CHAPTER - 8

STUDY OF UNDOPED NANO-WIRED ZnO, Cu DOPED ZnO NANO-STRIPS AND Fe DOPED ZnO NANO-NET THIN FILMS FOR APPLICATION IN METHANE SENSING

8.1 Introduction

This chapter deals with the special nano-structures based thin films such as undoped ZnO Nano-Wired containing thin film, 8 % Cu doped ZnO ($Zn_{0.92}Cu_{0.08}O$) Nano-Strips containing thin film and 8 % Fe doped ZnO ($Zn_{0.92}Fe_{0.08}O$) Nano-Net containing thin film were utlized as sensor for application in methane sensing. The testing of methane detection in the concentration range of 100 to 500 ppm at 100 ^{o}C, 150 ^{o}C, 200 ^{o}C, and selectivity in presence of hydrogen is briefly descript and presented in this chapter for thesis.

8.2 Results and Discussion for application of undoped Zinc oxide (ZnO) nano-wired based thin film in methane sensing

It methane was exposed on undoped ZnO nano-wired thin film sensor, we observed that resistance of film decreased and reached to stable value. When gas flow is closed and removed from testing chamber, then resistance increased and recovers to original resistance.

Fig.8.1, show the undoped ZnO wired thin film based sensor response for 500 ppm methane at 250 ^{o}C. In the graph, point A show to the gas inlet and point C show the outlet conditions. The resistance of the sensor decreases 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 sensing. The approximate response and recovery time are 120 sec, 165 sec respectively for 500 ppm methane at 250 ^{o}C.

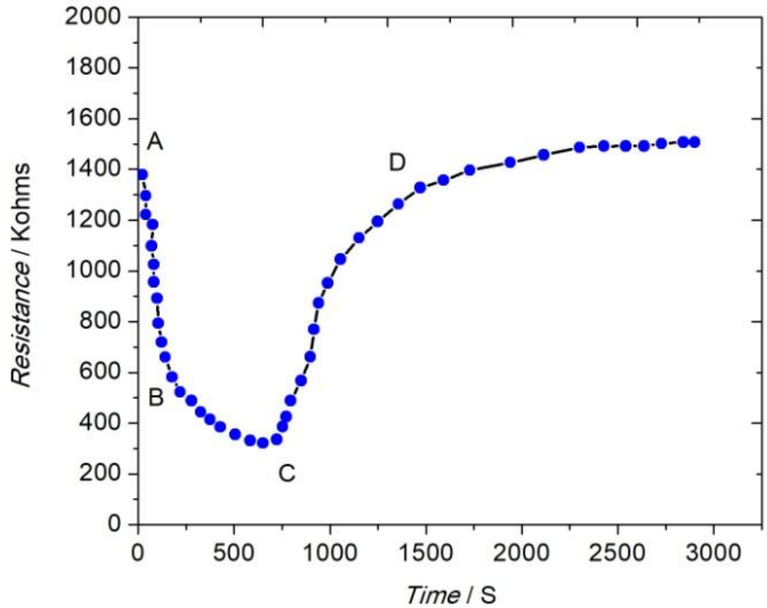

Fig.8.1. Sensor response of undoped ZnO nano-wired thin film with methane as target gas at 250 °C.

Response in percentage at different operating temperatures, ranging from 100 °C to 250 °C with various concentrations of methane such as 100 ppm, 300 ppm and 500 ppm is shown in the Fig.8.2. In the graph show that the response increases with increase in temperature and gas concentrations. Fig.8.3**,** show the resultant value of response for 100 ppm, 300 ppm and 500 ppm methane at 100 °C, 150 °C, 200 °C, 250 °C operating temperatures. The lowest value was approximately 3.8 % for 100 ppm at 100 °C and highest value was 49 % for 500 ppm at 250 °C. The response was higher than undoped ZnO flat thin film and lower than the nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ based thin film sensor. The desorption start above 250 °C.

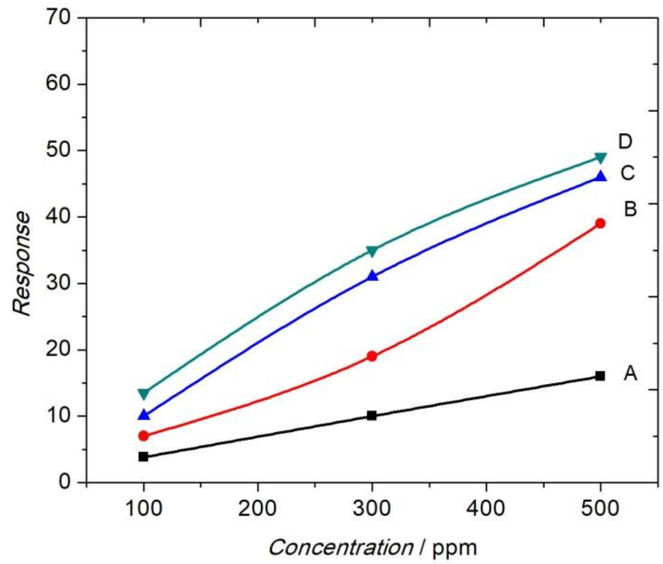

Fig.8.2. Response of the sensor on various concentrations (100 to 500 ppm) and curve A, B, C, D as 100 °C, 150 °C, 200 °C, 250 °C respectively (Response versus Concentration).

