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Highly conductive grain boundaries in copper oxide thin films

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High conductivity in the off-state and low field-effect mobility compared to bulk properties is widely observed in the p-type thin-film transistors of Cu₂O, especially when processed at moderate temperature. This work presents results from *in situ* conductance measurements at thicknesses from sub-nm to around 250 nm with parallel X-ray photoelectron spectroscopy. An enhanced conductivity at low thickness is explained by the occurrence of Cu(II), which is segregated in the grain boundary and locally causes a conductivity similar to CuO, although the surface of the thick film has Cu₂O stoichiometry. Since grains grow with an increasing film thickness, the effect of an apparent oxygen excess is most pronounced in vicinity to the substrate interface. Electrical properties of Cu₂O grains are at least partially short-circuited by this effect. The study focuses on properties inherent to copper oxide, although interface effects cannot be ruled out. This non-destructive, bottom-up analysis reveals phenomena which are commonly not observable after device fabrication, but clearly dominate electrical properties of polycrystalline thin films. *Published by AIP Publishing.*
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I. INTRODUCTION

A significant economic potential lies within low-temperature fabrication of transparent oxide electronics.¹ A successful commercialization is primarily held back by the development of a complementary p-type transistor element. With a band gap of 2.17 eV,² Cu₂O is one of the candidate p-type materials, but shows a pronounced discrepancy between bulk electrical properties and device behavior. Deposition by reactive magnetron sputtering at room temperature results in a Hall mobility of 1 cm² V⁻¹ s⁻¹, however additional annealing at 200 °C for 1 h in air increases the mobility to 32 cm² V⁻¹ s⁻¹ (own data, similar to results from the literature^{3,4}). In contrast, bottom-gated thin-film transistors (TFTs), produced at temperatures up to 200 °C, show field-effect mobilities in the order of 10⁻³ cm² V⁻¹ s⁻¹.^{5,6} A higher annealing temperature above 500 °C (Refs. 7–9) is typically needed for a field-effect mobility closer to the bulk value. This is commonly related to an increased grain size. An estimation of sub-gap density of states close to the valence band maximum in a Cu₂O transistor annealed at 800 °C has resulted in a value an order of magnitude higher than that of amorphous silicon or organic TFTs.¹⁰ However, the intermediate temperature approach (below 200–300 °C) has been shown to be feasible by an adequate choice of bottom-gate dielectric substrate material, leading to field-effect mobilities of 2 cm² V⁻¹ s⁻¹ on AlN and 0.5 cm² V⁻¹ s⁻¹ on SrTiO₃.^{11,12}

Already one year after the first report on epitaxial Cu₂O as active channel in a TFT,¹³ the interpretation of

bulk properties has led to the conclusion that the low on-off current ratio and the low field-effect mobility can be either due to a secondary phase of CuO or ionization of intrinsic donors (oxygen vacancy).¹⁴ In the case of high-quality epitaxial films, such defects have to be localized at interfaces and/or surfaces. Apart from a well known surface oxidation of Cu(I) in Cu₂O to Cu(II),¹⁵ a porosity of Cu₂O and an interdiffused layer due to high temperature processing have been discussed to be the reasons for bad transport properties at the interface between the polycrystalline Cu₂O and the dielectric substrate.^{16,17} In the here presented study, a surface oxidation is excluded as the electrical analysis was entirely conducted in an ultra-high vacuum (UHV).

Cu₂O has been reported to exist in non-stoichiometric form, both polycrystalline and monocrystalline, when quenched from high temperatures.^{18,19} At room temperature and in ambient air, Cu₂O is thermodynamically unstable, but the eutectoid decomposition into Cu and CuO below 375 °C is kinetically hindered.²⁰ A structural stabilization has been reported by (110) stacking faults in minerals of Cu₂O, which are understood as a missing plane of copper ions and give rise to a formal increase in copper valency of the adjacent cations.²¹ Grain boundaries, in general, have been shown to present regions of an increased conductivity with respect to monocrystalline material²² and act as a sink for intrinsic defects.²³ Apart from segregation of intrinsic defects, inhomogeneity may also exist in the form of oxidation states different from the parent material. In Cu₂O, precipitate phases containing either Cu(0) or Cu(II) might be present.²⁰ Cu(0) is metallic and forms a Schottky barrier to Cu₂O.²⁴ Cu(II) occurs in another stable p-type oxide, CuO, which generally exhibits a higher charge carrier concentration and lower Hall

