ELECTRICAL AND THERMO-ELECTRIC CHARACTERIZATION OF CdO THIN FILMS PREPARED BY A MODIFIED REACTIVE THERMAL DEPOSITION PROCESS

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Abstract

Highly conductive cadmium II oxide thin films were deposited on glass substrates by a modified reactive vacuum evaporation technique in the oxygen partial pressure range 0.0133 - 0.0933 Pa. The carrier concentration, resistivity, mobility and thermo-electric power of the films were found to be strongly influenced by the oxygen partial pressure during film deposition. A minimum resistivity of \(7.4 \times 10^4\) \(\Omega\)m and a maximum carrier mobility of \(1.14 \times 10^2\) m\(^2\)/Vs were obtained for films deposited at an oxygen partial pressure of 0.04 Pa. Film thicknesses obtained were in the 156 - 420\(\mu\)m range. Room temperature Hall effect measurements on the films yielded resistivities \((7.4 - 17.7) \times 10^5\) \(\Omega\)m, carrier densities \(6.0 \times 10^{23} - 2.3 \times 10^{24}\) m\(^3\) and mobilities \((46 - 114) \times 10^4\) m\(^2\)/Vs, depending on the oxygen partial pressure during film deposition. The high conductivity of the films was mainly due to their high mobility and carrier concentration. The thermo-electric power of the films investigated in the temperature range from room temperature to 473K gave values in the range (3 - 120) \(V/K\). Data treatment suggests that the dominant carrier scattering mode is by ionized impurities.

Keywords: CdO thin films, electrical conductivity, thermoelectric power, Oxygen Partial Pressure

1. Introduction

Cadmium oxide, CdO which is an n-type II-VI semiconductor with a NaCl structure, is among a large variety of transparent conducting oxides that simultaneously exhibit high electrical conductivity and high transparency in the visible region of the electromagnetic spectrum (Vossen, 1977). Its high transparency in the visible region is because of its relatively wide band gap (E.g. \(\sim 3.0 - 2.70\) eV). The variation in the band gap has been ascribed to large Burstein-Mott shifts (Burstein, 1954).

Nonstoichiometric undoped CdO thin films usually exhibit low resistivity due to native defects of oxygen vacancies or cadmium interstitials, which act as doubly charged donors (Koffyberg, 1970). Hence, low resistivity films can be obtained by controlling these native defects. With these physical characteristics, CdO thin films, like SnO\(_2\), In\(_2\)O\(_3\), ITO, ZnO and Cd, SnO\(_2\), films, have found a wide range of applications in electronic and optoelectronic devices: solar cells (Chu et al., 1990; Champness et al. 1995), transparent electrodes for liquid crystal displays (Benko et al., 1986), phototransistors (Su et al., 1984), photodiodes (Kondo et al., 1971), and gas sensors (Liu et al., 1997). On the other hand, the need to obtain the lowest resistivity and highest visible transparency in parallel with clarifying the physical properties of CdO films have led to various methods of their deposition, such as spray pyrolysis (Gurumurugan et al., 1994; Sravani et al., 1994) solution growth (Varkey et al., 1994), reactive evaporation (Eze, 1998), activated reactive evaporation (Sravani et al., 1996; Phatak et al., 1994), sol-gel (Zunigo-Romero et al., 2001), pulsed laser (Yan et al., 2001), chemical vapour deposition (Coutts et al., 2000), metal-organic chemical vapour deposition (Zhiyong Zhao et al., 2002), ion-beam sputtering (Chu et al., 1990) and reactive sputtering (Subramanyam et al., 1998). With the sputtering techniques CdO thin films of very low resistivity \((\sim 7.4 \times 10^4\) \(\Omega\)m) and very high visible transmittance \((\geq 80\%\) could easily be obtained. Similar results are obtained with spray pyrolysis and activated reactive evaporation.

In a previous work (Eze, 1998) we described a simple, modified but non activated reactive
vacuum evaporation technique for depositing good quality CdO thin films of resistivity \( \sim 1.45 \times 10^3 \, \text{m} \), high optical transmittance (70-92\%) in the visible and near infrared regions, a mobility of 59.77 cm\(^2\)/Vs and a carrier density of 7.35 \times 10^{20} \, \text{m}^{-3}. \) Recently we reported that both the structural and compositional characteristics of the films were strongly dependent on the partial pressure of oxygen during film deposition (Eze, 2005). Nevertheless, the electrical properties of the films have not been studied in detail. Such information will facilitate the optimization of the deposition process for producing device quality films. This paper deals with the electrical and thermo-electric characterization of cadmium oxide thin films prepared by a modified reactive vacuum evaporation process. The effects of the oxygen partial pressure on the electrical and thermolectric properties of the films are also reported.

