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All-Oxide $\text{MoO}_x/\text{SnO}_x$ Charge Recombination Interconnects for Inverted Organic Tandem Solar Cells

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Multijunction solar cells are designed to improve the overlap with the solar spectrum and to minimize losses due to thermalization. Aside from the optimum choice of photoactive materials for the respective sub-cells, a proper interconnect is essential. This study demonstrates a novel all-oxide interconnect based on the interface of the high-work-function (WF) metal oxide MoO_x and low-WF tin oxide (SnO_x). In contrast to typical p-/n-type tunnel junctions, both the oxides are n-type semiconductors with a WF of 5.2 and 4.2 eV, respectively. It is demonstrated that the electronic line-up at the interface of MoO_x and SnO_x comprises a large intrinsic interface dipole (≈ 0.8 eV), which is key to afford ideal alignment of the conduction band of MoO_x and SnO_x , without the requirement of an additional metal or organic dipole layer. The presented $\text{MoO}_x/\text{SnO}_x$ interconnect allows for the ideal (loss-free) addition of the open circuit voltages of the two sub-cells.

There is a variety of recent reports on single junction organic solar cells (OSCs) with a power conversion efficiency (PCE) exceeding 10%.^[1–4] The highest efficiencies in single junction cells have been achieved in the so-called inverted device layout, where electrons are collected via the bottom (substrate) electrode while holes are extracted via the top contact.^[5–7]

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Multijunction OSCs, e.g., tandem or triple cells, where two or three sub-cells with different photoactive layers are stacked and connected in series bear the potential to unlock efficiency levels beyond 15%.^[8,9] As of today, multijunction OSCs have been shown to reach a PCE of 13.8%.^[10]

Aside from the optimum choice of photoactive materials for the respective sub-cells along with a sophisticated optical design of the stacked device structure, a proper interconnect between the sub-cells is essential. In an inverted tandem solar cell, the holes extracted from the bottom sub-cell must recombine with the electrons stemming from the upper sub-cell, ideally without any loss of voltage and fill factor (FF). Thus, tandem cells involve an electronic interface between a hole extraction layer (HEL) and an electron extraction layer (EEL). Typical HEL materials are poly(3,4-ethylenedioxythiophene) polystyrene (PEDOT:PSS) or high-work-function (WF) transition metal oxides (TMOs),^[11] like MoO_x ^[12] or VO_x .^[13] As EEL, materials like titanium oxide (TiO_x)^[14] and zinc oxide (ZnO)^[15,16] have been established. More recently, Trost et al. reported SnO_x as an advantageous EEL for OSCs.^[17,18] As an alternative, conjugated polyelectrolytes (CPEs) have been considered as EELs.^[19,20]

Aside from its electronic functionality, the interconnect must be optically transparent, and in the case of solution processed photoactive materials, the interconnect must concomitantly provide chemical protection for the bottom cell against dissolution due to the solvents involved in the deposition of the upper sub-cell. This set of requirements severely limits the freedom in the design of the interconnect and the choice of materials. The state of the art of interconnects for multijunction OSCs has been reviewed by several authors.^[21–23] A plethora of interconnects is based on PEDOT:PSS as HEL and TiO_x or ZnO as EEL.^[24,25] However, PEDOT:PSS has been evidenced to be an origin of reliability issues in organic electronic devices^[12,26,27] and it suffers from a limited optical transmittance, which becomes a significant issue if more than one interconnect is required, e.g., in a triple junction cell.^[28] Due to a lack of promising alternatives, most multijunction OSCs still rely on the use of PEDOT:PSS in their interconnects.^[29,30]

The pH-neutralized variant (n-PEDOT:PSS) is sometimes used to avoid etching of the adjacent ZnO layer.^[31] For n-PEDOT:PSS a substantially lowered work function, about

0.5 eV lower than that of conventional PEDOT:PSS, has been reported, which disqualified the material to properly interface to photoactive materials with deep highest occupied molecular orbital (HOMO) levels.^[32]