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mobility than Cu_2O .^{25–27} This is due to the partial Cu 3d⁹ occupancy, which subjects the hole state to strong antiferromagnetic coupling.²⁸ The higher carrier concentration is also related to the Cu 3d⁹ configuration, since it introduces strong electron-electron coupling to the valence band, which shifts its maximum closer towards the Fermi energy.²⁹ The value of the band gap is approximately 1.5 eV.³⁰

In order to describe the morphology of a film grown from the vapor phase, a structure zone model has been developed.³¹ When grown without substrate heating, grains have fibrous structure, predominantly oriented orthogonal to the substrate surface.³ The grain size in this direction is equal to the film thickness d , which is related to the lateral extension of the grains L according to Equation (1).³² The exponent n mediates the curvature of the grain faces

$$d \propto L^n. \quad (1)$$

Inhomogeneous electrical properties in polycrystalline semiconductors most commonly exist in the form of poorly conductive, thin intergranular regions, with respect to the grains. Consequently, most of the literature on electrical properties of inhomogeneous semiconductors focuses on this case.^{33–35} A rather simple model, which accounts for highly conductive grain boundaries, has been developed for polycrystalline CeO_2 on SiO_2 , growing with columnar morphology. In this contribution, a similar model is used to correlate thickness-dependent conductance data for Cu_2O with the morphology of the material. In parallel, changes in the copper oxidation state are studied to reveal the origin of the inhomogeneous electrical properties.

II. EXPERIMENTAL

Sample preparation for *in situ* X-ray photoelectron spectroscopy (XPS) was done at the DArmstadt Integrated SYstem for MATerial research (DAISY-MAT), a cluster tool which provides UHV transfer between deposition and characterization chambers.³⁶ Cu_2O thin films were grown by reactive radio frequency (RF) magnetron sputtering without substrate heating. A 2 in. metallic copper target of 99.999% purity purchased from Lesker was sputtered at 25 W (2.53 W in.^{−2}) and 0.5 Pa total pressure. Similar to earlier studies,³⁷ the stoichiometry of Cu_2O was optimized by adjusting the gas flow ratio of oxygen with respect to the total gas flow in the range of 3.7%–4.3%. This value had been found to depend on target consumption. Figures of merit for optimized deposition conditions were stoichiometry, obtained from areal peak intensities divided by atomic sensitivity factors provided for the instrument,³⁸ the absence of the Cu 2p satellite structure of Cu(II),³⁹ and a Fermi energy $E_F - E_{\text{VB}} \leq 0.3$ eV. Fermi energies of 0.5–0.6 eV were found a more sensitive indicator for small amounts of Cu(0) than the Cu LMM Auger emission.⁴⁰ LMM refers to the orbitals in X-ray level notations, which are involved in the Auger emission, more precisely $\text{L}_{3,4,5}\text{M}_{4,5}$. Comparatively high Fermi energies in Cu_2O can be related to a depletion by the formation of Schottky barriers to nanocrystalline copper precipitates.^{41,42} Samples of CuO were grown with similar condition, but using an oxygen gas flow ratio of 10%.

