Properties of spray coated $(PbO)_x$ $(CdO)_{1-x}$ thin films

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Transparent conducting oxide (TCO) films find extensive application in the field of optoelectronics and other solid state devices [1–3]. PbO and CdO thin films have been prepared by spray pyrolysis technique by other workers [4, 5]. PbO is reported to exist in a low temperature tetragonal α-PbO phase and a high temperature orthorhombic β-PbO [6] phase. The difficulties encountered in preparing exclusively single-phase α-PbO or β-PbO have been pointed out by many authors [4, 6]. Thin films of the low temperature α-PbO phase have been obtained by pulsed laser deposition method [6] and spray pyrolysis route from 0.1 M aqueous lead nitrate solution [4, 7]. Heat treatment beyond 489 °C is said to transform the α-PbO phase to the metastable β-PbO phase [8]. CdO films have been grown by spray pyrolysis method [5] with cubic structure. Both PbO and CdO have high transparency in the visible and near infrared region of the electromagnetic spectrum and both the materials show n-type conductivity [9, 10]. The electrical conduction in these films has been attributed to the existence of oxygen vacancy in the oxides [11].

$(PbO)_x(CdO)_{1-x}$ films were grown on ultrasonically cleaned glass substrates using an indigenously fabricated spray pyrolysis set-up. The spray solution was prepared by dissolving appropriate volumes of 0.1 M lead acetate and 0.1 M cadmium acetate in deionised water. The substrate temperature, nozzle diameter, spraying angle, and nozzle to substrate distance were optimized for obtaining good quality films of high transparency. The optimized parameters were 350 °C, 0.25 mm, 45 ° and 300 mm, respectively. High purity N_2 gas was used as the carrier gas at a pressure of 4×10^4 kg m^{-2}. The as-deposited films were annealed *in-situ* at 350 °C for 15 min. The powder X-ray diffraction data were obtained with a powder X-ray diffraction system (Seifert XRD 3003 T/T) equipped with a grazing incidence device (GID) attachment. Cu K_α radiation (1.541 Å) was used with a Ni filter. The optical band gap (E_{opt}) of the films was obtained from absorbance measurements made using a spectrophotometer (Shimadzu 3101 PC). The electrical resistivity at room temperature and thickness of the thin films were measured using Van der Pauw and multiple-beam interferometer methods [12], respectively. Thermoelectric power measurements were performed using an indigenously fabricated set-up.

The X-ray diffraction patterns of the $(PbO)_x(CdO)_{1-x}(0 \leq x \leq 1)$ thin films grown with different compositions are shown in Fig. 1. For the $x = 0$ film, the five diffraction peaks observed were identified as the reflections from (111), (200), (220), (311), and (222) planes of cubic CdO phase with a lattice parameter of 4.6948 Å [ICDD PDF file No: 75-591]. The most prominent peak for the $x = 0$ (CdO) sample was the reflection from the (111) plane. The diffraction peaks corresponding to (111), (200) and (220) planes were sharp in comparison to those from (311) and (222) planes. For the $x = 1$ (PbO) sample, nine peaks which could be related to (001), (101), (110), (002), (112), (003), (211), (202), and (103) planes of the tetragonal α-PbO phase were observed with cell parameters, $a = b = 3.96$ Å and $c = 5.01$ Å. The broad peak at $2\theta = 54.9^\circ$ is a combination of three peaks, i.e., (003) and (211) of the tetragonal α-PbO phase and (220) of the cubic CdO phase. Similarly, the broad peak at $2\theta = 60^\circ$ is a combination of two peaks, namely, (202) and (103) of α-PbO phase. According to our observation, PbO could be grown as a single (tetragonal) PbO phase, when the films were deposited at 350 °C. For the $x = 0.25$ sample, the peaks corresponding to (001) and (202) and (103) planes of the tetragonal PbO phase were not observed. For $x = 0.5$ sample, all the peaks corresponding to both the tetragonal PbO as well as cubic CdO phase were present. For $x = 0.75$ sample, the diffraction peaks corresponding to (311) and (222) planes of cubic CdO phase were not observed. This may be due to the low crystallinity of CdO along these planes at this composition. The present data could be fitted well to PDF Files 72–151 and 75–591.

