CHAPTER - 4

NANO-WRINKLED Fe DOPED ZnO THIN FILM FOR APPLICATION IN METHANE DETECTION

4.1 Introduction

This chapter deals with the application of up to 8 % Fe doped ZnO ($Zn_{0.92}Fe_{0.08}O$) thin film in the methane sensing. The testing of methane detection in the concentration range of 100 - 500 ppm at operating temperature between 75 ^{o}C to 200 ^{o}C with selectivity with hydrogen, a brief description of all is presented in this chapter.

4.2 Results and Discussions

Fig.4.1, show the wrinkled based sensor response for 500 ppm methane at 200 ^{o}C. In the graph, point A show to the gas inlet and point C show the outlet conditions. The resistance of the sensor decreased in the presence of methane from point A to B and was stable form point B to C and between point C to D, the sensor recovered to its original status in the absence of methane. Point A to B indicates the sensor response of the film for methane. The approximate response and recovery time are 96 sec, 107 sec respectively for 500 ppm methane at 200 ^{o}C. 5 and 10 % Fe doped ZnO samples showed poor response compared to 8 % Fe doped ZnO samples. By Sol-gel process we used in our study, only maximum 10 % Iron doping is possible. That is why we concentrated our studies at 8 % Fe doped samples to develop superior methane sensors.

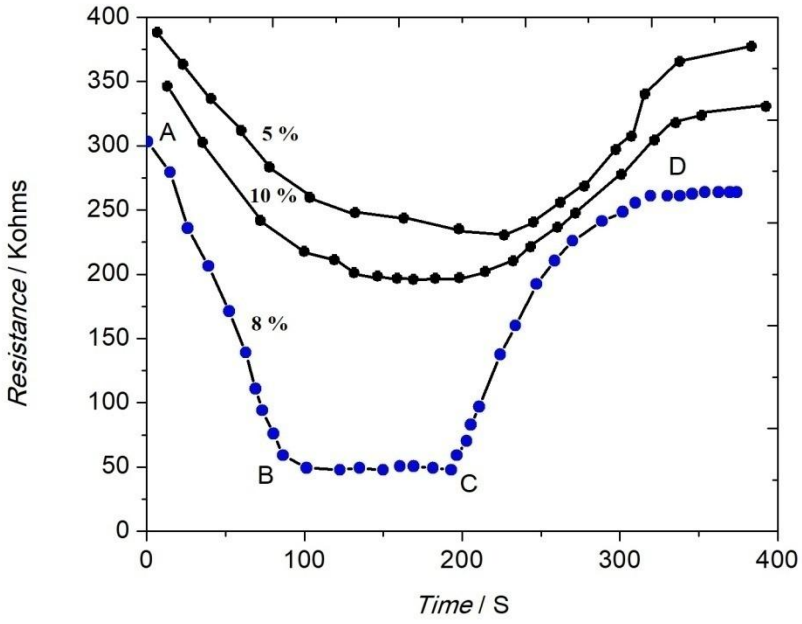

Fig.4.1. Sensor response of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film with methane as target gas at 200 °C.

Response in percentage at different operating temperatures, ranging from 75 °C to 200 °C with various concentrations of methane such as 100 ppm, 200 ppm, 300 ppm, 400 ppm and 500 ppm is shown in the Fig.4.2 and Fig.4.3. In this graph, It was visible that response increases with increase in temperature and gas concentrations. Fig.3.2 and Fig.3.3**,** show the resultant value of response for 100 ppm, 200 ppm, 300 ppm, 400 ppm and 500 ppm methane at various operating temperatures such that 75 °C, 100 °C, 125 °C, 150 °C, 175 °C, 200 °C. The lowest value was 4% for 100 ppm at 75 °C and highest value was 83.4 % for 500 ppm at 200 °C, because increased adsorption sites and space charge layer decreased formed on surface can trap the electrons into the conduction band. The response was better than undoped ZnO based flat thin film sensor.

