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Structural, electrical and surface morphological studies of Cd_2SnO_4 and Mg doped Cd_2SnO_4 thin films

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Abstract

The technologically important conductive Cadmium stannate (Cd_2SnO_4) and Magnesium doped cadmium stannate (Cd_2SnO_4: Mg) thin films were prepared using Cadmium acetate and stannous chloride by spray pyrolysis technique. Films prepared are crystalline and have cubic CdO phase with SnO_2. The X-ray diffraction patterns of both thin films shows perfect crystalline structure and from the data, the particle diameter of both films were calculated. Atomic Force Microscopy (AFM) of both films reveals the uniform thickness of the films and the presence of uniform grain growth in Cd_2SnO_4 and Mg doped Cd_2SnO_4 thin films. Thickness of Cadmium stannate film is 725nm and that of Magnesium doped Cadmium stannate film is 285nm. The indirect band gap energy of Cd_2SnO_4 film is 2.71eV and for magnesium doped Cd_2SnO_4 is 2.97eV were observed from the UV-Visible absorption spectrum studies. Presence of uniform grain growth is found in both thin films. The doping of Magnesium in Cadmium stannate film improves the electrical properties without affecting its structural properties.

1. Introduction

Transparent conducting oxides (TCO) have attracted the scientific world because of its wide range of applications in opto-electronic devices including flat panel displays, organic light-emitting diodes (OLEDs), micro sensors and photovoltaics (PVs) [1]. The most popular TCO, tin-doped indium oxide (ITO) has some shortcomings limiting its applications in PVs and OLED structures [2,3]. This stimulated an intense research on alternative TCO materials and is now the subject of numerous investigations for alternative material to ITO for PVs device structures [4]. From the literatures, Cd_2SnO_4 thin films are an n-type defect semiconductor material exhibiting promising properties such as low metal-like electrical resistivity (10^{-6} Ωm) and high transmission (>90%) in the visible range of the light spectrum and high reflectivity in the IR range. Cd_2SnO_4 transparent conducting oxide (TCO) films have several significant advantages over conventional TCOs when applied to CdS/CdTe thin-film devices. They are more conductive, more transparent, have lower surface roughness, are patternable, and are exceptionally stable. Possible applications of Cd_2SnO_4 films as a perspective electrode material for various electrochemical applications, [5–7]. Nozik and later Haacke et al. were the first to report Cd_2SnO_4 TCO films deposited by r.f. sputtering [8, 9]. Recent improvements in r.f. sputter-deposited Cd_2SnO_4 and post-deposition processing have yielded films with superior properties [10,11] In this study, the nanocrystalline films of Cadmium stannate and magnesium contained Cadmium stannate were grown by spray pyrolysis techniques and its structural, electrical and morphological studies were carried out.

2. Experimental

Cadmium stannate and Magnesium doped Cadmium stannate thin films were prepared by home made spray pyrolysis setup constructed by the authors. The parameters such as the size of the spray nozzle, distance between the spray nozzle and the substrate and the angle between the nozzle and the substrate were adjusted to get good quality continuous films.

Thin films of Cadmium stannate were fabricated by spraying a mixture of aqueous solutions of $Cd(CH_3COO)_2$ and $SnCl_2.2H_2O$ in the molecular weight ratio 4:1. A few ml of concentrated Hydrochloric acid was added to get clear solution. The resultant solution was sprayed on the preheated glass substrate at a substrate temperature of 300ºC. Magnesium doped Cadmium stannate thin film was also prepared by the same method, the mixture of aqueous solution was prepared by mixing aqueous solutions of Cadmium stannate and Magnesium chloride in 5% weight ratio. The fabricated films were thoroughly checked by a metallurgical microscope and good surface featured films were selected for studies. Computer controlled Philips X-ray diffractometer was employed to record X-ray diffraction pattern of films. The morphological studies were done by Atomic Force Microscopy. The optical absorption studies, the Sheet resistivity of the films and dielectric properties were also done.

