6.1 Introduction

The percentage of atoms of different species present in the films is measured using the energy dispersive X-ray analysis (EDX) studies of undoped and metals doped ZnO thin films prepared by SILAR [1-4]. The compositional analysis mainly carried out for the confirmation of doping metals incorporation in ZnO matrix.

6.2 ZnO thin films

To study stoichiometry of the film quantitative analysis was carried out using the EDX technique. Fig. 6.1 shows atomic percentage values of ZnO films are deposited at various molar concentrations. The 0.01 M concentration prepared film exhibited 45.23:54.77 ratio of Zn:O, respectively. When zinc sulphate concentration is increased from 0.01 M to 0.02 M, the oxygen atomic percentage decreased from 54.77 % to 52.37 % as well the zinc percentage increases from 45.23 % to 47.63 % when the concentration of the solution is 0.03 M the zinc content in ZnO thin film prepared increases from 45.23 to 47.63. Also oxygen content decreased from 52.37% to 50.59%. This is due to the zinc ions was replacing the oxygen ions in zinc oxide thin films when the zinc sulphate concentration was increased.
Fig. 6.1: Atomic percentage values of ZnO thin films prepared at various molar concentrations
6.3 Nickel doped ZnO (NZO) thin films

The composition of Ni doped ZnO thin films are estimated using EDX analysis. Fig. 6.2 shows the atomic percentage values of NZO films are deposited at various doping concentrations. The 5mM NiSO₄ prepared NZO film exhibited atomic percentage respectively, Zn: O as 40.10:57.29 and the Ni percentage is 2.61. This Zn composition value is quite low compared with undoped ZnO thin films and the oxygen content is observed to be high. When nickel sulphate concentration increases from 5 mM to 10mM, the oxygen atomic percentage decreases from 57.29 % to 55.1 % as well as the zinc percentage increases from 40.10 % to 41.12% and the Ni content increased from 2.61% to 3.78 % in NZO thin film. Also nickel atomic percentage increased from 3.78 % to 4.3% in NZO thin film prepared at 15mM nickel sulphate concentration prepared film and also Zn:O ratio is observed to be 44.9:50.8. This is due to the nickel ions replacing the zinc metal ions in NZO thin films when the nickel sulphate concentration was increased in the solution bath.

The NZO thin films annealed at various temperatures the concentrations are estimated. Fig. 6.3 shows the atomic percentage values of NZO thin films that are annealed at various temperatures from 200°C to 400°C. The atomic percentage of oxygen and nickel content decreased as the zinc content increases. This happens when post annealing temperatures are increased. The 200°C annealed NZO thin films oxygen atomic percentage decreases from 50.8 % to 50.5 % as well as the zinc percentage increases from 44.9 % to 45.6 % and the Ni content reduced from 4.3% to 3.9 %. Also the nickel atomic percentage decreases from 3.9% to 3.3% in NZO thin film annealed at 400°C. These results show that the atomic percentage of oxygen in Ni-doped ZnO thin film decreased to lower values after annealing.
**Fig. 6.2:** Atomic percentage variation of NZO thin films prepared at various NiSO$_4$ concentrations

**Fig. 6.3:** Atomic percentage variation of Ni, Zn and O of thin films annealed at various temperatures
As temperature of annealing is increased more oxygen is absorbed in the process that could cause a decrease in the oxygen content in the films.

### 6.4 Manganese doped ZnO (MZO) thin films

The atomic percentage values of Mn doped ZnO thin films are estimated using EDX analysis. Fig. 5.4 shows the atomic percentage value of MZO films that are deposited at various doping molar concentrations. The 5 mM MnSO₄ concentration prepared MZO film exhibited the composition of Zn:O as 42.60:55.29 and Ni percentage as 2.11. The lower percentage of manganese ions are incorporated when ZnO matrix was doped with MZ compared to NZO thin films. Also Zn atomic percentage is slight by high when compared to NZO. When manganese sulphate concentration increases from 5 mM to 10 mM, the oxygen atomic percentage decreases from 55.29 % to 52.10 % as well as the zinc percentage increases from 42.60 % to 44.00 % respectively and Mn content increase from 2.11% to 3.90 % in MZO thin film. Also nickel atomic percentage is increases from 3.90 % to 4.4% in MZO thin film prepared at 15 mM manganese sulphate concentration and also Zn:O ratio is exhibited as 46.5:49.1. This is due to the manganese ions replacing the zinc metal ions in MZO thin films when the manganese sulphate concentration increases in solution bath.

