

# Interface Stoichiometry Control in ZnO/Cu<sub>2</sub>O Photovoltaic Devices

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**Abstract** — Cu<sub>2</sub>O is a potential earth-abundant alternative to established thin photovoltaic materials (CIGS, CdTe, etc.) because of its low cost, high availability, and inexpensive processing, but Cu<sub>2</sub>O has seen limited development as a photovoltaic device material owing to challenges in measurement and control of interface stoichiometry and doping. We report measurements of Cu<sub>2</sub>O interface stoichiometry and the effect of interface composition on heterojunction device performance. ZnO/Cu<sub>2</sub>O interface stoichiometry was varied by adjusting the ZnO window layer deposition conditions and stoichiometry was measured by X-ray photoelectron spectroscopy. Current-voltage characteristics of ZnO/Cu<sub>2</sub>O heterojunctions indicate open circuit voltages of  $V_{oc} \sim 530$  mV for devices where the Cu<sub>2</sub>O layer is stoichiometric at the interface and  $V_{oc} \sim 100$  mV for devices where Cu<sub>2</sub>O is nonstoichiometric at the interface.

**Index Terms** — copper compounds, oxygen, photovoltaic cells and semiconductor materials.

## I. INTRODUCTION

Cuprous oxide (Cu<sub>2</sub>O) is an interesting candidate as a solar absorber due to its low processing and material costs and the abundance of its component elements in the earth's crust. Furthermore, Cu<sub>2</sub>O has a direct gap and a detailed balance efficiency for a homojunction of  $\sim 25\%$  under AM1.5G illumination. It is a native p-type semiconductor with relatively high absorbance in the visible region above the gap [1, 2, 3]. Long minority carrier diffusion lengths and high hole mobilities have also been reported [1, 4, 5].

One of the major challenges to Cu<sub>2</sub>O photovoltaics has been the difficulty of creating devices with high quality interfaces. Cu<sub>2</sub>O is a uniquely reactive oxide due to its low enthalpy of formation, which is  $-176$  kJ/mol. Thus Cu<sub>2</sub>O may be both either oxidized or reduced easily, as it is in the copper (I) oxidation state. The effect of interface reactions on device performance has been well characterized for Cu<sub>2</sub>O Schottky diodes [1], but little is known about how interface reactions affect heterojunction device performance.

In this manuscript we describe the stoichiometry of Cu<sub>2</sub>O surfaces and Cu<sub>2</sub>O/ZnO interfaces. The phase of the samples was analyzed using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Photovoltaic devices with different interface compositions were also tested.

## II. EXPERIMENTAL

The Cu<sub>2</sub>O wafers used in these experiments were grown by thermal oxidation of copper foils (99.9999%, Alfa Aesar).

The copper foils were hung vertically from copper wires during oxidation. Cu substrates were heated to  $900$  °C in a tube furnace under nitrogen flow. This temperature was chosen because it is within the stability range of the Cu<sub>2</sub>O phase in the Cu-O phase diagram at 1 Torr O<sub>2</sub> [6, 7]. Samples were then oxidized for 24 hours at  $900$  °C and 1 Torr O<sub>2</sub>. Substrates were then cooled to room temperature under nitrogen flow.

ZnO was deposited on the Cu<sub>2</sub>O wafers by rf magnetron sputtering from a compound ZnO target. Samples were deposited at 100 W and a sputtering pressure of 5 mTorr. The heterojunction was sputtered under both a pure Ar atmosphere and a 0.25 mTorr partial pressure of O<sub>2</sub> in Ar.

XRD measurements were performed using a high resolution diffractometer; scans were performed using the  $\omega$ -2 $\theta$  geometry. The surface stoichiometry and interface stoichiometry of the samples were measured using high resolution XPS.

Photovoltaic devices were made from the ZnO/Cu<sub>2</sub>O heterojunctions sputtered under different O<sub>2</sub> partial pressures. 10 nm of ZnO was deposited on Cu<sub>2</sub>O both with and without O<sub>2</sub>. 50 nm of AZO and 100 nm of ITO were then sputtered as a top contact. Gold was sputtered for a back contact. Current density vs. potential measurements were performed both in the dark and under AM 1.5 1-sun illumination.

