DOI: 10.1002/ ((please add manuscript number))

Article type: Full Paper

Zr-doped Indium Oxide (IZRO) Transparent Electrodes for Perovskite–Based Tandem Solar Cells

Erkan Aydin¹, Michele De Bastiani¹, Xinbo Yang¹, Muhammad Sajjad¹, Faisal Aljamaan¹, Yury Smirnov³, Mohamed Nejib Hedhili², Wenzhu Liu¹, Thomas G. Allen¹, Lujia, Xu¹, Emmanuel Van Kerschaver¹, Monica Morales-Masis³, Udo Schwingenschlögl¹, and Stefaan De Wolf^{*1}

¹King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Physical Sciences and Engineering Division (PSE), Thuwal 23955-6900, Kingdom of Saudi Arabia

²King Abdullah University of Science and Technology (KAUST), KAUST Core Lab, Thuwal 23955-6900, Kingdom of Saudi Arabia

³University of Twente, MESA+ Institute for Nanotechnology, Enschede 7500 AE, The Netherlands

E-mail: stefaan.dewolf@kaust.edu.sa

Keywords: perovskite tandem solar cells, indium zirconium oxide, improved near-infrared response, transparent electrodes, high mobility

Parasitic absorption in transparent electrodes is one of the main roadblocks to enable power conversion efficiencies (PCEs) for perovskite-based tandem solar cells beyond 30%. To reduce such losses and maximize light coupling, the broadband transparency of such electrodes should be improved, especially at the front of the device. Here, we show the excellent properties of Zr-doped indium oxide (IZRO) transparent electrodes for such applications, with improved near-infrared (NIR) response, compared to conventional In-doped tin oxide (ITO) electrodes. Optimized IZRO films feature a very high electron mobility (up to $\sim 77 \text{ cm}^2/\text{V}\cdot\text{s}$), enabling highly infrared transparent films with very low sheet resistance ($\sim 18 \text{ }\Omega/\square$ for annealed 100 nm films). For devices, this translates in a parasitic absorption of only $\sim 5\%$ for IZRO within the solar spectrum (250–2500 nm range), to be compared with $\sim 10\%$ for commercial ITO. Fundamentally, we find that the high conductivity of annealed IZRO films is directly linked to promoted crystallinity of the indium oxide (In_2O_3) films due to Zr-doping. Overall, on four-terminal perovskite/silicon tandem device level, we obtained an absolute 3.5

mA/cm² short-circuit current improvement in silicon bottom cells by replacing commercial ITO electrodes with IZRO, resulting in improving the PCE from 23.3 to 26.2%.

1. Introduction

Tandem solar cells are the most straightforward way to exceed the Shockley-Queisser limit of single-junction solar cells.^[1] In particular, perovskite/silicon tandems hold great promise for commercialization, now showing 28% certified PCE on a laboratory scale.^[2] Transparent electrodes are essential components in the tandem stack, particularly at their sunward side. Ideally, these electrodes feature simultaneously a high lateral conductivity and broadband transparency to minimize resistive losses and to increase the performance throughout the solar spectrum on device level, respectively. Sputtered transparent conductive oxides (TCOs) are the first choice for transparent electrodes since they fulfill relatively well the seemingly contradictory transparency/conductivity requirements. In addition, TCOs can be processed at a low temperature and with proven industrial scalability. In perovskite-based tandems, the perovskite top cell should efficiently harvest the blue part of the solar spectrum whereas the bottom cell, which can be silicon, copper-indium-gallium-selenide, or another metal halide perovskite do so for the near-infrared part.^[3, 4] Importantly, the top cell should also be highly NIR transparent. For perovskite absorbers this requirement is fulfilled by their steep absorption edge and absence of deep optical states.^[5] Based on these arguments, for highly efficient devices, it is critical that the transparent electrodes should combine a wide bandgap with minimal free carrier absorption (FCA), to avoid parasitic absorption in the blue and red parts of the solar spectrum, respectively. Losses associated with FCA can be reduced by decreasing the carrier density of the transparent electrode.^[6] However, to maintain a low sheet resistivity, strategies to increase carrier mobility are then required. Motivated by these criteria, some TCOs based on doped In₂O₃ have already been explored in literature for tandem solar cells such as ITO, Zn-doped In₂O₃ (IZO), and ITO/H-doped In₂O₃ (In₂O₃:H) bilayer

electrodes.^[4, 7] In this, ITO, whereas being well established, is of limited appeal because of its low mobility due to the ionized impurities and high parasitic absorption, especially in the NIR range.^[8] Conversely, crystalline $\text{In}_2\text{O}_3\text{:H}$ has a very high mobility and optical transparency.^[9] Unfortunately, this TCO may degrade the device performance due to water vapor effusion.^[10] IZO, which is another promising TCO, enables a mobility of $\sim 60 \text{ cm}^2/\text{V}\cdot\text{s}$ without the need of post-annealing.^[11] However, due to its amorphous nature, its band edge is ‘blurry’, causing parasitic absorption in the blue part of the spectra.^[11] Alternatively, other transition metals such as Ti, Ce, W, Mo, Zr can also be used for heteroatom doping of In_2O_3 . However, such dopants have not been explored widely in tandem solar cells because of high-temperature annealing requirements to activate these materials.^[12] Recently, IZRO has been explored as a high-mobility and NIR transparent TCO, resulting in improved short circuit current density (J_{sc}), compared to conventional TCOs in silicon heterojunction (SHJ)solar cells.^[13] Excellent optoelectronic properties such as high transparency, wide bandgap ($>3.5 \text{ eV}$) and high conductivity, combined with high NIR transparency make IZRO a promising electrode for perovskite single-junction and perovskite-based tandem solar cells.

In this study, we thoroughly studied the structural and optoelectronic properties of radio frequency (RF) sputtered IZRO films, using 2 wt% zirconium oxide (ZrO_2) doped In_2O_3 targets. This doping ratio has already been successfully proven to obtain maximum conductivity for In_2O_3 .^[6, 13, 14] Here, we investigated critical processing parameters for application in perovskite solar cells (PSCs), such as process pressure, oxygen partial pressure $p(\text{O}_2)$, and film thickness for as-deposited and annealed (at 200°C in ambient air) samples, aiming at gentle deposition on the soft perovskite thin films. Finally, we tested our IZRO electrodes in four-terminal perovskite/silicon tandem solar cells.

