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Microstructural and Electrical Properties of Mn Doped Nanostructured CdO Thin Films

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Abstract: A great deal of research efforts was directed towards investigating the physical properties of thin film in order to improve the performance of device and for finding new applications. In this study, undoped cadmium oxide and manganese doped cadmium oxide (CdO) film were prepared using home built spray pyrolysis technique. Structural properties of undoped and Mn (manganese) doped CdO films shows polycrystalline FCC (Face Centered Cubic) crystal in nature with preferential orientation along (111) plane. X-ray peak line broadening technique was adopted to estimate grain size and strain. Film resistivity was obtained using linear four probe method. From the resistivity verses temperature plot, activation energy was estimated. It was observed that the activation energy decreases as Mn concentration in the precursor solution increases. The effect of Mn level on microstructural parameters like grain size and microstrain as well as activation energy were analyzed and reported.

Key words: Thin film, spray pyrolysis, CdO, activation energy

INTRODUCTION

Cadmium oxide is a n-type semiconducting material with higher mobility. Cadmium oxide in the form of transparent conducting film has been used in various applications such as photodiodes, phototransistors, photovoltaic cells, LCD (Liquid Crystal Display), gas sensor, thin film resistors etc. (Kulkarni *et al.*, 1999; Ito *et al.*, 2006; Lim *et al.*, 2007). There are various physical and chemical deposition techniques used to prepare cadmium oxide film. The spray pyrolysis technique (Jeyaprakash *et al.*, 2010; Ferro *et al.*, 2001) was used to deposit cadmium oxide thin film due to its simplicity, mass production capability over large area and ease of adding doping material. By doping different materials, the physical properties of the film will change. Various dopants were incorporated in CdO films such as in (Freeman *et al.*, 2000), Sn (Zhao *et al.*, 2002; Yan *et al.*, 2001), F (Ghosh *et al.*, 2004), Ti (Gupta *et al.*, 2009a) and Al (Maity and Chattopadhyay, 2006; Khan *et al.*, 2010; Gupta *et al.*, 2009b). The literature survey showed that there are limited numbers of reports on Mn incorporated CdO films obtained by different techniques.

Today various materials which have become insufficient for device that needs higher performance and technology needs to introduce novel materials. With this objective we produce undoped cadmium oxide and Mn doped cadmium oxide thin film using spray pyrolysis technique and the physical properties were investigated.

From the physical property and crystallographic data we conclude that the Mn doped cadmium oxide film will be a promising material for technological applications. By doping Mn in cadmium oxide thin films the physical properties changes and there is raise in chemical stability of the film.

MATERIALS AND METHODS

The undoped and manganese doped cadmium oxide films were prepared using home built spray pyrolysis technique. The aqueous solutions were prepared by mixing appropriate volume of cadmium acetate dihydrate and manganese acetate tetrahydrate dissolved in deionized water. The prepared aqueous solution was sprayed through the nozzle on the glass substrate. The distance between the nozzle and the substrate were maintained at 20 cm. The main parameter to be considered is optimization. The films were prepared with 50 mL of solution which was sprayed for 30 min at the temperature of 230°C that was maintained using thermocouple. The Mn doped CdO were prepared with different concentration which is shown in Table 1.

Table 1: Prepared CdO-Mn concentration

Material	Cd(CH ₃ COO) ₂ ·2H ₂ O	Mn(CH ₃ COO) ₂ ·4H ₂ O	Total volume (mL)
Undoped CdO	50 mL (0.05 M)	-	50
CdO-Mn	25 mL (0.05 M)	25 mL (0.001 M)	50
CdO-Mn	25 mL (0.05 M)	25 mL (0.002 M)	50
CdO-Mn	25 mL (0.05 M)	25 mL (0.002 M)	50

The structural and electrical studies were investigated using XRD (X-ray diffraction) and four probe method. The obtained result from XRD and four probe methods were reported.

RESULTS AND DISCUSSION

Structural studies: Structural studies were carried out to confirm the crystallinity, X-ray diffractometer with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) in the range of 10-70 $^\circ$ in steps of 0.025 at a scan speed 2 $^\circ \text{ min}^{-1}$. Typical XRD spectrum reflects polycrystalline FCC crystal with preferential orientation along (111) plane. The XRD results show that the samples contain Montepontite phase of cadmium oxide. The broadness of the XRD peaks indicates the nanocrystalline nature of undoped and Mn doped cadmium oxide thin film which is shown in Fig. 1.

