NiN-Passivated NiO Hole-Transport Layer Improves Halide Perovskite-Based Solar Cell

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ABSTRACT: The interfaces between inorganic selective contacts and halide perovskites (HaPs) are possibly the greatest challenge for making stable and reproducible solar cells with these materials. NiO, an attractive hole-transport layer as it fits the electronic structure of HaPs, is highly stable and can be produced at a low cost. Furthermore, NiO can be fabricated via scalable and controlled physical deposition methods such as RF sputtering to facilitate the quest for scalable, solvent-free, vacuum-deposited HaP-based solar cells (PSCs). However, the interface between NiO and HaPs is still not well-controlled, which leads at times to a lack of stability and $V_{oc}$ losses. Here, we use RF sputtering to fabricate NiO and then cover it with a Ni$_3$N layer without breaking vacuum. The Ni$_3$N layer protects NiO doubly during PSC production. Firstly, the Ni$_3$N layer protects NiO from Ni$^{3+}$ species being reduced to Ni$^{2+}$ by Ar plasma, thus maintaining NiO$_x$ conductivity. Secondly, it passivates the interface between NiO$_x$ and the HaPs, retaining PSC stability over time. This double effect improves PSC efficiency from an average of 16.5% with a 17.4% record cell to a 19% average with a 19.8% record cell and increases the device stability.

KEYWORDS: halide perovskites, solar cells, nickel oxide, nickel nitride, passivation, interface

INTRODUCTION

Halide perovskite solar cells (PSCs) have been extensively researched since 2009, and their power conversion efficiency (PCE) has improved toward their Shockley–Queisser limit. One of the main factors for the high PCE in PSCs composed of polycrystalline thin films is the intrinsically low defect concentration in the bulk of halide perovskites (HaPs). However, PSCs are not constructed from HaPs alone, and defect states at interfaces between HaP films and adjacent layers adversely affect the conversion efficiency, long-term stability, and reproducibility of PSCs.

Nickel oxide (NiO$_x$) is a sturdy and efficient hole-transport material (HTM), which has been reported to improve the stability of PSCs over that achieved with organic HTMs.

Radio-frequency (RF) sputtering is a scalable fabrication method for metal oxides with a highly controlled oxygen partial pressure. Wang et al. have shown that sputtered NiO at low temperatures has controlled transparency and conductivity that affect the efficiency of the PSC. Moreover, sputtered NiO is preferred over wet-chemically processed NiO$_x$ because it leaves no residues of solvents or precursors that can damage the stability and efficiency of the final device. However, sputtered NiO$_x$ hole-transport layers (HTLs) with no further treatment have parasitic resistance that leads to PSCs with moderate fill factors (FFs) and efficiencies.

One of the challenges of using NiO$_x$ as HTM is its nonstoichiometric composition; Ni$^{3+}$ readily oxidizes into Ni$^{4+}$. Then, charge balance leads to a Ni-poor material, NiO$_x$ with, i.e., $x < 1$, which is a p-type semiconductor due to Ni vacancies. Excess oxygen in more conductive NiO$_x$ leads to more Ni$^{3+}$ species. On the one hand, the Ni$^{3+}$ cations are essential as dopants to improve NiO$_x$ conductivity. On the other hand, the same Ni$^{3+}$ cation is highly reactive and leads to degradation of the adjacent HaP layer in the solar device.

Earlier attempts to passivate the NiO$_x$/HaP interface have improved PSC efficiency and stability. Most passivation techniques have so far included deposition of a buffer layer through spin coating or introducing additives into the HaP solution. These passivation approaches are not suited for the fabrication of larger area perovskite devices that would inevitably need solvent-less methods, for both active layer deposition and interface modification.
In this work, we use RF magnetron sputtering for an alternative in-situ route to passivate the HaP/NiO interface. The approach is well-suited for upscaling PSC throughput via all vacuum-processed device fabrication techniques. We deposit nickel nitride (Ni$_x$N), a very small bandgap semiconductor, as an ultra-thin ∼2 nm layer on NiO$_x$ essentially an in-situ modification of the NiO$_x$ surface without breaking vacuum. This Ni$_x$N interlayer becomes a buffer between the oxide and the HaP film. We then investigate its effects on PSC performance and stability.