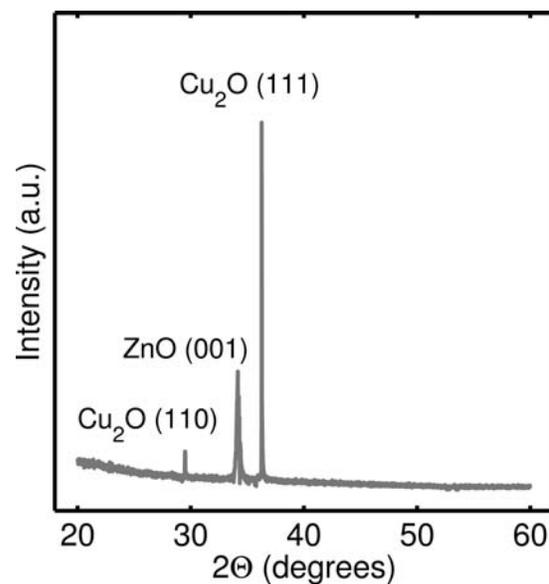


Fig. 1. Typical XRD spectra of ZnO deposited on Cu<sub>2</sub>O.

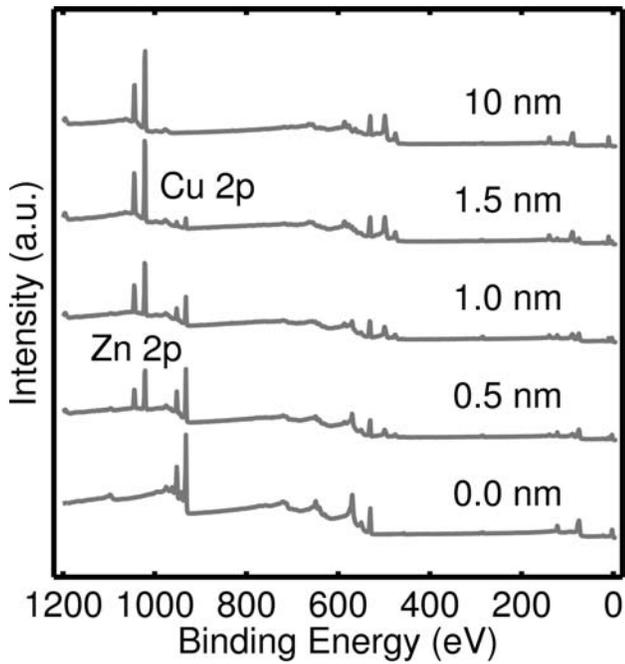


Fig. 2. XPS spectra of ZnO/Cu<sub>2</sub>O heterojunctions. Thickness of ZnO layer is indicated.

### III. RESULTS AND DISCUSSION

An XRD spectrum (see Fig. 1) for a typical ZnO/Cu<sub>2</sub>O heterojunction shows that the Cu<sub>2</sub>O wafers are phase pure, with no Cu or CuO present in the bulk form. The spectra also shows some preferential orientation for the (110) and (111) directions. These directions are the close packed planes so it is hypothesized that the grains nucleate with this preferential orientation to minimize surface energy. Furthermore the ZnO

is also phase pure with no Zn inclusions, even when sputtered in pure Ar. The ZnO also shows a strong texture along the c-axis, which is common in sputtered ZnO.

XPS spectra (see Fig. 2) were collected for bulk ZnO and Cu<sub>2</sub>O as well as for several thicknesses of ZnO on Cu<sub>2</sub>O. Thickness for the ZnO range from 0.5 nm to 1.5 nm such that the ZnO was electron transparent. This allows the stoichiometry of the Cu<sub>2</sub>O at the interface with ZnO to be measured by XPS. Peaks for both Zn and Cu can be seen in XPS spectra meaning we are indeed effectively probing the ZnO/Cu<sub>2</sub>O interface.

The stoichiometry of the interface was analyzed using high resolution XPS scans (see Fig. 3) of the Cu 2p<sub>3/2</sub> and Cu Auger peaks. Analysis of these peaks allows us to determine the oxidation state of Cu. The as grown Cu<sub>2</sub>O surfaces (0.00 nm) show some amounts of trace CuO. This is to be expected as Cu<sub>2</sub>O is the high temperature phase of copper oxide, and while the substrates are cooling they must pass through pressure and temperature conditions in which CuO is the thermodynamically favored phase. This leads to a layer of CuO on the surface, and the thickness of this layer can be predictably controlled by adjusting the cooling conditions.