2. Results and Discussion

We developed our IZRO electrodes by targeting high conductivity and transparency by using low power densities, and room temperature depositions to avoid damaging the

underlying soft layers. **Table S1** summarizes the results for tested process parameters. We found that as-deposited films processed at a total process pressure [$r(\text{O}_2) + r(\text{Ar})$] of 1 mTorr, with $r(\text{O}_2) = 0.12\%$ give the highest mobility and lowest sheet resistivity (**Figure 1a**) as well as excellent optical transparency (**Figure S1a** and **S1b**). Next, we studied the role of the thickness of IZRO films and found that increased film thickness yields a decrease in sheet resistivity (**Figure 1c**) and optical transparency (**Figure S1e** and **S1f**) for as-deposited as well as annealed samples. When the film thickness reached 100 nm, the electron density (N_e) and mobility (μ_e) remained in a similar range compared to thinner films. For films post-annealed at temperatures lower than 200 °C, no substantial changes are found in the structural and electronic parameters. However, above 200 °C, the resistivity increases drastically, as summarized in **Table 1**. We correlate this to an amorphous-to-crystalline phase transition, occurring at 200 °C, as apparent from XRD spectra, shown in **Figure 2c**. For the samples post-annealed at 200 °C, we obtained the combination of the lowest sheet resistivity ($18 \Omega/\square$, with $\mu_e = 77 \text{ cm}^2/\text{V}\cdot\text{s}$, **Table S1**) with the highest optical transparency (**Figure 4a**). The increased carrier concentration after annealing at 200 °C can be attributed to enhanced Zr^{4+} ion doping activation.^[6] Here, Zr acts as a shallow donor via substituting In^{3+} by Zr^{4+} (generating one electron per Zr atom), making the In_2O_3 degenerately doped.^[6] Further increasing the temperature resulted in a decrease in free-carrier density, and thus decreased conductivity, probably because of further oxidation. It is worth noting that annealing of IZRO at 200 °C in an inert atmosphere (nitrogen filled glove box, $<0.1\text{ppm O}_2$ and H_2O) resulted in similar optoelectronic properties, which indicates that ambient-specific annealing is not a requisite.

Figure 1. The change of sheet resistance (R_s), Hall mobility (μ_{Hall}) and free carrier concentration (N_e) as a function of a) process pressure ($r(O_2) + r(Ar)$), b) $r(O_2)$ in plasma gas mixture, c) thickness of the films and d) post-annealing temperature of IZRO films. Open circles (o) show the as-deposited while closed circles (●) show annealed samples at 200 °C (except for annealing temperature part, d). Whereas the influence of process pressure has been tested with $r(O_2) = 0.09\%$ and 100 nm films, the $r(O_2)$ has been tested for 1 mTorr optimized process pressure. The thickness of the films has been studied for 1 mTorr process pressure and $r(O_2) = 0.12\%$. Post-annealing of the films has been performed for 100 nm films processed at 1 mTorr process pressure and $r(O_2) = 0.12\%$.

Figure 2c shows the X-ray diffraction (XRD) patterns of the as-deposited and annealed (at 200 °C) IZRO films. As-deposited films show an amorphous nature without characteristic reflections; crystallization and grain growth become notable when samples are post-annealed above 200 °C. However, further increasing the annealing temperature did not increase the crystallinity which can be witnessed from the XRD spectra given in **Figure S3**. Based on these results, it appears that annealing at 200 °C for 25 minutes suffices to obtain fully

crystalline films (no remnants of amorphous tissue) as also suggested by the top-view scanning electron microscope (SEM) images in **Figure 2b**. After post-annealing, IZRO films showed a preferred orientation in growth to the (400) plane, characteristic of the unit cell of cubic In_2O_3 (PDF 01-071-2194). The 2θ positions of the detected peaks and assigned crystallographic planes are listed in **Table S3** together with PDF data. Most of the peaks show a small shift towards higher angles which may be correlated with the presence of interstitial Zr atoms in the lattice; substitutional Zr doping is not likely to cause stress to the lattice due to the similar atomic radii of In^{3+} (80 pm) and Zr^{4+} (72 pm).^[6] The absence of peaks originating from impurity phases may indicate the formation of a solid solution with Zr-doping.

In agreement with the XRD analysis, SEM top-view images revealed that as-deposited films are mainly amorphous, and after annealing at 200 °C for 25 minutes the films become crystalline (**Figure 2b**). This behavior is similar to that of non-doped and Zr-doped In_2O_3 films (**Figure S4**). The XRD spectra also confirm the increased crystallinity of the films compared to their non-doped counterparts by showing an increased intensity of the main peak (**Figure S5**). These results indicate that Zr doping of the In_2O_3 films notably promotes the formation of larger grains, compared to the non-doped films (see also SEM images in **Figure S4**). A similar annealing behavior was earlier reported for H doping of In_2O_3 .^[15] Following the Scherrer formula, we calculated the average crystal size in IZRO films as 105 nm, to be compared with 47 nm for a non-doped sample.^[16] This remarkable improvement in crystal size arguably helps IZRO films to have higher mobility and conductivity. Indeed, earlier, Koida *et al.* correlated the increased mobility of $\text{In}_2\text{O}_3\text{:H}$ films with a longer optical relaxation time, rather than with a smaller effective electron mass in the crystallized films (as compared with the as-deposited films).^[15]

To further elucidate the effect of annealing on the conductivity and electron transport properties of IZRO films, we performed temperature-dependent Hall-effect measurements in a

range from 300 K down to 10 K (**Figure 2d**). For this, as-deposited (amorphous) and annealed (crystalline) IZRO films were compared. For both films, N_e is independent of temperature as expected for degenerate semiconductors. Regarding the electron mobility, the amorphous film shows only a relative change of 13% with cooling down, while the crystalline film shows a relative change of 33% (reaching 115 cm²/V·s at 10 K). Temperature-dependent Hall-effect measurements were performed using a Quantum Design Physical Property Measurement System (PPMS) and $\mu_{e,annealed}$ was found 87 cm²/V·s at room temperature, which is slightly higher than results obtained with a Lake-Shore system. For the as-deposited IZRO film, the weak dependence of μ_e with temperature is indicative of transport dominated by ionized or neutral impurity scattering, as observed for several doped amorphous oxides.^[17] Contrary to this, for the crystalline sample, the increment in μ_e with cooling down from 300 to 100 K is indicative of lattice (phonon) scattering. Sources of lattice scattering can arise from optical and/or acoustic phonons. Polar optical phonon scattering has been generally proposed as the main contributor to phonon scattering in In₂O₃.^[18, 19] Using the approximation for polar optical phonon scattering, $\mu \propto T^p$, we determined $0.24 < p \leq 0.45$ for the annealed IZRO sample (**Figure 2d**). This is lower than the $p = 2.2$ reported for unintentionally doped epitaxially grown In₂O₃ films.^[19] The small slope for our polycrystalline IZRO suggests that although photon scattering dominates, ionized impurities and/or grain boundaries still contribute to the scattering of carriers in the IZRO films.

Next, we verified the Zr content of the films by energy dispersive spectroscopy (EDS) analysis. EDS spectra shown in **Figure S6** reveal that as-deposited films contain 1.4 at.% Zr, similar to annealed films with 1.6 at.%. The Zr concentration in thin films is slightly lower than the target composition, which is expected for sputtered films from doped targets since different metals have different energy distributions of sputtered atoms. Additionally, the O/In ratio increased by annealing, which confirms the higher O intake due to the oxidization of

Zr^{4+} or O vacancies. The EDS analysis also revealed that the white spots observed on the films have the same elemental composition as the rest of the films for both doped and non-doped films (**Figure S6c**). We believe therefore that these regions are the seeding points for the crystal growth during the post-annealing.

