

## Performance of H<sub>2</sub>S Sensors Based on Undoped And Doped Zinc Oxide Thin Films

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### 5.1 Introduction

There have been enormous research efforts in the development and characterization of materials and pursue their applications during the past few decades. Most of these novel materials show unusual multifunctional behavior which may be exploited for new and interesting applications. The hexagonal wurtzite zinc oxide (ZnO) is one of such popular versatile materials. It is an n-type semiconductor material with wide band gap (3.37eV at 300K) and large exciton binding energy (60meV) and has a variety of potential applications such as photo-voltaic devices, surface acoustic wave devices, optical wave guides, displays and heaters etc. While using ZnO film for optoelectronics has become a trend nowadays; this nontoxic metal-oxide has materialized as a probable gas sensor. Presently, ZnO gas sensors primarily occur in three forms, including sintered bulk, thin film and thick film. Although sintered ceramic components have gained greater attention, ZnO thin film gas sensors also remained thought of the researchers due to beneficial features, such as high sensitivity under ambient conditions, low cost, high stability with long product life and simplicity in fabrication [1]. It is believed that, ZnO is sensitive to variety of combustible and harmful gases/vapors viz. LPG, ozone, humidity, H<sub>2</sub>, NH<sub>3</sub>, CO<sub>x</sub>, NO<sub>x</sub>, Cl<sub>2</sub>, alcohol and hydrocarbons.

Conversely, less attempts have been devoted to detect reducing gas like hydrogen sulfide (H<sub>2</sub>S), which often founds in the sewage, coal, coal-oil or natural gas industries and other industrially important hydrocarbon feed stocks [2, 3]. Although H<sub>2</sub>S is colorless; it can be sensed at concentrations as low as 0.5 ppm, however, inhalation of excessive levels of H<sub>2</sub>S gas in a confined space destroys the ability of the olfactory nerve to detect the gas and can result in loss of consciousness, respiratory failure, and death [4]. In this decade, efforts have

been made to develop ZnO based gas sensors which could detect lower concentration of H<sub>2</sub>S gas at low working temperature. Variety of techniques viz. hydrothermal [5], thermal evaporation [6], reactive vapor deposition [7], direct precipitation [8], vapor phase transport [9], vapor phase growth method [10] etc. have been used to prepare ZnO based H<sub>2</sub>S gas sensitive elements. One of the strategies to improve the sensitivity of oxide based gas sensors is the structural engineering; which gives a great emphasis to the fabrication of oxides with a very high surface area. The simple and inexpensive chemical spray pyrolysis is well capable of producing such large area deposition. C. M. Ghimbeu et al have achieved sensitivity of  $S=1.3$  at 573K to 12 ppm hydrogen sulphide for electrostatic spray deposited ZnO films [11]. Whereas, S. S. Badadhe et al have examined the response towards H<sub>2</sub>S for sprayed undoped and indium doped ZnO thin films; and found  $S=13000$  response at 523K for indium doped ZnO films to 1000 ppm of H<sub>2</sub>S gas. However, undoped ZnO films haven't showed any response [12]. However, in above cases, sprayed ZnO films were deposited at high substrate temperatures i. e. above 623K.

Herein, ZnO thin films are prepared using advanced spray pyrolysis at different preparative conditions [Core temperature variation / Substrate temperature variation / Thickness variation / layer by layer (LBL) deposition] , copper (Cu) and tin (Sn) doping concentrations are tested for gas sensing against hydrogen sulphide as a probing gas. The H<sub>2</sub>S sensing response and other parameters are tested against operating temperatures and low gas concentrations for all the ZnO thin films.

## **5.2 Experimental Setup of Gas Sensor study**

The gas sensing properties of ZnO films were studied in the home made gas sensor assembly comprising temperature controller, Chromel-Alumel thermocouple, electric heating plate, gas chamber, etc as described in section 1.3. (B) 9 of chapter one. For measurement of H<sub>2</sub>S gas response, the film sensors were loaded in an airtight housing having a volume of 250 cm<sup>3</sup>. A measured quantity of gas concentration (ppm) was introduced in the housing using a syringe and resistance of the samples was measured as a function of time.

The electrical resistance of ZnO film in air ( $R_a$ ) and in gas atmosphere ( $R_g$ ) was measured to evaluate the gas sensitivity defined as follows

$$\text{Sensitivity } S (\%) = \frac{R_a - R_g}{R_a} \times 100 \text{-----} (5.1)$$

where,  $R_a$  is the stabilized resistance of zinc oxide in air atmosphere and  $R_g$  is the resistance in the presence of target gas.

