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ABSTRACT
Recently, the transition metal oxide thin film has been actively investigated for doping-free heterojunction Si solar cells. However, most of the research on characterizing the chemical state and work function of the metal oxide thin film has been conducted on its surface, while there has been little work on the characterization on the subsurface of the metal oxide thin film. Here, we systematically investigate the chemical state and work function of the evaporated nickel oxide (NiOx) thin film on a Si substrate as a function of the depth position. We found that the chemical state of the NiOx thin film is highly affected by the surface chemical reaction. For instance, an air-exposed NiOx surface exists more in nickel hydroxide [Ni(OH)2] than in nickel monoxide (NiO). In addition, we discern that NiOx near the Si substrate exists in nickel silicide (NiSi). The changed chemical state of the NiOx thin film creates a high variation in the work function as a function of the depth position in the range of 4.4–5.4 eV. We also investigate the heterojunction Si solar cell with the NiOx thin film. We found that the performance of the heterojunction Si solar cell was determined according to the air exposure on the NiOx thin film inducing an undesirable chemical reaction. The heterojunction Si solar cell with the air-exposed NiOx thin film shows a relatively low efficiency of 11.84% by the reduced work function of the NiOx thin film, while one with the controlled NiOx thin film exhibits an enhanced efficiency of 14.23%.

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I. INTRODUCTION
Crystalline Si (c-Si) photovoltaic (PV) has dominated the worldwide PV industry for decades because of its stability, low cost, and appropriate energy bandgap. The majority of commercialized c-Si PV device architectures are the diffused junction type Si solar cells, which enable extraction of the photoexcited carriers by formation energy band bending, called a pn junction, with different dopant types and/or concentrations. Although these diffused junction-type PV devices have a simple device structure, it inevitably suffers by free-carrier absorption, Auger recombination, Shockley-Read-Hall (SRH) recombination loss in the heavily doped region of an emitter, and a back surface field layer.1 An alternative approach to surpass the limitations of the conventional c-Si PV device architecture is a heterojunction-type solar cell. The basic concept of a heterojunction-type solar cell is extraction of the photoexcited carriers by formation asymmetric surface band bending in a Si absorber with a deposited thin film that has a high (or low) work function. For instance, for lightly doped p-type Si, the Schottky contact formation at the surface (i.e., downward band bending) induced by a low work function thin film enables facile extraction of photoexcited electrons and prevents photoexcited holes in their path from the Si absorber to the outer metal electrode terminals, and it is called the selective electron contact.
The ohmic contact formation at the opposite surface (i.e., upward band bending) caused by the high work function thin film allows efficient transport of photoexcited holes and blocks photoexcited electrons, and it is called the selective hole contact. 17-20 The introduced heterojunction-type Si solar cell without incorporation of a dopant in a Si absorber can avoid the dopant related fundamental problems as we mentioned above and has a potential for cost reduction by precluding a doping related complicated process such as high temperature (> 800 °C) annealing and phosphorus silicate glass (PSG) removal.

As we mentioned, the surface band bending in a Si absorber can be controlled by the work function of the heterojunction thin film, so careful material choice for the heterojunction thin film with regard to the work function is of paramount importance. Recently, profound efforts were made to demonstrate an efficient heterojunction Si solar cell with thin films, which has an extremely low or high work function (e.g., organic polymers, 21 alkali metal fluorides, 1 and transition metal oxides 6-9). Among the materials reported so far, transition metal oxide thin films show high performance as heterojunction contact materials by proper selection of their extremely low or high work function. 6-9 For instance, thermally evaporated molybdenum oxide (MoO 3 ) was reported as an efficient metal oxide material for a heterojunction Si solar cell by its high work function value (> 6 eV). 6 Bullock et al. demonstrated a heterojunction Si solar cell with an efficiency of 19.4% by a formation asymmetric heterojunction containing a selective hole transport contact with the MoO 3 thin film and a selective electron transport contact with the lithium fluoride thin film. 8 Geissbühler et al. achieved a conversion efficiency of 22.5% with a heterojunction Si solar cell by the formation of selective hole transport contact with the MoO 3 thin film and process optimization. 17

