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Physical Properties of Spray Deposited Mg Doped CdO Thin Films

[1]M. Vigneshwaran, [1]R. Chandiramouli, [1,2]B.G. Jeyaprakash and [1]D. Balamurugan
[1]School of Electrical and Electronics Engineering, SASTRA University, Thirumalaisamudram, Thanjavur, 613 401, India
[2]Centre for Nanotechnology and Advanced Biomaterials, SASTRA University, Thirumalaisamudram, Thanjavur, 613 401, India

Abstract: Cadmium oxide is the very crucial material in the field of solar cells, optoelectronic devices, flat panel displays due to its high transparency and narrow band gap. In this study, Mg doped CdO thin films were prepared using the home made spray pyrolysis unit and its structural and electrical properties were studied. The XRD results show that the grain size decreases upon increasing the dopant concentration from its broadened peak. Atomic Force Microscopy (AFM) analysis indicates that the roughness of the surface decreases upon increasing Mg concentration. The activation energy, I-V characteristics were studied using Four probe method. The results were analyzed for three different concentration of Mg doped CdO films and are reported.

Key words: Spray pyrolysis, thin films, CdO, grain size

INTRODUCTION

Generally transparent semiconductors have the wide range of application in many areas. In that CdO is one of the dominant member used in different fields like solar cells, smart windows, light-emitting diodes, photo-transistors, sensors (Grado-Caffaro and Grado-Caffaro, 2008; Li *et al*., 2008; Lee *et al*., 2008; Lokhande *et al*., 2009) etc. It has a narrow band gap of ~2.20-2.40 eV (Demchenko *et al*., 2011) and high transparency in visible and NIR spectral regions with cubic face centered crystal structure (Demchenko *et al*., 2011). CdO has activation energy of 0.32-0.90 eV (Uplane *et al*., 2004) with electrons as the majority carriers due to the oxygen vacancies (Dakhel 2009a). The resistivity of CdO thin films ranges from 10-2-10-4 Ω cm (Dakhel, 2011a). Many dopants like Al, Cu, Dy, Ce, Sn, In, Ti, F (Dakhel, 2009b, 2010, 2011b; Chattopadhyay *et al*., 2007; Ghosh *et al*., 2005; Gupta *et al*., 2011; Atay *et al*., 2006). Were doped in order to improve the electrical properties of the CdO.

In the current work Mg was chosen as the dopant in order to enhance the structural and electrical properties. The ionic radius of Mg^{2+} ion is 86 and Cd^{2+} is 109 pm since Mg has lower ionic radius than Cd it may cause considerable change in its electrical property (Dakhel, 2011a). Mg was incorporated at different weight percentage from 2-6 wt.%. The method chosen for the preparation of film is homemade spray pyrolysis unit. Because it is simple method to achieve nanostructured thin films and also bulk production can be achieved. Some of the physical properties of Mg doped CdO has been reported (Atay *et al*., 2011) but according to the best of our survey no work has been done on their electrical properties.

MATERIALS AND METHODS

The precursors used in spray pyrolysis method are cadmium acetate dihydrate (99.9% purity, Merck, India) in constant concentration of 0.05 M and magnesium acetate tetra hydrate (99.9% purity, Merck, India) in varying concentration of 0.001, 0.002 and 0.003 M. Deionized water was used as solvent and the clear solution was obtained. The compressed air was used as the carrier gas at the pressure of 2 kg cm^{-2}. The distance between the spray nozzle and substrate was maintained at 30 cm to obtain maximum coverage throughout the film. Solution was dispersed through the glass nozzle on to the ultrasonically cleaned, preheated glass substrate at temperature of 503±2 K and the spray gun angle was 45°. The temperature was assured by K-type thermocouple. Total volume of 50 mL solution was sprayed in 30 min at the flow rate of 1 mL for every 40 sec to get the perfect nucleation. The coated films were annealed at 623 K for 60 min in order to improve its stability and electrical properties. Mg was implanted at

