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Reactive magnetron sputtering of Cu_2O : Dependence on oxygen pressure and interface formation with indium tin oxide

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Thin films of copper oxides were prepared by reactive magnetron sputtering and structural, morphological, chemical, and electronic properties were analyzed using x-ray diffraction, atomic force microscopy, *in situ* photoelectron spectroscopy, and electrical resistance measurements. The deposition conditions for preparation of Cu(I)-oxide (Cu_2O) are identified. In addition, the interface formation between Cu_2O and Sn-doped In_2O_3 (ITO) was studied by stepwise deposition of Cu_2O onto ITO and vice versa. A type II (staggered) band alignment with a valence band offset $\Delta E_{\text{VB}} = 2.1\text{--}2.6$ eV depending on interface preparation is observed. The band alignment explains the nonrectifying behavior of p- Cu_2O /n-ITO junctions, which have been investigated for thin film solar cells. © 2011 American Institute of Physics. [doi:10.1063/1.3592981]

I. INTRODUCTION

In contact with oxygen, copper oxidizes to either singly charged Cu(I) or doubly charged Cu(II). The crystal structure of Cu_2O is cubic cuprite with a lattice constant of 4.27 Å (Ref. 1) and a direct bandgap of 2.17 eV.² CuO crystallizes as monoclinic tenorite with an optical bandgap of 1.47 eV.³ In air and at room temperature, CuO is thermodynamically stable with a transition to Cu_2O at 1031 °C.⁴ Nevertheless, the transition from Cu_2O to CuO is kinetically hindered, which makes Cu_2O stable for technical applications in air and at room temperature.⁵ Its semiconducting properties are known since 1926.⁶ The p-type conductivity of nearly stoichiometric Cu_2O originates from copper vacancies.⁷ Recent calculations confirm this result and indicate an ionization energy of the copper vacancy of 0.28 eV,⁸ which was also experimentally observed.⁹

Cu_2O has been investigated for applications as p-type thin film transistors,¹⁰ thin film solar cells,¹¹ and gas sensors.¹² Bottom gate thin film transistors of Cu_2O were prepared using indium tin oxide (ITO) as gate electrode with an insulating layer of a superlattice of Al_2O_3 and TiO_2 (ATO). Indium zinc oxide (IZO) served as source and drain electrode materials. These devices show a field effect mobility of 1.2×10^{-3} V s and an on/off ratio of 200, as well as an average optical transparency of 85%.¹⁰ Solar cells made of Cu_2O have been prepared mainly as Schottky junctions using metallic copper as contact material or as semiconductor heterojunction with transparent semiconducting oxides (TCOs), for example, ITO.^{13–15} The highest conversion efficiency of 2% has been obtained with a layer structure $\text{Cu}_2\text{O}/\text{ZnO}/\text{ITO}$.¹¹ Essential for the photovoltaic performance is the band alignment at the p-n junction, which has been part of the investigations presented here.

The oxidation state of Cu can directly be determined from photoelectron spectroscopy. The Cu $2p_{3/2}$ emission of Cu_2O and CuO have a binding energy difference of

1.2 eV.^{16,17} Cu(II) can further be clearly distinguished from Cu(I) by the occurring shake-up satellites at around 9 eV higher binding energies.¹⁸ This makes it possible to detect already small amounts of Cu(II) on the surface of Cu_2O .

In this study we report on the properties of copper oxide thin films prepared by reactive magnetron sputtering. The structural, morphological, chemical, and electronic properties of the films are analyzed using *in situ* photoelectron spectroscopy, x-ray diffraction, atomic force microscopy, and electrical resistance measurements.

II. EXPERIMENTAL

Thin film deposition and photoelectron spectroscopy were performed at the Darmstadt Integrated System for Material research (DAISY-MAT).¹⁹ The system provides a central sample distribution chamber, which combines a Physical Electronics PHI 5700 multitechnique surface analysis system with several preparation chambers, allowing for rapid sample transfer between preparation and analysis chambers without breaking ultrahigh vacuum (UHV) conditions.

