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Impact of Nickel silicide Rear Metallization on Series Resistance of Crystalline Silicon Solar Cells

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Abstract: The Silicon-based solar cell is one of the most important enablers toward high efficiency and low-cost clean energy resource. Metallization of silicon-based solar cells typically utilizes screen printed silver-Aluminium (Ag-Al) which affects the optimal electrical performance. To date, metal silicide-based ohmic contacts are occasionally used as an alternative candidate only to the front contact grid lines in crystalline silicon (c-Si) based solar cells. In this paper, we investigate the electrical characteristics of nickel mono-silicide (NiSi)/Cu-Al ohmic contact on the rear side of c-Si solar cells. We observe a significant enhancement in the fill factor of around 6.5% for NiSi/Cu-Al rear contacts leading to increasing the efficiency by 1.2% compared to Ag-Al. This is attributed to the improvement of the parasitic resistance in which the series resistance decreased by 0.737 $\Omega\cdot\text{cm}^2$. Further, we complement experimental observation with a simulation of different contact resistance values, which manifests NiSi/Cu-Al rear contact as a promising low-cost metallization for c-Si solar cells with enhanced efficiency.

Introduction

Crystalline silicon (c-Si) solar cell has proven reliability and efficiency, holding the dominant market share compared to the varied Photovoltaics (PV) technology market due to its advantages like non-toxicity, abundance, and stability. Silicon has an energy band gap of 1.12 eV corresponding to a broad spectral absorption range with a cut-off wavelength of about 1160 nm. Thus, silicon has a very close optimum solar-to-electric energy conversion using single semiconductor optical absorber.^[1] Further performance per cost enhancement signifies a great effort to fulfill the global demand for renewable energy. Improving the efficiency of c-Si solar cells while exploring the total cost reduction signifies a huge effort.^[2] In that regard, one key area is contact engineering in c-Si solar cells, which utilize screen printed silver (Ag) as the primary metallization technology due to its remarkable current collecting properties with the relative simplicity of the procedure. On the other hand, screen printed Ag exhibits high contact resistance since the current must flow through Ag crystallites formed during firing, then tunnel through an insulating glass layer, organic binders, and solvents to reach the metal finger bulk, resulting in metallization-induced recombination losses.^[3] Recent advances in silicon solar cells research are heightening an evolutionary approach to increase the cell efficiency of the industry via exploring silicidation on the front contacts.^[4] Metal silicides based on ohmic contact formation principle, have proven to be great contact materials in complementary metal oxide semiconductor (CMOS) technology because of their low specific resistivity, minimal junction penetration, and high thermal stability.^[5] Additionally, metal silicides have demonstrated great promise in energy harvesting devices.^[6] In

particular, Nickel silicide has been under investigation to be used for c-Si solar cells.^[4e, 7] Plated Ni/Cu contacts have also been used to achieve 18.1% on large area multi-crystalline substrates using a single-sided buried contact design.^[8]

In this work, we investigated Nickel mono-silicide NiSi/Cu ohmic contact on the rear side, especially that 49% of the recombination losses are taking place at the rear side at the maximum power point.^[1b] Our approach is unique to be applied on the back side to discover its impact on enhancing the solar cell's efficiency by increasing the Fill Factor (FF) which is defined by:

$$FF = \frac{P_m}{V_{oc} I_{sc}} \quad (1)$$

Where P_m is the maximum output power, V_{oc} is the open circuit voltage and I_{sc} is the short circuit current. The power of the solar cells is dissipated through the resistance of the contacts and through a leakage current around the sides of the device as can be shown below:

$$P_m = I_{mp}^2 \left(R_s + \frac{R_{sh}}{X} \right) \quad (2)$$

$$\text{Where } X = \frac{I_0 R_{sh}}{n V_{th}} \exp \left(\frac{V_{mp} + I_{mp} R_s}{n V_{th}} \right) + 1 \quad (3)$$

R_s is the series resistance, R_{sh} is the shunt resistance, I_0 is reverse saturation current of the diode, n is the diode quality factor, V_{mp} and I_{mp} are the voltage and current at the maximum power point, respectively.^[23] We assume that using the nickel silicide ohmic contact on the rear side will reduce the FF due to its influence on the R_s as can be seen from equations (1, 2 and 3), especially that nickel silicide forms ohmic contact with p-type silicon with a barrier height of 0.5 eV.^[9] Also, NiSi works as an appropriate barrier to prevent copper diffusion in silicon.^[10]

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Supporting information for this article is given via a link at the end of the document.

