Chapter IV

PREPARATION AND CHARACTERISATION OF Al DOPED CdO THIN FILMS

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4.1 Introduction

Transparent conducting oxide (TCO) thin films have great importance in the field of optoelectronic devices. They are widely used for flat panel display, organic light emitting diodes and photovoltaic applications [1–3]. Among these TCOs, cadmium oxide (CdO), doped zinc oxide (ZnO), tin oxide (SnO_2) and indium oxide (In_2O_3) are used as n-type transparent conducting oxides, while silver doped In_2O_3, doped ZnO, $CuAlO_2$ and $SrCu_2O_2$ are used as p-type transparent conducting oxides [4–11]. In particular, CdO is been considered a promising material for photovoltaic applications due to its high electrical conductivity and optical transmittance in the visible region of solar spectrum [12].The simultaneous occurrence of high optical transparency in the visible region and high electrical conductivity is not possible in an intrinsic stoichiometric material. The only way to obtain good transparent conductors is to create electron degeneracy in wide band gap (greater than 3 eV) oxides by controllably introducing non-stoichiometry and appropriate dopants [13].

CdO is an n-type semiconductor with band gap of 2.5 eV [14].Due to its low optical band gap, CdO is not widely used as transparent conducting electrodes, although CdO thin films show low resistivity due to defects of oxygen vacancies and cadmium interstitials [15]. Different techniques have been used to deposit CdO thin films. Literature survey reveals that there is no report on Al doped CdO thin films by spray pyrolysis deposition technique. In this work an attempt is made to study the effect of Al doping on the optical and electrical properties of CdO thin films synthesized by spray pyrolysis technique.

4.2 Experimental details

4.2.1 Substrate cleaning

The micro slides glass substrates were used for Al doped CdO thin film deposition by spray pyrolysis technique. The substrates were cleaned using procedure discussed in section 3.2.4

4.2.2 Solution preparation

Freshly prepared double distilled water is used to prepare the solution. Initial ingredients used to deposit Al doped CdO thin films in aqueous medium are as follows

i) A. R. grade Cadmium acetate ($Cd(CH_3COO)_2\ 2H_2O$), grade supplied by s. d. fine chem. limited, Boisar, Mumbai.

ii) A. R. grade Aluminum nitrate $Al(NO_3)_3$, supplied by s. d. fine chem. limited, Boisar, Mumbai.

iii) Double distilled water

4.2.3 Film Deposition Procedure

Al doped CdO thin films were deposited by the spray pyrolysis technique. The experimental steps involved in the deposition of thin films using a spray pyrolysis technique are as discussed in section 3.2.5

4.3 Results and discussion

The structural, surface morphological, optical and electrical Characterization of the aluminum doped cadmium oxide films deposited was carried out by means of X-ray diffraction, Scanning electron microscopy (SEM), optical absorption, electrical resistivity.

4.3.1 X-ray diffraction

The XRD pattern of aluminum-doped cadmium oxide thin film for different Al-doping is shown in Fig. 4.1. Which reveals that the material deposited is polycrystalline.

These XRD patterns do not show the presence of any aluminum compound in the films, which indicates the absence of an impurity phase in the films. The average crystallites size is deduced using the well known scherrer's formula,

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

Where λ is the X-ray wavelength, β is the full width at half maximum of the (200) diffraction line and Θ is the diffraction angle of the XRD spectra. The average crystallite size is found to be 15.6 nm.

