Realizing the Potential of RF-Sputtered Hydrogenated Fluorine-Doped Indium Oxide as an Electrode Material for Ultrathin SiO\textsubscript{x}/Poly-Si Passivating Contacts

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ABSTRACT: In high-efficiency silicon solar cells featuring carrier-selective passivating contacts based on ultrathin SiO\textsubscript{x}/poly-Si, the appropriate implementation of transparent conductive oxide (TCO) layers is of vital importance. Considerable deterioration in passivation quality occurs for thin poly-Si-based devices owing to the sputtering damage during TCO deposition. Curing treatment at temperatures above 350 °C can recover such degradation, whereas the opto-electrical properties of the TCO are affected as well, and the carrier transport at the poly-Si/TCO contact is widely reported to degrade severely in such a procedure. Here, we propose straightforward approaches, post-deposition annealing at 400 °C in nitrogen, hydrogen, or air ambience, are proposed to tailor material properties of high-mobility hydrogenated fluorine-doped indium oxide (IFO:H) film. Structural, morphological, and opto-electrical properties of the IFO:H films are investigated as well as their inherent electron scattering and doping mechanisms. Hydrogen annealing treatment proves to be the most promising strategy. The resulting layer exhibits both optimal opto-electrical properties (carrier density = 1.5 × 10\textsuperscript{20} cm\textsuperscript{-3}, electron mobility = 108 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}, and resistivity = 3.9 × 10\textsuperscript{-4} Ω cm) and remarkably low contact resistivities (∼20 mΩ cm\textsuperscript{2} for both n- and p-contacts) in poly-Si solar cells. Even though the presented cells are limited by the metallization step, the obtained IFO:H-base solar cell show an efficiency improvement from 20.1 to 20.6% after specific hydrogen treatment, demonstrating the potential of material manipulation and contact engineering strategy in high-efficiency photovoltaic devices endowed with TCOs.

KEYWORDS: hydrogenated fluorine-doped indium oxide (IFO:H), transparent conductive oxide (TCO), carrier-selective passivating contacts, ultrathin SiO\textsubscript{x}/poly-Si passivating contacts, hydrogen annealing

1. INTRODUCTION

In efficiency-driven photovoltaic (PV) industry, the market-dominating crystalline silicon (c-Si) technology evolved from the traditional aluminum back surface field (Al-BSF) cell to passivated emitter rear contact (PERC) cell architecture, resulting, at the production level, in power conversion efficiency (PCE) well above 20%.\textsuperscript{1} However, PERC cells feature localized metal-silicon contacts, which still suffer from high recombination.\textsuperscript{2} To push forward the practical PCE, c-Si solar cells featuring carrier-selective passivating contacts (CSPCs) are developed, which have demonstrated viable novel cell concepts with PCE well above 25%.\textsuperscript{3} Such CSPCs enable low contact resistance and good passivation quality of the c-Si surface, thus appreciably enhancing the contact selectivity as compared to conventional diffused junctions.\textsuperscript{3} Applying CSPCs based on ultrathin SiO\textsubscript{x}/poly-Si in front/back-contacted (FBC) silicon solar cells remains to be further exploited due to the significant optical loss caused by parasitic absorptive layers.\textsuperscript{4,5} In fact, in FBC c-Si solar cells featuring ultrathin SiO\textsubscript{x}/poly-Si passivating contacts at both front and rear sides (so-called poly-Si solar cell), parasitically absorptive poly-Si layers cannot be deposited thick enough to provide sufficient lateral conductivity for the current transport toward the metal grid. To solve this dilemma, transparent conductive oxide (TCO) layers on top of a thin poly-Si layer ensure the required lateral conductivity and constitute a more transparent front window.\textsuperscript{1,6} However, commonly used sputtering technology is known to degrade the passivation quality of thin poly-Si contacts.\textsuperscript{4} Owing to the high thermal
stability of poly-Si contacts, an effective curing can be achieved at ~350 °C to restore the passivation.6 Nevertheless, carrier transport at the poly-Si/TCO contact is widely reported to degrade severely for temperatures above 250 °C, likely due to the formation of an interfacial SiOx with oxygen diffusing from the TCO.5,6,9–10 Such drawbacks in carrier transport need to be solved to achieve a high PCE in FBC poly-Si solar cells.

As for the TCO alternatives, it is well known that there is a trade-off between optical transparency and electrical conductivity in TCO material design.10 High carrier mobility (μ) is generally required for the TCO films used in PV applications to ensure a low sheet resistance (Rsh) at a moderate carrier density (Nc) level, providing high transparency with reduced free carrier absorption (FCA) in the visible and near-infrared regions (NIR).10,11 To this end, various doped TCOs were developed over the past decades, mostly with cationic metallic dopants such as Ce, Zn, Ti, Zr, W, Mo, Hf, etc.12–15 (with or without hydrogen as co-dopant), in which Mo,13 Ce,16 and Zr14 have been identified as resonant dopants, i.e., they provide donor states without perturbing the conduction band, thus allowing high electron mobilities. TCOs of In2O3 doped with Ce4 and Zr1+ have been shown to have very low FCA in the absorption range of c-Si solar cells. Apart from this, anionic dopants such as fluorine provide another attractive approach in producing TCO films with relatively high lateral conductivity in conjunction with low optical absorption loss.12,17,18 In our previous work,12 we developed a high-μ hydrogenated fluorine-doped indium oxide (IFO:H) film, in which fluorine and hydrogen act as co-dopants in a bixbyte In2O3 structure. Specifically, fluorine dopants enhance the electrical properties of In2O3 film via (i) substituting for oxygen atoms thus generating free electron carriers, (ii) occupying oxygen vacancy sites thus eliminating electron trap sites, (iii) lowering the transport barrier at the grain boundaries, while the introduction of hydrogen further enhances the electrical properties of the fluorine-doped In2O3 film by acting as shallow donors and passivating defects in the film. The application of the IFO:H film in different c-Si solar cells with passivating contacts has been demonstrated. For the low thermal-budget architecture such as silicon heterojunction solar cells, our IFO:H-based devices showed comparable fill factor (FF) as the ITO-based counterparts. In this sense, we might say that IFO:H outperforms its close relative hydrogen-doped indium oxide (IO:H), which has been reported to face FF losses in silicon heterojunction devices.19,20 However, it remains elusive to realize the potential of the IFO:H film in high thermal-budget devices, especially due to the aforementioned carrier transport problem for poly-Si passivating contacts in a passivation restoring step. It has been reported that the electrical behavior of polycrystalline In2O3 from room temperature to 800 °C is influenced by impurities and oxygen vacancies (Vox) that act as donor states in degenerated TCO layers.21–24 In addition, amphoteric hydrogen provides donor states in metal oxide, inducing alteration and changing the opto-electrical properties in the host matrix.20,23–25 On the other hand, in the case of semiconductor application with Si/SiO2 interface, atomic hydrogen is found to simultaneously passivate and depassivate silicon dangling bonds,26 resulting in different passivation qualities at the device level. Furthermore, hydrogen effused from TCO could help to passivate interfaceal defects.27 Therefore, engineering these defect states is of vital importance in tailoring both the opto-electrical properties of the TCO and contact at specific poly-Si polarity.

