COMPATIBILITY OF THE ALTERNATIVE SEED LAYER (ASL) PROCESS WITH MONO-Si AND POLY-Si SUBSTRATES PATTERNED BY LASER OR WET ETCHING

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ABSTRACT

An alternative seed layer (ASL) process is proposed in order to increase the efficiency of silicon solar cells by forming a low cost, front metal contact with reduced contact resistance and increased line conductivity and aspect ratio. A nickel seed layer is deposited directly on silicon to form a low resistivity nickel silicide (NiSi) ohmic contact and this contact is thickened by light induced plating (LIP) of nickel and copper. Unlike the traditional screen printing process currently used in industry, the ARC layer must be patterned to expose the silicon surface for nickel deposition. This paper investigates the compatibility of the ASL process with two different ARC patterning methods: 1) masking & wet chemical etching, and 2) laser ablation. In addition, the ASL process is demonstrated on both mono-crystalline and polycrystalline silicon substrates with ARC layers from different sources. The nickel seed layer and resulting NiSi layer are evaluated using scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS) and focused ion beam (FIB) cross section. X-ray photoelectron spectroscopy (XPS) is used to investigate the completeness of the ARC removal step. In addition, contact resistance testing will be performed to determine the quality of the ohmic contact formed from the ASL process. The importance of chemistry optimization in the development of a robust ASL process that is compatible with mono-Si and poly-Si substrates and exposed to two different ARC patterning methods will be discussed.

INTRODUCTION

It has been shown that an alternative seed layer (ASL) process coupled with light induced plating (LIP) of nickel and copper can produce high quality, low cost front metal contacts for industrial high efficiency silicon solar cells [1]. Nickel mono-silicide (NiSi) has been discussed as the favored metal silicide for formation of ohmic contacts in silicon solar cells due to a low silicide formation temperature and low silicon consumption [2]. However, in order to form this NiSi ohmic contact on a silicon solar cell, the ARC layer, typically silicon nitride, must be removed in order to expose a clean silicon surface.

Selectively removing the ARC layer without damaging the underlying silicon emitter layer is challenging, especially for a high efficiency silicon solar cell with a shallow junction emitter depth of 200-250 nm. Two of the more common approaches used for patterning the ARC layer are 1) masking & wet chemical etching and 2) laser ablation [3]. In the masking & etching process, a photo resist is used to pattern the ARC layer, exposing only the gridline and bus bar pattern. A wet chemical etching solution removes the silicon nitride in the exposed areas. The second technique is to ablate the ARC layer with a laser beam.

Once the ARC layer is removed, the NiSi ohmic contact can be formed by depositing a nickel seed layer directly on the exposed silicon surface and annealing to form NiSi. For solar cells with shallow junction emitters, the NiSi formed must be thin and uniform or the shallow emitter may be shunted [3]. In order to form a uniform, thin NiSi ohmic contact at a low temperature, the interface between the deposited nickel metal and the silicon must be free from any contamination. The presence of an oxide or other type of interlayer between the nickel metal and silicon will serve as a kinetic barrier to the formation of NiSi at the desired low temperature. [4,5] The ARC patterning and activation steps, prior to nickel deposition, play a very important role in determining the quality of the interface between the nickel metal and silicon.

For example, the masking & wet chemical etching step is expected to result in less damage to the shallow silicon emitter layer [1,3]; however, the standard etching solution may not be effective on all varieties of ARC layers that are deposited by different cell manufacturers. Although laser ablation requires less processing steps and is able to produce very fine lines, the laser parameters need to be tightly controlled to ensure the ARC layer is ablated without melting the underlying silicon and damaging the shallow emitter layer [6,7]. Both of these patterning techniques require optimization for use on both mono-Si and poly-Si substrates. Therefore, one of the challenges with ASL is to develop a robust process that is compatible with mono-Si and poly-Si cells having varying ARC compositions and patterned with different methods.

