



Article Potential of NiO_x/Nickel Silicide/n⁺ Poly-Si Contact for Perovskite/TOPCon Tandem Solar Cells

Jiryang Kim ^{1,†}, Dowon Pyun ^{2,†}, Dongjin Choi ², Seok-Hyun Jeong ², Changhyun Lee ², Jiyeon Hyun ², Ha Eun Lee ², Sang-Won Lee ², Hoyoung Song ², Solhee Lee ², Donghwan Kim ², Yoonmook Kang ¹ and Hae-Seok Lee ^{1,*}

- ¹ Graduate School of Energy and Environment (KU-KIST Green School), Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Korea; kjr951@korea.ac.kr (J.K.); ddang@korea.ac.kr (Y.K.)
- ² Department of Materials Science and Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Korea; dowon0212@korea.ac.kr (D.P.); donggenie@korea.ac.kr (D.C.); jsh7983@korea.ac.kr (S.-H.J.); changhyuni@korea.ac.kr (C.L.); hjy1214@korea.ac.kr (J.H.); sylvia0121@korea.ac.kr (H.E.L.); tv12m@korea.ac.kr (S.-W.L.); ghdudlg@korea.ac.kr (H.S.); rnlxlsla@korea.ac.kr (S.L.); solar@korea.ac.kr (D.K.)
- * Correspondence: lhseok@korea.ac.kr; Tel.: +82-2-3290-3713
- + These authors contributed equally to this work.

Abstract: In this work, nickel silicide was applied to tandem solar cells as an interlayer. By the process of thermal evaporation, a layer of NiO_x, hole transport layer (HTL) was deposited on n⁺ poly-Si layer directly. Nickel silicide was simultaneously formed by nickel diffusion from NiO_x to n⁺ poly-Si layer during the deposition and annealing process. The I–V characteristics of NiO_x/n⁺ poly-Si contact with nickel silicide showed ohmic contact and low contact resistivity. This structure is expected to be more advantageous for electrical connection between perovskite top cell and TOPCon bottom cell compared to the NiO_x/TCO/n⁺ poly-Si structure showing Schottky contact. Furthermore, nickel silicide and Ni-deficient NiO_x thin film formed by diffusion of nickel can improve the fill factor of the two sub cells. These results imply the potential of a NiO_x/nickel silicide/n⁺ poly-Si structure as a perovskite/silicon tandem solar cell interlayer.

Keywords: perovskite/silicon tandem solar cells; nickel silicide; NiO_x/n^+ poly-Si contact; X-ray photoelectron spectroscopy

1. Introduction

With great efforts from the photovoltaic (PV) research community, photoconversion efficiency (PCE) of silicon solar cells is now almost close to the practically achievable limit of 27.1% [1] and the theoretical limit of 29.56% [2]. The highest reported PCEs with tunnel oxide passivated contact (TOPCon) and heterojunction interdigitated back contact (HJ-IBC) structures were 25.8% [3] and 26.7% [4], respectively. In addition to increasing efficiency, silicon solar cells are reaching grid parity, while occupying about 95% of the PV market. Perovskite is also an emerging material in the PV field. The PCE of perovskite solar cells has risen sharply from 3.8% [5] to 25.5% [6] in only a few years. In addition to PCE, various fields have been studied about perovskite solar cells such as: long-term stability, vacuum deposition process, or conformal deposition technology [7–9]. Moreover, perovskite solar cell is suitable as the top cell of a tandem solar cell due to its band gap tunability over a wide range of 1.4–2.3 eV. Based on the well-commercialized market of silicon solar cells and the high PCE of perovskite solar cells with easy band gap control, 2-terminal (2-T) perovskite/silicon tandem solar cells have been widely studied [10–19].

