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Structural, optical and electrical properties of In-doped Cd_2SnO_4 thin films by spray pyrolysis method

R. Kumaravel, K. Ramamurthi*

Crystal Growth and Thin Film Laboratory, School of Physics, Bharathidasan University, Tiruchirappalli 620 024, India

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ABSTRACT

Preparation of highly conducting and transparent In-doped Cd_2SnO_4 thin film by spray pyrolysis method at a substrate temperature of 525 °C is reported. In-doping concentration is varied between 1 and 5 wt.%. The effect of In-doping on structural, optical and electrical properties was investigated using different techniques such as X-ray diffraction, atomic force microscopy, optical transmittance and Hall measurement. X-ray diffraction studies revealed that the films are polycrystalline with cubic crystal structure. The undoped and In-doped Cd_2SnO_4 films exhibit excellent optical transparency. The average optical transmittance is ~87% in the visible range for 3 wt.% In-doping. Further In-doping widens the optical band gap from 2.98 ± 0.1 eV to 3.04 ± 0.1 eV. A minimum resistivity of $1.76 \pm 0.2 \times 10^{-3}$ Ω cm and maximum carrier concentration of $9.812 \pm 0.4 \times 10^{19}$ cm^{-3} have been achieved for 1 wt.% In-doping in Cd_2SnO_4 thin films.

1. Introduction

Transparent conducting oxide (TCO) thin films have been extensively studied in recent years, because they not only exhibit high optical transparency in the visible region of the spectrum but also possess high electrical conductivity [1]. These unique features made them useful in many optoelectronic applications, including flat panel displays, photovoltaic electrochromics, solar cells and energy efficient windows [2–6]. Research in this field has been carried out with the aim of discovering new materials with higher mobilities or improving the mobilities of the existing materials. The established materials such as indium tin oxide (ITO), SnO_2 and ZnO have been thoroughly investigated to improve their properties and it seems unlikely that improvements would result from these studies [7]. Among the various transparent conducting films, cadmium stannate (Cd_2SnO_4), a ternary TCO material, combines with many beneficial characteristics of both SnO_2 and CdO. Cd_2SnO_4 film possesses electron mobility up to 100 $cm^2 V^{-1} s^{-1}$ with high electrical conductivity and low absorption in the visible region. These properties make it potentially suitable material for a wide range of applications [8–10].

In the case of wide bandgap semiconductors, addition of impurities often induced dramatic changes in their electrical and optical properties. The effects of n-type doping on the electrical properties of Cd_2SnO_4 thin films [9,11] and thick films [12] have been extensively studied. Sb-doped Cd_2SnO_4 films are characterized by NMR, EPR and spectroscopic studies [13–15]. Dou and Egdell [13,16] have reported that In-doping in Cd_2SnO_4 improves its electrical properties. However, a detailed study on the effects of In-doping on the properties of Cd_2SnO_4 films remains to be clarified. Further various deposition methods have been employed to prepare Cd_2SnO_4 thin films [17–26]. However, the practical use of Cd_2SnO_4 thin films requires a cost-effective preparation method and relatively low cost precursors with the potential to produce thin films with improved physical properties. In this respect, the inexpensive spray pyrolysis method was effectively employed by early workers for producing highly transparent and conductive thin films [27–30]. Hence in this work we report on the preparation of In-doped Cd_2SnO_4 thin films for the first time employing the spray pyrolysis method and the effects of In-doping on the structural, electrical and optical properties of Cd_2SnO_4 films.

2. Experimental procedure

The spray aqueous solution was prepared mixing cadmium acetate and tin II chloride precursors in 8:1 mole ratio, respectively. Then a few drops of hydrochloric acid was added to this to get a clear solution. To achieve In-doping, aqueous solution of $InCl_3$ was mixed with the precursor solution. The resultant solution was sprayed on to the preheated substrates (Corning 1737 bare glass plate) at a temperature of 525 °C using the spray pyrolysis experimental setup described elsewhere [31]. The optimized deposition parameters such as spray nozzle–substrate distance (35 cm), spray angle (about 45°), spray time (4 s) and the spray interval (30 s) were kept constant. The total duration of film coating was adjusted to get film thickness of ~500 nm. The pressure of the carrier gas (compressed air) was 4.412 MPa. For each concentration, several sets of films were prepared and their structural, optical and electrical qualities were found to be highly reproducible and stable. The X-ray diffraction patterns were recorded using the computer controlled Philips X Pert

* Corresponding author. Tel.: +91 431 2407057; fax: +91 431 2407045.
E-mail address: krmurthin@yahoo.co.in (K. Ramamurthi).