EXPERIMENTAL DETAILS

Industrially supplied 156 x 156 mm mono-Si and poly-Si textured solar cells with an n-type emitter layer and screen printed Al backside are processed through both 1) masking & wet chemical etching and 2) laser ablation processes. The solar cells are from multiple sources so the ARC layer composition and deposition method for each sample is different. Figure 1 illustrates the ASL process used to fabricate these cells with the option of ARC patterning by both processes. For the masking & wet chemical etching step, TechniSol UV-PR etch resist [8] is screen printed over the ARC layer of the textured silicon solar cell, both mono-Si and poly-Si, in order to define the desired pattern for metallization. A proprietary wet etching solution developed by Technic Inc. is used to remove the ARC layer in the open areas of the resist pattern. Alternatively, the laser ablation process is performed by various suppliers and the cells are received with the laser ablated lines completed in order to test the ASL process. A proprietary activating solution developed by Technic Inc. is used to prepare the laser ablated cells for the nickel seed layer deposition.

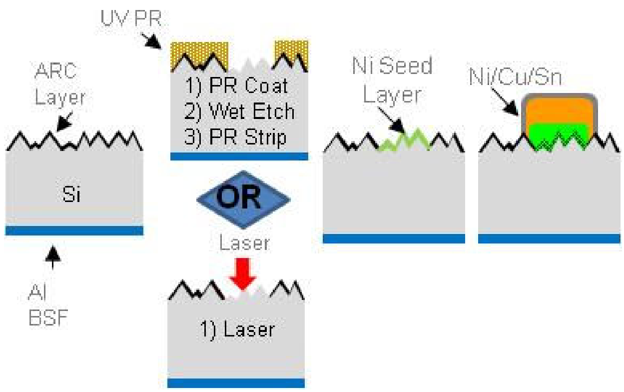

Fig. 1: Alternative Seed Layer (ASL) process for either 1) Mask & Etch or 2) Laser Ablation

The nickel and copper layers are deposited using Technic Inc.'s laboratory scale light induced plating (LIP) tool designed to keep the backside of the solar cell dry during plating. A proprietary nickel solution developed by Technic Inc. is used to deposit the nickel seed layer directly on the silicon surface. The copper layer is deposited using TechniSol Cu 2440 [8]. The nickel silicide ohmic contact is formed after an anneal ranging in temperature from 350-750 °C.

The resulting NiSi layer and the nickel/copper contact lines are characterized using scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS) and focus ion beam (FIB) cross-section. An X-ray diffraction (XRD) method is used to characterize the formed nickel silicide phases on both the mono-Si and poly-Si cells after annealing. The specific contact resistance of the NiSi contact is estimated using the Transmission line model (TLM) method. For the masking & wet chemical etching samples, x-ray photoelectron spectroscopy (XPS) technique is used to investigate the completeness of the ARC removal step. Solar cell characterization on 156 x 156 mm silicon solar cells are currently in progress and will be reported in future publications.

RESULTS

Masking & Wet Chemical Etching Samples

Complete removal of the silicon nitride ARC layer is necessary for successful metallization with the ASL process. Previously [1] it was demonstrated that thin, uniform NiSi layer with a thickness less than 200 nm could be formed on mono-Si cells using Technic Inc.'s ASL process with masking & wet chemical etching for patterning the ARC layer. The type of solar cell substrate and the composition of the ARC layer can greatly impact the performance of the wet etching solution. For example, textured poly-Si cells from two different sources, ARC1 and ARC2, were tested with the proprietary wet etching solution previously demonstrated [1] on mono-Si cells. Figures 2a & b show top down SEM images for ARC1 and ARC2 after wet etching and nickel plating. The nickel seed layer shown in Figure 2a has full coverage; whereas, the nickel seed layer shown in Figure 2b is not complete. XPS analysis was performed on the silicon surface after removal of the silicon nitride layer using this initial wet etching solution. The nitrogen signal on the silicon surface after wet etching for ARC1 was ~1.5 at%. In comparison the nitrogen signal for ARC2 was 10 times higher at ~15 at%. These results indicate that the silicon nitride was not completely removed from ARC2 prior to nickel deposition. Whereas, the same etching solution removed the silicon nitride layer from ARC1 and the mono-Si cell previously tested [1].

