High-Mobility In$_2$O$_3$:H Electrodes for Four-Terminal Perovskite/CuInSe$_2$ Tandem Solar Cells

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ABSTRACT: Four-terminal (4-T) tandem solar cells (e.g., perovskite/CuInSe$_2$ (CIS)) rely on three transparent conductive oxide electrodes with high mobility and low free carrier absorption in the near-infrared (NIR) region. In this work, a reproducible In$_2$O$_3$:H (IO:H) film deposition process is developed by independently controlling H$_2$ and O$_2$ gas flows during magnetron sputtering, yielding a high mobility value up to 129 cm$^2$ V$^{-1}$ s$^{-1}$ in highly crystallized IO:H films annealed at 230 °C. Optimization of H$_2$ and O$_2$ partial pressures further decreases the crystallization temperature to 130 °C. By using a highly crystallized IO:H film as the front electrode in NIR-transparent perovskite solar cell (PSC), a 17.3% steady-state power conversion efficiency and an 82% average transmittance between 820 and 1300 nm are achieved. In combination with an 18.1% CIS solar cell, a 24.6% perovskite/CIS tandem device in 4-T configuration is demonstrated. Optical analysis suggests that an amorphous IO:H film (without postannealing) and a partially crystallized IO:H film (postannealed at 150 °C), when used as a rear electrode in a NIR-transparent PSC and a front electrode in a CIS solar cell, respectively, can outperform the widely used indium-doped zinc oxide (IZO) electrodes, leading to a 1.38 mA/cm$^2$ short-circuit current ($J_{SC}$) gain in the bottom CIS cell of 4-T tandems.

KEYWORDS: hydrogenated indium oxide, carrier mobility, perovskite, tandem solar cell, optical analysis

Thin film photovoltaics (TFPVs), benefiting from their light weight, outstanding flexibility, and high compatibility with low-cost and high-throughput roll-to-roll manufacturing, are specifically attractive for the huge potential markets in buildings, wearable/portable electronic devices, vehicle- and airship-integrated photovoltaics (PVs), etc. As a class of TFPVs, organometal halide perovskite solar cells (PSCs) have made significant progress in the past decade, and their certified power conversion efficiency (PCE) reaches 25.2% on research lab-scale (0.1 cm$^2$) devices. This value surpasses many other commercialized TFPV technologies, such as Cu(In,Ga)$_2$(S,Se)$_2$ (CIGS) (23.6%), CdTe (22.1%), and amorphous silicon (14.0%). In addition, the roll-to-roll processability of PSCs allows for reducing their manufacturing cost, resulting in a very short estimated energy-payback time (EPBT) of 0.22 year. Another exciting prospect is to implement them in tandem solar cells in combination with other existing TFPVs. In such a tandem architecture, two subcells absorb solar light with different photon energies in an optimum manner. As a result, the tandem devices have the potential to overcome the 33.7% single-junction efficiency limit and theoretically reach over 40% efficiency by minimizing the thermalization losses. Among various tandem TFPVs, perovskite/CIGS tandems are very promising for three reasons. (I) Absorber bandgaps in the two PV technologies (1.5−1.7 eV for perovskite and 1.0−1.1 eV for CIGS, specifically 1.0 eV for CIS) are adjustable and well-suited for tandem application; (II) both subcells have demonstrated high PCEs; (III) the CIGS solar cell is in high technology readiness levels for production on both glass and flexible foil substrates. Technology upgrades for tandems...
can be directly realized on the existing CI(G)S manufacturing lines.

In a perovskite/CI(G)S tandem solar cell, the near-infrared (NIR) transparent PSC can either be mechanically stacked on top of a CI(G)S solar cell in a four-terminal (4-T) configuration or monolithically grown on a CI(G)S cell in a two-terminal (2-T) configuration. Simulation studies indicate that 4-T perovskite/CI(G)S tandems outperform 2-T tandems in terms of PCE and annual energy yield because current matching between two subcells is not required. Experimentally, 4-T perovskite/CI(G)S tandems have demonstrated PCEs up to 25.9%, higher than single-junction devices and 2-T tandems but still much lower than their theoretical efficiency limit.

