Chapter 7

Summary and Conclusions

Present work is on the development of highly conductive and transparent Zinc Oxide (ZnO) thin film using Chemical Spray Pyrolysis (CSP). First we introduced an innovative post deposition treatment for enhancing the conductivity of ZnO, which we called as “Zero-Energy Process”. Further work was on enhancing the conductivity by doping of different elements Aluminum (Al), Indium (In), Tin (Sn) and co-doping using Indium & Fluorine (In+F) and Aluminum & Fluorine (Al+F).

ZnO thin films were deposited on soda lime glass substrate with following parameters kept as constant [Temperature- 450°C ± 5°C, Molarity- 0.3M, Volume-100 ml and spray rate -7ml/min]. After the deposition of the film, two type of post deposition treatments were tried on the samples. One is ‘Regular cooling (Z-R)’ and the other is ‘Inversion cooling (Z-I)’. X-ray photo-electron spectroscopy analysis showed that Zn/O ratio increased after the inversion process and the ratio is uniform throughout the thickness of the samples. All films had orientation along (002) plane. Above all electrical resistivity of Z-I decreased from 80 Ω cm to 2.4 ×10⁻² Ω cm. Photoluminescence studies revealed that the intensity of ‘Blue-green emission’ [which was due to the transition to the Oxygen antisite (O_{zn})] was decreased after the inversion. The process could also enhance the crystallinity and the optical transmittance. Vacuum annealing does not bring any further changes in electrical properties of Z-I samples. But After the vacuum annealing of Z-R, resistivity decreased from 80Ω cm to 1.8×10⁻² Ω cm. Thus the Zero-Energy process resulted in samples of high electrical conductivity and optical transmission avoiding the post deposition [and energy consuming] processes like vacuum annealing.

Deposition parameters of ZnO thin films like molarity, spray rate, precursor medium and pH of the solution were optimised to get the good quality and large area thin films. The samples were prepared at different spray rate, varied from 3 ml/min to 12 ml/min after fixing all the other parameters constant. Structural analysis proved that with increasing the spray rate from 5 ml/min to 7ml/min, orientation of films tuned from (101) to (002). By the variation of spray rate we could fine tune the intensity of ‘Blue- Green emission’; it
decreased after the orientation of grains shifting to (002) plane. The film with spray rate of 7ml/min achieved the lowest resistivity of $2.4 \times 10^{-2} \ \Omega \ cm$. Keeping the spray rate at 7 ml/min, samples were prepared using different molarities of Zinc acetate solution [from 0.2 M to 0.6 M]. At the lower molarity, samples exhibited poly crystalline nature with the planes orienting along (002) and (101) directions. After reaching 0.3M, intensity of peak corresponding to the plane (101) decreased while that of the plane (002) increased. Resistivity of the samples increased with increasing the molarity of the solution. After optimizing spray rate (7ml/min) and molarity (0.3M), next move was to vary the precursor medium. In this work two types of spray solutions were used. In the first one, this aqueous solution was mixed with ethanol while in the other type the aqueous solution was mixed with propanol. Volume of alcohol added to the aqueous solution was varied as 0, 20, 30, 50, 60 and 70 ml so that the total volume of spray solution was always 100 ml. Crystallite size, optical transmission and electrical conductivity of the films enhanced with increase of alcohol concentration. Intensity of Blue-green emission varied with percentage as well as with the type of alcohol used in the precursor solution, supporting the results from electrical and optical characterisations. Propanol based samples had lower resistivity than the ethanol based samples. The lowest value of $2 \times 10^{-2} \ \Omega \ cm$ was obtained for the sample prepared using water and propanol in 1:1. In the next step, pH of the solution was varied from pH-3 to pH-6. From the pH-3.5 to pH-4, the orientation of grains was shifted to (002) direction. But in the case of lower and higher pH, (101) was the preferential orientation. Precursor solution with pH-4 exhibited the lowest value of resistivity in the order of $2 \times 10^{-2} \ \Omega \ cm$. Finally spray rate was fixed 7ml/min and molarity of the spray solution, at 0.3M. The precursor medium was selected as the one having deionised water and propanol in the ratio 1:1 with pH equal to 4. We used these optimised condition for the preparation of doped ZnO thin film for the further studies.

