Enhanced absorption in tandem solar cells by applying hydrogenated \text{In}_2\text{O}_3 as electrode

Guanchao Yin,$^{1,\text{a}}$ Alexander Steigert,$^2$ Phillip Manley,$^1$ Reiner Klenk,$^2$ and Martina Schmid$^{1,3}$

$^1$Nanooptische Konzepte für die PV, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 14109 Berlin, Germany
$^2$Institut für Heterogene Materialsysteme, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 14109 Berlin, Germany
$^3$Fachbereich Physik, Freie Universität Berlin, 14195 Berlin, Germany

(Received 11 August 2015; accepted 10 November 2015; published online 23 November 2015)

To realize the high efficiency potential of perovskite/chalcopyrite tandem solar cells in modules, hydrogenated \text{In}_2\text{O}_3 (IO:H) as electrode is investigated. IO:H with an electron mobility of 100 cm$^2$ V$^{-1}$ s$^{-1}$ is demonstrated. Compared to the conventional Sn doped \text{In}_2\text{O}_3 (ITO), IO:H exhibits a decreased electron concentration and leads to almost no sub-bandgap absorption up to the wavelength of 1200 nm. Without a trade-off between transparency and lateral resistance in the IO:H electrode, the tandem cell keeps increasing in efficiency as the IO:H thickness increases and efficiencies above 22% are calculated. In contrast, the cells with ITO as electrode perform much worse due to the severe parasitic absorption in ITO. This indicates that IO:H has the potential to lead to high efficiencies, which is otherwise constrained by the parasitic absorption in conventional transparent conductive oxide electrode for tandem solar cells in modules. © 2015 AIP Publishing LLC.

[http://dx.doi.org/10.1063/1.4936328]

Despite great progress achieved in photovoltaics in the last decades, energy from photovoltaics is still less competitive compared to the conventional fossil energy. Therefore, it is desirable to further improve the efficiencies of solar cells at low cost. Tandem solar cells are a concept exceeding the Shockley-Queisser efficiency limit of 30% without light concentration.\textsuperscript{1} Related work has been intensively done based on various combinations of two single-junction solar cells.\textsuperscript{2–8} However, efficiencies beyond 20% were not yet experimentally reported among thin-film tandem solar cells. The underlying challenges mainly lie in Refs. 9 and 10: (a) there is lack of high performing high-bandgap solar cells on the top; (b) sub-bandgap transparency from the top cell is poor due to parasitic absorption, which inhibits the realization of high efficiencies of the bottom cell.

The recent emergence of organic–inorganic \text{CH}_3\text{NH}_3\text{PbI}_3 perovskite solar cells may provide a way out of this tandem stalemate.\textsuperscript{11–13} Organic–inorganic \text{CH}_3\text{NH}_3\text{PbI}_3 perovskite solar cells have achieved an efficiency above 20% up till now.\textsuperscript{14} \text{CH}_3\text{NH}_3\text{PbI}_3 is the absorber and has a relatively large bandgap of 1.6 eV.\textsuperscript{15} It also has a high absorption coefficient and exhibits a steep absorption edge and little sub-bandgap absorption.\textsuperscript{16} All these features render the perovskite solar cell an appealing candidate for the top cell in tandem architecture. In the last two years, the perovskite/CIGSe (Si) tandem solar cells in both monolithic (two-terminal) and mechanically stacked (four-terminal) architectures have been intensively investigated, and efficiencies beyond 30% have been theoretically predicted.\textsuperscript{9,17–22} One of the assumptions made is an excellent sub-bandgap transparency from the perovskite cell. The perovskite solar cells typically have a transparent conductive oxide (TCO) and an Au electrode. To realize semi-transparency, TCOs were recommended for replacing the typical Au electrode in a mechanically stacked architecture.\textsuperscript{19} For a monolithic tandem structure, only the top TCO electrode is required for the top perovskite cell, also see Fig. 2(a).