We find that Ni$_x$N protects NiO$_x$ from the reduction of Ni$^{3+}$ cations to Ni$^{2+}$ during the Ar plasma cleaning step, typically used to improve the wettability of the oxide, thus maintaining NiO$_x$ conductivity. The Ni$_x$N layer also passivates the interface between NiO$_x$ and MAPbI$_3$, and inhibits the reaction between MAPbI$_3$ and Ni$^{2+}$. Although Ni$_x$N is conductive and could be expected to introduce trap states that damage PV performance, we show that thin enough Ni$_x$N can passivate the interface between NiO$_x$ and HaP, thereby improving device efficiency and stability.

## EXPERIMENTAL SECTION

### Fabrication. Substrate Cleaning.
Fluorine-doped tin oxide (FTO, KINTEC Company)-coated glass substrates (TEC 15, 1 inch × 1 inch) were cleaned in a sonication bath with soap (Decon 90) and deionized water and then rinsed in deionized water followed by dry ethanol.

NiO$_x$ and Ni$_x$N were deposited using RF sputtering (AJA International Inc.) from 2-inch NiO and Ni targets, respectively (Kurt J. Lesker, 99.9%). NiO$_x$ deposition was done at room temperature with an Ar gas flow of 30 sccm and a total chamber pressure of 3 mTorr. Ni$_x$N deposition was done at room temperature and a total chamber pressure of 3 mTorr, with Ar and N$_2$ gas flows of 15 and 45 sccm, respectively. In the first stage, the NiO$_x$ target was set to 80 W for 1 h, then the chamber was purged for 10 min, and finally, the Ni target was set to 60 W for 3 min. Ar plasma cleaning was performed by applying a power of 30 W on the substrate with an Ar flow of 30 sccm.

MAPbI$_3$ was synthesized from MAI (Greatcell Solar) and PbI$_2$ (Sigma-Aldrich, 99.999%) precursors in a 1:1 ratio at a concentration of 1.5 M. The precursors were dissolved overnight at 60 °C in γ-butyrolactone (GBL, Alfa Aesar, 99%) and dimethyl sulfoxide (DMSO, Sigma-Aldrich, anhydrous) at a 7:3 ratio. The solution was spin-coated at 4000 rpm for 35 s with 800 μL of a toluene (Sigma-Aldrich, anhydrous) anti-solvent drip after 30 s. For device fabrication, 20 mg of PCBM was dissolved in 1 mL of chlorobenzene overnight, spin-coated at 2000 rpm for 30 s, and annealed for 10 min. After 15 min of cooling, a solution of 3 mg of bathocuproine in 6 mL of isopropanol was spin-coated at 4000 rpm for 30 s. Finally, thermal evaporation was performed to deposit round Ag contacts of 3 mm diameter. A scheme of the device structure is given in the Supporting Information (SI) (Figure S1).

### Characterization.
Ultraviolet photoemission spectroscopy (UPS) was used to probe the vacuum level and the position of the Fermi level with respect to the valence band edge, leading to the determination of the work function (WF) and ionization energy (IE) of the measured materials at a resolution of 0.15 eV. UPS was performed in an ultrahigh vacuum (10$^{-10}$ Torr) with He I photons (21.22 eV) generated by a He discharge lamp, with a pass energy of 5 eV and a 0.02 eV step size.

X-ray photoelectron spectroscopy (XPS) with an Al Kα anode (1486.6 eV) was used to probe the Ni 2p, N 1s, and C 1s core levels at a resolution of 0.8 eV. Scans were taken with a pass energy of 25 eV and a 0.05 eV step size at a low base pressure of 10$^{-9}$ Torr. UPS and XPS were conducted on the samples before and after a 5 s Ar$^+$ etching. The Ar$^+$ etching was performed using an Ar ion gun at a pressure of 5.5 × 10$^{-3}$ Torr, a 1000 V acceleration voltage, and a 20 mA emission current. The current measured during the etching process was around 15 μA. All UPS, XPS, and Ar$^+$ etching steps were performed in the same vacuum chamber without sample exposure to ambient atmosphere.