It is important to select the material for the heterojunction thin film with an appropriate work function, but it is also crucial to examine a variation of work functions in the fabrication process of the selected material. During the deposition process of a metal oxide thin film on the target substrate, the chemical state of the metal oxide thin film often appears in an undesirable form, and the changed chemical state of the metal oxide has a great influence on the work function. 1 For instance, a thermally evaporated MoO 3 thin film readily reacts with moisture in an air atmosphere, and then, chemisorbed oxygen is present on the MoO 3 surface. As a result of the changed chemical state at the surface of the MoO 3 thin film by surface adsorbrates, the work function of the MoO 3 thin film dramatically decreased from 6.8 eV to 5.3 eV. 18 In addition, an undesirable chemical reaction also occurs at the interface of the transition metal oxide and the deposited target substrate. Greiner et al. also reported that the evaporated MoO 3 thin film was present in a reduced form in the interface of the MoO 3/metal substrate. 19 This reduced MoO 3−x has a lower work function than stoichiometric metal oxide (e.g., $\Phi = 6.8$ eV for MoO 3 and $\Phi = 5.9$ eV for MoO 2). 20 As reported above, the altered chemical state and work function of the metal oxide thin film highly affect the performance of the heterojunction Si solar cell, which is unlike what we expected from the work function of the bulk metal oxide. Therefore, the chemical state and work function of the metal oxide thin film especially at the surface and interface with the Si substrate have to be carefully investigated for efficient heterojunction Si solar cells.

In this work, we focused on the characterization of the chemical state and work function of the evaporated metal oxide thin film on a Si substrate, especially depending on the depth position of the metal oxide thin film, to investigate the transformed chemical state and work function by an undesirable chemical reaction at its outermost surface and the interface of the metal oxide/Si substrate. Nickel oxide (NiO x ) has been chosen as a model material system owing to its advantages for efficient heterojunction thin film candidates; NiO x has a high work function and is optically transparent in the visible region. 21-24 From its outermost surface to near the Si substrate, the NiO x thin film existed in a mixed form with nickel hydroxide [Ni(OH) 2 ], nickel monoxide (NiO), metallic nickel (Ni), and nickel silicide (NiSi 2 ). By the modified chemical state of the NiO x thin film on the Si substrate as a function of the depth position, the work function of the NiO x thin film dramatically changed. In addition, we characterized the performance of the heterojunction Si solar cell with the NiO x thin film depending on the air exposure condition. Because air exposure on the NiO x thin film induces an undesirable chemical reaction and reduction of the work-function, the heterojunction Si solar cell with the air-exposed NiO x thin film shows a low efficiency of 11.84%, while one with the controlled NiO x thin film exhibited a high efficiency of 14.23%.

II. EXPERIMENTAL SECTION
A. Material characterization

Samples for transmission electron microscopy (TEM), depth profiling X-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS) measurements were fabricated by deposition of the NiO x thin film on a mirror-polished Czochraski (CZ) monocrystalline lightly doped p-type Si (100) wafer. The Si wafers were cleaned by the conventional cleaning method using acetone, methanol, and deionized water. Then, the Si wafers were immersed in a diluted HF (5%) solution for a while to remove native oxide. The NiO x thin film was deposited on a Si substrate with a thickness of 15 nm using an e-beam evaporator. Before characterization of the NiO x thin film deposited on a Si wafer, the sample was exposed to air for about 24 h. For high-resolution imaging and chemical mapping with energy dispersive X-ray spectroscopy (EDS), a TEM (Titan cubed G2 60-300, FEI Co.) with an acceleration voltage of 200 kV was used. For the depth profiling XPS and UPS measurement, Ar + ions of 3 keV energy at a scan size of 2 mm × 2 mm and a 240 s sputter interval were used. The core level was referenced to a C 1s peak at 284.8 eV. A secondary electron cutoff was performed using X-ray excitation with a negative bias of − 5 eV to extract the cutoff edge.