In this study, we demonstrated different straightforward approaches to alter the opto-electrical properties of the IFO:H film. Particularly, we examined the influence of post-deposition annealing (PDA) treatment in different gaseous ambiances on the IFO:H structure, morphology, and opto-electrical properties. Corresponding inherent electron scattering mechanisms were also elucidated. We found that a specific PDA treatment provides the most promising strategy to tailor material’s properties while retaining a good contact for carrier transport across poly-Si/TCO contact. As a proof of that, FBC poly-Si solar cells were then manufactured and those that underwent the PDA treatment exhibited increased fill factor (FF).

2. EXPERIMENTAL SECTION

2.1. TCO Deposition and Post-deposition Annealing (PDA) Treatments. TCO films were prepared using RF magnetron sputtering. The IFO:H film was sputtered from a commercially available fluorine-doped In2O3 target from Advanced Nano Products Co., Ltd. The process parameters were chosen for optimum opto-electrical properties of the as-deposited films, which were as follows: Ar flow = 50 sccm, substrate temperature = 100 °C, chamber pressure = 2.50 × 10−3 Pa, water vapor partial pressure = 1.6 × 10−5 Pa, and power density = ~1.8 W/cm2. These conditions yielded a IFO:H deposition rate of ~6.0 nm/min. The F/In atomic ratio in the film is ~17% from X-ray photoelectron spectroscopy (XPS) analysis.27 For comparison purpose, ITO films were deposited from a target containing 90 wt % of In2O3 and 10 wt % of SnO2 with Ar flow = 50 sccm, substrate temperature = 100 °C, chamber pressure = 2.20 × 10−3 Pa, and power density = ~1.8 W/cm2. The ITO deposition rate was ~6.5 nm/min. Before deposition, the targets were usually pre-sputtered for 5 min to remove any contaminants and eliminate any differential sputtering effects. During the deposition, a rotation of the sample holder of 5 rpm was maintained to ensure the uniformity of the TCO films. Samples were subject to different post-deposition annealing (PDA) treatments as tabulated in Table 1. We note that in

Table 1. Post-deposition Annealing (PDA) Treatments on Different IFO:H Samples

<table>
<thead>
<tr>
<th>sample</th>
<th>temperature (°C)</th>
<th>ambience</th>
<th>a pressure (Pa)</th>
<th>b duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-dep</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2-ann</td>
<td>400</td>
<td>pure nitrogen</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>H2-ann</td>
<td>400</td>
<td>pure hydrogen</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>air-ann</td>
<td>400</td>
<td>air</td>
<td>400</td>
<td>10</td>
</tr>
</tbody>
</table>

“We did annealing tests in different tools, such as rapid thermal annealer in Kavli nanolab, Mapper annealing tube, and different multi-chamber PECVD systems in EKL lab. The results from the same ambience showed similarity, even though the pressure control levels were different among the annealing tools. The results from Cascade PECVD were used in this article for a better gas controllability, and 50 Pa was used to keep a constant oxygen partial pressure and avoid overheating of our poly-Si cell precursors, 400 °C annealing temperature above 400 °C facilitated considerable changes in electrical properties (a duration of 10 min was used in the annealing tests, “stable” means that the sheet resistance change upon annealing is within 5% compared to the as-deposited film). To avoid overheating of our poly-Si cell precursors, 400 °C was chosen to our various annealing tests regarding the single TCO layer, our IFO:H films were stable up to 300 °C in N2, H2, and air ambiances, and annealing temperature above 400 °C facilitated considerable changes in electrical properties (a duration of 10 min was used in the annealing tests, “stable” means that the sheet resistance change upon annealing is within 5% compared to the as-deposited film). To avoid overheating of our poly-Si cell precursors, 400 °C was chosen to...
stimulate opto-electrical properties change in TCO and to maintain the passivation quality at the Si/SiO2 interface.26,28

2.2. Material Characterization. Approximately 80 nm-thick IFO:H thin films were deposited on Corning glasses substrates (Figure 1a) unless otherwise specified. Their opto-electrical properties were evaluated with a Hall effect measurement setup HMS-5000 (ECOPIA CORP.) and a spectroscopic ellipsometry (SE) M-2000DI system (J.A. Woollam Co., Inc.). In Hall measurements, carrier density ($N_d$), carrier mobility ($\mu_{\text{Hall}}$), and resistivity ($\rho$) are determined, in which the Hall scattering factor is assumed to be unity in our degenerate TCO samples.23 Apart from room temperature measurements, temperature dependence of the electrical properties was also evaluated from 200 to 350 K. The data from 70°-860° scan range of 10°-90° were selected for analysis due to its ideal graphing different angle variations on one sample. The data from 70° were selected for analysis due to its ideal graphing different angle variations on one sample.

Further, the presence of open-volume defects was studied by Doppler broadening positron annihilation spectroscopy (DBPAS) using the mono-energetic low-positron beam VEP at Delft University of Technology.38 A liquid nitrogen-cooled high-purity Ge (HPGe) detector with an energy resolution of 1.3 keV was utilized to determine the energy of the emitted positron-electron annihilation $\gamma$-rays. The line shape parameter $S$ was calculated as the ratio of the central region ($\Delta E_1 < 0.8$ keV) of the 511 keV annihilation $\gamma$-ray photopake to the total area, and the wing parameter $W$ was defined as the ratio of wing regions ($2.1$ keV < $\Delta E_1 < 6.0$ keV) to the total area. The Doppler depth profiles collected in the range of $0.1-24$ keV were fitted to extract $S$ and $W$ parameters of corresponding samples using the VEPFIT program. The extracted thicknesses of IFO:H films from VEPFIT analysis were approximately 280, 280, 80, and 80 nm for as-dep., N2-ann., H2-ann., and air-ann. layers, respectively, providing a qualitative measure of their thicknesses. The VEPFIT analysis demonstrated that the two thicker layers consisted of a double layer, with a top ~70 nm-thick IFO:H layer, consistent with the quantitative spectroscopic ellipsometry analysis.

