

Tuning the Surface Electron Accumulation Layer of In₂O₃ by Adsorption of Molecular Electron Donors and Acceptors

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In₂O₃, an n-type semiconducting transparent transition metal oxide, possesses a surface electron accumulation layer (SEAL) resulting from downward surface band bending due to the presence of ubiquitous oxygen vacancies. Upon annealing In₂O₃ in ultrahigh vacuum or in the presence of oxygen, the SEAL can be enhanced or depleted, as governed by the resulting density of oxygen vacancies at the surface. In this work, an alternative route to tune the SEAL by adsorption of strong molecular electron donors (specifically here ruthenium pentamethylcyclopentadienyl mesitylene dimer, [RuCp*mes]2) and acceptors (here 2,2'-(1,3,4,5,7,8-hexafluoro-2,6-naphthalene-diylidene)bis-propanedinitrile, F₆TCNNQ) is demonstrated. Starting from an electron-depleted In₂O₃ surface after annealing in oxygen, the deposition of [RuCp*mes]2 restores the accumulation layer as a result of electron transfer from the donor molecules to In₂O₃, as evidenced by the observation of (partially) filled conduction sub-bands near the Fermi level via angle-resolved photoemission spectroscopy, indicating the formation of a 2D electron gas due to the SEAL. In contrast, when F₆TCNNQ is deposited on a surface annealed without oxygen, the electron accumulation layer vanishes and an upward band bending is generated at the In2O3 surface due to electron depletion by the acceptor molecules. Hence, further opportunities to expand the application of In₂O₃ in electronic devices are revealed.

1. Introduction

Indium oxide (In_2O_3) , one of the most relevant conducting materials for commercial use, simultaneously exhibits superior electrical conductivity and high optical transparency in the visible range.^[1-3] In₂O₃ doped with Sn, that is, indium tin oxide (ITO), is widely employed as a transparent electrode in (opto)electronic devices,^[4] including organic light emitting diodes,^[3,5] solar cells,^[6,7] field effect transistors,^[8] and other devices.^[3,9–11] Unintentionally doped In₂O₃ shows an inherent n-type conductivity, as a surface electron accumulation layer (SEAL) is commonly formed within only a few nanometers at the top surface.^[12] This is similar to other transparent oxides, for example, ZnO,^[13] Ga_2O_3 ,^[14] and SnO₂,^[15] for which the partially filled conduction band can be directly detected by ultraviolet photoemission spectroscopy (UPS).^[16] The formation of the SEAL is usually attributed to surface oxygen vacancies,^[16,17] leading to a downward band bending at the surface.^[18]

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For emerging applications of In₂O₃, a tunable SEAL is highly desirable in order to form an Ohmic or a Schottky contact^[19,20] with a variety of other materials, depending on the interface electronic features desired for devices such as transistors,^[21,22] sensors,^[23] or perovskite solar cells.^[24] For example, by doping with Sn,^[25] the SEAL can be promoted, while it can be inhibited by doping with Mg or Ni.^[26] An alternative way to vary the SEAL is by performing oxygen-based surface treatments. For instance, when exposing to ultraviolet illumination^[27] or by annealing in an oxygen-free environment,^[12,28] adsorbed oxygen desorbs from the surface and more electronically active oxygen vacancies/In-adatoms^[29] are formed, which leads to an enhancement of the SEAL. In contrast, when conducting oxygen plasma treatment^[27,30] or annealing in oxygen,^[12,31] the SEAL can be fully depleted, which is then accompanied by an upward surface band bending. These changes happen between electron-accepting oxygen adsorbates^[11,19,28] and electron-donating O-vacancies^[12] or In-adatoms^[25] on the surface. Furthermore, Gong et al. have reported that the SEAL of In_2O_3 can also be depleted, with the change from downward to upward surface band bending, when a 4 nm p-type NiO layer is deposited on top.^[32] Clearly, the SEALs can be tuned by charge transfer upon contacting with a layer of electron donating/ accepting materials, as an alternative route to impurity doping and annealing methods. However, to effectively pursue this route, it is necessary to extend the range of available materials for modifying SEALs in a controlled manner. Notably, organic (or metal-organic) molecular electron acceptors and donors constitute a variety of materials that could be relevant in this context. It has been shown that (metal-)organic molecules can be employed to modify the surface electronic properties of inorganic semiconductors such as Si,^[33] ITO,^[34,35] and ZnO.^[36] However, it remains to be elucidated whether such molecules are able to tune SEAL of In_2O_3 .^[37,38]

