# CHAPTER - 7

# METHANE DETECTION USING Ni DOPED ZnO THIN FILM

## 7.1 Introduction

This chapter deals with the application of 8 % Ni doped ZnO ($Zn_{0.92}$ $Ni_{0.08}O$) thin film in the methane sensing.. The testing of methane detection in the concentration range of 100 - 500 ppm between the operating temperature range 75 $^{o}$C to 200 $^{o}$C and selectivity in presence of hydrogen, is also briefly described. When methane was exposed on $Zn_{0.92}Ni_{0.08}O$ thin film sensor, we observed that resistance of film was decreased and reached to a stable value. When gas flow was closed and gas was removed from testing chamber, then resistance increased and recovered to original resistance.

## 7.2 Results and Discussions

Fig.7.1, show the $Zn_{0.92}Ni_{0.08}O$ thin film 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 were 120 sec, 180 sec respectively for 500 ppm methane at 200 $^{o}$C.

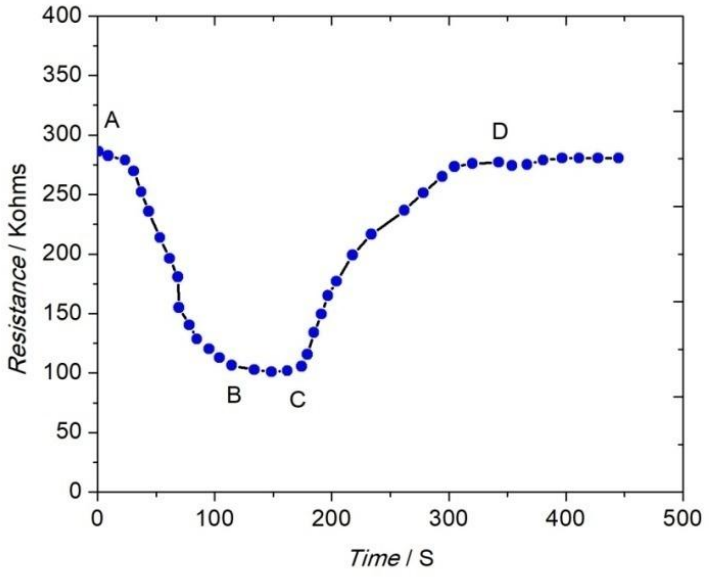


**Fig.7.1. Sensor response of $Zn_{0.92}Ni_{0.08}O$ thin film with methane as target gas at 200 °C.**

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.7.2. The graph show that response increased with increase in gas concentrations and temperatures. Fig.7.3**,** show the resultant value of response for 100 ppm, 200 ppm, 300 ppm, 400 ppm and 500 ppm methane at 75 °C, 100 °C, 125 °C, 150 °C, 175 °C, 200 °C operating temperatures. The lowest value was ~3.23 % for 100 ppm at 75 °C and highest value was ~ 63.79 % for 500 ppm at 200 °C. The response was higher than the undoped ZnO thin film sensor and lower than the nano-wrinkled $Zn_{0.92}Co_{0.08}O$ , $Zn_{0.92}Fe_{0.08}O$ thin film and $Zn_{0.92}Cu_{0.08}O$ thin film sensors.

