Evolution of Optical, Electrical, and Structural Properties of Indium Tungsten Oxide upon High Temperature Annealing

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Optical, structural and electrical properties of thermally co-evaporated indium tungsten oxide (IWO₂) thin films with varied stoichiometry, from pure tungsten oxide to pure indium oxide (InO₂) are investigated upon stepwise annealing, up to 700 °C. The thin films are candidate materials for carrier selective contacts in different types of solar cells, such as silicon hetero junction and perovskite solar cells. Three different phases for the thin films with different stoichiometry and crystallization temperatures of $T_c > 500$ °C for tungsten-rich layers and $T_c \approx 200$ °C for indium-rich layers are found. The pronounced optical absorption of the as-deposited InOₓ-rich layers is strongly decreased after crystallization. Tungsten oxide rich layers show low optical absorption in the as-deposited state as well as for all applied annealing temperatures. The lateral conductivity of the pure indium oxide can be increased from $1.24 \times 10^{-2}$ up to 0.83 S cm⁻¹ after 700 °C annealing. The conductivity of the pure tungsten oxide increases slightly after crystallization from $2.55 \times 10^{-5}$ to $8.25 \times 10^{-5}$ S cm⁻¹ after annealing at 700 °C. However, for mixed oxide layers with $\approx 25\%$ InOₓ-fraction in the mixture, the highest conductivity of $4.0 \times 10^{-6}$ S cm⁻¹ cannot be increased by the applied annealing process.

1. Introduction

Metal oxide thin films find multiple applications in modern solid-state electronic devices. Among the most prominent ones are transparent conductive layers in optoelectronic devices, such as flat panel devices, catalysts for water splitting, and charge carrier extracting layers in different solar cell technologies, for example, in silicon heterojunction,[1,2] lead halide perovskite,[3] chalcopyrite,[4] and organic molecule-based[5] solar cells. In particular for new types of tandem solar cells[6] as carrier selective contact, they can be a key technology toward high efficiency and high stability.[7] Novel contact stacks, in which thin layers of different transition metal oxides are applied as carrier selective contacts,[8] have become a broad field of interest. Especially, high work function materials, such as MoO₃,[1,9,10] VOₓ,[11] and WOₓ,[1,12,13] have the potential to improve carrier selectivity and, therefore, both the device’s open circuit voltage and the fill factor.[14]

Tungsten(VI) oxide (WO₃) is a well-known material, used as electrochromic layer in shading windows[15] and as anode in water splitting devices.[16] Its high work function of up to 6.5 eV,[17] good thermal stability,[17] and wide bandgap[16] also led to applications as front side hole extracting layer in different solar cell technologies. The drawback of stoichiometric tungsten(VI) oxide as contact layer is the comparably low conductivity.[12,18] Other metal oxides, e.g., indium(III) oxide (In₂O₃), are known for their high conductivity, which can be even increased by doping with various elements, such as hydrogen,[19] zinc,[19] molybdenum,[20] and tungsten.[21] Different to the well-known dopant tin, these dopants increase the conductivity by increasing not only the charge carrier concentration, but also the charge carrier mobility.[13] On the other hand, indium oxide possesses a rather low work function of about 4.7 eV[21]

Because of these contrary characteristics, an obvious idea is to combine both materials, to reach an optimum of the high work function of tungsten oxide while keeping the high conductivity of the indium oxide. Here, the aim is to alloy both metal oxides to form either a more conductive amorphous mixture or a mix of segregated phases that possesses a higher conductivity than the pure tungsten oxide. Note that there have also been studies of tungsten-doped indium oxide[21-23] (In₂O₃:W) as transparent conductive oxide (TCO)—thus, In₂O₃ with the addition of a few percent of tungsten, but with a different purpose: The indium oxide was doped to increase the conductivity. The work function is not significantly increased for small amounts of tungsten doping.[23] Here, we aim at keeping the high work function of the tungsten oxide, to obtain a material, that is suitable as recombination contact for common solar cell absorbers, such as silicon. In previous studies, we already showed how the indium tungsten oxide (IWOₓ) work function and band bending at the interface toward crystalline silicon can be manipulated by
changing the material composition. In that study, we found a strong Fermi-level pinning at the IWO/(n)c-Si interface with a pinning factor of \( S = 0.1 \). On the other hand, a high band bending of up to 600 meV toward (n)c-Si was observed for pure tungsten oxide, which should provide sufficient selectivity if applied as a hole extracting layer in silicon heterojunction solar cells. Although layer thicknesses of typical carrier selective contacts are only about a few nanometers, the low conductivity of pure tungsten oxide leads to significant increase in series resistance losses and, hence, needs to be increased. Thus, the idea of this study is to increase the conductivity by increasing the indium oxide fraction of IWO. Furthermore, we investigate how optical properties and the electrical conductivity, measured post-annealed at room temperature, change after high temperature treatments by annealing the thin films at the temperatures of up to 800 °C.