We note that the conventional TCOs (e.g., \text{In}_2\text{O}_3:Sn—ITO; \text{SnO}_2:F—FTO; and \text{ZnO}:Al—AZO) inherently suffer from transparency loss, which lowers the illumination for the bottom cell. For lab-scale cells in small size, the TCO can be relatively thin since the current collection can be assisted by metal grids on top of the TCO.\textsuperscript{23} The resulting parasitic absorption in TCO is moderate. However, when the solar cell is up-scaled to module size, the modules are generally scribed into multiple stripes of cells, which are monolithically connected without metal grids. A much thicker top TCO electrode is required to minimize the resistive loss due to the lateral transportation of current through the TCO.\textsuperscript{23} The resulting parasitic absorption from TCO is expected to be quite serious and the potential for high efficiency can be thus restrained. The conductivity of TCOs is determined by carrier concentration as well as carrier mobility. In conventional TCOs, a higher free carrier concentration indicates a better conductivity but at the cost of sacrificing transparency. To improve transparency without compromising conductivity, a high-mobility TCO is desirable. Therefore, in this contribution, we will investigate the opto-electronic properties of high-mobility TCO. Using optical simulations, we then evaluate how much of optical benefit can be gained by applying a high-mobility TCO compared to a conventional one as the thick top electrode in a module.

We select hydrogenated \text{In}_2\text{O}_3 (IO:H)\textsuperscript{24} as the high-mobility TCO due to the high electron mobility and ITO as the conventional in this work. Table I presents the carrier...
concentration and mobility values of ITO and IO:H films obtained by Hall measurement, which are individually averaged from 3 different thicknesses (200 nm, 300 nm, 400 nm). The corresponding resistivity is then calculated. Both ITO and IO:H in Table I were prepared by RF sputtering from ceramic target on glass substrate without intentional substrate heating. Ar was used as the working gas. For ITO, the In$_2$O$_3$/SnO$_2$ composition of the target is 90:10 wt. %, and the sputtering process was done at a pressure of 4 × 10$^{-3}$ mbar and a power of 60 W. For IO:H, the target is pure In$_2$O$_3$. The dopant is H$_2$O and was introduced from a reservoir through a needle valve. The water partial pressure was adjusted to 2 × 10$^{-5}$ mbar before starting the Ar$_2$ gas flow. The deposition was then conducted with Ar$_2$ at a pressure of 5 × 10$^{-3}$ mbar at a power of 60 W. Afterwards, the as-deposited IO:H sample was annealed in air for around 10 min. IO:H features an electron mobility as high as 100 cm$^2$ V$^{-1}$ s$^{-1}$ but a much lower electron concentration compared to ITO. As a combined effect of improved electron mobility and decreased electron concentration, IO:H exhibits a resistivity in the same order as ITO. To gain insight into optical properties of ITO and IO:H, we applied an in-house software RefDex based on transfer matrix method and extracted optical constants ($n$, $k$) of ITO$^{25}$ and IO:H as examples based on the measured reflection (R) and transmission (T), which are plotted in Fig. 1. R/T curves for 200 nm thick TCO layers are shown in Fig. S1 of the supplementary material. To be representative, the optical constants in Fig. 1 are also averaged from 200, 300, and 400 nm thick TCO layers. From the extinction coefficient ($k$), IO:H exhibits a lower absorption in the full wavelength range (350–1600 nm) compared to ITO. The absorption in the short wavelengths for both ITO ($\lambda < 450$ nm) and IO:H ($\lambda < 400$ nm) is related to the inter-band transition. ITO also shows strong near infrared absorption starting from 700 nm and is gradually increasing as the wavelength increases. This is ascribed to the absorption of free carriers, which is typically observed in conventional TCOs. For IO:H, this absorption is weak, which can be mainly interpreted by the reduced electron concentration confirmed in Table I. According to the Drude model,$^{28}$ the wavelength $\lambda$ of the bulk plasma frequency for free charge carriers is proportional to $1/\sqrt{N}$ ($N$ is the free carrier concentration), the reduced electron concentration in IO:H therefore redshifts the wavelength of plasma resonance of free carriers beyond 1200 nm. For refractive index $n$, IO:H exhibits a moderate decreasing trend as the wavelength is increasing. ITO generally follows a similar trend but starts to drop faster from the wavelength of 700 nm, where the extinction coefficient $k$ in ITO starts to increase.