2. Experimental details

The details of our modified reactive vacuum evaporation process had been given in a previous report (Eze, 1998). Cadmium pellets of 99.999% purity were evaporated in vacuum at a pressure range 0.0133-0.0933 Pa from a molybdenum crucible by the resistive heating method. The substrates were quartz plates of dimensions 5 mm x 5 mm x 1 mm which were heated at temperatures from room temperature to 433K during the deposition. After the ultimate vacuum pressure of 9.33 \times 10^{-4} \, \text{Pa} had been reached the pumping was switched to only one diffusion pump and high purity oxygen gas was passed through a needle valve into the vacuum chamber. The total gas pressure during evaporation was kept in the 0.0133-0.0933 Pa pressure range to facilitate the oxidation of the films, the background pressure being about 6.65 \times 10^{-3} \, \text{Pa}. The film thicknesses obtained were in the range 156-420 nm. The film thickness was measured by a Talsysurf instrument (Taylor Hopson, London). The temperature variation of the electrical conductivity of the films was investigated in the room temperature to 473K range while the Hall effect measurements were carried out at room temperature and at a magnetic field of 3.8kG. A van der Pauw/Hall effect system (MMR Technologies, Inc.) interfaced with a computer, was used for these electrical measurements. To make the measurement, indium electrodes were evaporated onto the four corners of the samples, in a square geometry, through a perforated brass mask. Contacts to the CdO films were then made by placing the four hair size copper wires provided in the measuring system on the indium electrodes, using silver paste. The ohmic nature of the contacts was confirmed using a cathode ray oscilloscope arrangement. Thermoelectric power measurements were carried out using a differential temperature technique. In this method, copper constantan thermocouples were attached to the ends of the samples for the measurement of the temperature difference \( \Delta T \) and the thermal emf in the film copper circuit. The reference junctions of the thermocouples were electrically insulated and placed in an ice-water bath at 0°C. The temperature difference \( \Delta T \) between the cold and hot junctions was maintained by means of an electric heater. The variation of thermoelectric power \( S \) with temperature \( T \) was investigated in the range from room temperature to 473K.

3 Results and Discussion

3.1 Theoretical considerations

The CdO films studied were polycrystalline, semiconducting, degenerate and n-type. The films contained defects, such as grain boundaries, dislocations and surface charge layers (Eze, 2005). For such materials the electrical conduction is caused by ionized impurities, lattice scattering, surface scattering and grain boundary scattering (Smith, 1978). The electrical conduction mechanism in the CdO films may be explained using Seto's polycrystalline model for semiconductors (Seto, 1975). The model prescribes that the electrical conduction in a polycrystalline semiconducting thin film at higher temperatures is effected by thermionic emission of charge carriers over the intergrain potential barriers in the film, viz:

\[
\sigma = \frac{e^2 \ln}{2 \pi m^* kT} \exp \left( \frac{-E_0}{kT} \right)
\]

where \( \sigma \) is the dc electrical conductivity, \( e \) is the electronic charge, \( l \) is the average grain size of the film, \( n \) is the average carrier concentration, \( m^* \) is the effective mass of the carriers at the Fermi energy, \( k \) is the Boltzmann constant, \( E \) is the activation energy.
for the grain boundary limited conduction and $T$ is the absolute temperature. On the other hand, for degenerate semiconductors the thermoelectric power $S$ can be shown to have the form (Smith, 1978):

$$ S = \frac{\pi^2 k^2 T}{|e|E_F} \left( \frac{1}{2} + \frac{p}{3} \right) $$

(2)

where $p$ is the scattering parameter with $p = \frac{1}{2}$ (acoustic mode phonon scattering), $p = + \frac{1}{2}$ (optic mode phonon scattering), $p = \frac{1}{2}$ (ionized impurity scattering) and $p = 0$ (neutral impurities). Relative to the bottom of a parabolic conduction band, the Fermi energy $E_F$ may be expressed as:

$$ E_F = \frac{\hbar^2}{2m^*} \left( \frac{3\pi^2 n}{2} \right)^{\frac{2}{3}} $$

(3)

where $n$ is the carrier density, $m^*$ is an effective mass and represents Planck’s constant. Using equation (3) which defines $E_F$, equation 2 can be re-written as:

$$ S = \frac{2\pi^{\frac{1}{3}} k^2 m^* \left( \frac{1}{2} + \frac{p}{3} \right) T}{|e| \hbar^2 (3n)^{\frac{2}{3}}} $$

