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Using photoelectron spectroscopy, we investigate the band alignments of the Cu₂O/ZnO heterointerface and compare the findings with the corresponding values for Cu₂O/GaN. While for Cu₂O/ZnO, we find a valence band offset (VBO) of 2.17 eV and a conduction band offset (CBO) of 0.97 eV, both values are considerably reduced for Cu₂O/GaN where the numbers are 1.47 eV (VBO) and 0.24 eV (CBO), respectively. The large CBO between ZnO and Cu₂O will very likely result in low photovoltaic power conversion efficiencies as is the current status of Cu₂O/ZnO solar cells. © *2012 American Institute of Physics.* [doi:10.1063/1.3685719]

Making photovoltaics (PVs) a reliable and sustainable source of energy requires a critical look at the availability of the elements used in the construction of the cell modules. Indium and Tellurium have been identified as critical raw materials which could limit the growth of the corresponding PV technologies, i.e., $CuInGaSe_2$ (CIGS) and CdTe, respectively.[1] When thinking about alternatives, Cu_2O is often named as a promising material, its sustainability, non-toxicity, and ease of formation of thin films on a large scale by industrial techniques, such as sputtering, are some of the pros. In terms of optical and electronic properties, there are serious restrictions: the room temperature energy band gap of 2.1 eV of Cu_2O results in an attainable efficiency limit of ~20% using the AM1.5 spectrum normalized to 1000 W/m². The absorption coefficient is only slowly rising with higher energies (above 2.5 eV), finally reaching values of around 10^5 cm^{-1}, where the maximum attainable efficiency has decreased to 17%.[2] Although being a p-type semiconductor by nature, with hole concentrations being controllable by nitrogen doping,[3] mobilities in thin films based on sputtering deposition techniques are lower by a factor of more than 100, if compared to single crystals or films with large grain sizes (>10 μm). As there is apparently no n-type Cu_2O available, solar cells have to be constructed as heterojunctions with an n-type, wide band gap window material, typically out of the family of transparent conducting oxides. So in the past, many efforts have been concentrated on p-Cu_2O/n-ZnO heterojunctions,[3–7] despite the fact that simple estimates predict large valence (VBOs) and conduction band offsets (CBOs) between the two semiconductors (for a review, see Ref. 8). It was therefore our interest to determine the band alignments in Cu_2O/ZnO and to compare it to the band alignments in Cu_2O/GaN, since GaN has a nearly identical band gap energy.

The x-ray photoelectron spectroscopic (XPS) investigations were performed on a VG Instruments set up consisting of an UHV vacuum chamber equipped with a MARK II dual anode x-ray tube (Al Kα: 1486.6 eV; Mg Kα: 1253.6 eV). Spot size on the surface was 8×8 mm². By sputtering with argon, the surface could be cleaned, polished, and etched at a rate between 10 and 20 nm/h. The samples were prepared by RF magnetron sputtering (20 nm p-type Cu_2O on 400 nm n-type ZnO and 20 nm Cu_2O on 1-μm thick metalorganic chemical vapor deposition (MOCVD)-grown n-GaN templates). Immediately after growth, the samples were transferred into the XPS measuring system. All sputtered copper oxide samples were also checked by x-ray diffraction (XRD) to state that it is Cu_2O. We found a preferred orientation of (200) for Cu_2O.

To investigate the VBO of the heterostructures Cu_2O/ZnO and Cu_2O/GaN via photoelectron spectroscopy, the energy difference between the core level (CL) and valence band maximum (VBM) of the pure materials as well as between the core levels at the interface of the heterostructures are needed. The valence band offset is given by

$$\Delta E_{VBO} = \Delta E_{CL}^{Int} + (E_{CL}^{Cu_2O} - E_{VBM}^{Cu_2O}) - (E_{CL}^{X} - E_{VBM}^{X}) \quad (1)$$

with

$$\Delta E_{CL}^{Int} = E_{CL}^{X,Int} - E_{CL}^{Cu_2O,Int},$$

following the method from Kraut *et al.*[9] By means of the band gaps, the CBO can be calculated as

$$\Delta E_{CBO} = \Delta E_{gap} + \Delta E_{VBO,} \quad (2)$$

with

$$\Delta E_{gap} = E_{gap}^{Cu_2O} - E_{gap}^{X}, \quad (3)$$

where X = ZnO for Cu_2O/ZnO and X = GaN for Cu_2O/GaN.