Corresponding Author: D. Balamurugan, School of Electrical and Electronics Engineering, SASTRA University, Thirumalaisamudram, Thanjavur, 613 401, India

different ranges of 0, 2 , 4, 6% and named M0, M1, M2, M3, respectively. To study the structural property X-Ray Diffraction(XRD) patterns were obtained from (Model XPERT-PRO) Cu-Kα radiation (λ = 1.54056 Å) with continuous scanning mode and range of 2θ varying from 10-90° to detect the possible peaks. Surface properties of the film were studied using AFM. Electrical properties were studied through the standard four probe technique.

RESULTS AND DISCUSSION

Structural analysis: XRD patterns obtained for undoped and Mg doped CdO were given in Fig. 1. The diffracted peaks showed that it has polycrystalline nature with cubic face centered crystal structure which was confirmed from JCPDS (No. 5-0640). Both undoped and Mg doped films showed the preferential orientation along (111) plane. There are no additional peaks upon doping which indicates the stability of the crystal structure. The grain size was calculated using Scherrer formula (Gurumurugan *et al*., 1994) for preferential planes. The grain size decreased rapidly upon increasing the Mg concentration. The grain size of the undoped film was found to be 43 nm which decreased to the minimum of 17 nm for 6 wt.% of Mg. Peak shifts towards higher angles were also noted from XRD results which indicate the compression in unit cell. This may be due to the lower ionic radius of Mg when compared to Cd ionic radius. Strain value was minimum for undoped film but increased in relation with Mg wt.% which is evident for decrease in grain size. The values of peak angle, grain size and strain obtained for both undoped and doped CdO films are given in Table 1.

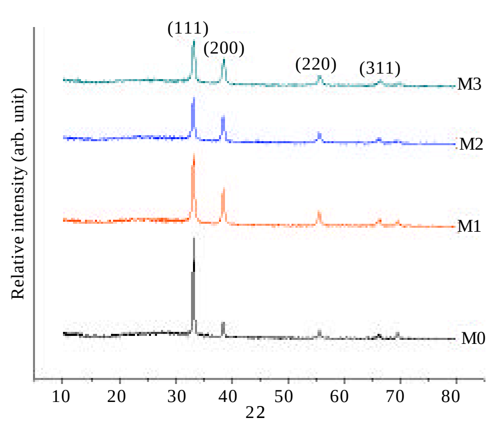

Fig. 1: XRD patterns for undoped and Mg doped CdO

Surface analysis: Figure 2 shows the AFM (Atomic force microscopy) images obtained for undoped and doped CdO films. The roughness of the surface was estimated by calculating the Root Mean Square (RMS) value. The surface of Mg doped CdO seems to be more rough than the undoped CdO. Mg doping increases the surface roughness upon increase in Mg wt.%.

Electrical properties: Linear I-V characteristics was obtained for all Mg doped CdO films which show they obey ohms law and shown in Fig. 3. R vs. T plot given in Fig. 4 indicates that the 2 wt.% Mg doped CdO has the decrease in resistance value for increase in temperature which has the negative temperature coefficient and behaves as the semiconductor. For 4 and 6 wt.% Mg

Table 1: XRD data obtained for undoped and Mg doped CdO

Doping concentration (wt.%)	2θ (deg.)	Grain size (nm)	Strain
Undoped CdO	33.23	43.2	0.000024
2 wt.% Mg doped CdO	33.235	23.1	0.000045
4 wt.% Mg doped CdO	33.245	22.2	0.000047
6 wt.% Mg doped CdO	33.27	17.7	0.00006