The preparation of copper oxide by reactive radio-frequency (rf) magnetron sputtering was carried out in a custom-made sputter chamber at 25 W, sputtering a 2 in. metallic copper target of 99.999% purity purchased from Lesker. As reactive gas component, oxygen was introduced to the argon atmosphere during deposition. The oxygen content was varied between 4 and 9%. To achieve the desired atmosphere the gas flow rate was controlled at a constant pressure of 5×10^{-3} mbar. 6 to 1 sccm of pure argon where mixed with 4 to 9 sccm of an Ar-O₂ mixture containing 10% oxygen. Soda-lime glass was used as substrate for the deposition. During one of the depositions the substrate was heated to 500 °C by a halogen lamp installed under the sample holder. Without substrate heating, the substrate temperature T_S is assumed to remain below 100 °C during deposition. The target to substrate distance was set to 8.4 cm.

For the preparation of the interface, Cu_2O was deposited without intentional heating of the substrate at 5% oxygen

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content in the process gas. ITO was prepared by rf magnetron sputtering at 25 W from a 2 in. target of indium tin oxide containing 10 wt. % tin oxide and a purity of 99.99% also purchased from Lesker. The atmosphere was pure argon at 5×10^{-3} mbar at a flow rate of 6.6 sccm. The distance between target and substrate was set to 10 cm. Typical conductivities of the films are 2×10^4 S/cm. Electrical, optical and surface properties of the ITO films are described elsewhere.²⁰

In order to avoid charging of the material during photoelectron spectroscopy, 5 mm wide and about 100 nm thick films of Pt were deposited on two opposing sides of 25×15 mm² glass substrates before film deposition, leaving a square of 15×15 mm² without platinum in the middle of the substrate. The platinum electrodes served as electrical contacts for sample grounding.

X-ray photoelectron spectroscopy (XPS) was performed using monochromatic Al $K\alpha$ radiation with an energy of 1486.6 eV and an overall energy resolution of less than 0.4 eV. Binding energies are reported with respect to the Fermi level, which was calibrated measuring a sputter cleaned metallic silver sample. The integral intensities of the photoelectron emission lines serve for determination of the sample's stoichiometry using atomic sensitivity factors.²¹ Ultraviolet photoelectron spectra (UPS) for determination of work function $\phi = E_{\text{vac}} - E_F$ and ionization potentials $I_P = E_{\text{vac}} - E_{\text{VB}}$ were acquired under normal emission and a sample bias of -1.5 V using He I radiation ($h\nu = 21.2$ eV) from a gas discharge lamp with an overall energy resolution of less than 0.2 eV. The work function of the films are determined from the binding energies of the secondary electron cutoff E_{sc} according to $\phi = h\nu - E_{\text{sc}}$. With core level binding energies and valence band maximum from XPS and work function determined by UPS, the energy band diagram of the interface can be constructed.

Electrical resistance was measured on films deposited on substrates prepared with Pt electrodes as described above. The Pt electrodes were contacted to perform measurements in-plane in two-point geometry.

III. RESULTS AND DISCUSSION

A. Thin film deposition

XPS survey scans of the freshly prepared samples where performed in a binding energy range from 0 to 1400 eV. The spectra, which are displayed in Fig. 1, show only emission from copper and oxygen. There is no surface contamination such as carbon, which has its most intense emission at 285 eV binding energy.²¹ The intensity ratio of Cu to O changes with different depositions conditions. A film which has been deposited at 500 °C substrate temperature for reference shows some small Na emission, which is attributed to diffusion of Na from the glass substrate.

Relevant emissions of copper and oxygen together with the valence band spectra are shown in Fig. 2. The peak shape of the main Cu $2p_{3/2}$ emission does not change significantly between 4 and 6% oxygen during deposition, indicating a predominant phase of Cu₂O. Only in more oxidizing atmosphere (9% O₂) the shape and position change and strong sat-

FIG. 1. XPS survey spectra of copper oxide films prepared by reactive magnetron sputtering. The oxygen content in the process gas and substrate temperature T_s during deposition are annotated. The emission lines are identified for the topmost spectra. No surface carbon contamination at ~ 285 eV binding energy is observed.

ellites occur, which are related to a noticeable amount of Cu(II) in the sample.¹⁸ A closer look at the satellite spectra reveals a certain amount of Cu(II) also in the sample prepared under 6% oxygen.

FIG. 2. Detail XP spectra of the Cu $2p_{3/2}$ emission, its satellite lines, the O 1s and Cu LMM emissions and the valence band. The films were deposited at RT and various oxygen contents in the process gas, which are indicated in the graphs. Emission features related to Cu(II) are indicated by triangles while metallic Cu is indicated by a circle.