Substantial work has been devoted to replace PEDOT:PSS by a high-work-function TMO, e.g., MoO_x , in next generation interconnect architectures. Interestingly, the one-by-one exchange of PEDOT:PSS by MoO_x to form a MoO_x /EEL interconnect did not result in satisfactory cell characteristics, and thus a thin metal layer (thickness: $\approx 0.5\text{--}10\text{ nm}$) had to be thermally evaporated in-between, e.g., $\text{MoO}_x/(\text{Al,Au})/\text{ZnO}$,^[33,34] $\text{MoO}_x/\text{Al}/\text{TiO}_x$,^[35] or $\text{MoO}_x/\text{Ag}/\text{CPE}$.^[36,37] The addition of the metal mitigates the formation of a detrimental counter diode, helps to form an ohmic contact,^[33] and increases the number of “recombination centers” in the recombination contact.^[38,39] In any case, the metal layer critically affects the optical properties of the interconnect and severely compromises its transmittance. Moreover, it is challenging to deposit thin metal films with sub-nm control and large-area homogeneity.

Shim et al. reported a metal-free, oxide-based interconnect $\text{MoO}_x/\text{Al}:\text{ZnO}/\text{polyethylenimine ethoxylated}$ (PEIE).^[40] The $\text{Al}:\text{ZnO}$ has been prepared by atomic layer deposition (ALD) as a so-called nanolaminate of Al_2O_3 and ZnO . The PEIE polyelectrolyte was important to properly interface to the fullerene acceptor of the upper sub-cell. The interconnect afforded tandem cells with a PCE of 6.5%, which however did not significantly exceed that of the single junction devices (PCE = 6.4%). Lu et al. have reported an interconnect consisting of MoO_x (“dipole layer”/ TiO_x).^[41] Here, the “dipole layer” was formed by a conjugated polymer with highly polar amino-*N*-oxide functionalized side groups.^[42] Without the insertion of the polar moiety, only extremely poor characteristics of the tandem cells were achieved.

In this communication, we demonstrate a novel all-oxide recombination interconnect, which is based on the interface of the high-WF metal oxide MoO_x and low-WF tin oxide (SnO_x). Remarkably, both oxides are *n*-type semiconductors with a WF of 5.2 and 4.2 eV, respectively. The electronic line-up at the interface of MoO_x and SnO_x comprises a large intrinsic interface dipole ($\approx 0.8\text{ eV}$), which affords near to ideal alignment of the conduction band of MoO_x and SnO_x , without the

requirement of an additional metal or organic dipole layer. As a result, electrons extracted via the SnO_x from the upper sub-cell are efficiently handed over from the SnO_x to the MoO_x . The actual recombination of electrons with holes takes place at the interface of organic/ MoO_x at the lower sub-cell. The mechanism of charge recombination in our tandem cells is in inverse analogy to that evidenced previously in multijunction organic light emitting diodes (OLEDs), where the individual light emitting units are connected by so-called charge generation layers which comprised high-WF TMOs.^[43] Moreover, the working principle in our interconnects contrasts the established picture used in the case of highly doped organic *p*/*n*-type tunnel junctions, which have been frequently used in tandem cells.^[39] There, charge recombination occurs in the center of the interconnect as electrons tunnel from the lowest unoccupied molecular orbital (LUMO) of the *n*-doped electron transport layer to the HOMO of the *p*-doped hole transport layer.

The presented $\text{MoO}_x/\text{SnO}_x$ interconnect allows for the ideal addition of the open circuit voltages (V_{oc}) of the two sub-cells. In stark contrast to the vast majority of TiO_x or ZnO based tandem interconnects, which require activation by UV light (“UV light-soaking”),^[44,45] our interconnect functions even in the absence of UV spectral components. We reason that this novel all-oxide interconnect will be generally applicable for the design of monolithically integrated organic multijunction solar cells.