3. Results and discussion

3.1 Structural and morphological studies

The X-ray diffraction pattern of Cadmium stannate thin film is shown in Fig. 1. Figure 2 shows the X-ray diffraction pattern of Magnesium doped Cadmium stannate thin film. From the figure, it is found that the addition of Mg slightly shifted the position of peaks; this may be due to generation of strain induced in the lattice by Mg ion. The particle diameter of both films are calculated and tabulated in Table 1 and Table 2. It is found that the average particle size of Magnesium doped Cadmium stannate thin film is greater than that of pure Cadmium stannate film. From the XRD pattern analysis, the film is polycrystalline in nature and confirms the presence of cubic CdO phase in major [JCPDS file: 750592] with SnO_2 phase peak (110), Similar results have been reported by A. Abrutis et al. [12],

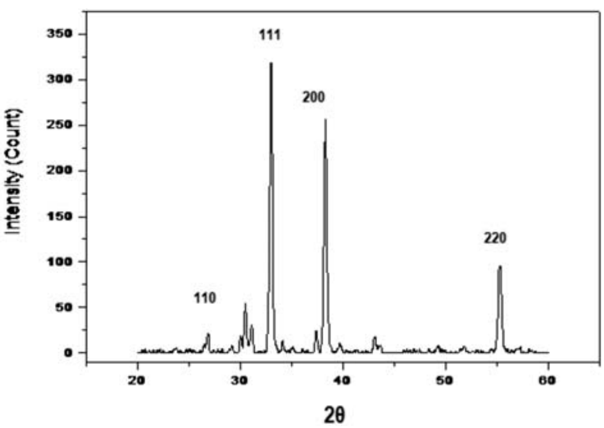

Fig. 1 : X-ray Diffraction pattern of Cadmium Stannate thinfilm

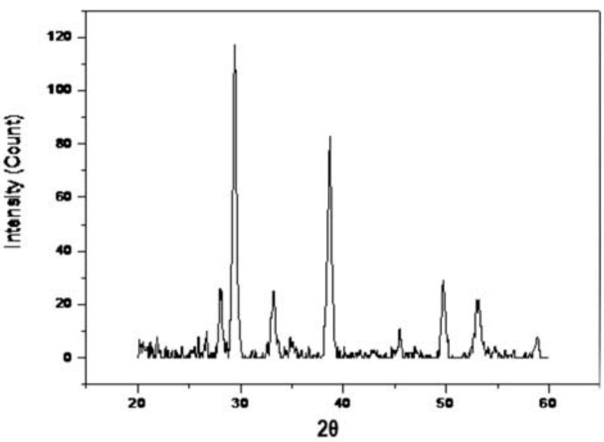

Fig. 2 : X-ray Diffraction pattern of Magnesium doped Cadmium Stannate thinfilm

The surface morphology of all the as-deposited films were studied using AFM , dealing with the thickness of the film, surface roughness and section analysis, Figures 3-6. The studies reveal the uniform thickness of the films and the presence of uniform grain growth in Cadmium stannate and Magnesium doped Cadmium stannate thin films. Thickness of Cadmium stannate film is 725nm and that of Magnesium doped Cadmium stannate is 285nm. It is observed from the roughness analysis that the root mean square value of surface roughness is 99.285 nm for Cd_2SnO_4 and that of Cd_2SnO_4 :Mg is 13.982 nm, the roughness is comparatively small. The study reveals that surface of both films are smooth

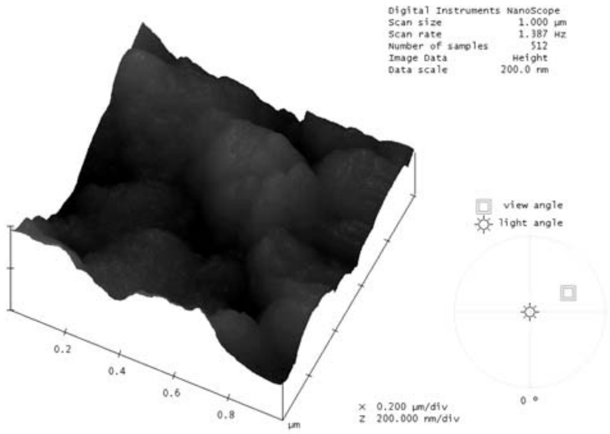

Fig. 3 : Surface topography of Cadmium Stannate thin film

and uniform. From the section analysis, it confirms the uniform grain growth in both films. The morphological study concludes that the roughness of the Cadmium Stannate is reduced due to the incorporation of Magnesium ions. This special behavior of these materials can be exploiting in gas sensors.