Four-terminal perovskite/CI(G)S tandems require three transparent electrodes. Optical loss analysis suggests that parasitic absorptions in these transparent electrodes can account for a total photocurrent loss of 4–5 mA cm⁻² in devices using state-of-the-art transparent conductive oxide (TCO) electrodes, such as aluminum-doped zinc oxide (AZO), indium tin oxide (ITO), and indium zinc oxide (IZO). Significant parasitic absorptions appear in the NIR wavelength range (800–1300 nm), owing to free-carrier intraband absorption. To alleviate the parasitic absorption losses while maintaining high electrical conductivity, TCOs with high electron mobility instead of high free carrier density are required. Zr-doped indium oxide (IZRO) shows high electron mobility of up to 77 cm² V⁻¹ s⁻¹ and has been demonstrated recently in high-efficiency perovskite-based tandem solar cells. Hydrogenated indium oxide (IO:H) also offers an excellent transparency–conductivity trade-off due to its extraordinarily high carrier mobility of over 100 cm² V⁻¹ s⁻¹ and a suitable carrier density in the 10²⁰ cm⁻³ range. It has been successfully implemented in Si heterojunction solar cells and recently in PSCs. Schultes et al. reported that the IO:H electrode can substantially decrease NIR absorbance (800–1300 nm) compared to ITO or fluorine-doped tin oxide (FTO), leading to a 23% 4-T perovskite/CI(G)S tandem solar cell. However, two challenges remain for the wide application of IO:H in 4-T perovskite/CI(G)S tandems.

(I) Hydrogen doping in high-mobility (>100 cm² V⁻¹ s⁻¹) IO:H films is typically realized by injecting water vapor, i.e., IO:H(H₂O), during the sputtering process. However, delicate control of a trace amount of water vapor (0.1–1 mPa) is technically challenging, leading to poor batch-to-batch reproducibility. Alternatively, H₂ gas is used for hydrogen doping, i.e., IO:H(H₂), which improves processing reliability. But these IO:H films usually suffer from low carrier mobility (50–90 cm² V⁻¹ s⁻¹). Therefore, a CIS solar cell, can outperform the cells with widely used IZO electrodes, leading to a 1.38 mA/cm² short-circuit current (Jₛ) gain in the bottom CIS cell.

RESULTS AND DISCUSSION

Optical and Electrical Properties of the Highly Crystallized IO:H Films. Hydrogen doping in the IO:H films can be realized by injection of H₂ and O₂ during magnetron sputtering. Previous experimental results and density functional theory (DFT) calculation suggest that H⁺ passesivate oxygen vacancies (VO⁻) by forming substitutional (H⁺O⁻) and interstitial (H⁺) sites, which reduces free carrier scattering and accordingly provides a suitable density of free carriers. O₂, on the other hand, prevents metallic indium formation and therefore improves film transparency. H₂ and O₂ gas flow rates can affect substantially the optical and electrical properties of IO:H films.

We deposited IO:H films on soda-lime glass (SLG) substrates by magnetron sputtering at different H₂ partial pressures (pp(H₂)) and different O₂ partial pressures (pp(O₂)). The films, showing similar thicknesses around 140 nm, were crystallized via postannealing at 230 °C for 30 min in a N₂ atmosphere. To quantitatively assess absorption losses caused by IO:H from a 4-T perovskite/CI(G)S tandems point of view, a parameter considering absorptance (A), quantum efficiency (Q), and solar spectral irradiance (S), designated as AQS, is introduced:

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AQS(\lambda) = \frac{\int_{300 \text{nm}}^{1300 \text{nm}} (100% - A(\lambda)) \times EQE(\lambda) \times S(\lambda) \, d\lambda}{\max_{\lambda = 360 \text{nm}}^{} (\text{EQE}(\lambda) \times S(\lambda))}
\]

where the nonabsorbed light from SLG.IO:H is weighted by the perovskite/CI(G)S 4-T external quantum efficiency (EQE) and the AM 1.5 solar spectral irradiance (S) and normalized with the maximum value of EQE weighted by the solar spectral irradiance (see calculation details in the Supporting Information; average absorptance values (A) weighted by AM 1.5 solar spectral irradiance (S) are also shown in Supporting Table 1). A higher integrated AQS value represents a lower absorption loss. When pp(O₂) is minimal (close to 0 mPa), increasing pp(H₂) from 1.0 mPa to 3.4 mPa significantly.

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increases IO:H absorbance in the wavelength range of 300–600 nm (Figure S1). This is due to the formation of metallic indium, which causes substantial optical losses in the top PSC (Figure 1a).14 The trend is less significant when pp(O2) is increased (Figure 1a, Figure S1). When pp(O2) is 1.0 mPa, integrated AQS at the whole investigated pp(H2) range reaches a value of 490, which is higher than the commercial ITO (460) or IZO (473.0) developed in our lab34 and comparable to that of IO:H(H2O) (489.7) (Table S1).26 On the other hand, a low sheet resistance ($R_{sh}$) region appears when pp(O2) is at 0.4 mPa. The region becomes broader toward higher pp(O2) when pp(H2) is increased (Figure 1b). The lowest $R_{sh}$ of IO:H is 18.5 $\Omega$/sq, similar to IZO34 and IO:H(H2O),26 but slightly higher than ITO (Table S1).