To further understand the effect of Zr doping, we performed density functional theory (DFT) calculations on a bixbyite In_2O_3 lattice system. We obtain a lattice parameter of 10.30 Å, which is 1.7% higher than the previously reported experimental value.^[20] In order to study Zr doping, we replaced one of the thirty-two In atoms with Zr such that the doping concentration is 3.125%, finding that the lattice constant slightly expands to 10.31 Å. The crystal structure of Zr-doped In_2O_3 is shown in **Figure 2a**. The formation energy of Zr substitution is calculated as $E_{\text{FE}} = E_{\text{IZO}} - (E_{\text{IO}} + \mu_{\text{In}} + \mu_{\text{Zr}}) = 4.89$ eV, where E_{IZO} and E_{IO} are the total energies of the Zr-doped and pristine In_2O_3 crystals, respectively, and μ_{In} and μ_{Zr} are the chemical potentials of In and Zr obtained from their bulk phases. Usually, the chemical potentials depend on the growth conditions. We calculated the bandgap to be 0.92 eV for In_2O_3 . This is in agreement with a previously reported DFT value of 0.90 eV^[21], but notably underestimates – as expected for DFT^[22] – the experimental value of ≥ 2.7 eV for a single crystal.^[23] From the partial density of states (**Figure S10**), the valence band maximum (VBM) is found to be primarily due to O (p) states, but also includes contributions of In (p and d) states. The conduction band minimum (CBM) is due to hybridized In (s) and O (p) states, and we found that the addition of Zr does not cause hybridization with these CBM states. Similar behaviour has been found for Ce doping in In_2O_3 .^[24] Since the dispersion of the CBM does not change by Zr substitution, we attribute the increment in the measured electron mobility to the enhanced grain size.

Figure 2. a) Crystal structure of In_2O_3 crystal with Zr substitution of In atoms. Pink, red, and green colors represent In, O, and Zr atoms, respectively. b) SEM top view of the IZRO films before and after the annealing process showing the formation of large crystals after annealing at 200 °C explicitly. c) XRD spectra of the IZRO films before and after annealing confirming the phase transition from amorphous to crystalline. d) Temperature-dependent Hall-effect measurements for as-deposited and annealed samples between 10 and 300 K. The thin straight line qualitatively represent asymptotic mobility due to polar optical phonon scattering only.

We performed X-ray photoelectron spectroscopy (XPS) to characterize the chemical composition of the IZRO films and to determine the oxidation state of Zr. Survey spectra proved the presence of In, O, Zr and C elements in the structure before and after annealing of the films (**Figure 3c**). The determined Zr/In atomic ratio from the XPS survey spectrum was found to be equal to 0.01 in consistent with EDS results. **Figure 3d** displays high-resolution XPS spectra of the In 3d core level for the samples. This level shows two peaks corresponding to In $3d_{5/2}$ – In $3d_{3/2}$ doublet located at 444.6 eV and 452.2 eV, respectively, characteristic of In_2O_3 .^[25] No significant changes were observed comparing as-deposited and annealed samples. High-resolution XPS spectra of O 1s core level of both as-deposited and annealed IZRO

shows a peak located at 530.0 eV with a shoulder at high binding energy around 531.8 eV (**Figure 3d**). The dominant peak at 530.0 eV corresponds to the oxygen bond of In–O–In, the small peak situated at higher binding energy 531.8 eV refers to a combination of hydroxide and oxygen defects in the matrix of metal oxide and organic oxygen.^[25] Previously, this peak was reported to disappear by annealing of In₂O₃:H films.^[26] The high-resolution XPS spectra of Zr 3d core level for the as-deposited sample shows two characteristic peaks of ZrO₂ corresponding to Zr 3d_{5/2} – Zr 3d_{3/2} located at 182.2 eV and 184.8 eV, respectively (**Figure 3d**).^[27] After annealing, we observed a small shift of about 0.2 eV to higher binding energy, which can be attributed to further oxidation of Zr.

The work function (WF) of IZRO films is another important parameter to be considered for device engineering. Here, we obtained a WF of –4.2 eV from ultraviolet photoelectron spectroscopy (UPS) for both as-deposited and annealed IZRO films (**Figure 3a**). The measured values are very close to the previously reported WF of –4.3 eV for thick In₂O₃ films.^[28] We measured the WF of the non-doped In₂O₃ films, which are deposited with the same process parameters, to be –4.1 eV for both as-deposited and annealed samples, which can be seen in **Figure S4**. We also performed DFT calculations for the WF of O terminated (12 O atoms on each surface) and In terminated (8 In atoms on each surface) In₂O₃(100) slabs by using the expression $WF = E_v - E_F$, where E_v and E_F are the vacuum and Fermi energies, respectively. The WF of pure In₂O₃ is –7.51 eV for O-termination, decreasing to –6.85 eV when the surface oxidation is reduced (6 O atoms on each surface). Termination by In gives a WF of –4.60 eV and –4.38 eV for pure and Zr-doped In₂O₃, respectively, which is very close to experimental values. Experimental results confirmed the WF to be –4.2 eV (undoped –4.1 eV). This opposing behavior might be related to the dependency of the ionization potential and WF of In₂O₃ on the surface orientation.^[29]

Figure 3. UPS spectra showing the a) WF and b) VBM values. c) XPS survey of the IZRO films before and after the annealing process. WF values have been calculated by $WF = 21.2 - WF_{\text{cutoff}}$ (eV). VBM values have been calculated by $VBM = WF + VBM_{\text{cutoff}}$ d) Detailed view on XPS spectra of In 3d, O 1s, and Zr 3d states with direct comparison of as-deposited and annealed samples.

Compared to standard ITO, IZRO electrodes provide better transparency in the high energy part of the solar spectrum. **Figure 4a** shows the transmittance and absorbance of the films measured by UV-vis-NIR spectroscopy, revealing that the transparency of the films increases drastically by annealing, whereas the transparency of ITO changes only slightly. We correlate this improvement with increased crystallinity and decreased N_e , where the former also leads to improved carrier mobility. Solar-weighted absorbance plots indicate that while as-deposited IZRO absorbs 98.3 mW/cm^2 ($\sim 10\%$) of the solar spectrum, annealed IZRO films absorb only 48.9 mW/cm^2 ($\sim 5\%$) (**Figure 4b**). Contrasting with this, as deposited ITO film absorbed 111.9 mW/cm^2 ($\sim 12\%$) and annealed ITO 93.8 mW/cm^2 ($\sim 10\%$). This underlines the great

potential of IZRO to reduce the parasitic absorption losses in solar cells and hence improve their power output, especially for annealed samples. We calculated the optical bandgap values of the films by the extrapolation of the linear region of the $(\alpha h\nu)^2$ vs. $h\nu$ graph as shown in **Figure 4c**.^[30] Accordingly, whereas as-deposited films have a 3.55 eV bandgap, by annealing this value shifted to 3.75 eV; such broadening of the bandgap is often observed for wide bandgap TCOs.^[13, 31] DFT calculations revealed that Zr-doping enlarges the bandgap to 1.01 eV from 0.92 eV, suggesting that increased bandgap of the films might be due to the combined effect of promoted crystallinity and the Moss-Burstein shift observed for doped In_2O_3 films.^[13]

The refractive index (n) and extinction coefficient (k) are widely used optical parameters to understand the absorption losses and light in-coupling on the device level. The dependency of n and k values on the photon energy ($h\nu$) of the as-deposited and annealed IZRO films are shown in **Figure 4d** which were extracted from measured spectroscopic ellipsometry (SE) data. At short and long wavelengths, the k values decrease, and the absorption edge blue shifts. The improvement in short wavelengths can be attributed mainly to the improved crystallinity of the IZRO films after annealing whereas the improvement in the long wavelengths might be assigned decreased carrier density and thus FCA.^[32] Thanks to decreased FCA, parasitic absorption losses reduced which can be translated in improved light coupling of the NIR part of the spectrum in solar cells.

