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Copper zinc oxide: Investigation into a p-type mixed metal oxide system

P.J.M. Isherwood
Centre for Renewable Energy Systems Technology, Wolfson School of Mechanical Electrical and Manufacturing Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK

Abstract

In photovoltaics, ZnO is widely used both as an n-type window and buffer layer and as the basis for a range of transparent conducting oxide (TCO) top contact materials. Whilst there are reports of p-type doping, there have been no successful attempts to create a p-type ZnO-based TCO. Synthesis of an effective p-type TCO could be of significant benefit, enabling further development of technologies such as bifacial and multi-junction devices. This study investigates the effects of combining ZnO with CuO, an intrinsically p-type narrow band-gap metal oxide, with the aim of synthesising a range of mid to wide band-gap p-type alloys.

Alloying ZnO with CuO gave a range of p-type films with varying electrical, optical and structural characteristics. XRD patterns show that as copper content was increased above 24.5% of the total metal content, crystal structure changed from a typical ZnO wurtzite structure to a CuO tenorite structure. A second change occurred at 35% copper with the emergence of two further tenorite peaks. These structural changes correlate to significant local increases in band-gap, visible and infrared transmission, and resistivity. These dramatic changes correspond to relatively minor compositional variations. Through careful control of the alloy composition it is therefore theoretically possible to tailor the material properties to suit a wide range of applications, both in photovoltaics and in other fields.

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1. Introduction

Transparent conducting oxides (TCOs) are the dominant class of transparent conductive material [1,2]. Their uses are enormously varied and extremely widespread, from computer screens, flat-screen televisions and smartphone displays to thin-film photovoltaics, smart windows and transparent electronics [1–4]. They are wide band-gap metal oxide semiconductor materials which have been doped to such a high level that they become degenerate, exhibiting metallic conductivity [2].

The vast majority of metal oxide semiconductors are natively n-type [2,5]. Over the years, many groups have looked at ways of changing the primary carrier type in materials such as zinc oxide, tin dioxide and indium oxide with mixed success [6]. Others have worked with some of the few intrinsically p-type metal oxide materials, particularly the copper oxides (Cu2O and CuO). These latter materials have relatively narrow band-gaps, making them of interest as solar absorbers (Cu2O is one of the most studied photoactive semiconductors) and solar cell back contact materials, but of limited use as TCOs [5,7–12]. Other p-type oxides that have shown some promise include ZnRh2O4, NiO, CuAlO2, CuSrO2 and Cr2O3 [5,13–15].

Zinc oxide (ZnO) is a commonly used wide band-gap n-type semiconductor [16,17]. In photovoltaics, it is typically used as a buffer layer in its intrinsic form or as the transparent top contact when doped with aluminium [18,19]. P-type ZnO could have uses as a p-type transparent conductor and as a back contact electron reflector layer, and could enable development of n-type absorber layers by acting as a transparent donor layer in a heterojunction device. It has also been suggested for use in other fields such as transparent electronics, UV resistant materials and the synthesis of all-oxygen UV lasers and LEDs [6,17,20]. In common with most other metal oxides however synthesis of p-type ZnO is challenging [16,17].

P-type ZnO has been synthesised using a wide range of dopants and doping techniques [17,20–23]. The most successful results have largely been obtained using nitrogen as a dopant, which is in agreement with density functional theory (DFT) calculations.
Several groups have reported p-type ZnO doped with copper (e.g., [23,24]). Because the copper 3d subshell is energetically close to the oxygen 2p subshell, it has the effect of spreading the valence band and reducing the hole localisation effect typically exhibited by oxygen atoms in metal oxides. The result is a reduced hole effective mass, and hence increased hole mobility [5,10,25]. By alloying copper oxides with wider band-gap metal oxides, it is thought that synthesis of p-type materials with increased band-gaps could be achievable. This study investigates co-sputtering ZnO with cupric oxide (CuO).