### 5.3 Results and discussion

#### 5.3.1 The H<sub>2</sub>S Sensing Properties of ZnO Thin Films Prepared at Different Core Temperatures

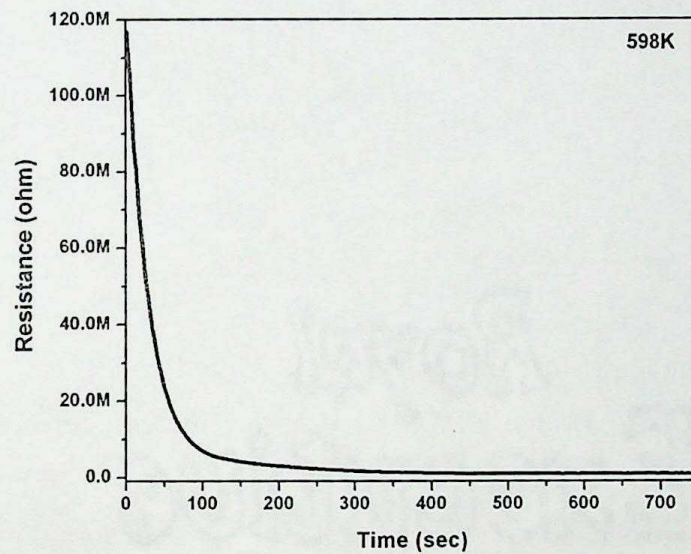


**Figure 5.1:** Typical initial stabilization curve of resistance of ZnO thin film prepared at 598K from non-equilibrium to equilibrium stage.

The typical initial stabilization curve of resistance of ZnO thin film prepared at 598K from non-equilibrium to equilibrium stage is shown in Figure 5.1. The stabilization of the ZnO film resistance in ambient air prior to exposure of gas is important, because it ensures stable zero level for gas sensing applications [13]. Initially, the resistance was decreased rapidly within ~200 seconds when the operating temperature increases from room temperature to 573K and then gradually exhibited a stable value. This can be ascribed to the generation of electrons as a result of thermal excitations. However, slight variation can be seen during gradual stabilization process due to extraction of some of these electrons from the conduction band of ZnO by oxygen adsorbed on the surface of the semiconductor [14].

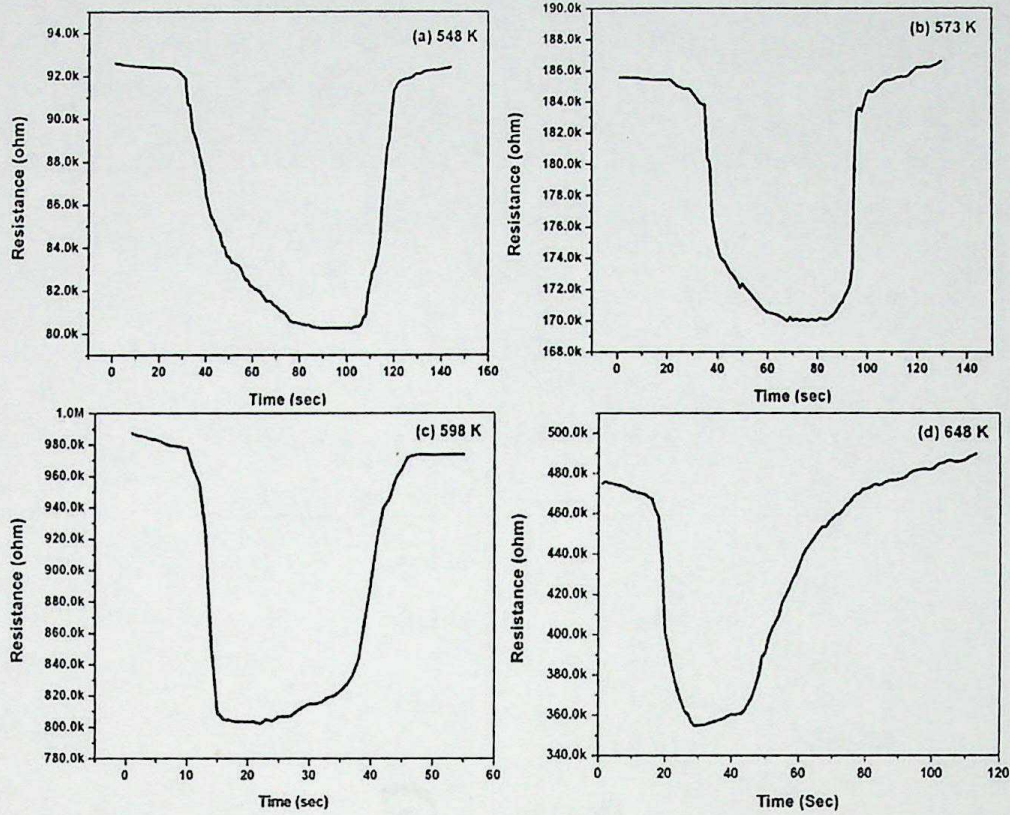
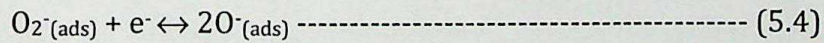
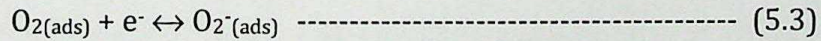
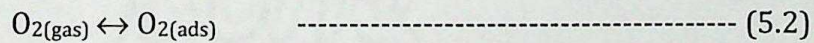