Figure 4. a) Transmittance (T) and absorbance (A) and b) solar weighted absorbance spectra of the sputtered IZRO and ITO films measured with integrating sphere. The shaded area shows the spectral irradiance for AM 1.5 conditions. c) The optical bandgap values of the IZRO from $(\alpha h\nu)^2$ vs. $h\nu$ graph. d) Refractive index (n) and extinction coefficient (k) for as-deposited and annealed IZRO films.

Subsequently, we tested the performance of the IZRO electrodes in four-terminal perovskite/silicon tandem solar cells. We fabricated semitransparent PSCs with the structure of $\text{NiO}_x/\text{MAPbI}_3/\text{PC}_{60}\text{BM}/\text{ZnO}/\text{BCP}/\text{IZRO}/\text{Ag}$ on either ITO or IZRO transparent electrodes (**Figure 5a**). For the low bandgap bottom cell, we used an *n*-type SHJ solar cell, which characteristically features a high V_{OC} .^[33] **Figure 5b** and **Figure 5c** show the cross-sectional SEM image of the stacked layers and the photograph of the fabricated semitransparent PSCs, respectively. First, we compared the semitransparent solar cell performance of ITO and IZRO front electrodes by keeping the IZRO back electrode in all cases. We found that, while ITO front electrode based devices were giving 1078 mV V_{OC} , IZRO based devices feature a V_{OC}

of 1042 mV on the soda-lime glass and 1008 mV on quartz substrates (**Table 2** and **Figure 5**). The V_{OC} difference between ITO and IZRO based devices might be attributed to the band alignment of the electrodes as UPS analysis revealed the work function of the IZRO films is -4.2 eV while ITO has -4.7 eV. The difference for the film deposited on soda-lime glass and quartz substrates might be related to substrate-specific film-growth dynamics. We found that IZRO-based semitransparent PSCs showed 0.9 mA/cm² current gain respect to ITO based devices. Thanks to the improved NIR transparency by IZRO electrodes compared to ITO, a 1.8 mA/cm² current gain was obtained on filtered c-Si bottom cells (**Figure 5e**). This difference became more notable when we used quartz substrates instead of soda-lime glass as can be seen in **Figure 5f**. $\Delta_{EQE} = EQE_{IZRO} - EQE_{ITO}$ analysis confirmed that IZRO electrodes enable improved light harvesting. Overall, across the whole absorption spectrum, we achieved an absolute current gain of 3.5 mA/cm² (using quartz substrates) compared to ITO based electrodes, and four-terminal tandem PCE reached to 26.2% which is comparable with other reported efficient devices.^[34] Importantly, 1-R plots show that employing IZRO electrodes enable an improved spectral response thanks to reduced reflection losses (**Figure 5e**). To verify the improved NIR response of the tandem solar cells, we compared the results with c-Si solar cells with electron-selective titanium dioxide (TiO₂) rear contact, which gives an excellent external quantum efficiency (EQE) response in both short and long wavelength range and high PCE (22.1%).^[35] We found that such devices provide 2.3 mA/cm² absolute current gain and overall four-terminal tandem PCE is 24.8% which is slightly lower than SHJ cells (**Figure S14**). Herein, SHJ cells get benefit of their high V_{OC} and better NIR response although they suffer from a somewhat moderate UV response originating from parasitic absorption at the front contact stack.^[36] Achieved PCE results highlight also the key role of the high V_{OC} of the silicon bottom cells to achieve high-efficiency tandems. Overall, these results revealed the full potential of IZRO electrodes on tandem solar cells by proving the improved light harvesting.

Figure 5. Schematics of the fabricated semitransparent perovskite top cells and c-Si bottom cells. b) Stacked layers of IZRO/ NiO_x / MAPbI_3 / PC_{60}BM / ZnO-np /IZRO structure imaged by cross-sectional SEM analysis c) together with the photograph of the devices. d) $J-V$ graphs and e) EQE spectra of the mechanically stacked perovskite/silicon tandem solar cells and individual top and bottom cells with 0.16 cm^2 top cell aperture area and 4.2 cm^2 bottom cell area. All measurements were done without any antireflection coating and foil. The shaded area shows the AM 1.5G spectra. f) $\Delta\text{EQE} = \text{EQE}_{\text{IZRO}} - \text{EQE}_{\text{ITO}}$ for both soda-lime and quartz glass substrates which is showing absolute current gain on SHJ bottom cells.

Table 1. Performance overview for the silicon solar cells, NIR transparent solar cells, and mechanically stacked solar cells.* Note that silicon solar cells are measured over 4.2 cm² aperture area while semitransparent solar cells over 0.16 cm². Four-terminal tandem solar cells are measured over 4.2 cm² aperture area by using full area perovskite devices as a filter on 1 inch² glass substrates

Devices	Voc (mV)	Jsc (mA/cm ²)	FF (%)	PCE (%)
c-Si	722	37.2	79.7	21.4
Filtered c-Si (ITO based)	704	15.6	79.2	8.7
Filtered c-Si (IZRO based)	704	17.4	79.0	9.7
Filtered c-Si (IZRO on quartz based)	708	18.8	79.3	10.6
Semitransparent PSC (ITO based)	1078	18.2	74.0	14.6
Semitransparent PSC (IZRO based)	1042	19.1	76.0	15.1
Semitransparent PSC (IZRO on quartz based)	1008	19.8	78.0	15.6
4T-Tandem (ITO based)	-	-	-	23.3
4T-Tandem (IZRO based)	-	-	-	24.8
4T-Tandem (IZRO on quartz based)	-	-	-	26.2

* IZRO back electrode is common for all semitransparent devices and these electrodes were used without any thermal treatment. No antireflection foils or layer has been utilized for the $J-V$ measurements.

3. Conclusion

In summary, we successfully implemented IZRO films as front and rear transparent electrodes on perovskite semitransparent solar cells for tandem applications, using low power density and low thermal budget to protect underlying soft layers. Our IZRO electrodes showed improved transparency and low sheet-resistance (41 and 18 $\Omega/\square$ for as-deposited and annealed films, respectively) which are encouraging to increase the finger spacing on the tandem solar cells, essential to increase the current in devices. Beyond this, the high conductivity of the IZRO films may help to decrease the thickness of the transparent electrodes, which directly translates in less indium usage. In the long term, this might help to decrease the price of the tandem solar cells. Besides, we foresee that IZRO can replace ITO as a recombination junction in monolithic tandem solar cells to improve the NIR response of the silicon bottom cells. Moreover, here we engineered IZRO films with a low thermal budget, which means such electrodes can be used on different low-temperature resilience substrates and device structures as well. Finally, IZRO electrodes may find applications in other electronic devices

beyond silicon and perovskite-based solar cells, such as IR sensitive quantum dot solar cells, thin film transistors, and organic light emitting diodes.

4. Experimental Section

Deposition of IZRO films: IZRO films were grown on soda lime glass substrates by RF sputtering technique (Angstrom Engineering). As a target material, 98 wt% In_2O_3 and 2 wt% ZrO_2 has been used. Argon and 2.5% oxygen/argon gas mixture were used as a process gas. It is of note that no water is intentionally introduced to the system and base pressure was kept $< 5 \times 10^{-7}$ Torr before the deposition to eliminate the contribution of the water during the processing. The deposition rate of the optimized IZRO films was $0.21 \text{ \AA/s}$. All deposition performed at room-temperature without any intentional heating. The gas flow ratio, process pressure and the thickness of the layers have been engineered as defined in the main text.