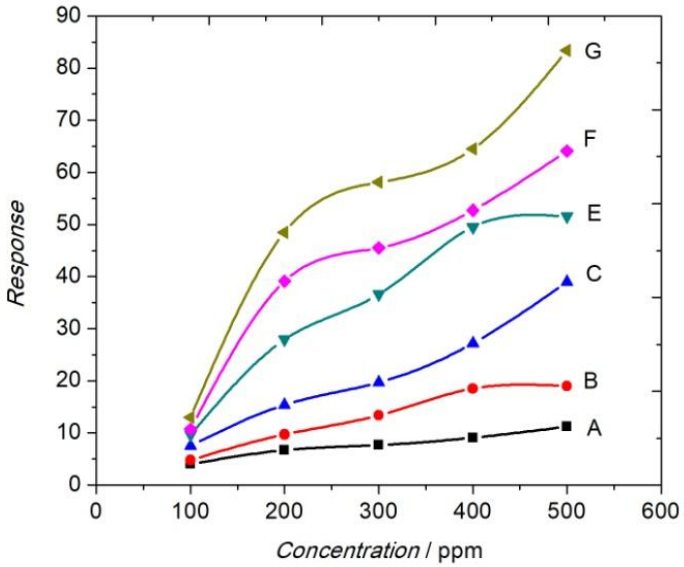

Fig.4.2. Response of the sensor on various concentrations and curve A, B, C, D, E, F as 75 °C, 100 °C, 125 °C, 150 °C, 175 °C, 200 °C respectively (Response versus Concentration).

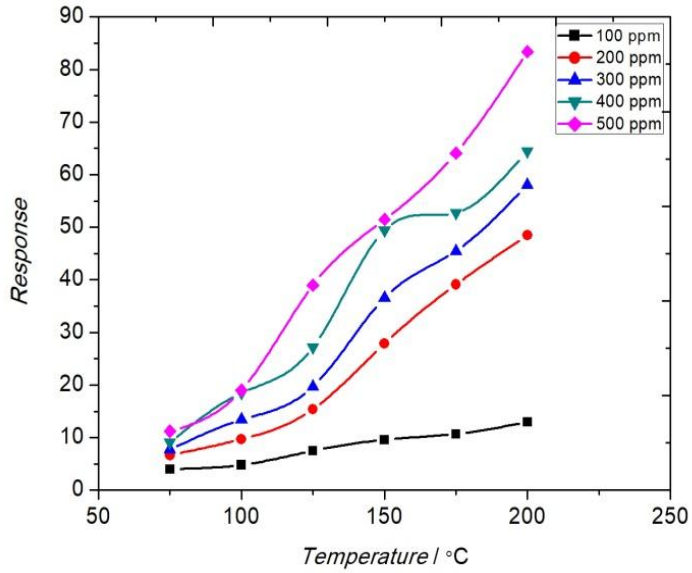

Fig.4.3. Response for 100 ppm, 200 ppm, 300 ppm, 400 ppm concentrations at 75 °C, 100 °C, 125 °C, 150 °C, 175 °C, 200 °C temperatures (Response versus Temperature).

Fig.4.4, show the response time of $Zn_{0.92}Fe_{0.08}O$ thin film methane sensor for 100 ppm, 200 ppm, 300 ppm, 400 ppm, 500 ppm of methane concentrations on operating temperatures at 75 °C, 100 °C, 125 °C, 150 °C, 175 °C, 200 °C. It was clear that response time was decreased with increasing concentrations and also with increase in operating temperatures (Fig.4.5). Quickest sensor response was achieved for 500 ppm methane concentration at 200 °C. The responses time was faster than undoped ZnO flat thin film for 100 - 500 ppm concentration range of methane at operating temperatures ranges of 75 °C - 200 °C. Fig.4.4 and Fig.4.5 are correlated to each other, and graph A, B, C, D, E, F denoted as operating temperature at 75°C, 100°C, 125°C, 150°C, 175°C, 200°C respectively.

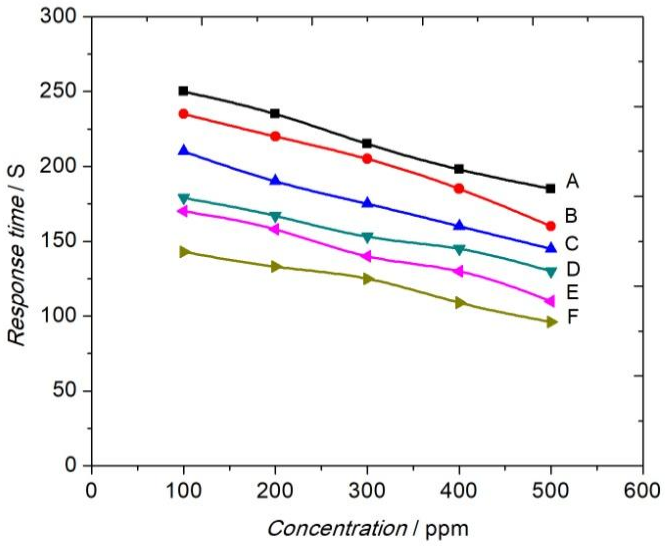

Fig.4.4. Show response time of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film methane sensor for 100 to 500 ppm at operating temperatures 75 °C to 200 °C (Response time versus Concentration).