The 2-T perovskite/silicon tandem solar cell is constructed by monolithically depositing the perovskite solar cell on the silicon solar cell. In the case of using TOPCon as the bottom cell, TCO is usually deposited on n^+ poly-Si or p^+ poly-Si, while the silicon emitter



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). is placed on the rear side, as shown in Figure 1a. TCO also acts as an electrode for the perovskite solar cell, which makes it a reasonable choice as an interlayer to connect the top and bottom cells. However, 2-T tandem devices with TCO as an interlayer require additional processing—such as sputtering—for deposition of TCO. Plasma damage, which occurs during the sputtering process, can negatively affect the V_{oc} of the bottom cell [20]. Although there were some reports that the passivation quality of TCO can be cured through heat treatment, it can also negatively affect fill factor (FF) [21] by forming an interfacial oxide on the silicon and TCO surfaces.



Figure 1. Schematic of 2-T perovskite/TOPCon tandem solar cell, where (**a**) indium tin oxide (ITO) and (**b**) NiO_x/n^+ poly-Si direct contact.

In this work, NiO_x was deposited on heavily phosphorus-doped n⁺ poly-Si. NiO_x is used as HTL in perovskite solar cells. Its majority carriers are holes, while electrons are the majority carriers in the n⁺ poly-Si. Since the majority carriers of the two materials are different, carrier transport mechanisms of the NiO_x/n⁺ poly-Si structure can be interpreted as band-to-band tunneling in a band diagram. However, during the evaporation and annealing, nickel silicide is formed at the NiO_x/n⁺ poly-Si interface, and the band structure is changed similar to NiO_x/TCO/n⁺ poly-Si, thereby changing the carrier transport mechanism of NiO_x/n⁺ poly-Si. In this study, NiO_x/n⁺ poly-Si direct contact and NiO_x/TCO/n⁺ poly-Si contact were compared through dark I–V characteristics, and carrier transport mechanisms of two structures were analyzed through band diagram. We also determined that nickel diffusion not only forms nickel silicide, but also changes the properties of NiO_x thin films. We confirmed the influence of nickel diffusion on TOPCon bottom cells. Through this study, we discussed the potential of a tandem structure with NiO_x/nickel silicide/n⁺ poly-Si as the interlayer, instead of using TCO, as shown in Figure 1b.

2. Materials and Methods

Samples A, B, and C were prepared and analyzed by following process. A schematic of process flow for the fabrication of sample A, B, and C is shown in Figure 2.



Figure 2. Schematic of process flow for the fabrication of sample A, B, and C.

2.1. $Au/NiO_x/(ITO)/n^+$ Poly-Si Contact Measurement Sample Fabrication (Sample A)

The Au/NiO_x/ n^+ poly-Si contact samples for measurement were prepared using a float-zone (FZ) monocrystalline n-type silicon (100) wafer. These silicon wafers were cleaned using the Radio Corporation of America (RCA) cleaning process. After cleaning, a silicon oxide layer of ~1.2 nm thickness was grown on the wafer by dipping it in hydrogen peroxide (H_2O_2) solution. P-doped poly-Si of ~300 nm thickness was then deposited on the silicon oxide surface, using low-pressure chemical vapor deposition at 600 °C. Next, native oxides were removed using dilute hydrogen fluoride (HF) solution. The NiOx layer of ~5 nm thickness was deposited by thermal evaporation, using nickel oxide granules (>99.9%, 3–6 mm) with a deposition rate less than 0.2 Ås⁻¹. After the NiO_x deposition, Au was deposited by thermal evaporation. In the case of metal/NiO_x/ITO/ n^+ poly-Si contact samples, an ITO layer with a thickness of ~20 nm was deposited by radio frequency magnetron sputtering before NiO_x deposition. NiO_x , (ITO), and Au were deposited as TLM patterns with shadow mask on the n⁺ poly-Si in order to calculate the contact resistivity. The TLM patterns were fabricated at intervals of 0.2, 0.4, 0.8, 1.2, 2.0, and 3.8 mm. The samples were then annealed using rapid thermal annealing at 300 °C, 400 °C, and 500 °C with a ramp-up period of 300 s within a $N_2 + H_2$ (95 + 5%) atmosphere. To confirm the I–V characteristics, dark current-voltage (I–V) measurements were taken at room temperature using a Keithley 238 source meter.