In this contribution, we investigate the potential of using (metal-)organic molecules with strong electron donor and acceptor character to tune the SEAL of In2O3. An unintentionally doped In₂O₃ (111) film, grown by plasma-assisted molecular beam epitaxy (PAMBE) on Al₂O₃ (0001),^[27] is employed, and the molecular donor ruthenium pentamethylcyclopentadienyl mesitylene dimer, [RuCp*mes]2,[36] and the acceptor 2,2'-(1,3,4,5,7,8-hexafluoro-2,6-naphthalene-diylidene)bispropanedinitrile, F₆TCNNQ,^[33] are selected to test the above hypothesis. Two different surface treatments of In2O3 were performed before molecule deposition, that is, annealing in ultrahigh vacuum (Avac) and annealing in low-pressure oxygen (A_{O2}) in a vacuum chamber, promoting or depleting the SEAL, respectively. X-ray photoemission spectroscopy (XPS) and angle-resolved photoemission spectroscopy (ARPES) were used to monitor the electronic structure evolution of In2O3 upon adsorption of the molecules. Starting with a depleted SEAL after annealing in oxygen (referred to as $In_2O_3-A_{O2}$), the initially absent SEAL was promoted again upon deposition of the [RuCp*mes]2 donor by electron donation, as evidenced by the detection of the partially filled conduction band using ARPES. In contrast, F₆TCNNQ deposition on In₂O₃ featuring an initial SEAL as achieved by annealing in vacuum without oxygen (referred to as In2O3-Avac) gradually depleted the SEAL by electron extraction and induced an upward band bending

at the In_2O_3 surface. In addition, two further experiments ([RuCp*mes]₂ on In_2O_3 -A_{vac} and F₆TCNNQ on In_2O_3 -A_{O2}) revealed that the SEAL can be further altered by electron donation/extraction after these corresponding surface treatments.

2. Results and Discussion

2.1. Electronic Structure of Bare In_2O_3 Annealed without O_2 and in O_2

Figure 1a-d demonstrates the changes of the electronic structure of In2O3 thin films after annealing without O2 in ultrahigh vacuum and subsequent annealing with O2 in high vacuum conditions. For the In₂O₃-A_{vac} surface, the work function (ϕ) is found at 4.12 eV and the valence band maximum (VBM) is at 3.05 eV binding energy (BE). A small feature close to Fermi edge (E_F) (Figure 1d) appears as a result of the partial filling of the conduction band. This is direct evidence for the presence of the SEAL due to surface oxygen vacancies or In-adatoms.^[12,29] It has also been reported that annealing without O₂ in ultrahigh vacuum at high temperature effectively removes carbon-based surface contaminations and other acceptor-like adsorbates,^[39] which promotes the detection of the SEAL. In comparison, after annealing in O_2 (In₂O₃-A_{O2}), the work function increases to 5.01 eV and the VBM shifts by about 0.37 eV to lower BE. Notably, the peak near E_F vanishes, implying the emptying of the previously partially filled conduction band. Concomitantly, a 0.25 eV shift in the O 1s peak to lower BE is observed (Figure 1e). Figure 1f shows the surface energy level diagram based on the UPS and XPS results. A value of 2.76 eV is chosen for the electronic band gap according to literature.^[40,41] The energy difference between E_F and the conduction band minimum (CBM) in the bulk is calculated to be 0.06 eV for a bulk electron density of 2×10^{17} cm⁻³.^[26] Thus. the presence of a SEAL at the surface leads to a downward band bending by ${\approx}0.35$ eV, and at the surface E_F is located ≈0.30 eV above the CBM. After annealing in O₂, due to the re-filling of the oxygen vacancies, the SEAL disappears and the shift of the VBM suggests a slight upward surface band bending of 20 meV occurs. Besides that, comparing the work function change ($\Delta \phi = 0.89$ eV) with the change in surface valence band positions after A_{Q2} (using the shift of the VBM, $\Delta VBM = 0.37 \text{ eV}$) shows that a large upward surface dipole Δ = 0.52 eV arises. We note that the shift of the VBM and O 1s core level of In₂O₃ annealed in O₂ relative to those of a sample annealed in vacuum is smaller than the 0.70 eV achieved by oxygen plasma treatment,^[39] suggesting that oxygen plasma treatment is more efficient in filling the oxygen vacancies than annealing in O₂, consistent with observations that oxygen plasma is more prone to react leading to deeper penetration of oxygen atoms into the surface region.[30]