Carrier density and mobility are studied using Hall effect measurement to understand the effects of deposition conditions. Two low carrier density regions ($N_e \approx 1.5 \times 10^{20}$ cm$^{-3}$) appear at low pp(H2) (Figure 1c). Free carrier absorption of IO:H at these conditions is mitigated, as reflected by low absorbance in the NIR range (Figure 1a, Figure S1). Comparison of the optical losses between the two low carrier density regions suggests that the higher pp(O2) region outperforms the low pp(O2) region, taking advantage of lower absorption loss in the UV–vis range. Carrier mobility increases with the increment of pp(O2) and the decrement of pp(H2) and reaches 129 cm$^2$ V$^{-1}$ s$^{-1}$. To the best of our knowledge, this is the highest reported mobility value for IO:H with hydrogenation realized by H2 gas (Figure 1d). Electrical conductivity is carrier-density-limited at low pp(H2) and mobility-limited at high pp(H2).

**Solar Cell Performance.** The highly crystallized IO:H films deposited at 1.9 mPa H2 and 1.0 mPa O2 and subsequently annealed are used as front electrodes in PSCs, which show a sheet resistance of 16.5 $\Omega$/sq (240 nm thick) and absorbance less than 3% between 380 and 1300 nm. Parasitic absorption loss in the NIR range is significantly mitigated compared to the commercial ITO electrode (Figure 2a). Planar-structured PSCs with a stack of glass/IO:H/SnO2/perovskite/spiro-MeOTAD/MoOx/IZO/(Ni–Al grid) were fabricated (Figure 2b) to evaluate the IO:H performance. The perovskite used in the study is composed of (Cs0.1FA0.9PbI3)0.97(MAPbBr3)0.03 with a bandgap of 1.58 eV. A small amount of K+ was introduced in the perovskite to reduce the $J$–$V$ hysteresis.35 A thin layer of MoOx is deposited between the spiro-MeOTAD and IZO layer to mitigate the sputter damage during IZO deposition.4

IO:H front electrodes enable PSCs to reach a high average transmittance of 78% (spectrally weighted) between 820 and 1300 nm in the region without the metal grid (Figure S2). This value is a 23% (spectrally weighted) absolute enhancement compared with the device using commercial ITO as front contact (Figure S2). Implementation of MgF2
antireflective coatings mitigates the reflective losses, leading to an average transmittance of up to 82% (spectrally weighted) in this range (Figure 2c, Figure S3), which is among the highest values achieved on the NIR-transparent PSCs.8,36 The devices were measured in the superstrate configuration to evaluate their PCE. The best PSC shows a PCE of 17.0% (reverse to forward scan) and 16.5% (forward to reverse scan) on an active area of 0.3 cm² (Figure S4). Short-circuit current density ($J_{sc}$) is 22.0 mA/cm² from $J$–$V$ measurement, which agrees well with the value (22.1 mA/cm²) obtained from the integration of the EQE spectrum (Figure 2d). PSCs prepared in eight different batches show very similar PCEs with small variations, suggesting an excellent batch-to-batch reproducibility (Figure S5, Table S2). In addition, large-area homogeneity of IO:H bottom contacts was confirmed by very similar EQE responses on 12 PSCs that were distributed on a total area of 5 cm × 5 cm (Figure S6 and inset).

We further characterized the PCE of the best PSC with an antireflection foil, which has shown to increase the $J_{sc}$ because of the increased optical path length and reduced reflective

Figure 2. Performance of NIR-transparent PSCs with highly crystallized IO:H front electrode. (a) Absorptance of the IO:H and ITO electrode. (b) Scheme of a NIR-transparent PSC. (c) Optical property of the NIR-transparent PSCs. No Ni–Al grid is deposited for the optical measurement. (d) External quantum efficiency, (e) $J$–$V$ characteristics, and (f) steady-state efficiency of the best NIR-transparent PSC measured with an antireflection foil.

Figure 3. Performance of the 4-T tandem solar cells. (a) $J$–$V$ characteristics and (b) external quantum efficiency of the 4-T perovskite–CIS tandems. The EQE curve of the perovskite–CIS tandem (green curve in (b)) is obtained by adding the EQE curve of the perovskite top cell (blue curve) and the CIS bottom cell (red curve).
loss.\textsuperscript{37} Indeed, the $J_{sc}$ increases to 22.9 mA/cm$^2$, leading to a high PCE value of 17.6% (reverse to forward scan) (Figure 2e, Table S3). The series resistance of the PSC, derived from the dark $J$–$V$ curve using the one-diode model, is comparable to the devices with the ITO front electrode (Figure S7). This suggests that the solar cell PCE is not limited by the electrical conductivity of the IO:H front electrode. When measured at the maximum power point tracking condition, the best PSC shows a steady-state efficiency of 17.3% at 0.83 V (Figure 2f).