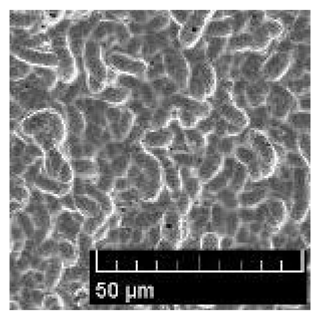

Fig. 2a) Initial Wet Etch & Ni Plating for ARC1

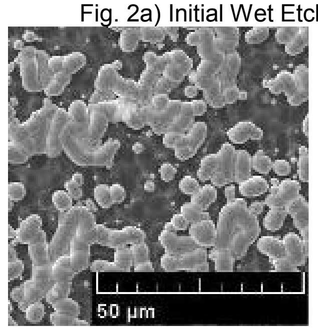

Fig 2b) Initial Wet Etch & Ni Plating for ARC 2

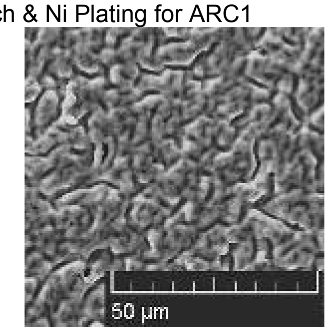

Fig. 2c) Re-formulated Wet Etch & Ni Plating for ARC2

This wet etching solution was reformulated to achieve a robust chemistry that would remove the silicon nitride layer on all cells tested. The top down SEM image in Figure 2c demonstrates that full coverage of the nickel seed layer was achieved on the poly-Si ARC2 cell using the reformulated wet etching solution. Table 1 summarizes the XPS results for the poly-Si cells processed through the wet etching process. The nitrogen signal for ARC2 after wet etching with the reformulated chemistry was not detectable.

Table 1: XPS Results for poly-Si samples after Wet Etch

ARC Type	Wet Etch	Nitrogen (at%)
ARC 1	Initial formulation	1.5
ARC 2	Initial formulation	15
ARC 2	Re-formulated	Not detected

After patterning of the ARC layer using the masking & wet etching process, a nickel seed layer is deposited and annealed to form the NiSi ohmic contact. Figure 3a & b show FIB cross-sections of the thin, uniform NiSi layers obtained for (a) mono-Si and (b) poly-Si substrates processed through the ASL process.

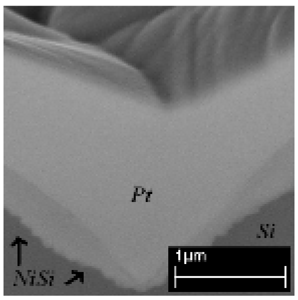

Fig. 3a) Mono-Si with thin NiSi layer

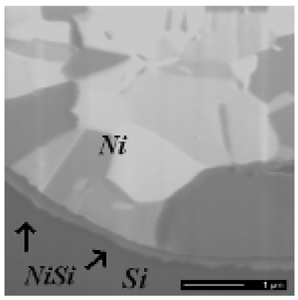

Fig. 3b) Poly-Si with thin NiSi layer

Normal θ-2θ XRD spectra were collected from mono-Si and poly-Si textured solar cell substrates processed through the masking & wet chemical etching, ASL nickel, and low temperature annealing processes. The XRD spectra were compared with reference patterns from the standard Joint Committee for Powder Diffraction Standards (JCPDS) powder diffraction file (PDF). Figure 4 shows that the XRD spectra collected for both mono-Si and poly-Si cells have reflection peaks at the main NiSi orientations confirming that nickel mono-silicide is successfully formed on both substrate types using the ASL process.

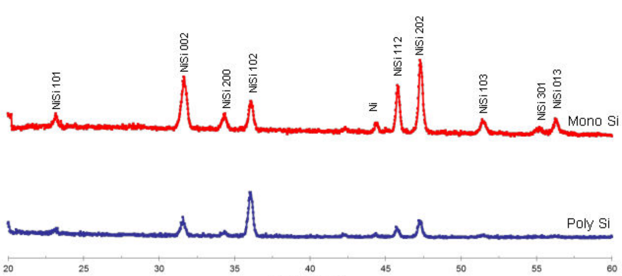

Fig. 4) Normal θ-2θ XRD spectra for NiSi layer on mono-Si and poly-Si substrates

Laser Ablated Samples

Laser ablation can also be used to pattern the ARC layer prior to the formation of a NiSi ohmic contact. Laser ablation has fewer processing steps than the masking & etching method; however, the shallow silicon emitter layer may be melted or a thermally grown SiNx layer may form on top of the silicon if non-optimized laser parameters are used during the ablation process [6,7]. After the laser ablation step, the silicon surface may form an oxide layer when exposed to air. Therefore, an activation step may be required after laser ablation and before the nickel seed layer deposition to ensure a clean interface between the nickel and silicon. Since the ARC layer is exposed during this activation step, the activating solution must not damage the ARC layer.