As substrates, SiO_2 quartz glass, Al_2O_3 and Bi_2O_3 were used. The quartz glass substrates had been provided by CrysTec. Al_2O_3 was deposited by an atomic layer deposition (ALD) in a home-made chamber at 200 °C substrate temperature. The complete process is described elsewhere.⁴³ In addition, Al_2O_3 incorporated in a bottom-gate stack of a multi-layer structure of Al_2O_3 and TiO_2 by ALD (250 nm) on sputter-deposited indium tin oxide (ITO, 160 nm) was used as substrate. In the following, this substrate is referred to as ATO. The dielectric surface and the interface to ITO consist of 25 nm pure Al_2O_3 . Planar Systems (now Beneq) provided these substrates, which are used for the fabrication of p-type oxide TFTs, as reported in the literature.^{5,12,44,45} Bi_2O_3 was reactively sputtered from a 2 in. metallic Bi target provided by Alineason Materials Technology at 15 W (RF, 1.52 W in.^{−2}) without substrate heating. A gas flow ratio of 10% oxygen was maintained at 0.5 Pa total pressure. Bi_2O_3 is an interesting material due to its high dielectric constant of approximately 40, which has been studied previously in the system.^{46,47}

XPS was performed in a Physical Electronics PHI 5700 multi-technique surface analysis unit, using monochromatic Al K α radiation with an energy of 1486.6 eV, a take-off angle (TOA) of 45°, and a pass energy of 5.85 eV, resulting in an overall energy resolution of less than 0.4 eV. The system is equipped with an electron flood gun for charge compensation. *In situ* measurements of conductance G were realized by connecting a Keithley 6487 picoammeter/voltage source to the sample through two electrical feedthroughs installed on the XPS chamber. The substrate had been prepared with two sputter-deposited gold electrodes in planar geometry. The width w and the length l of the measured sample area were in the range of 6.5–8.3 cm and 1.2–1.3 cm, respectively. The ohmic contact to both electrodes was confirmed by current-voltage sweeps. As the measured currents have been in the range of picoampere especially at low thickness, the conductance was determined by applying a constant voltage of 1 V until the current reached a steady state. Then, the voltage bias was set to zero and the current was read again until steady state was reached. The difference of both steady-state currents was used for calculation of the conductance. The amount of voltage was chosen as compromise between high signal-to-noise ratio of the measurement and little current stress on the thin film.

The *in situ* XPS and IV characterization was done on Cu_2O films deposited onto plane quartz glass and onto quartz glass coated either with 25 nm Al_2O_3 or 45 nm Bi_2O_3 . Furthermore, ATO was investigated in two runs. One of the ATO runs involved an additional cleaning step by heating the substrate in 0.5 Pa oxygen at 200 °C for 2 h immediately before film deposition. Then, two substrates of ATO coated with additional 45 nm Bi_2O_3 were studied in two separate runs. With respect to deposition parameters, both runs were identical.

The quartz substrate showed rather pronounced charging during XPS measurement, which was partially compensated by the electron flood gun. For the analysis of the films on quartz glass coated with Al_2O_3 and Bi_2O_3 , a second quartz substrate was sputter-coated with an additional gold layer

prior to the respective deposition of Al_2O_3 and Bi_2O_3 , which was added on the same sample holder next to the insulating substrate. While the insulating substrate served for conductance measurement, the conductive substrate was used for XPS analysis. In this way, the use of the electron flood gun could be avoided. The ATO substrates were subjected to less pronounced charging, so they did not require the use of charge compensation to obtain the spectra, however disregarding binding energies. In any case, charging disappeared as soon as a sufficiently thick Cu_2O film had been deposited.

An Asylum Research MFP-3D atomic force microscope (AFM) was used to obtain surface roughnesses and average grain sizes at the surface, as well as current maps in contact mode with a voltage of 2 V applied to the tip (Asylum Research PPP-CONTPT). Scanning electron microscopy (SEM) was done with a Carl Zeiss Auriga. To obtain cross-sectional images of the films, the samples had been manually broken prior to measurement. The Hall effect was measured with a custom Hall effect system⁴⁸ as well as with a commercial BioRad HL5550. X-ray diffraction (XRD) measurements were done with a PANalytical X'Pert Pro Diffractometer in Bragg-Brentano geometry. Film thickness was measured by profilometry and the deposition rate was assumed to be independent on film thickness.