A perovskite cell structure as an optical filter (without metal grid) was fabricated using the same method and mechanically stacked on top of a CIS bottom cell (1.0 eV bandgap)\textsuperscript{5} to investigate its application in 4-T tandems (Figure S8). Measured with an antireflection foil, the PCEs of the CIS cell without and with the perovskite filter are 18.1% and 7.3%, respectively (Figure 3a). Combining with the 17.3% efficiency (mpp value) perovskite top cell, a PCE of 24.6% is realized in the 4-T tandem configuration (Figure 3a, Table 1). This is a 7.3% absolute PCE gain compared to the top PSC and a 6.5% absolute PCE gain compared to the bottom CIS cell and well within the range of the current record efficiencies of four-terminal all-thin-film tandems (Table S4). The PCE of such 4-T tandems is largely limited by the $J_{sc}$ of the bottom cell, manifested by the relatively low EQE response in the NIR wavelength range (Figure 3b). EQE improvement in such a wavelength range is expected by mitigating parasitic absorption losses in the rear electrode of the NIR transparent PSC and front electrode of the CIS solar cell.\textsuperscript{7} Aiming at improving the EQE response of the CIS bottom cell in the NIR region, the IO:H films were explored as the rear electrode in PSC and front electrode in CIS solar cells. However, the previous results were not satisfactory for two reasons.\textsuperscript{4,9,24} (I) The IO:H films were not adequately crystallized due to low processing temperature, resulting in low carrier mobility; (II) the deposition atmosphere was not optimized, in our opinion, for these amorphous or partially crystallized IO:H films. Therefore, efforts should be made to decrease the IO:H film crystallization temperature and to optimize the deposition atmosphere of the amorphous or partially crystallized IO:H films for further enhancement in the efficiency of tandem devices.

**Effect of Deposition Atmosphere on the IO:H Crystallization Process.** To investigate the effect of the deposition atmosphere (Figure 1a) on the IO:H crystallization process, we deposited four IO:H films at conditions A (0.6 mPa H$_2$ and 0 mPa O$_2$), B (0.6 mPa H$_2$ and 1.0 mPa O$_2$), C (3.4 mPa H$_2$ and 1.0 mPa O$_2$), and D (3.4 mPa H$_2$ and 1.0 mPa O$_2$) (Figure 1a). All the as-deposited films show the amorphous phase (Figure S9a and Figure S10), which starts to crystallize upon annealing at around 150 °C (films are designated as partially crystallized, Figure S9b and Figure S10) and become highly crystallized at 230 °C (Figure S9c and Figure S10). However, the crystallization processes are kinetically different for films deposited in different atmospheres (Figure 4a). In the partial-crystallization regime (samples annealed at 150 °C), higher pp(O$_2$) substantially accelerates the crystallization process (Figure 4a). This can be explained by the existence of a higher amount of hydroxyl groups in the film, which facilitate formation of intergrain In–O–In bonding.\textsuperscript{25} Higher pp(H$_2$) delays the crystallization process, possibly due to the consumption of the hydroxyl group via formation of H$_2$O. Such different crystallization kinetics in the partial-crystallization regime determine the film crystallinity at the high-crystallization regime (Figure 4a), which eventually affects the optical and electrical properties of the IO:H films. Besides, in the partial-crystallization regime, IO:H films deposited at higher pp(H$_2$) show diffraction peaks at a lower 2-theta degree, indicating that H$^+$ causes lattice expansion (Figure 4b). The lattice shrinks to a similar size in films deposited at lower pp(H$_2$), corresponding to the high-crystallization state (Figure 4c). Similar lattice constant changes have been observed for IO:H$_2$(H$_2$O) films, but the phenomenon is less pronounced for IO:H$_3$(H$_2$O)$_2$.\textsuperscript{14}