For allowed direct transition, the absorption coefficient $\alpha \propto (h\nu - E_{\text{opt}})^{1/2}$, where E_{opt} is the optical band gap and $h\nu$ is the photon energy, α^2 versus $h\nu$ plot obtained for various compositions of $(PbO)_x(CdO)_{1-x}$ films are shown in Fig. 2. All the films were found to exhibit direct allowed transitions. The optical band gap, E_{opt}, is determined by extrapolating the linear portion of the graph to $\alpha = 0$. It can be seen from Fig. 3 that E_{opt} increased from 2.28 to 2.56 eV for samples with $x = 0$ to 0.5 and then decreases to 1.93 eV for $x = 1$ sample. The present results agree well with the reported data of 2.25–2.37 eV for CdO and 1.9 eV for PbO [4, 5, 13]. The single band-gap exhibited by $(PbO)_x(CdO)_{1-x}$ and its non-linear variation with x are two aspects of interest in this mixed crystal system. The non-linear variation of E_{opt} shows that the PbO and CdO may not be miscible.

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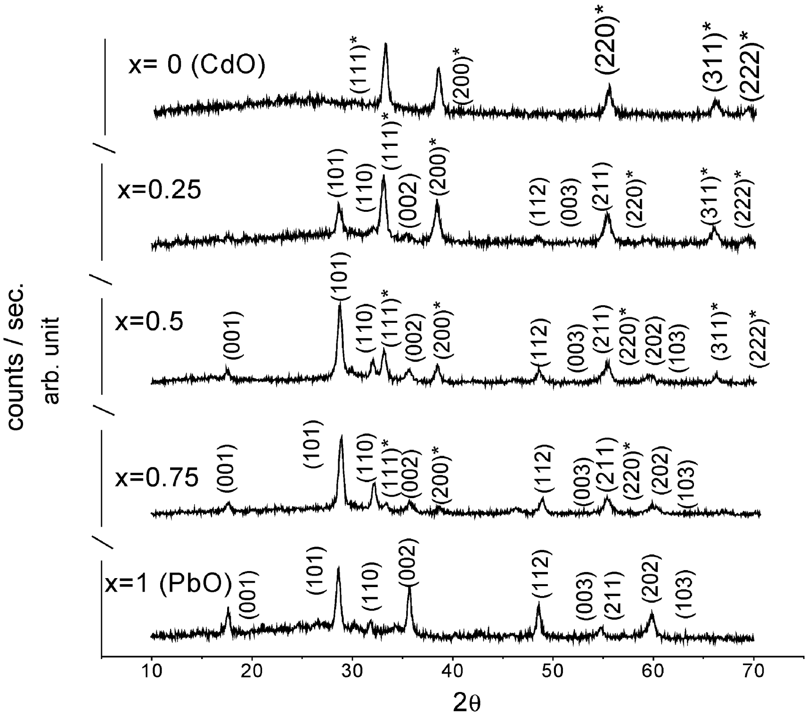

Figure 1 X-ray diffraction patterns of $(PbO)_x(CdO)_{1-x}$ films ["*" indicate cubic CdO].

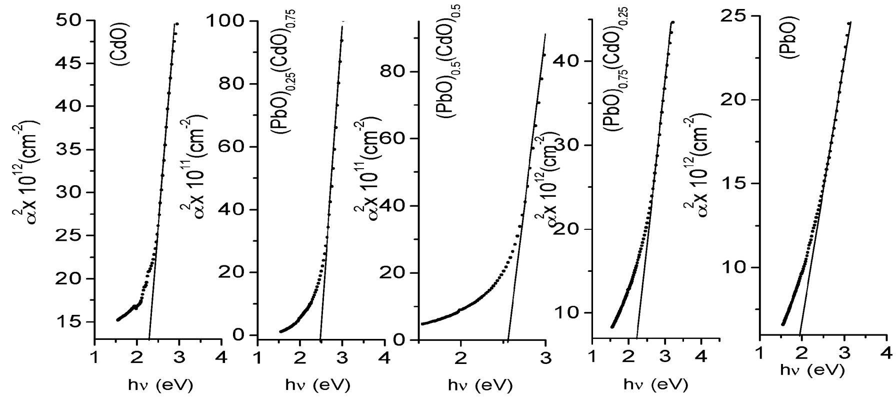

Figure 2 α^2 vs. $h\nu$ plots of $(PbO)_x(CdO)_{1-x}$ films.

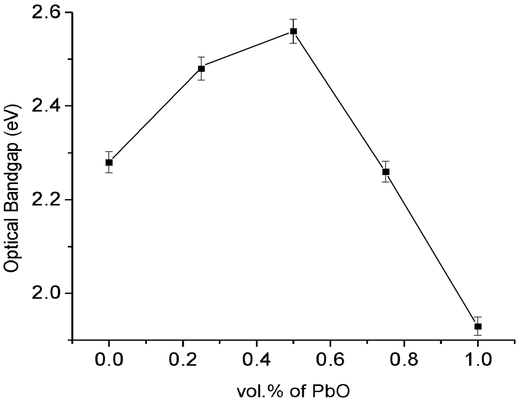

Figure 3 Variation of E_{opt} with composition for $(PbO)_x(CdO)_{1-x}$ films.