XPS in Bar-Ilan University (BIU) was performed using a Thermo Scientific Nexus spectrometer XPS system with an Al Kα anode (1486.6 eV) at a base pressure of ∼7 × 10$^{-8}$ Pa (∼5 × 10$^{-10}$ Torr). The binding energy (BE) was calibrated vs carbon (C 1s = 285 eV). Survey scans were collected with a pass energy of 200 eV and a 1.0 eV step size, followed by high-resolution scans with a pass energy of 50 eV and a step size of 0.1 eV. The samples were exposed for ∼1 min to air during the sample transfer.

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**Figure 1.** Narrow-range XPS plots of the (a) N 1s peak of a reference NiO$_x$ (black) and Ni$_x$N-modified NiO$_x$ (red), (b) C 1s peak of a reference NiO$_x$ (black) and Ni$_x$N-modified NiO$_x$ (red), before (dashed) and after (solid) Ar$^+$ etching, (c) O 1s and (d) Ni 2p peaks of a reference NiO$_x$ before (dashed) and after (solid) Ar$^+$ etching, and (e) O 1s and (f) Ni 2p peaks of a Ni$_x$N-modified NiO$_x$ before (dashed) and after (solid) Ar$^+$ etching.
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We used RF sputtering to deposit a NiO film, illuminated by a deuterium (D₂) atmosphere, using an air photoemission system (ASKP150200, KP Technology Ltd.), illuminated by a deuterium (D₂) UV source, coupled with a motorized grating monochromator.

Transient PL decay measurements on the HaP thin films deposited on NiO/FTO substrates with and without a NiN interlayer were measured in ambient conditions. The HaP thin films were excited with a 450 nm picosecond pulsed laser diode source, and PL decay characteristics in the 760–765 nm emission wavelength range were recorded with a photomultiplier tube.

■ RESULTS AND DISCUSSION

We used RF sputtering to deposit a NiO film from a NiO target on an FTO-coated glass substrate. To modify the NiO surface, we used reactive sputtering treatment of the Ni target with a plasma composition of 25% Ar and 75% N₂.

To examine the reactive sputtering effect on the NiO surface, we used XPS on NiO samples modified and unmodified by reactive sputtering. The XPS spectra from both NiO samples show a broad and shallow nitrogen signal around a binding energy of 399 eV, which typically fits the signal of nitrogen in organic matrices (Figure 1a). However, the NiO layer after a reactive sputtering treatment of a Ni target with a plasma composition of 25% Ar and 75% N₂ exhibits a clear, sharp nitrogen peak at a binding energy of 397.7 eV that fits metal nitrides.

To examine the effect of the Ni,N modification on NiO, we conducted 5 s of Ar⁺ etching to clean the surface of contaminants and mimic the layers built into the solar cells. After Ar⁺ etching, the intensity of C 1s is reduced, indicative of the surface cleaning effect of the s etching process. The BE of the C 1s core level increases by 0.3 eV, from 284.9 to 285.2 eV, for both unmodified NiO and Ni,N-modified NiO. Any carbon present in the layers is adventitious, and the BE difference is most likely due to a change in the chemical environment between the top and sub-surface species, as the surface is Ar⁺ etched (Figure 1b).

Nickel and oxygen are not adventitious; hence, their BE can be directly linked to the Fermi level (E_F) position in the material. The O 1s feature is a superposition of two core level peaks corresponding to oxygen bound to Ni⁢²⁺ and Ni⁢³⁺. The BE of the O 1s peak is found to increase by 0.6 eV upon Ar⁺ etching, from 528.6 to 529.2 eV, for NiO (Figure 1c) but only by 0.2 eV, from 528.7 to 528.9 eV, for Ni,N-modified NiO (Figure 1c). O 1s peak fitting details can be found in Figure S2. Similarly, the BE of the tallest Ni 2p peak increases by 0.4 eV from 852.7 to 853.1 eV for NiO (Figure 1d) but remains unchanged at 853.2 eV for Ni,N-modified NiO (Figure 1f).