2. Experimental details

CuO and ZnO were co-sputtered using an AJA International Orion 8HV sputter coater. CuO was deposited using an AJA International 600 series RF power supply, and ZnO was deposited using an Advanced Energy pulsed DC supply. Pressure was maintained at 1 mTorr (0.133 Pa). Films were deposited at room temperature. Argon flow rate was maintained at 7 standard cubic centimetres per minute (SCCM) and pure oxygen input was maintained at 4 SCCM, resulting in an oxygen partial pressure of 0.048 Pa. ZnO power was varied from 105 W to 180 W, and CuO power was varied from 120 W to 60 W.

Characterisation of deposited films involved measuring film thickness, sheet resistance, transmission and Hall mobility, analysis of material composition and crystal structure, and observation of the film surface using SEM. Transmission was measured using a Varian Cary 5000 spectrophotometer, and film band-gaps were calculated from transmission data using the Tauc method [26]. Thickness was measured using an Ambios XP2 stylus profilometer, and Hall mobility measurements were carried out using an Ecopia HMS 3000 Hall effect device. Carrier type was confirmed by exploiting the Seebeck effect and measuring the output voltage. Sheet resistance was measured using a four-point probe, and these data were used to verify the resistivities measured using the Hall effect system. SEM was carried out using a Carl Zeiss Leo 1530 VP field emission gun scanning electron microscope. The aperture size was 30 μm and the operating voltage was 5 kV. Images were taken using a secondary electron detector at 50,000 times magnification.

Crystal structure was examined by X-ray diffraction (XRD) using a Bruker D2 Phaser benchtop diffractometer equipped with a Cu-Kα X-ray gun and a lynxeye™ detector. The beam slit was 1 mm wide, and the anticratter plate was positioned 3 mm above the sample. Samples were rotated at 15 rpm. Compositional data were obtained using a Thermo Scientific K-Alpha™ X-ray photoelectron spectrometer equipped with a monochromated Al-Kα X-ray gun (hv = 1486.6 eV), an EXO6 ion source, and a 180° double focussing hemispherical 128 channel analyser. Measurements were run at a base pressure of 3 × 10⁻⁷ mBar. The survey scan range was 0–1350 eV, with a pass energy of 200 eV. Step size was 1 eV. Data were collected over 10 scans, with 10 m dwell time per step. High-resolution scans were run with a pass energy of 50 eV. Step size was 0.1 eV, and data were collected over 5 scans with 50 m dwell time per step. Samples were subjected to a 60 s low power Ar⁺ etch (200 eV beam energy) prior to measurement so as to remove adventitious surface contamination. Peaks were identified and fitted using the Thermo Advantage analysis suite, using Smart (a Shirley variant) background subtraction.

3. Results and discussion

Crystal structure was found to change significantly as the film composition changed. Films with a high zinc content show XRD patterns characteristic of sputtered ZnO, with a single prominent peak at a 2θ angle of 34° corresponding to the ZnO wurtzite structure (002) plane. As the proportion of copper present in the film increases this peak is reduced, and disappears at copper contents above 23% (as a percentage of total metal content). More copper rich films instead show a single small, broad CuO (111) peak at a 2θ angle of around 39–40°. A second change in crystal structure is seen as copper content is increased beyond 35%. The single broad peak increases in size and two smaller secondary peaks begin to emerge, which correspond to CuO (−111) and (110) planes (Fig. 1).

The crystal structure could not be observed using SEM, indicating that whilst the films clearly are crystalline the grain size is extremely small. Film surfaces do however show a number of patterns and undulations, the causes of which are unknown (Fig. 2).

The observed changes in crystal structure were found to correspond to significant changes in both optical and electrical properties. As the proportion of copper in the films increased the band-gap was found to show a rapid reduction, up to a copper content of around 24.5%. Further increases caused a slight increase in band-gap, after which it decreased again at a reduced rate. A second shift occurs at a copper content of around 40% (Fig. 3). Changes in band-gap with increased copper content were expected to produce either a straight line decrease, or more likely a curve as shown by amorphous alloy systems such as Ga(As,N) and (In,Ga)As [27,28]. The overall trend is very clearly a general decrease in band-gap with increased copper content, disrupted only at those points which correlate with the observed structural changes.

