induced electroplating (LIP) of silver metal over front grid contacts shows promise to reduce line resistance and increase cell power output [1, 2, 3]; however, the cost of plating a precious metal layer may limit acceptance into the industry. The feasibility of replacing silver plating with low cost nickel and copper plating has been demonstrated by Technic Inc [4] and provides the opportunity to improve solar cell performance without the introduction of costly precious metal plating. However, this method still involves the use of a precious metal paste to form front contact grid lines with limited line resolution. A two-step process has been proposed to form the front grid lines through the use of advanced electrodeposition techniques: 1) deposition of a nickel seed layer directly on the silicon to form a low resistivity nickel silicide ohmic contact and 2) thickening of the nickel seed layer with plating in order to achieve a high conductivity, high aspect ratio contact line [5-7].

Electroless nickel plating is a low cost and manufacturable method to deposit a nickel seed layer. Significant work has been done to show that low resistivity nickel silicide ohmic contact layers can be formed on silicon using electroless nickel plating coupled with a low temperature anneal [5-12]. However, much of this work has been performed on smooth silicon surfaces such as silicon wafers used to fabricate complementary metal–oxide–semiconductor (CMOS) devices or laser grooved trenches in silicon solar cells to create buried contacts [8-12]. Formation of a uniform nickel silicide layer onto the current PV industrial textured silicon surface requires modification of the electroless nickel plating process to ensure that both the tips and the base of the pyramids that result from the texturing process have uniform coverage.

Light induced plating (LIP) of nickel and copper over the nickel silicide ohmic contact has been proposed to reduce cost and increase the conductivity of the front grid line [6]. A successful LIP process requires optimization of the chemistry, light source, and backside potential applied via an external power supply. The negative potential induced by the light source should attract the positively charged metal ions out of the bath while the current applied to the backside minimizes the anodic dissolution of the Al. In addition, the plated nickel layer must serve as a diffusion barrier to copper migration.

This paper will discuss a low cost process utilizing an alternative seed layer (ASL) process coupled with light induced plating (LIP) of nickel and copper to fabricate high efficiency Si-based solar cells. The quality and uniformity of the nickel silicide layer that is formed on the textured surface of an industrial silicon solar cell using two different ASL processes will be discussed. In addition, LIP of nickel and copper over the nickel silicide contact layer will be demonstrated.

2 EXPERIMENTAL

Figure 1 illustrates the low cost process used to fabricate high efficiency Si-based solar cells from front side ARC patterning through contact line metallization. Industrial supplied textured silicon solar cells with an n-type emitter layer and a silicon nitride ARC layer are used to evaluate the low cost fabrication process depicted in Figure 1. TechniSol UV-PR etch resist [13] is screen printed over the ARC layer of the textured silicon solar cells in order to define the desired pattern for metallization. A proprietary non-HF etching solution developed by Technic Inc is used to remove the ARC layer in the open areas of the resist pattern. Two different alternative seed layer (ASL) processes using electroless nickel plating are evaluated for deposition of the nickel seed layer: 1) chemically activated or 2) light

assisted. The chemically activated electroless process is tested using two different formulations, Process A and Process B. The electroless nickel chemistry utilized is a proprietary chemistry formulated by Technic Inc. The pH of the electroless nickel bath is 8-10, the metal source is $NiSO_4$, and the reducing agent is hypophosphite. The bath is operated between 75 - 90 °C. The targeted nickel seed layer thickness is 100 – 200 nm. Anneal temperatures ranging from 350 – 750 °C are investigated for conversion of the nickel seed layer into the nickel silicide ohmic contact. TechniSol Ni 2420 [13] and TechniSol Cu 2440 [13] are deposited on the contact area using LIP plating.
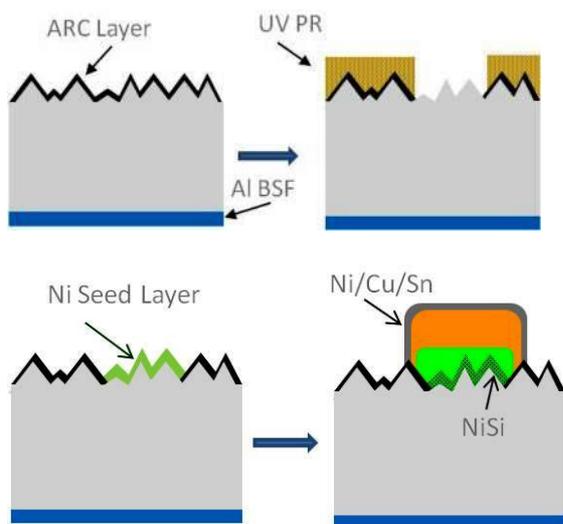