2. Results and Discussion

The study of the material properties will be presented in four different sections. We first discuss the chemical composition to find the exact stoichiometry of the co-evaporated samples. Afterward, we analyze the crystallization temperature as well as the crystal structure of the thin films, which leads to a deeper understanding of the film compositions. At the end, we evaluate the optical and electrical properties of the IWO films and their potential application as material for carrier selective contacts.

2.1. Chemical Composition

First, we determine the layer stoichiometries by means of X-ray photoelectron spectroscopy (XPS) using the core levels In 3d\(_{3/2}\) and W 4f. The measured data, after subtraction of a Shirley background and normalized with the sum of the In 3d and W 4f core-level peak area, are shown in Figure 1. The data shown here are not yet weighted with the sensitivity factors. We observe that the binding energies of the same core level deviate up to 10.7 eV between the different samples. The core-level spectra might be shifted due to different reasons: 1) The Fermi-level position relative to the band edges; 2) the sample surface gets charged; or 3) the chemical state of the investigated materials changes. Here, glass substrates were used with no additional conductive layer on the substrate. For thin, non-conductive films, this is likely to lead to surface charge effects. Note that the peak area, which is used to determine the layer composition, is not affected by this. To allow an easier visualization of peak area changes, the spectra in Figure 1 are shifted along the binding energy axis (shown as \( E_{\text{Bind}} \) shift in the graph). The core-level position of the sample with 26% indium oxide fraction was set as an arbitrary reference point. The investigated layers cover the whole range from pure tungsten oxide to pure indium oxide with the intended closer spacing for high tungsten oxide fractions. As it can be seen from the raw data, for the layer with an indium oxide fraction of \( C_{\text{In}} \approx 7\% \), the XPS spectra were accidentally measured with a larger step width and shorter measuring time per spot. This is why the uncertainty of the stoichiometry for this layer is assumed to be much larger (10%) than for the other layers (5%). The uncertainty of 5% is reasonable for a quantitative determination of the composition by XPS and results out of a plethora of origins, such as mean square deviation between raw data and fitted model or inhomogeneity in the layer itself, but also systematic errors introduced by uncertainties of the sensitivity factors.

2.2. Crystal Structure

Next, we investigated the crystallization process of the IWO thin films. We will discuss the crystallization temperature and then analyze the crystal structures after crystallization for different compositions of the layers.

As an example, Figure 2a shows the obtained X-ray diffraction (XRD) patterns of the pure tungsten oxide layer for all post-annealed states. As-deposited, the layer showed an amorphous structure; i.e., no diffraction peaks were visible in the pattern. After annealing at a temperature of \( T = 450^\circ \text{C} \), this layer crystallized in the monoclinic crystal structure with the most intense diffraction peak at \( 2\theta \approx 24^\circ \). As the annealing was conducted in steps of 50 °C, the actual crystallization temperature (\( T_c \)) lies between 400 and 450 °C. This is in accordance with other studies, where the temperatures of \( T \approx 400^\circ \text{C} \) were found for the crystallization of pure tungsten oxide. All other IWO layers were analyzed in the same way, and the resulting crystallization temperatures are shown versus the indium oxide fraction, \( C_{\text{In}} \), in Figure 2b. The pure indium oxide phase crystallized at 200 °C, which is in accordance with other studies of \( \text{In}_2\text{O}_3 \). The as-deposited indium oxide also showed slight indications...
of the presence of the known monoclinic In$_2$O$_3$ phase with a much less pronounced 222 peak; at 200 °C, it is then fully crystallized. This might result from small crystallites, which form already during the deposition process. For the mixed oxide layers, we find that the range of crystallization temperatures is divided into two parts. For layers with $C_{\text{In}} < 50\%$, i.e., tungsten oxide-rich mixtures, we observe the high crystallization temperatures of $T_C = 450$ and 500–600 °C for the layers with $C_{\text{In}} = 7\%$ and $C_{\text{In}} = 41\%$, respectively. For the three indium oxide-rich layers with $C_{\text{In}} = 50\%$, we find significantly lower crystallization temperatures of $T_C = 200$–250 °C. As the passivation quality of intrinsic amorphous silicon is very sensitive to temperatures above 200 °C, we conclude that tungsten-rich IWO$_x$ would only be suitable for application in (i)α-Si passivated silicon heterojunction solar cells in its amorphous state.