The layer sequence of the inverted tandem OSCs in this study is shown in **Figure 1a**. The bottom sub-cell is based on poly[*N*-9'-heptadecanyl-2,7-carbazole-alt-5,5'-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT):[6,6]-phenyl-C71-butyric acid methyl ester (PC_{70}BM) as photoactive material, while the upper sub-cell comprises poly[(2,5-bis(2-hexyldecyl)-2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-*c*]pyrrole-1,4-diyl)-alt-([2,2':5',2''-terthiophene]-5,5''-diyl)] (PDPP3T):[6,6]-phenyl-C61-butyric acid methyl ester (PC_{60}BM).^[46] The molecular structure of the donor polymers and the respective absorption spectra of the photoactive layers are shown in **Figure 1b,c**. We decided to use well-established photoactive materials^[28] to test and to demonstrate the functionality of our novel all-oxide interconnect. We are aware that these photoactive materials may impose limits for the achievable overall efficiency of the tandem device, but we

Figure 1. a) Layer sequence of the inverted tandem OSCs with $\text{MoO}_x/\text{SnO}_x$ interconnect. b) Molecular structure of the absorber polymers poly[*N*-9'-heptadecanyl-2,7-carbazole-alt-5,5'-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) and poly[(2,5-bis(2-hexyldecyl)-2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-*c*]pyrrole-1,4-diyl)-alt-([2,2':5',2''-terthiophene]-5,5''-diyl)] (PDPP3T) used for the bottom and top sub-cells, respectively. c) Absorption spectra of both photoactive materials as used in the sub-cells of the tandem device.

want to note that the presented interconnect will be applicable to future photoactive systems which may allow for elevated efficiencies. As EEL we use SnO_x , which is grown by atomic layer deposition at temperatures as low as 80 °C (see the Experimental Section for details of the preparation). In single junction OSCs, we have shown that SnO_x forms a universal EEL with a low-work-function, which does not rely on activation with UV light.^[17] Moreover, we have demonstrated that by the use of SnO_x we can avoid the occurrence of photoinduced degradation of the FF and V_{oc} , which is commonly encountered in ZnO based devices upon prolonged exposure to solar radiation.^[18] Recently, SnO_x has also been considered as EEL for solar cells based on hybrid perovskites with improved efficiency and long-term stability.^[47–50]

Initially, we have prepared single junction reference devices with a thickness of the photoactive layers identical to that of the sub-cells in the tandem devices. The optimum thickness of the active layers for current matching has been determined by an optical simulation taking into account the absorption characteristics of the photoactive layers in the tandem cell and the external quantum efficiency (EQE) of the single junction devices (Figure S1, Supporting Information). The optical simulation indicated an optimum thickness of the active PCDTBT:PC₇₀BM layer in the bottom sub-cell of about 130 nm and a concomitant thickness of >135 nm for the upper PDPP3T:PC₆₀BM active layer. Unfortunately, our batch of PCDTBT did not allow us to prepare devices with a layer thickness substantially in excess of 90 nm without severe losses in FF (Figure S2, Supporting Information). Moreover, the J_{sc} did not increase significantly for a thickness higher than 90 nm. The reasons may be due to the molecular weight of the PCDTBT which did not allow for an optimum BHJ morphology. As such, we decided to use 90 nm for the PCDTBT:PC₇₀BM sub-cell. For current matching, the thickness of the active PDPP3T:PC₆₀BM layer in the upper cell was consequently chosen ≈80 nm (Figure S1d, Supporting Information).

The respective characteristics of the single junctions are shown in Figure S3 (Supporting Information) and Table 1. The resulting tandem cells based on the monolithic series connection of these single junctions by a $\text{MoO}_x/\text{SnO}_x$ interconnect have been characterized according to a protocol detailed elsewhere.^[51] Briefly, the EQE of the sub-cells in the tandem devices has been determined by using an appropriate choice of electrical and optical bias. For example, for the characterization of the PCDTBT:PC₇₀BM sub-cell, the PDPP3T:PC₆₀BM has been optically biased at 730 nm. Conversely, the PCDTBT:PC₇₀BM sub-cell has been biased at 530 nm. The resulting EQE spectra are shown in Figure 2a. The J – V characteristics of the sub-cells have been obtained from the single junctions by tuning the illumination to afford the J_{sc} calculated from the respective EQE spectrum (Figure 2b). From these data, the J – V characteristics of the tandem cell have been constructed. In addition the J – V characteristics of the tandem cell measured with appropriate corrections for spectral mismatch are shown. Importantly, in the tandem cells an ideal addition of the V_{oc} of the sub-cells is achieved, demonstrating the functionality of the $\text{MoO}_x/\text{SnO}_x$ interconnect. We find a device efficiency of up to 8.0% (7.6%, average over 11 devices) for the tandem cell, which is substantially higher than 5.4% and 4.2% for the PCDTBT:PC₇₀BM and the PDPP3T:PC₆₀BM sub-cells, respectively.