Fabrication of semitransparent perovskite solar cell: First, NiO_x layers were deposited on the pre-cleaned commercial ITO coated (Xin Yan Technologies, $15 \text{ } \Omega/\square$) or homemade IZRO coated glass substrates via RF magnetron sputtering technique at room temperature and with high uniformity as we reported previously.^[37] Perovskite precursor was prepared by dissolving 507 mg PbI_2 (TCI) and 175 mg methylammonium iodide (Greatcell Solar) in 970 μl N,N-dimethylformamide and 75 μl dimethyl sulfoxide (both Sigma Aldrich). This precursor dropped onto the substrate's NiO_x surface, and the spin process was started (4000 rpm for 30 seconds). 24 seconds before the end of the spin cycle (in other words, after 6 seconds), 100 μl chlorobenzene (Sigma Aldrich) was pipetted onto the spinning substrate. Samples were annealed in a nitrogen-filled glovebox at 100°C for 10 minutes before cooling to room temperature. Next, a 20 mg/ml solution of PC_{60}BM ($>99.5\%$, Lumtec) in chlorobenzene was spin-coated onto the perovskite films at 1300 rpm for 30 seconds. As a buffer layer, ZnO nanoparticle solution (Avantama) was spin cast on PCBM layer as defined previously without any annealing step.^[38] Finally, an ultra-thin layer of bathocuproine (Sigma

Aldrich) cathode modification layer was spin-coated at 5000 rpm for 10 seconds from a 0.5 mg/ml solution in anhydrous ethanol. 100 nm IZRO transparent electrodes was deposited by RF sputtering ($41 \text{ } \Omega/\square$). Devices were completed by the thermal evaporation of a 100 nm thick silver contact at 10^{-6} mTorr.

Fabrication of the TiO_2 passivated silicon bottom cell: The bottom silicon cell (4.2 cm^2), featuring a high-performance full-area $\text{SiO}_2/\text{TiO}_2$ electron-selective contact at the rear side, were fabricated on n -type FZ-Si wafers ($1.0 \text{ } \Omega \text{ cm}$). The textured front side with random pyramids has a boron diffused p^+ emitter, passivated by $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack. The front fingers ($\sim 30 \text{ } \mu\text{m}$) were prepared by thermal evaporation of a Cr/Pd/Ag seed layer and subsequent thickened by silver electroplating. The fabrication details can be found in reference.^[35, 39] The bottom silicon cell exhibits an excellent EQE response in the long wavelength range, thanks to the full-area $\text{SiO}_2/\text{TiO}_2$ electron-selective contact, enabling low carrier recombination and a low contact resistivity.

Fabrication of the n -type SHJ bottom cell: We used 250–280 μm thick float-zone double-side-polished 4 inches wafers (n -type, resistivity 1–5 $\Omega\text{-cm}$) to fabricate SHJ cells. Texturing was performed by concentrated KOH solution. After the texturing process, the wafers are rinsed three times in a dedicated DI water bath and finished with the RCA cleaning process. The wafers were passivated and carrier-selective contacts were created by deposition of intrinsic and doped hydrogenated amorphous silicon layers. The cells were then finished with ITO deposition and metallization with full-area silver on the rear-side and screen-printed silver grid on the front-side.

Solar cell measurements: J – V characteristics of the semitransparent perovskite solar cells were characterized using a custom-made temperature controlled jig as defined in previous studies.^[40] To avoid back reflections to semitransparent perovskite solar cells, the back side of

the jig was mate black painted. All devices were tested under 1-sun illumination conditions (100 mW/cm², AM 1.5G, 25 °C) employing Wavelabs LED-based solar simulator which is calibrated by Fraunhofer certified c-Si calibration cell. Semitransparent devices had 0.16 cm² aperture area. Note that the reverse scan is from V_{OC} to J_{SC} (1.2V → − 0.1V), and the forward scan is from J_{SC} to V_{OC} (− 0.1 V → 1.2V). No preconditioning protocol has been used before the measurement. Silicon solar cells were measured with a scan rate of 1.4 V/s. For four-terminal tandem measurements, the bottom cell was measured by using the perovskite top cell (without metal contacts) as a filter by illuminating from the glass side. No antireflection layer and foil was employed.

EQE measurements: The external quantum efficiency (EQE) spectra of our perovskite cells were measured with a commercial EQE system (Newport) equipped with a xenon lamp and under dark conditions and without any biasing and preconditioning. Semitransparent solar cells have been illuminated from the glass side. The c-Si bottom cell was filtered by semitransparent solar cells during the EQE measurements. EQE of the c-Si bottom cells was measured by focusing the beam between two metal fingers. The calibration of the EQE tools was performed by a silicon and germanium diodes.

Characterization—Hall-effect: Room temperature Hall-effect measurements were performed on Lake Shore Hall-effect system at dark conditions. Samples were prepared in Van der Pauw geometry. Connections of silver wires for the electrical measurements were made by conductive silver paste. After drying process of the paste, the ohmic behavior of the metal contacts was checked by the linear variation of the current-voltage (I–V) characteristics which was observed to be independent of the polarity of the applied current and the contact combinations for each sample. Measurements were done under 10 kG magnetic field. The sample size was 10 × 10 mm². Temperature-dependent Hall-effect measurements were

performed using a Quantum Design Physical Property Measurement System (PPMS) in the temperature range of 10 – 300 K at a current level of 10 μ A and magnetic field of ± 9 Tesla. Sample preparation was identical to the one described for room temperature Hall-effect measurement.

Characterization—SEM-EDX: Surface and cross-sectional images of the samples were taken by a Carl Zeiss AURIGA® CrossBeam® Workstation using in-lens detectors. A 5 kV voltage was used to accelerate the electrons, and the working distance was 5 mm. EDX analysis was performed at 10 keV accelerating voltage using Oxford X-max 20 detector under a pressure of typically 10^{-9} mBar.

Characterization—Transmittance/Reflectance: A PerkinElmer Lambda 950 UV-vis-NIR spectrophotometer was used to investigate the transmittance of samples between 200 and 2500 nm range with the integrating sphere. Absorptance of the films calculated by $A = 100 - (T + R)$ method.

XPS and UPS measurements: XPS studies were carried out in a Kratos Axis Supra DLD spectrometer equipped with a monochromatic Al K_{α} X-ray source ($h\nu=1486.6$ eV) operating at 150 W, a multichannel plate and delay line detector under a vacuum of $1\sim 10^{-9}$ mbar. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV, respectively. Samples were mounted in a floating mode in order to avoid differential charging for the XPS measurements. Charge neutralization was required for all samples. Binding energies were referenced to the C 1s peak of (C-C, C-H) bond which was set at 284.8 eV. The data were analyzed with commercially available software, CasaXPS. The individual peaks were fitted by a Gaussian(70%) – Lorentzian (30%) (GL30) function after linear or Shirley type background subtraction. UPS measurements were performed in the same instrument using a He I excitation ($h\nu = 21.22$ eV). A bias of -9 V was applied to the

sample surface for UPS measurements. Samples were mounted in contact mode for the UPS measurements.

XRD measurements: Bruker D8 Advance diffractometer was used for XRD analysis. The tool was operated at 30 kV, 10 mA at 2θ (Cu K_{α} , ($\lambda = 0.15418$ nm)) $30 - 80^{\circ}$, step 0.02° and scan speed $2.5^{\circ} \text{ min}^{-1}$.

