

Thin, Free-Standing Cu₂O Substrates via Thermal Oxidation for Photovoltaic Devices

Samantha S. Wilson, Chengxiang Xiang, Yulia Tolstova, Nathan S. Lewis, and Harry A. Atwater
California Institute of Technology, Pasadena, California, 91125, United States

Abstract — Cu₂O is a promising, earth-abundant alternative to traditional photovoltaic materials (CIGS, CdTe, etc.) because of its low cost, high availability, and straightforward processing. We report a method to fabricate Cu₂O substrates with thicknesses of less than 20 microns which may be handled and processed into devices. Development of thinner Cu₂O substrates is essential as extrinsic doping has been impossible thus far, and intrinsic Cu₂O is highly resistive. Hall measurements indicate that the substrates had Hall mobilities of 10-20 cm²V⁻¹s⁻¹ and carrier concentrations on the order of 10¹⁴ cm⁻³. Current-voltage characteristics of these Cu₂O substrates were derived from liquid junction Schottky barrier device measurements which indicate open circuit voltages of Voc ~ 600 mV.

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

I. INTRODUCTION

Cuprous oxide (Cu₂O) is an interesting candidate as a solar absorber due to its low processing and materials costs and the abundance of its component elements in the earth's crust. Furthermore, Cu₂O has a direct gap we measured to be 2.1 eV and a detailed balance efficiency for a homojunction of ~20% [1]. 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 Cu₂O photovoltaics has been the inability to dope the Cu₂O wafers extrinsically without negatively impacting minority carrier properties. There have been some reports of doping in Cu₂O, especially in thin films [6, 7, 8]. However, these results have either not been replicated in bulk wafers, or devices made with these dopants were less efficient than intrinsically doped Cu₂O wafers [9, 10]. The lowered efficiency of the doped devices was probably due to impurities creating new recombination paths for minority carriers. As a result, all recent high efficiency devices have been intrinsically doped [9, 11]. Intrinsically doped Cu₂O is highly resistive (~1,000 Ω-cm), leading to devices with poor fill factors. Since doping methods currently cannot reduce the resistivity of bulk wafers, we have looked into making ultrathin Cu₂O wafers.

In this manuscript we describe the electronic and structural properties of 20 micron Cu₂O substrates grown by thermal oxidation of 12 micron copper foils. The phase of the samples was analyzed using X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). The grain structure and sample thickness were analyzed using a scanning electron

microscope (SEM). The electronic properties were analyzed by Hall effect measurements. Devices made with liquid junctions that were not optimized are reported.

II. EXPERIMENTAL

The Cu₂O wafers used in these experiments were grown by thermal oxidation of copper foils (99.99%, ESPI Metals). The copper foils were supported during oxidation by 0.5-1 mm thick Cu. Cu substrates were heated to 1050 °C in a tube furnace under nitrogen flow. This temperature was chosen because it is within the stability range of the Cu₂O phase in the Cu-O phase diagram at atmospheric pressures of oxygen, (see Fig.1) [12, 13]. Samples were then allowed to sit in air for 30 minutes at 1030 °C. Substrates were then cooled to room temperature under nitrogen flow. The thicker Cu₂O frame was then used as a handle for the resulting 20 μm Cu₂O membrane. (see Fig. 2)

XRD measurements were performed using a high resolution diffractometer; scans were performed using the ω-2θ geometry. The surface stoichiometry of the samples was measured using XPS after the samples had been sitting in air for several days.

In order to perform Hall effect measurements, the thin wafers were removed from the thicker Cu₂O handles by

