Chapter 7

Summary and Conclusions

7.1 Introduction

ZnO nano structured thin films were prepared with three different doping elements and at three different doping concentrations. The structural, electrical and optical characterization of the films were done with different characterization techniques. The films were then used for the sensing of three different gases; ethanol vapour, LPG and biogas. The main conclusions revealed from the study are included in this chapter.

7.2 Properties of ZnO thin films prepared for the study

ZnO thin films prepared by SILAR method were smooth and continuous and from the XRD, it was obtained that the films had a particle size varying between 28 nm to 58 nm. XRD patterns obtained for Al, Sn and Cd doped samples at all doping concentrations had been analyzed for the study. The cell parameters; a, b c determined from XRD were in good agreement with that of the values in the JCPDS data. All the
peaks obtained in the XRD pattern were compared with that in the JCPDS values and the cell volume in each case was determined. The maximum intensity peak in all cases were found to be (002) peak and was at a '2 theta' value around 34°. All the samples used in the study were having hexagonal wurtzite structure and had an average cell volume, calculated from XRD as 35x10^{-30}m^3. The comparison of XRD patterns between different doping elements and doping concentrations were found to have slight difference in appearance but the particle size was found decreasing according to an increase in doping concentration. The films with comparatively small particle size were found to have low value of film resistance and good sensitivity to reducing gases.

Electron dissipative X ray analysis (EDAX) gave the mass percentages of oxygen and zinc in the prepared ZnO samples. The stoichiometric mass percentages, as theoretically expected, for zinc and oxygen were 80.30% and 19.70% respectively. The atomic percentage of oxygen as obtained from EDAX were 27.39% for pure and 23.92% for Al doped samples. From the values, it was clear that the doping concentration reduces the oxygen content of the samples. This means the samples with high doping concentration had more oxygen vacancy. Doping with Al, Sn and Cd will create oxygen vacancies due to the substitution of Zn by the corresponding doping element.

The UV-Vis-NIR analysis revealed the samples were of semiconducting nature and had an average band gap of 3.2 eV. The Sn doped samples had the least band gap and Cd doped samples had the highest gap. Band gap variation with doping elements followed the pattern

\[ \text{BG}_{\text{Sn}} < \text{BG}_{\text{Al}} < \text{BG}_{\text{Cd}} \]

A comparison between doping elements revealed that Sn was the best choice because it was having minimum resistance and maximum sensitivity compared to Al and Cd doped
samples at same doping concentrations. Doping with strontium, calcium, gallium and iodine had been done in the laboratory and Sr doped samples were found to have good sensitivity to ammonia gas. Iodine doped ZnO samples were found to be having antibacterial and anti microbial activity too.

Band gap of the samples found decreasing according to an increase in doping concentration. The variation in Band gap of the samples with different doping concentration, of all the three doping elements, followed the pattern

\[ BG_{7\text{ at }\%} < BG_{5\text{ at }\%} < BG_{3\text{ at }\%} \]

7.3 Optimum film preparation conditions

ZnO films deposited by SILAR method were found to have more surface continuity, low resistance high gas sensitivity and low response time compared with the films deposited by other methods. Three different concentrations of ZnSO\(_4\) had been used in the preparation 0.075 molar, 0.1 molar and 0.125 molar. They vary a little in electrical and gas sensing properties. Molarity of ZnSO\(_4\) was selected as 0.1 molar for the preparation of all the samples used for the gas sensing studies. The molar concentration of NaOH was always 2 molar for all the films.

In comparison of ZnO films with respect to four other parameters; (1) number of dips, (2)Drying delay, (3)dipping delay (4) pH of sodium zincate solution and (5) temperature of hot water bath, best film was obtained at the following conditions

(1) Number of dips:100

(2) Drying delay: minimum

(3) Dipping delay: 10 seconds
7.4 Effect of annealing temperature and annealing atmosphere

A set of annealing temperatures varying from 100°C to 500°C were considered and practiced. Among which 450°C was found to be the most suitable. The disadvantage of temperatures above 450°C was that the film was coated on microscope glass slides and the temperature at which the glass slide softens was very near to 500°C. So the annealing temperature was fixed to 450°C for a time of 1 hour.

