CHAPTER 7

Conclusions and Future Scope
Summary and Conclusion

This chapter outlines a summary of all major conclusions of the present thesis with respect to the synthesis methods, characterization and application of pure and doped ZnO as both oxidizing and reducing gas sensor. In addition, the photoluminescence and field emission investigations have also been carried out.

As mentioned earlier the present work involves different synthesis methods to obtain pure and doped ZnO nanostructures with various morphologies. Different experimental techniques such as XRD, SEM / TEM / HRTEM, DTA / TGA, ESR, DRS, PL, FE and GS (gas sensing) were employed to characterize and study these samples. The different syntheses methods used include wet chemical routes namely co-precipitation, citrate gel, hydrazine and a physical method (thermal evaporation). Four different elements such as aluminum (Al), ruthenium (Ru), copper (Cu) and tin (Sn) were chosen as dopants to study their influence on physico-chemical characteristics of ZnO. These samples were tested for various gases right from the reducing (LPG, acetone, and ethanol) to oxidizing gases (NO2 and Cl2) at different operating temperatures and for various gas concentrations. The response and recovery time were also recorded.

The incorporation Al in ZnO was done during co-precipitation process. In co-precipitation technique, SDS (sodium dodecyl sulphate) was used as a surfactant to decrease the particle size and their avoid agglomeration. The variation in resistivity of ZnO was studied with respect to Al contents. The Al acting as a donor compensated by free electrons in conduction band at lower concentrations in ZnO thereby decreasing the resistivity. The Al doping modifies the defect species resulting in high sensitivity for oxidizing gas like NO2. The sensitivity, selectivity and an optimum operating temperature were determined as a function of Al content. The response and recovery time were also recorded for selected samples. Both ESR and DRS techniques provide strong evidences for NO2 adsorption on these samples. A probable mechanism for this effect (NO2 sensing) using ESR and DRS results obtained from samples before and after exposure to NO2 gas has been presented. This property is very interesting and needs more investigations for optimization since ZnO in general is well known as a reducing gas sensor. The field emission studies revealed that Al doped ZnO showed non-linearity in the F-N plot.
characteristic of semiconductor. This usually depends on factors such as band gap, defect states and saturation of emission current from conduction band and defect states.

The citrate gel method commonly used to prepare simple to complex ternary oxides has been adopted in the present work to prepare Ru doped ZnO samples. Even though this method has several advantages over other techniques, the major drawback of this procedure is possible carbon contamination. The XRD studies results in addition to average particle size (Scherrer formula), the magnitude of strain (Hall equation) and texture coefficient (Harris analysis) calculation. On Ru addition, the tensile lattice distortion changes to compressive mode as indicated by systematic XRD studies. The variations of all these parameters were investigated as a function Ru doping. The room temperature PL studies and gas sensing characteristics at different operating temperatures were also carried out for these samples. Pure ZnO samples respond to LPG selectively while on incorporation of ruthenium both the sensitivity and selectivity increases towards ethanol. This change can be attributed to the possibility of different defect species produced due to aliovalent ion (Ru) doping and morphology of the particles.

The hydrazine process has been employed to synthesize pure and Cu doped ZnO. The microstructure of these powders was dominantly dictated by the ratio of zinc precursor to hydrazine. The amount of hydrazine was varied during the synthesis process to find its influence on the morphology and hence the average particle size. The presence of cupric oxide was detected in the XRD for higher concentrations of Cu incorporation. The particle size was also found to increase slightly with Cu doping. The conductivity of cupric oxide being 'p’ type in contrast to host n-ZnO, the resistivity increases with copper addition. The doping of copper does not improve the gas sensing property and also decreases selectivity. The operating temperature for gas sensing was varied from 250 °C to 350 °C to determine optimum conditions for sensing.

Thermal evaporation process was utilized to produce Sn doped ZnO nanostructures. Since ZnO and SnO₂ are well-known gas sensors and Sn doping is known to enhance the electrical properties and hence its study as gas sensor has been explored. The presence of SnO₂ (tetragonal, rutile phase) was detected in the XRD for higher concentrations of Sn
incorporation. The reduction in resistance of ZnO with Sn addition suggests that Sn acts as a donor, as expected. However no improvement in gas sensing properties was observed on Sn incorporation in ZnO.

Thus, the fundamental issues tackled in the present thesis are (i) the effect of synthesis method on the morphology and average particle size (ii) variation in gas sensing mechanism on doping of various elements (iii) Correlation of gas sensing with the electron paramagnetic resonance and diffused reflectance spectra results and (iv) photoluminescence and field emission studies for pure and doped ZnO nanostructures.

**Future scope**

Technological and scientific potentials of high aspect ratio structures of semiconducting oxides are immense and the future of these nanostructured materials is certainly bright as revealed in the present study on ZnO structures. Moreover, the ultimate use of these structures is strongly dependent upon the ability to precisely control their dimension, shape, composition, surface property, phase purity and crystal structure. Additionally, these unique structures represent promising candidates for fundamental studies of low dimensional physics and applications in various fields like nanoelectronics, nanosensors etc.

All these results point out that with suitable synthesis method and dopant, a solid state semiconducting sensor can be realized which can also be economical and amenable for large scale production. The most important ‘3S’ parameters: selectivity, sensitivity and stability can also be modified. Although we have not investigated the influence of noble metal ion on ZnO, the available literature data suggest it may produce beneficial effects on important parameters of gas sensing. Yet another promising way to make a very good gas sensor is to alter the morphology of nanosized powder by way of using a surfactant during synthesis so that mesoporous structure is created. Hence realization of room temperature gas sensor is not far away from reality.