B. Fabrication and measurement of metal/NiO x/p-Si contact devices

The top side of the metal/NiO x/p-Si contact device was fabricated by first depositing a 2 nm-thick NiO x thin film on a p-type Si substrate using an e-beam evaporator. For air exposure conditions, the 2 nm-thick NiO x deposited Si substrate was unloaded from the evaporator chamber and exposed to air for about 24 h, and then, a circular shaped Pd/Ag (50/500 nm) metal patch with
a diameter of 4 mm was sequentially deposited by means of a shadow mask. For without air exposure conditions, a circular shaped NiO$_x$/Pd/Ag (2/50/500 nm) was sequentially deposited on a p-type Si substrate without breaking the vacuum state. A full area Pd/Ag (50/500 nm) metal was deposited on the rear side of the Si substrate for ohmic contact formation. Dark current density-voltage (J-V) measurements were taken at room temperature using a Keithley 236 source-measure unit and probe station (MST-8000C).

C. Fabrication and measurement of heterojunction Si solar cell with NiO$_x$ thin film

Heterojunction Si solar cells with a rear NiO$_x$ thin film were fabricated on pyramidal textured p-type c-Si wafers with a thickness of 180 $\mu$m. All wafers were cleaned using the conventional RCA process: deionized water/H$_2$O$_2$/NH$_4$OH (RCA1) at 80 $^\circ$C for 10 min and followed by diluted HF dip (10 wt. %), and deionized water/H$_2$O$_2$/HCl (RCA2) at 80 $^\circ$C for 10 min and followed by 10% HF dip (10 wt. %). Then, the n-type hydrogenated amorphous Si (n$^+$/a-Si:H) thin film with a thickness of 7 nm was deposited on the top side of the Si wafer by the capacitively coupled-plasma (CCP) radio-frequency (RF, 13.56 MHz) glow discharge plasma enhanced chemical vapor deposition (PECVD) method at substrate temperatures ranging from 175 to 200 $^\circ$C. The bottom side of the Si wafer was deposited by a 2 nm-thick NiO$_x$ thin film and a Pd/Ag (50/500 nm) back metal using a thermal evaporator. We conducted the NiO$_x$/Pd/Ag stack using the same method as described above to form the NiO$_x$ thin film with and without air exposure conditions. First, we characterized the surface and interfacial morphology and the elemental atom distribution of the evaporated 15 nm-thick NiO$_x$ thin film on a Si substrate using TEM and EDS, respectively. The cross-sectional TEM image in Fig. 1(b) shows clearly, from the outermost surface of the NiO$_x$ thin film to the Si substrate, poly-crystalline NiO$_x$, 4.5 nm-thick bright amorphous regions, 2 nm-thick dark amorphous regions, and a crystalline Si substrate. This suggests that the chemical reaction took place between the NiO$_x$ and the Si substrate, thereby forming a distinguishing layered structure at the NiO$_x$/Si interface. To characterize the formed interfacial layer between the NiO$_x$ and the Si substrate more clearly, high angle annular dark-field scanning TEM (HAADF-STEM) imaging and corresponding energy dispersive spectrometer (EDS) elemental mapping were conducted [Figs. 1(c)–1(f)]. This STEM image clearly showed the distinguishing dark and gray color regions at the NiO$_x$/Si interface. Figure 1(d) shows a Ni deficient layer at the NiO$_x$/Si interface [a region marked by the yellow arrow line in Fig. 1(d)], and this region matches the dark color region of the STEM image in Fig. 1(c).