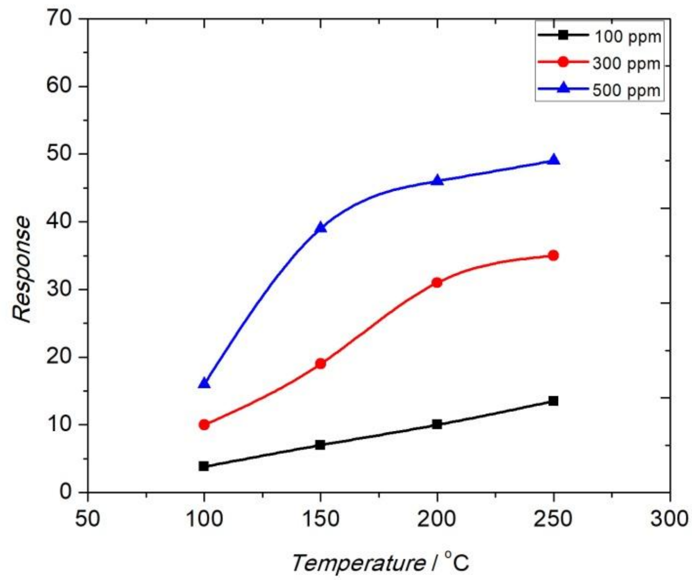

Fig.8.3. Response for 100 ppm, 300 ppm, 500 ppm concentrations at 100 °C, 150 °C, 200 °C and 250 °C temperatures (Response versus Temperature).

In Fig.8.4 and 8.5, show the determined the response time of ZnO thin film for 100 ppm, 300 ppm, 500 ppm concentrations of methane at different operating temperatures ranging from 100 °C to 250 °C. The response time decreased with increasing concentrations 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 approximately 242 sec for 100 ppm at 100 °C and 120 sec for 500 ppm at 250 °C. Sensor response was fast for 500 ppm methane at 250°C. The responses time was quicker than undoped ZnO flat thin film for 100 - 500 ppm at ranges of 100 °C - 250 °C. In Fig.8.4, graph A, B, C, D denoted as operating temperature at 100°C, 150°C, 200°C, 250°C respectively.

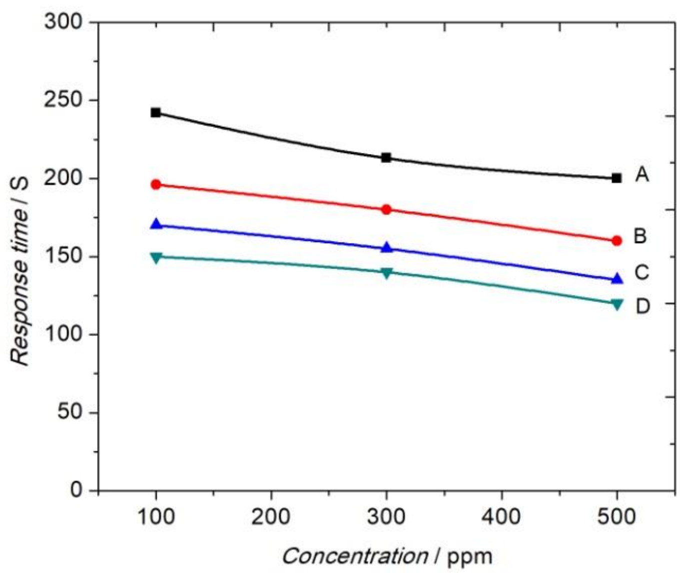

Fig.8.4. Show response time for 100 to 500 ppm at operating temperatures 100 °C to 200 °C (A to D) (Response time versus Concentration).

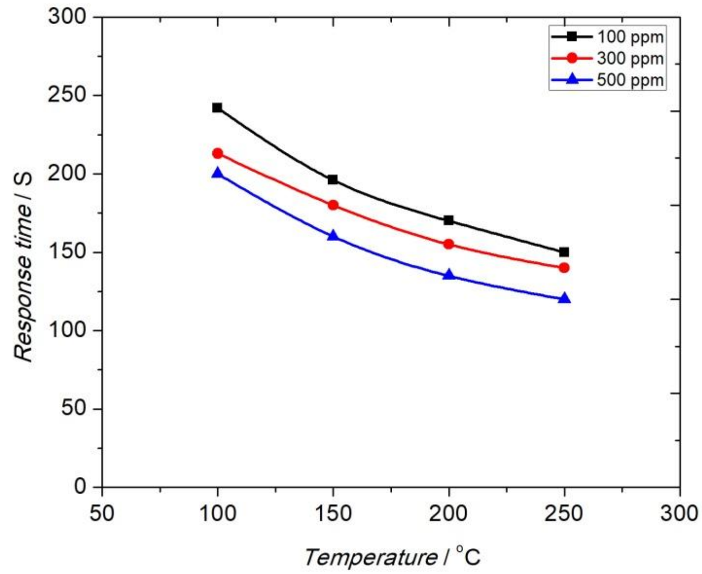

Fig.8.5. Show response time for 100 to 500 ppm at operating temperatures 100 °C to 250 °C (Response time versus Temperatures).

Recovery time increased with increasing concentration at constant operating temperature, while decreased with increasing of operating temperature for same concentration. Resultantly, recovery time decreased with the combined effect of increasing of concentration and temperatures. Fig. 8.6 and 8.7 show the recovery time for 100 ppm, 300 ppm, 500 ppm methane at operating temperatures 100 °C, 150 °C, 200 °C, 250 °C. Recovery time was approximately 120 sec for 100 ppm at 100 °C and 165 sec for 500 ppm at 250 °C. This thin film based sensor was sensitive up to 250 °C and desorption of gas molecules start above 250 °C. In Fig.8.6, graph A, B, C, D, denoted as operating temperature at 100°C, 150°C, 200°C, 250°C respectively.