When tested using the Seebeck effect, all films apart from pure ZnO were found to show p-type behaviour. Carrier concentration and mobility measurements carried out using the Hall effect system were found to be highly variable, making the resulting data unreliable. This is thought to be caused by the films having a mobility below that of the device’s measurement limit (less than 1 cm²/V.s).

Resistivity was initially found to decrease roughly exponentially as copper content is increased (Fig. 3). This is thought to be caused...
by a combination of increasing carrier concentration and reduced hole effective mass as the proportion of copper present increases; unfortunately this could not be confirmed because of the unreliable Hall mobility and carrier concentration data. In theory however the copper 3d subshell reduces the hole effective mass through having a similar energy level to that of the oxygen 2p level, which forms the valence band in most metal oxides [29,30]. This means that in copper-based oxides the valence band is both less flat and has a greater spread. Electron holes consequently have a lower effective mass, being less localised and so able to move around more freely. As copper content is reduced this effect is gradually removed, hence the increased resistivity. Although increased copper content was found to cause an overall reduction in resistivity, at two places there is a sudden and dramatic increase, which is counter to the general trend. These are at 24.5% and 35% copper contents, and directly correlate with the observed changes in crystal structure. Furthermore, resistivity of films with high copper contents (>35%) was found to be greater than those with intermediate copper contents (24.5–35%). This implies that crystal structure has a significant impact on the material’s electrical properties. The resistivity of the most Zn-rich films was unfortunately too high to be measured reliably.

In general, transmission was found to decrease with increasing copper content. The overall trend is the same as for band-gap, with marked increases at copper contents of 24.5% and 35%. It was thought that this trend might be influenced by the position of the band-gap for more copper-rich samples, but analysis of the average near-infrared transmission produces the same trend. Average infrared transmission was however typically found to be around 10–12% higher than total average transmission (Fig. 4).

It is clear from these data that there is a strong correlation between crystal structure and optical and electrical properties. The significant increase in resistivity corresponding to the emergence of two further CuO peaks however is markedly larger than any of the changes seen in band-gap or transmission, and is arguably greater than that exhibited at the change from ZnO-dominated to CuO-dominated structure. It is thought likely that the changes in crystal structure have a direct causal effect on the optical and electrical properties, as has been observed in other materials (e.g., [1,31,32]). This may be purely coincidental with the actual cause being as yet unidentified, however given how closely the changes correlate this seems unlikely. As crystallinity and crystal structure are heavily affected by deposition temperature, any further investigation into this system should also endeavour to examine the impact of heat. Identification of a method for successfully analysing the carrier concentration and mobility of p-type metal oxide films would also be of use in further confirming the cause of the observed behaviour.

The overall increase in resistivity at wider band-gaps and higher optical transmissions mean that this material is unlikely to be suitable for use as a potential p-type TCO. Nonetheless, other possible applications for thin-film photovoltaics include back contact, p-type window and electron reflector layers. The changing crystal structure with compositional variation mean that it is theoretically possible to optimise the crystal lattice and hence reduce mismatch issues through careful compositional control. This ability to tailor material behaviour through simple alteration of the composition could also be of value in the design of other thin film optoelectronics devices such as LEDs and lasers.

4. Conclusions

This study demonstrates that alloying ZnO with even a small
quantity of CuO produces p-type behaviour. Unlike other mixed semiconductor alloys, this suite of materials shows crystalline behaviour. Crystal structure was found to show significant changes within the range investigated, at copper contents of 24.5% and 35% (relative to the total metal content). The latter change is from the emergence of two further CuO peaks (at 111 and 110). These changes correspond to significant variations in material band-gap and transmission (both total and infrared), and to significant local increases in resistivity. With the exception of these variations, both band-gap and resistivity decrease approximately linearly with increased copper content.

It is likely that the optical and electrical effects are caused by the change in crystal structure, but further work is required to demonstrate this with certainty. Nonetheless, it is very clear that by tweaking the film composition, the optical, electrical and structural properties of the material can be controlled. The material could therefore be tailored to meet the requirements for a range of applications, including p-type window and electron recycling layers and non-transparent p-type back contacts.

References

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