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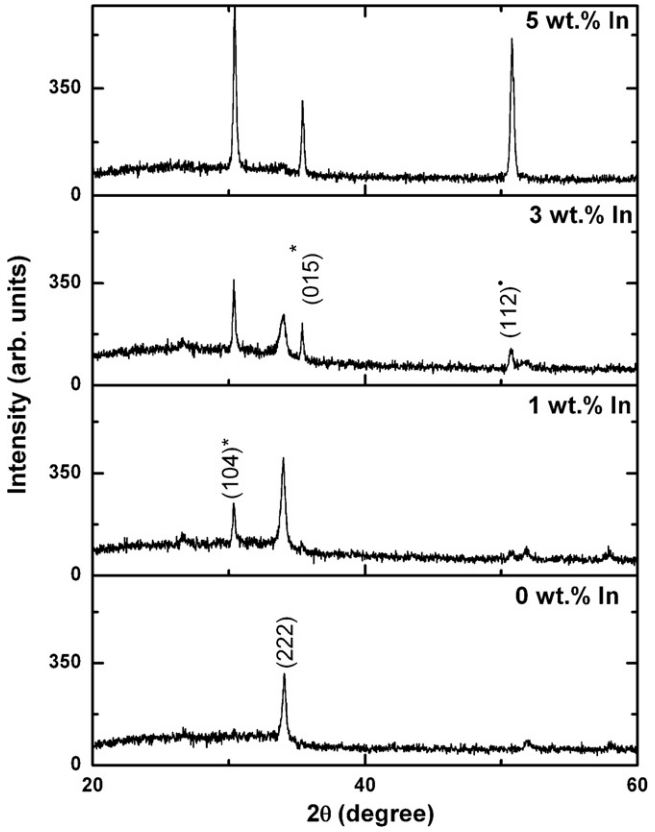

Fig. 1. X-ray diffraction pattern of In-doped Cd_2SnO_4 thin films deposited at 525 °C.

PRO X-ray diffraction system (Cu $K\alpha_1$ radiation; $\lambda = 1.54056$ Å) in Bragg–Brentano geometry ($\sigma/2\theta$ coupled). The surface morphology of the samples has been evaluated by atomic force microscopy (Nanoscope IIIa). Optical transmittance spectrum in the wavelength range of 300–1100 nm was recorded using UV–vis–NIR spectrometer (Shimadzu, UV–1601). The electrical studies were carried out using Hall measurements setup in van der Pauw configuration.

3. Results and discussion

The effect of In-doping on the structural properties of Cd_2SnO_4 thin films was investigated using X-ray diffraction studies. The 2θ value was varied from 20° to 80° and the films exhibit polycrystalline structure (Fig. 1). The undoped film exhibits cubic crystal structure with preferential orientation along the (2 2 2) direction and this peak fits well with JCPDS data (34-0928) [32]. The diffraction from the (2 2 2) peak is the strongest in the undoped and 1 wt.% In-doped films. In addition to cadmium stannate phase, secondary phase of $CdSnO_3$, (1 0 4)* and (0 1 5)* reflections is also observed when the doping concentration increases to 1 wt.%. As the Indium concentration increases additional peak of (1 1 2)• of SnO_2 phase appeared. Increase in In concentration enhances the $CdSnO_3$ phase growth.

The grain size (G) was calculated using the Debye Scherrer equation [33]

$$G = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where λ (1.54056 Å) is the wavelength of the X-rays used; β is the full width half maximum of the corresponding peak and θ is Bragg angle. The average grain size of (2 2 2) $h\,k\,l$ plane is decreased from 27.3 to 17.5 nm as the In doping concentration increased from 0 to 3 wt.%.

Optical transmittance spectra (Fig. 2) reveal high transmittance and a widening of visible transparency window with increasing

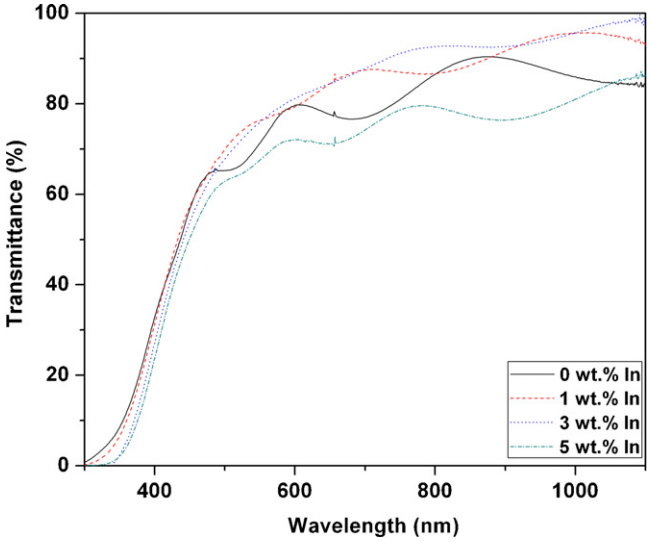

Fig. 2. Transmittance spectra of In-doped Cd_2SnO_4 thin films.