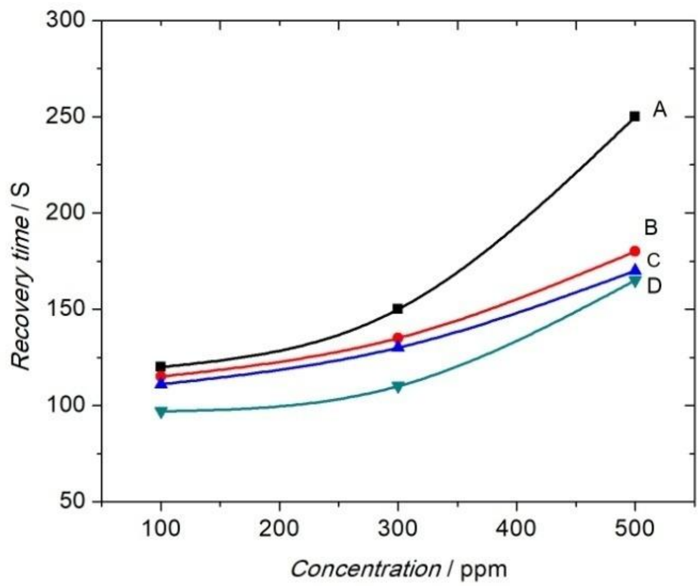

Fig.8.6. Show recovery time for 100 to 500 ppm at operating temperatures 100 °C to 250 °C (A to D) (Recovery time versus Concentration).

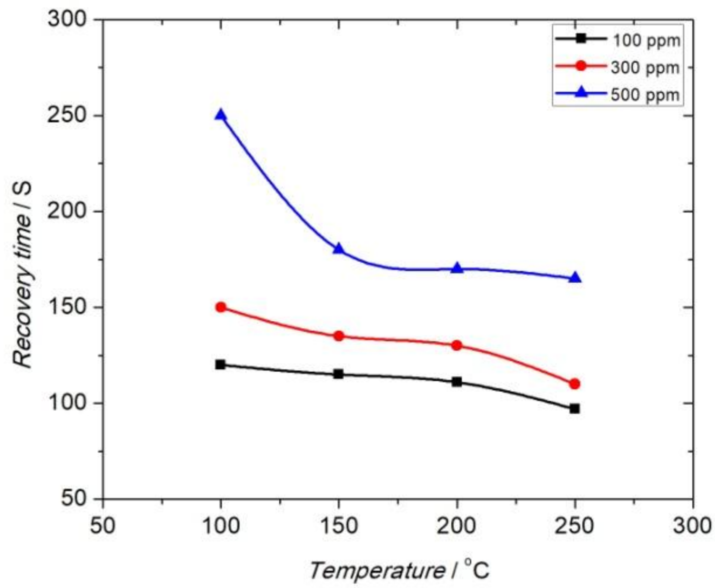

Fig.8.7. Show recovery time for 100 to 500 ppm at operating temperatures 100°C to 250 °C (Recovery time versus Temperature).

8.3 Selectivity

In separate experiment, undoped ZnO nano-wired based thin film sensor showed is high selectivity in presence of hydrogen for 500 ppm of methane at the operating temperature range of 200 °C to 250 °C. High response was observed in the range of 100 °C to 200 ^{o}C for 500 ppm of H_2.

8.4 Results and Discussion for application of 8 % Cu doped Zinc oxide nano-strips based thin film in methane sensing

Fig.8.8, show the $Zn_{0.92}Cu_{0.08}O$ nano-strip 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 response and recovery time were 70 sec, 115 sec respectively for 500 ppm methane at 200 ^{o}C. The sensitivity and response time was better than undoped ZnO nano-wired thin film sensor.

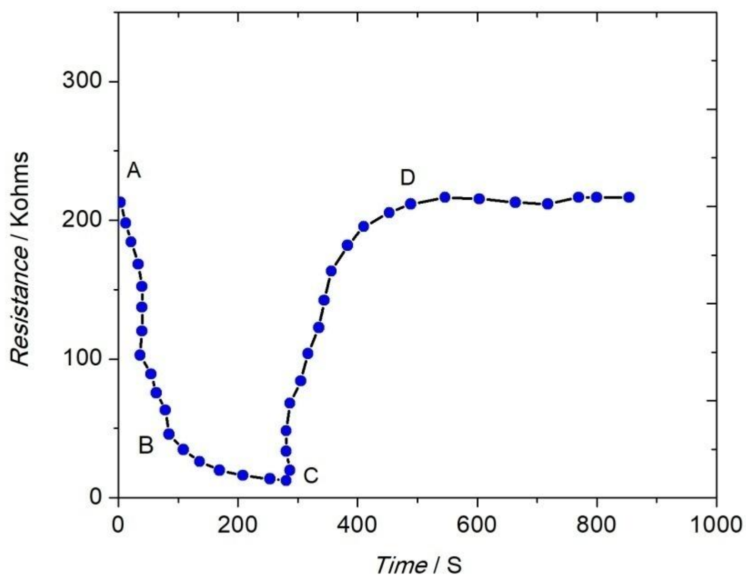

Fig.8.8. Sensor response of $Zn_{0.92}Cu_{0.08}O$ nano-strip thin film based sensor with methane as target gas at 200 °C.