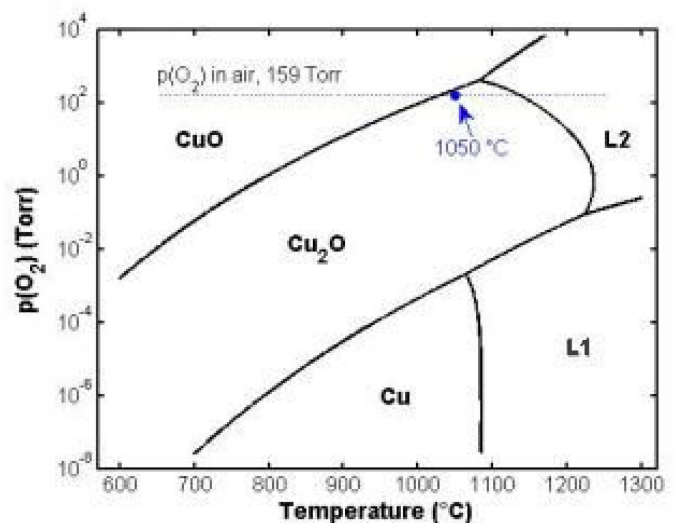


Fig. 1 Phase diagram for Cu-O system after Xue et.al. [12, 13] The dashed line indicates the partial pressure of oxygen in the atmosphere and the experimental conditions are marked by the blue dot.

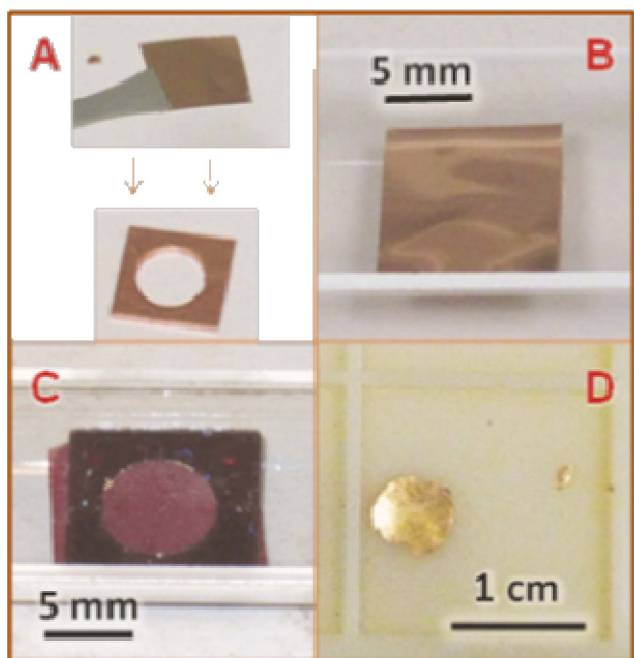


Fig. 2 Process for creating 20 μm free standing Cu_2O wafers is described. First 12 μm copper foils are placed on .5-2 mm thick copper (A). Stack is then placed into quartz boat (B). Stack is oxidized in furnace and fuses together (C). ~ 100 nm of gold is deposited on thin Cu_2O wafer and wafer is removed from thicker handle (D).

double stick tape and mechanically supported on a glass substrate. Samples were then shaped to be approximately square with an area 9 mm². Contacts were patterned in the corners of the mounted samples using gold paste, and room temperature Hall effect measurements were performed.

The Cu_2O membranes with thickness < 20 microns were removed from the thicker Cu_2O substrates after ~ 100 nm of gold was deposited by DC magnetron sputtering. Once the layer of metal was deposited, the thin substrates could be handled without breaking (see Fig 2D).

Current density vs. potential (J-E) measurements were taken in non-aqueous regenerative photochemical cells, which are described in detail in reference [14]. The gold coated Cu_2O substrates were sealed in epoxy and contacted with silver paste. The liquid junction was made with $\text{Cu}_2\text{O}/\text{CH}_3\text{CN}-\text{CoCp}^{2+/0}$, and data was collected at 50 mV s⁻¹ using a Princeton Applied Research (PAR 273) potentiostat. White light from a Sylvania ELH-type halogen bulb was passed through a quartz diffuser to provide the equivalent of air mass 1.5 illumination calibrated using a Si photodiode electrode inside the cell. The conventional three-electrode photoelectrochemical cells were assembled and tested in an inert atmosphere glove box.