As the concentration of Mn increases in the precursor solution the broadness of XRD peak increases. Based on XRD peak line broadening technique the grain size and microstrain were determined. The grain size were determined using Debye-Scherrer's equation:

$$d = \frac{0.9\lambda}{\beta \cos\theta}$$

and it was found that there is a decrease in grain size when the Mn doping level increases and the average grain size is found to be 10.58 nm.

Decrease in the grain size increases microstrain which indicates peak movement without change in the shape of the peak. The dislocation density which also increases with decrease in grain size.

Electrical studies: The I-V characteristics curves for the prepared film were analyzed using four probe method. In four-point probe technique two probes are used for current injection and the other two probes are used to measure the voltage drop. The I-V curve shows the linear relationship between current and voltage this convey the prepared film which are ohmic in nature. The electrical resistance of the film was obtained from I-V curves by calculating the gradient of the curves shown in Fig. 2.

The electrical resistivity for the prepared films was calculated at each temperature. The resistivity of each film were determined using the relationship:

$$\rho = \frac{It}{\ln 2} \left(\frac{V}{I} \right)$$

where, ρ is the resistivity ($\Omega\text{-cm}$), t is the sample thickness (cm), V is the measured voltage and I is the source current (mA).

Figure 3 shows the dependence of resistivity with temperature. Thus it is clearly evident that when there is an increase in temperature the resistivity of the film decreases which indicate the semiconducting property of the thin film.

The activation energy of the film were determined from the straight portion of the curve between $\log R$ and