Now, we want to investigate the crystal structure after crystallization of the thin films. It is important to understand whether the thin films form a phase composition with superposition of different mixed phases, or whether they segregate into pure phases. Therefore, we compare the XRD patterns after annealing at 700 °C with the powder diffraction file (PDF) 4+ database provided by the International Center for Diffraction Data (ICDD).

Depending on stoichiometry, we find three or four different phases, as shown in Figure 3a–d: Layers contain either a single phase, or they segregate into a combination of two phases, depending on $C_{\text{In}}$. Note that the patterns are all normalized to their maximum intensity. For some layers, especially the one with $C_{\text{In}} = 41\%$, the intensity was lower than for others, which is why in the normalized data the pattern appears more noisy than for others. As the film thickness was similar for all layers between 19 and 30 nm, this can be addressed to a reduced fraction of crystallized material and a larger amorphous part in the thin film. According to the ICDD powder data, the resulting phases match the composition determined by means of XPS, as it is shown in Figure 3. The monoclinic tungsten oxide phase (WO$_3$, space group P21/n, PDF 04-005-4272) appears in layers with $C_{\text{In}} \leq 22\%$. The layer with $C_{\text{In}} = 26\%$ crystallizes in the pure monoclinic tungsten oxide phase (In$_2$(WO$_3$)$_3$, space group P121/c, PDF 04-007-5763), which also makes up a part of the layers with slightly lower ($C_{\text{In}} = 22\%$) and higher ($C_{\text{In}} = 41\%$) indium oxide fraction. For $C_{\text{In}} = 41\%$, we find a composition of two phases. The −204 and 115 diffraction peaks of In$_2$(WO$_3$)$_3$ are still visible, where additionally two other reflexes appear at $2\theta = 31\°$ and $2\theta = 36\°$. As the pattern of the rhombohedral hexa- silindium tungsten oxide phase (In$_4$WO$_{12}$, space group R-3, PDF 04-007-6814) is very similar to the pure cubic indium oxide phase (In$_2$O$_3$, space group I213, PDF 01-073-6440), it is hard to distinguish these phases with the low intensity obtained from the measurements of the thin films. One indication is the small peak close to 12-1 toward smaller angles, which broadens the 12-1 peak as compared with the 222 peak of the pure indium oxide phase. However, the resolution at these low intensities is not sufficient to clearly distinguish these two phases in the pattern.

Richard et al. investigated powder samples of solid-state reacted IWO$_x$ mixtures and found four different phases: In$_2$O$_3$, In$_2$(WO$_3$)$_3$, In$_4$WO$_{12}$, and WO$_3$. Our results show that the thermally evaporated thin films crystallize in combinations of these phases, and that no additional phases could be detected from our XRD measurements. However, for $C_{\text{In}} > 50\%$, it is not clear, if only In$_2$O$_3$ and no In$_4$WO$_{12}$ is present, or if a combination of both phases is present in the layers. The tungsten oxide fraction in these mixtures either stays amorphous, or the W$^{6+}$ ions partially substitute...
the In$^{3+}$ ions in the crystal structure, due to their similar ionic radii of 0.74 and 0.94 Å, respectively.\cite{23}

In Figure 4, a tentative crystallization diagram, based on these observations, is shown. Note that the layers were annealed at $T_{\text{Anneal}}$ first and then measured at room temperature. The data on which the crystallization diagram is based are obtained from the eight samples of this series, marked as black dots in Figure 4. In addition, there might also appear the rhombohedral In$_6$WO$_{12}$ phase, which could not be resolved in the XRD pattern obtained in this series and is, hence, not indicated in the diagram.