2.3. Contact Study and Solar Cell Fabrication. In this work, n-type <100> oriented, 280 µm-thick, 1–5 Ω cm, double-side polished float zone (FZ) wafers were used as substrates unless otherwise specified. Figure 1b,c shows different test structures and solar cell schematic. After dipping the c-Si wafers into 0.55% HF for 4 min to remove the native oxide, the tunneling SiO2 layer was formed by the method of nitric acid oxidation of silicon (NAOS).39 In our case, we dipped the wafers in 68% HNO3 bath for 1 h at room temperature. In order to obtain 250 nm-thick p+ poly-Si layer for utilization at the rear side in our FBC poly-Si solar cells, a Varian Impplanter ES00HP was used to implant boron (B) atoms into the low-pressure chemical vapor deposition (LPCVD) intrinsic a-Si layer, with a fixed implantation energy of 5 keV and implantation dose of $5 \times 10^{15}$ cm$^{-2}$. Afterward, an annealing step in N2 and O2 mixed ambience at 950 °C for 3 min was conducted to activate and drive in the dopants. The ramping rate for heating or cooling was 10 °C/min, and the doping level in the p-type poly-Si layer after activation and drive was around $1 \times 10^{20}$ cm$^{-3}$.40 To obtain the 24 nm-thick n+ poly-Si layer on a textured surface for utilization at the front side in our FBC poly
Si solar cells, we first textured the c-Si bulk in a mixture solution of TMAlH and ALKA-TEX 8 from GP-Solar-GmbH followed by NAOS; then, intrinsic a-Si growth and subsequent doping by POCl3 diffusion were carried out with Nv as a carrier gas in LPCVD at 800 °C for 43 min. The doping level in the n-type poly-Si layer after diffusion was measured by electrochemical capacitance-voltage (ECCV) as around 2 × 10^{20} cm^{-3}. Forming gas (10% H2 in N2) annealing was used to hydrogenate the poly-Si passivating contacts in precursor samples (400 °C, 30 min). Further details about the fabrication process can be found elsewhere.39,40 For solar cell fabrication, the samples were single-side textured prior realizing rear and front ultrathin SiOx layers and an in-house EQE setup. For solar cell metallization, and the curing condition was 170 °C for 5 min to restore the contacts resistivity of n-contact (n-ca-Si/TCO/metal) and p-contact (p-ca-Si/TCO/metal) from vertical dark current (I-V) measurements,6,41 full-area 1 μm-thick Ag was evaporated on both sides of test structures in Figure 1b, in which n-type and p-type c-Si were utilized as substrates, respectively. The measurements were carried out on a Cascade33 Microtech setup in Else Kooli Lab at Delft University of Technology, with a four-point mode to eliminate the influence from the chuck and ensure accuracy of the extracted resistance R_{total} (R_{total} = R_{bus} + 2 \times R_{contact}). Screen-printing Ag was used for solar cells metallization, and the curing condition was 170 °C for 30 min with a subsequent 350 °C for 5 min to restore the passivation in samples without TCO PDA treatments. During the fabrication of the contact stack and solar cells, we tracked the precursor passivation qualities (e.g., implied V_{oc,i}−iV_{oc}) by using a Sinton WCT-120 with quasi-steady-state photodconductance (QSSPC) mode. SunsVoc measurements were performed as well for evaluating the electrical transport properties in our devices via a Sinton Suns-Voc-150 Illumination-Voltage Tester. We characterized the I−V performance and external quantum efficiency (EQE) of the solar cell by using an AAA class Wacom WXS-156S-L2 solar simulator and an in-house EQE setup.

3. RESULTS AND DISCUSSION

3.1. Opto-electrical Properties upon PDA Treatments.

Figure 2 illustrates data points of (Nv, μ_{Hall}) of the IFO:H films under different PDA treatments, i.e., Hall mobilities (μ_{Hall}) versus corresponding carrier densities (Nv) plot. Resistivity (ρ) lines are also provided according to the relation log(ρ) = −log(Nv) + log(1/μ_{Hall}).42 Hall measurements show that all the films exhibit n-type conductivity. The mobilities (μ_{Hall}) are plotted versus the corresponding carrier densities (Nv), with our lab-standard 80 nm-thick ITO data serving as a reference. Compared to the ITO reference, the as-dep. IFO:H film shows a bit higher resistivity, while the N2-ann. and H2-ann. layers show lower resistivity values. We note that the properties of the ITO layer also change with PDA treatments, but the topic is outside the scope of this article, thus will not be elaborated here. Among the IFO:H films, with respect to the as-dep. film, the reduced resistivity values in the N2-ann. and H2-ann. films result from improvements in both Nv and μ_{Hall}. In sharp contrast, the air-ann. sample shows instead an obvious deterioration in electrical properties, caused by largely reduced Nv and μ_{Hall}. The specific data of Np, μ_{Hall} and sheet resistance (R_{sh}) of the IFO:H films under PDA are summarized in Table 2. The optimal material properties were obtained after PDA in hydrogen, with carrier density = 1.5 × 10^{20} cm^{-3}, electron mobility = 108 cm² V^{-1} s^{-1}, and resistivity = 3.9 × 10^{-4} Ω cm. In addition, the N2-ann. sample shows comparable electrical properties as the H2-ann. film, and detailed elucidation and supplement of these observations will be discussed in the following sections.

Furthermore, the optical properties of the IFO:H films were evaluated, as compared to the commonly used ITO. Figure 3a displays the measured wavelength-dependent transmittance/reflectance of the IFO:H films under different PDA treatments, with our lab-standard ITO layer as a reference. In the ultraviolet (UV) range, the transmittance edge of the ITO film and the air-ann. IFO:H sample basically showed a red shift with respect to the other IFO:H layers. These results imply optical band gap (E_g) differences of the IFO:H films, which are illustrated Figure 3b. The transmittance/reflectance differences around the 400−600 nm region among the IFO:H films might be caused by the different film thicknesses after PDA treatments (as shown in Table 2). Figure 3b shows the absorption coefficient curves extracted from ellipsometry (SE) fittings. As one can observe, contrasting with the ITO film, the IFO:H layers show a marked sharper transition at the absorption edge in the UV part and a visible lower absorption in the NIR region, which is in accordance with our previous report and underlines the great potential of the IFO:H film in allowing an augmented light in-coupling into the absorber material of PV devices.12 Among the IFO:H films, with respect to the as-dep. film, the absorption edges of the N2-ann. and H2-ann. samples show blue shifts, while that of the air-ann. layer illustrates a red shift, indicating changes in E_g. The E_g for allowed direct electronic transition was extracted according to Tauc relation in Figure 3b, inset.18,42 The E_g values of 3.85, 3.94, 3.87, 3.76, and 3.78 eV were obtained corresponding to as-dep., N2-ann., H2-ann., air-ann., and ITO reference samples, respectively. The results of IFO:H films are in accordance with the Nv changes in Hall measurements (as shown in Table 2), which can be explained by the Moss–Burstein effect in the degenerate semiconductors (∆E_F ∝ Nv^{2/3}).44 The wavelength-dependent complex refractive index of the films are reported in Supporting Information Figure S1, and repeated experimental opto-electrical parameters of IFO:H films under different PDA treatments can be found in Table S3.