For doping studies we tried various methods and elements with the aim of reducing the resistivity of the sample. In ‘ex-situ doping’, a thin layer of In/Sn was deposited over the undoped ZnO thin films using vacuum evaporation [Pressure ~ $2 \times 10^{-5}$ mbar] method and this bilayer films were annealed in vacuum [Pressure ~ $2 \times 10^{-5}$ mbar; Temperature-100 $^\circ$ C; Time- 60 min]. Different masses of In/Sn (2, 4, 6, 8 and 10 mg) were deposited over the surface of ZnO sample. There was small variation of band gap after the doping. Resistivity
of the Z-8mg-In reduced from \(28 \times 10^{-3} \ \Omega \text{cm}\) to \(8\times 10^{-3} \ \Omega \text{cm}\). Transmittance of the sample decreased when the doping percentage increased. In-situ doping using Indium (indium nitrate) was an excellent method for enhancing the conductivity of the sample. Incorporation of 1% Indium through in-situ method resulted in giving the lowest resistivity of \(2 \times 10^{-3} \ \Omega \text{cm}\) and >80% transmission in visible region. PL analysis also supported the results from electrical characterisation studies of the samples.

Aluminum was doped by adding the required quantity of aluminum 2,4 pentanedioninate in the spray solution itself [In-situ method]. Doping percentage of Aluminum was varied from 0.5 to 3.5%. Samples doped with aluminum in the range 2 to 2.5% had resistivity of \(1.5 \times 10^{-3} \ \Omega \text{cm}\). Annealing of these samples in vacuum further lowered the resistivity [\(6 \times 10^{-4} \ \Omega \text{cm}\)], with optical transmittance [in visible region] remaining in the range 85 to 90%. Transmission in the NIR region decreases after the vacuum annealing. A phenomenon that is common in all other transparent conductors [like ITO] with higher carrier concentration. Room temperature PL revealed that the intensity of the blue-green emission (520 nm) decreased in these samples. Lowest intensity for the PL emission was also obtained for the sample having the optimum doping.

In the case of ‘co-doping’ of both Aluminum and fluorine, required quantities of Aluminum 2,4 pentanedioninate and ammonium fluoride were added into the spray solution; here percentage of aluminum in the solution was kept constant (2.5% of Al) while the concentration of fluorine was varied from 0.5 % to 3% and for this, ammonium fluoride was added to the spray solution in calculated quantities. In the case of Z:Al-F film the crystallite size increased and also there was observable variation in (101) plane. Here the transmittance and resistivity were increased. Co-doping of both Indium and fluorine was done by adding required quantities of indium nitrate and ammonium fluoride in to the spray solution; here percentage of Indium in the solution was kept constant (1% of In) while the concentration of fluorine was varied from 0.2 % to 3%. Intensity of (002) plane peak decreased and crystallite decreased after the co-doping of indium and fluorine. Z:In-F exhibited increase in optical transmission. But the electrical resistivity slightly increased after the co doping using fluorine and indium. Fig.7.1 shows resistivity value through various stages of ZnO film.
Fig. 7.1. Resistivity values of ZnO thin films achieved in the present work.

**Future scopes**

1) Automation of Inversion process has to be done as it guarantees more than 95% uniform resistance over the sample surface.
2) Development of nano ZnO using chemical spray pyrolysis.
3) Fabrication ZnO/nano ZnO based all sprayed Thin film solar cell.

Main aim of our research work is the fabrication of very low cost and eco-friendly thin film solar cells using easily available materials. In our lab, thin films of In$_2$S$_3$, CuInS$_2$ are prepared using Chemical Spray Pyrolysis technique. Suitable combinations of these compounds, in bilayer thin film structure, can form p-n junction (ZnO/In$_2$S$_3$/CuInS$_2$/Ag) and hence find application in solar cell technology with sprayed ZnO as the electrode instead of high cost ITO. Development of ‘Extremely Thin Absorber [ETA]’ layer solar cells having ZnO [possibly with nano rods] as the TCO layer [using spray pyrolysis for the deposition of all the three layers] will be the ideal aim in this type of work.