Furthermore, as shown in Figure 1e, when comparing changes of energy levels between $\rm In_2O_3\text{-}A_{O2}$ and $\rm In_2O_3\text{-}A_{vac}$ treatments, we find that the energy shift of the O 1s core level (ΔO 1s = 0.25 eV) is smaller than the change in valence bands (ΔVBM = 0.37 eV); a similar phenomenon has also been observed in another $\rm In_2O_3$ study, but it was not further explained.^[28] As the SEAL is confined to the surface (<8 nm)^[12]





Figure 1. Characterization of an In_2O_3 surface annealed in UHV without O_2 (In_2O_3 - A_{vac} , black curve) and in O_2 (In_2O_3 - A_{O2} , red curve). a) Secondary electron cutoffs (SECO), b) survey UPS spectra, and c,d) UPS spectra of the near- E_F region on log- and linear-intensity scale, respectively. e) XPS O 1s core levels. f) UPS-determined energy level diagrams of In_2O_3 - A_{vac} and In_2O_3 - A_{O2} . The unit for all values is eV. g) Chemical structures of the donor and acceptor molecules, [RuCp*mes]₂ and F_6TCNNQ , respectively.

and UPS is more surface sensitive than XPS (electron mean free path ≈0.6 nm for UPS and ≈2.6 nm for XPS with the photon energies used here),^[42,43] our observation can be rationalized following two possible arguments. i) Photoelectrons from the O 1s core level and VB states experience different effective screening due to the charge density variation along the surfacenormal direction. When the SEAL is enhanced, larger energy shifts are expected for the electrons coming from the immediate surface region (i.e., VB electrons) with stronger screening than those coming also from deeper within the sample (i.e., core level electrons); the effective screening will be similar for both types of photoelectrons when the SEAL is depopulated. Alternatively, ii) the different information depth of UPS and XPS can account for the different BE shifts in UPS and XPS, as different near-surface regions (and thus different band bending magnitude along the surface-normal) are probed. Given that electronic screening is rather efficient in In₂O₃ overall, it is more likely that scenario (ii) gives rise to the difference in BE shifts between the core levels and VB states in our experiments.

The observed evolution of the electronic structure of In_2O_3 upon annealing treatments in (ultra)high vacuum without or with O_2 , even though showing slight variations, are consistent with previous reports,^[12,27,39] which allows us to further test the ability to tune the SEAL via the adsorption of the molecular donors and acceptors.

2.2. Electronic Properties of the Electron Donor [RuCp*mes]₂/In₂O₃ Interfaces

As shown above, after annealing in UHV without O₂ (In₂O₃-A_{vac}), the SEAL is well developed in conjunction with downward surface band bending. Incremental deposition of [RuCp*mes]2 only slightly increases the O 1s BE (Δ O 1s \approx 0.05 eV) and the VBM position (Δ VBM \approx 0.08 eV), as seen in Figure 2a. In contrast, the work function dramatically decreases by about 1.31 eV with only 2 Å of nominal molecular coverage and further by 1.88 eV for the 64 Å thick [RuCp*mes]₂ layer (secondary electron cutoff-SECO spectra shown in Figure S1, Supporting Information). This indicates that upon deposition of [RuCp*mes]₂, electrons are transferred from the donor molecule (presumably resulting in formation of monomeric RuCp*mes⁺ cations, as in other solution and surface redox reactions of this species)^[36,44] to the conduction band of In₂O₃, leading to a small increase of the downward surface band bending and the formation of a large dipole across the In2O3/[RuCp*mes]2 interface