DFT modelling: We use the Vienna Ab-initio Simulation Package^[20] to perform DFT calculations for an 80-atoms cell of In_2O_3 (space group: $\text{Ia}\bar{3}$, No. 206), using a cut-off energy of 500 eV and $2 \times 2 \times 2$, $4 \times 4 \times 4$, and $8 \times 8 \times 8$ k-meshes for the structure relaxation, self-consistent calculation, and non-self-consistent calculation, respectively. In the structure relaxation, we use the Perdew-Burke-Ernzerhof^[21] flavor of the generalized gradient approximation for the exchange-correlation functional and converge the Hellmann–Feynman forces to $0.01 \text{ eV } \text{\AA}^{-1}$ for all atoms. To calculate the WF, In_2O_3 (100) slabs are constructed, as the most prominent peak (200) in the XRD data corresponds to the (100) growth direction. A vacuum region of $18 \text{ \AA}$ thickness is added to separate the repeating geometries.

Spectroscopic Ellipsometry: Spectroscopic ellipsometry measurements of the IZRO/c-Si stacks were performed by using J.A. Woollam M-2000DI at 65° and 75° . The c-Si substrate was a single-polished float-zone wafer ($525 \pm 25 \text{ }\mu\text{m}$) and IZRO film was deposited on the polished side. Such a substrate can effectively impede interference caused by light reflection from the rear side. An optical model of air/surface roughness/IZRO/c-Si is used to fit the (Ψ, Δ) raw data. The IZRO layer is analyzed by a combination of three oscillators: a Tauc-Lorentz oscillator, a Gaussian and, a Drude oscillator. The surface roughness is analyzed using Bruggeman effective medium approximation (BEMA), composed of 50 vol% air and 50 vol% IZRO material.

Supporting Information

Supporting Information is available from the Wiley Online Library or the author.

Acknowledgements

The research reported in this publication was supported by funding from King Abdullah University of Science and Technology (KAUST) under award no. OSR-CARF URF/1/3079-33-01.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] K. Yoshikawa, H. Kawasaki, W. Yoshida, T. Irie, K. Konishi, K. Nakano, T. Uto, D. Adachi, M. Kanematsu, H. Uzu, K. Yamamoto, *Nat. Energy* **2017**, 2, 17032.
- [2] NREL, Best Research-Cell Efficiency Chart, <https://www.nrel.gov/pv/cell-efficiency.html>, accessed: February, **2019**.
- [3] D. T. Grant, K. R. Catchpole, K. J. Weber, T. P. White, *Opt. Express* **2016**, 24, A1454; S. Altazin, L. Stepanova, J. Werner, B. Niesen, C. Ballif, B. Ruhstaller, *Optics Express* **2018**, 26, A579; L. G.-E. D. Forgács, D. Pérez-Del-Rey, C. Momblona, J. Werner, B. Niesen, C. Ballif, M. Sessolo, H. J. Bolink, *Adv. Energy Mater.* **2016**, 7, 1602121; F. Sahli, J. Werner, B. A. Kamino, M. Bräuninger, R. Monnard, B. Paviet-Salomon, L. Barraud, L. Ding, J. J. Diaz Leon, D. Sacchetto, G. Cattaneo, M. Despeisse, M. Boccard, S. Nicolay, Q. Jeangros, B. Niesen, C. Ballif, *Nat. Mater.* **2018**, 17, 820.
- [4] F. Fu, T. Feurer, S. Pisoni, E. Avancini, C. Andres, S. Buecheler, *Nat. Energy* **2016**, 2, 16190.
- [5] S. De Wolf, J. Holovsky, S. J. Moon, P. Loper, B. Niesen, M. Ledinsky, F. J. Haug, J. H. Yum, C. Ballif, *J. Phys. Chem. Lett.* **2014**, 5, 1035; M. Ledinsky, T. Schönfeldová, J.

Holovsky, E. Aydin, Z. Hájková, L. Landová, N. Neykova, A. Fejfar, S. De Wolf, *J. Phys. Chem. Lett.* **2019**, *10*, 1368.

[6] T. K. a. M. Kondo, *J. Appl. Phys.* **2007**, *101*, 063705.

[7] J. Werner, G. Dubuis, A. Walter, P. Löper, S.-J. Moon, S. Nicolay, M. Morales-Masis, S. De Wolf, B. Niesen, C. Ballif, *Sol. Energy Mater. Sol. Cells* **2015**, *141*, 407; K. A. Bush, A. F. Palmstrom, Z. J. Yu, M. Boccard, R. Cheacharoen, J. P. Mailoa, D. P. McMeekin, R. L. Z. Hoye, C. D. Bailie, T. Leijtens, I. M. Peters, M. C. Minichetti, N. Rolston, R. Prasanna, S. Sofia, D. Harwood, W. Ma, F. Moghadam, H. J. Snaith, T. Buonassisi, Z. C. Holman, S. F. Bent, M. D. McGehee, *Nat. Energy* **2017**, *2*, 17009; J. Werner, C. H. Weng, A. Walter, L. Fesquet, J. P. Seif, S. De Wolf, B. Niesen, C. Ballif, *J. Phys. Chem. Lett.* **2016**, *7*, 161.

[8] M. Morales-Masis, S. D. Wolf, R. Woods-Robinson, J. W. Ager, C. Ballif, *Adv. Electron. Mater.* **2017**, *3*, 1600529; M. Chen, Z. L. Pei, X. Wang, Y. H. Yu, X. H. Liu, C. Sun, L. S. Wen, *J. Phys. D: Appl. Phys.* **2000**, *33*, 2538.

[9] T. Koida, H. Fujiwara, M. Kondo, *Jpn. J. Appl. Phys.* **2007**, *46*, L685.

[10] T. Koida, H. Fujiwara, M. Kondo, *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 851.

[11] M. Morales-Masis, S. M. D. Nicolas, J. Holovsky, S. D. Wolf, C. Ballif, *IEEE J. Photovolt.* **2015**, *5*, 1340.

[12] M. F. A. M. van Hest, M. S. Dabney, J. D. Perkins, D. S. Ginley, *Thin Solid Films* **2006**, *496*, 70; H. Ryota, A. Yoshiyuki, N. Tokio, *Appl. Phys. Express* **2008**, *1*, 015002.

[13] M. Morales-Masis, E. Rucavado, R. Monnard, L. Barraud, J. Holovský, M. Despeisse, M. Boccard, C. Ballif, *IEEE J. Photovolt.* **2018**, *8*, 1202.

[14] H. Kim, J. S. Horwitz, G. P. Kushto, S. B. Qadri, Z. H. Kafafi, D. B. Chrisey, *Appl. Phys. Lett.* **2001**, *78*, 1050.

[15] T. Koida, M. Kondo, K. Tsutsumi, A. Sakaguchi, M. Suzuki, H. Fujiwara, *J. Appl. Phys.* **2010**, *107*, 033514.

[16] N. D. Sankir, E. Aydin, H. Unver, E. Uluer, M. Parlak, *Sol. Energy* **2013**, *95*, 21.