To understand the effect of Ar⁺ etching on the electronic structure of the NiO surface, we used UPS to determine the WF and IE of the NiO films, both with and without NiN modification. The valence band maximum (VBM) positions obtained by linear extrapolation of the leading edge of the filled states are shown in Figure 2a. Notably, the NiO valence band shows a 0.39 eV shift away from E_F upon Ar⁺ etching, whereas the Ni,N-modified NiO valence band remains at the same position (negligible shift of 0.03 eV). Comparing the valence bands of the NiO reference and Ni,N-modified NiO after 5 s of Ar⁺ etching, we find the VBM to be 0.30 eV closer to the Fermi level for Ni,N-modified NiO (1.00 eV below E_F) than for the unmodified NiO (1.30 eV below E_F) (Figure 2). This trend is further investigated by measuring a 40 nm thick Ni,N on NiO whose VBM reaches all the way to the Fermi level, forming almost a Fermi step (Figure S3).

The resulting energy diagrams for NiO (left) and Ni,N-modified NiO (right) before and after 5 s Ar⁺ etching, plotted relative to the vacuum level (E_vac), are shown in Figure 2b. For clarity, similar energy diagrams, plotted relative to the Fermi energy (E_F), as they were measured, are shown in the SI.

Figure 2. (a) Normalized UPS valence spectra plotted with respect to the Fermi level (E_F) for NiO (black) and Ni,N-modified NiO (red) before (dashed) and after (solid) 5 s Ar⁺ etching. (b) Energy diagrams for NiO (left) and Ni,N-modified NiO (right) before (dashed) and after (solid) 5 s Ar⁺ etching. All energy levels are plotted with respect to the vacuum level (E_vac). Energy diagrams plotted relative to the Fermi energy (E_F) are shown in the SI (Figure S4).
corroborated by the unchanged energies of the valence states during subsequent processing steps, which is further evidenced by the NiO$_x$ surfaces, we used 60 s RF sputtering with Ar plasma to etch the NiO$_x$ (Figure 2b). The UPS and XPS data suggest that the NiO$_x$ presence of NiO$_x$ vacancies (V$_{Ni}$) part of the gap (Figure 2b), we infer that the NiO$_x$ BEs of the Ni 2p and O 1s core levels, reflecting a Fermi level shift measured by UPS (a decrease in E$_F$) decrease after NiO$_x$ etching leads to a decrease in the NiO$_x$ surface. Oxygen vacancies can reduce the charge carrier concentration as $V'_O + O'^- + \frac{1}{2}O_2 \rightarrow \frac{1}{2}V'O_2$, and thereby reduce the p-doping level of the NiO$_x$ films. Ni$_x$N-modified NiO$_x$ is more resistant to such a process, as shown by the XPS and UPS results, demonstrating the passivating effects of Ni$_x$N on the NiO$_x$ surface. This passivating effect makes the Ni$_x$N-modified NiO$_x$ film less prone to electronic structure changes during subsequent processing steps, which is further corroborated by the unchanged energies of the valence states with respect to the Fermi level in Figure 2a.

As a minor point, the decrease in the adventitious C 1s peak intensity upon Ar$^{+}$ etching of both surfaces (Figure 1b) is consistent with a ∼0.4 eV vacuum level ($E_{vac}$) shift, which agrees with the 0.42 eV change in the Ni$_x$N-modified NiO$_x$ WF measured by UPS (a decrease in $E_{vac}$ from 4.52 to 4.10 eV as seen in Figure S4) above $E_F$ upon Ar$^{+}$ etching (Figure 2b). For unmodified NiO$_x$, however, the WF decreases by 0.8 eV, a combination of an ∼0.4 eV decrease in $E_{vac}$ and an ∼0.4 eV downward shift of the band edges with respect to $E_F$. To check if the effect of Ar$^{+}$ etching performed in the XPS measurements resembles that of the Ar plasma cleaning, performed via RF sputtering, of the unmodified NiO$_x$ and Ni$_x$N-modified NiO$_x$ surfaces, we used 60 s RF sputtering with Ar plasma to etch NiO$_x$ with and without Ni$_x$N modification, to imitate the conditions before MAPbI$_3$ spin coating.