2.2. NiO_x, NiSi Material Characterization (Sample B)

Samples for NiO_x and nickel silicide were fabricated by depositing approximately 5 nm thickness of NiO_x thin film on n⁺ poly-Si/SiO_x/n-type c-Si substrate. Energy dispersive spectroscopy (EDS) and TEM (Talos F200X) were applied to investigate the diffusion of Ni atom into the polysilicon film. Depth profiling XPS (PHI 5000 VersaProbe) was used to determine nickel silicide and NiO_x by Ar⁺ ion sputtering (2 kV) with a scan size of 1 mm \times 1 mm.

2.3. NiO_x/TOPCon Bottom Cell Fabrication (Sample C)

TOPCon solar cells with NiO_x film were fabricated on 280 μ m n-type FZ c-Si wafers. The wafers were cleaned using the RCA process. Both sides of the wafers were doped using BBr₃ diffusion at 985 °C. Borosilicate glass and native oxide were etched on both sides using dilute HF solution. The front side p⁺ emitter was etched by dipping it in 80 °C texturing solution (DI:KOH:IPA = 10:0.25:0.78, volume ratio). Silicon oxide layer and n⁺

poly-Si layer were deposited in the same way as that of sample A. Rear side n⁺ poly-Si layer was etched by dipping it in 80 °C tetramethylammonium hydroxide (TMAH, 20 wt.% in H₂O, Aldrich, St. Louis, MO, USA) solution. Rear side silicon oxide and native oxide were etched using dilute HF solution sequentially. Then, NiO_x/Au (5/100 nm) was sequentially deposited on the front side of the wafers. Next, a ~1 μ m thick Ag layer was deposited on the rear side of the samples. The measurements for TOPCon bottom cells with NiO_x layer were performed at room temperature, using a light current-voltage, Keithley 2400 source meter under the illumination of an AM 1.5G solar simulator (100 mW/cm²). Quantum efficiency (QE) measurements were carried out by scanning the UV-Vis-Infrared spectrum at room temperature.

3. Results and Discussion

3.1. Contact Property of NiO_x/n^+ Poly-Si

First, the contact properties of the two different structures— NiO_x/n^+ poly-Si and $NiO_x/TCO/n^+$ poly-Si—were measured and compared. Figure 3a,b show the dark I–V characteristics of the samples before and after ITO annealing. Non-ohmic I–V was measured as shown in Figure 3a,b. Furthermore, during the annealing process the SiO_x phase was formed between the n⁺ poly-Si and the ITO [22], which increased the Schottky barrier width and threshold voltage (0.16 -> 0.35 V) of the n⁺ poly-Si/ITO/n⁺ poly-Si Schottky diode.



Figure 3. Dark I-V characteristics of Au/NiO_x/ITO/n⁺ poly-Si structure: (**a**) with annealing; (**b**) without annealing; (**c**) test sample structure. Transmission line measurement (TLM) structure with ~1.2 nm SiO_x; ~300 nm n⁺ poly-Si continuous layers with ITO/NiO_x/metal spacing of 0.2, 0.4, 0.8, 1.2, 2.0, and 3.8 mm.

Contact properties of samples without TCO were also measured using the method described above. Figure 4a,b show that the contact between NiO_x/n^+ poly-Si showed ohmic behavior both before and after annealing. Significantly, the contact resistivity measured by the TLM method was about 30 m $\Omega \cdot cm^2$, which was a low value considering that it was an entire surface contact. After annealing, the contact resistivity corresponded to before annealing the sample, as shown in Figure 4c.