3.2 Optical properties

A basic reason why TCOs are of concern is that they can show transparency in a limited and well-defined range, normally encompassing visible light in the 400nm to 700nm wavelength interval. In the infrared (IR) region their metallic property leads to reflectance and at sufficiently short wavelengths, in the ultraviolet (UV), they become absorbing due to excitations across an energy gap [13]. The UV-Visible absorption spectrum of the films were taken by SHIMADZU UV-Visible NIR spectrophotometer. Figure 7 shows the UV-Visible absorption spectrum of Cadmium stannate thin film. In this spectrum, a distinct absorption peak at 302nm is found. Figure 8 shows the UV-Visible absorption spectrum of Magnesium doped cadmium stannate thin film. A maximum absorption peak is observed at wavelength 296nm. From the absorption spectra, it's quite clear that both materials we prepared have excellent transparency in the visible range, the wavelength region ranging from 350nm to 900nm shows very low absorption of incident light and the doping of Mg reduces the absorption further. From the Tauc plot it is observed that both the films are having indirect band gaps, for Cadmium stannate thin film it is 2.71eV and in the case of Magnesium doped Cadmium stannate thin film, is 2.97 eV.

3.3 Electrical properties

The major investigation on a Transparent Conducting Oxide material is its metal like resistivity and good electronic conduction. To investigate the electrical behavior of TCOs, the four-probe method is competitive one. The sheet resistivities of the material, activation energy, are reported in the section. The sheet resistivities of both films were measured by four probe method. Figures 9 and 10 show the variation of sheet resistivity with temperature of Cd_2SnO_4 and Cd_2SnO_4: Mg thin film respectively. The activation energy for Cadmium stannate thin film calculated from graph is 0.21eV and for Magnesium doped Cadmium stannate film, it is 0.18eV. Both films show increase in conductivity with increase in temperature which confirms the semiconducting behaviour of the material of both thin films. Decrease in activation