FIG. 3. XRD of copper oxide films prepared at different substrate temperature with different oxygen content in the process gas. The expected positions and intensities of Cu₂O (PDF-2 card 5-667) and CuO (PDF-2 card 5-937) reflections are indicated.

The O 1s emission shows a clearly different binding energy and shape at 9% oxygen during deposition compared to lower oxygen contents. With 6% oxygen during deposition the shoulder at lower binding energy also indicates the presence of Cu(II). In the Cu LMM Auger emission, a shoulder attributed to metallic copper¹⁷ occurs at oxygen contents in the process gas lower than 5%. Besides the differences in spectral shape, the emissions of copper, oxygen, and the valence band maximum E_{VB} of the 6% sample are at lower binding energies compared with the ones prepared at 5 and 4% oxygen. This indicates a lower value of $E_F - E_{VB}$ at higher oxygen contents in the process gas, which corresponds to a higher doping level of the film.

The results of XRD measurements are shown in Fig. 3. At RT and 4% oxygen during deposition there is evidence for traces of metallic copper in Cu₂O. After deposition at RT and 5% O₂ the material is pure Cu₂O (the Pt signal is due to thin films of platinum on the edges of the glass substrate in order to ground the sample to avoid charging during photoemission). Deposition at 500°C in the same atmosphere produces a mixture of cuprite (Cu₂O) and tenorite (CuO), accompanied by narrower diffraction peaks, indicating larger grains than for films deposited at room temperature. The larger grains are also evident in AFM pictures, which are shown in Fig. 4.

The sample deposited at RT and 6% oxygen does not show a tenorite phase, it shows only cuprite reflections. This indicates that the traces of Cu(II) detected with XPS form either amorphous or very small crystallite tenorite precipitations in the cuprite matrix.

The lattice parameter of the cuprite structure is increased after deposition at RT with 6% O₂ compared to the films prepared with lower oxygen content (see Fig. 3). A possible explanation for this is that the increased oxygen content leads to

FIG. 4. AFM images of copper oxide samples deposited under 5% oxygen at RT and 500°C.

a formation of nonstoichiometric cuprite with an increased amount of copper vacancies. This is consistent with the lower binding energy values and enhanced p-doping and conductivity (see below) of the film. The lattice expansion is then explained by the increased repulsive Coulomb interaction of charge uncompensated oxygen anions. A positive vacancy formation volume is attributed to singly charged copper vacancies as it is the case for singly charged zinc vacancies in ZnO.²²

Table I summarizes important values obtained from photoelectron spectroscopy of samples prepared at RT and various oxygen partial pressure on glass or ITO as substrate. The stoichiometry after deposition with 5% oxygen on glass substrate corresponds to single phase Cu₂O. Lower oxygen content in the process gas leads to a higher amount of copper in the compound, higher oxygen content decreases it, as expected. As already mentioned, the Fermi energy ($E_F - E_{VB}$) decreases if the oxygen content during deposition exceeds 5%.

The films deposited onto ITO substrates show a higher oxygen content than those deposited onto glass with the same conditions, which may be explained by diffusion of oxygen from the ITO substrate into the growing film. The release of oxygen from ITO substrates has previously been observed during deposition of organic molecules.²³ It is related to the high concentration of interstitial oxygen in ITO (Refs. 24 and 25) and their high mobility.²⁶ The different substrates also affect the work function ϕ and the ionization potential I_p of the Cu₂O film. Higher values are obtained when deposited on glass.

Different values of $E_F - E_{VB}$, ϕ and I_p for Cu₂O on ITO in dependence on the substrate temperature during ITO deposition may be related to temperature dependent crystallinity and orientation of the ITO film.^{27–29} The two-point resistances of the samples (see Table I) also correlate with the oxygen content during deposition. The highest resistance is observed for the sample prepared with 5% oxygen, which is closest to the Cu₂O stoichiometry. At lower oxygen content during deposition the resistivity decreases, probably caused by metallic copper precipitations. In more oxidizing atmosphere the resistance also decreases, which corresponds well with the enhanced p-doping of the film as indicated by the lower Fermi level position.

