Thickness dependent electrical properties of CdO thin films prepared by spray pyrolysis method

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Abstract. A large number of thin films of cadmium oxide have been prepared on glass substrates by spray pyrolysis method. The prepared films have uniform thickness varying from 200–600 nm and good adherence to the glass substrate. A systematic study has been made on the influence of thickness on resistivity, sheet resistance, carrier concentration and mobility of the films. The resistivity, sheet resistance, carrier concentration and mobility values varied from $1.56\text{--}5.72 \times 10^{-3} \Omega\text{-cm}$, $128\text{--}189 \Omega/\square$, $1.6\text{--}3.9 \times 10^{21} \text{cm}^{-3}$ and $0.3\text{--}3 \text{cm}^2/\text{Vs}$, respectively for varying film thicknesses. A systematic increase in mobility with grain size clearly indicates the reduction of overall scattering of charge carriers at the grain boundaries. The large concentration of charge carriers and low mobility values have been attributed to the presence of Cd as an impurity in CdO microcrystallites. Using the optical transmission data, the band gap was estimated and found to vary from 2.20–2.42 eV. These films have transmittance around 77% and average reflectance is below 2.6% in the spectral range 350–850 nm. The films are *n*-type and polycrystalline in nature. SEM micrographs of the CdO films were taken and the films exhibit clear grains and grain boundary formation at a substrate temperature as low as 523 K.

Keywords. Spray pyrolysis; CdO thin films; structure and morphology; II–VI semiconductor; optical properties; energy gap.

1. Introduction

CdO is a degenerate, *n*-type transparent semiconductor with wide energy gap and high electrical conductivity. Its high conductivity is due to the increased crystallite size at high substrate temperature, moderate electron mobility and high carrier concentration. The properties of CdO films can be controlled to a suitable parameter value to suit a particular application, by controlling some of the process parameters viz. the film thickness, concentration of the solution, temperature of the substrate and the solution flow rate etc. Though CdO was the first transparent conducting oxide film, studied by Badeker in 1907 (Holland 1966; Jarzebski 1973), not many investigations have been done for quite a long time. For the last few years CdO is being extensively investigated both in bulk and thin film forms. CdO has interesting properties like large band gap, low electrical resistivity, high transmission in the visible region etc. These properties make it useful for a wide range of applications such as photo-diodes (Kondo *et al* 1971), phototransistors (Su *et al* 1984), photovoltaic (Champness *et al* 1985), transparent electrodes (Benko and Koffyberg 1986) besides liquid crystal displays, IR detectors and anti-reflection coatings (Ocampo *et al* 1993). CdO has been prepared by various

deposition techniques such as activated reactive evaporation (Sravani *et al* 1991; Phatak and Lal 1992), dc magnetron reactive sputtering (Phatak and Lal 1992; Subramanyam *et al* 1997), spray pyrolysis (Chu and Chu 1990; Gurumurugan *et al* 1995) and chemical bath deposition techniques (Ocampo *et al* 1994; Varkey and Fort 1994). One of the simple, low cost techniques and a novel approach to make thin films is through spray pyrolysis. Though this technique has been widely employed for the study of transparent conducting oxide (TCO) films, the properties of the films vary from one pyrolysis setup to the other. The properties of the films are also influenced by the geometry of the experimental setup. This process has good control over the thickness uniformity. The films prepared by this method are pin hole free and have good adherence to the substrate. Improving the film quality, characteristics and reproducibility prompted us to prepare thin films of cadmium oxide by spray pyrolysis method. The objective of the current investigation is to prepare CdO films with larger grains under optimum conditions and then to study their structural, electrical and optical properties. More precisely to increase the grain size by controlling the film thickness.

2. Experimental

A simple glass nozzle was fabricated to give a fine and very small droplets when the solution is driven by either

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air from the compressor or nitrogen from the gas cylinder. CdO films were prepared by spraying the resultant solution of 0.1 M concentration of cadmium acetate on a heated substrate. Compressed air was used as carrier gas in our experiment. The spraying solution was prepared by dissolving a known quantity of cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) in deionized water and methanol in the ratio 1 : 1. The experimental arrangement is shown in figure 1.