III. RESULTS

A. Electrical film properties

The different types of insulating substrates investigated in this study are referred to by the names as shown in Table I. Stoichiometry, Fermi energy and *in situ* conductivity σ from planar geometry of thick Cu_2O and CuO are reported. The conductivity is calculated according to Equation (2), where Y is the reduced conductance, corrected for the electrode geometry

$$\sigma = \frac{I G}{w d} = \frac{Y}{d}. \quad (2)$$

The film thickness of the samples listed in Table I was generally 254 nm, except for sample ATO (1) (42 nm) and for CuO on ATO (366 nm). All surfaces of thick Cu_2O films are stoichiometric within an error of 5%. Accordingly, they were free of the characteristic spectral features described in Sec. II, which indicates the absence of $\text{Cu}(0)$ and $\text{Cu}(\text{II})$. However, the conductivities at 254 nm film thickness are

TABLE I. Stoichiometry, Fermi energy, and conductivity (estimated from planar geometry).

Substrate	Ratio Cu/O	$E_F - E_{\text{VB}}$ (eV)	σ ($\text{S cm}^{-1} \times 10^{-3}$)
Quartz (q)	1.98	0.26	0.3
q/ Al_2O_3	2.13	0.23	2.2
q/ Bi_2O_3	1.93	0.24	4.4
ATO (1)	1.89	0.27	10.2
ATO (2)	1.99	0.33	3.4
ATO/ Bi_2O_3 (1)	2.05	0.29	8.6
ATO/ Bi_2O_3 (2)	2.05	0.28	15.3
CuO on ATO	0.86	0.06	166.6

quite different according to the type of substrate. Cu_2O on quartz shows the lowest value, followed by the Al_2O_3 substrates. The low conductivity on quartz is not due to a measurement artifact, since a similarly low value was obtained on a sapphire substrate (not shown here). The highest conductivities in Cu_2O are obtained on Bi_2O_3 with further increase when deposited on ATO/ Bi_2O_3 . In CuO , the conductivity is comparatively high in accordance with the low Fermi energy. The remainder of this article is concerned with the wide range of conductivities observed in Cu_2O by evaluating the data with respect to film thickness.

Figure 1 shows the change in reduced conductance with an increasing copper oxide thickness on a linear scale and in double-logarithmic representation. The value of Y before any film deposition is at least five orders of magnitude lower than the final reduced conductance for all experiments. As the measurements were performed in the vacuum system directly after deposition, this observation is related to the film properties and not to an extrinsic surface effect, which may be caused, for example, by adsorbates. The most striking observation from Figs. 1(a)–1(c) is the strong initial increase of conductance at thicknesses below 10 nm, compared to the slope at higher thicknesses. This is found both for Cu_2O and CuO . Figs. 1(d) and 1(e) reveal the different thicknesses, at which the onset of conduction occurs. The root mean square (RMS) roughness of ATO-based substrates is about 5 nm, which explains the observed higher conduction onset thickness compared to q/ Al_2O_3 and q/ Bi_2O_3 . The quartz-based substrates have a similar RMS roughness of 0.4 nm. The reason for the relatively high onset thickness on quartz compared to q/ Al_2O_3 and q/ Bi_2O_3 is therefore supposed to be related to a different substrate-film interaction. In Figure 1(f), it is noteworthy, that for thicknesses below 5 nm, the conductance of Cu_2O is nearly identical to CuO .

B. XPS analysis

Depending on film thickness, systematic changes in Cu $2p_{3/2}$ satellite intensity from the Cu_2O films could be identified by XPS. Figure 2 shows the Cu $2p_{3/2}$ spectra of all Cu_2O thicknesses on q/ Al_2O_3 as representative example. In order to obtain a semi-quantification of the relative amount of satellite emission with respect to film thickness, the following procedure was applied to each experiment: The background was removed according to the method of Shirley in the binding energy range of Cu $2p_{3/2}$ including the satellite region (around 927 eV–948.5 eV). Then, the areal intensity of this region was calculated, and the spectra were normalized to the respective area. The difference between the spectra of each thickness and of the final film was then calculated and integrated in the region, where Cu $2p_{3/2}$ satellites typically appear (around 938.3 eV–945.8 eV). The relative satellite sensitivity of Cu_2O is zero by definition and around 0.3, when calculated for CuO .