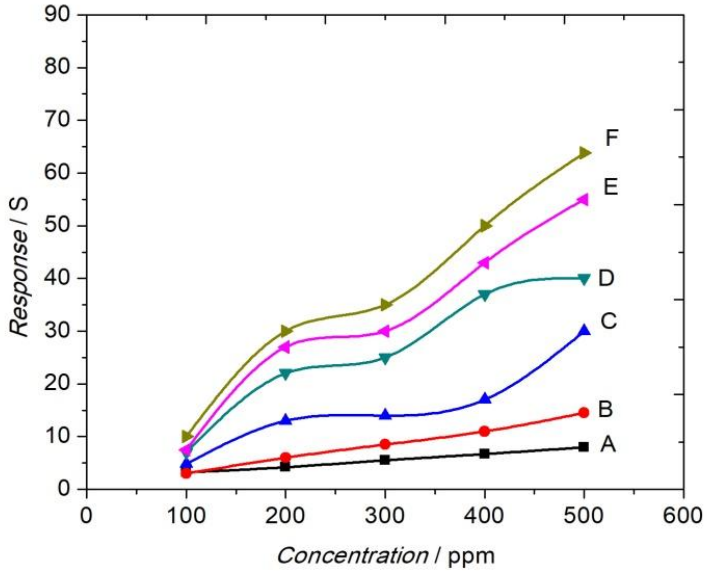


**Fig.7.2. Response of the sensor on various concentrations and curve A, B, C, D, E, F as 75 °C, 100 °C, 125 °C, 150 °C, 175 °C, 200 °C respectively (Response versus Concentration).**

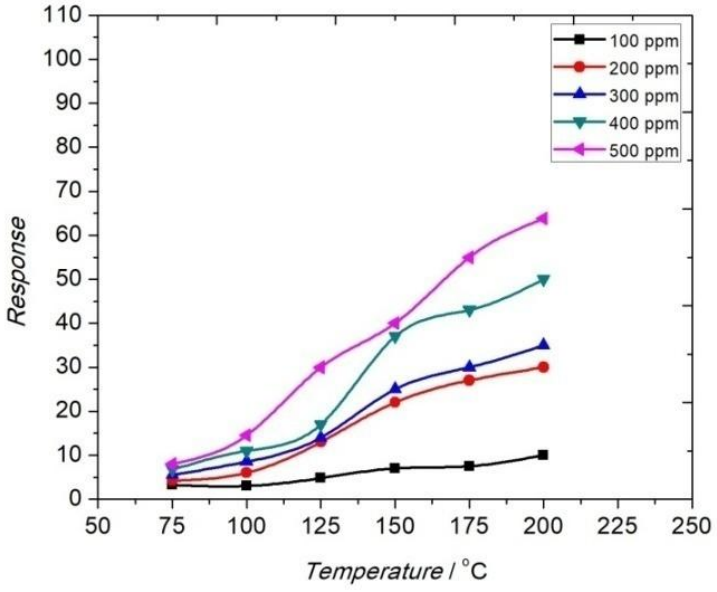


**Fig.7.3. Response for 100 ppm, 200 ppm, 300 ppm, 400 ppm concentrations at 75 °C, 100 °C, 125 °C, 150 °C, 175 °C, 200 °C temperatures (Response versus Temperature).**

Fig.7.4 and Fig.7.5, shown the determined the response time of ZnO thin film for 100 ppm, 200 ppm, 300 ppm, 400 ppm, 500 ppm concentrations of methane at different operating temperatures ranging from 75 °C to 200 °C. The response time decreased with increasing concentrations of methane at constant operating temperature. The response time decreased with increasing operating temperatures for same concentration. Resultantly, response time decreased with the combine effect of increasing of concentration and temperatures. Response time was 330 sec for 100 ppm at 75 °C and 120 sec for 500 ppm at 200 °C. Sensor response was fast for 500 ppm methane at 200 °C. Response time was slower than $Zn_{0.92}Co_{0.08}O$ thin film, nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film and $Zn_{0.92}Cu_{0.08}O$ thin film sensors for 100 - 500 ppm at ranges of 75 °C - 200 °C. Response time was faster than undoped ZnO thin film sensor for 100 - 500 ppm at ranges of 75 °C - 200 °C. In Fig.7.4, 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.