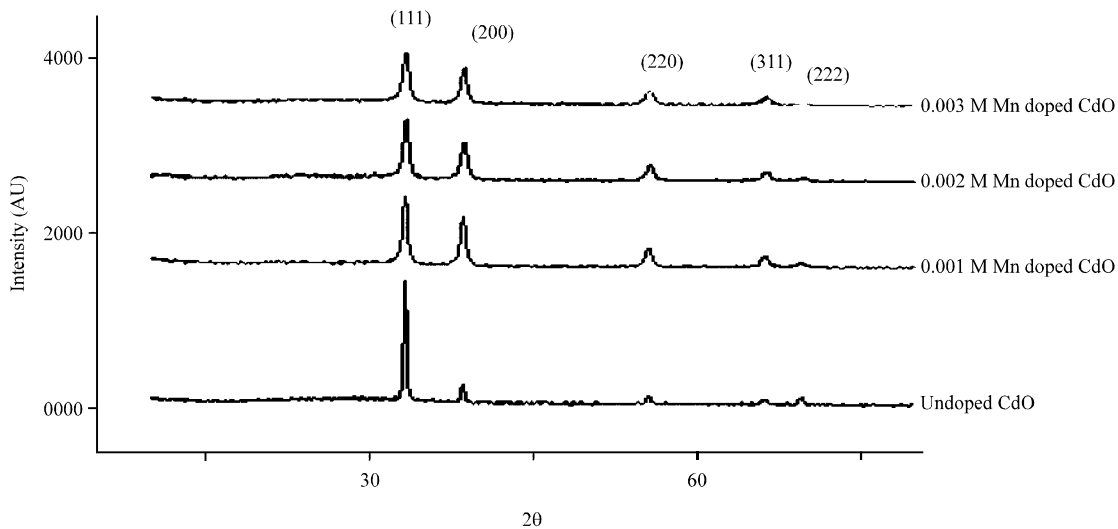


Fig. 1: XRD pattern of undoped and Mn doped CdO

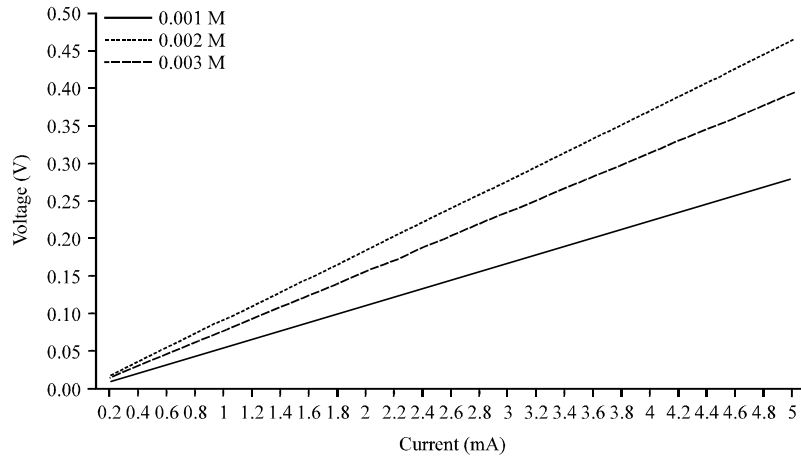


Fig. 2: I-V characteristics curve for different Mn concentration

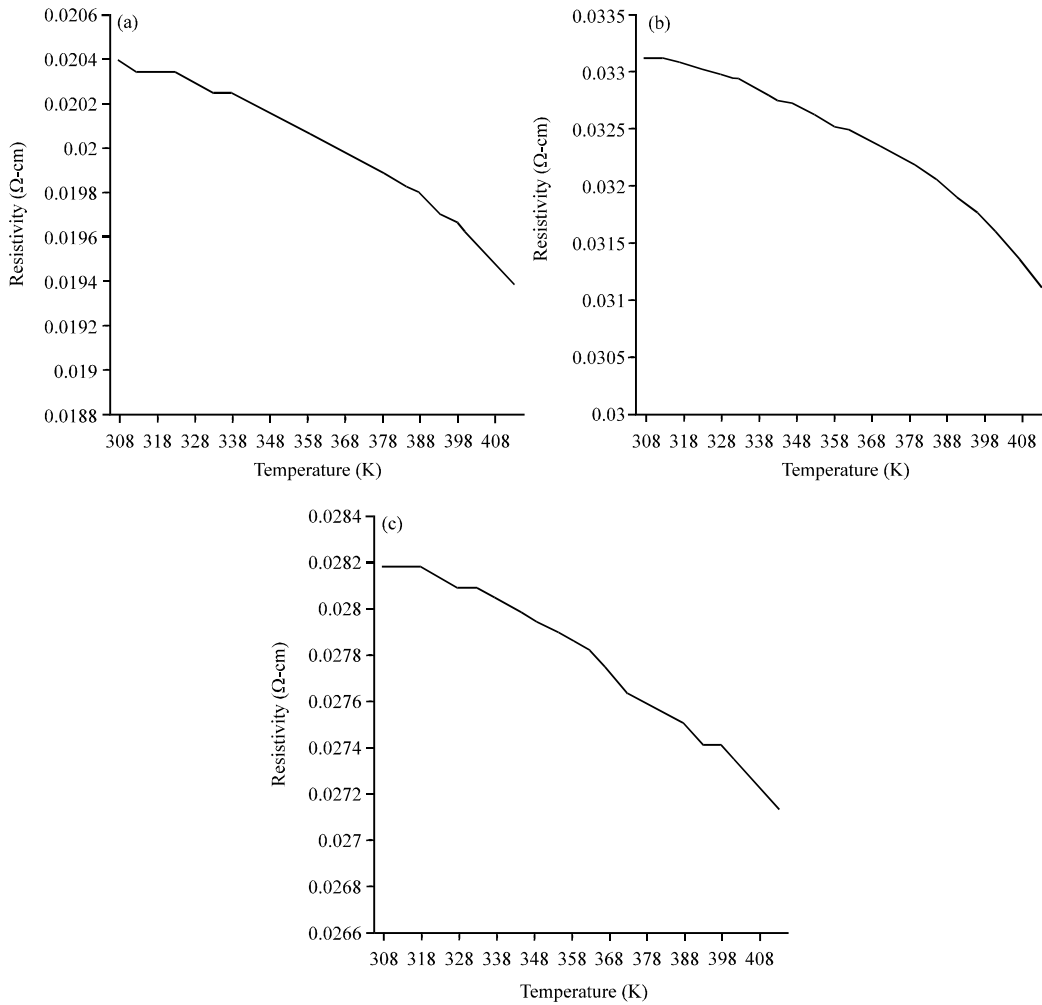


Fig. 3 (a-c): Plot of resistivity vs. temperature for different Mn concentration; (a) 0.001 M, (b) 0.002 M and (c) 0.003 M