The relative intensity of the Cu $2p_{3/2}$ satellite emission with respect to the main line intensity is plotted against Cu_2O film thickness in Figure 3(a). In order to compare the data to the conductance results, the conductivity σ is shown in Figure 3(b). A general accordance of $\text{Cu}(\text{II})$ satellite

FIG. 1. *In situ* reduced conductance data are shown with respect to increasing copper oxide thickness (a)–(c) on linear and (d)–(f) on double-logarithmic scale. The type of substrate is indicated, using the same nomenclature as in Table I. (c), (f) The data on CuO, in comparison to Cu₂O on ATO (2). The values left of the broken line correspond to the uncoated substrate (at arbitrary thickness).

intensity and conductivity is apparent. However, the maximum satellite intensity is generally observed at lower thicknesses than the maximum conductivity. Note that the substrate ATO (1) had been heated at 200 °C in 0.5 Pa oxygen for 2 h prior to film deposition. This additional surface cleaning step may be the reason for the lower satellite intensity compared to that of Cu₂O on ATO (2). However, this does not affect the film conductivity, which is similar for both samples.

C. Morphology

There is obviously a relationship between the excess conductivity and the Cu(II)-related satellite intensity,

FIG. 2. Spectra of the Cu 2p_{3/2} satellite region of copper oxide on q/Al₂O₃ are shown as example to illustrate the thickness-dependent amount of Cu(II) satellite emission and the procedure for semi-quantification. The blue curve is the spectrum after the final deposition step, which is supposed to represent pure Cu₂O. The dark brown to light brown curves are the spectra at intermediate thicknesses. The green curve represents data of CuO.

observed at low and intermediate Cu₂O thicknesses. In order to investigate whether grain boundaries have an effect on conductivity, the morphology of Cu₂O is included into the analysis. XRD has shown the material to be of

FIG. 3. (a) The relative amount of Cu 2p_{3/2} satellite emission is displayed with respect to Cu₂O film thickness. XPS data of intermediate film thicknesses on ATO (2) has been acquired only at a thickness of 2.8 nm. (b) Conductivity with respect to Cu₂O thickness as calculated from reduced conductance data.

FIG. 4. Cross-sectional SEM images of Cu₂O (a) on corning glass and (b) on q/Al₂O₃.

polycrystalline cuprite phase without preferential crystallographic orientation, similar to the previous work.³⁷ No CuO phase could be detected by XRD (not shown here). Cross-sectional SEM images of Cu₂O on corning glass and q/Al₂O₃ are displayed in Figure 4. A fibrous grain structure is found, with a lateral grain size which increases with thickness.³ AFM topographies have been used to obtain a rough estimate of the grain size at the surface after complete film deposition. An average value of 35 ± 15 nm was obtained, without systematic dependency on the substrate material.

Conductive atomic force microscopy (CAFM) was measured to obtain direct evidence for an increased grain boundary conductivity. The best results were obtained on a 100 nm thick sample deposited on ITO-coated glass in a commercial stand-alone sputtering chamber by AJA International. On these samples, Cu₂O phase purity without preferential crystallographic orientation was confirmed by XRD and optical transmittance spectroscopy (not shown here). Topography and current map are presented in Figure 5. The thin bright lines of increased current between the grains are clear evidence for the increased grain boundary conductivity.

IV. DISCUSSION

When the lateral grain size L increases with thickness according to Equation (1), the volume fraction of grain boundaries decreases with increasing thickness. Consequently, if a grain boundary effect is at play, enhanced conductance at low thicknesses can only be explained by the existence of more conductive grain boundaries with respect to the grain interior. Göbel *et al.* have described the increase in grain boundary conductance for the columnar morphology of their samples by a model of cuboid grains of horizontal dimensions L and a vertical extension equal to the film thickness d .⁴⁹ Grain boundaries perpendicular to the current flow are

FIG. 5. (a) Topography and (b) current map of Cu₂O on ITO-coated glass.