(4)

It had been suggested (Bhattacharyya et al., 1985) that the Fermi energy should be allowed to vary linearly with temperature as:

$$ E_F = E_{Fe}[1 - \alpha T], $$

(5)

where $E_{Fe}$ is the reduced Fermi energy and the temperature coefficient of the Fermi energy. However, considering a rigid band in which the density of states varies as a positive power $p$ of the energy it can be shown that the temperature dependence of the Fermi Dirac distribution function leads naturally to a quadratic temperature dependence in Fermi energy:

$$ E_F = E_{Fe} \left[ 1 - \frac{(P - 1)(\pi k T / E_{Fe})^2}{6} \right] $$

(6)

If we also define $C = \sqrt{\frac{13.62E_{Fe}}{C}}$, then eqn. 2 transforms to:

$$ S = \frac{13.62E_{Fe}}{C} \left[ \alpha - \frac{1}{T} \right] $$

(7)

### 3.2 Electrical transport data

The variation in electrical resistivity, mobility and carrier density $n$, with $pO_2$ are shown in Fig.

The figure clearly shows a minimum in the resistivity at a $pO_2$ of $4 \times 10^7$ Pa. The increase in resistivity on either side of the optimum $pO_2$ is attributable to the additional oxygen that is accumulated at the grain boundaries which then acts as scattering centres for the electrons. A partial pressure of oxygen greater than that which produces a stoichiometric film would result in an increase in film resistivity and a consequent reduction in mobility as observed experimentally. Nevertheless, the higher resistivity at lower than the optimum $pO_2$ could be explained in terms of the existence of phases of cadmium oxide other than CdO.

These phases would result in nonstochiometric films. However, X-ray diffraction patterns of the films did not confirm any trace of CdO. This notwithstanding, there was evidence of pure, unoxidized cadmium in the X-ray diffraction spectra of the as-deposited films taken for lower $pO_2$ values (Eze, 2005). Annealing of such films in an oxygen atmosphere, though was found to reduce the resistivity, could not achieve complete film oxidation. This was confirmed via X-ray fluorescence analyses which revealed that while the [Cd]/[O] atomic ratio for the films deposited at the optimum $pO_2$ value of $4 \times 10^7$ Pa was 1: 0.96, the ratio for films deposited at a typical lower $pO_2$ value of $1.33 \times 10^5$ Pa was 1: 0.71 (Eze, 2005). It should be noted that the mobility values obtained here are comparable to those reported for sputtered films (Gurumurugan et al., 2006).
al., 1996) but significantly less than values in excess of 200 cm² / V s reported on CVD films (Coutts et al., 2000) and sintered CdO powder (Koffyberg, 1971). Our mobility values are also higher than those reported for CdO films prepared by atmospheric MOCVD (Zhiyong Zhao et al., 2002) and activated reactive evaporation (Zunigo-Romero et al., 2001). Fig. 1 also shows that the carrier concentration initially decreases gradually with increasing pO₂, attains a minimum value of about 7 × 10⁻⁵ m⁻³ in the pO₂ range 2.67 × 10⁻⁴ - 5.33 × 10⁻⁵ Pa. Thereafter, it increases with pO₂, reaching a maximum value of about 3 × 10⁻⁶ m⁻³ at a pO₂ value of 9.33 × 10⁻³ Pa.

The n values obtained here are comparable to those reported for activated reactive evaporation films (Ramakrishna Reddy et al., 1998), sprayed films (Ferro et al., 2001) and CVD films (Coutts et al., 2000) but lower than values reported for MOCVD films (Yan et al., 2001). The differences may well be due to the different methods of preparation employed. Following eqn. 1, the conductivity is plotted semilogarithmically in Fig. 2 as a function of inverse temperature with pO₂ as parameter. The E values deduced from the Arrhenius plots are shown in Table 1. It is interesting to note that the lowest and highest E values of 0.03 eV and 0.06 eV occur at pO₂ values of 9.33 × 10⁻³ Pa and 1.33 × 10⁻² Pa, respectively. The E values agree with the values reported on sprayed films (Uplane et al., 2000). Fig. 2 also shows that the variation of pO₂ during film deposition increased the electrical conductivity by nearly two orders of magnitude.

3.3 Thermoelectric Power Data
All our data have been analyzed by plotting S versus T as suggested by equation 4. The results for the CdO samples deposited at the indicated oxygen partial pressures are shown in Fig. 3. The data for all the samples exhibited linear behaviour when plotted in this manner. The temperature rise thermoelectric power values obtained here are comparable to values of 118 V/K reported for heat treated films (De et al., 2000) but larger than the values of 89 V/K reported for sprayed films (Gurumurugan et al., 1994; Uplane et al., 2000).