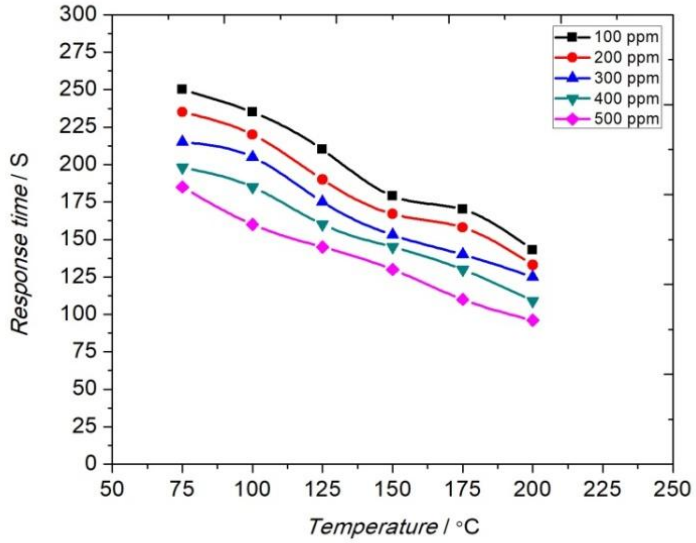

Fig.4.5. Show response time of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film methane sensor for 100 to 500 ppm at operating temperatures 75 °C to 200 °C (Response time versus Temperatures).

Fig.4.6, show the recovery time for 100 ppm, 200 ppm, 300 ppm, 400 ppm, 500 ppm concentration of methane at operating temperatures 75 °C, 100 °C, 125 °C, 150 °C, 175 °C and 200 °C. The response and response-recovery time were functions of gas concentrations. If concentration increases then more gas molecules adsorb on surface and increased adsorption and space charge layer decreased formed on surface can trap the electrons into the conduction band, resulting in the increase in conductivity, while recovery time is a consequence of desorption rate and it was slower at the increased concentrations. The gas molecules desorption rate is high above 200 °C for the Fe-doped ZnO wrinkled sensor. Recovery time decreases with increase in operating temperatures for same concentration of gas (Fig.4.7). Resultantly recovery time decreases with increasing concentrations of test gas and operating temperatures. In comparison with undoped ZnO flat thin film sensor, we observed that recovery time of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film were faster for 100- 500

ppm concentration range at operating temperatures ranges of 75 °C - 125 °C and above this operating temperatures, recovery time was slow, while faster in comparison to undoped ZnO flat thin film at operating temperature ranges of 150 °C - 200 °C. In Fig.4.6, graph A, B, C, D, E, F denoted as operating temperature at 75°C, 100°C, 125°C, 150°C, 175°C, 200°C respectively.

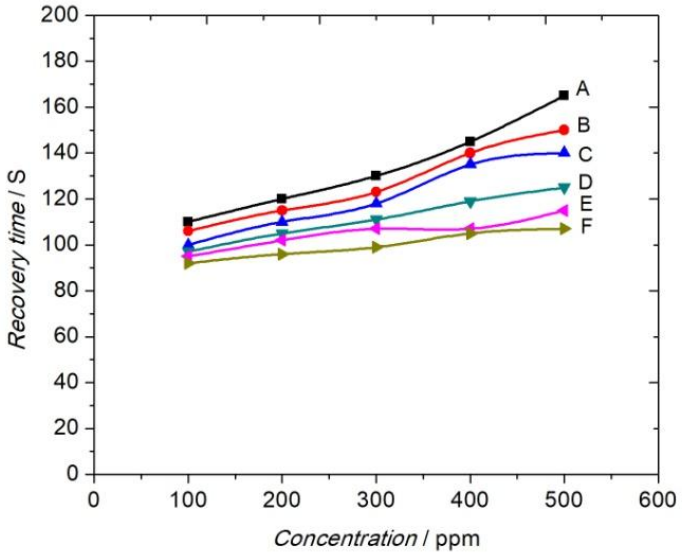

Fig.4.6. Show recovery time of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film methane sensor for 100 to 500 ppm at operating temperatures 75 °C to 200 °C (Recovery time versus Concentration).