Figure 1: Low cost fabrication process with an alternative seed layer (ASL) process and LIP of nickel, copper, and tin.

The resulting nickel silicide layer and nickel/copper contact lines were characterized using sheet resistance measurements and scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS) and focus ion beam (FIB). An X-ray diffraction (XRD) method was deployed to characterize the formed nickel silicide phases after the annealing treatment. Transmission line model (TLM) method was used to estimate the contact resistivity [14-15] based on a TLM pattern consisting of isolated square contacts separated by variable distances. The TLM pattern was fabricated using the process depicted in Figure 1. The resistance between each set of contacts was measured using a 4pt probe and the results were fitted to the TLM model to extract the specific contact resistance. Solar cell characterization on 156 x 156 mm silicon solar cells are currently in process and will be reported in future publications.

3 RESULTS / DISCUSSION

Screen printing of the TechniSol UV-PR etch resist on the silicon nitride ARC layer followed by etching of the silicon nitride with a non-HF chemistry is a low cost method for patterning the ARC layer without damaging the silicon emitter layer. In this study, line widths ranging from 100 – 160 um are investigated; however, future work will focus on reducing these lines widths

either through optimization of the TechniSol UV-PR screen printing process or development of an alternative method for deposition of the etch resist. The resulting silicon surface exposed after etching is free of silicon nitride and the emitter layer is not damaged by the etching solution. Deposition of a thin and uniform nickel seed layer directly on the exposed silicon surface has been demonstrated for both the chemically activated and light assisted electroless processes. Figure 2 shows a typical FIB cross section of the textured silicon solar cell with a uniform nickel seed layer deposited directly over the silicon having a thickness of 145 ± 20 nm. However, uniform deposition of the nickel seed layer does not ensure a uniform, thin formation of nickel silicide post annealing. The quality of the interface between the deposited nickel seed layer and the silicon impacts the formation of the nickel silicide layer.
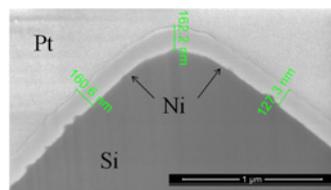

Figure 2: FIB cross section of nickel seed layer on textured silicon solar cell.

For example, the top down SEM image shown in Figure 3a is the silicon surface after the anneal is completed. The bright areas on the surface are the islands of nickel silicide formed. Even though the orginal nickel seed layer deposited using the light assisted electroless process was uniform across the entire surface, the resulting NiSi after anneal is not uniform. Figure 3b illustrates an improvement in the uniformity of the nickel silicide coverage when the chemistry and light source for the light assisted deposition method are modified to improve the interface between the deposited nickel seed layer and the silicon surface. Chemistry improvements have also been made to the chemically assisted seed layer process to improve the uniformity of the nickel silicide formed over the textured silicon surface. In addition, the annealing time and temperature requires optimization for each seed layer process used. Figure 4a, shows the SEM top down image of a sample created with the chemically activated seed layer process and annealed at an un-optimized condition. The same chemically activated seed layer process has been used on the sample depicted in Figure 4b but the annealing time and temperature have been modified to produce a more uniform coverage of NiSi on the surface of the silicon.
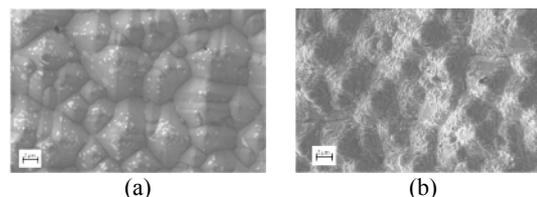