The impact of the Ar plasma on the optical transparency of the unmodified NiO$_x$ and the Ni$_x$N-modified NiO$_x$ was examined via total transmission measurements over a range of 370–950 nm. We found that in the visible range, Ar plasma treatment did not change the transparency of the unmodified NiO$_x$. The Ni$_x$N modification reduced NiO$_x$ transparency by ∼1.5%, which is expected because of the narrow band gap of Ni$_x$N. The Ar plasma treatment etched away part of the Ni$_x$N and improved the transparency to bring it closer to that of the unmodified NiO$_x$ (Figure 3a). The Ar plasma effect on the Ni$_x$N-modified NiO$_x$ together with the lack of change in the $E_F$ position in the material’s gap seen by XPS and UPS, suggests that the Ni$_x$N forms a protective layer on top of the NiO$_x$, preventing a reaction between the NiO$_x$ and the Ar plasma.

The NiO$_x$ film protection by the Ni$_x$N layer from the Ar plasma was investigated via two-probe electrical measurements, inspecting the resistance along the Z axis (perpendicular to the surface) between the FTO electrode and the NiO$_x$ surface with and without a Ni$_x$N layer, both before and after Ar plasma treatment. The Ar plasma treatment dramatically increased the unmodified NiO$_x$ resistance ∼40X, from 1.9 MΩ before to 80 MΩ after. The Ni$_x$N layer reduced the NiO$_x$ resistance from 1.9 to 0.09 MΩ before plasma treatment, but even more critically, after Ar plasma treatment, the resistance increased about three times to 0.3 MΩ, lower than that of the unmodified NiO$_x$ (Figure 3b). The dramatic resistance increase of the unmodified NiO$_x$ after the Ar plasma treatment via RF sputtering indicates a decrease in O$^-$ concentration in the NiO$_x$ film, which reduces the NiO$_x$ surface. This interpretation fits the results from XPS, which shows that Ar$^{+}$ etching leads to a decrease in the Ni$_{39}$/Ni$_{29}^+$ ratio. The likely cause is that RF Ar plasma sputtering, similar to Ar$^{+}$ etching, removes more of the lighter oxygen atoms than of the heavier Ni atoms, leading to V$_O$ and reduction in the NiO$_x$ p-doping levels. The result is that the NiO$_x$ is less p-type and becomes less conductive. The Ni$_x$N layer modification decreases the resistance by around 20%, while it increases after Ar plasma, the resistance is still six times smaller than that of NiO$_x$ before Ar plasma treatment. The XPS measurements suggest an explanation for preserving the low resistance after Ar plasma by applying the Ni$_x$N layer, namely, that the original Ni$_{39}^+$ concentration is retained. The results from UPS are consistent with the resistance decrease after Ni$_x$N modification of NiO$_x$. The energy of the VBM is closer to $E_F$, from 5.1 eV, to 4.10 eV for Ni$_x$N-modified NiO$_x$, with and without Ni$_x$N modification, to imitate the conditions before MAPbI$_3$ spin coating.