Figure 1. Schematic illustration of crystalline silicon solar cells with NiSi/Cu and Al rear contacts. (b) Optical photo of the rear side. (c) NiSi/Cu contacts on the textured silicon rear surface.

This investigation includes studying the electrical and micro-structure characterization of NiSi/Cu-Al on the rear side c-Si commercial solar cells as the schematics illustrate in Figure 1. Figure 1(a) depicts all the components of the solar cells with dopant-diffused silicon homo-junction solar cell where electrons and holes are generated in the p-type silicon, then extracted via phosphorus-doped (front, yellow) and boron-doped (back, black) regions with an n-type emitter layer and screen-printed Ag grids/bus bar as the front and rear contacts besides the aluminum back surface field (BSF). Figure 1(b) shown an optical photo of the solar cell rear side. Figure 1(c) reveals the cross-sectional scanning electron microscope (SEM) image showing NiSi/Cu contacts on the textured silicon rear surface.

The characterization and analysis of the microstructure of NiSi are performed with the help of scanning electron microscopy (SEM), near glancing incidence x-ray diffraction (GIXRD) and Transmission electron microscopy (TEM).

Furthermore, we investigate the effect of utilizing NiSi/Cu-Al rear contacts for the first time compared to Ag-Al metallization of c-Si solar cells. To evaluate the electrical behavior of both contacts, the J–V characteristics are compared in the dark as well as under 0.7 and 1 sun. The measured data is used for the determination of R_s using two different approaches.

Experimental approach

Optimization of NiSi

The optimization process is done using a lightly doped, p-type c-Si (100) substrates with a sheet resistance (ρ_{sh}) of 330 Ω/sq . First, the wafers were first RCA cleaned followed by dipping in dilute HF solution for superficial silicon native oxide removing. Then, two different thicknesses (20 nm and 50 nm) of nickel were deposited to achieve the minimum resistance using electron-beam deposition (0.5 $\text{\AA}/\text{s}$ deposition rate) on. Next, the samples were annealed in an inert Argon (Ar) atmosphere at different temperatures ranging from 300 $^{\circ}\text{C}$ to 750 $^{\circ}\text{C}$ using rapid thermal annealing (RTP) for 60 seconds. Finally, removal of unreacted Ni was done using piranha ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$) at 120 $^{\circ}\text{C}$ for 120 seconds. Figure 2(a) shows the sheet resistance as a function of the annealing temperature. For temperatures below 350 $^{\circ}\text{C}$, Nickel disilicide (Ni_2Si) was formed first until all Ni was reacted. This formation was followed by Nickel mono-silicide (NiSi) phase transformation at temperatures between 400–600 $^{\circ}\text{C}$. Further material characterization is carried out on the samples which achieve the minimum Rsh value of 2.8 Ω/sq by depositing 50 nm of Ni and annealed at 450 $^{\circ}\text{C}$.

GIXRD is performed by fixing the angle of incidence of the X-ray generator with reference to the plane of the sample at 3 $^{\circ}$ while moving the detector with respect to the sample at a 2-theta angle. GIXRD confirms the nickel mono-silicide formation of the optimized formation recipe in Figure 2(b). Also, TEM samples are prepared via dual-beam using Pt/C deposition for sample protection. Then TEM images were obtained using an FEI Titan ST electron microscope operated at 300 kV used to study the microstructure of NiSi phase. TEM samples are prepared via dual-beam using Pt/C deposition for sample protection. Then TEM images were obtained using an FEI Titan ST electron microscope operated at 300 kV used to study the microstructure of NiSi phase. Fig. 1(c) shows the cross-sectional TEM image of the resulting structure of NiSi with a thickness of ~ 44 nm. Energy-dispersive X-ray (EDX) spectroscopy shows the elemental composition of silicon and nickel which have an approximately 49.24% and 50.76% atomic percentages, respectively, indicating that around 22 nm of silicon is consumed for NiSi structure (see Figure S1 and Table S1 in the supplementary material for details for the EDX study of NiSi layer).