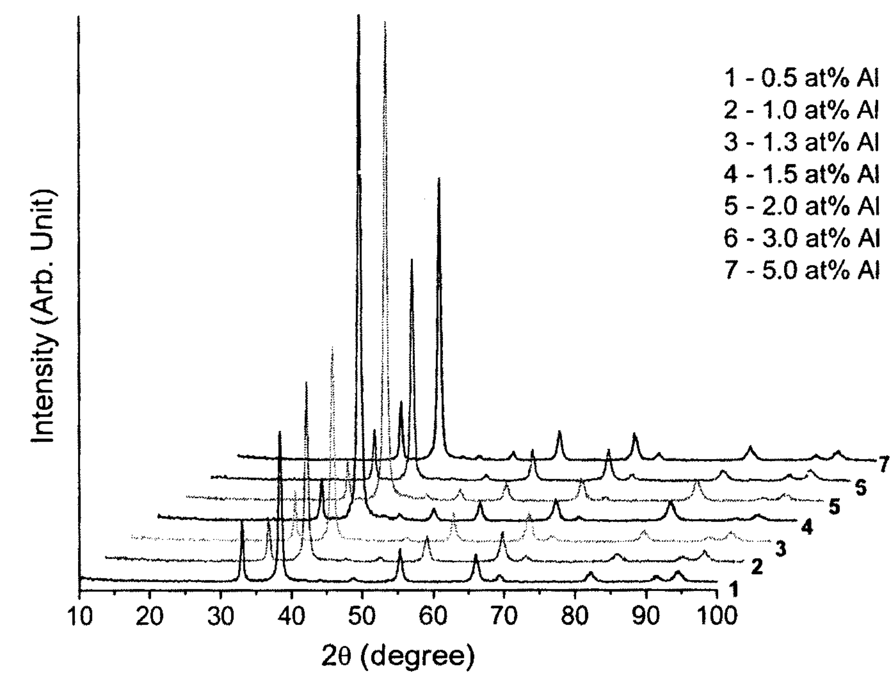


Fig.4.1Superposed X-ray diagram of Al: CdO thin films deposited at different atomic percent of Al [JCPDS Card No.65-2908].

Texture coefficients of the films are calculated by using equation 3.2. The variation of texture coefficient with different doping percents of Al is shown in fig .4.2.maximum texture coefficient (3.22) is obtained for 1.3% Al doping. The lattice constants calculated from the Bragg equation are plotted against the Nelson-Riley function (NRF) (fig.4.4). By extrapolation technique, the true value of lattice parameter is found to be a= 4.69 Å.

Table 4.1 observed and standard d values for the Al: CdO thin film with 1.3% Al doping

Sr. No.	Standard d value Å	Observed d value Å	(hkl) planes.
1	2.7112	2.7184	(111)
2	2.3480	2.3495	(200)
3	1.6602	1.6626	(220)
4	1.4158	1.4130	(311)
5	1.3556	1.3571	(222)
6	1.1740	1.1761	(400)

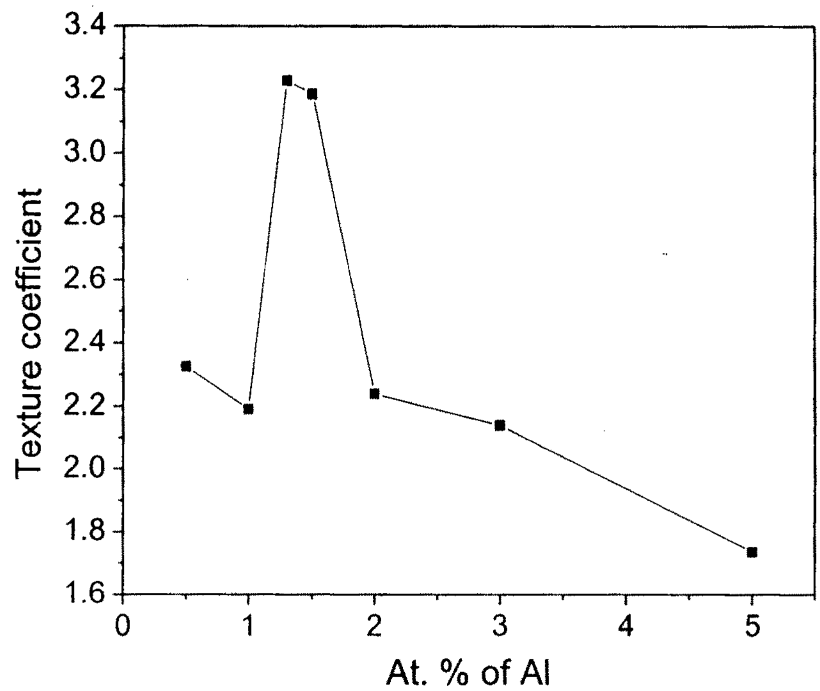


Fig.4.2Variation of texture coefficient for (200) plane of Al: CdO thin films deposited at different atomic percent of Al.