III. RESULTS AND DISCUSSION

The main work underlying this paper was an investigation on the chemical state and work function of the NiO$_x$ thin film on a Si substrate as a function of the depth position. The NiO$_x$ thin film with a thickness of 15 nm was deposited on a monocrystalline p-Si wafer, and the NiO$_x$ thin film was exposed to air before material characterization [see Fig. 1(a) for a characterization sample diagram]. First, we characterized the surface and interfacial morphology and the elemental atom distribution of the evaporated 15 nm-thick NiO$_x$ thin film on a Si substrate using TEM and EDS, respectively. The cross-sectional TEM image in Fig. 1(b) shows clearly, from the outermost surface of the NiO$_x$ thin film to the Si substrate, poly-crystalline NiO$_x$, 4.5 nm-thick bright amorphous regions, 2 nm-thick dark amorphous regions, and a crystalline Si substrate. This suggests that the chemical reaction took place between the NiO$_x$ and the Si substrate, thereby forming a distinguishing layered structure at the NiO$_x$/Si interface. To characterize the formed interfacial layer between the NiO$_x$ and the Si substrate more clearly, high angle annular dark-field scanning TEM (HAADF-STEM) imaging and corresponding energy dispersive spectrometer (EDS) elemental mapping were conducted [Figs. 1(c)–1(f)]. This STEM image clearly showed the distinguishing dark and gray color regions at the NiO$_x$/Si interface. Figure 1(d) shows a Ni deficient layer at the NiO$_x$/Si interface [a region marked by the yellow arrow line in Fig. 1(d)], and this region matches the dark color region of the STEM image in Fig. 1(c).
Interestingly, we observed the dominant composition of Si and O atoms at the Ni deficient layer. The EDS mapping data also show the intermixing layer of Ni and Si without O atoms at the bottom region of the Ni deficit layer [the region marked by a red arrow line in Fig. 1(d)], and this region matches the gray color region of the STEM image in Fig. 1(c).

For quantitative analysis of the element distribution on the NiO\textsubscript{x}/Si substrate, we conducted an EDS line scan as shown by the white dotted line in the cross-sectional STEM image [Fig. 1(c)], and the corresponding atomic percentage curves as a function of the distance from the NiO\textsubscript{x} surface are shown in Fig. 1(g). Until a distance of 6 nm below the outermost surface of NiO\textsubscript{x}, only the Ni and O elements exist, and the measured atomic percentage is about 60% and 40%, respectively. Closer to the interface of the NiO\textsubscript{x}/Si substrate, the atomic percentage of Si begins to increase from a distance of 6 nm by diffusion from the Si substrate. The atomic percentage of Ni gradually decreases from distances of 6 nm to 12 nm. At this position, the Ni elements were even reduced to an atomic percentage of 9% from 60%, but the atomic percentage of O and Si was about 47% and 44%, respectively, showing the apparent Ni deficit layer in the NiO\textsubscript{x} thin film. After a distance of 12 nm, the atomic percentage of Ni increases until 14 nm, and then it decreases again showing a hump curve. The peak atomic percentage of Ni and Si is 39% and 53%, respectively, and O is only ~8% at a distance of 14 nm, which means that the atomic composition of Ni and Si is dominant, and this state is obviously different from NiO\textsubscript{x} at the outermost surface and the Ni deficit layer.

We analyzed the chemical state of the 15 nm-thick NiO\textsubscript{x} thin film on a Si substrate as a function of the depth position using depth-profiling XPS. Figure 2(a) shows the measured XPS spectra of Ni 2p\textsubscript{3/2} as a function of Ar-ion etching time. The spectrum of the NiO\textsubscript{x} thin film at the outermost surface shows the NiO peak at 853.84 eV (violet solid lines) and the Ni(OH)\textsubscript{2} peak at 855.74 eV (magenta solid lines). After the surface etching process on the NiO\textsubscript{x} thin film in a vacuum chamber, we observed a change in the XPS spectra of Ni 2p\textsubscript{3/2}. At the etching time of 2.4 ms, the NiO peak intensity slightly increased, and the metallic Ni peak at 852.13 eV (green solid lines) was newly observed, while the Ni(OH)\textsubscript{2} peak intensity decreased. When we increased the etching time to 3.1 ms, the metallic Ni peak intensity appeared prominently, and the intensity of both NiO and Ni(OH)\textsubscript{2} was dramatically decreased. Then, the etching time increased to 3.6 ms, and the metallic Ni, NiO, and Ni(OH)\textsubscript{2} peaks were no longer observed; instead, there was a NiSi peak at 853.44 eV (orange solid line). Figure 2(b) shows the measured XPS spectra of O 1s on the NiO\textsubscript{x} thin film as a function of the etching time. The XPS spectra of the NiO\textsubscript{x} thin film at the outermost surface show the NiO bonding state at 529.51 eV and hydroxide (OH) bonding at 531.13 eV. After a surface etching time of 2.4 ms, the intensity of OH bonding is dramatically decreased. Interestingly, SiO\textsubscript{x} bonding at 532.18 eV is observed at an etching time of 3.1 ms, and the intensity of the NiO bond state is dramatically decreased. The XPS spectra of Si 2p\textsubscript{3/2} also show the SiO\textsubscript{x} formation at the NiO\textsubscript{x}/Si substrate at an etching time of 3.1 ms (see Fig. S1 of the supplementary material). These results indicate that NiO is reduced at the interface of the NiO\textsubscript{x}/Si substrate, and Si is oxidized instead. After an etching time of 3.6 ms, a small amount of the OH peak is observed. We believe that the negligible amount of the measured OH bond is due to the diluted HF treatment followed by a DI water rinse on the Si substrate for native oxide removal.

