Chapter V

Summary and Conclusions

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Applications of metal oxide semiconductors (MOS) in the bulk as well as in thin film form are tremendously increasing research field for the last few decades for the researchers. MOS are of immense value for developing optoelectronic devices, gas sensors, photocatalysts, smart window electrochromic materials, heat resistive materials, solar cells, photovoltaic cells, supercapacitors, transparent conducting oxides etc. Further properties of MOS can be enhanced by employing it in the thin film form. MOS could find wide applications owing to their small tiny size, high value of quality factor Q, high surface to volume ratio, high chemical as well as physical stability, high efficiency. Rather than using MOS like TiO_2, In_2O_3, ZnO, CdO, WO_3, oxides doped with special and suitable dopant is an alternative way over the globe which tailors properties of thin films. Properties being tailored are electrical conductivity, photoactivity, band gap, optical transmittance in visible spectral region and gas response. This is required for various devices such as photo-detectors, solar cells, gas sensors, and antireflection coatings. Remarkable efforts have been promoted for the search on ZnO thin films doped with different elements which can be used as active components in many devices. Various methods have been tried to deposit ZnO thin films and doped ZnO thin films. Due to the unique electronic, optical, and piezoelectric property, doped ZnO semiconductors are set up as an important multifunctional material for fabrication of devices such as semiconducting multilayers, photothermal conversion system, gas sensors and optical position sensors, surface acoustic wave filters, piezoelectric thin film. From all the studied MOS, ZnO has come out as a promising MOS, due to its electrical and optical properties; also it has high chemical as well as mechanical stability, together with its abundance in nature, which makes it a lower cost material when compared to the most currently used MOS.

In the particular case, study is based on developing reliable ZnO thin films doped with Co and Ni which are ferromagnetic in nature and due to its properties it gives desired changes in the physical and chemical properties of the materials. In many respects, Co and Ni are found to be most suitable dopants for device applications owing to relatively low cost precursors and superior properties which could suitably tailor ZnO. Total work is divided in to five chapters.

Chapter I includes general introduction along with in detailed literature survey of the ZnO thin films and applications in different fields. Also the studies on Ni and Co doped thin films using different methods are reported. The information about different characterization techniques such as X-ray diffraction technique (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform Raman spectroscopy (FT-Raman), scanning electron microscopy (SEM), optical studies– transmittance, reflectance and absorbance, photoluminescence (PL), electrical, dielectric and impedance measurements, thermoelectric power studies etc are described. Working principle as well as instrumentation of the techniques required for the samples characterizations and data acquisition is studied. In the end statement of the problem is discussed in detail.

Chapter II focuses deeply and discusses about the different thin film preparation techniques. It covers classification of the thin film techniques and discussion about the spray pyrolysis technique. Basics of spray pyrolysis technique are given along with the factors governing spray pyrolysis technique. Effect of the preparative parameters such as spray rate, solution quantity, deposition temperature, nozzle to substrate distance on the properties of thin films is as well given. Preparation of ZnO thin films along with the detailed information about substrate cleaning, preparation of spraying solution is discussed. Mechanism of formation of ZnO thin films in various steps such as atomization of precursor solution, aerosol transport, decomposition of precursor solution at different distance, and film formation is studied for pure ZnO as well as doped ZnO thin films.

Chapter III explains the work based on nickel-doped ZnO thin films in the perception of their transparent and electrically conducting properties. The transparent Ni-doped ZnO thin films were successfully prepared by spray pyrolysis in an aqueous medium. Structural analysis shows that the pure and Ni-doped ZnO films are polycrystalline with a hexagonal (wurtzite) crystal structure. The observed highest visible range transmittance is about 80– 85%. The influence of Ni doping on to structural, morphological, optical, electrical, dielectric and impedance properties of zinc oxide host lattice has been investigated. Nickel doped ZnO thin films were grown by chemical spray pyrolysis technique onto corning glass substrates using following precursors: Zinc acetate [$Zn(CH_3COO)_2.2H_2O$] and Nickel nitrate [$Ni(NO_3).6H_2O$] dissolved in double distilled water. The atomic percentages of [Ni]/[Zn] were varied as 0.5%, 1%, 1.5% and 2.5%. Other spray parameters such as substrates temperature (450°C), air flow rate (22 LPM), spray rate (5cm^3/min), distance between the atomizer and the substrates (30 cm), and volume of solution (100 ml) were kept constant for all experiments. Ni doped ZnO thin films were characterized using various characterizations techniques, viz. X-ray diffraction, Scanning electron microscopy, UV-Vis spectroscopy and dielectric measurements.