The typical energy band diagrams of NiO_x/ITO/n⁺ poly-Si and NiO_x/n⁺ poly-Si are shown in Figure 5a,b. As mentioned before, the dark I–V results of the ITO sample were non-ohmic, which was consistent with the band diagram shown in Figure 5a. The work function of ITO is higher than that of n⁺ poly-Si and lower than that of NiO_x, therefore a Schottky barrier was formed on both ITO/n⁺ poly-Si and ITO/NiO_x interfaces, which resulted in non-ohmic dark I–V results. However, in the case of the NiO_x and n⁺ poly-Si—which are directly in contact—the band diagram of NiO_x/n⁺ poly-Si in Figure 5b was not consistent with those shown in Figure 4a,b, which were measured as an ohmic contact. In the NiO_x/n⁺ poly-Si interface, carrier transport was only possible through band-to-band tunneling, where carriers were transported from the conduction band of n⁺ poly-Si to the valence band of NiO_x due to the band structure, as shown in Figure 5b. It has been reported that diode behavior has been exhibited in the SnO₂/p⁺⁺ emitter [23]

and TiO_2/p^{++} emitter [24] interface, which is similar to the NiO_x/n^+ poly-Si. However, an ohmic contact was confirmed as shown in Figure 4a,b. It was expected that nickel silicide would be formed between NiO_x and the n^+ poly-Si during thermal evaporation, and that this nickel silicide will assist carrier transport into the NiO_x valence band and the n^+ poly-Si conduction band, as shown in Figure 5c.



Figure 4. Dark I-V characteristics of $Au/NiO_x/n^+$ poly-Si structure. TLM structure with $NiO_x/metal$ spacing of 0.2, 0.4, 0.8, 1.2, 2.0, and 3.8 mm: (a) with annealing; (b) without annealing; (c) contact resistivity according to annealing temperature; (d) test sample structure.



Figure 5. Energy band diagrams of: (a) $NiOx/ITO/n^+$ poly-Si; (b) $NiOx/n^+$ poly-Si; (c) NiOx/Ni silicide/ n^+ poly-Si.

3.2. Nickel Silicide Confirmation

The existence of nickel silicide was confirmed through TEM analysis. To confirm the distribution of Ni atoms, high angle annular dark-field scanning TEM (HAADF-STEM) and corresponding EDS were used. Figure $6a_e$ correspond to the images of the NiO_x/n⁺ poly-Si structure before and after annealing. In the STEM images NiO_x , SiO_x , and Si were represented as bright white, dark, and gray regions, respectively. In Figure 6a,e approximately 1.7 nm thick SiO_x was observed between NiO_x and n^+ poly-Si interfaces. This is due to SiO_x having a greater negative Gibbs formation energy (ΔG_0) value than that of NiO. Therefore, the oxygen in NiO oxidized Si, and the remaining Ni atoms diffused into n^+ poly-Si to form nickel silicide [25]. As shown in Figure 6a, white dot-shaped parts were detected under the SiO_x layer. It was confirmed from Figure 6b that this dot-shaped region was diffused Ni; nickel silicide is expected to be formed in this region. In addition, the shape of nickel silicide was different before and after annealing. After annealing, Ni atoms aggregated in the n⁺ poly-Si as shown in Figure 6f, which resulted in partial contact between nickel silicide and NiO_x . Attributing to the Ni aggregation, nickel silicide did not distribute uniformly, and this might be the reason for the non-ohmic graph of L1 in Figure 4b.



Figure 6. Comparison of NiO_x layer on n^+ poly-Si: (**a**) with annealing; (**e**) without annealing; (**a**,**e**) scanning transmission electron microscopy (STEM) images; (**b**–**d**,**f**–**h**) energy dispersive spectroscopy (EDS) mapping images.

The chemical state of the diffused Ni atom in n⁺ poly-Si was analyzed. A nickel silicide peak was detected using depth profiling XPS. Figure 7a,b show the XPS spectra of Ni $2p_{3/2}$ and $2p_{1/2}$ as a function of the depth position. The spectra of Ni $2p_{3/2}$ showed the Ni₃₁Si₁₂ peak at 853.0 eV (1 s), the Ni₂Si peak at 853.4 eV (2 s), and the NiSi peak at 853.9 eV (6 s). Likewise, the spectra of Ni $2p_{1/2}$ showed the Ni₃₁Si₁₂ peak at 870.2 eV (1 s), the Ni₂Si peak at 871.2 eV (6 s) [26]. As the etching time increased, the nickel silicide peak shifted to the left. These results indicated that the nickel silicide phase shifted from Ni rich silicide to the NiSi phase, depending on the depth. As a result, the nickel silicide formed during the evaporation process of NiO_x was placed on NiO_x/n⁺ poly-Si interface and assisted the contact between the two layers, which finally resulted in an ohmic contact and a low contact resistivity.