After measuring the transparency and resistance of NiO$_x$ with and without Ni$_x$N, before and after plasma etching, we marked Ni$_x$N-modified NiO$_x$ after plasma treatment as the best candidate for PSCs. Thus, we deposited MAPbI$_3$ on top of NiO$_x$ with and without a Ni$_x$N layer after plasma treatment and then performed time-resolved photoluminescence (TRPL) to measure differences in charge extraction after Ni$_x$N deposition and plasma treatment. A fit of the PL decay to a double exponential curve typically indicates two kinds of decay mechanisms, which are common when HAP is deposited on a selective contact. A short lifetime $\tau_1$ corresponds to
charge transfer and detrapping of charge due to light exposure, and a longer lifetime \( \tau_c \) corresponds to recombinations at the interface and within the absorber. Because \( \tau_x \) and \( \tau_z \) were hard to distinguish, we chose to calculate only \( \tau_x \) according to a monoexponential fit at a decay time \( >60 \text{ ns} \).\(^{35}\) Similar lifetimes, 31 and 29 ns for MAPbI\(_3\) on NiO\(_x\) and Ni\(_N\)-modified NiO\(_x\), respectively (Figure 4a), indicate that Ni\(_N\) modification did not cause more (or less) recombination at the interface. Furthermore, PEYS, AFM, SEM, and XRD measurements (Figure 4b and Figures S5–S7) do not differ between MAPbI\(_3\) layers deposited on Ni\(_N\)-modified or unmodified NiO\(_x\).

AFM imaging of the surfaces before and after Ni\(_N\) modification does not show any difference in morphology (Figure S5).

SEM and XRD (Figures S6 and S7) measurements show no significant difference in MAPbI\(_3\) morphology and crystallinity (peak presence, positions, and widths). Both XRD analysis and SEM micrographs did not show any signs of PbI\(_2\) beyond the peak-to-noise ratio level.

PEYS (Figure 4b) yielded the same values for the MAPbI\(_3\) IE between samples deposited on NiO\(_x\) or Ni\(_N\)-modified NiO\(_x\) in dry N\(_2\).

The MAPbI\(_3\) surface morphology similarities before and after Ni\(_N\) modification of NiO\(_x\) and the PEYS and XRD results indicate and even imply that the solar cell efficiency improvement in these samples is caused by the Ni\(_N\) layer effect on the NiO\(_x\) selective contact rather than an effect on the MAPbI\(_3\) layer.

To test the photovoltaic activity of the Ni\(_N\)-modified cells, \( I-V \) measurements, in the dark and under illumination, were recorded on all complete PSCs in both ascending and descending voltage scan directions (Figure S8), but only the descending direction is shown for simplicity (Figure 5a). Statistics on 30 PSCs reveal that the Ni\(_N\) passivation layer affects the entire device in two main ways. As the etching time is decreased, the Ni\(_N\) layer becomes thicker, and the \( V_{oc} \) decreases from an average of 1.05 V for cells with unmodified NiO\(_x\) to 0.8 V for Ni\(_N\) with no plasma etching (Figure 5b). \( V_{oc} \) highly depends on the Ni\(_N\) thickness, and most of the 0.25 V \( V_{oc} \) loss is gained back as the Ar plasma treatment increases, and Ni\(_N\) gets thinner, up to a negligible value of 0.01 V. This effect of the Ni\(_N\) thickness on \( V_{oc} \) can be linked to the UPS-measured VBM shift of up to 0.37 eV toward \( E_F \) as the \( \sim 2 \text{ nm} \) Ni\(_N\) thickness increases, all the way to the Fermi level when the Ni\(_N\) is 40 nm thick (Figure S3). The similarity in \( V_{oc} \) between these two samples is consistent with the similar results obtained by TRPL. At the same time, the FF improves dramatically from a 65% average with unmodified NiO\(_x\) to 75% with the Ni\(_N\) layer, regardless of its thickness or the etching time (Figure 5c). The FF improvement for the Ni\(_N\)-modified PSCs indicates that despite its metallic properties, the Ni\(_N\) layer was thin enough so that no obvious damaging trap states formed at the interface with MAPbI\(_3\).

The minor decrease in \( V_{oc} \) and the significant improvement in the FF yield an overall PCE improvement, from a 16.5% average and a 17.4% record cell for the reference NiO\(_x\) to a 19.2% average and a 19.8% record cell for NiO\(_x\) with a Ni\(_N\) layer after 60 s of Ar plasma (Figure 5d). A slight decrease of 2 mA in \( J_{sc} \) for PSCs with a shorter Ni\(_N\) etching time (Figure 5e) is consistent with a slightly lower external quantum efficiency (EQE) (Figure S9) for these samples and is explained by the decrease in transparency, as seen in Figure 3a. Therefore, the proposed optimum use of our Ni\(_N\) modification is to have as thin a Ni\(_N\) layer on NiO\(_x\) as possible, which can passivate the HTL with a minimum loss in \( V_{oc} \) and transparency.