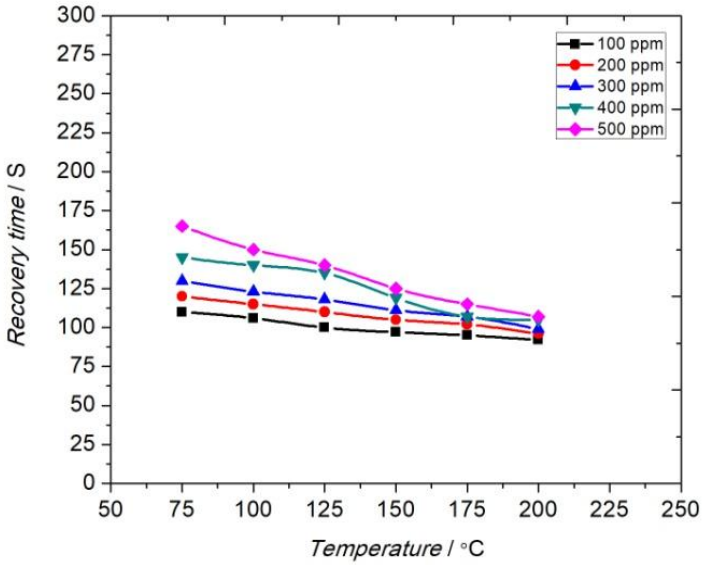

Fig.4.7. Show recovery time of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film methane sensor for 100 to 500 ppm at operating temperatures 75 °C to 200 °C (Recovery time versus Temperature).

4.3 Selectivity

We also studied selectivity of methane sensing in presence of hydrogen. A gas mixture of 10 % hydrogen balanced in methane was used for the study. Fe doped wrinkled sensor showed high selectivity for 500 ppm of methane in the operating temperature range of 150 °C to 200 °C. The selectivity response for H_2 and CH_4 shown in Fig.4.8. In this study, quickest response time was observed for 500 ppm of methane at 200 °C and selectivity response were better than undoped ZnO based flat thin film sensor. For H_2, high response was observed in the range of 75 °C to 150 ^oC for 500 ppm.

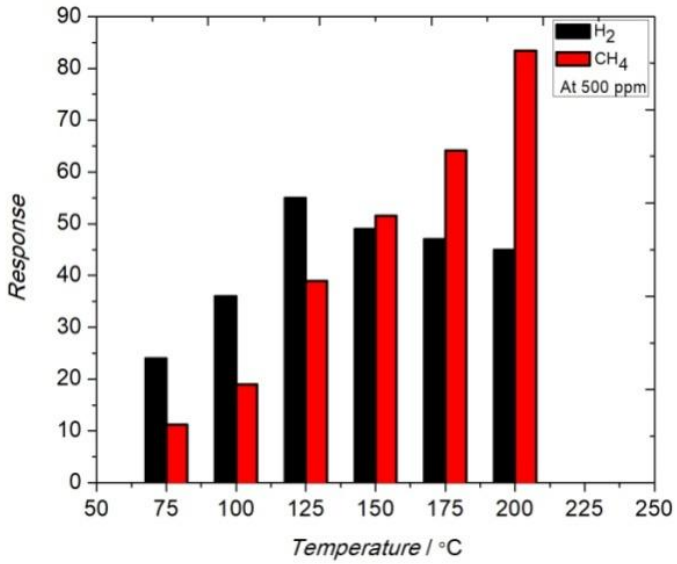

Fig.4.8. Selectivity response of $Zn_{0.92}Fe_{0.08}O$ wrinkled based sensor for methane and hydrogen for 500 ppm at the operating temperatures range of 75 ^{o}C to 200 ^{o}C

4.4 Conclusion

Nano-wrinkled based thin film was sensible for 100 – 500 ppm concentration of methane at operating temperatures range of 75 °C - 200 °C. The response was highest (83.4 %) for 500 ppm at 200 °C along with quick selectivity with hydrogen for 500 ppm at 200 °C. This film showed better performance than undoped zinc oxide flat thin film for methane sensing.