Figure 1 shows the XPS spectra of the pure materials (a)-(c) and of the heterostructures (insets). The surface of the pure materials was cleaned via argon sputtering for half an hour before the region from the 3p core level to the valence band edge was measured (a)-(c). The binding energy of the photoelectron signals was determined at FWHM by using Voigt functions. A linear function was used to fit the valence band edges of the XPS spectra, where the intersection with horizontal background, fitted in the same manner, unveils the approximate energetic position of the VBM (Figure 2). Because of the surface sensitivity of XPS experiments, the thin Cu_2O layers on top were removed step by step via argon

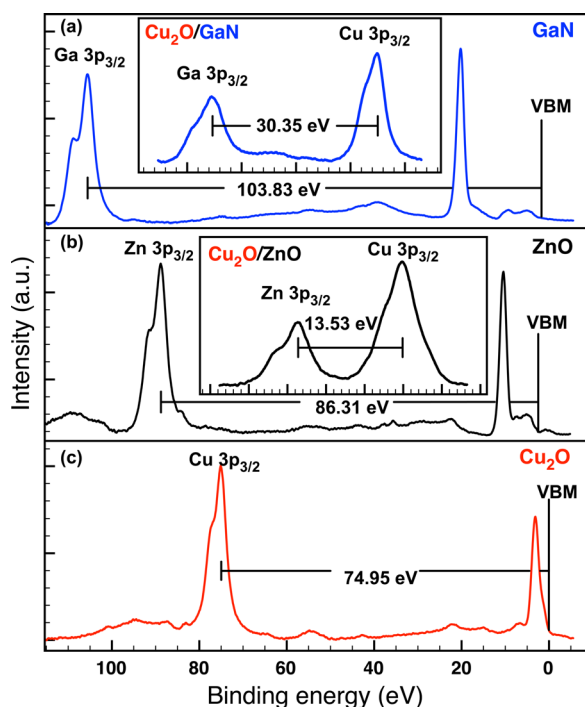a)Author to whom correspondence should be addressed. Electronic mail: Benedikt.G.Kramm@physik.uni-giessen.de.

FIG. 1. (Color online) XPS spectra of the pure materials (a) GaN, (b) ZnO, and (c) Cu_2O. The insets show the XPS spectra of the heterostructures (a) Cu_2O/GaN and (b) Cu_2/ZnO.

TABLE I. Binding energies for the core level, VBM, and the band gap energy.

	Cu_2O (eV)	ZnO (eV)	GaN (eV)	Cu_2O/ZnO (eV) (Interface region)	Cu_2O/GaN (eV) (Interface region)
Zn $3p_{3/2}$	—	88.78	—	88.61	—
Ga $3p_{3/2}$	—	—	105.55	—	105.34
Cu $3p_{3/2}$	74.98	—	—	75.08	74.99
VBM	0.03	2.47	1.72	—	—
E_{gap}	2.17	3.37	3.40	—	—

bombardment until nearly equal intensities of the core level signals at the interface were reached. The core level positions of both materials at the interface were investigated. From the depth profiling, the interface range is estimated between 10 nm and 20 nm. The values of the binding energies are listed in Table I. The C 1s signal from carbon was used for charge correction.

Finally, Eqs. (1) and (2) are used to obtain the values for the VBOs and CBOs. The calculated error for the band offset values is in the range of 0.20-0.40 eV. The results are summarized in Table II. Figure 3 shows the band alignments of ZnO, GaN, and Cu_2O with respect to each other, as obtained from the experimentally determined band offsets.

We now compare our results with recent theoretical and experimental studies. Ichimura[10] performed calculations on two types of interfaces based on a density functional, pseudo potential method. In the first, the oxygen atoms are arranged at the interface as in ZnO, in the second as in Cu_2O (values in round brackets in Table II). The valence band offsets range between 1.3 and 1.6 eV. Their experimentally measured VBO and CBO values 1.7 eV and 0.5 eV (values in square brackets in Table II) matches well with the theoretical calculations of the second model. The discrepancy of about

0.5 eV to our band offset values is partially due to the fact that the Cu_2O films from Ichimura and Song[10] have a (111) orientation unlike ours. Furthermore, the authors used the Cu 3d and Zn 3d level as core level to determine the valence band offset via XPS, knowing these are valence band states. The influence of the heterointerface to the valence band states probably another reason for the difference to our band offset values. Robertson and Clark[11] used local density approximation (LDA) with a screened exchange hybrid density functional. As can be seen from Table II, their values come close to the experimental values, especially in the case of Cu_2O/GaN. Wong *et al.*[12] used x-ray photoelectron spectroscopy for a heterojunction of Ga-doped ZnO with Cu_2O and obtained significantly higher values for the CBO and VBO. Ozawa *et al.*[13,14] performed x-ray photoelectron (and angle resolved) spectroscopy, and as can be seen from Table II, their values nicely agree with ours. In general, the XPS results of this work and in the references are in the range of the band offsets[13–17] estimated via Andersons law,[18] an established theoretically model for calculating band offsets, using electron affinities of 3.2–3.3 eV for Cu_2O and 4.1–4.2 eV for ZnO.

For the Cu_2O/GaN heterostructure, there is only the theoretical work of Robertson and Clark[11] to compare to, and as mentioned above, there is an excellent agreement with the experiment. Assuming transferability, one can estimate the band offsets between ZnO and GaN from the CBOs and VBOs of the heterostructure systems Cu_2O/ZnO and Cu_2O/ GaN (see Table II), which are to be compared to the theoretical and experimental data of Robertson and Clark,[11] Hong *et al.*,[19] and Liu *et al.*[20] Hong *et al.* gave two values, before and after cleaning (value in brackets) with Ar^+-ion irradiation of the surfaces, while Liu *et al.* investigated the influence of polar and non-polar (values in brackets in Table II) surfaces on the CBO and VBO.

