CuI-TiO₂ Composite Thin Film for Flexible Electronic Applications

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Copper iodide (CuI) is a p-type transparent conductor that can be synthesized and doped at low temperature (≤ 100 °C) while maintaining its high-conductivity and high optical transmittance (> 75 %). The realization of such simultaneously high conductivity and transparency makes CuI useful for applications in both active and passive flexible electronics. However, a few of the major disadvantages of CuI include its optical and electronic stability at ambient atmosphere and reduced transparency with iodine doping. In this report, instead of using pure CuI, we fabricate CuI-TiO₂ composite thin films which are highly transparent and stable at ambient conditions whilst maintaining degenerate p-type conductivity. The CuI-TiO₂ composite film is >80 % transparent (450–2000 nm range), highly conducting (~ 77 S/cm), heavily doped ($> 1.2 \times 10^{20}$ /cm³), with a mobility of ~ 3.5 cm²V⁻¹s⁻¹.

1. Introduction

Transparent conductors (TCs) are a class of materials that display close to metal conductivity ($\sim 10^4$ S cm⁻¹) while maintaining high transparency (> 80 %) in the visible region [1,2]. These transparent conductors have been widely used for applications in solar cells, LEDs, transistors, thermoelectrics, diodes, etc. Commonly used TCs are generally heavily doped n-type wide-bandgap semiconductors such as In₂O₃, SnO₂, ZnO, GaN, etc., whereas, high-performance p-type TCs are not well developed [1-3]. Cu⁺-based oxides such as delafossite CuMO₂ (M: Al³⁺, Ga³⁺, In³⁺, Sc³⁺, Y³⁺) have been investigated as a p-type TC but are unable to match the performance of n-type transparent conductor in terms of conductivity and/or transparency [3-5]. Most recently, La_{2/3}Sr_{1/3}VO₃, a Mott–Hubbard insulator of LaVO₃ has been reported to achieve a high conductivity of 742.3–872.3 S cm⁻¹, however, the transparency of a 48 nm-thick film decreases to ~ 55 % in the visible region [5]. Also, these p-type transparent conducting oxides need high processing temperature (> 400 °C) which makes them unsuitable for organic and flexible electronics. Copper iodide on the other hand can be synthesized and doped at low temperature (≤ 100 °C) while maintaining its high-conductivity and high optical transmittance (> 75 %) and thus can be used for both active and passive flexible electronic applications. However, pure CuI is both optically and electrically unstable in the ambient environment. Our work is based on previous reports on use of insulating oxides to increase the conductivity of metal halides [6,7]. Amongst, several of the insulating oxides used, TiO₂ and Al₂O₃ have most widely been used to improve the conductivity of metal halides. Also, oxygen has also been reported to increase the long-

term stability of CuI [8,9]. In this work, we are using TiO₂ as an insulating oxide to improve both the conductivity and the stability of copper iodide, simultaneously. We fabricate CuI-TiO₂ composite thin films which are highly transparent and stable at ambient conditions whilst maintaining degenerate p-type conductivity.

2. Materials and Methods

Copper and TiO₂ were co-sputtered at the same time in an ATC 1800 UHV sputter chamber using a 99.99 % pure copper and TiO₂ targets. The DC power to the copper target was set at 50 W, whereas TiO₂ concentration in the film was controlled by varying the RF power of the TiO₂ target between 60 to 180 W. All sputter depositions were performed in an argon environment at a pressure of 1.5 mTorr with a flow of 10 sccm. The glass slides with copper-TiO₂ thin film were then transferred into a petri dish and covered with 100 grams of iodine beads and tightly packed using a parafilm. The film became transparent after an hour of reaction time at room temperature. However, to obtain a heavily doped film, the sample was left for another 48 hours in the petri dish at room temperature. These heavily doped CuI-TiO₂ samples are then rinsed in IPA/acetone until the surface iodine is totally removed.

The surface and morphology of CuI-TiO₂ thin film was analysed using a Zeiss UltraPlus analytical field emission scanning electron microscope (FESEM). UV-Vis spectroscopy was performed to measure the transmittance and reflectance of CuI-TiO₂ samples using a Shimadzu 3000 spectrophotometer. Finally, the electronic properties such as resistivity, carrier density and hole mobilities were obtained using a Lakeshore 8400 series HMS Hall effect system.

Figure 1. (a) Transmittance and reflectance spectra of CuI-TiO₂ film measured using UV-Vis spectroscopy. (b) Resistivity and carrier density of CuI-TiO₂ samples at different magnetic field.

3. Results and Discussion

The co-sputtered copper and TiO₂ thin film iodized with solid iodine resulted in a transparent layer of about 240 nm $\pm$ 15 nm thickness. Because the deposition rate of TiO₂ was maintained sufficiently low, no significant change in thickness was observed in the Cu-TiO₂ film with RF power of the TiO₂ target. However, the electronic and optical properties of the CuI-TiO₂ composite thin film was distinctly affected. The best optical and electrical result was obtained for TiO₂ deposition rate of $\sim$ 0.6 nm/min (180 W power). The UV-Vis spectra and Hall effect measurements for the best CuI-TiO₂ film are shown in Fig. 1 (a) and 1 (b), respectively. The CuI-TiO₂ film has a low resistivity of $\sim$ 13 mohms-cm (conductivity of $\sim$ 77 S/cm) while maintaining a transparency of $>$ 65-85% in the 450 -1800 nm wavelength region. An average carrier density of $\sim$ 1.45 $\times$ 10²⁰ /cm³ is measured, while the mobility is $\sim$ 3.5 cm²V⁻¹s⁻¹.

The morphology and surface of CuI-TiO₂ samples are shown by the electron microscopy images in Fig. 2. It is quite apparent that the grains of the CuI-TiO₂ sample are closely packed leading to a smooth thin film. Also, we find that CuI-TiO₂ film is stable at ambient conditions for at least six months, with no appreciable change in its electrical conductivity or optical transparency during this time.

Figure 2. FESEM images of CuI-TiO₂ sample at different magnification.

4. Conclusion

We have successfully grown CuI-TiO₂ thin films which show promise for applications as p-type transparent contacts. UV-Vis spectroscopy and Hall effect measurements show that the CuI-TiO₂ thin films have a high conductivity of $\sim$ 77 S/cm, while, maintaining a transparency of $>$ 65% in the visible spectrum region. Moreover, the CuI-TiO₂ thin films do not show any degradation in their optical or electrical characteristics over a period of more than six months.

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6. References

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