2.3. Optical Properties

To apply the IWO$_x$ thin films on the front side of solar cells, a low optical absorption is necessary, because such parasitic absorption would lead to a current loss in the device. The reflection (dashed lines) and transmission (solid lines) spectra of the different mixtures of indium oxide and tungsten oxide are shown in Figure 5 for as-deposited (Figure 5a) as well as annealed layers, with the annealing temperatures of 200 °C (Figure 5b), 250 °C (Figure 5c) and 800 °C (Figure 5d). The black curve in Figure 5 indicates the transmission and reflection of the bare glass substrate (Corning). The investigated layers all have a device relevant thickness of 19–30 nm. The surface roughness increases from 2 to 16 nm.

In general, but especially for low annealing temperatures and as-deposited layers, we observe a decrease in transparency (solid line) for increasing indium oxide fraction in the mixture over the whole wavelength range. After annealing at 200 °C (Figure 5b), the poor transparency of the indium oxide-rich layers between 350 and 1200 nm is already improved, whereas the mixed oxides as well as the pure tungsten oxide almost do not change. After 250 °C annealing (Figure 5c), the crystallization of the In$_2$O$_3$ phase is completed, and the transparency in the lower wavelength range increases further. The same holds for the mixed oxide layers, which also show a further increased transmission. Note that the tungsten oxide-rich layers already show a high transmission for the as-deposited amorphous thin films and only improve slightly. After complete crystallization (Figure 5c, after 800 °C annealing), according to the XRD measurements, all layers similarly show a very high transparency.

Now, we focus on the reflectance data (dotted lines). For the as-deposited layers, the reflection decreases with increasing indium oxide fraction. The reflection does not significantly change upon annealing up to an annealing temperature of 250 °C. With further increasing annealing temperature, the reflection decreases, especially for the tungsten oxide-rich layers.

To assess the applicability of IWO$_x$ for application as a front contact in a solar cell, we calculated an estimate of the loss in short circuit current density due to parasitic absorption. We modeled a stack of the glass substrate and the IWO$_x$ layer on top using the software SpectraRay/3 by Sentech Instruments. The reflection and transmission data were fitted using Swanepoel's method$^{30}$ with a model of up to three Tauc–Lorentz oscillators.

Figure 4. Crystallization diagram of thin-film mixtures of tungsten oxide and indium oxide, based on grazing incidence X-ray diffraction measurements. The measurements were conducted at room temperature, and the annealing was conducted in ambient conditions. The black dots indicate the composition and the crystallization temperature, $T_c$, of the layers investigated here (Figure 3). The colored areas show the different appearing phases in the mixtures after crystallization.

Figure 5. Reflection (dashed lines) and transmission (solid lines) spectra for different indium oxide fraction in mixtures of indium oxide and tungsten oxide, a) after deposition and after annealing at b) 200 °C, c) 250 °C, and d) 800 °C. The black line indicates the corresponding spectrum of the bare Corning glass substrate.
and one Drude term. From the fitted extinction coefficient, \( k(\lambda) \), the absorption coefficient, \( \alpha(\lambda) \), was calculated via \( \alpha = 4\pi \times k(\lambda) \). The resulting spectrally resolved absorption for a 10 nm thick layer was calculated, multiplied with the AM1.5g solar spectrum and integrated over the wavelength range of 280–1200 nm. We assumed a film thickness of 10 nm as the upper limit for application as carrier selective contact. This yields an upper limit of the possible loss in short circuit current density of c-Si solar cells by parasitic absorption for the given films and preparation conditions in single pass limit. Figure 6 shows this equivalent \( J_{SC,loss} \) for films with different indium oxide fraction in dependence of the annealing temperature.

For as-deposited 10 nm thick indium oxide layers, applied as a front side layer on a solar cell, the short circuit current density might decrease by up to \( J_{SC,loss} = 3.2 \text{ mA cm}^{-2} \) due to parasitic absorption in the indium oxide. Increasing the tungsten oxide fraction leads to a strong decrease in parasitic absorption to \( J_{SC,loss} \approx 0.5 \text{ mA cm}^{-2} \) for the layers with the \( C_{\text{In}} \) of 53% and 64%. The four mixtures with \( C_{\text{In}} = 7\%\), 22%, 26%, and 41% show a slightly higher \( J_{SC,loss} \) of around \( J_{SC,loss} = 0.7 - 0.9 \text{ mA cm}^{-2} \). As-deposited, the pure tungsten oxide shows the lowest \( J_{SC,loss} \).