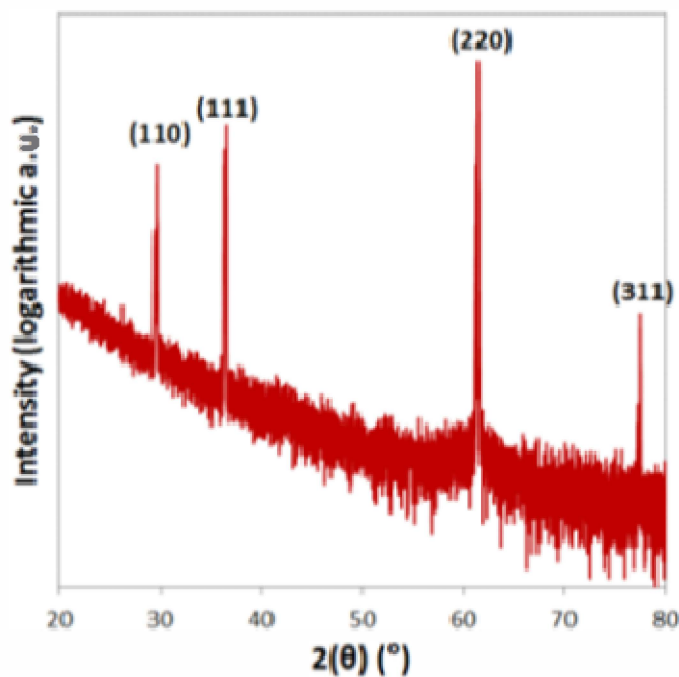


Fig. 3 XRD spectra for thin substrates. All peaks can be indexed as the Cu_2O phase.

III. RESULTS AND DISCUSSION

XRD data (see Fig. 3) shows that the Cu_2O 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 samples grow with this preferential orientation to minimize surface energy.

The SEM data (see Fig. 4) shows that the grain size of the wafers is large compared to the overall thickness of the sample. Typical grain size was 20-100 μm and the thickness varied across the samples from ~ 5 -20 μm . We have also measured diffusion lengths of Cu_2O wafers in the range of ~ 500 nm [14]. The grains spanned the entire height of the sample. A columnar grain structure with grain size much greater than the diffusion length is desirable for device applications, since in such a microstructure, photogenerated carriers suffer less grain boundary recombination relative to small-grain microstructures.

The XPS data (see Fig. 5) shows the $\text{Cu}(2p_{3/2})$ peak for a typical untreated substrate that has been left in air for a week. The spectra shows that the copper on the surface is mostly found in the Cu^{+1} oxidation state. This means that the surface is predominantly Cu_2O . The Cu_2O 2p_{3/2} peak did have a small shoulder which indicates there is some coverage of CuO , but it is less than a monolayer. CuO is the thermodynamically stable phase at room temperature, but conversion from CuO to Cu_2O

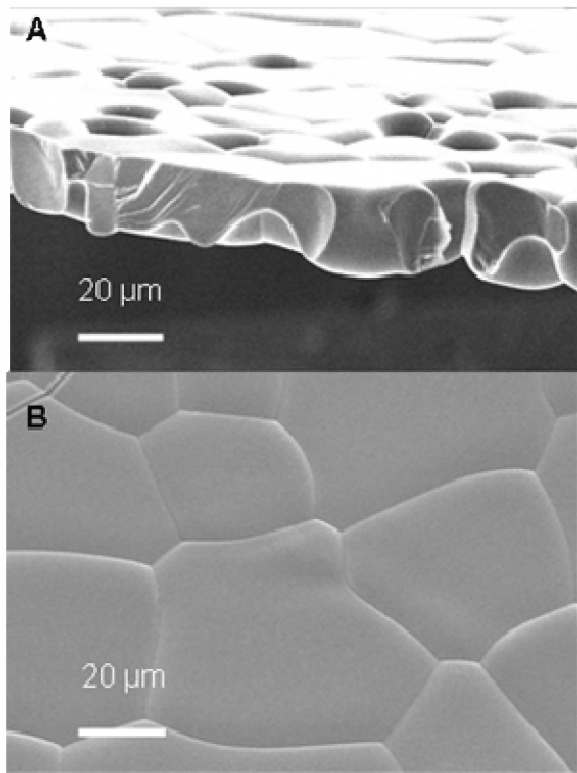


Fig. 4 SEM images of both a cross section (A) and the surface (B) of the Cu₂O substrates.

is slow. This makes Cu₂O kinetically stable at room temperature and pressure. This is shown by the fact that there was minimal growth of CuO after several days exposed to atmosphere. This kind of stability is ideal for a potential solar material. Also, the surface CuO can easily be removed by etching in nitric acid or by annealing in situ [14]. Furthermore, the surface of the wafers made by this bulk process is remarkably uniform and high quality due to the fact that this process requires no cutting or polishing steps. The processing needed to make these thin wafers is much easier and less wasteful than methods for making wafers of comparable thickness from other materials, such as silicon.

