CHAPTER 6

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

6.1 SUMMARY

This thesis elucidates the outline and importance of metal oxide films for technological applications. In this work, preparation of pure and doped zinc oxide, tin oxide and zinc tin oxide (zinc stannate) thin films, and their physical properties have been investigated. A detailed study has been performed in view of understanding the spray pyrolysis deposition method and dopant concentration variations for practical applications. The obtained results suggest that all these materials possess interesting structural, optical and electrical properties, which is well suited for transparent conducting oxide (TCO) electrode applications. However, some of the features of these films, both in film deposition as well as in characterization aspects, need to be studied further for better performance.

The chemical spray pyrolysis technique has been used for the film deposition. During the thin oxide film deposition processes, both chemical and thermal reactions were used. Using spray pyrolysis method, it was easy to grow uniform films with very high growth rates, in the order of several hundred nanometers per minute. The main advantages of this technique include reproducible deposition of uniform films on large area substrates such as architectural glass, easy stoichiometry control of the films with good reproducibility, etc. The composition of the films was determined by the energy dispersive X-ray diffraction spectroscopy technique. The structures of the films were identified by X-ray diffraction analysis. Optical properties
were studied by optical spectroscopy and variable angle spectroscopic ellipsometry methods. Computer simulations were performed to determine the optical constants by adopting different oscillator models. The electrical resistance of the films was studied by four probe method in the van der Pauw configuration.

The effect of dopants (Al and Cd) on the property modifications of zinc oxide films, has been studied. The films were prepared by chemicals spray pyrolysis method with various dopant concentration. The XRD measurements revealed the pure ZnO films having hexagonal wurtzite structure with the grains 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 of the films increased, the observation was same for the both doping elements. The surface morphology of the films was studied by SEM and AFM. It has been observed that when increasing the dopant concentration the surface morphology was changed continuously and roughness of the films found to be decreased. 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 3.10 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. In the case of Cd doping, the optical transmittance measurements showed a red shift of the absorption edge (band gap narrowing behaviour), which is also confirmed by the spectroscopic ellipsometry method. The band gap of the Cd doped films decreased largely from 3.12 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 1.90 to 2.15. The observed decrease of band gap together with an increase in refractive index is due to the large difference in the material properties of ZnO and CdO. The films posses a lowest sheet
resistance value of ~310 Ω/□ 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/□ (for pure ZnO) to 465 Ω/□ (for 25wt% of Cd doping) which may be due to the higher conductive nature of CdO than ZnO.

The effect of Zn doping on the properties of SnO₂ films has been systematically studied as a function of increasing Zn concentration. Thin films of tin oxide (SnO₂) and zinc doped tin oxide (Zn:SnO₂), with different Zn doping concentrations, were prepared on Si(1 0 0) and silica glass substrates by the spray pyrolysis technique at a substrate temperature of 400°C. The zinc dopant concentration was varied from 0 to 25 wt% and the films were characterized by different methods. From the EDX elemental analysis it has been observed that the Zn concentration in the solid film is slightly less than that of the starting solution. The XRD measurements confirmed that pure SnO₂ films possess tetragonal crystalline structure with a preferred orientation along the (1 1 0) direction. Upon increasing the zinc concentration the preferred orientation changes from the (1 1 0) plane to the (2 0 0) plane. This has also been confirmed by the rocking curve measurements. The Raman measurements revealed the tetragonal structure of the films. From the Raman spectra, in addition to the SnO₂ vibrational modes, the additionally observed peaks at 303 and 671 cm⁻¹ are attributed to the phonon confinement effect of SnO₂ grains. The HR-SEM measurements showed that upon increasing the Zn concentration, the surface morphology of the films changed continuously and the grains also deteriorated, which is attributed to the amorphization of the films upon increasing the Zn dopant concentration. The optical transmittance measurements of the films confirmed that the films are fully transparent in the visible region. Upon increasing the Zn concentration the band gap of the films was found to decrease from 3.86 to 3.58 eV. The increase of sheet resistance due to Zn doping is attributed to the
amorphization of films. The studies of physical properties as a function of Zn dopant concentration indicate that the properties of SnO₂ films can be finely tuned for a desired application with specific values.

Zinc stannate (Zn₂SnO₄) thin films have been deposited on Si (1 0 0) and quartz glass substrates by spray pyrolysis technique at a substrate temperature of 400°C. The films were annealed at 600°C and 800°C in Ar atmosphere and the physical properties of these films have been investigated in detail as a function of increasing annealing temperature. The elemental analysis of the films measured by EDX confirmed that the deposited films possess nearly Zn₂SnO₄ stoichiometry and became slightly Zn deficient after annealing at 800°C. The XRD analysis revealed the cubic structure of the films. The crystalline quality was found to be increased upon annealing at 800°C. Due to annealing both grain size and cell volume is found to be increased. The observed trend of increasing grain size as a function of temperature has also been confirmed by AFM studies. Optical transmission measurements of the zinc stannate films showed a high transmission (>75%) in the visible region. While increasing the annealing temperature, the average transmission of the films was increased, with the absorption edge shifted towards shorter wavelength. The spectroscopic ellipsometry measurements showed the optical constants such as refractive index (n) and band gap (E_g) of the films, increased from 1.95 to 2.1 and 3.35 to 3.87 eV, respectively due to annealing. The electrical resistivity measurements showed that the as-deposited films possess relatively higher sheet resistance value and this value is found to be decreased due to annealing. The observed improvement 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 ≈ 2 and nearly zero extinction coefficient in the visible region together with low sheet resistance values. The
ZTO films prepared for our experiments satisfy certain basic requirements and it can be used for TCO applications.

6.2 SUGGESTIONS FOR FUTURE WORK

In this work, we have shown that the binary and ternary oxide films deposited by spray pyrolysis possess attractive properties for several applications. The present work has been focused on the films prepared from aqueous solution. The samples were prepared at 400°C for a fixed substrate spray nozzle distance and also during deposition, the spray nozzle was kept perpendicular to the substrate. The experimental parameters play a major role on the microstructure and properties of the films. Hence, attempts can be made to deposit the films by varying the nozzle substrate distance and with slight inclination, which can enable to achieve higher homogeneity and yield films with higher density, and hence higher refractive indices can be achieved. Also the post-deposition annealing in various atmospheres (e.g. Nitrogen, Argon or Vacuum) and temperatures would result in the deposition of films with improved characteristics.

Further research effort can be made to enhance the understanding of additional characteristics of the doped ZnO, SnO$_2$:Zn and Zn$_2$SnO$_4$ thin films. The relation between the composition and the electrical resistivity needs to be clarified. The effect of grain boundaries and different types of electron scattering mechanism on the film resistivity needs to be studied using Hall measurements.

The sensitivity of the films in aggressive environments such as CO and CO$_2$ could be tested to assess their applicability for gas sensors applications.