B. Cu₂O-ITO energy band alignment

Three variations of the interface were prepared, distinguished by using the notation substrate (T_S)/film (T_S), where

TABLE I. Composition, Fermi level position $E_F - E_{VB}$, work function ϕ , and ionization potential I_p as determined by photoemission from Cu-oxide films deposited by reactive magnetron sputtering with near Cu_2O stoichiometry. Electrical two-point resistances R are given in the last column.

No.	O_2 during deposition	Substrate material	Ratio Cu/O	$E_F - E_{VB}$ (eV)	ϕ (eV)	I_p (eV)	R (Ω)
1	6%	glass	1.60	0.33			4×10^6
2	5%	glass	1.99	0.58			2×10^{10}
3	5%	ITO(400 °C)	1.91	0.34	4.95	5.29	
4	5%	ITO(RT)	1.93	0.29	4.74	5.03	
5	5%	glass	2.00	0.59	5.07	5.66	
6	4%	glass	2.64	0.53			5×10^4

T_S is the substrate temperature during deposition of the respective film:

1. ITO(400 °C)/ Cu_2O (RT),
2. ITO(RT)/ Cu_2O (RT),
3. Cu_2O (RT)/ITO(RT).

In all cases, the Cu_2O films were deposited at room temperature with 5% oxygen in the sputter gas. The other deposition parameters are the same as those given in the experimental section. For the third experiment, a 270 nm thick Cu_2O film was first deposited onto a glass substrate prepared with Pt electrodes in order to avoid sample charging during photoemission measurements.

Photoelectron spectra recorded during the interface formation ITO(RT)/ Cu_2O (RT) are shown in Fig. 5. The spectra recorded during the other interface experiments show an analogous behavior. Following the stepwise deposition of copper oxide, the intensities of the Cu $2p_{3/2}$ and Cu LMM emissions

increase while the In $3d_{5/2}$ signal is attenuated. No change of the line shape of the In 3d emission is observed during deposition. In addition, the shape of the Cu 2p and the Cu LMM emission correspond to those of Cu_2O for all deposition steps. The oxygen emission before film deposition is attributed to ITO, while afterwards it originates from copper oxide. The evolution of the core levels in the course of Cu_2O deposition is typical for formation of an abrupt interface.

For the ITO substrate and the 31 nm thick Cu_2O film also ultraviolet photoelectron spectra have been recorded. The binding energies of the valence band maxima derived from linear extrapolation of the leading valence band edge and of the secondary electron cutoffs derived from the half height of the high binding energy cutoff are indicated in the figure.

The energy band alignment at the interfaces are derived following the procedure outlined by Waldrop and co-workers.³⁰ The relative position of the Cu_2O and ITO valence band maxima are followed on the basis of the evolution of the core levels, which exhibit a material specific binding energy offset with respect to the valence band maximum. These offsets are determined from spectra of the clean substrate and of the film with sufficient thickness. The typical scatter of the offset for a large set of samples is ± 0.1 eV. When the offset is subtracted from the core level binding energy, a value for $E_F - E_{VB}$ of the substrate and the film is derived for each deposition step.

The evaluation of the binding energies for the three interface experiments is displayed in Fig. 6. Valence band offsets ΔE_{VB} are derived directly from the difference of substrate and film valence band maxima. Lowest and highest values of $E_{VB}(\text{ITO}) - E_{VB}(\text{Cu}_2\text{O})$ are indicated in Fig. 6. The band bending eV_{bb} is determined from the core level binding energy shift of the substrate with successive film deposition. The derived energy band diagrams, which are displayed in the bottom part of Fig. 6, are completed using fundamental band gaps of 2.1 eV for Cu_2O (Ref. 2) and of 2.8–2.9 eV for ITO.³¹ The interface dipole δ is derived from the work functions and the band bending.

A band bending in Cu_2O of approximately 250 meV is found for the interface $\text{Cu}_2\text{O}(\text{RT})/\text{ITO}(\text{RT})$. As the binding energy of Cu_2O related core levels show comparable shifts during the deposition of Cu_2O onto ITO, the same band bending is considered for the ITO(400 °C)/ $\text{Cu}_2\text{O}(\text{RT})$ and the ITO(RT)/ $\text{Cu}_2\text{O}(\text{RT})$ interfaces. The Fermi energy change in ITO during interface formation depends on its deposition temperature. ITO deposited at 400 °C shows no band bending in the course of Cu_2O deposition, whereas ITO deposited at

FIG. 5. Photoelectron spectra of the interface ITO(RT)/ $\text{Cu}_2\text{O}(\text{RT})$. The Cu_2O film thickness is indicated in nm. Numbers attached to the UPS spectra indicate the binding energies of the valence band maxima and the secondary electron cutoff, respectively.