In-doping. The transmittance (T%) in the visible region is found to increase with increasing dopant level up to 3 wt.% In, followed by a decrease for higher doping percentage (5 wt.%). The average optical transmittance in the range of 500–850 nm is 78, 83, 87, and 73% for 0, 1, 3 and 5 wt.% In-doping, respectively. The 3 wt.% In-doped Cd_2SnO_4 film shows a higher average transmittance of 87% in the wavelength range of 500–850 nm and this value is relatively higher than that of the previous reports of Cd_2SnO_4 films prepared by spray pyrolysis method [9,22,24,34,35]. The optical band gap of Cd_2SnO_4 and In-doped Cd_2SnO_4 films was calculated from the optical transmission spectrum. The direct bandgap determination is based on the extrapolated linear regression of the curve resulting from a plot of photon energy ($h\nu$) vs. $(\alpha h\nu)^2$. The absorption coefficient was calculated according to the equation

$$\alpha = \frac{\ln(1/T)}{d} \quad (2)$$

where d is the thickness of the film and T is the transmittance at the wavelength in question. The optical absorption α and the direct band gap of the semiconductor film, are related by the equation

$$\alpha h\gamma = A(h_\gamma - E_g)^{1/2} \quad (3)$$

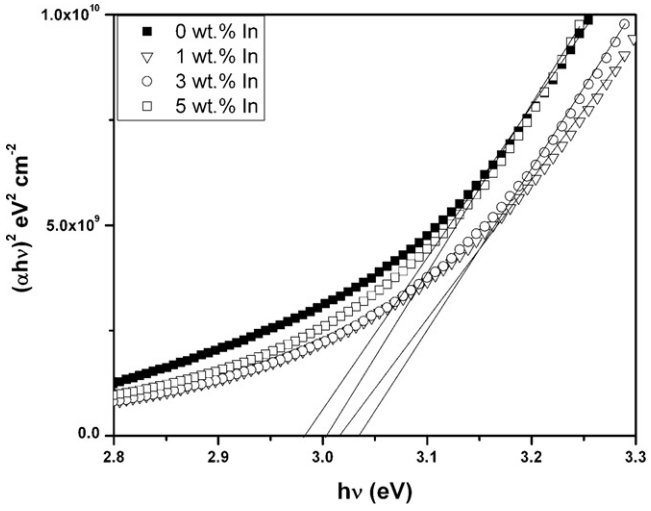

Fig. 3. $(\alpha h\nu)^2$ vs. photon energy for various In-doping level on Cd_2SnO_4 thin films.