(a)   (b)

Figure 3: Top down SEM image of nickel silicide coverage on textured silicon solar cell formed from a light assisted seed layer process: (a) non-uniform coverage, (b) improved coverage of nickel silicide
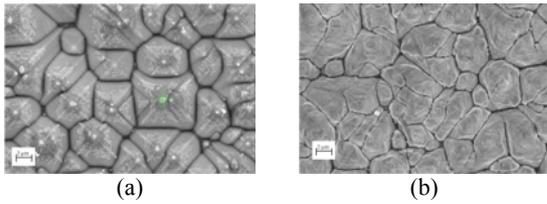
(a)   (b)

Figure 4: Top down SEM image of nickel silicide coverage on textured silicon solar cell formed from a chemically assisted seed layer process: (a) un-optimized annealing condition, (b) optimized annealing condition

In order to form a good ohmic contact, the NiSi not only needs to be uniform across the contact area but also thin. If the NiSi formed is too thick, it will shunt the emitter layer. This is especially problematic for solar cells with shallow junctions. For example, the NiSi layer that is created during annealing should not be thicker than 200 nm for some shallow junction solar cells. Control of the interface quality between the nickel seed layer and the silicon as well as optimization of the annealing time and temperature are key to formation of a thin, uniform nickel silicide layer. Figure 5 is a FIB cross-section of a thin, uniform NiSi layer formed on the textured silicon surface. The thickness of the NiSi is 100 ± 50 nm. Typically, the NiSi formation will be thicker at the tips of the pyramids and thinner in the valleys. Optimization of the chemistries used to deposit the seed layer greatly impact the uniformity of the nickel silicide formation across the textured features.
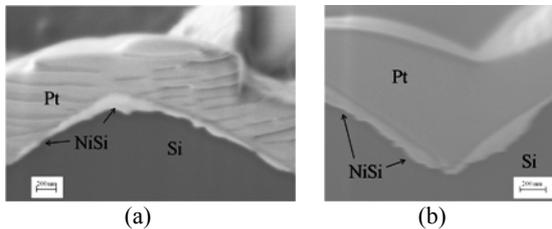

(a)   (b)

Figure 5: FIB cross section of textured silicon solar cell with thin, uniform NiSi formed (a) tip of pyramid, b) valley of pyramid

Normal θ-2θ XRD spectra comparing the nickel silicide crystalline phases that resulted from the different activation methods are shown in Figure 6. The XRD spectra were compared with reference patterns from the standard Joint Committee for Powder Diffraction Standards (JCPDS) powder diffraction file (PDF). The presence of reflection peaks at 31.67^o corresponding to NiSi(011), 45.84^o NiSi(112), and 47.33^o NiSi(211) confirm that nickel mono-silicide is formed on all the samples analyzed. The samples processed using both chemical activation processes A and B demonstrate well defined peaks for all of the main NiSi orientations, 23.1^o NiSi (101), 31.67^o NiSi(011), 34.25^o NiSi(200), 36.1^o NiSi(111), 45.84^o NiSi(112), 47.33^o NiSi(211), 51.4^o NiSi(103), and 56.4^o NiSi(020). There is clearly a predominant presence of NiSi phase in all samples.
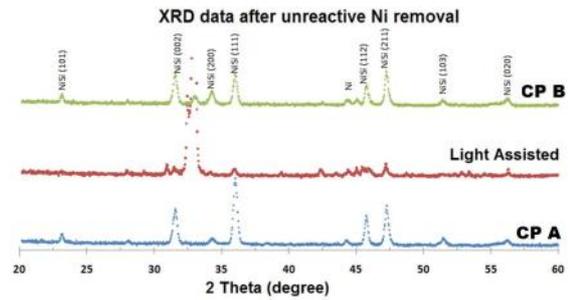

Figure 6: Normal θ-2θ XRD spectra for NiSi layer formed from chemically activated (CP A & CP B) and light assisted nickel seed layer processes.