Response in percentage at different operating temperatures, ranging from 100 °C to 200 °C with various concentrations of methane such as 100 ppm, 300 ppm, and 500 ppm is shown in the Fig.8.9. In this graph shown to the response increases with increase of gas concentrations. Fig. 8.10**,** show the resultant value of response for 100 ppm, 300 ppm and 500 ppm methane at 100 °C, 150 °C, 200 °C of operating temperatures. The lowest value was approximately 15 % for 100 ppm at 100 °C and highest value was 94 % for 500 ppm at 200 °C. The response was appear to be higher than undoped ZnO nano-wired thin film based sensor.

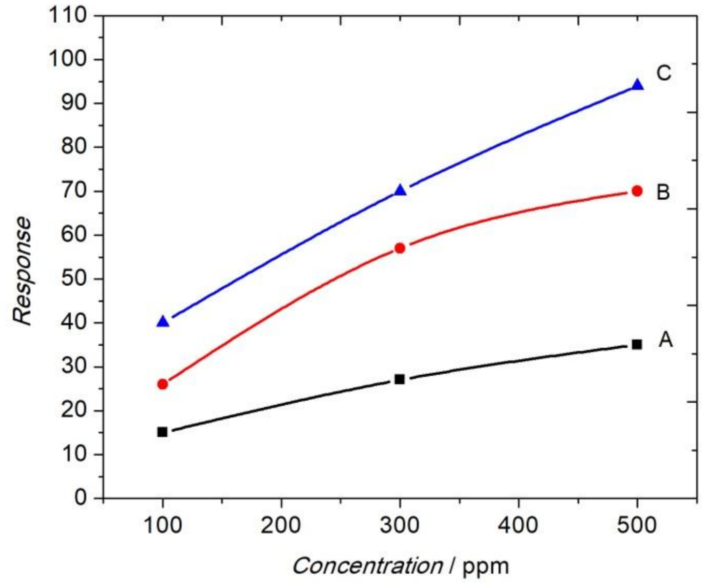

Fig.8.9. Response of the sensor on various concentrations (100 to 500 ppm) and curve A, B, C, as 100 °C, 150 °C, 200 °C respectively (Response versus Concentration).

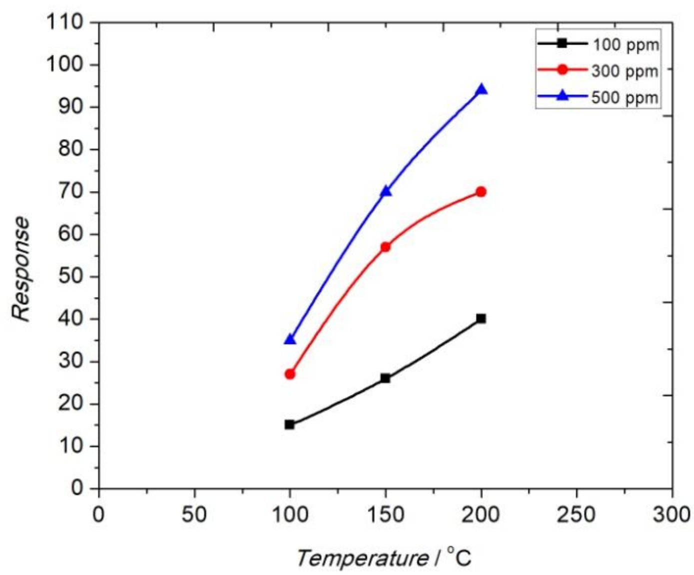

Fig.8.10. Response for 100 ppm, 300 ppm, 500 ppm concentrations at 100 °C, 150 °C, 200 °C temperatures (Response versus Temperature).

Fig. 8.11 and 8.12, show the determined the response time of ZnO thin film for 100 ppm, 300 ppm, 500 ppm concentrations of methane at different operating temperatures ranging from 100 °C to 200 °C. The response time decreased with increasing concentrations at constant operating temperature. The response time decreased with increasing operating temperatures for same concentration. Resultantly, response time decreased with the combined effect of increasing of concentration and temperatures. Response time was found 130 sec for 100 ppm at 100 °C and 70 sec for 500 ppm at 200°C. Sensor response was fast enough for 500 ppm methane at 200°C. The responses time was faster than undoped ZnO nano-wired thin film 100- 500 ppm at ranges of 100 °C- 200 °C. In Fig.8.11, graph A, B, C denoted as operating temperature at 100°C, 150°C, 200°C respectively.

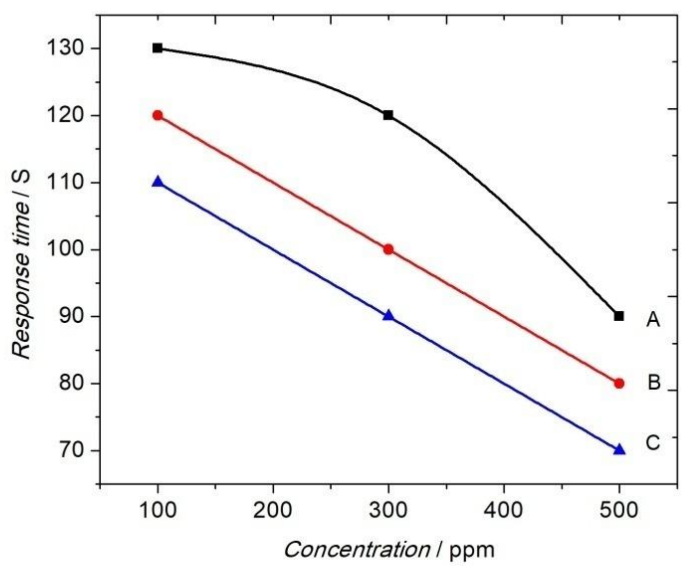

Fig.8.11. Show response time for 100 to 500 ppm at operating temperatures 100 °C to 200 °C (A to C) (Response time versus Concentration).