Table 1. Characteristics of the single junction and tandem devices. The cell characteristics of the bottom and top sub-cells in the tandem stack were obtained by illuminating the single junction devices with adapted intensity to match the J_{sc} determined from the EQE analysis of the tandem cell. Characteristics of the tandem cells were measured and constructed from the J – V curves of the sub-cells. Statistical data of 11 cells are also stated. The error margins denote the standard deviation found in the set of devices.

	V_{oc} [V]	J_{sc} [mA cm ^{−2}]	FF [%]	PCE [%]
Single junction devices				
PCDTBT:PC ₇₀ BM (nom. 90 nm)	0.849	10.3	62	5.4
PDPP3T:PC ₆₀ BM (nom. 80 nm)	0.627	10.7	63	4.2
Tandem device				
Bottom sub-cell	0.847	9.1	62	4.8
Top sub-cell	0.627	8.6	63	3.4
Tandem constructed	1.473	8.9	62	8.1
Tandem measured	1.468	9.1	60	8.0
Average of 11 devices	1.475 ± 0.012	8.4 ± 0.5	61 ± 2	7.6 ± 0.3

We note that the J – V characteristics of the tandem cells are in excellent agreement with those constructed from J – V data of the sub-cells, which evidences the loss-free connection of both sub-cells by the $\text{MoO}_x/\text{SnO}_x$ interconnect (Figure 2b).

To analyze the working mechanism of the $\text{MoO}_x/\text{SnO}_x$ interconnect in more detail, we have performed photoelectron spectroscopy (PES) as well as Kelvin probe (KP) analysis to assess the energy level line-up in the interconnect. To this end, we started with a 30 nm thick thermally evaporated MoO_x layer. Thereafter, we step-wise deposited SnO_x layers with a thickness of 0.5–50 nm on top. The X-ray photoelectron spectroscopy (XPS) spectra for Mo3d and Sn3d are shown in Figure S4 of the Supporting Information. No explicit band bending has been found in the MoO_x upon deposition of SnO_x on top. The resulting WF has been derived both from the secondary cut-off of the photoemission spectra (Figure S5a, Supporting Information) and the measured contact potential difference of our calibrated Kelvin probe, respectively. We repeated this experiment for several sets of samples (Figure 3a). In both PES and KP, a strong initial lowering of the WF is observed upon deposition of SnO_x on top of the MoO_x . We start with a WF = 5.1–5.3 eV for MoO_x , which is in agreement with previous reports on thermally evaporated MoO_x layers, which have seen a vacuum break.^[52] Note that our MoO_x has also been thermally evaporated, but we had to expose it to the glove-box atmosphere of our ALD system before deposition of the SnO_x .

According to KP data, we find an overall WF drop of $\Delta\text{WF} = 1.07$ eV after deposition of 30 nm of SnO_x , lowering the WF from 5.25 eV for MoO_x to a saturated value of 4.18 eV for SnO_x (Figure 3a). Taking the XPS core level measurements into account, we can further derive a contribution of $\phi_{\infty} = 0.28$ eV in this WF drop (from the binding energy shift of the Sn3d peak) that can be attributed to band bending (Figure 3b). The large remaining part of the WF drop $\Delta = \Delta\text{WF} - \phi_{\infty} = 0.79$ eV, which occurs for <5 nm of SnO_x , can be associated with an interface dipole.