To evaluate the conduction and valence band tail states change in the IFO:H film after various PDA treatments, we extracted the Urbach energy (E_U), which is presumed as the width of the tail of localized defect states in the band gap in low-crystalline, disordered, or amorphous materials.45 We followed the equation ln(α) = ln(α0) + (hν/E_U), where α is the absorption coefficient, α0 is a pre-exponential constant, and hν
interstitial H dopants and V OH shallow donor states plausibly caused by the hydrogen-induced defects such as crystallite size (fi ann., air-ann. IFO:H levels with our previous report.12 Among the IFO:H respectively. The data for the as-deposited layers are at similar 229, 224, 256, 224, and 420 meV with as-dep., N2-ann., H2-ann., and air-ann. samples, respectively, as observed in the H2-ann. layer, implying increased band tail position of the corresponding subgap states is still under debate.24,45 This is (generated by hydrogen occupation on V O sites), but the larger crystallite sizes and smaller strains in the annealed (211), (222), (400), (332), (440), and (622) planes of polycrystalline In2O3 with cubic bixbyite structure, 10,12,48,49 (222) orientation. No crystalline orientation change was observed along with different PDA treatments. Furthermore, from Gaussian (222) orientation. No crystalline orientation change was observed along with different PDA treatments. Figure 4 shows the X-ray diffraction (XRD) patterns of the IFO:H thin films under various PDA treatments. All films display XRD peaks at 2θ = 21.3°, 30.6°, 35.5°, 41.7°, 51.0°, and 60.6°, corresponding to (211), (222), (400), (332), (440), and (622) planes of polycrystalline In2O3 with cubic bixbyite structure,10,12,48,49 with the preferred (222) orientation. No crystalline orientation change was observed along with different PDA treatments. According to Scherrer’s formula,50 the mean crystallite size (Dcrystallite) values from the (222) orientation are calculated to be 22.08, 27.67, 25.03, and 25.91 nm for as-dep., N2-ann., H2-ann., and air-ann. samples, respectively, as is the incident photon.43 The fitting results show E\textsubscript{U} values of 229, 224, 256, 224, and 420 meV with as-dep., N2-ann., H2-ann., air-ann. IFO:H films, and reference ITO layer, respectively. The data for the as-deposited layers are at similar levels with our previous report.12 Among the IFO:H films, with respect to the as-dep. sample, a relatively higher E\textsubscript{U} value was observed in the H2-ann. layer, implying increased band tail states and promoted atomic structural disorder.24 This is plausibly caused by the hydrogen-induced defects such as interstitial H dopants and V OH shallow donor states (generated by hydrogen occupation on V OH sites), but the position of the corresponding subgap states is still under debate.24,45–47 By contrast, the N2-ann. and air-ann. samples exhibit a bit lower E\textsubscript{U} values with respect to the as-dep. sample, which might be attributed to the improved material quality during the annealing process.

3.2. Structure, Morphology, and Electron Scattering Mechanism of the IFO:H Films under Different PDA Treatments. 3.2.1. Structural/Morphological Changes under Different PDA Treatments. Figure 4 shows the X-ray diffraction patterns of IFO:H films under different PDA treatments. Figure 4a–d shows AFM images of the as-deposited, N2-ann., H2-ann., and air-ann. samples, respectively. In contrast to the as-dep. film, the annealed layers exhibit a rougher surface along with densely distributed granular structures. Enlarged grain sizes were observed in annealed samples compared to the as-dep. film, and we ascribe the observed agglomerated trend to the heating effect.24 These spontaneously formed nanostructures have a size range of 20–30 nm. The grain size (D\textsubscript{grain}) and the root-mean-square (RMS) roughness values of the samples are reported in Table 2.

3.2.2. Electron Scattering Mechanism in IFO:H Films under Different PDA Treatments. The carrier scattering summarized in Table 2. The small peaks appearing at 43° probably originate from substrate contamination since they can hardly be assigned to indium oxide/fluoride materials. We further measured the as-deposited samples, which were done previously, and 1 month later, no such signals were detected anymore.

Table 2. Extracted Material Parameters of the IFO:H Films under Different PDA Treatments

<table>
<thead>
<tr>
<th>Samples</th>
<th>D\textsubscript{h} (nm)</th>
<th>D\textsubscript{d} (nm)</th>
<th>N\textsubscript{D} (10\textsuperscript{21} cm\textsuperscript{-3})</th>
<th>(\mu)\textsubscript{Hall} (cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1})</th>
<th>R\textsubscript{J}(Ω cm)</th>
<th>D\textsubscript{crystallite} (nm)</th>
<th>D\textsubscript{grain} (nm)</th>
<th>RMS (nm)</th>
<th>(\mu)\textsubscript{Hall} (cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1})</th>
<th>E\textsubscript{U} (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-dep.</td>
<td>81.68</td>
<td>2.71</td>
<td>1.24</td>
<td>85</td>
<td>67</td>
<td>22.08</td>
<td>20.00</td>
<td>1.24</td>
<td>102</td>
<td>229</td>
</tr>
<tr>
<td>N\textsubscript{2}-ann.</td>
<td>89.91</td>
<td>4.90</td>
<td>1.74</td>
<td>106</td>
<td>35</td>
<td>27.67</td>
<td>23.53</td>
<td>1.75</td>
<td>121</td>
<td>224</td>
</tr>
<tr>
<td>H\textsubscript{2}-ann.</td>
<td>93.38</td>
<td>4.53</td>
<td>1.49</td>
<td>108</td>
<td>40</td>
<td>25.03</td>
<td>27.45</td>
<td>1.82</td>
<td>153</td>
<td>256</td>
</tr>
<tr>
<td>air-ann.</td>
<td>93.21</td>
<td>4.28</td>
<td>0.01</td>
<td>22</td>
<td>760</td>
<td>25.91</td>
<td>27.45</td>
<td>1.69</td>
<td>135</td>
<td>224</td>
</tr>
</tbody>
</table>


Figure 3. Optical properties of IFO:H films after various PDA treatments: (a) transmittance/reflectance spectra and (b) absorption coefficient curves from SE fitting; the inset is optical band gap plots.