Thick metallization above the NiSi ohmic contact is required to form low resistance contact lines. LIP of nickel and copper can be used to effectively build up the contact lines. A solderable layer such as tin should also be applied over the copper and will be evaluated in the future. The quality of the solar cell, the wavelength and intensity of the light source, and the current applied to the backside all impact the LIP process. A minimum light intensity is required to enable the LIP mechanism. Careful selection of the light source is required for successful nickel and copper deposition. Figure 7 illustrates the impact of light sources with different wavelengths on the copper plating rate at a given current applied to the backside. Changing the backside current density impacts this relationship and the plating rate.
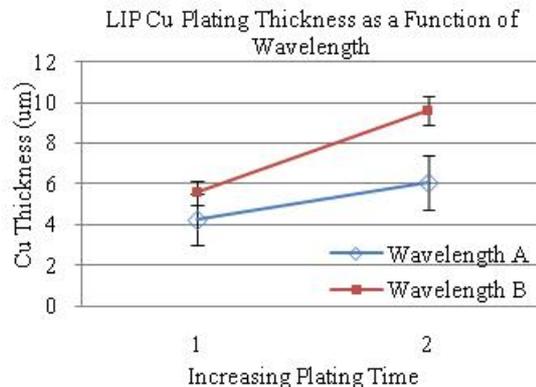

Figure 7: Impact of light source wavelength on LIP of copper

When the aluminum metallized backside of the solar cell is immersed in the LIP plating solution, the current applied to the backside should be sufficient to prevent aluminum from dissolving; however, too much applied current will initiate plating on the backside. A proposed high volume manufacturing LIP plating tool, TechniSol Si LIP 2400 [13] is designed to prevent the plating solution from coming in contact with the backside of the solar cell, easing the restrictions on the applied backside current. However, for this study, the backside was immersed in the plating solution so the light source wavelength and intensity were optimized taking into account the narrow range for the backside current density.

Figure 8 is a mechanically polished, cross sectional SEM image showing the resulting plated stack on the NiSi ohmic contact area of the textured silicon solar cell.

The nickel and copper metal layers are approximately 3 um and 8 um, respectively. The interface between each layer appears uniform and free from defects which indicates good adhesion of the stack. Studies to look at the adhesion of the stack across the 156 x 156 mm solar cell are currently in progress.
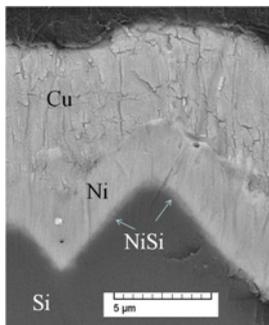

Figure 8: Mechanically polished SEM cross sectional image of the NiSi/Ni/Cu grid line on a textured silicon solar cell

Contact resistivity is estimated using transmission line modeling (TLM) [14-15]. As reported in the literature [16-17], contact resistivity measurements made using TLM on textured surfaces have different values than those measured on planar surfaces. In this study, contact resistivity for NiSi is measured after the final nickel and copper stack is plated to assure a proper contact between the probes and the metal pad. An initial specific contact resisitance measurement of 6 mΩ-cm^2 is reported. This is comparable to what has been reported for NiSi on textured surface [18]. Further optimization of the nickel silicide thickness and uniformity is currently in progress to achieve lower contact resistivity for shallow emitter solar cells.

4   CONCLUSIONS

A low cost process for fabrication of high efficiency Si-based solar cells from front side ARC patterning through contact line metallization has been demonstrated. Two different ASL processes, chemically activated and light assisted electroless plating, have been used to deposit a thin, uniform nickel seed layer on textured silicon solar cells with an n-type emitter layer. Optimization of the ASL process to control the nickel / silicon interface enabled the formation of a thin, uniform NiSi layer post annealing. This NiSi layer is less than 200 nm and should be compatible with shallow junction silicon solar cells. LIP of nickel and copper were successfully deposited over the NiSi contact areas.

5   FUTURE WORK

Complete characterization of a 156 x 156 mm industrially supplied silicon solar cell fabricated by this process is currently underway.

6   ACKNOWLEDGEMENTS

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