![Figure 6](image_url)

**Figure 6.** Estimated loss in short current density (\( J_{SC,loss} \)), calculated using the absorption coefficient \( \alpha(\lambda) \) as calculated from \( R, T \) (see text), due to parasitic absorption, when applying the IWO mixtures as a 10 nm thick front side layer on a solar cell for different indium oxide fraction in the mixture of indium oxide and tungsten oxide in dependence of the annealing temperature.

Now, considering the parasitic absorption after annealing the layers, the pure tungsten oxide does not change significantly up to \( T_{\text{Ann}} = 700 \text{ °C} \). For all other layers, the short circuit loss is decreased significantly by the first annealing steps, at \( T_{\text{Ann}} = 200–250 \text{ °C} \). For high indium oxide fraction, this is probably due to the crystallization of the indium oxide-rich phases. As the tungsten oxide-rich phases only crystallize at higher temperatures, the decrease in \( J_{SC,loss} \) cannot result from crystallization of the main phase. Instead, the improved transparency might be due to further oxidation of the initially slightly under-stoichiometric layers, as shown in Section 2.1. For higher annealing temperatures than 250 °C, all mixtures show a low parasitic absorption, which would make them, in principal, suitable for application on the front side of solar cells. As high annealing temperatures might be critical in a combination with other, more temperature sensitive layers, it is an advantage of the tungsten oxide-rich layers that their parasitic absorption is at a low level even in the as-deposited state and for low annealing temperatures. Compared with the standard p-type amorphous silicon hole-selective contact for silicon heterojunction solar cells, this low parasitic absorption on the front side can be a large advantage: Holman et al. determined the loss in short circuit current for a 10 nm thick (p)a-Si:H layer to be about 1.6 mA cm\(^{-2}\).[23] Hence, about 1.4 mA cm\(^{-2}\) might be gained in \( J_{SC} \) by replacing the a-Si:H selective contact with a thin layer of IWO\(_x\).

### 2.4. Conductivity

We further analyze the lateral conductivity of the thin films with mixtures of indium oxide and tungsten oxide to investigate whether mixing the tungsten oxide with the more conductive indium oxide or an annealing step can increase the conductivity of the pure tungsten oxide. In Figure 7, we see that the conductivity for the tungsten oxide containing mixtures in the as-deposited state is at least about three to four orders of magnitude lower than the conductivity of the pure indium oxide. The lower limit of the measurement is at \( \sigma = 10^{-6} \text{ S cm}^{-1} \), due to the internal resistance of the measurement setup. Only for three of the eight layers, i.e., with \( C_{\text{In}} = 100\%\), 22%, and 26%, a measurable conductivity could be obtained with \( 1.2 \times 10^{-2}, 3.4 \times 10^{-6}, \) and \( 4.0 \times 10^{-6} \text{ S cm}^{-1} \), respectively. The mixed oxide layers with \( C_{\text{In}} = 7\%, 41\%, 53\% \) and also the one with the highest indium oxide fraction \( (C_{\text{In}} = 64\%) \) are not conductive enough for this measurement method. The difference in composition from pure indium oxide to \( C_{\text{In}} = 64\% \) is quite high; however, the main gain in terms of applicability as hole selective contact (high work function) is observed for \( C_{\text{In}} < 40\% \)[24] which makes the indium-rich stoichiometries less interesting for our purpose. The pure indium oxide shows an overall increasing conductivity up to 0.39 S cm\(^{-1}\) after annealing at 700 °C. For \( T > T_{C} \), the pure tungsten oxide also shows an increasing conductivity of up to \( 1.6 \times 10^{-4} \text{ S cm}^{-1} \), whereas the conductivity of all mixed oxide layers stays below 10^{-6} \text{ S cm}^{-1} . Table 1 shows the measured specific conductivity, \( \sigma \), for three different compositions (pure indium oxide, pure tungsten oxide, and \( C_{\text{In}} = 22\% \)) and two different annealing states (as-deposited and after annealing for 10 min at 700 °C). From these results, we calculated the specific resistivity, \( \rho \), for a layer with 10 nm thickness, which is a relevant
assumption for an application as carrier selective contact in solar cells, we also estimated the series resistance contribution, \( R_s \). Note that, additionally, for a real layer stack, the contact resistance needs to be considered. The series resistance of the pure indium oxide in both annealing states, as-deposited and after 700 °C, is negligible compared with other contributions in series resistance in a solar cell. Contrary to that the as-deposited IWOx mixture with \( C_{\text{In}} = 22\% \) shows a significant \( R_s \) contribution, so a trade-off would need to be found in terms of layer thickness and a still functional hole selective contact. For the crystallized pure tungsten oxide, the \( R_s \) contribution is again negligible. However, these films require an annealing step, at least 450 °C, as we have seen earlier.