From TEM, EDS, and depth-profiling XPS analysis, we confirmed the dramatically changed chemical state of the evaporated NiO\textsubscript{x} thin film on the Si substrate as a function of the depth position. The change in the chemical state of the evaporated NiO\textsubscript{x} thin film depending on the depth position was due to the chemical
reaction at the outermost surface of the NiO\(_x\) thin film and the interface of the NiO\(_x\)/Si substrate. After deposition of the 15 nm-thick NiO\(_x\) thin film on the Si substrate in the evaporator vacuum chamber, the NiO\(_x\)/Si substrate was unloaded from the chamber and then exposed to air for ∼24 h before the depth-profiling XPS measurement. The air-exposed outermost surface of the NiO\(_x\) thin film reacted with the moisture in the air atmosphere, and the initial chemical state of metallic Ni and/or NiO transformed to a Ni(OH)\(_2\) state.\(^{25–27}\) At the NiO\(_x\)/Si interface, a reduction of evaporated NiO\(_x\) occurred, and Si was oxidized instead according to the TEM, EDS, and XPS results as presented in Figs. 1, 2(a), and 2(b). The reduction of the evaporated NiO\(_x\) thin film and oxidation of the Si substrate were explained by classical equilibrium thermodynamics. According to the oxygen-potential diagrams based on the Ellingham diagram and Gibbs formation energy (\(AG\)) principle, the \(\Delta G^0\)–T plots of the oxygen-potential diagram for 2NiO and SiO\(_2\) are presented in Fig. S2. In the Ellingham diagram, for instance, \(\Delta G^0\) of 2NiO and SiO\(_2\) at 300 K were −412 and −772 kJ/mol, respectively.\(^{28,29}\) Due to the more negative \(\Delta G^0\) of SiO\(_2\) than that of 2NiO, the oxidation of Si atoms by NiO was spontaneous at the interface of the NiO\(_x\)/Si substrate. In addition, we anticipated that some Ni atoms reduced from NiO were diffused to the Si substrate, and hence, NiSi\(_x\) was newly formed.

It is well known that the chemical state strongly influences a transition-metal oxide's electronic properties such as work function.\(^{30}\) The work function of the transition-metal oxide thin film is an important parameter for determining performance of a hole selective contact Si solar cell. Therefore, for designing an efficient heterojunction Si solar cell with the NiO\(_x\) thin film, it was necessary to investigate the effect of the surface reaction of the NiO\(_x\) thin film on the performance of the heterojunction Si solar cell.