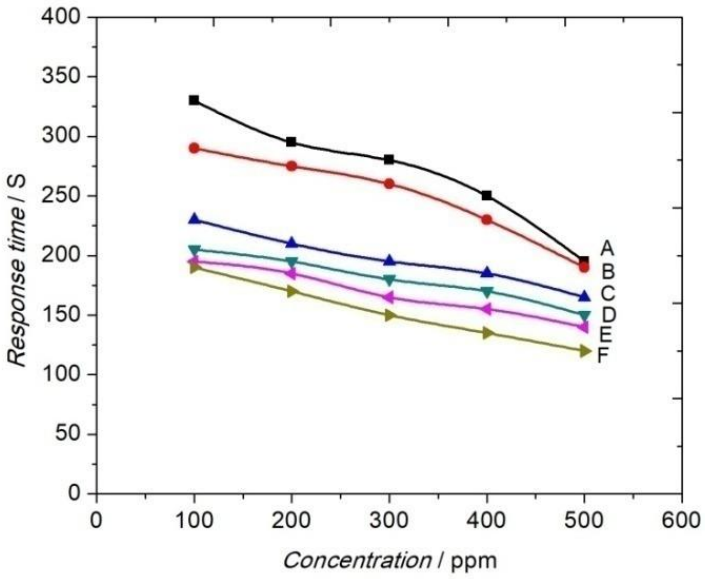


**Fig.7.4. Show response time of $Zn_{0.92}Ni_{0.08}O$ thin film methane sensor for 100 to 500 ppm at operating temperatures 75 °C to 200 °C (Response time versus Concentration).**

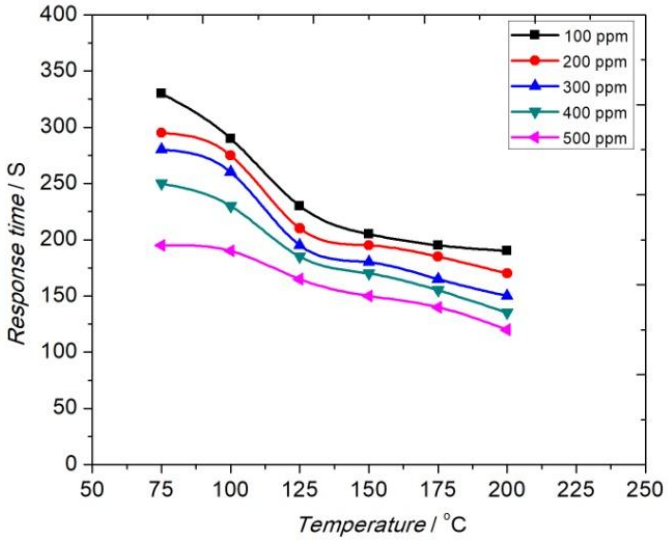


**Fig.7.5. Show response time of $Zn_{0.92}Ni_{0.08}O$ thin film methane sensor for 100 to 500 ppm at operating temperatures 75 °C to 200 °C (Response time versus Temperatures).**

Recovery time increased with increasing concentration at constant operating temperature, while decreased with increase of operating temperature for same concentration. Resultantly, recovery time decreased with the combine effect of increasing of concentration and temperatures. Fig.7.6 and Fig.7.7 show the recovery time for 100 ppm, 200 ppm, 300 ppm, 400 ppm, 500 ppm methane at operating temperatures 75 °C, 100 °C, 125 °C, 150 °C, 175 °C and 200 °C (graph A, B, C, D, E, F denoted as operating temperature). Recovery time was 200 sec for 100 ppm at 75°C and 180 sec for 500 ppm at 200 °C. This thin film based sensor was applicable up to 200 °C, but response was lower than the Cu doped, Fe doped ZnO wrinkled and Co doped based thin film sensor and higher than the undoped zinc oxide thin film. Desorption for gas molecules starts above 200 °C. Recovery time was slow or poor than $Zn_{0.92}Co_{0.08}O$ thin film, nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film and $Zn_{0.92}Cu_{0.08}O$ thin film sensors for 100 - 500 ppm at ranges of 75 °C - 200 °C. Recovery time was fast or better than undoped ZnO thin film sensor for 100 - 500 ppm at operating temperature at 75 °C.