3. Conclusion

Structural, optical, and electrical properties of thin films grown by thermal co-evaporation of mixtures of indium oxide and tungsten oxide were investigated, spanning the composition from pure indium oxide to pure tungsten oxide. The crystallization temperature of the thermally co-evaporated layers was determined by means of XRD. Layers containing less than 50\% indium oxide showed the crystallization temperatures of \( T_C = 400–600^\circ \text{C} \), whereas for layers with more than 50\% indium oxide, \( T_C = 200–250^\circ \text{C} \) was found. The layers were annealed up to 800 °C in ambient atmosphere. Optical reflection and transmission as well as the electrical conductivity were measured after each annealing step. An estimate for the loss in short current density due to parasitic absorption was calculated, assuming a device relevant film thickness of 10 nm. The high parasitic absorption of up to 3.2 \( \text{mA cm}^{-2} \) for as-deposited indium oxide was found to decrease with increasing tungsten oxide fraction, and with increasing annealing temperature. Layers with around 50\% tungsten oxide and pure tungsten oxide as well as all layers annealed at 250 °C showed low parasitic absorption with estimated photocurrent losses < 0.5 \( \text{mA cm}^{-2} \) for an assumed layer thickness of 10 nm. Even though the initial motivation was to increase the conductivity by adding highly conductive indium oxide to the lowly conductive tungsten oxide, this could not be demonstrated. The conductivity stays mostly below the lower measurement limit of conductivity at \( \sigma = 10^{-6} \text{ S cm}^{-1} \). For low annealing temperatures, only the pure indium oxide and the mixtures with an indium oxide fraction of 22\% and 26\% showed a measurable conductivity of \( 1.2 \times 10^{-5} \), \( 3.4 \times 10^{-6} \), and \( 4.0 \times 10^{-6} \text{ S cm}^{-1} \), respectively. The conductivity of the pure indium oxide could be increased by increasing the annealing temperature, up to 0.39 \( \text{S cm}^{-1} \) at \( T_{\text{Ann}} = 700^\circ \text{C} \). For \( T > T_C \), the pure tungsten oxide shows an increasing conductivity of up to \( 1.6 \times 10^{-5} \text{ S cm}^{-1} \). However, for the thicknesses of about 10 nm, the estimated series resistance contribution and the low parasitic absorption for \( C_{\text{In}} = 22\% \) and 26\% of tungsten-rich mixtures in combination with the high band bending toward crystalline silicon[24] and, therefore, a probably reduced contact resistance could still make it interesting in applications as carrier selective contact for solar cells.

4. Experimental Section

The IWOx layers were deposited on 1.2 mm thick, 1 × 1 in corning glasses by thermal co-evaporation in an ultrahigh vacuum chamber (base pressure <10^{-9} \text{mbar}) [see Menzel et al.[24] for details]. The substrate was not intentionally heated; however, a slightly elevated substrate temperature caused by the about 20 cm distant crucibles cannot be completely excluded. As the applied temperature range of the crucibles is small, the resulting effect should be comparable for all samples and is, therefore, neglected. Thermal co-evaporation is a simple and effective method for varying the composition of thin layers. Note that a slight deviation in the stoichiometry from the stoichiometric In\textsubscript{2}O\textsubscript{3} and WO\textsubscript{3} needs to be expected. The deposition method has an important influence on the electronic properties. It has been demonstrated that the oxygen vacancy density,[18] contamination with precursor residuals,[19] and the crystalline structure[19] depend on the applied deposition method.