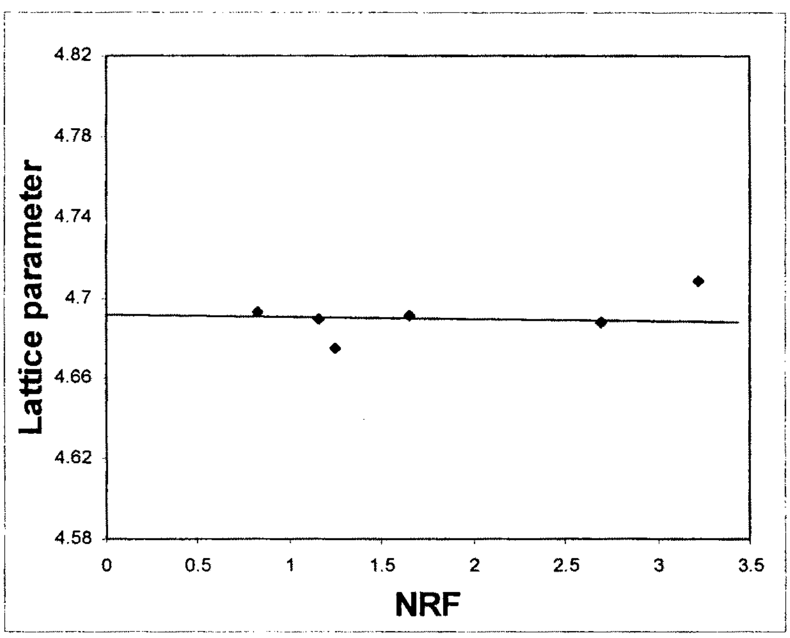
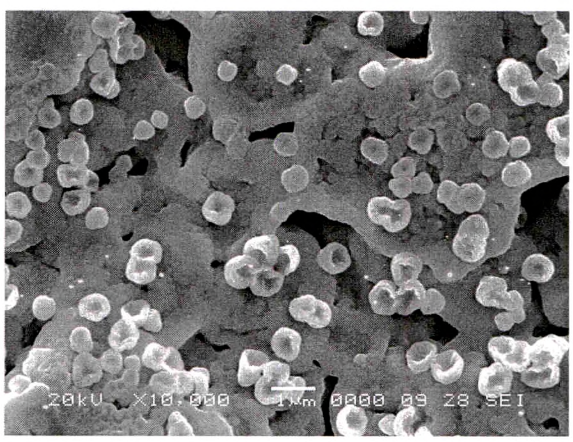


Fig.4.3 Plot of lattice parameters versus Nelson-Riley function for optimized sample

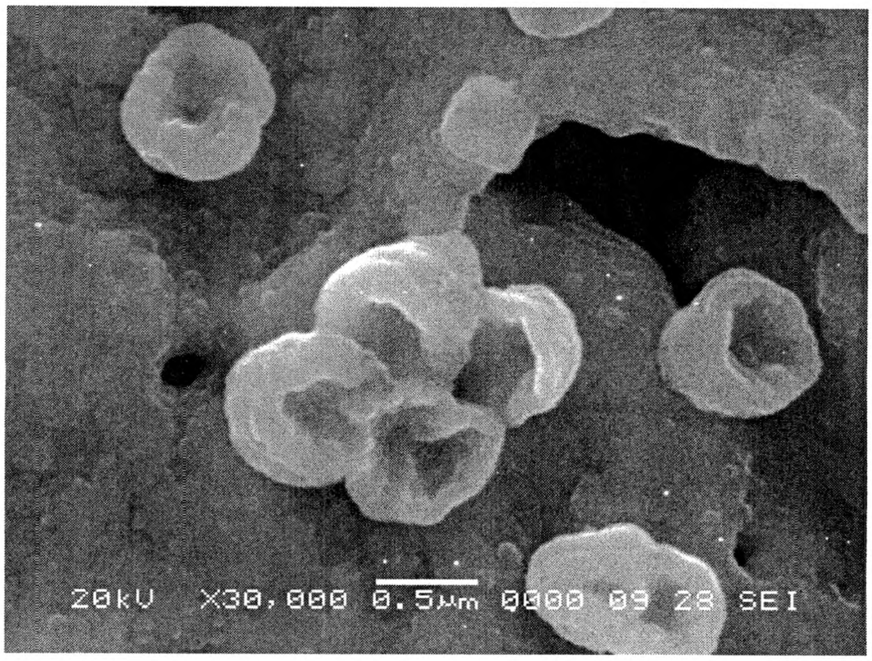
4.3.2 Scanning electron microscopy

Fig .4.4 shows SEM image of Al doped CdO thin films deposited on glass substrates at (a) X 10, 000 and (b) X 30, 000 magnifications. The micrograph shows the existence of well-crystallized grains, having a faceted cap like structure [16].

