SUMMARY AND FUTURE SCOPE

9.1 Summary

The main aims of this thesis was to improve the gas sensing properties of Zinc Oxide based sensors by the doping effect of transition metal ions such as Fe, Cu, Co and Ni and investigate the undoped and doped ZnO thin films fabricated for the application of methane detection for minimum concentration at low operating temperatures. The maximum doping up to 8 % of transition metal ions for improved sensing applications was carried out and gas testing confirm the better sensing performance for 100 - 500 ppm concentration of methane between operating temperature range of 75 °C - 200 °C. Thin films have been successfully deposited using spin coating on glass substrates. Metallization of developed sensor were carried out by using metal mask and silver pasted was used for deposition of electrodes. Chapter 2 presented the fabrication of thin film using same chemical route process with different precursors and solvents depending on the requirement for dissolution of materials. Common spin pattern of spin rpm (500 - 3000 rpm pattern) utilized for depositions of films. We observed that this pattern of spin-rpm is very much useful for thin film deposition. For the first time we successfully fabricated; nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film sensor for methane detection and, also other thin films such as undoped flat ZnO thin film, nanocrystalline $Zn_{0.92}Cu_{0.08}O$ thin film, $Zn_{0.92}Co_{0.08}O$ and $Zn_{0.92}Ni_{0.08}O$ thin film. These films were fabricated by same route followed same rpm patterns. The developed thin films were utlized in the methane sensing study. The sensing response was highest for nano-strips Zn_{0.92}Cu_{0.08}O among all thin films, and followed by nano-crystaline Zn_{0.92}Cu_{0.08}O thin film,

then nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film, then $Zn_{0.92}Co_{0.08}O$ thin film, then $Zn_{0.92}Ni_{0.08}O$ thin film, then nano-net $Zn_{0.92}Fe_{0.08}O$, then undoped ZnO nano-wired, then undoped ZnO flat thin film respectively. Selectivity in presence of hydrogen responses were quikest or fastest for nano-strips $Zn_{0.92}Cu_{0.08}O$ thin film followed by nano-crystalline $Zn_{0.92}Cu_{0.08}O$, nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film, Co doped and Ni doped thin film for 500 ppm concentration of methane at operating temperature 200 °C, while poor response was found for undoped ZnO thin film. It was shown that the properties of sensing improved by doping of transitions metal ions due to substitution into host lattice without creating any change of structure and were responsible for increased charge carrieres concentration in the developed thin films due to the non-soitchemetrics and defects effects.

The chapter 8, explained fabrication and sensing performance of special surface morphology such as nano-wired based structures as undoped ZnO nano-wired thin film, nano-strip Zn_{0.92}Cu_{0.08}O thin film and nano-net Zn_{0.92}Fe_{0.08}O thin film. The fabrication of undoped ZnO nano-wired was carried out using same slovent and precursor used as described in chapter 2, while aqua regia, zinc carbonate, copper sulphate, ferric oxide and melamine used in the fabrication of other doped thin films of chapter 8. Deposition technique used as spin coating on constinuiosly high rpm (2500 – 3000 rpm) and, for calcination / heating of films was done furnace kept at 400 °C (for undoped ZnO sample) / 700 °C (for Cu / Fe doped ZnO samples), temperature increased from 30 °C to 500 °C (for undoped ZnO sample) / 800 °C (for Cu / Fe doped ZnO samples), further samples were removed from furnace at the point when temperature just reached to 500 °C / 800 °C. Strategically different methods were employed for fabrication of special nano-structred thin films as described in chapter 2. The responses of undoped ZnO nano-wired and nano-net Zn_{0.92}Fe_{0.08}O thin film

based sensors were higher than undoped ZnO flat thin film based sensor described in chapters, for methane detection. The response of nano-strip $Zn_{0.92}Cu_{0.08}O$ thin film based sensor was highest among all the types of thin films in the various chapters of this thesis.

In conclusion, It can be said that undoped ZnO flat and nano-wired thin films, nanowrinkled $Zn_{0.92}Fe_{0.08}O$ thin film, nano-net $Zn_{0.92}Fe_{0.08}O$ thin film and nano-strip $Zn_{0.92}Cu_{0.08}O$ thin film were fabricated in unique nano-structured and demonstrated as sensor for the application of thin films in the detection of 100 - 500 ppm concentration of methane beteween the operating temperature range of 75 °C - 200 °C. Finally, it can be concluded at this point that up to 8 % Fe, Cu, Co, Ni doped Zinc oxide thin film were developed for application as sensor for methane with reasonably good sensitivity and selectivity in presence of hydrogen. Table 9.1. showing better sensitivity of developed thin film sensors at 200 °C.

Thin film based Sensors	Sensitivity for 500 ppm	Morphology
Nano-strips Zn _{0.92} Cu _{0.08} O Thin film	94	Nano-strips
Nano-crystalline $Zn_{0.92}Cu_{0.08}O$ Thin film	88.63	Nano-crystalline
Nano-wrinkled Zn _{0.92} Fe _{0.08} O Thin film	83.40	Nano-wrinkled
Zn _{0.92} Co _{0.08} O Thin film	74.07	Flat
Zn _{0.92} Ni _{0.08} O Thin film	63.79	Flat
Nano-net Zn _{0.92} Fe _{0.08} O Thin film	53	Nano-net
Undoped ZnO Nano-wired Thin film	49	Nano-wired
Undoped ZnO Flat Thin film	44.83	Flat

Table 9.1. Showing sensitivity of developed thin film sensors at 200 °C.

9.2 Future Scope

The undoped ZnO nano-wired thin film, nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film, nano-net $Zn_{0.92}Fe_{0.08}O$ thin film and nano-strip $Zn_{0.92}Cu_{0.08}O$ thin film were fabricated as unique nanostructured thin films and successfully utilized in the testing for methane sensing of 100 - 500 ppm concentration between operating temperature range of $100 \, ^{\circ}C - 200 \, ^{\circ}C$. These nanostructured based thin films were suitable for the methane detection / sensing and could be used in the fabrication of commercial sensors. The doping level of transition metal ion varied helping the morphology of thin film intact, and optimization of sensing activity of developed thin films can be carried out in future to develop superior sensors for methane detection. Further, these developed thin films can be investigated for the sensing of other environmental hazards such as NH₃, H₂, LPG, CO and CO₂.

9.3 Future Work

Followings steps are necessary to improve the sensitivity of sensor:-

- Reduce the size of testing set up.
- More study on grain size effects so that sensitivity can be improve.
- Study of other deposition techniques to improve the sensitivity.
- > Development of other, nano-structure based thin film sensors.