Two laser ablated poly-Si samples from two different sources were exposed to the activating solutions listed in Table 2 prior to the nickel seed layer deposition. The stronger the activating solution, the more potential damage to the exposed ARC layer if the time is not carefully controlled.

Table 2: Activating Solutions for Laser Ablated Substrates

Name	Strength	ARC Damage
AA10	Weak	No: 10+ min
AA0	Medium	No: 1 min maximum
AA1	Strong	No: 1 min maximum

Figure 5 shows top down SEM images of the two different laser ablated samples processed through the weakest activating solution, AA10. No ARC damage is observed with this activating solution up to 10 minutes, the maximum time tested. Sample #1 has incomplete coverage on the laser ablated surface; whereas, Sample #2 has complete coverage.

Figure 6 illustrates that both laser ablation samples have uniform coverage of nickel when a stronger activating solution, AA1, is used; however, the ARC layer will be damaged if this step is extended beyond 1 minute.

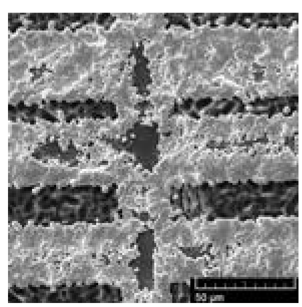

Fig. 5a) Sample #1, AA10, Incomplete coverage

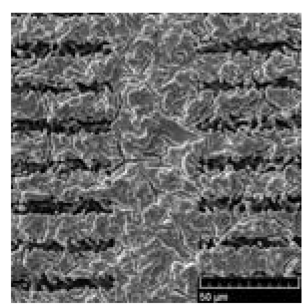

Fig. 5b) Sample #2, AA10, complete coverage

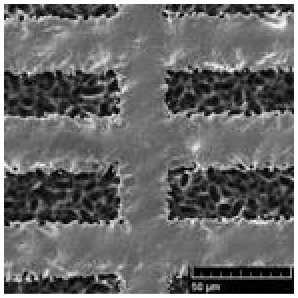

Fig. 6a) Sample #1, AA1, complete coverage

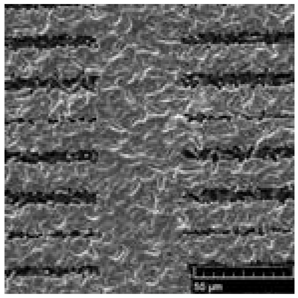

Fig. 6b) Sample #2, AA1, complete coverage

Industrially supplied and textured mono-Si and poly-Si laser ablated samples were processed through the activating solution and ASL nickel plating process. After a low temperature anneal, FIB cross-sections were obtained to look for NiSi formation. Figure 7a illustrates that a fairly uniform and thin NiSi layer is obtained for the mono-Si cell. However the poly-Si cell shown in figure 7b does not form NiSi. Although complete coverage of plated nickel is realized on this poly-Si sample, it did not form a uniform NiSi layer post annealing.