To further investigate the huge effect that the Ni\(_N\) layer has on the complete solar cell FF, we performed dark \( I-V \) measurements to determine the shunt resistance (\( R_{sh} \)) and the series resistance (\( R_s \)) of the SC (Figure 6a,b, respectively). \( R_{sh} \) increased with the Ni\(_N\) layer thickness, presumably due to the added coverage by the amorphous Ni\(_N\) layer, which inhibited electrical shorts between the layers. \( R_s \) dramatically dropped whenever Ni\(_N\) was deposited and decreased further with thicker Ni\(_N\) layers but with a minor trend. After summing up our former observations of UPS, XPS, transparency, and resistance, we conclude that the significant \( R_s \) decrease after Ni\(_N\) deposition is due to a higher Ni\(_{2+}\) concentration within
NiO$_x$ when the Ni$_x$N layer is present. The minor trend of $R_s$ decrease is inversely related to the Ar plasma etching time and follows the thickness of the Ni$_x$N layer. Based on the interpretation of the UPS measurement (Figure 2a and Figure S3), we ascribe this to a VBM shift toward the vacuum level that increases the driving force for hole extraction from the HaP film but at the expense of the $V_{oc}$ (Figure 6c).

To test the effect of the Ni$_x$N modification on cell stability, 18 cells were measured over 4 days at room temperature in a N$_2$-filled chamber with a controlled environment and relative humidity that did not surpass 5%. The cells were held in the dark between the measurements and were exposed to light for 4 h before and naturally during measurements. For both types of cells, the PCE decreased over the 4 days. However, on average, the reference cell PCE values were reduced by almost 50%, from 15.9 to 9%, while those of the Ni$_x$N-modified cells were reduced only by 15%, from 16.5 to 14% (Figure 7a).

Further investigation of the SC statistics reveals a different aging mechanism for cells with Ni$_x$N than those without it. The $V_{oc}$ and $J_{sc}$ of both types of cells show inverse changes over the 4 days of testing. The $J_{sc}$ of the reference cells decreased by 40% to, on average, 14 mA/cm$^2$, whereas the $J_{sc}$ of the Ni$_x$N-modified cells remained almost constant at 20 mA/cm$^2$ (Figure 7e). The $V_{oc}$ of the reference cells increased by 3% up to 1.1 V, and the $V_{oc}$ of the Ni$_x$N-modified cells decreased by 8% down to 0.95 V (Figure 7c). The FF values remained the same (63% without and 73% with Ni$_x$N modified-NiO$_x$, see Figure 7b). The series and shunt resistances of the reference cells increased gradually over 4 days by more than 90%. However, the series and the shunt resistances of the Ni$_x$N-modified cells remained constant for 3 days, and only on the fourth day did the series resistance increase by 30% (Figure 7d,f), still a much lower factor than that of the reference cells. The rapid $J_{sc}$ reduction and the $R_s$ increase in untreated PSCs are prominent evidence of a reaction at the NiO$_x$–MAPbI$_3$ interface inhibited by the Ni$_x$N treatment. The Ni$_x$N layer plays a dual role, as it helps maintain the Ni$^{3+}$ concentration, passivates the NiO$_x$–MAPbI$_3$ interface, and presumably prevents a reaction between the more active Ni$^{4+}$ and MAPbI$_3$. These two features of the Ni$_x$N layer improve the solar device FF and, most importantly, cell stability.