The final aluminum content in the films was determined by energy dispersive X-ray analysis (EDX) shown in fig.4.5. It was observed that, the Al/Cd atomic ratio inside the film was lower than that taken in the starting solution. For obtaining minimum resistivity in the deposited films, the presence of high concentration of Al ions in the starting solution was required.



(a)



(b)

Fig. 4.4 SEM image of Al doped thin film deposited with optimized deposition conditions at (a) X 10, 000 and (b) X 30, 000 magnifications.

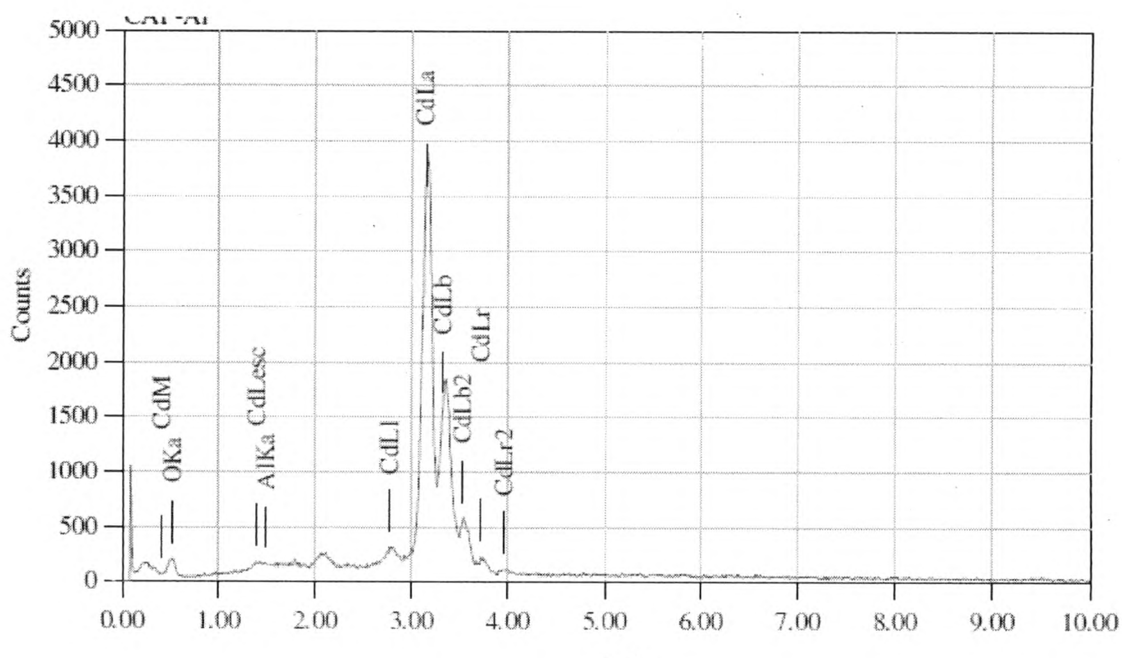


Fig. 4.5 Energy dispersive X-ray analysis of Al-CdO thin film deposited with optimized deposition conditions.

4.3.3 Optical absorption and transmission

Fig. 4.6 show the plot of $(\alpha h\nu)^2$ v_s. hν for spray deposited Al: CdO thin films. Extrapolation of linear portion of the plot to the energy axis at α = 0 gives the band gap energy of the material. The graph shows that, at lower doping percentage of aluminum, there is not much variation in the band gap energy. But at higher doping percentage of aluminum, the band gap energy changes significantly. Maximum band gap (2.15eV) is obtained for the film doped with 1.3 atomic percent Al.