ZnO was deposited on Cu<sub>2</sub>O under two different partial pressures of O<sub>2</sub>, 0.25 and 0.00 mTorr. The deposition conditions of the ZnO seem to have altered the interface stoichiometry of the Cu<sub>2</sub>O. When ZnO is deposited with O<sub>2</sub> (see Fig 3a), the Cu 2p<sub>3/2</sub> peak still has a shoulder, which indicates CuO at the interface. However, when ZnO is deposited without O<sub>2</sub> (see Fig 3b), this shoulder is no longer evident indicating the CuO layer is no longer present. We believe the lower amount of O<sub>2</sub> in the growth atmosphere makes the deposited ZnO slightly Zn rich, although not Zn rich enough to precipitate elemental Zn. The oxygen poor

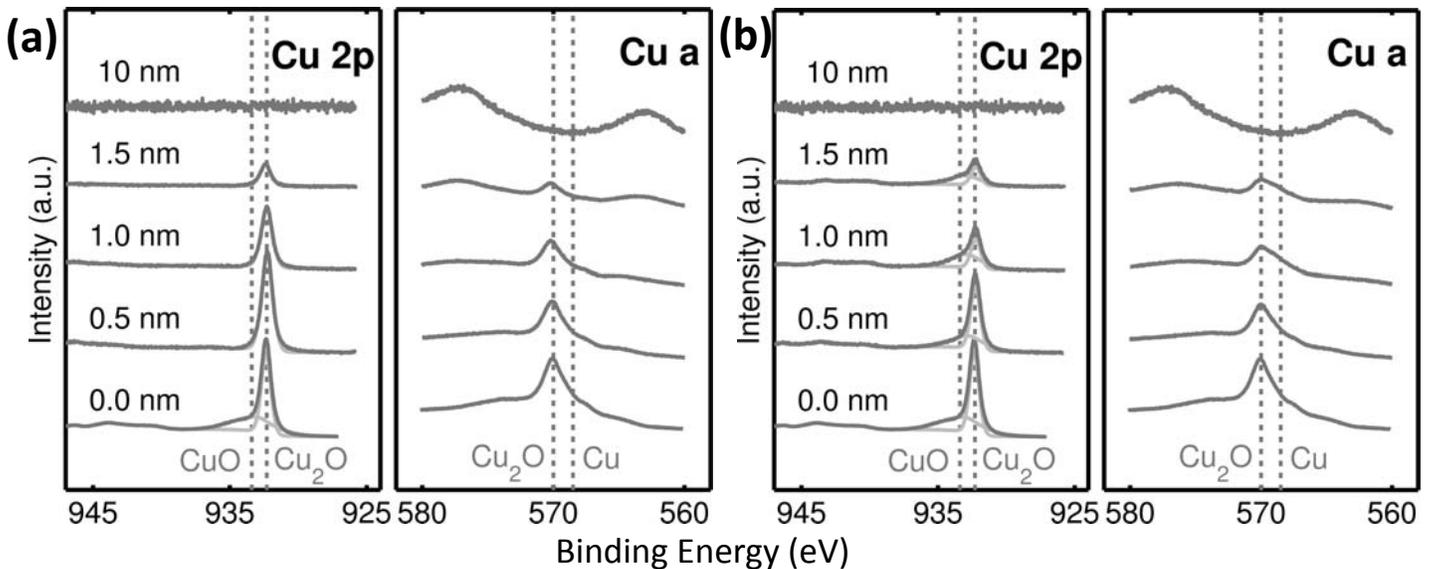


Fig. 3. XPS spectra for Cu 2p<sub>3/2</sub> peak and Cu Auger peak (a) ZnO on Cu<sub>2</sub>O deposited with 0.00 mTorr O<sub>2</sub>, thickness of ZnO is indicated. (b) ZnO on Cu<sub>2</sub>O deposited with 0.25 mTorr O<sub>2</sub>, thickness of ZnO is indicated.