Figure 7. XPS depth profiling of 5 nm thick NiO_x thin film on n^+ poly-Si (**a**) Ni $2p_{3/2}$ and (**b**) Ni $2p_{1/2}$ according to Ar⁺ etching time.

3.3. NiO_x Thin Film XPS Analysis

Pure stoichiometric NiO has extremely low electrical conductivity of 10–11 S·cm⁻¹ at room temperature [27]. However, excess oxygen results in Ni vacancy, which changes Ni²⁺ to Ni³⁺ for electrical neutrality. Ni³⁺ serves as an acceptor that donates a hole [28], which means NiO_x can act as a p-type semiconductor. In other words, the conductivity of NiO_x film can be indirectly compared from the ratio of Ni³⁺/Ni²⁺. The larger the ratio of Ni³⁺/Ni²⁺, the higher the conductivity of NiO_x film. Therefore, the XPS peak was measured to compare the tendency of NiO_x film conductivity.

The nickel atoms from NiO_x were diffused into silicon, therefore the NiO_x thin film deposited on n⁺ poly-Si was expected to be nickel-deficient NiO_x. Therefore, the Ni³⁺/Ni²⁺ ratio would be different from that of the NiO_x deposited on glass (0.69) [29]. As shown in Figure 8, annealing was conducted under four different conditions; as-deposited 300 °C, 400 °C, 500 °C, and the XPS data were separated into the NiO peak (Ni²⁺) and the Ni₂O₃ peak (Ni³⁺). For all annealing temperatures, the Ni₂O₃ peak intensity was measured to be greater than the NiO peak. As the annealing temperature increased from as-deposited to 500 °C, the Ni³⁺/Ni²⁺ ratio tended to increase to 1.77, 2.83, 3.16, and 7.93. That means that during the annealing process nickel is more diffused to silicon, making the NiO_x thin film more Ni-deficient. Therefore, because the Ni₂O₃ peak intensity is higher depending on the annealing temperature, it is expected to affect the electrical conductivity of NiO_x.

3.4. TOPCon Bottom Cell Analysis with NiO_x Layer

In the previous TEM and XPS analyses, the silicide formation and the Ni³⁺/Ni²⁺ ratio increase was confirmed. For further confirmation on how the characteristics of the TOPCon bottom cell changed with respect to NiO_x deposition and annealing, the structure shown in Figure 9d was fabricated. Figure 9 shows the external and internal QEs and JV curves of the $NiO_x/TOPCon$ sample. Regardless of the NiO_x deposition and annealing, the reflectance of the samples was almost the same. However, the QE data decreased overall after the NiO_x deposition and annealing, which was due to the parasitic absorption of nickel silicide [30]. Significantly, nickel silicide had high absorption coefficient at short wavelength [31]. As a result, Figure 9b shows further decrease in IQE at short wavelength in the case of NiOx deposition and annealing. As shown in Figure 9c and Table 1, Jsc also decreased after NiO_x deposition and annealing, similar to the trend observed with QE. On the contrary, FF increased from 53.55% to 63.07% from without NiO_x to after NiO_x annealing. These results indicate that the front surface sheet resistance was improved. Ni diffusion from NiO_x formed nickel silicide that assisted carrier transport. Ni^{3+}/Ni^{2+} ratio of NiO_x thin layer was also affected by Ni diffusion. Consequently, lateral conductivity of NiOx and n⁺ poly-Si interface was seen to improve.



Figure 8. XPS spectrum of Ni $2p_{3/2}$ according to: (**a**) as-deposited; (**b**) 300 °C; (**c**) 400 °C; (**d**) 500 °C annealing temperature.