Ni doped ZnO films exhibit hexagonal (wurtzite) crystal structure having preferred orientation along (002) plane. Crystal reorientation effect is seen as intensity of (002) increases while intensity of (101) plane decreases up to 1.5 at% and vice versa. The average crystallite size of the NZO thin films varies within 30-36 nm. XPS studies indicate that Zn is present in the oxidized state and its chemical state does not change even after Ni doping. [O]/[Zn] ratio is found to be decreasing with increase in Ni doping concentration from 0.97 to 0.95. XPS studies confirmed that Ni substitute Zn and incorporation of Ni in ZnO lattice is effective up to 1.5 % and at higher concentrations Ni remains as defect level than substituting Zn. SEM studies revealed that all the films are homogeneous, dense, adherent and grow with thin columnar grains perpendicular to the substrate. Decrease in the grain size with increasing [Ni]/[Zn] ratio up to 1.5 at% observed is due to the impurity effect of Ni. Optical transmittance studies shown strong interference fringes due to the multiple reflections at the interfaces indicating homogeneous film thickness. All the films are highly transparent having average transmittance around 85 %. The optical energy gap slightly increased with increase in doping concentration. Room temperature PL spectra of the NZO thin films studied in the visible range enlighten information of the defect states and concentration of defect levels. In PL three bands were observed: ultraviolet (UV), green, and orange. Near band edge emission (NBEE) is due to the existence of the Zn vacancies in the lattice. No specific trend in the peak intensity depicts that Zn vacancies are arbitrary in the films and are independent of the Ni doping. Also red emissions are due to the Zn and O at the antisites respectively. Intensity of the red emission increases with Ni doping up to 1% and decrease further at higher concentration. Resistivity of Ni doped ZnO thin films is higher than undoped films. A thermoelectric power study shows that films are of n type semiconductor. Thermo emf increased linearly with increase in the temperature gradient. Thermo emf is higher for the 1.5 at% Ni concentration and decrease on either side. Dielectric constant decreased abruptly at lower frequencies and remains nearly constant at higher frequencies, which is dispersion behavior of dielectric constant due charge transport relaxation time. The dielectric constant increases up to 1.5 at% Ni doping and then decreases. At lower frequencies, dielectric loss, tanδ, is large and it decreases with increasing frequency. The higher values of dielectric constant observed at 1.5 at% Ni is due to the large surface charge sorption of the Ni^{2+} ion in ZnO host lattice.

Chapter IV covers the mechanism of film formation of Co doped ZnO (CZO) thin films. It explains in detail solution preparation, characterization and also results of different characterization carried out. To prepare spraying solution Zinc acetate [$Zn(CH_3COO)_2.2H_2O$] and Cobaltous nitrate [$Co(NO_3).6H_2O$] were dissolved into double distilled water and [Co]/[Zn] ratio was varied as 1%, 2%, 3% and 5%. All other preparative parameters like spray rate (5cm^3/min), distance between the atomizer and the substrates (30 cm), and volume of solution (100cc) were kept constant for all Co concentrations. Films were characterized using different characterizations such as X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, UV-Vis spectroscopy, photoluminescence, and dielectric measurements technique. It has been found that cobalt ions, in the oxidation state of Co^{2+}, substitute Zn^{2+} ions in the ZnO lattice without changing its wurtzite structure with decrease in its oxygen deficiency. The observed highest visible range transmittance is about 70-85 %. Strongest blue emission which is characteristic of ZnO is observed at the wavelength of 487 nm. The band gap energy increases from 3.27 eV (pure ZnO) to 3.33 eV (2 at% CZO), which is responsible for the blue shifts of wavelength in UV absorption. Thus, the current doping method can be regarded as another effective technique to modulate the optical properties of ZnO thin films.