Formation of NiSi/Cu-Al rear contacts

The commercial c-Si solar cells which have screen printed Al and opening from NiSi were placed upside down inside the e-beam chamber to form the nickel mono-silicide as described in the previous step. Subsequently, an oxide etching step was required to remove the silicon oxide layer which grows during the annealing step using (BOE) for 120 seconds. Finally, we deposited 0.5 μm of Cu on the NiSi using magnetron sputtering process (400 W, 25 sccm, 5 mTorr). Cross-sectional SEM image was obtained for Cu/NiSi rear contact on the textured silicon as shown in Fig 1(c). (See Figure S2. In the supplementary material for SIMS depth profiling of the (Cu/NiSi/Si)).

Figure 2. (a) Sheet resistance of (Ni_xSi_y) crystalline silicon (100) as a function of Rapid Thermal Annealing (RTA) temperatures. (b) Glancing incidence x-ray diffraction (GIXRD) of NiSi and Ni (as-deposited). (c) Transmission electron microscopy (TEM) cross-sectional image of NiSi on silicon with thickness of ~ 44 nm.

Results and Discussion

Electrical characterization of the samples was done under simulated AM 1.5 sunlight (Spectra-Physics 91160–1000), calibrated to give 100 mW/cm² using a NREL-KG5-filtered silicon reference cell. The current density-voltage (JV) curves were recorded with a Keithley 2400. Figure 3 and Table 1 compare the output current of the optimized c-Si solar cells with NiSi/Cu-Al to Ag-Al rear contacts with an area of 1 cm². We observed significant increment in FF of approximately 6.5 % for NiSi/Cu rear contacts led to increased efficiency by 1.2 % compared to screen printed Ag solar cells. However, a modest improvement of ~ 0.01 V and 0.32 mA/cm² in V_{oc} and J_{sc} were found. This is typically expected for a lowered R_s as it mainly

Figure 3 Output current density vs. voltage of NiSi/Cu-Al (red circles) and screen printed Ag-Al (black squares) under one-sun illumination showing both of current and power density.

Table 1. Output parameters of c-Si solar cells with NiSi/Cu-Al rear contacts vs. Ag-Al rear contact of 1 cm² as measured under AM1.5 spectrum (100 mW/cm²) at 25 °C, means ± SD.

Solar Cell Parameters	NiSi/Cu-Al	Ag-Al
J_{sc} (mA/cm ²)	39.883 ± 0.213	39.562 ± 0.135
V_{oc} (V)	0.598 ± 0.0014	0.588 ± 0.0014
FF (%)	67.886 ± 1.945	61.383 ± 1.917
Efficiency (%)	16.254 ± 0.68	14.746 ± 0.443

affects FF and not V_{oc} or J_{sc} the silicide formation significantly affect the metal-specific contact resistance.

In this work, we used two different methods for R_s determination with high accuracy depending on the JV-curves under different illumination intensities (dark, 0.7 and 1 sun) comparing both of NiSi/Cu and screen-printed Ag rear contacts.[11] The first method depends on comparing one-sun with the dark JV-curves as shown in Figure 4(a). The principle of this method is based on a voltage difference at maximum power point (mmp) of one sun and the dark JV-curves.

$$R_{s,light_dark} = \frac{V_{dark,mmp} - V_{light,mmp}}{|J_{mmp}|} \quad (4)$$

Applying this method shows that $R_{s,light_dark}$ is reduced for NiSi/Cu-Al rear contact by 0.68 Ω.cm² compared to screen printed Ag. The electrical performance parameters for NiSi/Cu-Al and Ag-Al contacts at the maximum power [mmp] including J_{mmp} , ΔV_{light_dark} and $R_{s,light_dark}$ are summarized in table2 (see Figure S3 for graphical interpretation and table S2 for the detailed electrical parameters variation in the supplementary information).

Figure 4. Output current density vs. voltage of NiSi/Cu (red circles) and screen-printed Ag (black squares) under (a) one-sun and shifted dark measurements and (b) different illumination levels: 1 and 0.7 illumination intensities

The second method of R_s determination depends on the comparison of two JV-curves measured at different illumination intensities as shown in Figure 4(b). Measuring the JV-curves at different illumination intensities ends in two shifts between them. The first shift is in the current density due to the difference in the photo-generated current which is proportional to the incident illumination intensity.

Table 2. Variation of electrical performance parameters for NiSi/Cu-Al and Ag-Al contacts at the maximum power [J_{mpp}] value taken for series resistance determination ($R_{s,light_dark}$) for dark and 1 sun intensity illumination.