Figure 2. a) EQE spectra of the PCDTBT:PC₇₀BM (bottom) and PDPP3T:PC₆₀BM (top) sub-cells determined under appropriate biasing conditions (see the Experimental Section for details). b) *J*–*V* characteristics of the sub-cells as obtained from the single junction devices upon tuned illumination to achieve the *J*_{sc}, determined from the respective EQE spectra, as well as constructed and measured *J*–*V* characteristics of the tandem cell.

To understand the possible origin of the large interface dipole, it is important to note that earlier work has shown a substantial lowering of the initially high-work-function of MoO_x if the Mo⁶⁺ species at the surface are reduced to Mo⁵⁺

or Mo⁴⁺.^[53,54] Indeed, we also found an indication of reduced Mo⁶⁺ in the Mo3d XPS spectra, as a shoulder at lower binding energies of the main Mo⁶⁺ peak evolved upon deposition of SnO_x (Figure S6a, Supporting Information). Therefore, we can

Figure 3. a) Variation of the work function upon deposition of SnO_x on top of MoO_x determined by photoelectron spectroscopy (PES, solid symbols) and KP (open symbols) for several sets of samples. b) Binding energy shift derived from XPS core level data of the Sn3d signal. The red dotted line is inserted as a guide to the eye. c) The energy level line-up at the MoO_x/SnO_x interface, resulting from UPS/XPS and KP analysis (the line-up including core levels is shown in Figure S8, Supporting Information). The position of the conduction band minimum (CB) with respect to the valence band maximum has been determined from the respective optical band gap (see Figure S9, Supporting Information). Note that the gap states in MoO_x have been omitted for simplicity. Possible band bending due to adsorbed water molecules at the surface of SnO_x is also not shown.^[18] d) A schematic of the working mechanism of the interconnect in a tandem cell is shown in (d). For simplicity, only the energy levels of the acceptor of the top PDPP3T:PC₆₀BM cell and the donor of the bottom PCDTBT:PC₇₀BM cell are shown. The recombination of electrons and holes occurs at the interface of MoO_x/PCDTBT (marked in green). Note that the energy levels are not to scale in this schematic.

attribute the interface dipole to the partial reduction of Mo^{6+} . We want to note that the sudden drop of the WF upon deposition of SnO_x on top of the MoO_x is not limited to the combination of $\text{MoO}_x/\text{SnO}_x$. In fact, we could show that the WF of MoO_x likewise dropped by 0.7–1.1 eV upon deposition of a few nanometers of other metal oxides by ALD, e.g., ZnO , Al_2O_3 , etc. (see Table S1, Supporting Information). As such, the nucleation of the ALD precursors on top of the MoO_x layer gives rise to a reduction of the Mo^{6+} .

The WF of our SnO_x layers is remarkably low compared to the WF of 5.7 eV reported for single crystalline SnO_2 .^[53] We have previously shown that the lower WF of our ALD SnO_x results from Sn^{2+} surface species and adsorbed water molecules, which infer downward band-bending at the SnO_x surface.^[17,56] The observed binding energy shift in the $\text{Sn}3d$ peak corresponds to the variation of surface potential $\phi(d)$ with increasing the thickness d of the SnO_x (Figure 3b, red dotted line inserted as an eye guide). As can be seen in our discussion in Figure S7 of the Supporting Information, the progression of the surface potential $\phi(d)$ cannot be described by simple textbook semiconductor physics in the framework of the Schottky model over the total thickness range in this study. If we take defect induced gap states into account we can use a simplified distributed states model (DSM) that has been introduced by Mankel et al.,^[57] which provides a significantly better approximation of our experimental data. With the DSM, we cannot directly derive the carrier density in the SnO_x layer. With a rough estimate, at least within the first 10 nm based on the Schottky model, we estimate a carrier density of $>10^{19} \text{ cm}^{-3}$, which is orders of magnitude higher than the carrier density we derive from the position of the Fermi level for thick SnO_x layers (see below). This discrepancy can possibly be explained by taking into account the ALD specific nucleation phase in the first cycles of the ALD process, which may infer a higher number of defect states, that would give rise to a higher carrier density in the first few nanometers of layer growth. Unfortunately, the overall low electrical conductivity did not allow us to unambiguously determine the actual carrier density of the SnO_x layers by Hall techniques.

