Atmospheric pressure MOCVD of highly conductive thin films of CdO

D.M. Ellis [1)], ***S.J.C. Irvine*** [1)]

1) Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW (UK)

Thin conducting oxides (TCOs) are used in a variety of applications such as thin film solar cell technology (for front contacts and window layers) and applications such as gas sensors and functional glass windows [1−3]. To be competitive, the films have to be of high quality in terms of optical transmission and electrical conductivity.
In this study, atmospheric pressure MOCVD (metal organic chemical vapour deposition) of CdO thin films have been deposited using a novel oxygen precursor. Alcohols have been used successfully for deposition of ZnO, avoiding the gas phase pre−reaction between the zinc precursor and oxygen or water vapour [4]. An alcohol source, when dry, can prevent unwanted pre−reactions with the cadmium precursor, dimethylcadmium (Me_2 Cd).
CdO films were deposited in a purpose designed MOCVD reactor. A horizontal reactor cell was maintained at atmospheric pressure and a resistive heater was used to heat the substrate in the range 250−310 ºC. The precursors were dimethylcadmium (Me_2 Cd), adduct grade, supplied by Epichem Ltd., and for the novel oxygen source: n−butanol (99.8% anhydrous), supplied by Aldrich. The thin film growth was monitored by an in−situ laser interferometer using a 635 nm. This monitoring gave accurate measurement of thickness during growth and information about the film properties such as the reflectance and roughening.

The results were taken from two experimental recipes. In the first the film was grown to 700 nm thick at temperatures between 240 to 310 ºC and the precursor ratio increased for different films. In the second set, the films were grown at a fixed ratio or 4:1 (Me_2 Cd:n−butanol) to 400 nm thick over the same range of temperatures as the first batch of samples. The films were found to be light yellow to orange in colour.
From the onset it was apparent that there was a peak in the growth rates between 270 and 290 ºC. Also, as the ratio of DMCd:n−butanol increased there was an increase in the growth rate whereas an excess of the alcohol inhibits the growth, this is in contrast to growth with an oxygen precursor where the rate increases with increasing oxygen concentration. It is postulated that as the reaction is considered to be a surface catalysed reaction that the bonding of the precursors to the surface is a rate limiting step in the growth rate. The increase in n−butanol molecules bonded to the surface of the film appears to inhibit the growth rate.

AFM analysis indicated a change in the grain size and as temperature increases, grain size decreases up to a temperature of 270 to 280 ºC, increasing again in size thereafter. This corresponds to the range of temperatures where a maximum is observed in the growth rate. The mean height range (for single layer experiments) decreased from 140 to 50 nm with the roughness (root mean square) dropping from 33 to 14 nm.

Transmission is important for the application of TCO films and the transmission spectrum gives an indication of its band−gap. The transmission spectrum in figure 1 shows high transmission for the films in the red−green part of the spectrum. The films measured were all approximately 700 nm thick. Results show that as the film deposition temperature increases up to the optimum temperature range, the transmission of the film also increases. For the higher temperatures 80 to 90% transmission can be seen. An extrapolation of the photonic energy vs. $(aE)^2$ gave a measure of the band−gap increasing with temperature from 2.4 and 2.7 eV.