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Figure 2. Angle-integrated UPS spectra of the valence band region near E_F and the evolution of ϕ , VBM, and O 1s for a) [RuCp*mes]₂ deposition on In_2O_3 -A_{vac}, b) [RuCp*mes]₂ deposition on In_2O_3 -A_{vac}, b) [RuCp*mes]₂ deposition on In_2O_3 -A_{o2}, c) F₆TCNNQ deposition on In_2O_3 -A_{vac}, and d) F₆TCNNQ deposition on In_2O_3 -A_{o2}. For each system, the energy shift of the ϕ , VBM, and O 1s are reported.

that accounts for the decrease of ϕ . We also note that the [RuCp*mes]₂ adsorption gradually suppresses the signal from the partially filled conduction band near E_F , despite the fact that more electrons populate the conduction band. This can be readily explained by considering the In₂O₃ signal attenuation by the adsorbed organic layer, given the small inelastic mean free path in UPS experiments. Furthermore, the slightly larger ΔVBM as compared to ΔO 1s can be again rationalized by considering that UPS is more surface sensitive compared to XPS.

For In_2O_3 -A_{O2}, the SEAL is depleted and no partially filled conduction band can be detected (Figure 2b). Upon deposition of 2 Å [RuCp*mes]₂, a peak near E_F clearly emerges and a large change in ϕ of -1.64 eV is observed. The spectral weight of the peak at E_F increases further for 4 and 8 Å molecular coverage, but decreases for subsequent depositions. The observation of this density of states evidences for the re-filling of the conduction band upon electron transfer from [RuCp*mes]₂ to In_2O_3 - A_{O2} , resulting in a downward surface band bending with E_F located above the CBM, similar to the case of bare In_2O_3 -Avac. However, the amount of surface band bending and CBMderived intensity upon molecular surface-doping of In2O3-AO2 are smaller than those of In_2O_3 -A_{vac}. This could be explained by the fact that the density of oxygen-vacancies in the surface region of In2O3-Avac may be larger than the density of [RuCp*mes]₂ in the monolayer; that is, the coverage at which most of the charge transfer process with In2O3-AO2 is expected

to take place. This is confirmed by monitoring the ϕ evolution, which exhibits a steep decrease by 2.23 eV up to 4 Å coverage (\approx 1 monolayer), which represents about 80% of the total work function change. Furthermore, the electron transfer saturates at 8 Å [RuCp*mes]₂ coverage as ϕ does not change notably beyond that coverage (see Figure S2, Supporting Information, for SECO spectra). The VBM and O 1s core level shift to higher BE by 0.37 and 0.18 eV, respectively, consistent with the formation of the SEAL.

2.3. Electronic Properties of the Electron Acceptor F₆TCNNQ/In₂O₃ Interfaces

Having demonstrated the possibility to promote the SEAL for In_2O_3 - A_{O2} using a donor molecule, we now investigate the reverse process, which is to deplete the SEAL of In_2O_3 - A_{vac} using an acceptor molecule. F_6TCNNQ with its deep-lying lowest unoccupied molecular orbital (LUMO) level exhibits an electron affinity of about 5.60 eV, which renders this molecule one of the strongest electron accepting molecules.^[45] When 2 Å F_6TCNNQ are deposited on In_2O_3 - A_{vac} (Figure 2c), the intensity of the filled conduction band reduces strongly, in much larger proportion than what would be expected solely from simple substrate signal attenuation by a molecular overlayer (cf. discussion above). This indicates that significant