X-ray diffraction patterns of CZO thin films shown that films are polycrystalline having hexagonal (wurtzite) crystal structure and preferred orientation along the (002) and (101) planes. It is observed that the intensity of the (002) peak is lower for the CZO film as compared with undoped ZnO thin films. This is due to the incorporation of Co dopant into the ZnO film creating more defects in the lattice. The crystallite size decreases with Co doping concentration and then increases at higher Co concentrations. XPS studies showed that CZO films are sub-stoichiometric in nature; Zn exits in the oxidized state. Effect of Co dopant on Co 2p doublet is described in detail and values are listed in table 5.1.

Concentration of Co (at%)	Ratio O/Zn	Measured concentration of Co (at%)
undoped ZnO	0.974	0
1	0.960	1
2	0.959	1.98
3	0.964	2.5
5	0.969	4.5

Table 5.1 Ratio of [O]/[Zn] and measured Co concentration of the CZO thin films using XPS.

Narrow scan XPS studies well described increase in Co doping concentration by measurement of area under the curve which is elaborated in detail and confirms increase in the concentration of Co in ZnO lattice. Also presence of Co in two valence states is confirmed by careful observation of the two Co 2p doublets. It is also shown that with increase in doping concentration, Co exists in +3 valence state also, hence rate of decrease in oxygen deficiency is low at higher doping concentrations. Raman analysis is used for the qualitative analysis of the ZnO network formation and illustrated information about the defects resulted due to incorporation of Co. Various bands with frequency characteristic of a wurtzite crystal structure of high-integrity; such as low-frequency E_2 modes (110, 168 cm^{-1}), involving mainly Zn motion, peak at 573 cm^{-1} is of A1 symmetry and due to LO overtones along Γ were explained in detail. Change in the surface morphology of the films due to the doping is observed and is studied well. Differences in morphologies were noticeable were observed. The average grain size is found to be 70–150 nm. Optical studies shown that all the films exhibit an average optical transmittance about 60–80 %. Transmittance decreases for higher Co content due to presence of impurities and disorder in ZnO lattice. Further well developed interference patterns are observed in the reflectance spectra using which thickness is calculated by fitting with standard reflectance pattern. Optical band gap (Eg) increased after Co doping from 3.23 eV (pure ZnO) to 3.33 eV (Co doped ZnO). It concludes that the active transitions involving 3d levels in Co^{2+} ions are present. PL studies confirmed presence of defects and are found to be increasing with increasing Co concentration, distortion in the films increases with increasing doping concentration. It is concluded by observing dc electrical resistivity that films are semiconducting in nature as resistivity decreases with increasing temperature. The decrease in resistivity of films with increasing Co doping has been explained by displacement of the electrons. The type of conductivity exhibited by the spray deposited CZO thin films is determined from thermoelectric power measurement. Thermoelectric power was found within range 0.08 mV/K to 0.16 mV/K. Thermo emf decreased with doping concentration up to 2 at% and then increased for higher concentrations. The dielectric constant (ε') decreases at lower frequencies and almost remains constant at higher frequencies, showing the dispersion behavior of dielectric constant at lower frequencies owing to the charge transport relaxation time. The dielectric constant decreases up to 2 at% Co doping and then increases. The impedance spectrum is characterized by the appearance of semicircle arcs whose pattern changes, but not its shape, when the doping concentration is increased. Grain boundary resistance decreases with doping concentration up to 2 at% and then increases, it seems to the fact that grain boundary effect has assisted in lowering the barrier to the motion of charge carriers. Also Z' decreases with doping concentration up to 2 at% indicating an increase in conductivity as confirmed from electrical measurements.

Above conclusions indicate that properties of ZnO can be tailored by careful synthesis and doping it with Co and Ni. ZnO thin films doped with Ni and Co expected to show properties of soft magnetic materials because these films can easily be magnetised and also demagnetised. Due to Ni and Co doping in non magnetic material inherent ferromagnetic properties of Ni and Co are hindered by ZnO network resulting in forming soft magnetic materials. ZnO is a multifunctional material; attempt has been made to improve properties. Results indicate that these films are suitable to use as soft magnetic materials and also could be used as gas sensor electrode.