Figure 4. X-ray diffraction patterns of IFO:H films under different PDA treatments.
mechanism responsible for conductivity of the IFO:H thin films under different PDA treatments has been investigated. Note that, in terms of physical definition, \( \mu = e\tau/m^* \), where \( \mu \) is the carrier mobility, which directly correlates the conductivity parameter, \( \tau \) and \( m^* \) are carrier relaxation time and electron effective mass, respectively. It has been theoretically and experimentally\(^\text{10} \) found that high-\( \mu \) TCO films exhibit a similar \( m^* \) regardless of the material phase, and high \( \mu \) is mainly achieved through a larger \( \tau \) rather than a smaller \( m^* \).\(^\text{10} \) In polycrystalline films, the overall relaxation time is determined by scattering induced by grain boundaries (GBs), stacking faults, dislocations, charged centers such as ionized impurities, and phonons (lattice vibrations).\(^\text{10} \)

First, to distinguish whether GBs play roles on carrier scattering in the IFO:H films under different PDA treatments, we made a comparison between the \( \mu_{\text{Hall}} \) and \( \mu_{\text{opt}} \) as summarized in Table 2. One can clearly see that \( \mu_{\text{Hall}}/\mu_{\text{opt}} < 1 \) occurs for all the samples, yielding information that grain boundary scattering contributes to the carrier scattering in both as-deposited and annealed IFO:H films (especially for the air-ann. sample). To corroborate that, we further calculated the mean free path (MFP) of the charge carriers, which might represent an estimation of the upper limit for the distance between scattering centers.\(^\text{33,54} \) Using the Fermi velocity \( v_F = \hbar (3\pi^2 N_e)^{1/3}/m^* \), where \( \hbar \) is the reduced Planck constant, and the scatter frequency \( \omega_s = e/(m^*\mu_{\text{opt}}) \), MFP = \( v_F/\omega_s \) values were found to be 10.38, 13.79, 15.92, and 2.33 nm for as-dep., \( N_2 \)-ann., \( H_2 \)-ann., and air-ann. samples, respectively. The MFP values are of the same order of magnitude as \( D_{\text{crystallite}} \) and \( D_{\text{grain}} \), implying that GBs could play a role in the conduction mechanisms of the IFO:H films. We note that for the air-ann. film, in which grain boundary scattering might be a dominating factor, the MFP value is less meaningful since grain boundaries do not really act as scattering centers in the intra-grain analysis.

Second, we carried out DB-PAS measurements to identify the open-volume defects and thus understand the doping mechanisms in the PDA-treated IFO:H layers. The positron is the antiparticle of the electron. The annihilation between positron and electron produces \( \gamma \)-quanta, which forms the detected signal. Since positrons are repelled by the positive charge of the atom cores, neutral and negatively charged vacancy defects usually act as positron traps. In particular, we used DB-PAS as an additional tool to examine whether \( V_O \) or \( V_C \) vacancy defects are present as well known to act as donors in In\(_2\)O\(_3\)-based TCOs. While the positively charged \( V_O \) (or \( V_C \)) defects do not trap positrons, \( V_O \) defects are detectable in DB-PAS when they are complexed with cation vacancies (namely, \( V_{In}nV_{O} \) complex).\(^\text{52,53} \) Figure 6a shows the collected best-fit positron Doppler broadening \( W \)-parameters as a function of \( S \)-parameters of the IFO:H films using VEPFIT analysis, in which the as-dep. film denotes an \( S=W \) reference point, and error bars were calculated as the average deviation of fitted values to measured data in the energy range of 1–2.5 keV where the targeted IFO:H film is probed (see Supporting Information, Figure S2 and Table S1). Specifically, the \( S \)-parameter provides sensitivity to the presence of open-volume defects, while the \( W \)-parameter is more dependent on the type of atoms surrounding the annihilation site.\(^\text{53,54} \) From Figure 6a, the \( S \)-parameter of the \( N_2 \)-ann. layer and of the as-dep. sample are basically the same within the error bar region, indicating similar defect concentrations in the films or possibly saturation trapping of positrons at the vacancy sites. This phenomenon does not explain the notable increase in carrier density \( N_e \) of

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Figure 5. AFM micrographs of the (a) as-dep., (b) \( N_2 \)-ann., (c) \( H_2 \)-ann., and (d) air-ann. IFO:H films.

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Figure 6. (a) \( S=W \) parameters of the IFO:H films extracted from DB-PAS measurements. (b) Hall mobilities versus carrier densities in the IFO:H films in temperature-dependent Hall measurements; the arrows indicate the increasing direction of measurement temperature from 200 to 350 K.
≈40% as shown in Table 2. The discrepancy plausibly results from the effective interstitial H dopants generated during the annealing procedure, which contribute to the increased density in conduction band electrons but are invisible in DB-PAS measurements. In addition, the resulting S-parameter of the H2-ann. sample is decreased by ≈2.1% compared to the as-dep. layer, implying a less vacancy-related defective film structure. The reduced S may come from (i) a decrease in the size of V\textsubscript{O} sites due to their occupation by H, making singly charged V\textsubscript{O}H the major donor states in the film together with interstitial H\textsubscript{i}, which could explain the increased carrier density \(N\) in Table 2, and (ii) a reduction in the size of V\textsubscript{In} sites due to their interaction with H impurities. The above results outline the role of hydrogen-related donors as a dominant singly charged dopant in our IFO:H films, especially in N\textsubscript{2}-ann. and H\textsubscript{2}-ann. films. Furthermore, in the case of the air-ann. sample, the S-parameter is 2.5% lower than that of the as-dep. sample, indicating elimination of the V\textsubscript{In}-nVo complex due to local oxidation, which is also supported by a reported phenomenon and the degraded electrical properties as shown in Hall measurements (Figure 2). On the other hand, all the W-parameters of the annealed samples show increased values with respect to the as-dep. layer, demonstrating a change in the local environment of vacancy defects, such as O occupying the V\textsubscript{O} sites, or more effective fluorine impurities that order on neighboring V\textsubscript{In} sites with improved crystallinity upon annealing (the fluorine impurities alone cannot act as positron annihilation sites). The experimental S- and W-parameter depth profiles and fit curves as a function of positron implantation energy for the IFO:H films under PDA are illustrated in Supporting Information, Figure S2, and the VEPPFIT fitting parameters are provided in Table S1.

Third, we performed temperature-dependent Hall measurements to analyze the specific scattering mechanisms in the IFO:H films under different PDA treatments, as shown in Figure 6b. One can see that the \(N\) of the films does not show a temperature dependence as expected given the degenerate nature of the semiconductor. In addition, the temperature dependence of the mobility of IFO:H greatly varies with different PDA treatments. Apart from the air-ann. sample, films exhibited a marked increase in \(\mu\) with cooling direction with negligible change in \(N\) implying that phonon scattering plays a notable role in the as-dep., N\textsubscript{2}-ann., and H\textsubscript{2}-ann. films.