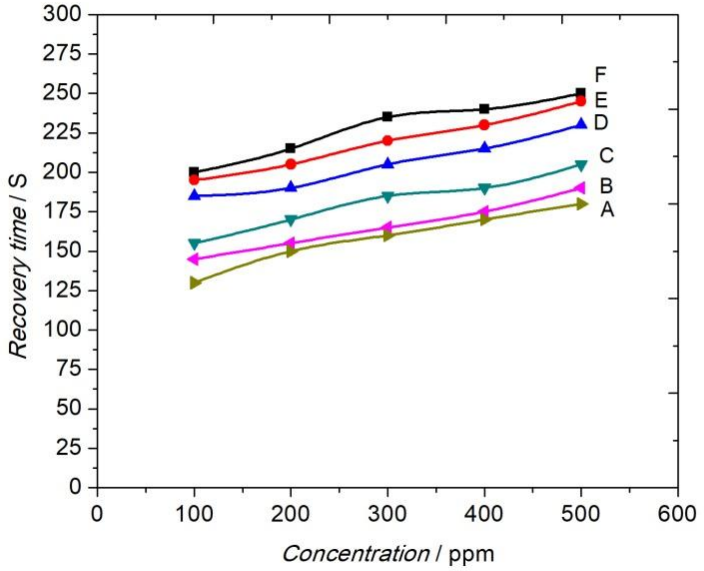


**Fig.7.6. Show recovery time of $Zn_{0.92}Ni_{0.08}O$ thin film methane sensor for 100 to 500 ppm at operating temperatures 75 °C to 200 °C (Recovery time versus Concentration).**

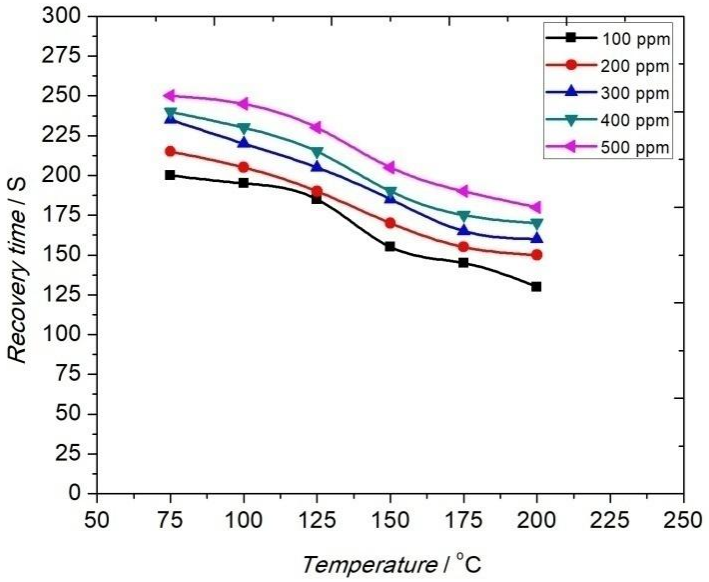


**Fig.7.7. Show recovery time of $Zn_{0.92}Ni_{0.08}O$ thin film methane sensor for 100 to 500 ppm at operating temperatures 75 °C to 200 °C (Recovery time versus Temperature).**

## 7.3 Selectivity

Observation of selectivity in presence of hydrogen for $Zn_{0.92}Ni_{0.08}O$ thin film methane sensor, It was found that high selectivity for 500 ppm of methane in presence of hydrogen was observed at the operating temperature range of 150 °C to 200 °C. In this study, in presence of $H_2$ high response was observed in the range of 75 °C - 150 $^oC$ for 500 ppm of $H_2$. The performance of selectivity for this film was poor than other types of developed films such represent in chapter 3 to 5, such as nano-wrinkled thin film, copper doped nano-crystalline and cobalt doped thin film based sensors.

## 7.4 Conclusion

Methane sensing for 100 – 500 ppm concentration at operating temperatures of 75 °C - 200 °C was studied. The response was highest (63.79 %) for 500 ppm at 200 °C. Selectivity in presence of hydrogen for 500 ppm of methane at 200 °C was better than undoped ZnO flat thin film. This film showed better response than undoped zinc oxide flat thin film for methane sensing.