For the co-evaporation, In\textsubscript{2}O\textsubscript{3} (99.99\%) and WO\textsubscript{3} powders (99.99\%) were evaporated from aluminum oxide and tungsten crucibles, respectively. During deposition, the substrate was rotated with about 1.3 rotations per second. By independently setting the temperature of both crucibles, different evaporation rates, thus compositions from pure tungsten oxide to pure indium oxide, could be obtained. For tungsten oxide, the crucible temperature was varied from 930 to 1020 °C and for indium oxide...
from 1280 to 1325 °C. With the deposition rates of 0.2–0.8 nm min⁻¹, a final layer thickness of d = 19–30 nm was reached. The layer thickness was determined ex situ by means of a Bruker Dektak XT profilmeter.

To determine the exact film stoichiometry and the In-to-W ratio of the metal oxide mixtures, in situ XPS with non-monochromized Al–Kx excitation was carried out directly after deposition, without breaking the vacuum. The XPS analysis was focused on the W 4f and In 3d core levels. The model used for fitting the W 4f spectra consists of Voigt profiles, representing the doublet with a spin–orbit splitting of 2.12 eV and an area ratio of 3:4 and the different oxidation states, 6+, 5+, and 4+. The model for In 3dₓᵧ consists of individual peaks for metallic indium (In), In with oxidation state 3+, and indium hydroxide species. For each core level, the full widths at half maximum for all individual peaks were constrained to be identical. For more detailed information about the fitting models, see also the previous study. The In and W fractions of the metal oxide mixtures were calculated using sensitivity factors obtained from WO₃ and In₂O₃ samples, which have been oxidized post-deposition by an oxygen plasma at 10⁻³ mbar for 10 min and were, therefore, fully stoichiometric. The ratio of the metal peak area to the O 1s peak area, each divided by the known number of the respective atom in the chemical formula of the metal oxide, was used as a sensitivity factor. We used the sensitivity factors of 17.07 for In 3d and 3.83 for W 4f to determine the fraction of InOₓ, in the mixture of indium oxide and tungsten oxide, Cₓ = Aₓ / (Aₚ + Aₜ). As already mentioned earlier, the aim is to keep the work function as high as possible. As the work function of the mixture decreases from 6.3 to 4.5 eV for pure tungsten oxide and ≈50% indium oxide fraction, respectively, we consequently focus on tungsten-rich layers.

For the annealing study, the eight samples with different compositions were heated from 200 to 600 °C in the steps of 50 °C for 5 min on a high vacuum atmosphere at 700 and 800 °C for 10 min. After every annealing step, the samples cooled down to room temperature and were measured afterward. Reflection and transmission measurements were conducted to investigate the changes in optical reflection, absorption, and transmission. Grazing incidence XRD with an incidence angle of 0.5° was measured at room temperature using a Bruker D8 diffractometer with Cu–Kα irradiation and an energy dispersive Sol-X detector. The patterns were detected in a range of 2θ = 10°–60° in the steps of 0.04° and a counting time of 6 s step⁻¹. In addition, the lateral conductivity was investigated using a mercury probe measurement setup with a lower measurement limit of 10⁻⁶ S cm⁻¹, which is given by the internal resistance of the setup.

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Conflict of Interest
The authors declare no conflict of interest.

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[32] R. E. Agbenyeke, E. A. Jung, B. K. Park, T. M. Chung, C. G. Kim, J. H. Han, *Appl. Surf. Sci.* 2017, 419, 758.
[33] A. Akl, H. Kamal, K. Abdel-Hady, *Physics B* 2003, 325, 65.
[34] F. Bussolotti, L. Lozzi, M. Passacantando, S. L. Rosa, S. Santucci, L. Ottaviano, *Surf. Sci.* 2003, 538, 113.
[35] J. S. Lee, I. H. Jang, N. G. Park, *J. Phys. Chem. C* 2012, 116, 13480.
[36] P. Koscielniak, J. Mazur, J. Henek, M. Kwoka, L. Pawela, J. Szuber, *Thin Solid Films* 2011, 520, 927.
[37] J. Ip, T. P. Nguyen, P. Le Rendu, *Synth. Met* 2003, 138, 107.