Three annealing atmospheres were used for the comparative study; air, vacuum and oxygen. Among which, oxygen annealed samples were found to be having the least resistance and more sensitivity to gases.

7.5 Effect of aging and repeated heatings

The effect of repeated heating had been studied by heating the film, then cooling to room temperature and again heating, then cooling to room temperature and repeating the procedure up to 5 times. It was evident from the results that the effect of repeated heating on the resistance of the film was negligibly small. It guarantees the re-usability of the same film again and again. Aging of the films also found to have minute effects on sensitivity as well as resistance of the films. Even if the surface resistance at room temperature was found too high for old films due to aging, it reduced to the same low value when heated to 300°C or near.
7.6 Optimum Gas sensing conditions

The whole gas sensing study revealed that ZnO thin films prepared by SILAR method was very good in sensing of ethanol vapour, LPG and biogas. On a comparison of the results from chapters 4, 5 and 6, Al, Sn and Cd doped ZnO thin films are having maximum sensitivity to ethanol vapour than LPG or biogas. The sensitivity to these gases can be arranged as

\[ \text{Sensitivity}_{\text{ethanol}} > \text{Sensitivity}_{\text{LPG}} > \text{Sensitivity}_{\text{biogas}} \]

A graph showing the comparison of sensitivity of 5 atomic percent Al doped ZnO to ethanol, LPG and biogas are given in figure 7.1

![Sensitivity comparison between different gases](image)

Figure 7.1

The corresponding graph of sensitivity of 3 atomic percent doping and 7 atomic percent doping is given in figure 7.2 and 7.3 respectively
Response time of all the samples regardless of doping element and doping concentration, was found 1 second for all the three gases; ethanol vapor, LPG and biogas. But the recovery time seem to be varying to doping concentration and sensing gas. Among the three gases ethanol was found to be having minimum recovery time and biogas the maximum. It followed the relation
Figure 7.4 shows the variation of recovery time of 5 atomic % doped samples to ethanol vapour, LPG and biogas. The corresponding graph of 3 and 7 at % are given in figures 7.5 and 7.8 respectively.
7.7 Effect of electron irradiation

High energy electron beam irradiation enhanced the sensitivity of the films to a great extent. The films which were given electron beam irradiation showed an enhanced sensitivity than the non-irradiated films of same preparation conditions. So it was evident that the sensitivity of ZnO thin films to reducing gases can be increased considerably by electron beam irradiation. A graph showing the variation in sensitivity percentage of 5% Al doped ZnO according to sensing gas is shown in figure 7.7. Minimum value of gas sensitivity observed in the case of irradiated films was 19% which was shown by 3 atomic percent Cd doped ZnO during LPG sensing. Maximum sensitivity percentage observed was 82% which was in the case of 7 atomic percent Sn doped ZnO during ethanol sensing. Least difference between non-irradiated and irradiated samples observed was 15% and was shown by 5 atomic percent Al doped ZnO during LPG sensing.
Highest difference between non-irradiated and irradiated samples was observed as 24%. It was observed in the case of 7 atomic percent Sn doped ZnO during the sensing of ethanol. Sensitivity of the sample increased to 82% while the corresponding non-irradiated film showed a sensitivity of 58%.

Recovery time of the samples also found decreasing due to electron irradiation. Electron irradiated samples regained their original resistance faster than corresponding non-irradiated samples. The difference in recovery time between irradiated and non-irradiated samples were of the order of 5 - 10 seconds and it was same in the case of all gases irrespective of doping.

Electron beam irradiation was given in two different dosages to compare the effect of dosage of irradiation; 6 K Gray and 8 k Gray. But it was found that dosage of irradiation had no effect on the gas sensing properties of Al, Sn and Cd doped ZnO thin films. Response time of the samples were also found not changing according to a change in sensing gas, dosage of irradiation, doping element or doping concentration.
7.8 Suggestions for further studies

This study is being concluded as Al, Cd and Sn-ZnO nano structured thin films at a doping concentration varying from 3 atomic percentage to 7 atomic percentage and prepared by SILAR method can be used effectively as fast and high response sensor to ethanol vapour, LPG and biogas. The response time of all the samples were found as 1 second irrespective of doping element, concentration, electron irradiation and the sensing gas. The reason for this stability in sensing time can be further investigated.