We prepared a batch of IO:H films with varied thicknesses, all layers exhibit a high mobility (91–120 cm$^2$ V$^{-1}$ s$^{-1}$) and a low carrier concentration (1.3–1.7 × 10$^{20}$ cm$^{-3}$). This results in a negligible parasitic sub-bandgap absorption compared to the ITO. The calculated optical constants are also similar among IO:H layers in different thicknesses. Therefore, as a good approximation, we assume that the opto-electronic properties of TCO are thickness independent and take the values in Table I and Fig. 1 as references.

To illustrate the impact of TCOs on the performance of perovskite tandem solar cell in module size, a planar monolithic architecture is proposed in this work and only the top most TCO needs to be considered. The architecture is illustrated in Fig. 2(a) and consists of glass/EVA/TCO/C60/CH$_3$NH$_2$NH$_3$PbI$_3$/MoO$_3$/AZO/ZnO/CIGSe/Mo. Interface roughness is not taken into account. ITO and IO:H presented above are taken as top TCO electrodes. Glass and ethyl vinyl acetate (EVA) are incorporated to make the architecture comparable to the module. C60 and MoO$_3$ are electron and hole transporting layers, respectively. Optical constants of TCOs are according to Fig. 1 and those of other layers are taken from Refs. 20, 30, and 31. The CIGSe layer has a bandgap of 1.1 eV. For the optical simulations of the tandem device, we inversely import optical constants of each layer into RefDex and calculate the reflection/transmission/absorption (R/T/Abs). For the monolithic tandem, best efficiencies are achieved when the short circuit current density of the top cell ($J_{sc,\text{top}}$) matches that of the bottom one ($J_{sc,bot}$). In the following, all simulation results shown are thereby under the condition of matched current density $J_{sc,\text{match}}$, $J_{sc}$ is integrated from the absorption in the perovskite and CIGSe layer without collection loss under AM 1.5 solar illumination. The typical thickness of CIGSe layer is 2–3 μm for absorbing most of the incident light. Further increasing the thickness of the CIGSe absorber will not improve $J_{sc,\text{match}}$ and reducing the thickness to below 2 μm will lead to incomplete absorption and a resulting lower $J_{sc,\text{match}}$, thereby reducing the performance of the cell. For realizing the maximum efficiencies of tandem solar cells, we set the CIGSe thickness to 3 μm in this work. The thickness of the perovskite layer is varied to reach the condition of $J_{sc,\text{match}}$ as the top TCO electrode changes its thickness. All other layers are constant in thickness, as shown in Fig. 2(a).

For a high performing module, the sheet resistance of the top electrode is required to be less than 10 Ω/sq. The TCO thickness is 320 nm for a sheet resistance of 10 Ω/sq.

![FIG. 1. Optical constants (refractive index n, extinction coefficient k) of ITO$^{25}$ and IO:H derived from transmission/reflection (R/T) via transfer-matrix method.](image-url)

TABLE I. Comparison of electrical parameters of ITO and an IO:H layers.