- [17] E. Rucavado, Q. Jeangros, D. F. Urban, J. Holovský, Z. Remes, M. Duchamp, F. Landucci, R. E. Dunin-Borkowski, W. Körner, C. Elsässer, A. Hessler-Wyser, M. Morales-Masis, C. Ballif, *Phys. Rev. B* **2017**, 95, 245204; A. J. Leenheer, J. D. Perkins, M. F. A. M. van Hest, J. J. Berry, R. P. O'Hayre, D. S. Ginley, *Phys. Rev. B* **2008**, 77, 115215.
- [18] S. Husein, M. Stuckelberger, B. West, L. Ding, F. Dautou, M. Morales-Masis, M. Duchamp, Z. Holman, M. I. Bertoni, *J. Appl. Phys.* **2018**, 123, 245102; N. Preissler, O. Bierwagen, A. T. Ramu, J. S. Speck, *Phys. Rev. B* **2013**, 88, 085305.
- [19] O. Bierwagen, J. S. Speck, *Appl. Phys. Lett.* **2010**, 97, 072103.
- [20] M. Marezio, *Acta Crystallogr.* **1966**, 20, 723.
- [21] Z. Chen, L. Huang, Q. Zhang, Y. Xi, R. Li, W. Li, G. Xu, H. Cheng, *J. Phys. Chem. C* **2015**, 119, 4789.
- [22] A. Seidl, A. Görling, P. Vogl, J. A. Majewski, M. Levy, *Phys. Rev. B* **1996**, 53, 3764.
- [23] V. Scherer, C. Janowitz, A. Krapf, H. Dwelk, D. Braun, R. Manzke, *Appl. Phys. Lett.* **2012**, 100, 212108; R. L. Weiher, R. P. Ley, *J. Appl. Phys.* **1966**, 37, 299.
- [24] E. L. Runnerstrom, A. Bergerud, A. Agrawal, R. W. Johns, C. J. Dahlman, A. Singh, S. M. Selbach, D. J. Milliron, *Nano Lett.* **2016**, 16, 3390.
- [25] J. Stankiewicz, F. Villuendas, M. P. Lozano, I. Díez, *J. Appl. Phys.* **2013**, 114, 083703; J. Gan, X. Lu, J. Wu, S. Xie, T. Zhai, M. Yu, Z. Zhang, Y. Mao, S. C. I. Wang, Y. Shen, Y. Tong, *Scientific Reports* **2013**, 3, 1021.
- [26] H. Wardenga, M. Frischbier, M. Morales-Masis, A. Klein, *Mater.* **2015**, 8, 561.
- [27] D. Barreca, G. A. Battiston, R. Gerbasi, E. Tondello, P. Zanella, *Surf. Sci. Spectra* **2000**, 7, 303; L. Armelao, E. Tondello, L. Bigliani, G. Bottaro, *Surf. Sci. Spectra* **2001**, 8, 268.
- [28] O. Lang, C. Pettenkofer, J. F. Sánchez-Royo, A. Segura, A. Klein, W. Jaegermann, *J. Appl. Phys.* **1999**, 86, 5687.
- [29] A. Walsh, C. R. A. Catlow, *J. Mater. Chem.* **2010**, 20, 10438.

- [30] J. Tauc, R. Grigorovici, A. Vancu, *physica status solidi (b)* **1966**, *15*, 627; N. D. Sankir, E. Aydin, E. Ugur, M. Sankir, *J. Alloys Compd.* **2015**, *640*, 468.
- [31] J. I. Pankove, *Optical processes in semiconductors*, Courier Corporation, **1975**.
- [32] M. Balestrieri, D. Pysch, J. P. Becker, M. Hermle, W. Warta, S. W. Glunz, *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 2390; H. Fujiwara, M. Kondo, *Phys. Rev. B* **2005**, *71*, 075109.
- [33] C. Battaglia, A. Cuevas, S. De Wolf, *Energ. Environ. Sci.* **2016**, *9*, 1552.
- [34] J. Werner, L. Barraud, A. Walter, M. Bräuninger, F. Sahli, D. Sacchetto, N. Tétreault, B. Paviet-Salomon, S.-J. Moon, C. Allebé, M. Despeisse, S. Nicolay, S. D. Wolf, B. Niesen, C. Ballif, *ACS Energy Lett.* **2016**, *1*, 474; T. Duong, Y. Wu, H. Shen, J. Peng, X. Fu, D. Jacobs, E. Wang, T. C. Kho, K. C. Fong, M. Stocks, E. Franklin, A. Blakers, N. Zin, K. McIntosh, W. Li, Y. Cheng, T. P. White, K. Weber, K. Catchpole, *Adv. Energy Mater.* **2017**, *7*, 1700228; M. Jaysankar, B. A. L. Raul, J. Bastos, C. Burgess, C. Weijtens, M. Creatore, T. Aernouts, Y. Kuang, R. Gehlhaar, A. Hadipour, J. Poortmans, *ACS Energy Lett.* **2018**, *4*, 259; C. O. Ramirez Quiroz, Y. Shen, M. Salvador, K. Forberich, N. Schrenker, G. D. Spyropoulos, T. Huemueller, B. Wilkinson, T. Kirchartz, E. Spiecker, P. J. Verlinden, X. Zhang, M. Green, A. W. Y. Ho-Baillie, C. J. Brabec, *J. Mater. Chem. A* **2018**, *6*, 3583.
- [35] X. Yang, E. Aydin, H. Xu, J. Kang, M. Hedhili, W. Liu, Y. Wan, J. Peng, C. Samundsett, A. Cuevas, S. Wolf, *Adv. Energy Mater.* **2018**, *8*, 1800608; X. Yang, K. Weber, Z. Hameiri, S. De Wolf, *Prog. Photovoltaics: Research and Applications* **2017**, *25*, 896.
- [36] S. De Wolf, A. Descoeur, Z. C. Holman, C. Ballif, *Green* **2012**, *2*, 7.
- [37] E. Aydin, J. Troughton, M. De Bastiani, E. Ugur, M. Sajjad, A. Alzahrani, M. Neophytou, U. Schwingenschlögl, F. Laquai, D. Baran, S. De Wolf, *ACS Appl. Energy Mater.* **2018**.
- [38] E. Ugur, A. D. Sheikh, R. Munir, J. I. Khan, D. Barrit, A. Amassian, F. Laquai, *ACS Energy Lett.* **2017**, *2*, 1960.

- [39] X. Yang, Q. Bi, H. Ali, K. Davis, W. V. Schoenfeld, K. Weber, *Adv. Mater.* **2016**, 28, 5891.
- [40] J. Peng, J. I. Khan, W. Liu, E. Ugur, T. Duong, Y. Wu, H. Shen, K. Wang, H. Dang, E. Aydin, X. Yang, Y. Wan, K. J. Weber, K. R. Catchpole, F. Laquai, S. Wolf, T. P. White, *Adv. Energy Mater.* **2018**, 0, 1801208; M. De Bastiani, E. Aydin, T. Allen, D. Walter, A. Fell, J. Peng, N. Gasparini, J. Troughton, D. Baran, K. Weber, T. P. White, S. De Wolf, *Adv. Electron. Mater.* **2018**, 0, 1800500.

Improved near-infrared response of the perovskite/silicon tandem solar cells has been achieved by replacing conventional ITO electrodes with developed IZRO (Zr-doped In_2O_3) electrodes. Engineering the optoelectronic properties of the IZRO electrodes resulted in $18 \, \Omega/\square$ sheet resistivity with improved transparency. Overall, the power conversion efficiency of the mechanically stacked perovskite/silicon tandem solar cells have been improved from 23.3 to 26.2%.