electron transfer from the SEAL to F6TCNNQ occurs. For F_6TCNNQ layers of thicknesses beyond 8 Å, the signal from the partially filled conduction band can no longer be observed, implying an efficient depletion of the SEAL. When the coverage reaches 16 Å, further electron transfer from the fully depleted SEAL is therefore not further possible as confirmed from the saturation of the ϕ increase, which amounts to 2.07 eV. Depleting the SEAL with F₆TCNNQ further results in reversing the surface band bending of In₂O₃-A_{vac} from downward to slightly upward, as seen from ΔVBM and ΔO 1s in Figure 2c, in line with previous observations at other F₆TC-NNQ-inorganic semiconductor interfaces, such as GaN,^[46] ZnO,^[13] and Si.^[33] Finally, for a 64 Å F₆TCNNQ thick film, ϕ increased by ≈2.11 eV (Figure S3, Supporting Information), and both VBM and O 1s of In2O3-Avac shift to lower BE by ≈0.52 and 0.31 eV, respectively. All these observations are in line with a depletion of the SEAL.

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For comparison, the electronic properties of the F₆TCNNQ/ In₂O₃-A_{O2} interface were also investigated with the corresponding data shown in Figure 2d. Here, the SEAL is depleted to start with and the UPS spectrum shows no filled conduction band. Upon F₆TCNNQ deposition, electrons are still transferred from In₂O₃-A_{O2} to the LUMO of F₆TCNNQ, and a broad peak with an onset at 0.5 eV BE emerges, which we attribute to the singly occupied LUMO-derived level of the F₆TCNNQ anion.^[47] After deposition of 64 Å F₆TCNNQ, $\Delta\phi$, Δ VBM, and Δ O 1s of 0.82, 0.16, and 0.11 eV are determined, respectively (Figure S4, Supporting Information). This corresponds to an upward band bending (0.18 eV) at the In₂O₃ surface and an additional interface dipole of 0.66 eV between In₂O₃ and the partially negatively charged F₆TCNNQ layer.

2.4. Electronic States near E_F (Partially Filled Conduction Band)

To obtain more insight on the influence of molecular donor/ acceptor adsorption on the SEAL, ARPES measurements were performed on bare In_2O_3 with several molecular coverages (1, 2, and 4 Å) of $[RuCp*mes]_2$ and F_6TCNNQ , as shown in Figure 3. As In_2O_3 has a direct band gap at the Γ point of its Brillouin zone,^[2,12] close to normal emission ARPES spectra were taken. The angle integrated (over +/-14° emission angle) UPS spectrum exhibits a Fermi edge for the bare In2O3-Avac substrate, with two additional features peaking at ≈0.30 and 0.08 eV BE, as can be seen in Figure 3a,c, while the dispersive behavior of these two features is shown in Figure 3b,d. These second derivative images were obtained by using the procedure proposed by Zhang et al.,^[48] and a rational background subtraction was implemented to the raw ARPES data to account for Debye-Waller effects and inelastic scattering^[49,50] before the second derivative operation (Figure S5, Supporting Information). The presence of the Fermi edge in the angle-integrated spectra stems from scattering (e.g., by phonons, electron-electron interaction, or charged defects) of photoelectrons from the top dispersing bands.^[51] We also note that the Fermi edge is absent in the In₂O₃-A_{O2} angle-integrated UPS spectrum, for which no SEAL is present.

The two peaks at 0.30 and 0.08 eV BE in Figure 3a,c correspond to the two sub-bands in Figure 3b,d, which arise from

the quantized states of the confined 2D electron gas (2DEG) due to the SEAL of the bare In_2O_3 - A_{vac} surface.^[12,28] Previous work proposed the upper sub-band to retain substantial 3D character while the lower one was proposed to be purely 2D.^[12] In the following, we will mostly focus on the lower sub-band as its dispersion is better resolved.