To further investigate the current reduction source, we measured $I$–$V$ characteristics over 4 days, but this time we repeated the $I$–$V$ measurements for 100 cycles every day (Figure 8a,b). The reference cells exhibit an obvious current reduction when the number of cycles increases, while the Ni$_x$N-modified cells do not. Although in the initial response, the shunt resistance of the reference cell is higher than that of the Ni$_x$N-modified SC, its series resistance is higher by 150%, which leads to the two types of cells having equal FFs. After 4 days of cycling, the series resistance of the reference cell increased by 70%. Similar to what Khenkin et al. showed, the initial $V_{oc}$ of the reference PSC started every day at 1.1 V but decreased as the number of cycles progressed, which is not the case for the Ni$_x$N-modified cells. We interpret this finding as an acceleration of the reaction at the interface by the constant change in the electric field applied to the SC under working conditions. The $J_{sc}$ and $R_s$ reductions suggest that an insulating interfacial layer formed between NiO$_x$ and MAPbI$_3$. In contrast, in the cells prepared with Ni$_x$N-treated NiO$_x$, $J_{sc}$ only undergoes a 3 mA/cm$^2$ loss over the 100 cycles. The constant $R_s$ and $R_{sh}$ over time indicate no change in charge transport and therefore no change of the material under working conditions. These results altogether support that Ni$_x$N modification inhibits reaction at the NiO$_x$–MAPbI$_3$ interface and prevents the formation of a blocking layer that deteriorates the SC performance.

**CONCLUSIONS**

We used a physical vapor deposition method to improve NiO$_x$ HTLs with Ni$_x$N inorganic layers, which is the first time that such a modification was ever done. We showed that Ni$_x$N plays a dual role, improving the PSC’s efficiency and stabilizing the NiO$_x$–HaP interface. The Ni$_x$N layer formed on NiO$_x$ retains the Ni$^{3+}$ species within the nickel oxide bulk, preserving its conductivity and thereby improving the overall cell efficiency. Furthermore, the same Ni$_x$N layer protects HaP from the reactive Ni$^{4+}$ species, necessary for nickel oxide conductivity, and prevents degradation of HaP, giving devices superior stability over those built with untreated reference NiO films. Although, with time, some of the Ni$_x$N might be oxidized by the NiO$_x$ layer, in a well-encapsulated device, the interfacial reactivity can be kept below the level where charged defects
will start to change the overall defect density of the transport and absorber layers. These interactions should be investigated further beyond the scope of this study. We also showed that when Ni,N is thin enough, its small energy gap, which can block sunlight and introduce traps for charge carriers at the interface, has a negligible effect on the overall SC efficiency. Our first reported solid-state, inorganic, in situ passivation route via RF sputtering deposition presents a major step toward solvent-free fabrication of reproducible and stable PSCs.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c11701.

Scheme of the cell structure, XPS peak fitting of the O 1s peak, UPS and IPES measurements of ∼40 nm Ni,N energy diagrams for the NiOx and Ni,N-modified NiOx vs E resisted AFM scans, SEM micrographs of MAPbI3, XRD plot for MAPbI3, I−V curves in ascending and descending directions, and EQE of PSCs with different Ni,N etching times (PDF)

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**Author Contributions**

A.I. and X.H. contributed equally.

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D.C. and A.I. conceptualized the project. D.C. and A. Kahn supervised the project. A.I. synthesized and fabricated the layers and the solar cells and investigated and carried out the electrical measurements, XRD, and SEM characterization. X.H. investigated and carried out most of the XPS, IPES, and UPS characterization. A. Kama helped with RF sputtering depositions and helped with the draft writing. S.K. carried out TRPL measurements and helped with the draft writing. M.E. carried out some of the XPS measurements. The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors thank Dr. Eti Teblum (BIU) for AFM measurements, Shay Tirosh for his help with the EQE measurements, and Ziv Ben Daniel for insightful discussions. A.I. thanks the Israel Ministry of Science & Technology for the PhD fellowship support. This research was supported by Grant No. 2018349 from the United States-Israel Binational Science Foundation (BSF). S.K. held an Israel Council of Higher Learning PBC/VATAT PD fellowship at Bar-Ilan University. At the Weizmann Institute of Science, the work was supported by the WIS Sustainability and Energy Research Initiative (SAERI).

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