Current density vs. potential data (see Fig 6) was collected in contact with CH₃CN-CoCp₂⁺⁰ electrolytes. Cu₂O photoelectrodes with active areas of ~ 5 mm² were fabricated from several 20 μm thick wafers. In contact with CoCp₂⁺⁰ redox couple, the Cu₂O photoelectrode exhibited V_{oc} ~ 600 mV and energy-conversion efficiency of ~ 0.4%. The V_{oc} was comparable to V_{oc}'s made from thicker wafers with larger grains with the same liquid junction [14]. The design of the electrochemical cell was not optimized, as there is significant parasitic absorption in the solution and contact to the wafer was not optimized. These problems probably contribute to the low efficiency and fill factor. However, the J-E curves do show that shunting is a minimal problem for the devices. This

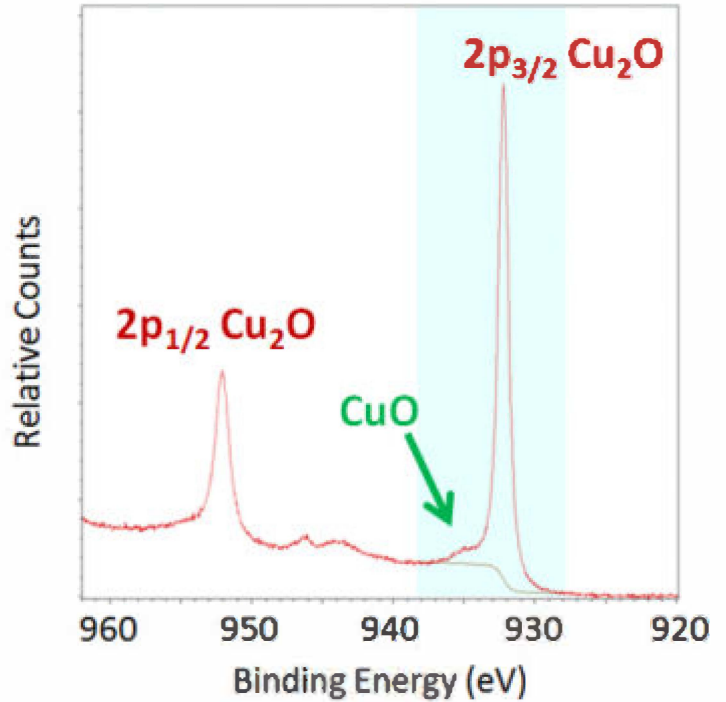


Fig. 5 XPS Spectra of Cu (2p_{3/2}) peak on untreated Cu₂O surface after one week in air.

is promising since it means if there are any pinholes in the devices, they are not having a significant impact on device performance. Therefore, from these results we can confirm that these wafers can be processed into devices with measureable efficiencies, and could potentially make efficient solid state devices.

IV. CONCLUSIONS

We report a novel approach to synthesizing thin (<20 micron) Cu₂O wafers by a bulk synthesis method. The procedure represents a relatively easy and low cost way to synthesize thin substrates compared to methods used for other materials. These substrates were phase pure Cu₂O with minimal CuO growth on the surface. The grains were on the order of 50 μm and penetrated all the way through the substrates. Furthermore we show that these substrates can be processed into devices by testing these wafers in a liquid junction cell.

ACKNOWLEDGEMENT

The authors acknowledge The Dow Chemical Company for funding and collaborating in this work.