	J_{mpp} (A/cm ²)	ΔV_{light_dark} (V)	$R_{s,light_dark}$ ($\Omega \cdot \text{cm}^2$)
NiSi/Cu-Al	0.0368	0.051	1.38
Ag-Al	0.0329	0.066	2.06

The second shift is in voltage which is caused by the smaller series resistance loss, at a lower light intensity: $\Delta V = R_{s,light} \Delta J_{sc}$. Where ΔJ_{sc} is the variance in the two short-circuit current densities. The series resistance value using this method ($R_{s,intvar}$) can be calculated using the following equation:

$$R_{s,intvar} = \left| \frac{\Delta V}{\Delta J_{sc}} \right| \quad (5)$$

Figure 5. Comparison of JV curves of the dark current: (a) experimental measurements (inset is equivalent circuit including series (R_s) and shunt (R_{sh}) resistance). (b) simulated data as a function contact resistance.

The second method confirms that $R_{s,intvar}$ is reduced for NiSi/Cu-Al with $0.794 \Omega \cdot \text{cm}^2$ compared to the Ag-Al (see Figure S4 for graphical interpretation and Table S3 of electrical parameters variation in the supplementary material). The previous calculations using both methods reveal the R_s reduction and approve the impact using the NiSi/Cu-Al contact on improving the FF which results in enhancing the efficiency of the solar cells as proposed in equations (1, 2 and 3).

Further investigation of the solar cells dark measurements was studied since the series resistance near the open circuit strongly affects the JV curves. We explored the dark current for NiSi/Cu-Al and Ag-Al rear contacts of the cells in Fig 3(a). For voltages above $V_{oc} \sim 0.6 \text{ V}$, we see an increase in the dark current for the NiSi/Cu-Al cells as compared to Ag-Al. Additionally, R_s values extracted according to PV simulator software (nanohub) from dark JV characteristics.^[12] The results confirmed a series resistance reduction from $0.966 \Omega \cdot \text{cm}^2$ for the screen-printed Ag to $0.55 \Omega \cdot \text{cm}^2$ for NiSi/Cu-Al rear contact.

To verify the contact resistance effect, we have simulated a solar cell of similar structure which is in contact with Ag-Al and the NiSi/Cu-Al contacts using TCAD Synopsys Sentaurus software (see Table S4. for the simulation parameters in supplementary materials). Ohmic contact was assumed for the emitter contact with zero contact resistance. However, the p^{++} collector contact was simulated with different contact resistivity values to simulate the effect of series resistance on dark JV curves. Previous studies showed that the screen-printed Ag-Al

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pastes have specific contact resistance (ρ_c) is in the range of 10^{-4} – $10^{-5} \Omega \cdot \text{cm}^2$ on the heavily doped silicon.^[13] On the other hand, the ρ_c of NiSi ohmic contact is in the range of 10^{-7} – $10^{-8} \Omega \cdot \text{cm}^2$ on the same highly doping concentration.^[14] Figure 5(b) shows that the on-current value is affected by the contact resistivity, showing similar trend to the experimental behavior in Figure 5(a). According to the results in Figure 5(b), as the contact resistance increases from 10^{-4} to $10^{-7} \Omega/\text{cm}^2$, the current increases by 17% from 152 A/cm² to 179 A/cm². Although the simulation overestimates the current density, due to not taking into account an experimentally validated mobility model and patristic recombination effects, it still qualitatively shows the effect of the series resistance reduction on the dark JV which we believe to play a significant role in the case of NiSi/Cu-Al cell.

Conclusions

In summary, we found that the NiSi/Cu ohmic contact is an efficient metallization candidate on the rear side of c-Si solar cells instead of the conventional Ag paste. We have reported experimental improvement of both of the FF and efficiency for NiSi/Cu compared to Ag paste by 6.5% and 1.2%, respectively. This is attributed to the average reduction of the $R_s \sim 0.737 \Omega \cdot \text{cm}^2$ which supported by performing simulations to understand the effect of the contact resistance on the dark electrical performance of the cells. Future work will be directed to replace the Ag paste by NiSi/Cu on both of front and rear contacts using advanced electrodeposition of a nickel seed layer to meet the automatic production line for manufacturing solar cells.

Supplementary information: See supplementary material for NiSi elemental quantification Figure S1 and Table S1, SIMS depth profiling of NiSi/Cu rear contact Figure S2, R_s graphical interpretation Figure S4, S5 and Table S2–S3 and Table S4 for the simulation parameters.

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Keywords: c-Si solar cells • Nickel silicide • Ohmic contact • screen printed silver • CMOS

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Layout

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