As to a transparent conducting front contact in heterojunction solar cells, GaN and ZnO share many properties; among them the nearly identical band gap energy of around
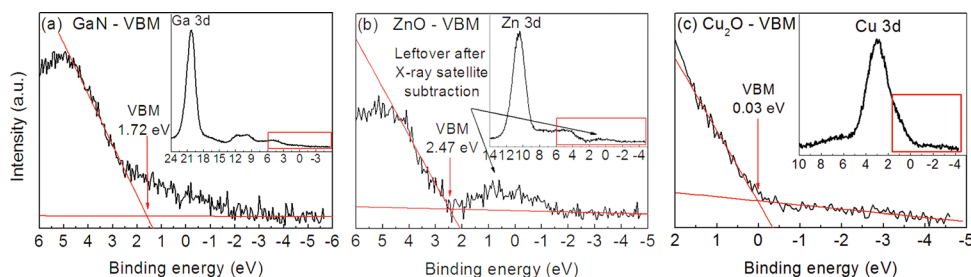

FIG. 2. (Color online) Determination of the valence band maximum by linear extrapolation with two functions. High resolution XPS valence band spectra (insets) of the bulk materials (a) GaN, (b) ZnO, and (b) Cu_2O were used.

TABLE II. Band offsets for the heterostructures.

System	VBO (eV)	CBO (eV)	Reference
Cu$_2$O/ZnO	2.17	0.97	this work
	1.3 (1.6) [1.7]	0.1 (0.4) [0.5]	10
	2.4	0.8	11
	2.82	1.81	12
	2.3	1.0	13 and 14
	2.4	1.0	13 and 14
	2.27	1	15
	2.2	1	16 and 17
Cu$_2$O/GaN	1.47	0.24	this work
	1.4	0.3	11
ZnO/GaN	0.70	0.73	this work
	1.0	0.8	11
	1.0 (0.8)	—	19
	0.7 (0.9)	0.8 (1.0)	20

3.3–3.4 eV. In solar cell applications, the heterojunctions ZnO/Cu$_2$O and GaN/Cu$_2$O are to be characterized as window-absorber structures, i.e., an electron current is needed to cross the interface. The holes are to be extracted by ultimately employing a metal back contact. Here, a Schottky barrier of the wrong kind has to be avoided in any case, which can be achieved by using gold contacts. Minemoto *et al.*[21] calculated the behavior of such solar cell devices against the value of the conduction band offset. Is the conduction band of the absorber much lower (>0.4 eV) than the conduction band of the window layer, the electrons cannot overcome the energy step and the short circuit current brakes down. On the other hand, if the conduction band of the absorber gets higher than the conduction band of the window layer, the electron hole recombination rate increases with the CBO and the open circuit voltage decreases simultaneously. Thus the optimal power conversion efficiency for such devices results for aligned conduction bands. The alignment of the conduction bands can be made possible by alloy-

ing GaN with Al. In Al$_x$Ga$_{1-x}$N, the band gap increases from 3.4 to 6.2 eV,[22] about 65% of the band gap difference is accommodated in the conduction band (up shift) and 35% in the valence band (down shift).[23] Thus, an Al-content of around $x = 0.2$ will be sufficient to align the conduction bands in Cu$_2$O and Al$_x$Ga$_{1-x}$N. For such small Al-contents, the electrical properties of the films are still excellent and easily controllable.[24] For Cu$_2$O on ZnO, the conduction band offset is 0.97 eV. To align the conduction band by alloying with Mg is much more difficult. The Mg$_x$Zn$_{1-x}$O alloy system shows a phase separation at around $x = 0.5$ from wurtzite to rock salt structure.[25] At $x = 0.5$, the band gap has increased from 3.3 ($x = 0$) to around 4.4 eV ($x = 0.5$).[25] This band gap difference is distributed to 70% to the conduction band and 30% to the valence band (as for AlGaN/GaN a type-I alignment).[26] So even for the highest composition, an offset in the conduction band between Mg$_x$Zn$_{1-x}$O and Cu$_2$O of 0.2 eV remains.
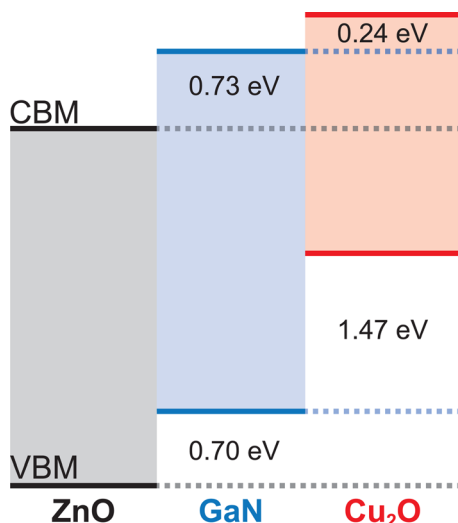
FIG. 3. (Color online) Band alignment for the heterostructures ZnO/GaN, Cu$_2$O/GaN, and Cu$_2$O/ZnO.

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