Figure 9. (a) External quantum efficiency (EQE); (b) internal quantum efficiency (IQE); (c) light current density-voltage (LJV) characteristics; (d) schematic structure of the NiO_x/TOPCon bottom cell.

	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
Without NiO _x	562.2	31.2	53.55	9.38
As-deposited NiO _x	557.6	25.1	60.21	8.42
Annealed NiO _x	565.3	21.6	63.07	7.72

Table 1. Comparison of the performance of a TOPCon solar cell with and without NiOx thin film and with and without annealing.

3.5. Potential of NiO_x/Nickel Silicide/n⁺ Poly-Si Interlayer Structure for Tandem

The 2-T tandem connects two sub cells in series; therefore, the role of the interlayer is very important. In particular, two different types of carriers must be recombined in the interlayer, and it is difficult to have ohmic contact with both sides of the interface. The interlayer interface with two sub cells has low barrier height on the energy band diagram. In Section 3.2, the formation of nickel silicide in NiO_x/n^+ poly-Si interface was confirmed. Nickel silicide has a work function of ~4.8 eV [32], which is similar to that of ITO $(4.6 \sim 4.8 \text{ eV} [33])$; nickel silicide played an important role in the ohmic contact between NiO_x and n^+ poly-Si. In addition, we also confirmed an increment in the Ni^{3+}/Ni^{2+} ratio of the NiO_x thin film. It has already been reported that an increase in the Ni^{3+}/Ni^{2+} ratio improves the carrier extraction and FF in perovskite solar cells [34–36]. In other words, in the case of the NiO_x /perovskite, many references show that an increase in Ni vacancy improves the electrical and optical properties of NiO_x , thereby improving the FF of perovskite solar cells. Therefore, the process of diffusion of Ni atoms into n^+ poly-Si from NiO_x by thermal evaporation and annealing improved the electrical property of our interlayer structure and the NiO_x film itself. These improvements were confirmed by an increase in FF in the bottom cell. Although J_{sc} reduction due to parasitic absorption of nickel silicide was confirmed, it is expected that J_{sc} can be improved by controlling the thickness of the nickel silicide by changing the deposition process or optimizing annealing temperature and time. For these reasons, NiO_x/nickel silicide/n⁺ poly-Si interlayer structure showed potential of increasing FF, as well as simplifying the fabrication process in perovskite/silicon tandem solar cells.

4. Conclusions

In this study the contact between NiO_x used as a hole transport layer of perovskite solar cell and n⁺ poly-Si of TOPCon solar cell was studied. Based on the band diagram, NiO_x/n^+ poly-Si was expected to exhibit non-ohmic behavior, because the carrier transport was only possible through band-to-band tunneling. However, an ohmic dark I–V was observed, and the contact resistivity was also measured to be approximately $30 \text{ m}\Omega \cdot \text{cm}^2$. These dark I–V results are attributed to the formation of nickel silicide between the NiO_x and n^+ poly-Si, which assisted the carrier transport between the interfaces. As a result of TEM and XPS analyses, the formation of nickel silicide was observed, which helped in carrier transportation. Nickel silicide peaks on Ni₃₁Si₁₂, Ni₂Si, and NiSi were observed depending on the depth. The deposited NiO_x showed Ni-deficient properties, which is attributed to the diffusion of Ni from NiO_x into n⁺ poly-Si. Therefore, the Ni₂O₃ peak was the main peak instead of the NiO peak. In addition, the ratio of Ni³⁺/Ni²⁺ increased as the annealing temperature increased, implying an improvement in the NiO_x film conductivity. We also fabricated a $NiO_x/TOPC$ on structure to confirm the electrical improvement by the formation of nickel silicide and Ni-deficient NiO_x . As a result, the FF improved after NiO_x deposition and annealing. By applying NiO_x/n^+ poly-Si contact as a tandem interlayer between the perovskite and silicon solar cell an enhanced electrical connection is expected compared to when using TCO.

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