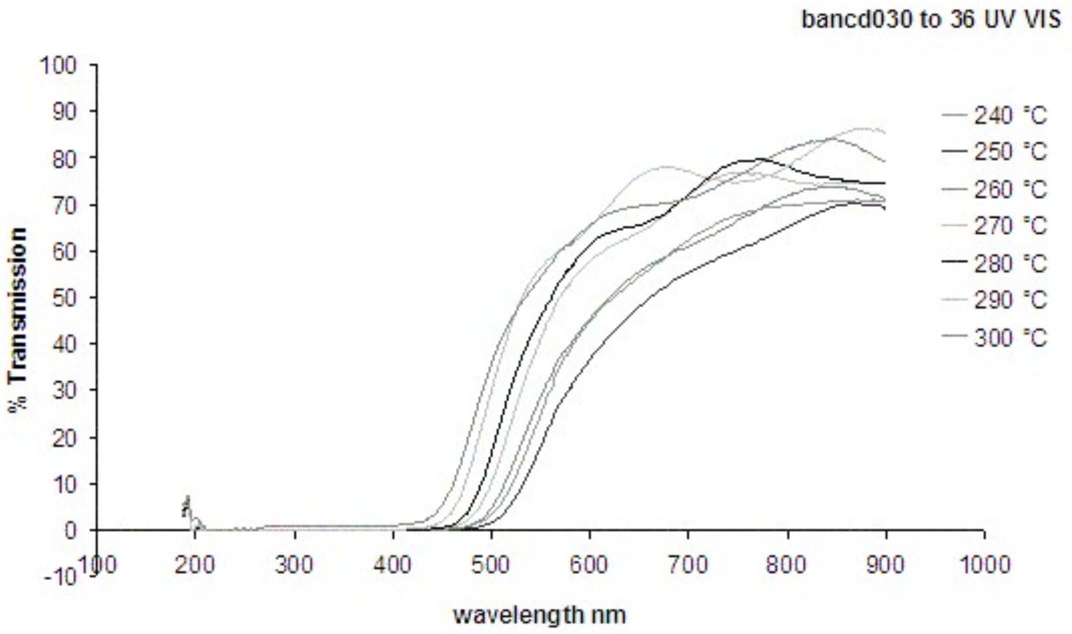

Fig. 1. Films, 700 nm thick, of CdO, grown over a range of temperatures 240 to 300 °C. Up to 290 °C, the transmission of visible light through the film increases to 90%.

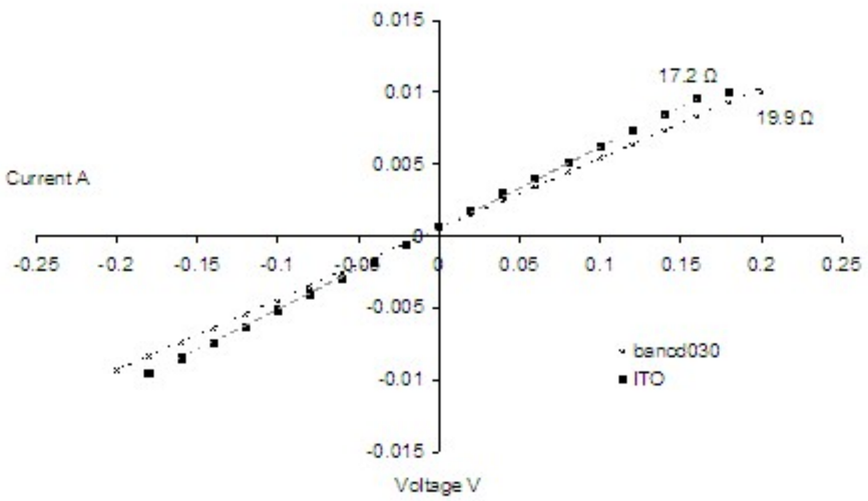

Fig. 2. I−V measurement between two evaporated gold spots 5 mm apart of a 700 nm CdO thin film grown at 290 °C compared with a commercially supplied ITO film measured under the same conditions.

I –V measurements were taken across two evaporated gold spots, 5 mm apart, to determine resistance. Figure 2 shows a comparison of a 700 nm CdO film grown at 290 ^{o}C with a thin film of ITO (Indium Tin Oxide) supplied by Delta Technologies Ltd. The spreading resistance measurement on the ITO films, using a four point probe, was 10 ohms per square. Both films show good ohmic characteristics and from the slope the CdO film gave a resistance of 19.9 ohms compared to the ITO sample of 17.2 ohms. The results signify a correlation between smaller grain size and lower resistivity. It also gives an indication of an optimum deposition temperature where the grain size and resistance is low, with the transmission high at deposition around 280 °C. The apparent optimum growth kinetics, within this temperature range, is associated with optimum film quality; giving lower electrical resistance that is not normally associated with small grain size

This study has shown that CdO can be grown at atmospheric pressure with a novel oxygen precursor. Very high transmittance up to 90 % in the visible region between 600 and 900 nm and low resistances comparable to ITO were obtained from the films. With growth rate monitoring, the films exhibit an optimum in growth rates and illustrates increasing the concentration of the alcohol precursor, reduces the growth rate implying a surface reaction.

References

1. W.P. Tai, J.H. Oh. *J. Mater. Sci: Mater. in Elec.* ***13*** (2002) 391.
2. B. Lewis. *MRS Bullitin.* ***25(6)***, (2000) 22.
3. N. Romeo. *Mater. Chem. and Phys.* ***66*** (2000) 210.
4. S. Oda, H. Tokunaga, N. Kitajima, J.I. Hanna, I. Shimizu, H. Kokado. *Jap. J. App. Phys.* ***24 (12)*** (1985) 1607.