Since mobility is inversely related to scattering, the separation into scattering processes is intuitively difficult. The interpretation becomes easier when using the inverse mobility. According to Preissler et al. and Macco et al., charged scattering centers from ionized impurities together with phonon scattering were found to be the dominant scattering mechanisms in both single-crystalline In\textsubscript{2}O\textsubscript{3} and polycrystalline hydrogenated In\textsubscript{2}O\textsubscript{3} films. Combined with the previous proven grain boundary scattering in our IFO:H films, we assume the temperature-dependent mobility can be expressed as follows from Matthiessen’s rule:

\[
\frac{1}{\mu} = \frac{1}{\mu_{GB}} + \frac{1}{\mu_{e}} + \frac{1}{\mu_{phonon}} \left( \frac{T}{T_{D}} \right)^{p}
\]

In this equation, \(\mu_{GB}\) represents the mobility results from grain boundary scattering, and \(\mu_{e}\) is from charged scattering centers (such as V\textsubscript{O} and V\textsubscript{O}H). The last component in eq 1 is the inverse phonon mobility (\(\mu_{phonon}\)), in which \(\mu_{e}\) denotes the phonon mobility at a reference temperature \(T_{D}\). The parameter \(p\) exponential fits temperature-dependent mobility data (see Supporting Information, Figure S3a). According to the literature, the fitted \(p\) values should be in the range of 2−4 if the temperature is below the Debye temperature (reported range for In\textsubscript{2}O\textsubscript{3} is 420−811 K). While our converged parameter \(p\) values were determined to be 1.35, 1.76, and 2.25 for as-dep., N\textsubscript{2}-ann., and H\textsubscript{2}-ann. samples, respectively. No converged \(p\) value was obtained for the air-ann. layer.

We note that, at the grain size range and carrier densities of interest (1×10\textsuperscript{20} to 2×10\textsuperscript{20} cm\textsuperscript{-3}), the grain boundary scattering can be either temperature-independent tunneling or temperature-dependent thermionic emission. By assuming \(\mu_{GB}\) as a temperature-independent component in eq 1, the latter case would not be displayed. That is why our obtained 1/\(\mu_{phonon}\) varies for different IFO:H films. On the other hand, the possible presence of thermionic emission can be roughly evaluated by the deviation on fitted \(p\) values from the above-mentioned reasonable range of 2−4 according to eq 1. From the above results, only the \(p\) value of the H\textsubscript{2}-ann. film is above 2 and is in accordance with the reported values for (un)intentionally hydrogen-doped In\textsubscript{2}O\textsubscript{3} films. This evidences that, in the H\textsubscript{2}-ann. film, grain boundary scattering is in tunneling mode, while in as-dep. and N\textsubscript{2}-ann. layers, thermionic emission and tunneling current may coexist at GBs. Additionally, we plotted \(1/\mu_{phonon}\sqrt{T}\) versus inverse temperature for the air-ann. sample (see Supporting Information, Figure S3b), which showed exponential dependence that well matches the scattering mechanism described by the Schottky barrier model in thermionic emission. It agrees with the report that, in the TCO film with rather low carrier densities (\(<10\textsuperscript{19}\text{ cm}^{-3}\)), transport across grain boundaries would be mainly through thermionic emission. Hence, we can conclude that thermionic grain boundary scattering is the dominant mechanism in the air-ann. layer.

Figure 7 plots a rough estimate on the inverse mobilities that accounts for carrier scattering from charged centers, phonons, and GBs based on eq 1. We decoupled components from the above mathematic fitting for the H\textsubscript{2}-ann. film, and the fitted phonon mobility is ~150 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}, which is in a similar range for In\textsubscript{2}O\textsubscript{3}.
level as predicted by Preissler et al.\textsuperscript{29} In the cases of as-dep. and N\textsubscript{2}-ann. films, thermionic emission at GBs results in converged \( \mu \) values deviating from the expected range for the phonon scattering component. The \( 1/\mu \) components in these films were assumed based on their \( p \) deviation from the H\textsubscript{2}-ann. film (uncertainties therein). In the air-ann. film, thermionic emission at GBs dominates in the film, and phonon scattering is assumed to be negligible. In addition, for statistically homogeneously distributed scattering centers, the charged center limited mobility (\( \mu_{cc} \)) were calculated following eq \textsuperscript{2}:\textsuperscript{33,60}

\[
\mu_{cc} = \frac{3(\varepsilon_0 \varepsilon_r)^{1/2} \hbar^3}{2m^* \varepsilon^3} \frac{N_e}{F_{cc}(\xi_0)} \frac{1}{N_i}
\]

In this equation, \( h \) is Planck’s constant, \( \varepsilon_0 \) and \( \varepsilon_r \) are the vacuum and relative permittivity (for In\textsubscript{2}O\textsubscript{3}, \( \varepsilon_r = 8.9 \)), respectively, and \( \xi_0 = (3\pi^2)^{1/3} \varepsilon_0 \varepsilon_r \hbar^2 N_e^{1/3}/m^* \varepsilon^2 Z^{1/3} \). \( Z \) is the charge state of the ionized impurity, and \( N_i \) the concentration of ionized impurities (taken to be \( N_e/Z \), i.e., full ionization is assumed). \( F_{cc}(\xi_0) \) is the \( N_e \)-dependent screening function for charged center scattering given non-parabolicity of the band structure.\textsuperscript{60} Considering the DB-PAS analysis in Figure 6a, it is well possible that singly charged hydrogen-related dopants are prevalent in our IFO:H films (especially in N\textsubscript{2}-ann. and H\textsubscript{2}-ann. films). Hence, we assume singly charged donors dominate in the IFO:H films, i.e., \( Z = 1 \).

From Figure 7, we note that \( \mu_{cc} \) almost remains at the same level for all the IFO:H films under different PDA treatments. In addition, in the as-dep. layer, \( \mu_{GB} \), \( \mu_{phonon} \), and \( \mu_{cc} \) co-play in the film, which is in accordance with reported electron scattering mechanisms on polycrystalline hydrogenated indium oxide films.\textsuperscript{61} In contrast to the as-dep. film, the N\textsubscript{2}-ann. sample shows a decreased \( \mu_{GB} \) contribution accompanied by an increased \( \mu_{phonon} \) component, which is presumably caused by diminished GBs from crystallite growth and increased GB passivation by diffusion hydrogen during the heating process.\textsuperscript{23,45} Furthermore, in the H\textsubscript{2}-ann. film, a pronounced \( \mu_{phonon} \) component is observed (as expected), indicating a further improved hydrogen passivation on GBs with respect to the N\textsubscript{2}-ann. sample. In addition, in the air-ann. sample, \( \mu_{GB} \) absolutely dominates in the film.