To gain insight into crystallization phenomena, we performed in situ TEM measurements. IO:H films were deposited on two TEM E-chips at condition A (designated as sample I) and B (designated as sample II), which were annealed at 10 °C min$^{-1}$ from 25 to 100 °C and at 5 °C min$^{-1}$ from 100 to 280 °C. Surprisingly, small IO:H nanocrystals (size <10 nm) were already formed for sample I when deposited at room temperature. These nanocrystals act as nuclei, start to grow at 200 °C, and reach sizes of tens of nanometers at 280 °C (Figure 4d and Supporting Video 1). The crystallization temperature mismatch between XRD and TEM characterizations and the morphology difference between SEM and TEM characterizations are due to the different annealing ramps applied in different environments. On the other hand, no IO:H nanocrystals were observed in sample II in as-deposited condition (Figure 4e and Supporting Video II). Crystalline nuclei grow from the amorphous IO:H matrix upon annealing at a temperature as low as 150 °C. The over 50 °C crystallization temperature decrease of sample II compared to sample I eventually results in IO:H nanocrystals 3–5 times bigger at 280 °C. Comparing TEM results of samples I and II, we revealed the effect of oxygen during the IO:H deposition on the film crystallization process. (I) In the investigated range, the IO:H film tends to be amorphous at higher pp(O$_2$) when deposited. (II) Higher pp(O$_2$) is beneficial for the crystal growth upon postannealing.

Selected area electron diffraction (SAED) patterns were acquired after cooling the samples to room temperature. The SAED patterns of both samples show broad, diffused rings together with many diffraction spots, indicating the coexistence of amorphous and crystalline phases (Figure 4g). The single-crystalline nature of the nanocrystals (Figure 4j) is confirmed by the zone-axis SAED patterns of Figure 4h,k, and the fast Fourier patterns of Figures S11 and S12. Energy dispersive X-ray (EDX) elemental mapping analysis shows

**Table 1. Photovoltaic Parameters of the All-Thin-Film Perovskite–CIS Solar Cells in Four-Terminal Tandem Configuration**

| solar cell                  | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF (%) | PCE (%) | PCE with MPP (%) | cell area (cm$^2$) |
|----------------------------|--------------|--------------------------|--------|---------|------------------|-------------------|
| perovskite top cell         | 1.09* (1.09$^*$) | 22.9 (22.9$^*$)         | 70.58* (69.45$^*$) | 17.62* (17.36$^*$) | 17.3              | 0.3               |
| CIS standalone              | 0.590        | 41.8                     | 73.2   | 18.1    | 18.1             | 0.509             |
| CIS bottom cell             | 0.564        | 17.5                     | 73.7   | 7.3     | 24.6             |                   |
| perovskite–CIS 4-T tandems  |              |                          |        |         |                  |                   |

*Data were obtained from the reverse scan direction. $^*$Data were obtained from the forward scan direction.
that In and O are uniformly distributed across sample I (Figure S13), while intensity of the In signal is slightly stronger in the crystalline phase as compared to the amorphous phase for sample II. To clearly reveal the lowest IO:H crystallization temperature, we deposited IO:H films at condition B, annealed them at 130, 140, 150, and 160 °C, respectively, for different times, and studied their crystallinity by XRD measurements. Interestingly, the IO:H crystallization...
process has already started at 130 °C. To the best of our knowledge, this is 20 °C lower than the lowest reported crystallization temperature value. Such a low crystallization temperature is expected to broaden the application of IO:H in heat-sensitive substrates and devices.

Optical and Electrical Properties of the Amorphous and Partially Crystallized IO:H. Understanding the effect of deposition atmosphere on the amorphous and partially crystallized IO:H is important in view of device processing temperature limitations, i.e., 80 °C for a PSC with a spiro-MeOTAD hole-transporting layer and 150 °C for the CIS solar cell. Fifteen amorphous IO:H films (pristine) and fifteen partially crystallized IO:H films (annealed at 150 °C) were prepared at a series of atmospheric conditions. AQS values decrease from the high pp(O2) and low pp(H2) region to the low pp(O2) and high pp(H2) region for both pristine films and partially crystallized films (Figure S1). This trend is similar to highly crystallized films (Figure 1a). However, the minimum AQS values in both cases are much lower than highly crystallized films, meaning that the effects of deposition atmospheres on the optical losses are more significant on the pristine and partially crystallized films. The highest integrated AQS values of these films are close to the highly crystallized IO:H film (485.6 for the pristine sample, 489.3 for the 150 °C, and 490.7 for the 230 °C) and substantially higher than the IZO film (473.0) (Table S1).

This implies that these IO:H films outperform the IZO electrodes, which have been used in the most efficient 4-T perovskite/CIGS tandems. A high-conductivity region appears when the O2 to H2 ratio is close to 0.4:1 for pristine samples (Figure S5c,d), which shows little change with postannealing at 150 °C (21.7 Ω/sq for the pristine sample, 21.3 Ω/sq for the 150 °C). On the other hand, changes in carrier density and mobility are significant when a comparison is made between the pristine and the partially crystallized IO:H films, especially for those deposited at high O2 partial pressure and low H2 partial pressure conditions (Figure S14). Specifically, high carrier mobility amorphous IO:H films (55 cm2 V−1 s−1) and partially crystallized IO:H films (76.9 cm2 V−1 s−1) are realized when deposited at 0.6 mPa H2 and 1.0 mPa O2.