We investigated the dark current density-voltage characteristic of the metal/NiO\(_x\)/p-Si contact. The thickness of NiO\(_x\) in the metal/NiO\(_x\)/p-Si contact is 2 nm as to maximize the impact of the surface reaction in the NiO\(_x\) thin films on the electrical property of the contact. In addition, thick NiO\(_x\) thin films could increase the series resistance of the contact and, therefore, decrease the efficiency of the heterojunction Si solar cells.\(^{31}\) Note that we used a 15 nm-thick NiO\(_x\) thin film for the material characterization in order to separately examine the influence of the surface reactions at the air/NiO\(_x\) and NiO\(_x\)/Si interfaces on the chemical states and work function of the NiO\(_x\)/p-Si contact. Figure 3(a) shows the different electrical contact behaviors of the metal/NiO\(_x\)/p-Si contact depending on the air exposure condition. First, for the sample of our investigation, we deposited a NiO\(_x\) thin film on p-Si, and the NiO\(_x\)/p-Si was exposed to air for 24 h. Then, we deposited sequentially Pd/Ag metal on NiO\(_x\).
The dark current density-voltage curve of metallic NiOx (with air-exposure)/p-Si contact structure shows Schottky contact behaviors [red line in Fig. 3(b)]. On the other hand, we fabricated a metal/NiOx/p-Si contact structure without air exposure of the NiOx thin film to minimize the chemical reaction at the outermost surface of NiOx. Interestingly, the metal/NiOx (without air exposure)/p-Si contact structure shows ohmic contact behavior [blue line in Fig. 3(b)].

The different electrical transport behaviors depending on the air exposure of the NiOx thin film were due to the work function of the outermost NiOx thin film. We characterized the work function of the NiOx thin film depending on the air exposure conditions. The work function of a 2 nm-thick NiOx thin film on a p-Si substrate with and without air exposure was also characterized using depth profiling UPS. The measured work function of the outermost NiOx thin film with air exposure was 4.13 eV by Ni(OH)2 formation, and the work function at the subsurface NiOx thin film was ~5 eV by NiSi formation [see Fig. S3(a) of the supplementary material]. The work function of the NiOx thin film without air exposure was lower than that of the p-type Si substrate (Φp-Si = 4.8–4.9 eV), and it induced Schottky contact formation at the NiOx (with air exposure)/p-Si heterojunction. Furthermore, we also characterized the work function of the NiOx thin film without air exposure by depositing a Pd metal capping layer with a thickness of ~5 nm. The measured work function of the NiOx thin film without air exposure after removal of the Pd capping layer was in the range of 5–5.3 eV. We anticipate that the NiOx thin film without air exposure can maintain the work function value to more than 5 eV by suppressing the Ni(OH)2 formation, and the work function also decreased to ~5 eV at the NiOx/Si interface by NiSi formation as we mentioned above. The work function of the NiOx thin film without air exposure was higher than p-Si, and it enabled ohmic contact formation at the NiOx (without air exposure)/p-Si heterojunction.

We confirmed that the electrical contact behavior was significantly affected by the surface property of the NiOx thin film. Furthermore, we also investigated the effects of the work function of the NiOx thin film on the heterojunction Si solar cell. The inset of Fig. 3(b) shows our fabricated heterojunction Si solar cell with a 2 nm-thick NiOx thin film. The heterojunction of n'-a-Si/p-Si at the front side made the Schottky contact to selectively extract photogenerated carriers. At the rear side, the heterojunction of NiOx/p-Si was formed, and the electrical contact was determined by status of the NiOx thin film as we confirmed the Schottky contact formation using the NiOx thin film with air exposure and ohmic contact formation using the NiOx thin film without air exposure. Figure 3(b) shows the illuminated current density-voltage curve of the heterojunction Si solar cell using a 2 nm-thick NiOx thin film with and without air exposure. The average value of photocurrent parameters of both heterojunction Si solar cells is also tabulated in Table I (see Tables S1 and S2 of the supplementary material). The heterojunction Si solar cell using the NiOx thin film with air exposure experiences a relatively low solar cell performance with an efficiency of 11.84% ± 0.08%, while the solar cell using the NiOx thin film without air exposure exhibited enhanced performance with an efficiency of 14.23% ± 0.08%.