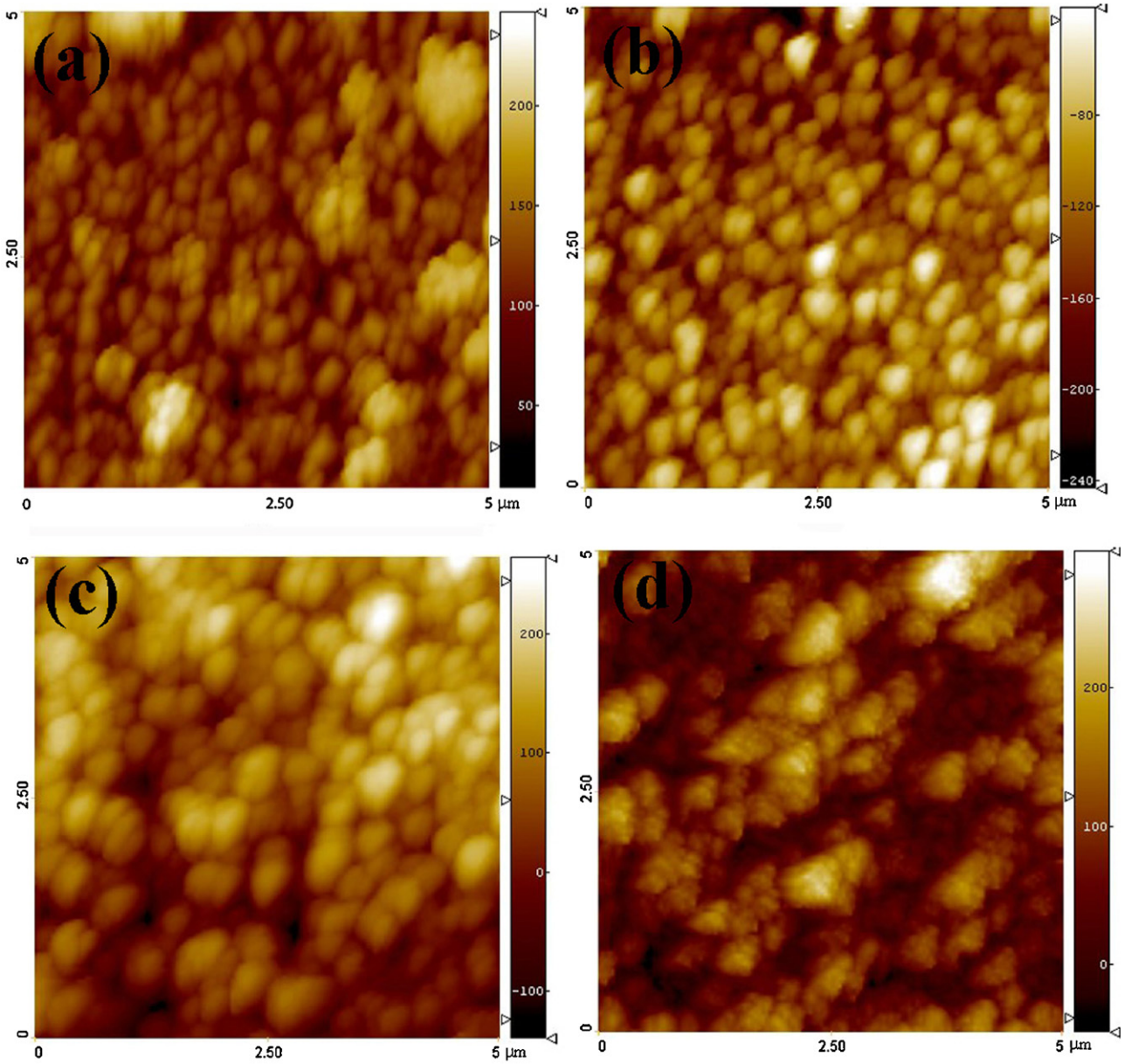

Fig. 4. AFM images of (a) un-doped, (b) 0.1 wt.%, (c) 0.3 wt.% and (d) 0.5 wt.% In-doped Cd_2SnO_4 thin films.

where A is a constant, E_g is the optical band gap and h is the incident photon energy. Plots drawn between $(\alpha h\gamma)^2$ and $h\gamma$ and the straight line fits of the pure and In-doped Cd_2SnO_4 films prepared in the present work are shown in Fig. 3. The direct energy gap of undoped Cd_2SnO_4 sample of the present work is $\sim 2.96 \pm 0.1$ eV, which agrees well with the earlier reports [8,22,36,37]. The energy gap increases and attains a maximum of $\sim 3.04 \pm 0.1$ eV for 3 wt.% In-doping.

Surface morphology of the undoped and In-doped Cd_2SnO_4 films was studied by AFM. The AFM images (Fig. 4) show that the In-doping modifies the surface morphology of the Cd_2SnO_4 films. The surface roughness of the undoped 1 wt.%, 3 wt.% and 5 wt.% In-doped Cd_2SnO_4 film is $13 \pm 2, 21 \pm 2, 15 \pm 2$ and 33 ± 2 nm, respectively. This higher surface roughness in the In:Cd_2SnO_4 (5 wt.%) is caused by variation in grain sizes and formation of cluster on the surface. The grain size in these spray deposited cadmium stannate films is not uniform. Fig. 5 shows the variation of electrical properties as a function of In-doping concentration in the Cd_2SnO_4 films. Hall measurement study confirmed that the prepared films are n-type semiconductor. The undoped Cd_2SnO_4 film shows a carrier concentration of $7.928 \pm 0.4 \times 10^{19}$ cm^{-3}. It is perceptible from Fig. 5 that the carrier concentration of the Cd_2SnO_4 film increases on initial In-doping of 1 wt.% ($9.812 \pm 0.4 \times 10^{19}$ cm^{-3}) but then decrease gradually with increasing In-doping level. This is due to the formation of secondary phase in the films. For initial doping concentration of indium, the mobility increases from 31.5 ± 1 (0 wt.%) to 36.12 ± 1 cm^2/V s for 1 wt%. and reaches a maximum of 44.8 ± 1 cm^2/V s for 3 wt.% In-doping. Thereafter the mobility decreases for 5 wt.% doping as shown in Fig. 5. The observed mobility values are relatively higher compared to the undoped Cd_2SnO_4 films reported in this work and also reported in the previous works by employing dc-sputtering [21], dip coating [23], electroless [9] and spray technique [34]. The mean free path (L) of the free carriers in these films was calculated using the equation

$$L = \left(\frac{h}{2e}\right)\left(\frac{3n}{\pi}\right)^{1/3}\mu_H \quad (4)$$