Optical Loss Reduction with Amorphous and Partially Crystallized IO:H Electrodes. In order to estimate the Jsc improvement in the bottom CIS cell by using amorphous and partially crystallized IO:H (Figure 6a), we simulated the optical response of the structures with the transfer matrix method (TMM) and considering all layers with their optical constants, i.e., n and k (Figure S15 and see discussion in the Supporting Information).

First, we selected IZO electrodes for optical modeling. Excellent agreements between simulation and experimental data were achieved for the NIR transparent perovskite solar
cell (Figure S16), the CIS solar cell (Figure S17), and the PSC filtered CIS solar cell (Figure S18), respectively. This validates the accuracy of our simulation models. Reflection loss of the complete device stack and absorptance loss in each sublayer were simulated, as shown in Figure 6b. In the wavelength between 800 and 1300 nm, the main optical loss originates from reflection at air/material interfaces, which accounts for a photocurrent decrease of 3.34 mA/cm² (Table S5). Absorptance loss is mostly associated with rear IZO of the PSC and front IZO of the CIS caused by free carrier absorption and spiro-MeOTAD caused by diffuse scattering (Table S5). Absorptance loss in the front IO:H of PSC is not significant (Table S5).

Second, we selected the amorphous IO:H as the PSC rear electrode and the partially crystallized IO:H as the CIS cell front electrode for optical modeling. Thicknesses of these IO:H films were adjusted so that the film $R_0$ are comparable to the IZO electrodes in devices. Four cases are studied, which are designated as case 1 (PSC (IO:H front electrode and IZO rear electrode) and CIS (IZO front electrode)), case 2 (PSC (IO:H front electrode and IO:H rear electrode) and CIS (IZO front electrode)), case 3 (PSC (IO:H front electrode and IZO rear electrode) and CIS (IO:H front electrode)), and case 4 (PSC (IO:H front electrode and IO:H rear electrode) and CIS (IO:H front electrode)), respectively (Figure S19). EQE responses increase in the sequence of case 1, 2, 3, and 4 (Figure 6c). Integrated current density in the CIS bottom cell is accordingly increased by 1.4 mA/cm² (8% relative improvement) in case 4 compared to case 1. Optical loss analysis was performed and shown in Tables S5 and S6. The EQE improvement is indeed because of mitigation of parasitic absorptance losses by replacing IZO electrodes with IO:H electrodes (Figure 6d). Specifically, $J_{sc}$ improvements are 0.78 mA/cm² from the perovskite solar cell rear electrode and 0.37 mA/cm² from the CIS front electrodes, respectively.

CONCLUSIONS

In this study, we developed a highly reproducible IO:H film deposition process that is realized by independently controlling H₂ and O₂ gas flows during magnetron sputtering. Optimization of partial pressures of H₂ and O₂ during sputtering not only allows an optimum balance of desired optical and electrical properties of the IO:H films but also facilitates a decrease in the crystallization temperature threshold to 130 °C. The IO:H films reach carrier mobilities of 55.0 cm² V⁻¹ s⁻¹ when as-deposited, 76.9 cm² V⁻¹ s⁻¹ when partially crystallized by postannealing at 150 °C, and a high value of 129 cm² V⁻¹ s⁻¹ when highly crystallized by postannealing at 230 °C. By using a highly crystallized IO:Hfilm as a front electrode in the NIR-transparent perovskite solar cell, a steady-state PCE of 17.3% and an average transmittance of 82% between 820 and 1300 nm are...
achieved. In combination with an 18.1% CIS solar cell, we demonstrate a 24.6% perovskite/CIS tandem device in 4-T configuration. Further optical analysis suggests that the low-temperature-processed amorphous and partially crystallized IO:H films, when used as the rear electrodes of NIR-transparent perovskite solar cells and the front electrodes of CIS solar cells, respectively, can outperform the 4-T tandem cells with widely used IZO electrodes. The decrease in optical parasitic absorption losses leads to 1.38 mA/cm² short-circuit current (Jsc) gain in the bottom CIS cell, suggesting the potential of appropriately processed IO:H films to enhance the efficiency of 4-T tandem devices. Besides, the IO:H films, with possible adaptions, may also be implemented in 2-T tandem solar cells to decrease the parasitic absorbance loss and improve the solar cell efficiency.