The carrier densities for all our samples have been determined by the Hall effect measurements and are listed in Table 1. However, there are no accurate measurements of the effective carrier mass in these samples effective mass of 0.23 m, for reductively sputtered CdO films with carrier concentrations in the range 5 × 10²⁴ - 2 × 10²⁶ m⁻³ while a value of 0.44 m, was reported for spray pyrolysed CdO films (Gurumurugan et al., 1994). Because of these uncertainties in m*, we have analyzed our data by assuming...
probable values of the scattering parameter $p$ in order to compute the values of $m^*$. From the slopes of the $S$ vs $T$ graphs in Fig. 3 we computed the values of $m^*$ using the measured values of the carrier densities. The calculated values of $m^*$ are listed in Table 1. For each sample the maximum value of $m^*$ corresponds to the choice $p = \frac{1}{2}$ (acoustic mode phonon scattering) and the minimum value corresponds to $p = \frac{3}{2}$ (ionized impurity scattering). The carrier effective mass $m^*$ values have been plotted in Fig. 4 as a function of carrier density at various oxygen partial pressures. The $m^*$ generally increases with increasing carrier density as expected. For most of the samples the best match with the effective masses reported by Tanaka et al. 1969 and Gurumurugan et al. 1994 corresponds to ionized impurity scattering. In some cases, however, optic mode phonon scattering leads to a better agreement. Values of $p$ such as $\frac{1}{2}$ for acoustic mode scattering suggest even larger effective masses. Nevertheless, it can be seen from Fig. 4 that the $m^*$ data at low carrier density tend to suggest a positive scattering exponent, implying that grain boundary scattering plays a significant role in these films. From the table an $m^*$ value of 0.30 m, was obtained for CdO films deposited at a PO$_2$ value of 0.040 Pa assuming ionized impurity scattering. The validity of this assumption is supported by the fact that for a carrier concentration of $6 \times 10^{23}$ m$^{-3}$ and an effective mass $m^* = 0.30$ m, the Fermi energy calculated using equation 2 yields $E_F = 0.19$ eV, suggesting further that at room temperature the CdO film is a degenerate semiconductor. Moreover, the mean free path of carriers was calculated using the expression (Noguchi et al. 1980) $\lambda = (8/\pi)(3n)/E_F$. For $n = 6 \times 10^{23}$ m$^{-3}$ and $E_F = 0.19$ eV, we have $\lambda = 4.8$ nm, which is much shorter than the grain size of about 28 nm obtained for the film. This result implies that grain boundary scattering is not dominant. Similar observations had been made by other workers on CdO (Gurumurugan et al., 1994) and In$_2$O$_3$ (Noguchi et al., 1980).

Equation 7 prescribes that a plot of $E_F$ versus $C$ should be a straight line with slope $13.62E_F/C$ and intercept $13.62E_F/C$. However, typical plots of $E_F$ versus $C$ (not shown) for all the samples revealed curves rather than straight lines.

It is noteworthy that the temperature dependence which equation 6 predicts is much smaller than the linear dependence given by equation 5 for all the samples. Besides, it is not entirely surprising that the data presented here are not consistent with the linear temperature dependence of $E_F$ because the Fermi energy given in equation 2 assumes a parabolic band whereas the CdO band is nonparabolic.

**Conclusions**

Thin films of cadmium oxide were prepared by a modified reactive thermal evaporation at various partial pressures of oxygen and
constant substrate temperature. The films were characterized by studying their electrical and thermo-electric properties. Resistivities in the range of (7.45- 17.7) x 10$^4$ m and film thicknesses of 156-420 nm were obtained. The high conductivity of the films was mainly due to their high carrier concentrations of (0.6-2.5) x 10$^{16}$/m$^2$ and carrier mobilities of (46- 114) x 10$^4$ m/Vs. The deposited films exhibited thermo-electric power values of 3-120 V/K. The partial pressure of oxygen during deposition was found to have remarkable effects on the electrical and thermo-electric properties. High mobility and high conductivity made possible by varying the pO$_2$ during film deposition imply that CdO has great potential for development as an effective transparent conducting oxide.

![Graph showing carrier concentration vs. effective mass](image)

**Fig. 4** Variation of the carrier effective mass, m* with partial resistance of oxygen, O$_{2}$ for the indicated CdO thin film

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**References**


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