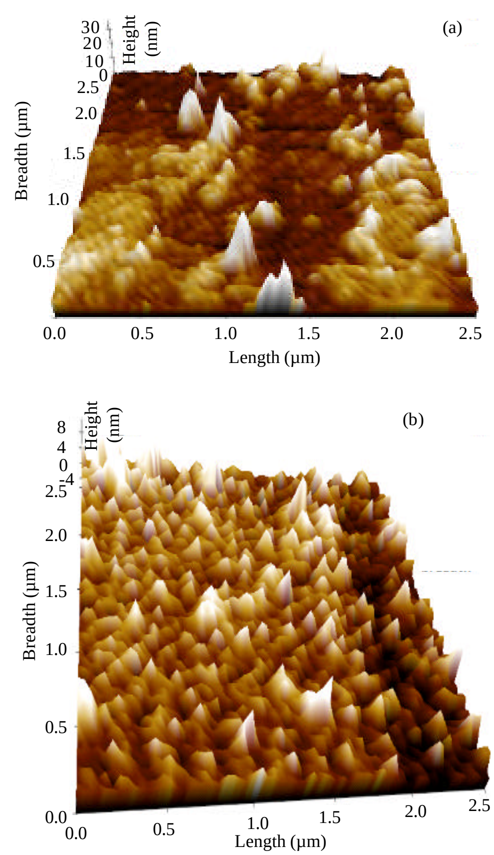

Fig. 2(a-b): AFM images of, (a) undoped and (b) 4 wt.% Mg doped CdO doped CdO exhibits the increase in resistance value for increase in temperature and has the metallic behaviour.

The resistivity values obtained for Mg doped CdO films are given in Table 2. Even though highly doped films exhibits the metallic character the resistivity of the films increases with concentration of Mg. This happens since they have less oxygen vacant sites when compared to 2 wt.% Mg doped films.

Activation energy of the films was found from Arrhenius plot Fig. 5 and the values are given in Table 2.

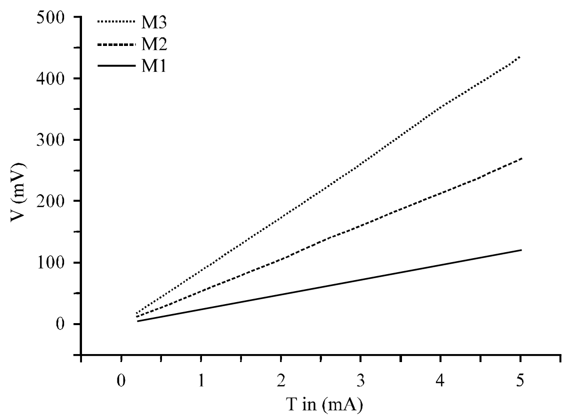

Fig. 3: Current-voltage characteristics of Mg doped CdO

The activation energy increases as the doping concentration increases this may be due to the increase in its optical band gap energy. Similar result was obtained for Mg doped In_2O_4 (Sanjeeviraja *et al*., 2008).