### 3.3. Contact and Device Application

FTIR measurements were carried out to evaluate the interfacial oxide
Figure 9. (a) Current–voltage characteristics of the best 3.92 cm² poly-Si solar cell devices using IFO:H and ITO with and without the H₂ annealing treatment, respectively. The values reported are the average based on three cells from the same batch, and more device results from different experimental batches can be found in Table S4. (b) Decomposition of series resistance ($R_s$) that corresponds to (a).

formation on symmetric structures with n⁺ poly-Si/IFO:H stack in Figure 1b; note that the FTIR results are collected on TCO coated poly-Si stacks. Figure 8a shows the baseline-corrected FTIR transmittance spectra of the IFO:H films under different PDA treatments by using the as-dep. sample as a reference baseline. In such a way, the noisy signals resulting from free carrier absorption of the TCOs in the infrared region were removed in the data reading so that the signal of our wanted n⁺ poly-Si/TCO interfacial formation was enlarged and became recognizable. The vibrations of the Si–O–Si network were observed at ~1076 and/or ~1236 cm⁻¹ in N₂-ann. and air-ann. samples, corresponding to its transverse mode (TO) and longitudinal mode (LO), respectively. According to Ishikawa et al. and Liu et al., the LO mode becomes lower when the film thickness decreases and the TO may become so weak with decreased SiO₂ film thickness or changed chemical composition that TO can be hardly recognized on the spectrum. Thus, the decreased LO intensity and undetected TO mode in the air-ann. sample might indicate a thinner interfacial SiO₂ layer compared to the N₂-ann. sample. Moreover, both the LO and TO characteristics were not detectable in H₂-ann. samples, implying a basically unchanged interfacial composition with respect to the as-dep. sample baseline.

The interfacial oxide has been assumed as a legitimate explanation for forming a transport barrier on the TCO/doped silicon layer and should be avoided in device application. Figure 8b displays the passivation test results on symmetric structures (Figure 1b). In contrast to the 24 nm-thick n-poly stack, the 250 nm-thick p-poly stack shows a higher stability against sputter-induced degradation and PDA treatments. The thickness-dependent characteristic can be attributed to the role of the poly-Si film as shielding the critical c-Si/SiO₂/poly-Si interface from emerging harmful species. The poly-Si thickness of 24 nm is in the reported range of 10–28 nm, in which the lifetime samples are dramatically sensitive during the subsequent process. Hence, one can see a clear implied $V_{oc}$ (i-$V_{oc}$) drop of ~20 mV on the thin n-poly stack samples after sputtering, which goes further down after PDA in N₂ ambiance while almost get fully restored after PDA in H₂ and air atmosphere. Hydrogen has been widely accepted as a crucial factor for ensuring good passivation quality in the poly-Si passivating contacts; thus, we attribute the passivation recovery to a sufficient hydrogen supplement to the n⁺ poly-Si/SiO₂/c-Si interfaces for the H₂-ann. sample. As for the air-ann. sample, with the existence of moisture (H₂O), the exchange of hydrogen at the n⁺ poly-Si/SiO₂/c-Si interfaces do not harm the passivation qualities since water vapor has been reported to effectively hydrogenate the poly-Si passivating contacts. While for the N₂-ann. contacts, the passivation degradation is plausibly caused by a dehydrogenation of the passivating contacts; in other words, hydrogen effuses from the n⁺ poly-Si/SiO₂/c-Si interfaces. Additionally, we extracted one group of contact resistivity values ($\rho_{c}$) of n-contact (n⁺ poly-Si/TCO/metal) regarding different PDA treatments, which showed the results of 21.68, 598.76, 22.05, and 265.05 mΩ cm², for as-dep., N₂-ann., H₂-ann., and air-ann. samples, respectively. We consider these values basically in accordance with Figure 8a, namely, the thicker interfacial oxide layer results in higher $\rho_{c}$ values. From all the above results regarding both TCO opto-electrical properties and device application, we can conclude that the H₂ annealing treatment provides a promising contact engineering approach in the high thermal-budget poly-Si solar cell design.

To verify that, we extracted $\rho_{c}$ values of n-contact (n⁺ poly-Si/TCO/metal) and p-contact (p⁺ poly-Si/TCO/metal) with and without the hydrogen annealing procedure, as shown in Figure 8c,d. Results on the lab-standard ITO layer were also provided for the audience’s reference. As it can be seen, low $\rho_{c}$ values below 40 mΩ cm² were observed for the contacts with as-deposited TCOs which decreased further to around (or below) 20 mΩ cm² after the hydrogen annealing treatment. For the p-contact, which will be used on the rear side of the device (Figure 1c), all the $\rho_{oc}$ values after annealing were observed well below 30 mΩ cm², which will add negligible transport and FF losses when this stack is applied as a full-area contact. As for the n-contact, to make a comparison, our $\rho_{oc}$ values with as-deposited TCOs are comparable with the reported data with the 35 nm-thick n⁺ poly-Si layer. However, carrier transport at the poly-Si/TCO contact have been widely reported to degrade severely for temperatures above 350 °C (even >10⁴ mΩ cm²). According to Tutsch et al., exposure at 380 °C in air significantly increased the $\rho_{c}$ of n-contact from 50 to above 700 mΩ cm², and Wietler et al. reported the unfavorable $\rho_{c}$ of ~800 mΩ cm² on a metal/ZnO:Al/poly-Si stack after air annealing at 400 °C. To our
knowledge, the $\rho_{c,n\text{-contact}}$ values are among the lowest values reported so far for the poly-Si/TCO/metal stack with a <30 nm thick polysilicon layer, especially after thermal annealing at a high temperature.

It is widely accepted that parasitic growth of the interfacial oxide in thermal annealing might be the reason for the reported high contact resistivity at poly-Si/TCO after the annealing procedure. According to the simulated results from Messmer et al., there is a critical parasitic oxide thickness of about 1.4 nm; below such value, the electron tunneling through the oxide is expected to be efficient to yield a low contact resistivity. Above this threshold, the contact resistivity grows exponentially with a linear increase in interfacial oxide thickness. Under this hypothesis, the un-increased contact resistivity values after our hydrogen annealing treatment at 400 °C probably result from the depression on the mentioned parasitic growth of interfacial oxide, which is also evidenced by our FTIR measurement results (Figure 8a). However, electric states at the interface between TCO and silicon can be very complicated (interface region can be even up to 50 nm67); thus, detailed investigation remains to be carried out. Additionally, we noticed that, for n-contact, ITO showed a lower $\rho_s$ and a more preferable contact compared to IFO:H, which is inconsistent with our previous results. This discrepancy might be explained by the high doping levels of the doped silicon layer and ITO,7,68 which facilitate electron tunnelings at the n’ poly-Si/TCO interface; thus, the work function matching becomes not as dominant as the case in ref 12.