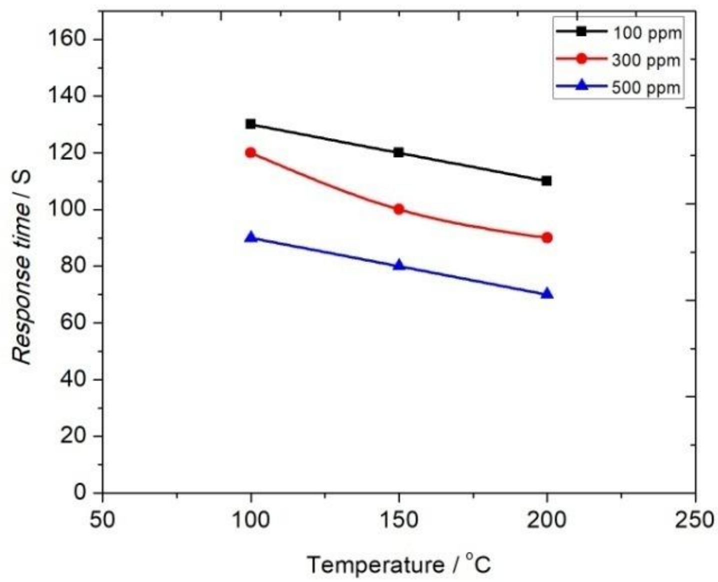

Fig.8.12. Show response time for 100 to 500 ppm at operating temperatures 100 °C to 200 °C (Response time versus Temperatures).

Recovery time increased with increased concentration at constant operating temperature, while decreased with increasing of operating temperature for same concentration. Resultantly, recovery time decreased with the combined effect of increasing of concentration and temperatures. Fig. 8.13 and 8.14 show the recovery time for 100 ppm, 300 ppm, 500 ppm methane at operating temperatures 100 °C, 150 °C, and 200 °C. Recovery time was found to be 75 sec for 100 ppm at 100 °C and 115 sec for 500 ppm at 200 °C. Recovery time was better than undoped ZnO nano-wired based thin film sensor. This thin film based sensor was suitable up to 200 °C. Desorption of gas molecules started above 200 °C. In Fig.8.13, graph A, B, C denoted as operating temperature at 100°C, 150°C, 200°C respectively.

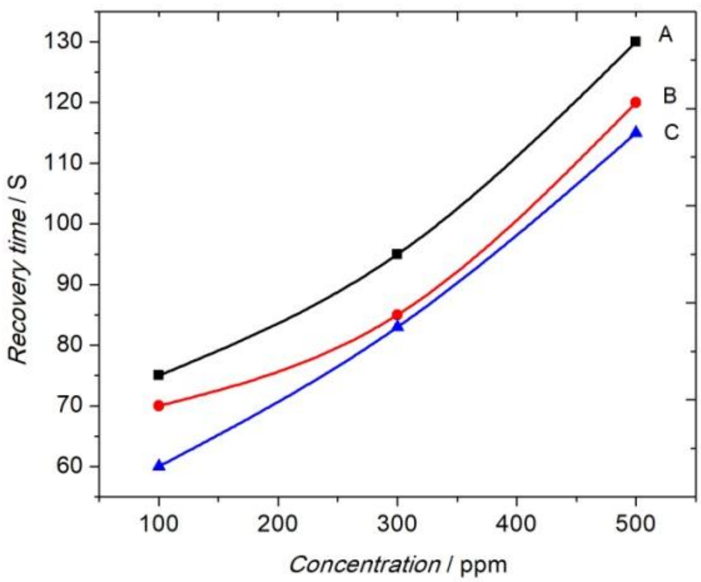

Fig.8.13. Show recovery time for 100 to 500 ppm at operating temperatures 100 °C to 200 °C (Recovery time versus Concentration).

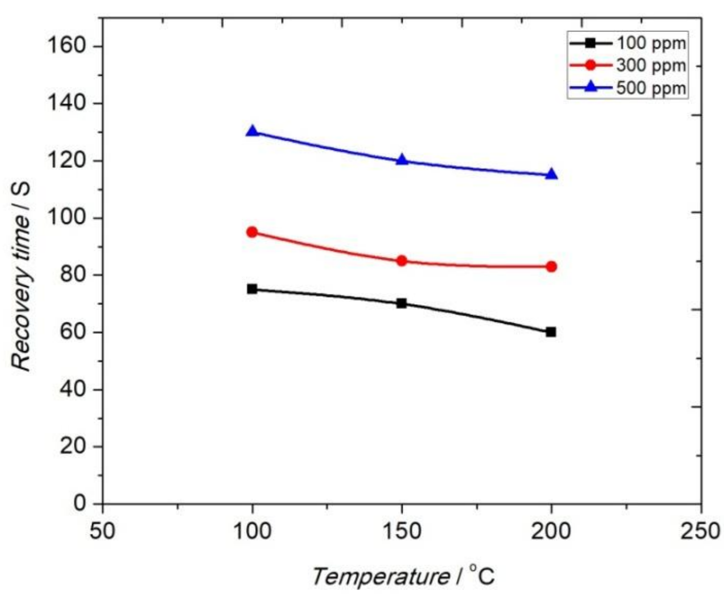

Fig.8.14. Show recovery time for 100 to 500 ppm at operating temperatures 100 °C to 200 °C (Recovery time versus Temperature).