The PES and KP data allow us to construct an energy level line up of the $\text{MoO}_x/\text{SnO}_x$ interface as shown in Figure 3c. Note that the WF and the band-bending is based on the results of the KP data. Using the WF from PES, instead, does not fundamentally change the line-up. It has to be noted that the position of the conduction band minimum (CB) has been obtained by adding the bandgap energy (E_g) of the respective material to the position of the valence band maximum that has been determined by UPS (Figure S5b, Supporting Information).

As shown in Figure 3c, both MoO_x and SnO_x are n-type semiconductors, and the large interface dipole $\Delta = 0.79 \text{ eV}$ between the two materials allows for a favorable alignment of the CB with only a minor energy offset on the order of 200 meV. It has to be noted that this energy offset in the CB is subject to the uncertainties in the determination of the energetic position of the CB in the respective material. We have found an E_g of 3.9 eV and 2.9 eV for SnO_x and MoO_x , from the respective Tauc-plots of their optical absorption spectra (Figure S9, Supporting Information). In the literature a bandgap for thermally evaporated MoO_x has been reported in the range of 2.8–3.2 eV.^[11] For SnO_x

grown by ALD at low temperature, ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) data provided a band gap of 3.72 eV.^[48] Taking the latter value as the band-gap in our line-up (Figure 3c) would even result in a CB offset between MoO_x and SnO_x close to zero.

From the distance of the Fermi level and the CB edge ($E_{\text{CB}} - E_{\text{F}}$), we can derive a complementary estimate of the carrier density in our SnO_x . The effective electron mass of SnO_2 is $m^* = 0.4 \times m_0$.^[58] With $(E_{\text{CB}} - E_{\text{F}}) = 0.12\text{--}0.3 \text{ eV}$ (depending on the technique to determine E_{CB}), the estimated carrier density varies between $4 \times 10^{13} \text{ cm}^{-3}$ and $5 \times 10^{16} \text{ cm}^{-3}$, which indicates a relatively low doping level of our SnO_x bulk layer. These values stand in contrast to the high carrier densities we derived from the band bending data for the first nanometers of SnO_x that we attributed to nucleation effects in the ALD growth at the $\text{MoO}_x/\text{SnO}_x$ interface, as outlined above.

The WF on both sides of the interconnect appears excellently suited to interface with the donor (PCDTBT) of the lower sub-cell and the acceptor (PC_{60}BM) of the upper sub-cell. Consequently, a schematic can be constructed which visualizes the working mechanism of the interconnect in the tandem cells (Figure 3d). Electrons which are extracted from the upper sub-cell via the $\text{SnO}_x/\text{PC}_{60}\text{BM}$ interface are efficiently transported in the CB of the SnO_x to the CB of the MoO_x where they further propagate to the PCDTBT/ MoO_x interface. There, they meet and recombine with the holes which are extracted from the PCDTBT. It has to be noted that even though MoO_x is used for hole extraction in organic solar cells, it is an n-type material with a high-WF and an extremely deep lying CB (high electron affinity). The electronic line up at the interface organic/ MoO_x has been determined for a range of organic compounds (e.g., 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP), tris(4-carbazolyl-9-ylphenyl)amine, and N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine).^[11] Typically, the energetic position of the CB minimum of the MoO_x is located close to the HOMO level of the adjacent organic material due to the formation of a large interface dipole. In addition, electron transfer from the organic material to the MoO_x has been evidenced, which resulted in an upward bending of the HOMO in the organic layer—in other words, interfacial p-type doping of the organic layer.^[11] A similar finding has been reported for the interface of other high-WF TMOs adjacent to organic semiconductors, e.g., WO_3/CuPc ,^[59] $\text{WO}_3/\text{spiro-MeOTAD}$,^[60] or $\text{V}_2\text{O}_5/\text{CBP}$.^[61]

We want to note that an interconnect based on a single layer of MoO_x (i.e., without the SnO_x) would not afford the same functionality. It has been shown that the electronic line-up at the interface of $\text{MoO}_x/\text{fullerene}$ comprises a large energy offset between the LUMO of the fullerene and the CB of the MoO_x even in cases where the MoO_x surface had been exposed to air prior to the deposition of the fullerene.^[62] As such, in the absence of SnO_x the energetic mismatch of MoO_x and fullerene would lead to substantial losses of V_{oc} for the tandem cell.