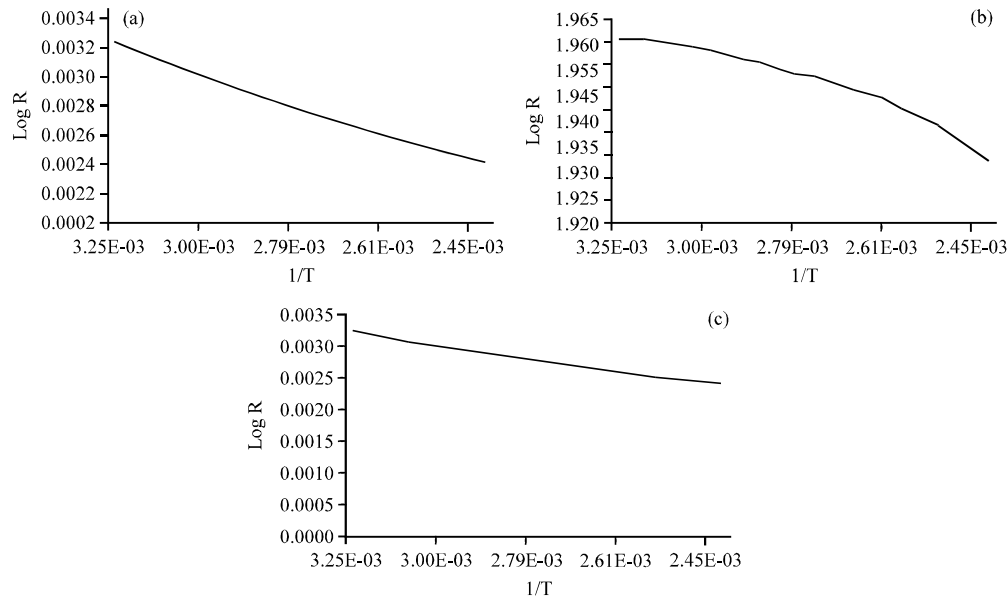


Fig. 4(a-c): Plot of log R vs. 1/T for different Mn concentration; (a) 0.001 M, (b) 0.002 M and (c) 0.003 M

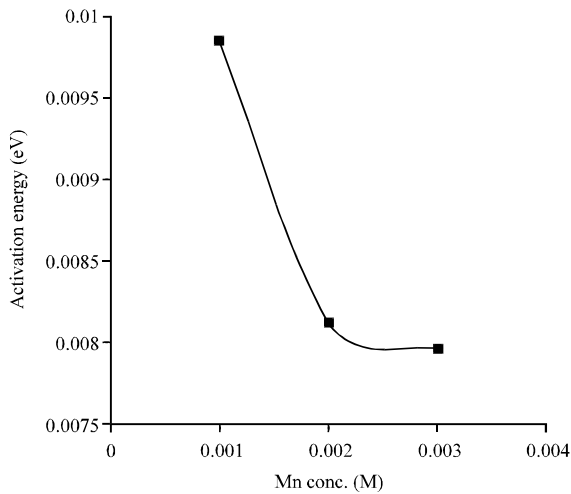


Fig. 5: Plot of activation energy vs. Mn concentration in precursor solution

1/T by using the relation which was shown in Fig. 4. Where k is the Boltzmann constant and T the absolute temperature in Kelvin. The calculated activation energy decreases as manganese concentration increases in the precursor solution which is shown in Fig. 5.

CONCLUSION

In this present study, undoped and Mn doped CdO films were prepared by home built spray pyrolysis technique on glass substrates. The preferred orientations in the samples were in (111) axes for undoped and Mn

doped cadmium oxide with FCC structure. As the concentration increases there is decrease in grain size and increase in microstrain. Electrical properties of the samples were studied by Four-probe method. I-V characteristics of the undoped and Mn doped thin film were determined which shows the ohmic nature of the film. It is evident from the result that there is a decrease in activation energy when the concentration of manganese in the precursor solution is increased which indicates the semiconducting property of the film.

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