8.5 Selectivity

Cu doped nano-wired based thin film sensor showed high selectivity for 500 ppm of methane at the operating temperature range of 150 °C to 200 °C. The selectivity response for H_2 and CH_4 shown in Fig.8.15. In this study, rapidly response time was observed for 500 ppm concentration of methane in the presence of hydrogen at operating temperature 200 °C. High response was observed in the range of 100 °C to 150 ^{o}C for 500 ppm of H_2.

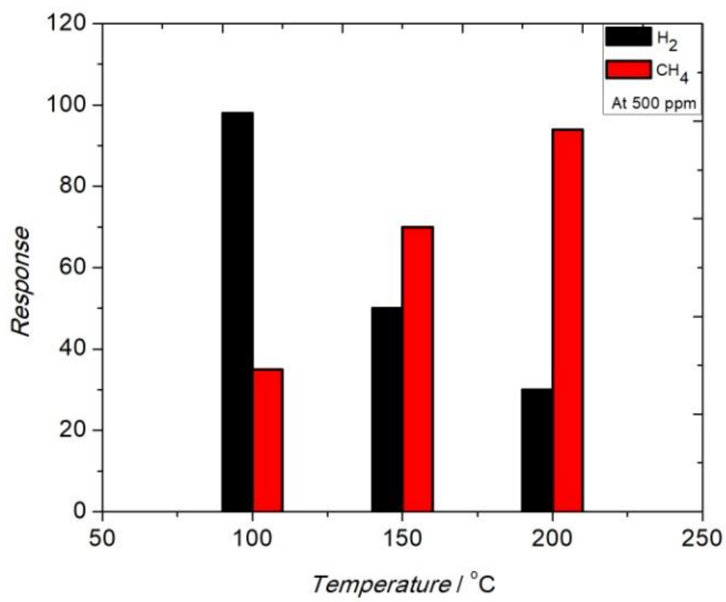

Fig.8.15. Selectivity response of $Zn_{0.92}Cu_{0.08}O$ nano-strips thin film based sensor for methane and hydrogen for 500 ppm at the operating temperatures range of 100 ^{o}C to 200 ^{o}C.

8.6 Results and Discussion for application of 8 % Fe doped Zinc oxide nano-net based thin film in methane sensing

Figure 8.16, show the $Zn_{0.92}Fe_{0.08}O$ nano-net 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 indicated the sensor response of the film for methane. The response and recovery time were approximately 110 sec, 125 sec respectively for 500 ppm methane at 200 ^{o}C.

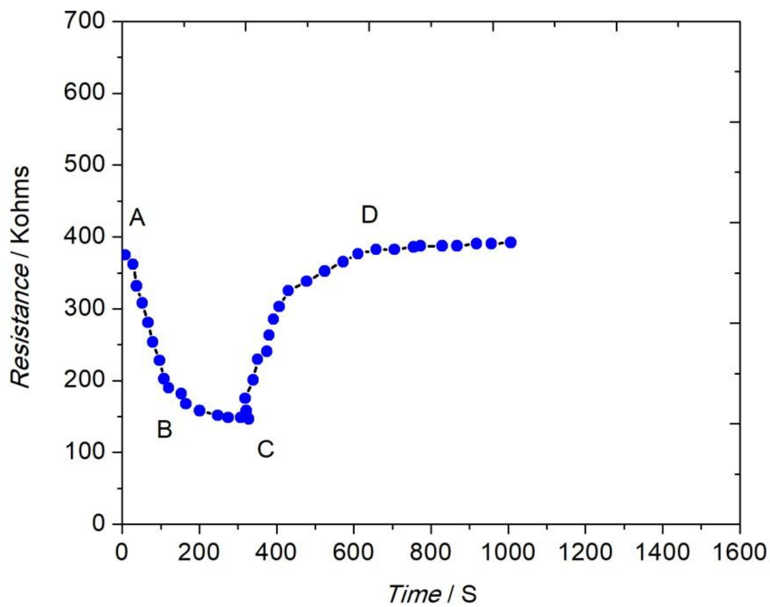

Fig.8.16. Sensor response of $Zn_{0.92}Fe_{0.08}O$ nano-net thin film based sensor with methane as target gas at 200 °C.

The response of the sensor was determined by using Equation (13) as described in chapter 1. Response in percentage at different operating temperatures, ranging from 100 °C to 200 °C with various concentrations of methane such as 100 ppm, 300 ppm, and 500 ppm is shown in the Fig. 8.17. In the graph show that the response increased with increase in gas concentrations. Fig. 8.18**,** show the resultant value of response for 100 ppm, 300 ppm, and 500 ppm methane at 100 °C, 150 °C, 200 °C operating temperatures. The lowest value was found to be 4 % for 100 ppm at 100 °C and highest value was found to be 53 % for 500 ppm at 200 °C. The response was higher than undoped ZnO nano-wired thin film and lower than $Zn_{0.92}Cu_{0.08}O$ nano-strip based thin film sensor.