As stated initially, SnO_x has shown notable advantages compared to ZnO or TiO_x based EELs in single junction organic solar cells. Among them the absence of light-soaking problems, in contrast to ZnO or TiO_x EELs, which need to be “activated” by UV light with photon energies larger than the band-gap of the metal oxide ($h\nu > E_g$).^[31,35,63–67] In this regard, the use of SnO_x is favorable in cases where UV light activation is undesired or

Figure 4. a) Layer sequence of the inverted tandem OSCs with MoO_x/ZnO or $\text{MoO}_x/\text{SnO}_x$ recombination layers. J - V characteristics of the corresponding devices under AM1.5 illumination b) with and c) without UV blocking filter ($\lambda > 435$ nm).

not even possible. In multijunction cells, the availability of UV photons to activate metal oxides in the recombination layers will be limited even without the dedicated use of UV-filters. There, the UV spectral range may be partially absorbed in the bottom sub-cell. To study this effect in our tandem cells, we fabricated tandem devices based on $\text{MoO}_3/\text{SnO}_x$ or MoO_3/ZnO interconnects (Figure 4a). As shown in Figure 4b,c, tandem cells with either $\text{MoO}_3/\text{SnO}_x$ or MoO_3/ZnO interconnects show similar characteristics when illuminated under full AM1.5 illumination, but both behave crucially different in absence of UV-light. Impressively, the use of SnO_x in the interconnect allows for well-behaved solar cell characteristics with high FF and PCE even under illumination with AM1.5, where the UV components have been blocked by a filter ($\lambda > 435$ nm), whereas the device comprising ZnO shows a strongly s-shaped J - V curve under the same conditions. Note that the drop of the WF of MoO_x inferred by the deposition of SnO_x or ZnO is comparable for both oxides (Table S1, Supporting Information). In earlier studies, the necessity of UV activation in case of ZnO EELs has been associated with the electronic alignment at the EEL/fullerene interface.^[25] Similar issues have been encountered for ZnO -based interconnects before.^[44]

In summary, all-oxide $\text{MoO}_x/\text{SnO}_x$ recombination interconnects for organic multijunction solar cells have been demonstrated. The electronic line-up at the interface of MoO_x and SnO_x has been studied in detail by photoelectron spectroscopy and Kelvin probe analysis. A large intrinsic interface dipole (≈ 0.8 eV) has been found to infer near to ideal alignment of the conduction band of MoO_x and SnO_x . This favorable line-up is essential for the working principle of the interconnect: Electrons extracted via the SnO_x from the upper sub-cell are efficiently handed over to the CB of MoO_x , while the actual recombination of electrons with holes takes place at the interface of organic/ MoO_x of the lower sub-cell. The presented $\text{MoO}_x/\text{SnO}_x$ interconnect allows for the ideal addition of the open circuit voltages (V_{oc}) of the two sub-cells. The resulting tandem devices significantly surpass the efficiency of the individual sub-cells. In stark contrast to similar devices based on MoO_x/ZnO which need to be activated by UV exposure, the $\text{MoO}_x/\text{SnO}_x$ based tandem cells function without any limitation even

in the absence of UV light. We assume that our concept of all-oxide $\text{MoO}_x/\text{SnO}_x$ interconnects is generally applicable to other organic/hybrid photoactive material systems.

Experimental Section

Materials Synthesis and Device Preparation: Tin oxide was prepared by atomic layer deposition in a Beneq TFS 200 system (base pressure 1.5 mbar). As precursors, tetrakis(dimethylamino)tin(IV) (TDMASn), kept at 45 °C and water, kept at room temperature, were used. At a substrate temperature of 80 °C the growth rate was 1.056 Å per cycle. The zinc oxide layers were deposited at the same conditions (substrate temperature: 80 °C, base pressure: 1.5 mbar) using diethylzinc and water as precursors (both kept at room temperature).