The various temperatures annealed MZO thin films are estimated by compositional analysis. Fig. 5.5 shows atomic percentage values of MZO thin films that are annealed at various temperatures. The atomic percentage of oxygen and manganese content decreases and zinc content increases with the increase of annealing temperatures. The 200°C annealed MZO thin films is observed at oxygen
atomic percentage decreases from 49.2 % to 48.9 % as well as zinc percentage increases from 46.5 % to 48.2 % and Mn content 4.4% to 2.9 % of MZO thin film. Also manganese atomic percentage is decreases from 2.9% to 2.1% in MZO thin film annealed at 400\degree C. These results show that the atomic percentage of oxygen in Mn-doped ZnO thin film decreased to lower values after annealing. As temperature of annealing is increased more oxygen is absorbed in the process that could cause a decrease in the oxygen content in the films.
Fig. 6.4: Atomic percentage variation of MZO thin films prepared at various MnSO$_4$ concentrations

Fig. 6.5: Atomic percentage variation of MZO thin films annealed at various temperatures
6.5 Manganese and Nickel co-doped ZnO (MNZO) thin films

The atomic percentage values of Mn & Ni doped ZnO thin films are estimated using EDX analysis. Fig. 5.6 show the atomic percentage values of MNZO films that are deposited at various molar ratio of Zn:Mn:Ni. The 100:1:1 molar ratio prepared MNZO film exhibited the Zn:O ratio as 46.16:51.01. Also the Mn and Ni atomic percentage is about 1.7 and 1.13, respectively as shown in fig. 5.6. The Mn and Ni content increased with increase of molar ratio of Zn:Mn:Ni in MNZO thin films. The maximum percentage of composition is observed as 2.38 % and 1.62 % of Mn and Ni, respectively for 100:3:3 molar ratio of Zn:Mn:Ni solution. From this study it is conformed that the manganese ions are the dominate spices of the ions in co-doped films compared with nickel ions. The Mn decides the property and Ni join as the guest.
Fig. 6.6: Atomic percentage variation of MNZO thin films prepared at various molar ratio of Zn:Mn:Ni.
6.6 Morphological studies of undoped and metal doped ZnO thin films

Scanning electron microscopy is primarily used for the morphology studies in solid materials. To study the morphology of a semiconductor film, simple reflection modes of the optical microscope can be extended. But these techniques are limited in spatial resolution to a few tenth of a micrometer. The extension of the resolution is allowed in electron beam techniques. The most versatile among these is Scanning Electron Microscopy (SEM). The convenience of conventional SEM is partly due to the long working distance between the final lens and the sample surface and partly due to the ability to directly study almost any free surface. The SEM photographs provide the nature of the surface (i.e) uniformity, smoothness and cracks, the nature of the grains (i.e) shape of particulate and grain size. A large number of scanning probe microscopy techniques utilizing various signals generation mechanism has emerged recent years scanning tunneling microscopy is the most important technique with the wide range of applications in science and technology. In these studies the surface morphology of prepared samples like ZnO, NZO, MZO and MNZO thin films were carried out using SEM and are discussed.