FIG. 6. (Color online) Band alignment of the interface between ITO and Cu_2O derived from three different interface experiments in the order substrate/film. The $E_F - E_{VB}$ calculated from core level binding energies (top) and a schematic representation of the energy diagrams (bottom) are graphically displayed. Values directly obtained from measurements are underlined. All values are given in eV.

room temperature shows a downward Fermi level shift of ~ 250 meV. The different behavior is attributed to the different free carrier concentrations in dependence on substrate temperature. Magnetron sputtered films of ITO prepared at 400°C show conductivities and electron concentrations ~ 2 orders of magnitude higher than those of films deposited at room temperature.^{20,27} Films deposited at higher temperature may therefore behave similar to a metal, showing no band bending during interface formation. When deposited at room temperature, ITO can behave more like a semiconductor due to a smaller free charge carrier concentration.

The downward shift of the Fermi level is surprising, as the composition of the Cu_2O films indicates that oxygen is diffusing from the ITO substrate into the Cu_2O film (see above). This should lead to an increase of the doping level, causing an upward shift of the Fermi level. However, the structural and defect properties of the ITO films deposited at room temperature are not well known yet and oxygen excess may also exist without being electrically active. The different structure of the ITO films after room temperature deposition is also reflected in the lower work function and ionization potential, which depends strongly on surface composition and termination.^{28,29}

Both experiments with ITO prepared at RT give a valence band offset of $\Delta E_{VB} = 2.1 \pm 0.2$ eV. Using ITO deposited at 400°C results in $\Delta E_{VB} = 2.6$ eV. Apparently, the valence band offset is affected by the substrate temperature during ITO deposition and not by the layer sequence. This may be related to the metalliclike behavior of ITO, leading to a strong pinning of the Fermi level. Pinning of the Fermi level must also occur in the deposited Cu_2O film in order to explain the different valence band offset. The Fermi level in the deposited Cu_2O adopts a value of $E_F - E_{VB} \approx 0.5$ eV. A valence band offset of 2.1 eV would require either a substantially higher Fermi level in Cu_2O (~ 1 eV) or an ~ 0.5 eV upward band bending in ITO. Apparently both are not possible. The low deposition temperature of the Cu_2O film will result in a high concentration of defects, which are likely the

origin of the Fermi level pinning in the Cu_2O film. A corresponding pinning related modification of energy band alignment has also been observed for $\text{In}_2\text{O}_3/\text{ZnO}$ and TCO/CdS interfaces.^{32,33}

Barrier heights of degenerately doped semiconductors strongly depend on the doping density. The higher the dopant concentration, the larger is the space charge density and the lower the band bending, as only a limited amount of charge has to be transferred across the interface to compensate the contact potential difference. The effect is well described by the fundamental electrostatic model of barrier formation outlined by Cowley and Sze.³⁴ It is included in the $\{\dots\}$ term of their famous expression, which empirically quantifies Fermi level pinning at semiconductor/metal interfaces in dependence on the density of interface states. The dependence of barrier height on doping concentration has been explicitly calculated for the SrTiO_3/Pt interface.³⁵ The barrier height essentially vanishes for doping concentrations $\geq 10^{20} \text{ cm}^{-3}$, which is less than the doping level of the ITO films deposited at 400°C .^{20,25} High doping levels also reduce the barriers at grain boundaries in polycrystalline thin films, thereby increasing the carrier mobility.³⁶

According to our experience, the band alignment at interfaces between different oxides is rather insensitive on interface preparation. In particular no dependence of barrier heights on interface orientation has so far been observed. The independence of barrier height on interface orientation has been demonstrated explicitly for the $\text{Pb}(\text{Zr,Ti})\text{O}_3/\text{RuO}_2$ interface.³⁷ Although an influence of a different interface structure on the band alignment cannot be excluded, it seems more likely that the difference in valence band offset for the interfaces prepared with low and high temperature deposited ITO films is related to the different carrier densities of the films.

