PREFACE

Transparent conductive oxide (TCO) films that are both transparent in the visible region and electrically conducting have been widely studied for over 20 years as a result of their extensive applications in optoelectronic devices. These include energy-efficient windows, burglar alarms and window heaters, and also electrodes for solar cells and especially for flat panel displays (FPDs) such as liquid crystal displays (LCDs), plasma display panels (PDPs), field emission displays (FEDs), organic electroluminescent (OEL) devices etc. The worldwide market of FPD is promising a stimulation of the present research of TCO films. In the case of solar cells and other applications, improvement in the performance of TCOs is essential because of their non-ideal properties that will eventually impact the performance of the complete device.

As the areas of the major applications of transparent conducting oxides increase, the demand will grow for materials having lower sheet resistance while retaining good optical properties. Simply increasing the film thickness is not acceptable because this would increase the optical absorptions. New materials must be developed with lower resistivities with optical properties superior to those of the present generation of TCOs. Fabrication of low resistivity whilst retaining high transparency in the visible region is the aim of many works carried out on TCO films. In this thesis the preparation of transparent conducting pure and doped cadmium oxide (CdO) and cadmium stannate (Cd$_2$SnO$_4$) thin films by spray pyrolysis method is reported and these films are characterized for their structural, electrical and optical properties. Further, the effects of swift heavy ion irradiation on their properties are reported.

The thesis consists of five chapters. Chapter 1 presents a brief introduction to renewable energy sources followed by a brief description about the transparent conducting oxides. Further this chapter briefly covers the features of pure and doped CdO and Cd$_2$SnO$_4$ films and including literature survey. A brief description of the spray pyrolysis experimental setup is given. The characterization techniques such as X-ray
diffracometry (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), UV-Vis-NIR double beam spectrometry and Hall measurement were employed to characterize the TCO films. As these experimental techniques were effectively utilized in the present work, the details on the schematic diagrams, working principle and application of these techniques are presented in this chapter.

Chapter 2 consists of three sections. Section I deals with the results obtained from a set of aluminium (Al) doped CdO films on glass substrates at a substrate temperature of 300 °C for different aluminium doping concentration in the range of 1 to 5 wt.%. The structural, optical and electrical properties of these films were investigated as a function of Al doping concentration. The films exhibit cubic crystal structure and the intensity of the peak decreases with increasing Al doping concentration up to 4 wt.%. The transmittance value increases with increasing Al doping concentration up to 4 wt.% and then it decreases for higher doping. The carrier concentration of the films increases with increasing doping concentration, which results in the reduction of electrical resistivity and increase in the band gap energy. A minimum resistivity of $3.4 \times 10^{-4}$ Ω cm with a maximum carrier concentration of $4.12 \times 10^{20}$ cm$^{-3}$ were achieved when the film is doped with 3 wt.% of Al. Thus Al doping in CdO films effectively increases the carrier concentration and reduces its resistivity. Section II deals with the preparation of indium (In) doped CdO thin films by spray pyrolysis on glass substrates for various concentrations of indium chloride (2-8 wt.%) in the spray solution. X-ray analysis shows that the undoped CdO films are preferentially orientated along (200) crystallographic direction. Increase of indium doping concentration increases the films packing density and reorient the crystallites along (111) plane. A minimum resistivity of $4.843 \times 10^{-4}$ Ω cm and carrier concentration of $3.73 \times 10^{20}$ cm$^{-3}$ with high transmittance in the range of 300-1100 nm were achieved for 6 wt.% indium doping. The band gap value increases with doping concentration and reaches a maximum of 2.72 eV for 6 wt.% indium doping from 2.36 eV of that of undoped film. Section III consists of the preparation of mixed thin films of (CdO)$_{1-x}$(PbO)$_x$ ($0 \leq x \leq 1$) on glass substrates at a substrate temperature of 350 °C. XRD studies confirm the cubic phase of CdO and orthorhombic phase of α-PbO in the mixed films. The crystallinity of (111)
diffracometry (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), UV-Vis-NIR double beam spectrometry and Hall measurement were employed to characterize the TCO films. As these experimental techniques were effectively utilized in the present work, the details on the schematic diagrams, working principle and application of these techniques are presented in this chapter.