Table 2: Activation energy obtained for Mg doped CdO

Doping concentration (wt.%)	Activation energy (eV)
2	0.00253
4	0.00811
6	0.00017

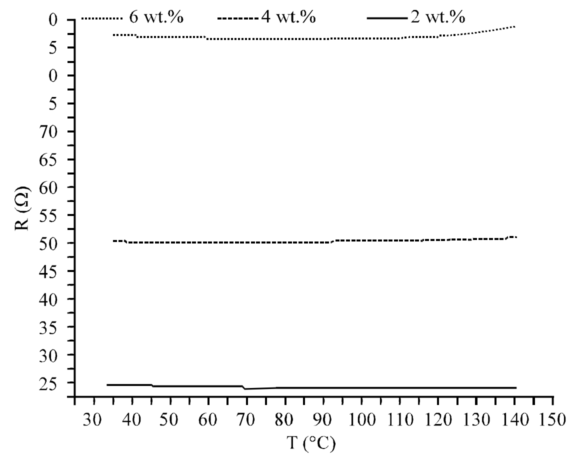

Fig. 4: R vs. T plot for Mg doped CdO

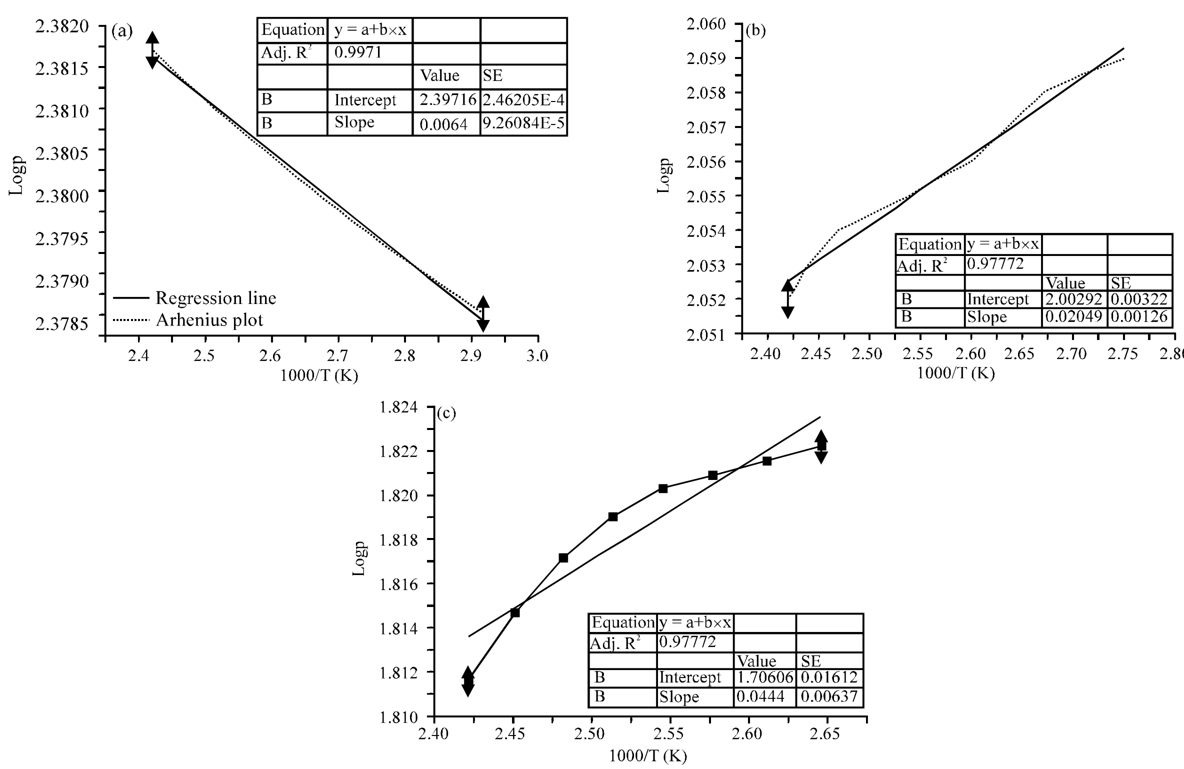

Fig. 5(a-c): Arrhenius plot for Mg doped CdO, (a) 2 wt.%, (b) 4 wt.% and (c) 6 wt.%

CONCLUSION

Mg doped CdO films are coated by spray pyrolysis technique. XRD patterns shows that it has polycrystalline nature with cubic face centered crystal structure with (111) plane as preferential orientation. The grain size decreased rapidly upon increasing the Mg concentration. Th grain size of the undoped film was found to be 43 nm which decreases to the minimum of 17 nm for 6 wt.% of Mg. Surface morphology studies showed that roughness of the films decreases as the doping concentration increases. Electrical studies revealed that higher doping cause the films to behave as metals. Linear I-V characteristics curve infers that they follow Ohms law. Activation energy of the 2 wt.% Mg doped films are almost four times lower when compared to undoped films which can be used for sensing applications at lower temperatures.

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