Figure 3a depicts the angle-integrated ARPES of the bare In₂O₃-A_{vac} and after subsequent [RuCp*mes]₂ deposition. The overall intensity of the partially filled conduction band does not show any clear enhancement upon 1 and 2 Å [RuCp*mes], deposition as compared to that of the bare In₂O₃-A_{vac}, even though electron transfer from the metal-organic donor to In2O3 occurred. The intensity of the two SEAL-derived peaks near E_F gradually but slightly decreases for the subsequent depositions partly due to the high surface sensitivity of UPS and partly because the molecular overlayer generates incoherent scattering of the substrate photoelectrons.^[52,53] The second-derivative image of the ARPES spectra displayed in Figure 3b shows that the dispersing bands become increasingly diffusive with increasing layer thickness, while the intensity of the related Fermi edge remains approximately constant. Similarly, this can be explained by the presence of the adsorbate layer, which leads to incoherent scattering of the substrate photoelectrons when escaping the sample surface. Therefore, scattering induces the loss of dispersion and the resulting second derivative image at 4 Å [RuCp*mes]₂ (Figure 3b) mostly exhibits a Fermi edge with blurred dispersion for the deeper band. However, the band minimum of the partially filled conduction band slightly shifts to higher BE from bare In₂O₃-A_{vac} to 2 Å [RuCp*mes]₂ film, as shown by the fitted parabolic curves for the lower sub-band. For 2D systems and assuming parabolic dispersion, the density of states is constant and given by the relation ρ (*E*) = $m^*/\pi\hbar^2$ where m^* is the charge-carrier effective mass and the charge-carrier density n_{2D} within a partially occupied conduction band can be calculated by the relation $n_{2D} = \int_{E_c}^{\infty} \rho(E) F(E) dE = \int_{E_c}^{E_F} \rho(E) dE$

where $E_{\rm C}$ is the energy of the CBM and $F(\rm E)$ the Fermi–Dirac distribution. A parabolic fit of the lower sub-band dispersion yields an electron effective mass of $(0.21 \pm 0.03) m_0$, in excellent agreement with previous ARPES measurements.^[12] The $n_{\rm 2D}$ determined for the lower sub-band amounts to $3.0 \times 10^{13} \rm \, cm^{-2}$ for the bare oxide and $3.6 \times 10^{13} \rm \, cm^{-2}$ with the 2 Å [RuCp*mes]₂ layer, evidencing an enhanced electron filling of the In₂O₃-A_{vac} CBM by [RuCp*mes]₂.

In contrast, when depositing the acceptor F_6TCNNQ on In_2O_3 - A_{vac} (Figure 3c), the overall intensity of the partially filled conduction band rapidly decreases, losing about 75% of its intensity when the layer thickness reaches 4 Å. This unambiguously indicates the efficient depletion of the SEAL. The measured band dispersion (Figure 3d) also becomes blurred from 2 Å on and cannot be distinguished for the 4 Å film, both as a result of the SEAL depletion and photoelectron scattering. The n_{2D} within the lower sub-band decreases from 3.3×10^{13} cm⁻² for the as-prepared bare indium oxide to 2.6×10^{13} cm⁻² for the 2 Å F₆TCNNQ layer. Thus, this further proves that an ultra-thin F₆TCNNQ layer can effectively extract electrons from the In_2O_3 - A_{vac} SEAL.

Finally, for the deposition of $[RuCp \star mes]_2$ on $In_2O_3 \hbox{-} A_{O2}$ (depleted SEAL) the intensity from the SEAL is initially



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Figure 3. Angle-integrated and corresponding (second derivative) ARPES spectra near E_F region around normal emission for a,b) [RuCp*mes]₂ deposition on In_2O_3 - A_{vac} , c,d) F_6TCNNQ deposition on In_2O_3 - A_{vac} , and e,f) [RuCp*mes]₂ deposition on In_2O_3 - A_{o2} . The second derivative images are fitted by parabolic curves (blue lines).

