ABSTRACT

Transparent conducting oxide (TCO) thin films are semiconducting materials having (i) large band gap values (typically $\geq 3$ eV), (ii) relatively high electrical conductivity, (iii) high optical transmittance in the visible region and (iv) high reflectance in the IR region. This unique combination of physical properties such as ‘high transmittance and electrical conductivity’ makes them suitable for a variety of applications in optoelectronic devices. TCOs can be prepared by multilayer coatings based on thin metal films, in which the conductivity arises from the metallic layer (dielectric/metal/ dielectric structure) or by a single layer based on wide band gap semiconductors like ZnO, SnO$_2$, In$_2$O$_3$ etc. Different deposition methods of both vacuum and non vacuum techniques have been used for the preparation of TCOs. The transparent and electrically conducting oxide films (TCOs), such as In$_2$O$_3$:Sn (ITO), SnO$_2$ (TO), ZnO and ZnO:Al (AZO), have been extensively studied due to their variety of applications in optoelectronic devices and also as gas sensors. However, ITO (In$_2$O$_2$) is widely used as a TCO material in industries because of its various applications. New materials must be developed with lower resistivity with better optical properties. The new family of transparent conducting oxide materials is based on the combinations of ZnO and SnO$_2$ materials and also with several dopants (Al, Cd, In, etc.). One of the attractive materials is zinc stannate with two phases, ZnSnO$_3$ and Zn$_2$SnO$_4$ which are non-toxic and inexpensive elements.
The present investigation deals with the preparation and characterization of Al and Cd doped ZnO, Zn doped SnO₂ and Zn₂SnO₄ thin films. The thin films were prepared by chemical spray pyrolysis process on Si (1 0 0), quartz and glass substrates.

ZnO is an alternative material for the conventional TCO (indium tin oxide). Several research groups are trying to develop ZnO based TCOs. In order to understand the effect of two different doping elements (Al and Cd) on the properties of zinc oxide film for TCO applications, both Al doped ZnO and Cd doped ZnO thin films have been prepared by chemical spray pyrolysis method. The films were deposited on different substrates like quartz, Si (1 0 0) and corning glass at 400°C. The XRD measurements showed the pure ZnO films possess hexagonal wurtzite structure with the grains preferentially oriented in the (0 0 2) direction. While increasing the dopant concentration, the grain orientation in the (0 0 2) axis deteriorated and the degree of polycrystallinity was found to be increased, for both the dopants. The surface morphology of the films was studied by SEM and AFM. Optical properties of the films have been studied by optical spectroscopy and spectroscopic ellipsometry methods. In the case of Al doping, the optical transmission measurements showed a blue shift (band gap widening) of the absorption edge. The spectroscopic ellipsometry measurement also confirmed this observation, i.e. increasing Al doping concentration increased the band gap of the films from 3.1 eV (for pure ZnO) to 3.34 eV (for 5 wt% Al doping), whereas there is no remarkable change in the refractive index of the films. Contradictorily, in the case of Cd doping, the optical transmittance
measurements showed a red shift of the absorption edge (band gap narrowing behaviour), which has also been confirmed by the spectroscopic ellipsometry method. The band gap of the Cd doped films decreased largely from 3.1 eV (for pure ZnO) to 2.96 eV (for 25 wt% Cd doping). On the other hand, the refractive index of the films increased from 1.9 to 2.15. The sheet resistance measurements showed a lowest sheet resistance value of ~310 Ω/$\square$ for 2 wt% of Al doping, and further increase of Al doping showed higher sheet resistance values. But, in the case of Cd doping the sheet resistance decreased continuously from 650 Ω/$\square$ (for pure ZnO) to 465 Ω/$\square$ (for 25 wt% of Cd doping), which is due to the higher conductive nature of CdO than ZnO.

The effect of Zn doping on the property modifications of SnO$_2$ thin films prepared by spray pyrolysis method has been studied in detail. The elemental analysis of the films measured by energy dispersive XRD spectroscopy showed that the Zn concentration in the solid film is slightly less than that of the starting solution. The X-ray diffraction (XRD) method showed that pure SnO$_2$ films possess tetragonal crystalline structure with the preferred (1 1 0) orientation. The Raman measurements also confirmed the tetragonal structure of the films for the entire range of Zn doping. High resolution scanning electron microscopy measurements revealed that upon increasing the Zn concentration, the surface morphology of the films change continuously and the grain growth also gets deteriorated. Optical transmittance measurements of the films revealed that the films are fully transparent in the visible region. Upon increasing the Zn concentration, the
band gap of the films decreased from 3.86 to 3.58 eV. The increase of sheet resistance due to Zn doping is attributed to the amorphization of films.

A new type of TCO material, zinc stannate (Zn$_2$SnO$_4$) a ternary compound has also been prepared by spray pyrolysis. The effect of post growth annealing on the properties of the films have also been investigated. EDX measurements confirmed that as-deposited films are nearly stoichiometric (Zn$_2$SnO$_4$). The XRD measurements revealed the cubic structure of the as-deposited films. Optical transmission measurements of the zinc stannate films showed a high transmission (>75%) in the visible region. The spectroscopic ellipsometry measurements showed the optical constants such as refractive index ($n$) and band gap ($E_g$) of the films, due to annealing, increased from 1.95 to 2.1 and 3.35 to 3.87 eV, respectively. The electrical resistivity measurements showed that the as deposited films possess relatively a higher sheet resistance value. The observed increase both in optical and electrical properties are attributed to the improvement in the crystallization of the films due to annealing. For TCO applications, a material should possess a refractive index of $n \approx 2$ and nearly zero extinction coefficient in the visible spectrum together with low sheet resistance values. The films prepared in this study satisfy certain basic requirements and it can be used for TCO applications.