Room temperature electrical resistivity of the $(PbO)_x(CdO)_{1-x}$ films is plotted as a function of composition in Fig. 4. The value of 1.5×10^{-2} Ω·cm obtained for CdO film ($x = 0$ sample) agrees well with earlier reports [5]. The increase in the resistivity with PbO content is due to the higher resistivity of PbO. Thermoelectric power measurements showed that all the films exhibited n-type conductivity. Composition dependence of the Seebeck coefficient is shown in Fig. 5. The Seebeck coefficient of 5.6×10^{-5} VK^{-1} obtained for CdO film ($x = 0$ sample) prepared by us could be compared 1.52×10^{-5} VK^{-1} reported earlier [13]. The difference in the Q value between the two reports may be due to the differences in the thickness of the samples used.

TABLE I Thickness, optical band gap (E_{opt}), room temperature resistivity (ρ) and Seebeck coefficient data for $(PbO)_x(CdO)_{1-x}$ ($0 \le x \le 1$) thin films

Composition	Thickness (Å)	E_{opt} (eV)	$\rho_{300} \times 10^{-2}$ (Ω·cm)	$Q_{348} \times 10^{-2}$ (mV K^{-1})
CdO	1020 ± 50	2.28 ± 0.02	1.5 ± 0.1	−5.6 ± 0.2
$(PbO)_{0.25}(CdO)_{0.75}$	1085 ± 50	2.48 ± 0.02	2.6 ± 0.1	−5.5 ± 0.2
$(PbO)_{0.5}(CdO)_{0.5}$	2665 ± 80	2.56 ± 0.02	8.6 ± 0.2	−3.4 ± 0.1
$(PbO)_{0.75}(CdO)_{0.25}$	1060 ± 50	2.26 ± 0.02	10.0 ± 0.2	−8.0 ± 0.2
PbO	2760 ± 90	1.93 ± 0.02	17.8 ± 0.3	−23.4 ± 0.3

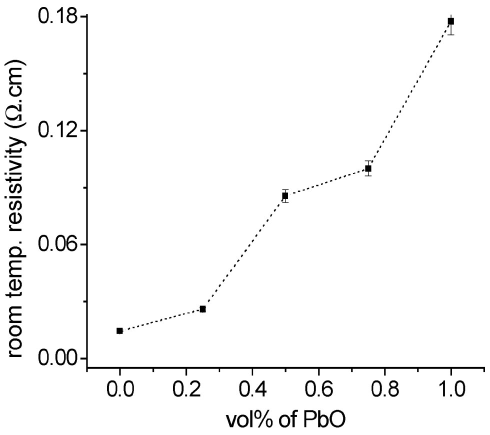

Figure 4 Variation electrical resistivity with composition of $(PbO)_x(CdO)_{1-x}$ films.

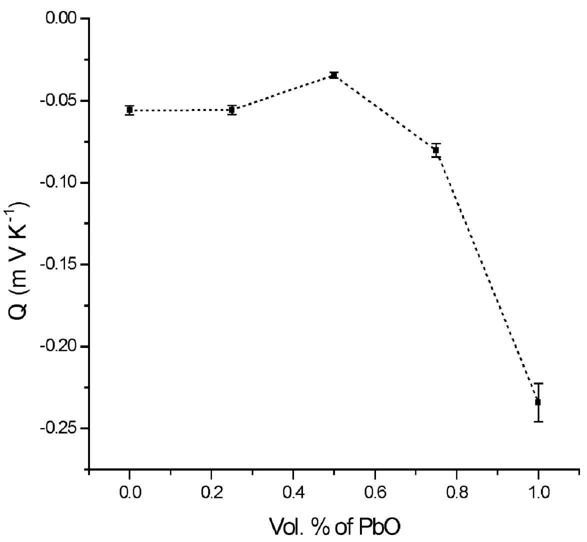

Figure 5 Composition dependence of Seebeck Coefficient of $(PbO)_x(CdO)_{1-x}$ films at 348 K.

In conclusion, $(PbO)_x(CdO)_{1-x}$ $(0 \leq x \leq 1)$ films with tetragonal PbO and cubic CdO phases have been prepared. These films exhibited a single direct (allowed) optical band gap. All the films showed n-type conductivity. An analysis of the preferred orientation of the crystallites in the films and the percentage of CdO and PbO crystallites in the films formed with different solution concentrations would throw light on the preferential growth of this mixed crystal system. The nonlinear variation of E_{opt}, Q and ρ show that the properties of this mixed oxide semiconductor crystal system could be tailored.

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