The large valence band offset between ITO and Cu_2O can be rationalized in terms of the contribution of Cu 3d states to the Cu_2O valence bands. While the valence bands in ITO are predominantly formed by O 2p orbitals,³⁸ Cu 3d and O 2p

FIG. 7. (Color online) Band alignment of different interfaces determined using photoelectron spectroscopy. The valence band maximum of Cu_2O is used as reference. Using transitivity of valence band offsets, the valence band maximum of Cu_2O is expected to be ~ 0.2 eV lower than that of Cu_2S and ~ 0.8 eV lower than that of Cu_2Te . The valence band offsets indicated are taken from Ref. 41 ($\text{Cu}_2\text{S}/\text{CdS}$), Ref. 42 ($\text{Cu}_2\text{S}/\text{CdS}$), Ref. 45 (CdS/CdTe), and from Ref. 46 ($\text{In}_2\text{O}_3/\text{CdTe}$), respectively. The conduction band minima are calculated bulk energy gaps of 2.1 (Cu_2O), 1.2 eV (Cu_2O), 1.04 eV (Cu_2O), 2.8–2.9 eV (In_2O_3), 1.49 eV (CdTe), and 2.42 eV (CdS), respectively.

orbitals form the valence bands in Cu_2O .³⁹ Due to the mixing of the Cu 3d and O 2p electrons, the valence band maximum is considerably shifted upwards in energy (p-d repulsion).⁴⁰ The upward shift of the valence band maximum is also reflected by the ionization potential of Cu_2O , which is ~ 2 eV smaller than that of ITO (see Table I and Ref. 28). Due to the comparable valence band offset and ionization potential difference only small interface dipoles δ result (see Fig. 6).

The determined valence band offset is in line with other valence band offsets of Cu-chalcogenides.^{41,42} Band alignments for different interfaces are shown in Fig. 7, where a ΔE_{VB} of 2.1 eV is used for the $\text{Cu}_2\text{O}/\text{ITO}$ interface, as this value appears to be less affected by the pinning effects discussed above. In combination with the different valence band offsets, an ordering of the valence band maxima of the Cu-chalcogenides can be established. Using transitivity of valence band offsets, the valence band maximum of Cu_2O is expected to be ~ 2 eV lower than that of Cu_2S and ~ 0.8 eV lower than that of Cu_2Te . This ordering is completely reasonable as it follows the same trend as the valence band maxima of Cd- and Zn-chalcogenides,⁴³ which is determined by the energy of sp^3 -orbitals of the chalcogens.⁴⁴

Considering the small built-in potential at the $\text{Cu}_2\text{O}/\text{ITO}$ heterojunction, which is a result of the energy band alignment between the two materials shown in Fig. 6, it is understandable that no rectifying behavior and only poor photovoltaic performance of $\text{Cu}_2\text{O}/\text{ITO}$ junctions are observed.^{11,15}

IV. SUMMARY AND CONCLUSIONS

Structural, morphological, chemical, and electronic properties of copper oxide films prepared by reactive magnetron sputtering were analyzed in this work. Methods of characterization included *in situ* photoelectron spectroscopy, x-ray diffraction, atomic force microscopy, and electrical resistance measurements. It is shown that near-stoichiometric cuprite films can be prepared by reactive magnetron sputtering at

room temperature with the possibility to influence intrinsic doping of the material with the concentration of copper vacancies by controlling the amount of oxygen in the process gas during deposition. A correlation between an elevated copper vacancy concentration depending on the oxygen partial pressure during RT deposition of Cu_2O and the intrinsic p-type doping of the material is observed. This may serve as a way to influence the doping of Cu_2O thin films simply by controlling the oxygen amount in the process gas.

The energy band alignment with ITO was analyzed in three variations revealing a valence band offset of $\Delta E_{\text{VB}} = 2.1 \pm 0.2$ eV for room temperature deposited ITO films, which exhibit considerably lower carrier concentration than ITO films prepared at higher substrate temperature. With higher carrier concentrations in the ITO film a 0.5 eV larger valence band offset is observed, which is ascribed to the pinning of the Fermi level resulting from a metalliclike behavior of ITO and a high defect concentration in Cu_2O .

The large valence band offset between Cu_2O and ITO is a result of the contribution of Cu 3d states to the valence bands of Cu_2O . It explains the absence of a strong rectifying current-voltage characteristic of p- $\text{Cu}_2\text{O}/\text{n-ITO}$ junctions and the photovoltaic behavior of this type of heterojunction.

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