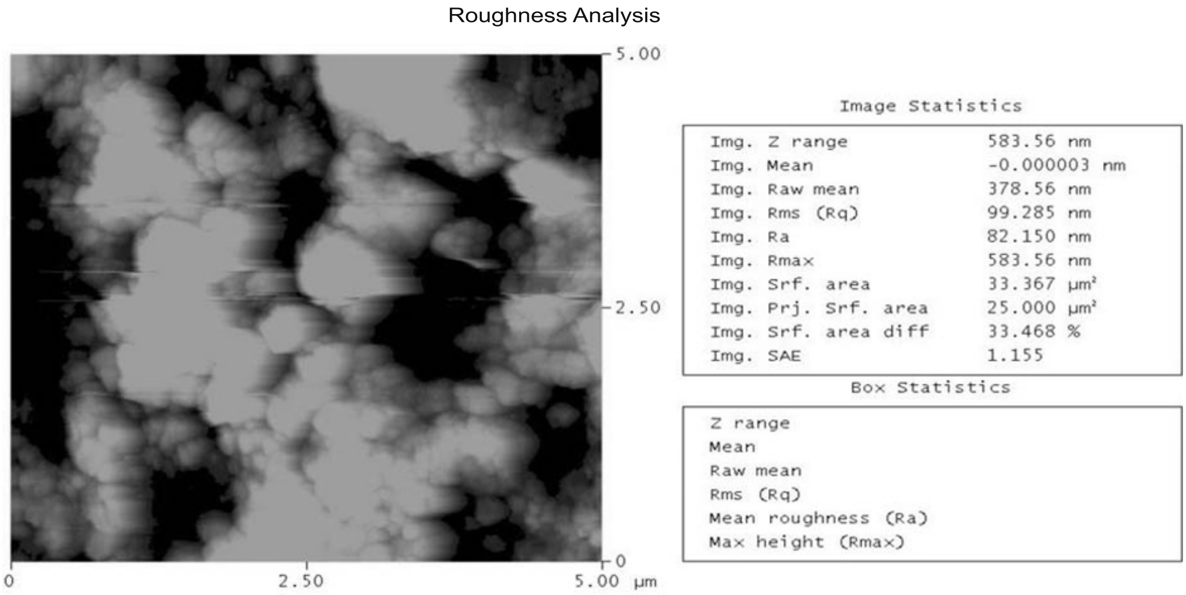

Fig. 4 : AFM of roughness analysis of Cd_2SnO_4

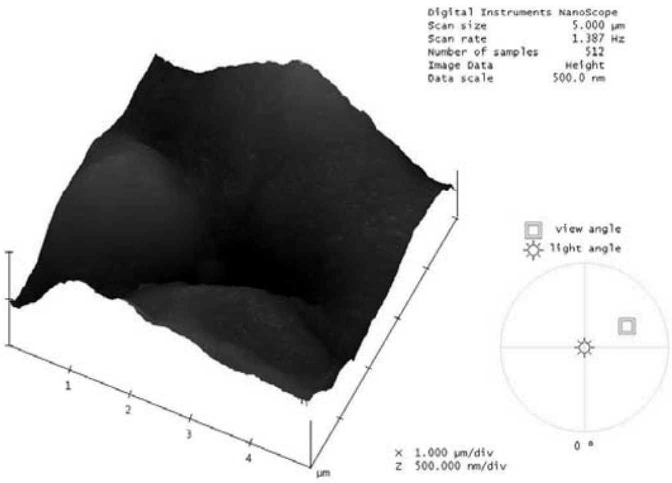

Fig. 5 : Surface topography of Magnesium doped Cadmium Stannate thin film

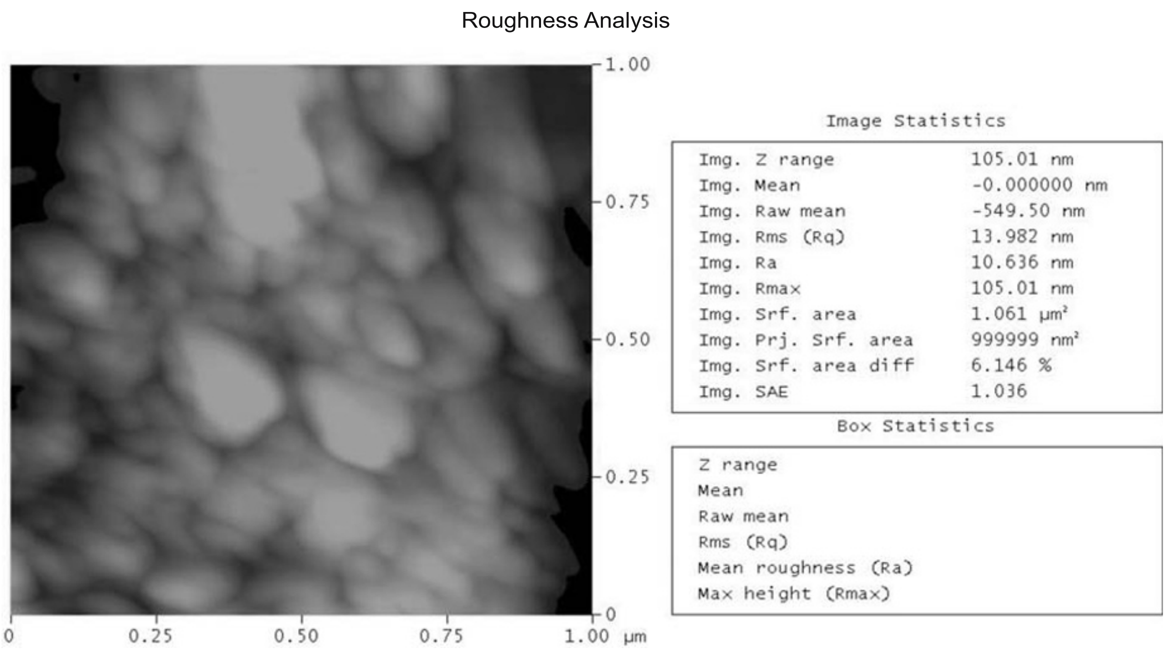

Fig. 6 : AFM of Roughness analysis of Cd_2SnO_4

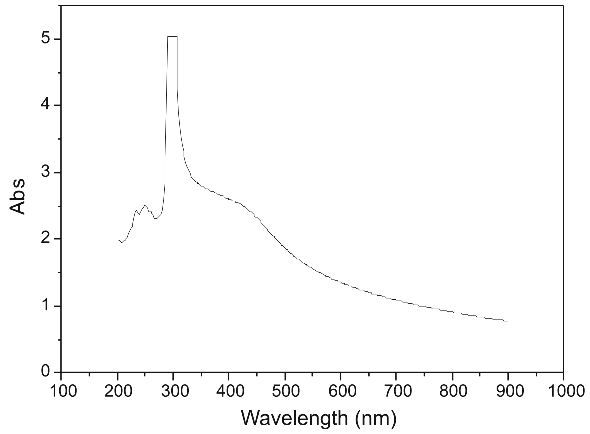