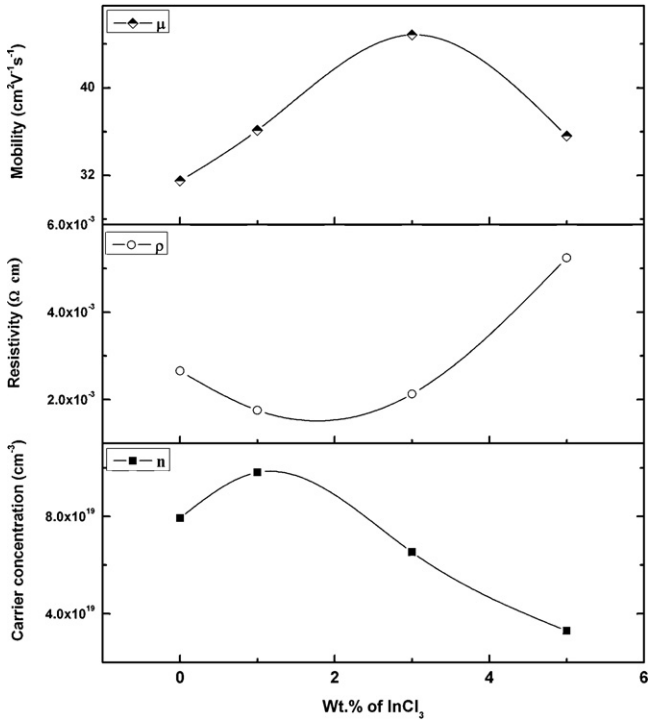

Fig. 5. Carrier concentration, resistivity and mobility as a function of In concentration.

where h is the Planck's constant, e is the electronic charge, n is the carrier concentration and μ_H is the Hall mobility [38]. The L values are in the range of 2.3–3.6 nm, which are very low compared to the grain size of ~17–27 nm derived by X-ray studies. It has been argued that grain boundary scattering is insignificant in these films because the carrier mean free path values are typically much smaller than the grain size of the prepared films. The Cd_2SnO_4 film has the resistivity of $2.657 \pm 0.2 \times 10^{-3}\ \Omega$ cm which decreases to $1.761 \pm 0.2 \times 10^{-3}\ \Omega$ cm for 1 wt.% In-doping and then gradually increases with the increasing concentration of In-doping. This is due to the decrease of the carrier concentration with increasing In-doping level. A slight decrease in the resistivity was observed in the In doped Cd_2SnO_4 thin films, this may be due to a less number of In^{3+} sites has replaces the Cd^{2+} sites. In doping gives carrier concentrations that are always lower than the dopant concentration. This could arise from compensation of In (III) substitution on Cd (II) sites by cation vacancies, although compensation of this sort does not pertain to CdO itself. However, a more likely explanation is that In (III) is distributed between Cd (II) and Sn (IV) sites. Whereas In (III) is a donor in the former, it is an acceptor on the latter. Thus, the availability of two different cation sites allows for substitutional incorporation of In with a carrier concentration lower than the nominal doping level [16].

4. Conclusion

Highly conducting and transparent In-doped Cd_2SnO_4 films have been deposited on Corning substrates at 525 °C using the spray pyrolysis technique. The undoped and In-doped Cd_2SnO_4 films exhibit polycrystalline structure and the average size of the crystallites is varied from 27 to 17 nm. A minimum resistivity of $1.76 \pm 0.2 \times 10^{-3}\ \Omega$ cm and maximum carrier concentration of $9.812 \pm 0.4 \times 10^{19}\ cm^{-3}$ occur for 1 wt.% In-doped films. Undoped and In-doped Cd_2SnO_4 films exhibit good optical transparency. The increase in transmittance of In-doped Cd_2SnO_4 film is due to the better crystallinity, less surface irregularity and less defect density. Doping of In in Cd_2SnO_4 films widens the band gap from 2.98 ± 0.1 to 3.04 ± 0.1 eV.

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