An electric heater was made from the kanthal wire wound on four silica tubes of 2.5 cm diameter and 30 cm length. The tubes were fixed parallel to each other, with a separation of 2.5 cm, inside a well insulated aluminium box $46 \times 30 \times 30$ cm with one half of the top open. The free ends of the wire were connected to a variac with an ammeter and voltmeter arrangement. A particular temperature could be achieved by supplying a suitable power through the variac. A digital temperature indicator was used with iron-constantan thermocouple to record the temperature. For uniform heating of the substrate an aluminium plate was kept about 2.5 cm above the coils on which the substrate was mounted. The spraying arrangement was in such a way that the spray of the solution directly fell on the substrate as shown in figure 1. Proper exhaust arrangements were made to remove the excess gas in the chamber. The thickness of the films was determined by weighing method, which was verified later by stylus technique. The various process parameters optimized for CdO thin film deposition are given below.

Nozzle	Glass
Nozzle-substrate distance	30 cm
Solution concentration	0.1 M
Solution flow rate	6.0 ml/min
Carrier gas	Compressed air
Gas pressure	5 kg/cm ²
Substrate temperature	523 K

Figure 1. Schematic diagram of spray pyrolysis apparatus. (1. Cadmium acetate solution; 2. spraying nozzle; 3. furnace; 4. heating element; 5. aluminium plate; 6. substrate; 7. thermocouple; 8. temperature indicator; 9. iron stand; 10. pressure regulator and gauge; 11. compressor; 12. exhaust fan; 13. auto transformer).

The optical transmittance, $T(\%)$ and reflectance, $R(\%)$ spectra were recorded using a Hitachi 330 double beam spectrophotometer with the wavelength ranging from 350–850 nm. The resistivity, sheet resistance, carrier concentration and mobility of the films were measured by using a standard Van der Pauw method. The XRD and SEM micrographs were recorded to study the structure and surface morphology of the CdO thin films.

3. Results and discussion

3.1a XRD studies: A typical XRD pattern of the deposited undoped CdO film prepared at a substrate temperature of 523 K is displayed in figure 2. The presence of different peaks in the figure shows that the films are polycrystalline in nature. Five strong diffraction peaks are observed at angles 32.98° , 38.32° , 55.20° , 66.00° and 69.22° and they correspond to $\langle 111 \rangle$, $\langle 200 \rangle$, $\langle 220 \rangle$, $\langle 311 \rangle$, and $\langle 2\bar{2}2 \rangle$ reflections, respectively. The comparison of observed 2θ , d , hkl , and (hkl) values for CdO thin films to that of the standard bulk values are shown in table 1.

3.1b SEM studies: Figure 3 shows SEM micrographs for the deposited CdO films of different thicknesses. The SEM micrographs show that a polycrystalline deposit is formed with a well defined circular grain and grain boundaries. The film having thickness of 600 nm shows a grain size of the order of $10\text{--}80\text{ }\mu\text{m}$ whereas a grain size of $0.3\text{--}0.5\text{ }\mu\text{m}$ was recorded for a film of thickness 200 nm. This shows that the disorder (Abd EL-Salam *et al* 1997) of the grain boundary increases as the thickness of the film increases. By comparing the micrographs it can be observed that the grain size increases with the increase in film thickness. Similar thickness dependence of grain

Figure 2. Typical XRD spectrum of sprayed CdO thin film prepared at 523 K.

size was reported for Al–Zn thin films by Abd EL-Salam *et al* (1997).

3.2 Optical properties

The optical transmittance and reflectance of CdO thin films were recorded as a function of photon energy ranging from 350–850 nm for three different samples and is shown in figure 4. It can be seen from the spectra that a transmission of 77% was observed for films of thickness 200 and 400 nm. A lower transmission of 73% was observed for a 600 nm film. The absorption coefficient

was determined from the transmittance data using the formula (Van der Pauw 1985), $\alpha = 2.303 \times \ln(1/T)$. The estimated α values were ranging from $2.81\text{--}3.20 \times 10^4$ at a wavelength of 500 nm, which are in consistent with the earlier reported values (Subramanyam 1997). For a direct transition, the absorption coefficient is related to band gap by the equation

$$\alpha(h\nu) = A(h\nu - E_g)^{1/2},$$

where A is a constant. Figure 5 shows the plot of $(\alpha h\nu)^2$ vs $h\nu$. The band gap was evaluated by extrapolating the linear portion of $(\alpha h\nu)^2$ vs $h\nu$ plot to the energy axis. The

Table 1. Comparison of 2θ , d , I/I_0 and $\langle hkl \rangle$ values of CdO thin films to that of standard bulk CdO.