Considering that H$_2$ annealing at 400 °C ensures good contact properties for both n-contact and p-contact, we tested the performance on completed devices. Figure 9a displays the poly-Si solar cell parameters in devices using IFO:H and ITO with and without the H$_2$ annealing treatment, respectively. Our devices experienced a general severe passivation loss accompanying the screen-printing procedure, which brought a big drop from $i$-$V_{oc}$ (~710 mV) on cell precursors to $V_{oc}$ values (~665 mV) in devices. This results from the damage of the metallization process on the (thin) poly-Si layer.7,69

Corresponding solutions are under investigation. Apart from the general $V_{oc}$ limitation on our devices, one can see that all the poly-Si solar cells showed similar $V_{oc}$ values, which is in accordance with the results as shown in Figure 8b. In addition, the FF was clearly improved by 0.9%abs. (from 78.6 to 79.5%) with the H$_2$ annealing treatment for IFO:H-based cells. To elaborate this, we performed Suns Voc measurements and calculated the series resistance ($R_{s,SunVoc}$) values of the devices according to eq 3:70

$$R_{s,SunVoc} = (PFF - FF) \frac{V_{sc}}{J_{mpp}}$$

In eq 3, PFF and $J_{mpp}$ represent the pseudo fill factor and current density at maximum power point condition in SunS Voc measurements, respectively.

The specific vertical resistance ($R_{s,\text{vertical}}$) and lateral resistance ($R_{s,\text{lateral}}$) in our devices were then derived according to eq 4 and 5, respectively. Figure 9b illustrates the calculative $R_{s,\text{vertical}}$ and $R_{s,\text{lateral}}$ results corresponding to the devices in Figure 9a.

$$R_{s,\text{vertical}} = \frac{\rho_{c,n\text{-contact}}}{A_{\text{front}}} + \frac{\rho_{c,p\text{-contact}}}{A_{\text{rear}}} + \frac{\rho_{\text{wafer}}}{A_{\text{cell}}}$$

(4)

In eq 4, $\rho_{c,n\text{-contact}}$ and $\rho_{c,p\text{-contact}}$ are corresponding average results from Figure 8c,d, respectively. $A_{\text{front}}$ and $A_{\text{rear}}$ denote the front metal coverage area, rear metal coverage area, and specific cell area, respectively. In our case, $A_{\text{rear}} = A_{\text{cell}}$, $\rho_{\text{wafer}}$ is the wafer resistivity (we took 3 Ω cm in the calculation), and $t_{\text{wafer}}$ is the wafer thickness (we took 270 µm as the single-side textured wafer). The vertical resistance values from our n’ poly-Si, p’ poly-Si, and TCO were negligible in the calculation:

$$R_{s,\text{lateral}} = R_{s,SunVoc} - R_{s,\text{vertical}}$$

(5)

From Figure 9b, the FF increase in the IFO:H ann. sample as compared to the IFO:H as-dep. sample is mainly caused by a decreased $R_{s,\text{vertical}}$ value, which can be reasonably attributed to the improved lateral conductivity of the IFO:H film (as shown in Table 2). Meanwhile, the $R_{s,\text{vertical}}$ almost remains unchanged in both kinds of samples, indicating that the small contact resistivity change as shown in Figure 8c,d did not bring an observable FF increase on IFO:H ann. devices with respect to IFO:H as-dep. cells. As for the comparative results on ITO-based devices, an average FF drop of 0.4%abs. after the hydrogen annealing treatment was observed. As it can be interpreted in Figure 9b, the FF drop is mainly caused by a decreased lateral conductivity of the ITO film, which plausibly results from stability issues of the ITO layer during the thermal treatments such as the firing steps in the screen-printing process. Such stability issues of ITO are beyond the scope of this article and will not be discussed here.

Furthermore, the as-deposited ITO-based devices showed a higher average FF of 79.0% than the 78.6% of the as-deposited IFO:H cell, which are consistent with our previous data (Figures 2a and 8c,d). Meanwhile, in the optical perspective, for specific TCO utilizations, slight $J_{shunt}$ improvements were observed after the H$_2$ annealing treatment, which might be interpreted by the compensation between $E_g$ and FCA with the PDA treatment (Figure 3 and Figure S1). However, all the IFO:H cells outperformed ITO cells due to the optical advantage of the high-$\mu_m$ IFO:H film.10,12 Subsequent improvements are under investigation regarding further reducing poly-Si layer thickness on the illuminated side, increasing internal reflection, etc.

Conclusively, the PDA with H$_2$ annealing at 400 °C was successfully utilized in high thermal-budget poly-Si solar cells, and no obvious FF loss was observed. An absolute 0.5% gain in active-area power conversion efficiency ($\eta_a$) was observed on IFO:H solar cells after the PDA treatment in H$_2$ ambience, mainly due to the FF improvement (0.9%abs.). Additionally, with respect to the widely used ITO, the PDA-treated IFO:H layer maintains its optical advantages in terms of higher $E_g$ and lower FCA while improves its lateral conductivity. This makes it a competitive transparent electrode for photovoltaic devices especially for high-thermal-budget solar cells.

4. CONCLUSIONS

In summary, we studied the opto-electrical properties of the hydrogenated fluorine-doped indium oxide (IFO:H) by means of post-deposition annealing (PDA) treatments at 400 °C in $N_2$, $H_2$, and air ambience. Through detailed analyses of the crystal structure, surface morphology, optical properties, and
temperature-dependent electrical properties, the inherent electron scattering and doping mechanisms of the IFO:H films were revealed and compared. Hydrogen annealing proved to provide an effective strategy that can simultaneously alter the opto-electrical properties of the TCO film and maintain a favorable carrier transport at the poly-Si/TCO stack. We highlight that the low contact resistivity of around (or below) 20 mΩ cm² was achieved on both n- and p-contacts with poly-Si/TCO stack after hydrogen annealing, which to our knowledge is among the lowest values especially on thermally annealed contacts at 400 °C. Beyond this, we successfully implemented the hydrogen-annealed IFO:H films on FBC poly-Si solar cells. A 0.9% improvement in fill factor was observed, which leads to an absolute 0.5% gain in active-area power conversion efficiency on poly-Si solar cells with IFO:H. We believe our findings will provide important insight for future material/contact engineering in various photovoltaic devices endowed with TCOs such as IFO:H.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.0c01206.

Complex refractive index from SE fitting, S- and W-parameters and corresponding fitting parameters in DBPAS analysis, temperature-dependent Hall mobilities, and repeated results from different batches (PDF)

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Notes

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