METHODS

Hydrogenated Indium Oxide Film Deposition. IO:H films were grown on soda lime glass substrates in a high-vacuum sputtering system (CT200, Allianceconcept) by RF sputtering of ceramic In2O3 targets (99.99%, 10 in. diameter, SPM AG) in a mixed Ar, O2, and H2 atmosphere at room temperature. The substrate to target distance is 69 mm. Before deposition, the base pressure was below 10⁻⁶ Pa. The pressure is much lower than the pp(H2O) when hydrogen doping in an IO:H film is realized by injection of H2O vapor. Therefore, the effect of H2O vapor in the system, if any, is not significant. A series of atmospheric conditions, i.e., pp(H2) and pp(O2), were studied, and the total processing pressure was kept at 0.225 Pa via adjusting the pp(Ar). The pp(H2) and pp(O2) were calculated from relative gas flows. The applied sputter power density was 0.5 W/cm². The deposition rate is 0.2 nm/s. Thicknesses of the IO:H films were 140 nm for optical and electrical measurements, 240 nm for solar cell fabrication, and 70 nm for the TEM characterizations. Some of the IO:H films were postannealed at 150 and 230 °C for 30 min in a N2 atmosphere.

Perovskite Solar Cell Fabrication. IO:H glass substrates were treated with a UV-ozone cleaner before use. A 10-nm-thick SnO2 electron transporting layer was spin-coated on the IO:H substrates using a SnO2 colloid precursor (5 wt % in H2O colloidal dispersion, Alfa Aesar) at 4000 rpm for 30 s, followed by annealing in the glovebox at 150 °C for 30 min. The perovskite layer was prepared via a two-step method. First, 1.3 M PbI2, 0.13 M CsI, and 0.025 M KI in the dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) mixed solvent (DMF:DMSO = 19:1 in volume ratio) was spin-coated at 1500 rpm for 30 s and annealed at 70 °C for 1 min inside the glovebox. Second, a mixture solution of FAI:MABr:MACl (60 μg:6 μg:6 μg in 1 mL of isopropanol) was spin-coated on the precursor film at 1300 rpm for 30 s in the glovebox, followed by annealing in ambient air (35% humidity) at 150 °C for 20 min. The spiro-MeOTAD layer was deposited atop the perovskite layer with a solution that contained 72.3 μg of 2,2′,7,7′-tetrakis(N,N′-di-p-methoxyphenylamine)-9,9′-spirobi fluorenone (Merck), 28.8 μL of tert-butylpyridine (98%, Sigma-Aldrich), and 17.5 μL of lithium bis(trifluoromethanesulfonil)imide (Li-TFSI) solution (520 mg of Li-TFSI:99%, Sigma-Aldrich) in 1 mL of acetonitrile (99.8%, Sigma-Aldrich) in 1 mL of chlorobenzene. A 20-nm-thick MoOx layer was deposited on top of the spiro-OMeTAD via thermal evaporation (3 × 10⁻⁴ Pa), which is then covered by 200-nm-thick IZO as the transparent electrode (200 W, sheet resistance 22 Ω/sq on a glass substrate). Ni/Al grids with a 50 nm/2500 nm thickness were deposited by e-beam evaporation at 2 × 10⁻⁴ Pa. Finally, MgF2 antireflection coatings were deposited on the front side (90 nm) and the rear side (175 nm) by e-beam evaporation.

CIS Solar Cell Fabrication. CIS solar cells were fabricated according to a reported method. In short, CIS absorbers were grown in a multistage evaporation process on soda lime glass with a sputtered Mo back contact. A two-step postdeposition treatment was performed first using NaF, followed by RbF. The absorbers were etched in 5% KCN solution for 1 min before deposition of 35-nm-thick CdS as a buffer layer via a chemical bath deposition process. A 70-nm-thick nonintentionally doped zinc oxide was sputtered atop the CdS layer. The IZO electrode (sheet resistance 60 Ω/sq on a glass substrate) with a thickness of 110 nm was deposited afterward by pulsed DC sputtering (0.81 W/cm²) at 110 °C. The CIS solar cells were finished with Ni/Al grids (50 nm/2500 nm) and a MgF2 antireflection coating (106 nm) by e-beam evaporation.