Figure 6.7 shows the SEM micrograph of ZnO thin film obtained at 0.03M ZnSO₄ concentration. The film surface exhibited the presence of hexagonal structured grains. The voids and non-uniformity has been observed in undoped ZnO thin film. However, in some parts of the surface the particles tend to agglomerate. This region may be due to the higher surface energy of the nanoparticles. For the gas sensors applications films with moderate conductivity that can be measured easily are needed. The size of the grains are estimated to be present in the range of 150 -200 nm. The SEM micrograph obtained for NZO film is shown in Fig. 6.8 for film grown
at 15 mM Ni$^{2+}$ ion concentration. It is observed that the surface are extremely smooth and uniform for all these films. The grain sizes are found to be increasing with Ni$^{2+}$ ion inclusion. The uniform rod shaped grains with nano protruding are observed in this NZO thin film. In some places voids are observed. The grains are in good electrical contact. However, SEM micrographs for the thin film grown with Ni: Zn (Fig. 6.8) show the presence of hexagonal rod shaped grains distributed uniformly with moderate grain sizes. This shows that the building up of the film surface is due to the competition for the lattice and vacancy sites between both metallic and non-metallic ions present in the solutions. The size of the grain is evaluated at 100 – 200 nm by SEM micrograph. At some parts of the surface examined a slight agglomeration of nano particles is observed. This type of nano-wires is useful for gas sensing properties [5]. The size of the grains could not be estimated correctly. This type of morphology may be due to the change of structural properties as given in fig. 5.6. The spherical shape collapsed nano grains are observed in 400°C annealed NZO thin film as shown in fig. 6.9. This may be due to the tensed state of surfaces exhibited for annealed samples.

The surface morphology of annealed and unannealed Mn doped ZnO thin films were examined by scanning electron microscopy (SEM). Figure 6.10 shows the SEM picture of Mn doped ZnO thin film prepared at 15 mM concentration of MnSO$_4$ concentration. The 15 mM concentration grown Mn doped ZnO films appears to be uniform with smaller grains and exhibits a structure with pores. The hexagonal shaped rod like grains with protruding of nano wires are exhibited in fig. 6.10. This result is due to the increase in nucleation over-growth and the deposits are more compact with uniform grain structure. It is observed from the scanning electron micrograph of Mn
doped ZnO film where average grain size about 250nm. The spherically shaped nano grains are observed by 400°C for annealed MZO thin film and are shown in fig. 6.11.

The Mn.Ni Co-doped thin films surface morphology studies are quite interesting. The presence of many novel shaped nano grains in the co-doped films shows that the morphology is greatly influenced by simultaneous dual doping. The nano fibers present very rarely in undoped and doped films tent to comout from the stacked nano rods and are forming a flowery pattern offering the infinite number of possibilities in morphological modifications.
Fig. 6.7: SEM micrograph of undoped ZnO thin film prepared at 0.03 M ZnSO$_4$

Fig. 6.8: SEM micrograph of Ni doped ZnO thin film prepared at 15mM NiSO$_4$
Fig. 6.9: SEM micrograph of Ni doped ZnO thin film annealed at 400°C

Fig. 6.10: SEM micrograph of Mn doped ZnO thin film prepared at 15mM MnSO₄
Fig. 6. 11: SEM micrograph of Mn doped ZnO thin film annealed at 400°C

Fig. 6. 12: SEM micrograph of Mn& Ni doped ZnO thin film at 100:3:3 molar ratio of Zn:Mn:Ni
6.7 Conclusions

The morphological analysis were performed using scanning electron microscopy. The studies agreed to a great extent with the structural studies results. The undoped films with good electrical conducting grains and moderate grain size were chosen for further applications. The doping revealed a distinct microstructure in Ni doped films. The change in morphology is minimal in Mn doped samples. This may be due to the similarity of the grains forming the film or due to the lattice matching between Zn and Mn. The morphological studies revealed excellent uniformity of the films. The formation of films with almost uniform surface energy during the growth determined by optimized conditions. The protruding of nanowire is used for gas sensing properties.

The compositional analysis performed using EDX analysis. The studies agree to a great extent. The compositional analysis revealed slight metallic excess in the undoped samples irrespective of the concentration of the Zn ion in solution. The metallic excess is reduced when adding metallic salts in the solution. A competition for the metallic and nonmetallic sites is created in the solution when more metallic salts are present and the formation of series of solid solutions is not possible due to the Zn ions dominating the competition. A doping level of 4.3 and 4.4 % of atomic concentration is observed in Ni and Mn, respectively. But even this low amount of doping is sufficient for our purpose and hence the doped samples were further used for gas sensor applications.
6.8 References