The inverted single junction OSCs are based on the following layer sequence: glass/indium-tin-oxide (ITO)/ SnO_x /photoactive layer/ MoO_x /Ag with an active area of 0.03 cm². As photoactive material for the wide band gap cell, PCDTBT (supplied by 1-Material) and fullerene (PC_{70}BM (SES Research)) with a weight ratio of 1:4 were used. The polymer was dissolved in chlorobenzene and stirred in N_2 atmosphere at 80 °C for 2.5 h followed by adding the fullerene (stirring for 1.5 h). The solution was filtered (5 µm PTFE Filter) and spin coated in N_2 atmosphere. On the anode side, MoO_x (10 nm) and Ag (100 nm) layers were thermally evaporated in high-vacuum (10^{-6} mbar).

For the low-bandgap cell, PDPP3T and fullerene (PC_{60}BM from American Dye Source) (weight ratio of 1:2) were dissolved in a mixture of chloroform and o-dichlorobenzene (6 vol% o-DCB) with an overall concentration of 15 mg mL⁻¹. After stirring at 90 °C for 1 h the still warm solution was spin coated in N_2 atmosphere.

Materials Characterization: Optical parameters of the tin oxide and molybdenum oxide layers were obtained by spectral ellipsometry (M-2000V from J.A. Woollam) for thin film samples deposited on top of a Si wafer with native oxide (Figure S10, Supporting Information). For determining transmission and reflection spectra a Deuterium Halogen lamp (DH-2000-BAL, OceanOptics) and a spectrometer with a range from 186 to 1041 nm (USB 2000+XR1-ES) were used. For transmission measurements, 200 nm thick SnO_x and 100 nm thick MoO_x layers were deposited on quartz substrates.

The measurements of the surface potential were done with a McAllister KP6500 Kelvin-Probe (KP) system in vacuum (10^{-6} mbar). Highly ordered pyrolytic graphite with a WF of 4.5 eV was used as reference.^[68,69]

The photoelectron spectra were measured without exposing the prepared samples to ambient environment. After preparation the

samples were stored in a glove-box and were transferred to the vacuum chamber in a dedicated vacuum shuttle. The XPS measurements were carried out using an ESCALAB 250 system from ThermoFisher. Monochromatic X-rays (1486.6 eV photoenergy) from an Al-K α source were used. A magnetic lens was used to have a maximum collection of photoelectrons from the sample. Data were collected with pass energy of 10 eV in normal emission. The binding energy was calibrated with the Cu3d, Ag3d, and Au Fermi edge.

The UPS measurements were performed using He-I α ($h\nu = 21.22$ eV) radiation. The experiments were carried out with a bias potential of 4 eV. The valence band maxima and the work function were determined from the linear extrapolation of valence band edge and secondary electron edge.

Device Characterization: The solar cells were characterized in ambient air without encapsulation using a Keithley 2400-C source meter and a solar simulator (300 W Newport, AM1.5G, 100 mW cm $^{-2}$).

The external quantum efficiency was determined using a calibrated tunable light source consisting of a 50 W tungsten halogen lamp (Osram 64610) and a monochromator (Oriel, Cornerstone 130) in combination with a lock-in amplifier (Stanford Research Systems SR 830). For the determination of the EQE of the tandem-cells a protocol was followed as recently reported.^[51] The sub-cells were therefore characterized under accurate bias light and voltage conditions. These measurements were performed using an in-house built system, where the bias light was provided by monochromatic power LEDs (Thorlabs M530L3, M730L4).

The J - V characteristics of the tandem cell were thereafter recorded upon illumination with a light source which was adjusted to compensate spectral mismatch for both active layers. Therefore, the power of the light source was changed such that the deviations between J_{sc} measured under the light source and the J_{sc} determined by EQE were equal for each reference single junction device.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

atomic layer deposition, charge recombination layers, inverted organic solar cells, organic tandem solar cells, tin oxide

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