neglected. The total reduced conductance Y with respect to thickness is expressed as parallel connection of grain conductance Y_{grain} and grain boundary conductance Y_{GB}

$$Y = Y_{\text{grain}} + Y_{\text{GB}}. \quad (3)$$

The situation is illustrated in Figure 6(a). Figure 6(b) shows a schematic representation of a film morphology with linear cone faces ($n = 1$). Upon an increase in average grain size L with d , regions close to the substrate interface remain at smaller L than regions close to the film surface. For this reason, the total conductance needs to be integrated over thickness

$$Y(d) = \int_0^d \sigma^*(z) dz. \quad (4)$$

When dividing $Y(d)$ by the film thickness d according to Equation (2), an average value for conductivity of the inhomogeneous thin film is obtained. An expression for $\sigma^*(z)$, which satisfies the interpretation by Göbel *et al.*, is given in the following equation:

$$\sigma^*(z) = \sigma_{\text{grain}} \frac{L(z)}{L(z) + W} + \sigma_{\text{GB}} \frac{W}{L(z) + W}, \quad (5)$$

σ_{GB} and σ_{grain} are the respective conductivities of grain boundary and grain. The grain boundary width W is below a nanometer, since it describes a rather highly doped region.⁴⁹ Figures 7(a) and 7(b) show results from the model, calculated with $W = 0.5$ nm. In the calculation, the grains begin to grow laterally only at a thickness of 1 nm, which is supposed to account for an interface layer of high conductivity, equal to σ_{GB} . The conductivity inside the grains is chosen equal to monocrystalline Cu₂O and the grain boundary conductivity is within the range of typical values for CuO (0.01 S cm^{-1} as single crystal and 1 S cm^{-1} as thin film, sputtered-deposited at room temperature).^{25,26,30} All curves have been calculated with $\sigma_{\text{grain}} = 10^{-6} \text{ S/cm}$ and $\sigma_{\text{GB}} = 0.1 \text{ S/cm}$. For comparison, Fig. 7(c) reproduces the measured conductivities on the same scale. Due to the limited amount of data points at different thicknesses for each substrate material, a reliable fitting of the data could not be conducted.

Fig. 7(a) illustrates the effect of different $L(z)$ on the calculated conductivity. Apart from of the linear relation ($n = 1$), a square dependency ($n = 2$) in red and a cubic one ($n = 3$) in gray are displayed. The more drastic the initial increase in L , the stronger is the conductivity decay with

FIG. 6. (a) The two parallel currents through the grain boundary (red) and through the grains (blue) are illustrated, together with the respective conductances. (b) Schematic representation of the film morphology, where L is the grain size, W is the width of the grain boundary, and d is the film thickness along z .

FIG. 7. Effective conductivity from calculation for different (a) grain growth models $L(z)$ and (b) interface layer thicknesses. The final grain size of $L=40$ nm is similar to the experimentally obtained values. (c) Conductivities from the experiment are shown with the same symbol coding as in Figs. 1 and 3.

increasing thickness. Fig. 7(b) shows that a similar change in σ can be obtained by considering an interface layer with conductivity equal to σ_{GB} and a monocrystalline bulk material of σ_{grain} .

It is apparent from Figure 7 that thickness-dependent analysis of conductance alone cannot distinguish whether an enhanced conductivity at low thickness is due to an interface or a grain boundary effect.⁴⁹ For this reason, additional experimental evidence needs to be considered. In the previous study, conductivity measurements on CuO thin films of different grain sizes with respect to temperature and atmosphere revealed the existence of more conductive grain boundaries in this material.³⁰ In the light of the present discussion, this corresponds well to the initially enhanced conductivity in CuO displayed in Figures 1(c) and 1(f). For bulk samples of Cu₂O, there is evidence in the literature to support the idea of the increased grain boundary conductivity.^{22,23} The Hall effect measurements on Cu₂O thin films by Lee *et al.* confirm this, although not discussed by the authors: As the average grain size is reduced by two orders of magnitude, (1) carrier concentration increases while mobility decreases up to the point that no stable Hall voltage is obtained. Simultaneously, (2) the concentration of ionized impurities increases, which dominate charge carrier scattering at low temperature.³ An increasing