The higher efficiency of the heterojunction Si solar cell with the NiOx thin film (without air exposure) compared to the one with the NiOx thin film (with air exposure) was due to the asymmetric band-bending formation in the p-Si absorber for more efficient photogenerated carrier extraction compared to the symmetric bending structure.4,14,32 In particular, at the heterojunction of NiOx/p-Si, a gradient of the hole carrier quasi-Fermi energy level occurs when the work function of the heterojunction layer is not sufficiently large.33,34 By the gradient of the hole quasi-Fermi energy level, the difference in the electron and hole quasi-Fermi energy level at the outside of the p-Si absorber was reduced, and it resulted in a diminished Voc in the heterojunction Si solar cell. Therefore, the heterojunction Si solar cell using the NiOx thin film (with air exposure) had a relatively low Voc of 507 ± 4.41 mV owing to the low work function of the NiOx thin film (with air exposure). By contrast, the cell using the NiOx thin film (without air exposure) had a higher Voc of 565 ± 0.71 mV resulting from the high work function of the NiOx thin film (without air exposure). The result also suggests that the NiOx thin film, without air exposure, provides reduced back surface recombination compared to that with air exposure. Such improved back surface passivation is attributed to decreased interface defect density in case of the film without air exposure. The Fermi level pinning effect, due to a large number of defects, results in formation of the Schottky barrier.33,35 The dark and the illuminated current density-voltage measurements in Figs. 3(a) and 3(b) indeed show good agreement in this aspect. Further works on interface defect control will introduce even higher Voc and improved carrier transport property and hence higher conversion efficiency solar cells. Another gain in the heterojunction Si solar cell using the NiOx thin film (without air exposure) was the improved fill-factor (FF) by an absolute 4.61% due to ohmic contact formation, which reduced the contact resistivity, as demonstrated in the result in Fig. 3(a).37,38 Therefore, we can conclude that the engineering of work function of metal oxide, which is highly affected by the chemical reaction at the outermost surface and adjacent materials, is important for controlling the electrical contact behavior and fabricating efficient heterojunction Si solar cells.

### IV. CONCLUSION

In this work, we systematically investigated the chemical state and work function of the evaporated NiOx thin film on a Si substrate. The chemical state of the NiOx thin film changed dramatically as a function of the depth position by the chemical reaction at the outermost surface of the air-exposed NiOx thin film and the interface of the NiOx/Si substrate. The outermost surface of the NiOx thin film exhibited a low work function of 4.2 eV by formation of Ni(OH)2, and the NiOx thin film near the Si substrate experienced a work function of ~5 eV by formation NiSi. We also investigated

### Table I. Comparison of the performance of a heterojunction Si solar cell with the NiOx thin film with and without air exposure.

| NiOx (with air exposure) | NiOx (without air exposure) |
|--------------------------|-----------------------------|
| Jsc (mA/cm²)            | 31.14 ± 0.11                |
| Voc (mV)                | 507 ± 4.41                  |
| FF (%)                  | 74.99 ± 0.83                |
| η (%)                   | 11.84 ± 0.25                |
| Jsc (mA/cm²)            | 31.65 ± 0.08                |
| Voc (mV)                | 565 ± 0.71                  |
| FF (%)                  | 79.60 ± 0.75                |
| η (%)                   | 14.23 ± 0.08                |
the electrical contact behavior of the heterojunction of NiO/α-Si and the performance of the heterojunction Si solar cell. The heterojunction of metal/NiO (with air exposure)/α-Si exhibited Schottky contact behavior, but the heterojunction of metal/NiO (without air exposure) showed ohmic contact behavior by suppressing the undesirable surface reaction of NiO with an air atmosphere. The work function of the NiO thin film had a huge impact on the performance of the heterojunction Si solar cell. The heterojunction Si solar cell with NiO (without air exposure) experienced a relatively high efficiency of 14.23% by a higher Voc and FF by forming a higher work function suitable for the hole selective contact structure compared to the one using NiO (with air exposure) with an efficiency of 11.84%. We anticipate that this achievement will pave the way for creation of efficient heterojunction Si solar cells with the appropriate work function of the metal oxide thin film by meticulously controlling the surface chemical reaction.

SUPPLEMENTARY MATERIAL

See supplementary material for additional data of X-ray photoelectron spectroscopy, standard Gibb's formation energy, work-function, and heterojunction Si solar cell performance.

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