Fig. 7 : UV-Visible absorption spectra of Cadmium Stannate thin film

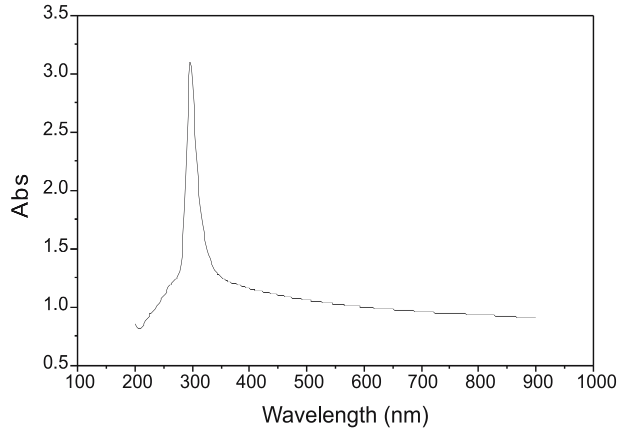

Fig. 8 : UV-Visible absorption spectra of Magnesium doped Cadmium Stannate thin film

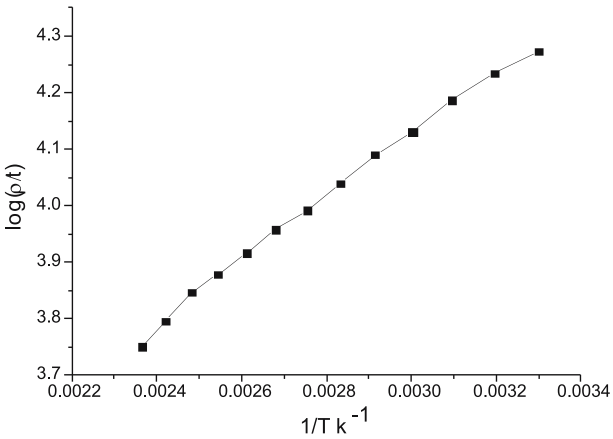

Fig. 9 : Sheet Resistivity of Cadmium Stannate thin Film as a function of temperature