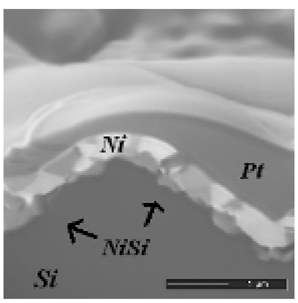

Fig. 7a) NiSi on mono-Si with original Ni solution

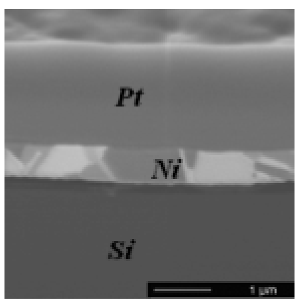

Fig. 7b) No NiSi on poly-Si with original Ni solution

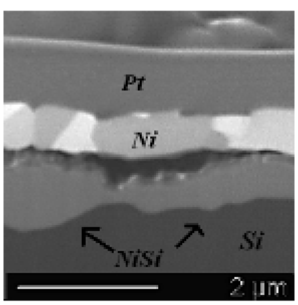

Fig. 7c) Thick NiSi on poly-Si with modified Ni solution

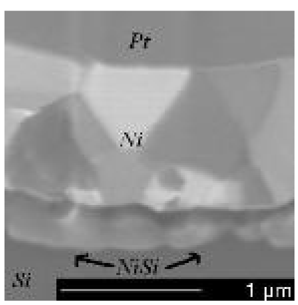

Fig. 7d) Thin NiSi on poly-Si with modified Ni solution & reduced annealing

A systematic study was performed to vary different components of the nickel plating solution in order to determine the impact of these components on the formation of NiSi. A poly-Si cell similar to that shown in Figure 7b was processed through the modified nickel solution. The same low temperature anneal was performed on this sample as the one from Figure 7b. Figure 7c shows that a very thick NiSi layer is formed on the poly-Si solar cell processed through the modified nickel solution. Figure 7d illustrates that a thin, uniform NiSi layer is achieved on the poly-Si solar cell by reducing the annealing time and temperature. The same activating and plating solutions are used for samples 7c & 7d, only the annealing conditions are changed. Therefore, it has been demonstrated that a thin, uniform NiSi layer can be achieved on both mono-Si and poly-Si laser ablated solar cells after modifying the activating and nickel plating solutions used. The modified nickel solution can also be used with the masking & wet etching patterning method. In addition, the thermal budget required to form a thin, uniform NiSi layer decreased as a result of using the modified nickel plating solution to deposit the nickel seed layer.

Formation of the thin, uniform NiSi contact layer is expected to reduce the specific contact resistivity of the solar cell. The contact resistance of the solar cell depends on the sheet resistance and doping level of the emitter layer and the quality of the ohmic contact formed between the front metallization and the silicon emitter. Two poly-Si laser ablated solar cells were processed through the same activating and nickel seed layer processes. One of these solar cells was annealed to form NiSi while the other cell remained as the control. The specific contact resistivity of these poly-Si laser ablated cells was estimated using the transmission line modeling (TLM) method [9,10]. The annealed sample shows a 38% decrease in specific contact resistivity compared to the control sample. This result confirms that the formation of a NiSi ohmic contact reduces the contact resistance of the solar cell.

Cu/Ni/NiSi Stack Samples

Thick metallization above the NiSi ohmic contact is required to form low resistance contact lines. LIP of nickel, copper, and tin can be used to effectively build up the contact lines. However, if the backside of the solar cell is immersed in the plating solutions during LIP the aluminum will be attacked. Technic Inc.'s laboratory LIP tool is designed to prevent the plating solution from coming in contact with the backside of the solar cell. With this configuration, LIP can proceed with or without backside rectification, depending on the desired plating parameters without restrictions from the backside dissolution problem. Full 156x156 mm solar cells patterned by either masking & wet etching or laser ablation have been processed through LIP of nickel and copper using the dry back configuration. The FIB-cross section in Figure 8 is an example of the Cu / Ni / NiSi stack obtained on a laser ablated mono-Si solar cell using the ASL process described in this paper.

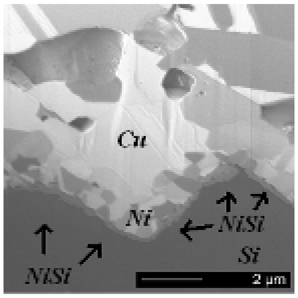

Fig. 8) FIB x-sec of Cu / Ni / NiSi layers on mono-Si solar cell

CONCLUSION

In order to develop a robust ASL process that is compatible with mono-Si and poly-Si cells with varying ARC compositions and patterned with different techniques, new proprietary chemistries were developed by Technic Inc. including a wet etching solution for removal of the ARC layer, activating solution for laser ablated silicon, and a nickel plating solution for deposition of nickel directly on silicon. By incorporating these new chemistries into the ASL process, a thin, uniform nickel silicide layer has been demonstrated on mono-Si and poly-Si cells processed through both masking & wet chemical etching and laser ablation ARC patterning processes. In addition, the ASL process has been scaled to 156 x 156 mm solar cells using a laboratory scale LIP plating tool designed by Technic Inc. that prevents damage to the backside of the solar cell during processing. The resulting NiSi contact has a 38% lower specific contact resistivity than the control sample. Future work will include electrical testing of the full solar cells processed using Technic Inc.'s proprietary wet etching/activation chemistries and plated in Technic Inc.'s dry back LIP plating tool using proprietary nickel, copper, and tin plating solutions.

ACKNOWLEDGEMENT

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