Solar Cell Performance Characterization. Photocurrent–voltage (J–V) characteristics were measured in four-contact mode at standard test conditions (100 mW cm⁻²) using a Keithley 2400 source meter. A solar simulator (ABA class, LOT-QuantumDesign) was calibrated using a certified monocrystalline silicon solar cell (RS-ID-5, Fraunhofer-ISE) and was used to simulate the AM 1.5 G one-sun illumination. Illumination is from the glass side. Active areas are 0.3 cm² for perovskite solar cells and 0.509 cm² for the CIS solar cell, determined by the areas that are mechanically scribed and optically scanned at 4800 dpi. All the J–V measurements were carried out in ambient (relative humidity, RH ~40%) at room temperature. Scan rates were 0.3 V/s in both forward and reverse directions, and the delay time was 10 ms. No pretreatment, e.g., bias or illumination, was applied before measurement. The steady-state efficiency as a function of time was recorded using an MPP tracker when applied voltage was adjusted to reach the solar cell maximum power point. The tandem devices in the four-terminal configuration were characterized using a perovskite filter (glass/IO:H/SnO2/perovskite/spiro-MeOTAD/MoOx/IZO).

The EQE characteristics were measured using a lock-in amplifier (SR830, Stanford Research). The probing beam was generated by a chopped white light source (900 W, halogen lamp, 260 Hz) and a grating monochromator. The beam size was adjusted to ensure that the illumination area was fully inside the device active area. A certified monocrystalline silicon solar cell (RS-ID-5, Fraunhofer-ISE) was used as the reference cell. A halogen light bias was applied during the measurement with ∼0.1 sun intensity.

Material Characterizations. Transmittance and reflectance of the films and devices were carried out with a UV–vis–NIR spectrophotometer (Shimadzu UV-3600) equipped with an integrating sphere. Absorptance (A) is calculated using the following equation: A = 100% − T − R. The sheet resistance of the IO:H films was measured using a sheet resistivity meter (SD-800, NAGY Instruments). XRD measurements were measured with the XPERT instrument (XPERT PRO, Panalytical). XRD patterns were obtained in Bragg–Brentano geometry with a 2θ–2θ scan (Cu Kr1 radiation, λ = 1.5406 Å) with a step interval of 0.0167°. Hall effect measurements were carried out on the IO:H films with an HEM 3000 Hall effect measurement system at room temperature using van der Paw Geometry Electron density and mobility were extracted from the characterization.

The IO:H film crystallization process was studied by in situ TEM measurements. Two IO:H films were deposited on two E-chips at conditions A (0.6 mPa H2 and 0 mPa O2) and B (0.6 mPa H2 and 1.0 mPa O2). The samples were annealed at 10 °C/min from 25 to 100 °C and at 5 °C/min from 100 to 280 °C in situ characterized by TEM. SAD, TEM, high-resolution TEM, and EDX spectroscopy were performed using a JEOL 2200 STEM/STEM microscope operated at 200 kV. A Protochips Fusion 500 holder (single-tilt) compatible with the JEOL 2200 microscope was used for the in situ experiments. Fusion thermal E-chips with a holey carbon film about 18 nm thick were used to grow the IO:H films. A hot plate (PZ28-2, Harry Gestiikg GmbH) was used for the IO:H film crystallization temperature study. Temperature accuracy of the hot plate is ±0.5 °C.

Ellipsometry measurements were performed on three IO:H films (pristine, annealed at 150 and 230 °C) and a SnO2 film that were deposited on silicon wafers using a Woollam M2000 VNIR instrument. The measurements were taken at a wavelength range between 370 and 1670 nm and at incidence angles of 50°, 60°, and 70°. The refractive indices of the different layers were determined by processing of reflectance, transmittance, and ellipsometry data using
the RefFit software. The dielectric functions were constructed as the sums of Lorentz and Tauc–Lorentz oscillators, ensuring consistency with the Kramers–Kroning relations. The optical propagation in the solar cell was simulated using the TMM implemented in the tmn python package.

ASSOCIATED CONTENT

1 Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c03265.

Movie (MP4)
Movie (MP4)
Additional absorptance and transmittance spectra, J–V characteristics and statistics, EQE curves, scheme of 4-T tandems, SEM images, XRD patterns, TEM characterizations, electronic properties, details of optical analysis (PDF)

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Author Contributions
Y.J. conceived the idea, designed the experiment, fabricated the perovskite solar cells, and analyzed the data. T.F. fabricated the CIS solar cell. R.C. helped with the optical simulation. G.T.S. helped with IO:H film deposition. T.M., S.P., and F.F. contributed to XRD and UV–vis measurements. R.E. and M.D.R. performed the TEM measurements. M.O.G. helped with optical loss analysis. R.H. carried out ellipsometry measurement. Y.J. with the help of F.F. and A.N.T. wrote the manuscript with inputs from all coauthors. All the authors contributed to interpretation of results and discussions on the research topics.

Notes
The authors declare no competing financial interest.

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