REFERENCES

- [1] L. C. Olsen, F. W. Addis and W. Miller, "Experimental and Theoretical Studies of Cu₂O Solar Cells" *Sol. Cells*, vol. 7, pp. 247-279, 1982.
- [2] B.P. Rai, "Cu₂O Solar Cells: A Review", *Sol. Cells*, vol. 24, pp. 265-272, 1988.
- [3] F. L. Weichman, "Photoconductivity of Cuprous Oxide in Relation to Its Other Semiconducting Properties", *Phys. Rev.*, vol. 117, pp. 998-1002, 1960.
- [4] J. A. Assimos and D. Trivich, "Photovoltaic properties and barrier heights of single-crystal and polycrystalline Cu₂O-Cu contacts" *J. Appl. Phys.* Vol. 44, pp. 1687-1693, 1973.
- [5] A. O. Musa, T. Akomolafe and M. J. Carter, "Production of cuprous oxide, a solar cell material, by thermal oxidation and a study of its physical and electrical properties", *Sol. Energy Mater. Sol. Cells*, vol. 51, pp. 305 – 316, 1998.
- [6] S. Ishizuka, S. Kato, Y. Okamoto, and K. Akimoto, " Nitrogen doping into Cu₂O thin films deposited by reactive radio-frequency magnetron sputtering." *Jap. J. of Appl. Phys.* Vol. 40, pp. 2765, 2001.
- [7] S. Ishizuka, S. Kato, Y. Okamoto, and K. Akimoto, "Control of hole carrier density of polycrystalline Cu₂O thin films by Si doping. *Appl. Phys. Letters*, 80, pp. 950, 2002.
- [8] M. Wei, N. Braddon, D. Zhi, P. A. Midgley, S. K. Chen, M. G. Blamire, and J. L. MacManus-Driscoll "Room temperature ferromagnetism in bulk Mn-doped Cu₂O" *Appl. Phys. Lett.* Vol. 86, 072514, 2005.
- [9] A. Mittiga, et al., "Heterojunction solar cell with 2% efficiency based on a Cu₂O substrate", *Appl. Phys. Lett.*, vol. 88, 163502, 2006.
- [10] F. Biccari, "Defects and Doping in Cu₂O" Ph. D. Thesis, Sapienza, University of Rome, 2009.
- [11] T. Minami et al., "High-Efficiency Oxide Solar Cells with ZnO/Cu₂O Heterojunction Fabricated on Thermally Oxidized Cu₂O Sheets", *Appl. Phys. Express*, 4, 2011, 062301 (3 pages).
- [12] M. Okeeffe and W. J. Moore, "Thermodynamics of the Formation and Migration of Defects in Cuprous Oxide" *J. Chem. Phys.*, vol. 36, 3009-3013, 1962.
- [13] J. Xue and R. Dieckmann, "The non-stoichiometry and the point defect structure of cuprous oxide (Cu_{2-δ}O)." *J. Phys. and Chemist. of Solids*, vol. 51 (1990), 1263
- [14] C Xiang, et al. "820 mV open-circuit voltages from Cu₂O/CH₃CN junctions", *Energy Environ. Sci.*, vol. 4, pp. 1311-1318, 2011

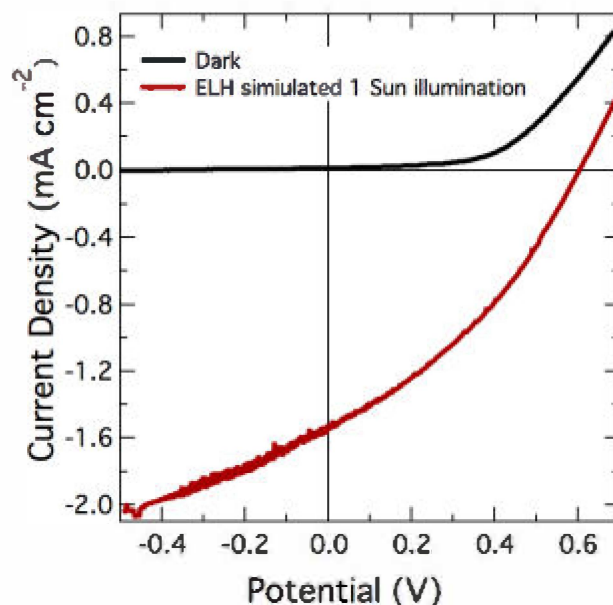


Fig. 6 Current density-potential characteristics of Cu₂O photocathodes in the dark (black trace) and under ELH-simulated 1 sun illumination (red trace) in contact with CH₃CN-1.0 M LiClO₄ containing 0.020 M CoCp₂⁺-0.002 M CoCp₂.