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and (200) planes of the cubic phase of CdO is found to increase with increasing PbO vol. % until x = 0.25 and then decreases for x = 0.50 whereas the crystallinity of the (001), (111) and (002) planes of PbO increases with increasing vol. % (x) from 0.25 to 1.00. The mean crystallite size calculated from XRD data is ranging from 19 to 67 nm. The average transmittance in the visible region (500 – 850 nm) varies between 40 and 68 %. The direct optical band gap value of these films varies between 1.96 and 2.69 eV.

Chapter 3 deals with the polycrystalline thin films of cadmium stannate (Cd$_2$SnO$_4$) deposited by spray pyrolysis method on the Corning substrates at the substrate temperature of 525 °C. Further, the films were annealed at 600 °C in vacuum for 30 minutes. The experimental results showed that the post-deposition annealing in vacuum has a significant influence on the properties of the films. The average grain size of the film was increased from 27.3 to 35.0 nm on heat treatment. The average optical transmittance in the visible region (500-850 nm) is decreased from 81.4% to 73.4% after annealing in vacuum. The minimum resistivity achieved in the present study for the vacuum annealed films is the lowest among the reported values for the Cd$_2$SnO$_4$ thin films by spray pyrolysis method. Further the preparation of highly conducting and transparent In-doped Cd$_2$SnO$_4$ thin film on Corning substrates at a substrate temperature of 525 °C is reported. In-doping concentration is varied between 1 and 5 wt.%. X-ray diffraction studies revealed that the films are polycrystalline with cubic crystal structure. In-doped Cd$_2$SnO$_4$ films exhibit excellent optical transparency. The average optical transmittance is ~ 87% in the visible range for 3 wt.% In-doping. Further In-doping slightly widens the optical band gap from 2.98 eV to 3.04 eV. A minimum resistivity of 1.76 × 10$^{-3}$ Ω cm and maximum carrier concentration of 9.812 × 10$^{19}$ cm$^{-3}$ have been achieved for 1 wt.% In-doping in Cd$_2$SnO$_4$ thin films.

Chapter 4 deals with the effect of swift heavy ion (SHI) irradiation on the physical properties of CdO and Cd$_2$SnO$_4$ thin films. The prepared films are irradiated using 120 MeV swift Ag$^{+}$ ions with the fluence in the range of 1 × 10$^{12}$ to 1×10$^{13}$ ions cm$^{-2}$. For CdO film the XRD peak intensity decreases with increasing ion fluence and then amorphization takes place at higher fluence of 1×10$^{13}$ ions cm$^{-2}$. The
transmittance of the films decreases with increasing ion fluence and also the band gap value decreases with increasing ion fluence. The resistivity of the film is increased from $2.66 \times 10^{-3} \ \Omega \ \text{cm}$ (pristine) to $5.57 \times 10^{-3} \ \Omega \ \text{cm}$ for the film irradiated with $1 \times 10^{13} \ \text{ions cm}^{-2}$. The mobility of the film decreased from 31 to 12 cm$^2$/Vs for the film irradiated with the fluence of $1 \times 10^{13} \ \text{ions cm}^{-2}$. For Cd$_2$SnO$_4$ thin films it is observed that the irradiated films amorphized at higher fluence of $1 \times 10^{13} \ \text{ions cm}^{-2}$. Surface morphology studies by atomic force microscopy show that the pristine film has a surface roughness of 23 nm and it increases with increase in ion fluence. The optical transmittance spectra show a decrease in transmittance with increase in the fluence.

Chapter 5 highlights the summary and overall conclusion of the results obtained in the present work.