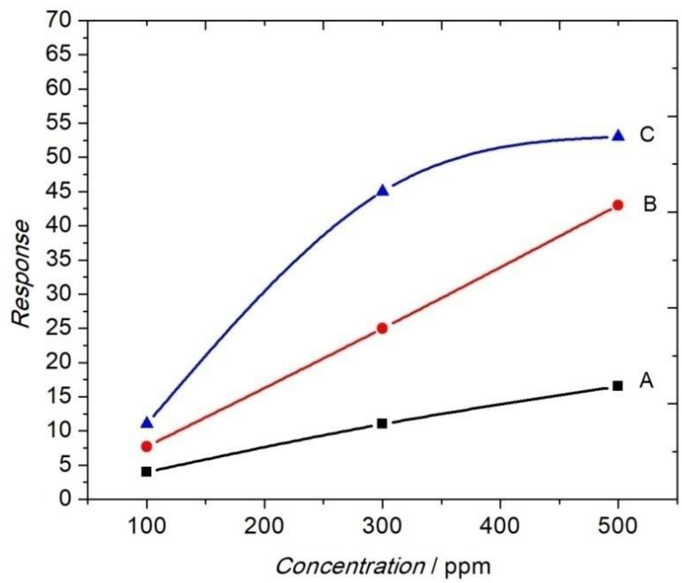

Fig.8.17. Response of the sensor on various concentrations (100 to 500 ppm) and curve A, B, C, as 100 °C, 150 °C, 200 °C respectively (Response versus Concentration).

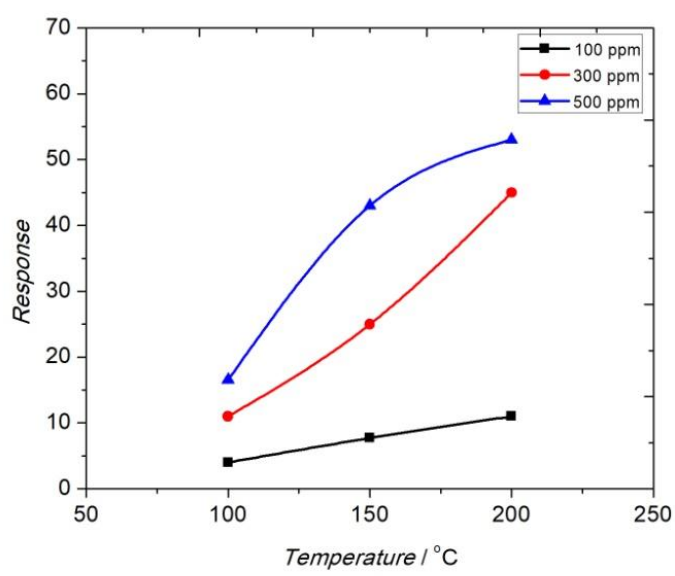

Fig.8.18. Response for 100 ppm, 300 ppm, 500 ppm concentrations at 100 °C, 150 °C, 200 °C temperatures (Response versus Temperature).

In Fig.8.19 and Fig.8.20, show the obtained the response time of $Zn_{0.92}Fe_{0.08}O$ nano-net thin film based sensor for 100 ppm, 300 ppm, 500 ppm concentrations of methane at different operating temperatures ranging from 100 °C to 200 °C. The response time decreased with increasing concentrations at constant operating temperature. The response time also decreased with increasing operating temperatures for same concentration. Resultantly, it can be said that response time decreased with the combined effect of increasing of concentration and temperatures. Response time was found 240 sec for 100 ppm at 100 °C and 110 sec for 500 ppm at 200°C. Sensor response was fast enough for 500 ppm methane at 200°C. The responses time was faster than undoped ZnO nano-wired thin film and slower than $Zn_{0.90}Cu_{.08}O$ nano-strip based thin film sensor for 100- 500 ppm at ranges of 100 °C- 200 °C. In Fig.8.19, graph A, B, C denoted as operating temperature at 100°C, 150°C, 200°C respectively.

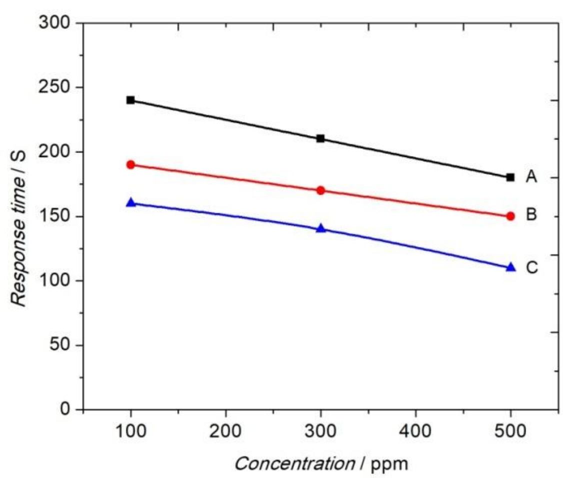

Fig.8.19. Show response time for 100 to 500 ppm at operating temperatures 100 °C to 200 °C (Response time versus Concentration).

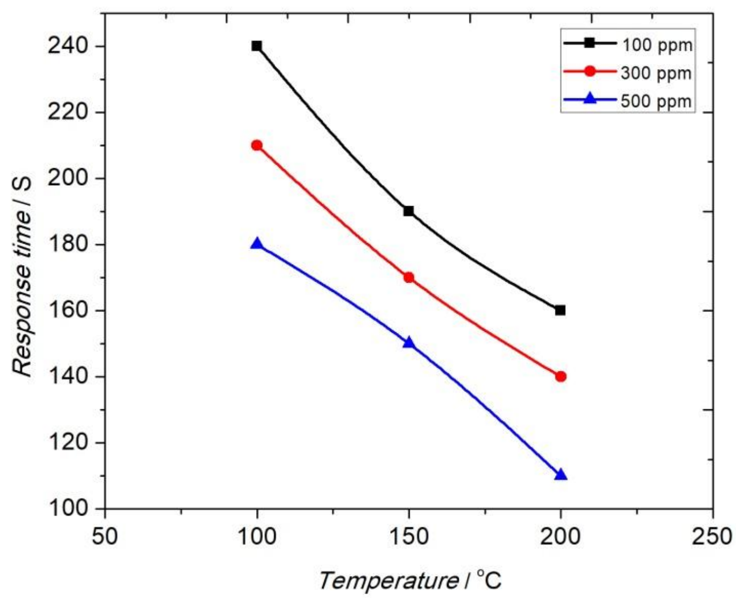

Fig.8.20. Show response time for 100 to 500 ppm at operating temperatures 100 °C to 200 °C (Response time versus Temperatures).