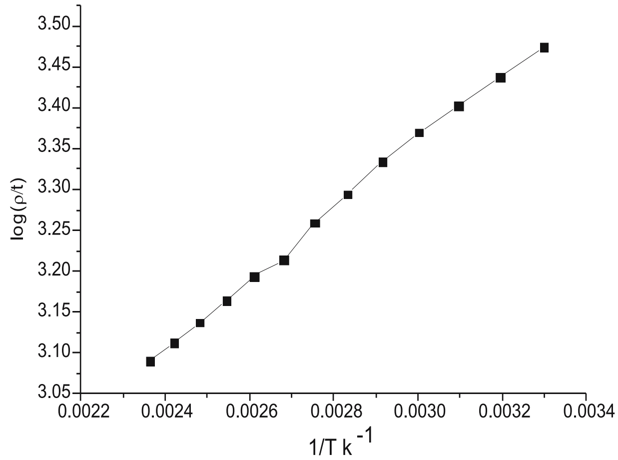

Fig. 10 : Sheet Resistivity of Magnesium doped Cadmium Stannate thin film as a function of temperature

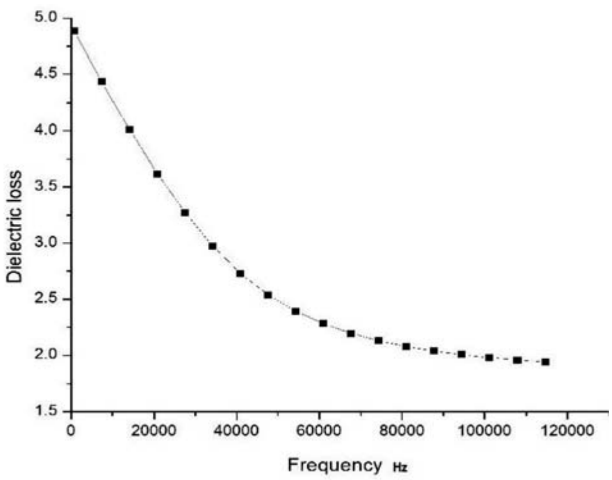

Fig. 11 : Dielectric loss of Cadmium Stannate thin film as a function of frequency

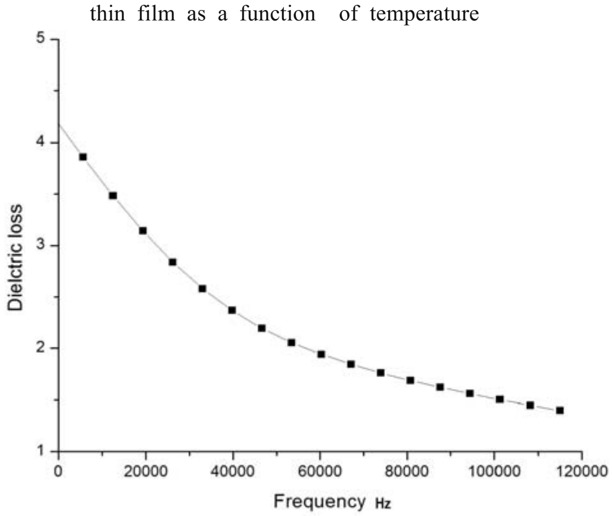

Fig. 12 : Dielectric loss of Magnesium doped Cadmium Stannate thin film as a function of frequency

energy in Magnesium doped Cadmium stannate is due to the presence of Mg ions.

The oxides are commonly dielectric in nature, the dielectric studies of the films were carried out by LCR HITESTER, and the films were sandwiched and made perfect contact between the two surfaces with silver paste. Figures 11 and 12 show the variation of dielectric loss with frequency for both samples. When the dielectric loss of above films were compared, it is found that Magnesium doped Cadmium stannate film has higher dielectric loss. These studies Magnesium doped Cadmium stannate thin film is more conducting than undoped Cadmium stannate thin film.

4. Conclusion

Cadmium stannate and Magnesium doped cadmium stannate thin films were prepared by employing home made spray pyrolysis technique using low cost precursors. Films prepared are polycrystalline with cubic CdO phase and SnO_2

phase. The indirect band gap energy of Cadmium stannate film is 2.71eV and for Magnesium doped cadmium stannate film, it is 2.97eV. Increase in the band gap energy of Magnesium doped film is due to the incorporation of Magnesium. Both films have very low absorption in the visible region. Presence of uniform grain growth is found in both thin films. The incorporation of Magnesium in Cadmium stannate film improves the electrical properties without affecting its structural properties.

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