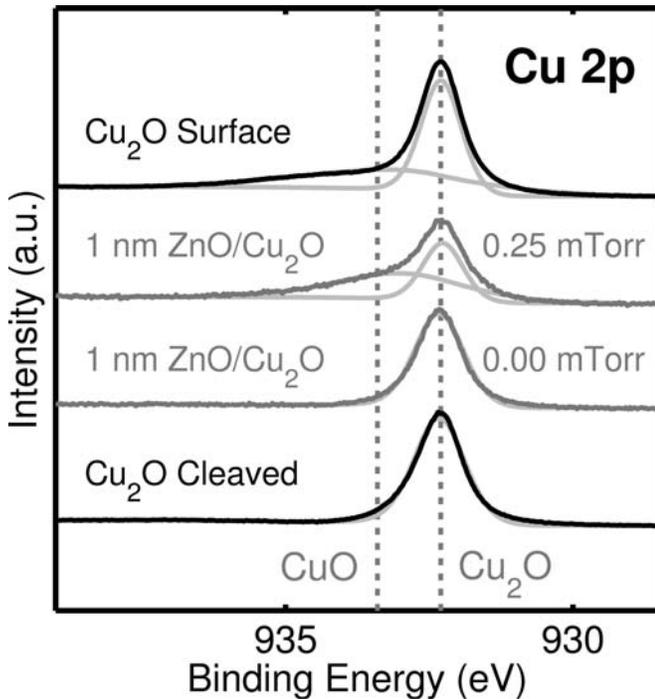


Fig. 4. XPS spectra for Cu  $2p_{3/2}$  peak for a  $\text{Cu}_2\text{O}$  wafer that has been cleaved in situ, 1 nm of ZnO/ $\text{Cu}_2\text{O}$  deposited with 0.00 mTorr  $\text{O}_2$ , 1 nm of ZnO/ $\text{Cu}_2\text{O}$  deposited with 0.25 mTorr  $\text{O}_2$ , and an as grown  $\text{Cu}_2\text{O}$  surface.

ZnO then reacts with the CuO layer to reduce it to  $\text{Cu}_2\text{O}$ , while the ZnO oxidizes slightly. The reaction then terminates once all the CuO is reduced, and analysis of the Cu auger peak shows no  $\text{Cu}_2\text{O}$  is reduced and no Cu is present. Because all deposited thickness show the same trend, we infer that this surface stoichiometry holds for thicker ZnO on  $\text{Cu}_2\text{O}$ .

We further analyzed the Cu  $2p_{3/2}$  peak (see Fig 4) for 1 nm ZnO/ $\text{Cu}_2\text{O}$  interfaces. We cleaved a  $\text{Cu}_2\text{O}$  wafer in situ in the XPS to obtain data for a stoichiometric interface. The Cu  $2p_{3/2}$  peak for the cleaved sample has no shoulder, indicating it is phase pure. The 1 nm ZnO/ $\text{Cu}_2\text{O}$  with 0.00 mTorr  $\text{O}_2$  has an identical peak shape to the cleaved sample, meaning it is indeed a stoichiometric interface. The 1 nm ZnO/ $\text{Cu}_2\text{O}$  with 0.25 mTorr  $\text{O}_2$  has a shoulder similar to the as grown  $\text{Cu}_2\text{O}$  surface, indicating there is CuO at the interface.

Differences in interface composition translated to differences in energy conversion efficiency in photovoltaic devices (see Fig. 5). Nine devices were made with ZnO deposited with a partial pressure of 0.25 mTorr  $\text{O}_2$  in the growth atmosphere. The devices had an average open circuit voltage of  $V_{oc} = 102.3 \pm 11$  mV. We hypothesize the layer of CuO present at the interface is probably pinning the Fermi level, limiting the diffusion voltage in the devices. Ten devices made with ZnO deposited in pure Ar had larger open circuit voltages with an average  $V_{oc} = 530.4 \pm 4$  mV.

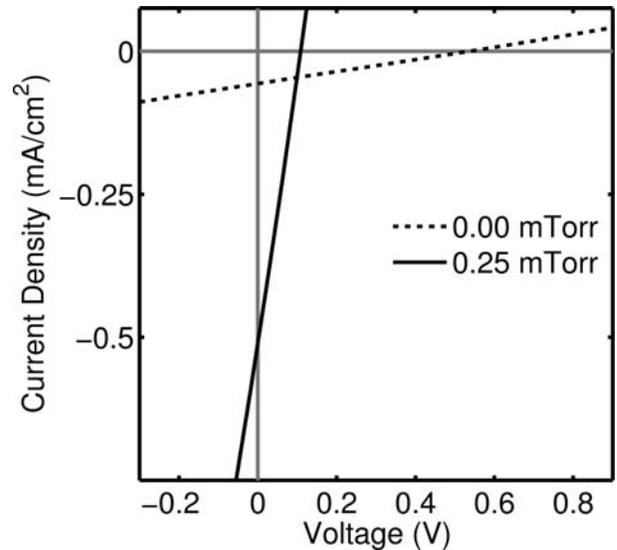


Fig. 5. Current density versus potential curves for ZnO/ $\text{Cu}_2\text{O}$  heterojunction devices. The partial pressure of  $\text{O}_2$  during deposition by rf magnetron sputtering is indicated. Devices made without  $\text{O}_2$  during deposition displayed higher open circuit voltages.

#### IV. CONCLUSIONS

We report a method for characterizing  $\text{Cu}_2\text{O}$  interface stoichiometry and used this technique to define deposition conditions for a stoichiometric ZnO/ $\text{Cu}_2\text{O}$  heterostructure photovoltaic device with increased efficiency. We have also demonstrated that a CuO layer formation at the interface appears to pin the Fermi level leading to reduced  $\text{Cu}_2\text{O}$  device efficiency.

#### ACKNOWLEDGEMENT

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