negligible but gradually increases from 1 to 4 Å coverage, before it starts to decrease with further [RuCp*mes]₂ deposition because of the surface sensitivity of UPS. The second derivative images give a direct picture of the evolution of the features around E_F: starting from bare In₂O₃-A_{O2} featuring no bands around E_F, predominantly the lower sub-band emerges with 1 Å [RuCp*mes]₂ coverage ($n_{2D} = 1.7 \times 10^{13} \text{ cm}^{-2}$). Only from 2 Å on, the upper sub-band can also be well observed. The charge density n_{2D} of the lower sub-band for 2 and 4 Å donor layers amount to 2.4×10^{13} and $2.8\times10^{13}~\text{cm}^{-2},$ respectively, close to the values determined for In₂O₃-A_{vac}. Thus, the SEAL can successfully be restored and a downward band bending reappears as a result of electron transfer from the [RuCp*mes]₂ to the In₂O₃-A_{O2}, but it only gradually reaches the same level as for the bare In_2O_3 -A_{vac} substrate, suggesting a way to very finely control the surface electronic properties of the indium oxide.

Based on the photoemission results, the energy level diagrams determined for $[RuCp*mes]_2$ and F_6TCNNQ deposited on $In_2O_3\text{-}A_{vac}$ and on $In_2O_3\text{-}A_{O2}$ are summarized schematically in Figure 4. Since photoemission is more surface sensitive than XPS, we use ΔVBM to evaluate the surface band bending in In_2O_3 . For In_2O_3 annealed without oxygen ($In_2O_3\text{-}A_{vac}$), a downward band bending and a SEAL are present at the

sample surface, as depicted in Figure 4a. Upon [RuCp*mes]₂ deposition, a large work-function decrease occurs, but the band bending on the In2O3 top surface only increases slightly by about 0.08 eV, which means that a large interface dipole (pointing upward from In₂O₃ to [RuCp*mes]₂) coexists with the band bending.^[13,54] For In₂O₃-A_{O2}, the SEAL is depleted as evidenced by the absence of a filled conduction band. After [RuCp*mes]₂ deposition, the conduction band of In₂O₃-A_{O2} becomes filled due to electron transfer from the molecules and an interface dipole also forms at this interface. The shift of the Fermi level above the CBM due to the CBM filling results in a downward band bending (Figure 4b) whose magnitude is a little smaller than that observed for the bare In₂O₃-A_{vac} surface, and the SEAL is restored. As shown in Figure 4c, due to electron transfer to the molecules, the deposition of F6TCNNQ on In₂O₃-A_{vac} fully depletes the SEAL and changes the initial downward band bending to an upward band bending, in addition to formation of a large interface dipole pointing downward (from F_6TCNNQ to In_2O_3) forms. This interface, therefore, appears as the reverse case with respect to the [RuCp*mes]2/In2O3- A_{02} interface. For the deposition of F_6TCNNQ on $In_2O_3-A_{02}$ (Figure 4d), the initial 0.02 eV upward band bending further increased to 0.18 eV along with the formation of a downward interface dipole of 1.18 eV.

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Figure 4. Schematic energy level diagrams for a) $[RuCp*mes]_2$ deposited on In_2O_3 - A_{vac} , b) $[RuCp*mes]_2$ deposited on In_2O_3 - A_{O_2} , c) F_6TCNNQ deposited on In_2O_3 - A_{vac} , and d) F_6TCNNQ deposited on In_2O_3 - A_{O_2} . In order to give a better illustration, values are not to scale. The values for the initial bare In_2O_3 surfaces are shown in grey. Units are eV for all values.

3. Conclusions

We demonstrated that annealing without or with the presence of O₂ in an overall vacuum environment can reversibly enhance or deplete the SEAL of In2O3 thin films. Next, we revealed the ability of organic donor/acceptor molecules to fine-tune the In₂O₃ SEAL occupation over a wide extent, and the electron acceptor F₆TCNNQ can even fully deplete the In₂O₃ SEAL. The electron donor [RuCp*mes]₂ can readily restore it for the SEAL depletion surface. Remarkably, we also show that by carefully controlling the [RuCp*mes]₂ deposition, it is possible to preferentially fill the lower SEAL sub-band, which has a more pronounced surface character. Finally, we established a precise picture of the surface energy level re-alignment of In₂O₃ upon adsorption of the molecular dopants, including the evolution of surface band bending, and the formation of large interface dipoles. The latter phenomenon could help to tune the energy levels of, for example, organic semiconductor layers eventually deposited on top of the molecularly modified surface. This proof-of-principle for employing an ultra-thin layer of organic acceptors/donors to control the electronic properties of In₂O₃ surfaces and its 2DEG offers huge potential for use in future opto-electronic devices.