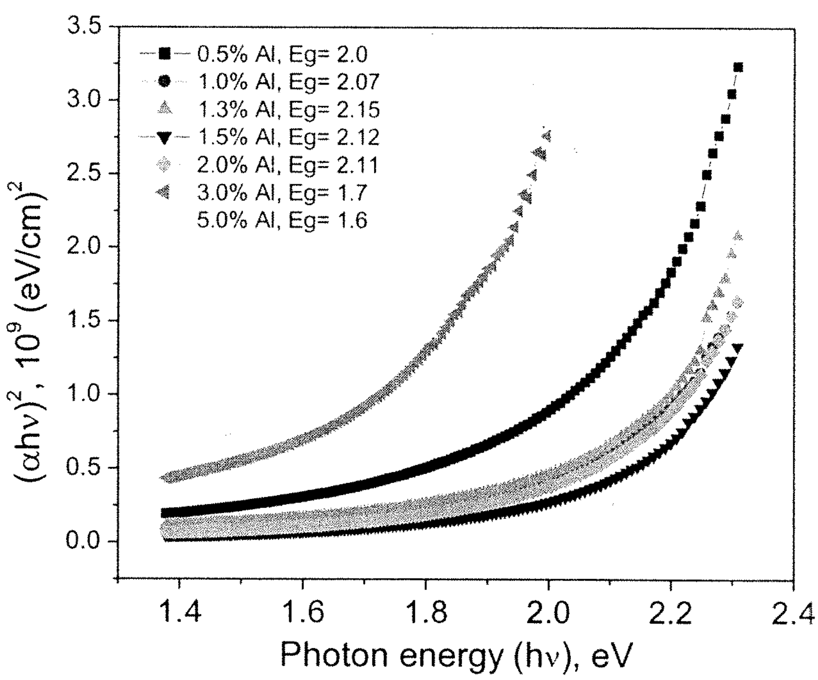


Fig 4.6 Variation of $(\alpha h\nu)^2$ versus hν for spray deposited Al: CdO thin films.

4.3.4 Electrical resistivity

The room temperature resistivity of Al: CdO film is measured by van-der pauw method. For different atomic percent of aluminum, the variation of resistivity is shown in fig. 4.7. Room temperature resistivity decreases from 1.7×10^{-4} to 1.2×10^{-4} (Ωcm) when the percentage of Al increases from 0.5 to 1.3, but further increase of Al increases the resistivity to 2.5×10^{-4} (Ωcm). This result is comparable to Aluminum-doped cadmium oxide thin films by the sol–gel dip-coating method [16], In-doped CdO thin films by the solution route [17], fluorine-doped CdO thin films by the sol–gel method [18] and fluorine-doped CdO thin films by the spray pyrolysis method [19]. The decrease in electrical resistivity due to aluminum doping can be explained as follows: the concentration of free charge carriers in CdO increases with the aluminum doping because, aluminum has one valance electron more than cadmium. We may consider that aluminum substitutes the cadmium atom, or it occupies the interstitial sites. In both cases aluminum acts as the donor. But excess Al-doping may destroy the crystalline structure, and due to the increased absorption of the free carriers, the resistivity in Al: CdO thin films increased [16].

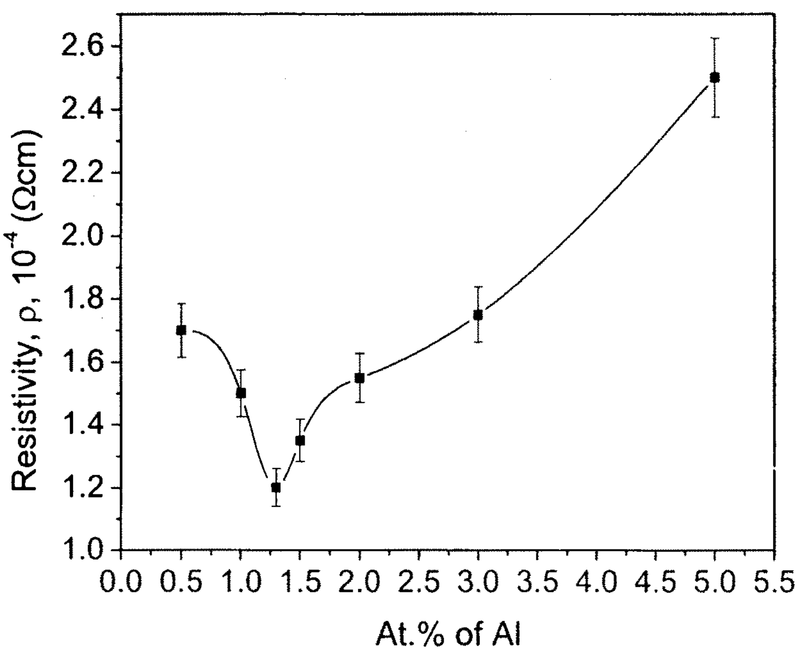


Fig.4.7 Variation of resistivity of CdO thin film with at. % of Al doping.

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