Supporting Information

Zr-doped Indium Oxide (IZRO) Transparent Electrodes for Perovskite–Based Tandem Solar Cells

Erkan Aydin¹, Michele De Bastiani¹, Xinbo Yang¹, Muhammad Sajjad¹, Faisal Aljamaan¹, Yury Smirnov³, Mohamed Nejib Hedhili², Wenzhu Liu¹, Thomas G. Allen¹, Lujia, Xu¹, Emmanuel Van Kerschaver¹, Monica Morales-Masis³, Udo Schwingenschlögl¹, and Stefaan De Wolf^{*1}

¹King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Physical Sciences and Engineering Division (PSE), Thuwal 23955-6900, Kingdom of Saudi Arabia

²King Abdullah University of Science and Technology (KAUST), KAUST Core Lab, Thuwal 23955-6900, Kingdom of Saudi Arabia

³University of Twente, MESA+ Institute for Nanotechnology, Enschede 7500 AE, The Netherlands

Table S1. Influence of process parameters on electronic parameters of as-deposited and annealed IZRO films. All measurements were performed on Lake Shore Hall-effect system at room temperature and dark conditions.

Parameters		R_s (As Dep.) ($\Omega/\square$)	R_s (Ann.) ($\Omega/\square$)	μ_{Hall} (As Dep.) (cm^2/Vs)	μ_{Hall} (Ann.) (cm^2/Vs)	N_e (As Dep.) ($cm^{-3} \times 10^{20}$)	N_e (Ann.) ($cm^{-3} \times 10^{20}$)
Process pressure (mTorr)	0.3	80.7	28.5	14.8	44.6	5.64	4.19
	0.5	78.9	29.0	16.7	45.1	4.84	3.97
	0.75	63.0	19.1	17.4	67.0	5.55	5.00
	1	41.0	18.0	25.7	76.9	6.18	3.18
	1.25	72.9	17.6	13.3	62.8	6.28	5.52
	1.5	75.9	21.9	14.5	54.0	6.47	4.56
Oxygen partial pressure r(O ₂) (%)	0.06	47.7	25.03	21.9	56.1	6.51	3.82
	0.09	42.7	22.9	26.6	61.7	5.73	2.96
	0.12	41.0	18.0	25.7	76.9	6.18	3.18
	0.17	43.4	29.4	28.3	57.8	5.40	3.09
	0.33	39.2	22.2	31.0	56.0	5.18	3.82
Film thickness (nm)	50	100.2	114.9	21.8	23.0	6.10	1.96
	75	63.7	42.2	24.4	25.7	5.50	2.92
	100	41.0	18.0	25.7	76.9	6.18	3.18
	150	33.8	12.8	23.0	57.7	5.52	4.09
	200	24.73	10.0	23.4	67.4	5.40	4.39
Annealing temperature (°C)	75	41.0	36.5	25.7	26.2	5.98	1.09
	100	41.0	33.3	25.7	28.6	5.98	6.18
	200	41.0	18.0	25.7	76.9	5.98	3.18
	300	41.0	43.2	25.7	63.6	5.98	5.98
	400	41.0	1181.4	25.7	30.0	5.98	1.09

Figure S1. UV-vis-NIR transmittance and absorptance spectra of the IZRO films depending on the process pressure for a) before and b) after annealing, $r(\text{O}_2)$ for c) before and d) after annealing, the thickness of the film e) before and f) after annealing, influence of the post-annealing temperature.

Figure S2. Influence of the post-annealing temperature UV-vis-NIR transmittance and absorbance spectra of the g) for 100nm-thick and h) 75nm-thick IZRO films.

Figure S3. XRD spectra of the as-deposited and annealed samples at different temperatures. Annealing processes have been performed in ambient air.

Table S2. The comparison of the 2θ peak position for sputtered IZRO films and PDF data card no: 01-071-2194.

(hkl)	2θ peak positions from PDF: 01-071-2194 (for In_2O_3)	2θ peak positions from Sputtered IZRO
(211)	21.5	21.6
(222)	30.5	30.5
(400)	35.4	35.5
(411)	37.7	37.8
(431)	45.7	45.7
(521)	49.3	49.4
(440)	51.0	51.1
(611)	56.0	56.0
(622)	60.6	60.7
(631)	62.1	62.2

Table S3. Comparison of electronic parameters of intrinsic and Zr-doped In_2O_3 films.

Samples	Temperature (°C)	R_s ($\Omega/\square$)	μ (cm^2/Vs)	N_e (cm^{-3})
In_2O_3	As Deposited	40.1	26.0	5.98×10^{20}
	Annealed	38.9	71.3	1.09×10^{20}
IZRO	As Deposited	41.0	25.7	6.18×10^{20}
	Annealed	18.0	76.9	3.18×10^{20}

Figure S4. SEM surface topography of the intrinsic and Zr-doped In_2O_3 films. The first row is showing the as-deposited films while the second one is showing the annealed samples. **Figure S5.** The comparison of the XRD spectra of the intrinsic and Zr-doped In_2O_3 films. Annealing processes have been performed in ambient air at 200 °C.

Figure S6. Area-based EDX spectra of the a) as deposited and b) annealed films. The average of the four different areas resulted in 60, 38.6 and 1.4% for as-deposited and 61.7, 37.6 and 1.6% for oxygen, indium, and zirconium atomic percentages for as-deposited and annealed films, respectively. c) EDX spectra of the white spots on the as-deposited films. The average of the two different spots resulted in 59.8, 38.9 and 1.4% for O, In, and Zr atomic percentages, respectively. This reveals that the observed white spots have an almost similar atomic ratio with respect to the rest of the films.

Figure S7. UV-vis-NIR transmittance and absorbance spectra of the a) as deposited and b) annealed of intrinsic and Zr-doped In_2O_3 films.

Figure S8. UPS spectra of the a) intrinsic and b) Zr-doped In_2O_3 films before and after the annealing process.

Figure S9. XPS spectra of the a) In 3d and b) O 1s states of the intrinsic and Zr-doped films before and after the annealing process.

Figure S10. Partial densities of states of a) non-doped and b) Zr-doped In_2O_3 .

Figure S11. Band structure of non-doped (left) and Zr-doped (right) In_2O_3 .

Figure S12. Average electrostatic potential of the (100)-In₂O₃ slab. E_v and E_F are the vacuum and Fermi energies, respectively.

Figure S13. Refractive index (n) and extinction coefficient (k) of the different thickness of IZRO films as a function of wavelength a) before and b) after the annealing process (at 200 °C). c) Influence of the post-annealing temperatures.

Figure S14. a) The comparison of the used device test structures with different silicon bottom cells. b) Regarding $J-V$ and c) EQE graphs for both device architectures. SHJ based devices delivers 39.5 mA/cm² current while TiO₂ passivated c-Si cell gives 40.3 mA/cm² (with 672 mV Voc, 82.2% FF and 22.1% PCE). Due to the front metal grid coverage, the measured J_{sc} values from $J-V$ measurements was around 37.2 mA/cm² which is slightly lower than EQE measurements. d) $\Delta_{\text{EQE}} = \text{EQE}_{\text{IZRO}} - \text{EQE}_{\text{ITO}}$ spectra for the filtered (quartz substrate based) SHJ and TiO₂ passivated c-Si cells which is clearly showing the advantage of using SHJ bottom cells for the better light harvesting in the NIR region of the solar spectra.