Recovery time increased with increasing concentration at constant operating temperature, while decreased with increasing of operating temperature for same concentration. Resultantly, recovery time decreased with the combined effect of increasing of concentration and temperatures. Fig. 8.21 and 8.22 show the recovery time for 100 ppm, 300 ppm, 500 ppm methane at operating temperatures 100 °C, 150 °C, and 200 °C. Recovery time was approximately 115 sec for 100 ppm at 100 °C and 125 sec for 500 ppm at 200 °C. The developed thin film based sensor was found suitable up to 200 °C for methane sensing applications. In Fig.8.21, graph A, B, C denoted as operating temperature at 100°C, 150°C, 200°C respectively.

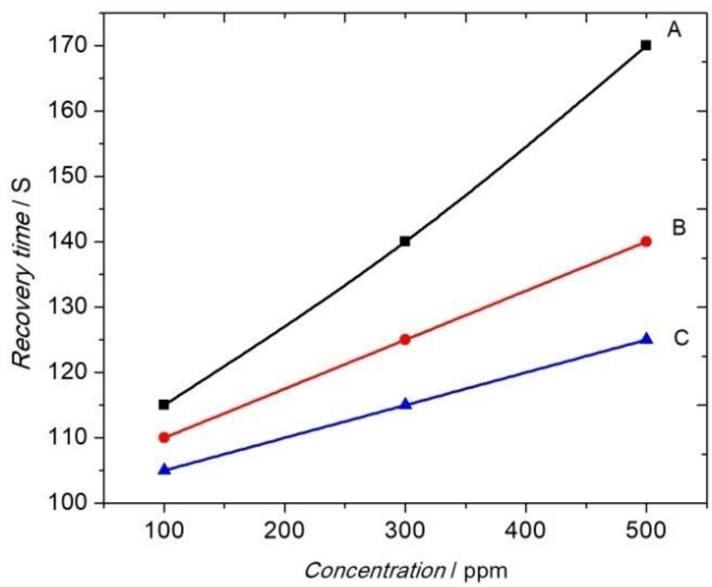

Fig.8.21. Show recovery time for 100 to 500 ppm at operating temperatures 100 °C to 200 °C (Recovery time versus Concentration).

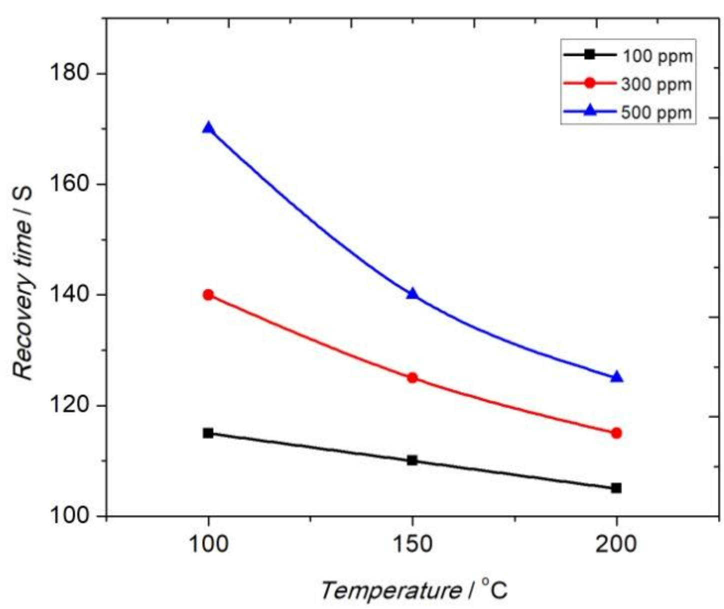

Fig.8.22. Show recovery time for 100 to 500 ppm at operating temperatures 100 °C to 200 °C (Recovery time versus Temperature).

8.7 Selectivity

$Zn_{0.92}Fe_{0.08}O$ nano-net thin film based thin film sensor showed the high selectivity for 500 ppm of methane at the operating temperature range of 150 °C to 200 °C in presence of hydrogen. In this study, rapid response time was observed for 500 ppm of methane at 200 °C. High response was observed in the range of 100 °C to 150 ^{o}C for 500 ppm of H_2.

8.8 Conclusion

Methane sensing study carried out for 100 – 500 ppm concentration range of CH_4 between the operating temperature range of 100 °C - 200 °C. The response was found to be 49 % for undoped ZnO based thin film sensor, 94 % for for $Zn_{0.92}Cu_{0.08}O$ nano-strips based thin film sensor and 53 % $Zn_{0.92}Fe_{0.08}O$ nano-net based thin film sensors for same concentaraions 500 ppm concentration of CH_4 at operating temperature 200 °C. These sensors response of selectivity in presence of hydrogen for 500 ppm at 200 °C, was highest or quickest for $Zn_{0.92}Cu_{0.08}O$ nano-strips based thin film sensor. Thus, it was clear from the study that, 8 % Cu and Fe doped ZnO based thin films were better than the undoped zinc oxide nano-wired thin film for methane sensing.