4. Experimental Section

Substrate and Surface Treatment: Textured, 500 nm thick, unintentionally doped In_2O_3 films were grown on (0001) oriented Al_2O_3 substrates by PAMBE under oxygen-rich conditions. The measured sheet resistivity and electron mobility for the $7 \times 7 \text{ mm}^2 In_2O_3$ films were 7 kΩ sq⁻¹ and 91 cm² V⁻¹ s⁻¹, respectively, with a bulk electron density of around 2×10^{17} cm⁻³. Ar-ion sputtering (bias voltage 500 V) in an ultra-high vacuum (UHV) chamber was used to clean the bare surface and remove the surface adsorbates. The annealing treatments were performed in the UHV chamber with 2×10^{-8} mbar base pressure. A pyrolytic boron nitride heater on the manipulator was used to anneal

the sample and the temperature was measured by thermocouple positioned near the sample. Two samples were used in the presented experiments and all annealing/cooling parameters of the samples were kept constant: the current for the resistive heating was applied gradually so that the expected temperature (600 °C) was typically reached in 30 min, and then the sample was kept at this temperature for 1 h. Sample cooling back to room temperature was done by sharply switching off the current supply and let the sample naturally cool down. Annealing in oxygen (A_{O2}) was performed at 600 °C for 1 h by introducing an oxygen partial pressure of 5×10^{-5} mbar in the same UHV system. This partial pressure was kept constant until the substrate temperature decreased to 80 °C. After reaching the room temperature, the sample was transferred to the analysis chamber for measurement.

Materials: The donor molecule $[RuCp\star mes]_2$ (synthesized as described in ref. $[55])^{[56,55]}$ and the acceptor molecule $F_6TCNNQ^{[57]}$ (purchased from Novaled) were evaporated from resistively heated quartz crucibles onto the In_2O_3 films at rates of 1 and 2 Å min^{-1}, respectively, which were monitored by quartz crystal microbalance.

Photoemission Spectroscopy Characterization: The characterization of the pristine substrates (annealing without O_2 or annealing in O_2) and F_6TCNNQ deposited on $In_2O_3\text{-}A_{O2}$ was performed by using UPS and XPS with a hemispherical electron analyzer (PHOIBOS-100, SPECS) using a non-monochromated AlK α (1486.6 eV) radiation of a dual anode X-ray source (SPECS XR 50) and a monochromated HeI α (21.22 eV) discharge lamp (Scienta Omicron HIS13 combined with a VUV5K monochromator). In order to probe the band dispersion of the partially filled conduction band, high resolution ARPES measurements (binding energy range: 1.0 to -1.0 eV) for the other three experiments ([RuCp*mes]₂ on In_2O_3 -A_{O2} and In_2O_3 -A_{vac} as well as F₆TCNNQ on In₂O₃-A_{vac}) were conducted at the ENERGIZE endstation at Bessy II with a hemispherical electron analyzer (DA30-L, Scienta Omicron) using an acceptance angle of $+/-14^{\circ}$ and a non-monochromated helium discharge lamp (Scienta Omicron HIS13). Angle-integrated UPS measurements (binding energy range: 10.0 to -1.0 eV) were also conducted at the same setup. A -10 V bias voltage was applied during the measurement of the SECO. All measurements were performed at room temperature. The Au $4f_{7/2}$ peak position (84.0 eV) and the Fermi edge (E_F) of a clean Au foil were used to calibrate the binding energy (BE) scale and all the UPS and XPS spectra were referred to the E_F at zero BE. The obtained angle-integrated data were analyzed using Origin and ARPES data were evaluated using Igor Pro (WaveMetrics).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

2D electron gas, charge transfer, In₂O₃, photoemission spectroscopy

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