impurity concentration gradually changes the electrical properties of Cu₂O to be rather similar to CuO. Given the possibility of highly conductive grain boundaries, a segregation of defects in the grain boundary can correlate observation (1) with observation (2). Consequently, grain boundaries are concluded to be the cause for the increased conductivity at low film thickness, as presented in this article. The results presented here show that XPS is able to detect the relevant change in cation oxidation state to prove the existence of Cu(II). The increased Cu(II)-related intensity at low film thickness where grain size is expected to be relatively small suggests that Cu(II) is present at the grain boundaries of Cu₂O. It is important for this assignment that the analysis is carried out in dependence on thickness, non-destructively, and in vacuum, which prevents surface oxidation.

The Cu₂O films are apparently rich in oxygen at low thickness, despite no sign for non-stoichiometry at high thickness (see Table I). Under more reducing deposition conditions, the formation of Cu(0) becomes more likely. The width of the depletion layer, caused by the Cu/Cu₂O Schottky junction is 0.5–1 μ m.²⁴ In case Cu(0) segregates in the grain boundaries, grains of similar size as in the present study would be fully depleted and no thickness dependence of conductivity could be observed by the here applied experimental procedure.

Given that Cu(II) is present at the grain boundaries in Cu₂O thin films, the film may be approximated by Cu₂O grains separated by CuO grain boundary phases. Transmission electron microscopy could confirm the existence of a CuO phase between Cu₂O grains, however an *in situ* sample preparation procedure would be required to prevent additional oxidation by exposure to ambient air, which was not available. In case any CuO phase is formed, the interface between Cu₂O and CuO is important for determining the grain boundary properties. As a direct determination of the energy band alignment between Cu₂O and CuO is not possible using photoemission, the corresponding alignment is derived here using the transitivity rule according to $\Delta E_{VB}(\text{Cu}_2\text{O}, \text{CuO}) = \Phi_B(\text{Cu}_2\text{O}, M) + \Phi_B(M, \text{CuO})$. Φ_B is the Schottky barrier for holes at the corresponding interface. M represents a common metal. This procedure has been successfully applied to interfaces of semiconducting oxides.^{50,51} Figure 8(a) schematically shows Fermi energies in Cu₂O and CuO at the contacts to RuO₂, ITO, and Au. The data have been obtained by photoemission according to the method by Kraut *et al.*⁵² and are partially taken from the previous studies.^{30,37,53} The valence band discontinuity between CuO and Cu₂O is 0.2 eV. In the case of a grain boundary segregation of CuO in Cu₂O, a schematic energy band alignment as sketched in Figure 8(b) will occur. The higher valence band maximum at the grain boundaries immediately explains the higher carrier concentration and therefore the higher conductivity of the grain boundary.

V. CONCLUSION

The analysis of conductance with respect to film thickness in UHV conditions has shown increased conductivity in polycrystalline Cu₂O thin films at low thicknesses. By

FIG. 8. (a) Fermi energies in the band gap of CuO and Cu₂O at the contact to different metals. Valence band and conduction band are designated as VB and CB, respectively. (b) Schematic energy band alignment between grains of Cu₂O and grain boundaries of segregated CuO.

simultaneous XPS measurement, this could be related to the occurrence of Cu(II), giving rise to a rather oxygen-rich region at low thickness, even in case of ideal stoichiometry at the surface of the final film. These extrinsic defects are likely to segregate to the grain boundaries, causing the electrical properties of the same to be similar to CuO and masking the low carrier concentration and high hole mobility of Cu₂O thin films. As grains grow with increasing thickness, the strongest conductivity enhancement occurs at the interface to the substrate. Additional effects at the interface also have to be considered, as they cannot be ruled out by this method. One requirement for fabrication of low-cost transparent electronics is a thin p-type semiconducting oxide, deposited at low temperature. The presented results provide an explanation for widely encountered difficulties in achieving this with Cu₂O. The high conductance of grain boundaries might also be responsible for the low conversion efficiencies of solar cells prepared from Cu₂O thin films.

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