Peak no.	$2\theta^\circ$	'd' spacing (10^{-10} m)		I/I_0		hkl
		Observed	Standard	Observed	Standard	
1	32.98	2.714	2.712	100	100	111
2	38.32	2.347	2.347	25	88	200
3	55.20	1.663	1.661	13	43	220
4	66.00	1.414	1.416	9	28	311
5	69.22	1.356	1.355	11	13	222

Figure 3. Scanning electron micrographs showing the surface topography of sprayed CdO thin films. Film thicknesses (a) 200 nm and (b) 600 nm.

Table 2. Observed electrical parameters of CdO thin films prepared at optimum conditions.

Sample no.	T_s (K)	t_s (nm)	ρ ($10^{-3} \Omega\text{-cm}$)	ρ_s ($\Omega/\square$)	n (10^{21}cm^{-3})	μ (cm^2/Vs)	T (%)
1	523	200	5.72	189	3.9	0.3	78
2	523	400	3.15	196	2.3	1.0	77
3	523	600	1.56	128	1.6	3.0	73

Figure 4. Optical transmission and reflectance @ data of CdO thin films for varying thicknesses, (a) 200 nm, (b) 400 nm and (c) 600 nm.

evaluated band gaps were ranging from 2.20–2.45 eV and these values are in accordance with the observed values of 2.35–2.50 eV for sprayed (Gurumurugan *et al* 1994) and 2.20 eV for chemically (Ocampo *et al* 1994) deposited CdO thin films.

3.3 Electrical properties

CdO films exhibit *n*-type conductivity as determined by hot probe method. The electrical resistivity, sheet resis-

Figure 5. Plots of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) for CdO films for varying thicknesses.

tance, carrier concentration and Hall mobility were evaluated by Van der Pauw technique (Van der Pauw 1985; Schroder 1990). Silver paste was used for electrical contacts. A typical current of 25 mA was fed through the sample using a Keithley programmable current source (Model 220). The voltage across the sample was measured by a Keithley digital multimeter (Model DMM 195). The estimated values of various electrical parameters are given in table 2. From table 2, it can be observed that the resistivity values decreases from 5.72 to $1.56 \times 10^{-3} \Omega\text{-cm}$ as the film thickness increases from 200 to 600 nm. The decrease in resistivity is probably due to the decrease in the number of grain boundaries with

increased film thickness which is in consistence with the observed mobilities in various samples (table 2). This result can be compared with the earlier result of Varkey and Fort (1994). In fact here, the observed mobilities are low compared to the higher values reported in the literature (Sravani *et al* 1991). Low mobilities of the charge carriers can be attributed to the presence of impurities in the microcrystallites as well as scattering of these carriers at the grain boundaries. The large concentration of charge carriers in our samples indicates the presence of cadmium as an impurity in the CdO microcrystallites which may be responsible for the reduction of mobility. The transmittance and sheet resistance show inverse thickness dependence which is in accordance with the result of Enoki *et al* (1991).

4. Conclusions

The CdO thin films prepared by spray pyrolysis have good adherence and thickness uniformity. The films were polycrystalline in nature as determined from the XRD profile. The surface structure of the CdO films could be seen clearly from SEM micrographs and the films exhibit clear grains and grain boundary formation. The prepared films were *n*-type in character. The electrical properties of CdO films viz. resistivity, sheet resistance, carrier concentration and mobility were found to vary from $1.56\text{--}5.72 \times 10^{-3} \Omega\text{-cm}$, $128\text{--}189 \Omega/\square$, $1.58\text{--}3.90 \times 10^{21} \text{cm}^{-3}$ and $0.3\text{--}3 \text{cm}^2/\text{Vs}$, respectively for film thickness ranging from 200–600 nm. The probable explanation for decreasing resistivity and increasing mobility with increasing thickness has been given. The observed low mobilities are attributed to the presence of scattering centres in the microcrystallites. The transmittance of the films was observed to be over 77% and the average reflectance was below 2.6% in the spectral range 350–850 nm. The optical band gap was found to vary from 2.20–2.42 eV.

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