<table>
<thead>
<tr>
<th></th>
<th>Electron concentration $N$ (cm$^{-2}$)</th>
<th>Electron mobility $\mu$ (cm$^2$/V × s)</th>
<th>Resistivity $\rho$ (Ω × cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>$6.7 \times 10^{20}$</td>
<td>29</td>
<td>$3.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>IO:H</td>
<td>$1.5 \times 10^{20}$</td>
<td>100</td>
<td>$4.2 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Fig. 2(b) represents R/Abs of the whole tandem device with 320 nm thick ITO and IO:H as top electrode, respectively. The optical losses can be divided into 3 parts: R, parasitic absorption in TCO (AbsTCO) and parasitic absorption in the rest layers (Absrest). For the tandem cell with ITO electrode, AbsTCO covers the whole spectrum of interest and dominates the parasitic absorption, corresponding to a current density of 6.1 mA/cm² and accounting for 81.3% of the whole optical losses. In contrast to this, AbsTCO is negligible for IO:H. Consequently, $J_{\text{match}}$ for the cell with IO:H is 2.5 mA/cm² higher than that for the cell with ITO. The disparity of $J_{\text{match}}$ between the cells with ITO and IO:H is expected to be larger as the TCO thickness increases. Fig. 3 plots the thickness of perovskite layer ($d_{\text{perovskite}}$) required for current match and the corresponding $J_{\text{match}}$ as a function of TCO thickness in the range of 320–1000 nm. As the ITO thickness increases, the parasitic AbsTCO is increasingly severe. To reach the condition of $J_{\text{match}}$, the thickness of the perovskite layer decreases to enable more light transmission into the bottom CIGSe cell. As a result, $J_{\text{match}}$ decreases from 16.2 to 12.1 mA/cm² when the ITO thickness increases from 320 to 1000 nm. In contrast, for the cell with IO:H top electrode, $d_{\text{perovskite}}$ and $J_{\text{match}}$ are independent of the TCO thickness and keep almost constant with a value of 355 nm and 18.7 mA/cm² as the IO:H thickness varies. The slight fluctuations in $d_{\text{perovskite}}$ are related to the influence of interferences originating from the variations of IO:H thickness. We note here for ITO: its optical properties vary to some extent due to different deposition parameters, but the broadband absorption ability is typical.

To assess the benefit of overall performance of cells from applying IO:H as top electrode, we calculated the efficiencies of tandem cells based on a monolithic model. The equivalent circuit is illustrated in Fig. 4(a). $J_{\text{sc}}$ is taken according to Fig. 3, and only the series resistance $R_s$ due to the lateral transportation of current through TCO is taken into account. The photoactive width ($l_1$) is assumed to be 10 mm, which is reasonable for realistic module geometry. Diode 1 (D1) and diode 2 (D2) correspond to a perovskite and a CIGSe solar cell with efficiencies of 16.7% and 21.7% (world record in the lab scale), respectively. Their...
Two the sum of the values of the two individual single cells and is lower, which is ascribed to the lower responsivity of lateral transport of current through TCO when cells are monolithically connected, only one single stripe is considered for simplicity here. Nevertheless, this is enough to reflect the trend of balance between transparency and serial resistance 

For the cell with IO:H as electrode, as the IO:H thickness increases, 

Assuming the quality of the two diodes can be maintained in the tandem structure, the \( J-V \) curves of the tandem solar cell were simulated as a function of TCO thickness. The corresponding efficiencies were extracted from \( J-V \) curves and are presented in Fig. 4(c). Since this is a monolithic structure, the open circuited voltage (\( V_{oc} \)) is approximately the sum of the values of the two individual single cells and is around 1.7 V. Two \( J-V \) curves for the cases of ITO thickness 350 nm and IO:H thickness 1000 nm are shown in Fig. S4 in the supplementary material.\(^{27}\) It should be marked here that in a realistic module several stripes of photovoltaic cells are monolithically connected, only one single stripe is considered for simplicity here. Nevertheless, this is enough to reflect the trend of balance between transparency and serial resistance \( R_s \) from TCO.

The authors acknowledge the funding from the Helmholtz-Assocciation for Young Investigator groups within the Initiative and Networking fund (VH-NG-928), and G. Yin specially acknowledges the support of funding from China Scholarship Council. The authors also acknowledge Hao-Wu Lin (National Tsing Hua University, Taiwan) for sharing the optical constants of C\(_{60}\).