**Figure 5.2:** Variation in resistance of (a) 548, (b) 573 and (c) 598 and (d) 648K as a function of time for a 20ppm H<sub>2</sub>S gas exposure and back at and operating temperature of 573K.

The oxygen adsorbed on the surface of oxide gas sensors undergoes the following reactions given by equations. (5.2) – (5.4) [15].

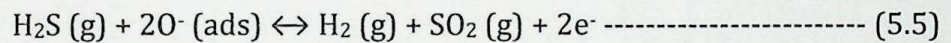


Accordingly, the equilibration of the chemisorption process gives rise to stabilization of surface resistance. Any process that perturbs this equilibrium causes changes in the semiconductors conductance [14]. The conductance change is associated with the concentration of noxious gases in an ambient air.

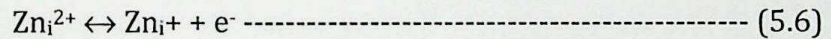
Throughout experiments, every time before exposing the hydrogen sulphide (H<sub>2</sub>S) gas on the ZnO film sensor, it was allowed to equilibrate inside the gas chamber at operating temperature (573K) for ~10 min. and the stabilized resistance was taken as R<sub>a</sub>. Figure 5.2 represents the change in resistance of samples prepared at different core temperatures viz. 548, 573 598

and 648K as a function of exposure time to H<sub>2</sub>S and subsequent exhaust of H<sub>2</sub>S gas.

The ZnO resistive sensors are highly resistive at room temperature due to the lower carrier concentrations and adsorption of atmospheric oxygen on the film surface that develops a potential barrier ( $\phi_b$ ) to charge transport. Even at working temperatures below 573K, the response of the films to reducing H<sub>2</sub>S gas is limited by the rate of the chemical reaction; since the gas molecules do not have sufficient thermal energy to react with the surface adsorbed oxygen species. However, at 573K the thermal energy acquired by ZnO thin film resistors is high enough to reduce the potential barrier ( $\phi_b$ ) and H<sub>2</sub>S reacts to the film surface to inject the electrons into conduction band so as to raise the electron concentration substantially [16]. This in turn leads to a decrease in film resistance. The reaction involved in H<sub>2</sub>S sensing [17] is,

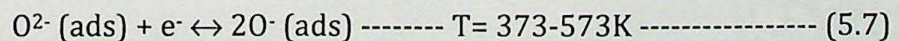


Moreover, in accordance with the Dayan et al. the intrinsic defects on the ZnO surface can ionize and contribute electrons to decrease in the resistance of sensor [18].



However, the factor by which the resistance changes due to H<sub>2</sub>S exposure; differs from sample to sample. This is due to the intrinsic electrical properties of ZnO thin films; that depend on the core temperature.

On the other hand, when H<sub>2</sub>S is removed (H<sub>2</sub>S out) molecular oxygen from the surrounding adsorbs on the ZnO surface that raises ZnO film resistance by entrapping the conduction band electrons. The depletion layers formed on the surface of ZnO film after sufficient oxygen adsorption decreases carrier concentration and hence increases the resistance of the film sensor. In this, the oxygen is adsorbed in the form of O<sup>2-</sup> depending on the operating temperature [19].



The H<sub>2</sub>S sensitivities of ZnO films deposited at different core temperatures evaluated using eq. (5.1), for 20 ppm H<sub>2</sub>S gas exposure and at 573K operating temperature are measured as a function of time. Figure 5.3 represents a typical plot of sensitivity as a function of time of ZnO film prepared at 598K for

a 20ppm  $\text{H}_2\text{S}$  gas exposure and back. The ZnO film prepared at 648K shows a maximum sensitivity of  $\sim 27\%$ . The variation of sensitivity of ZnO films prepared at different core temperatures is plotted in figure 5.4.

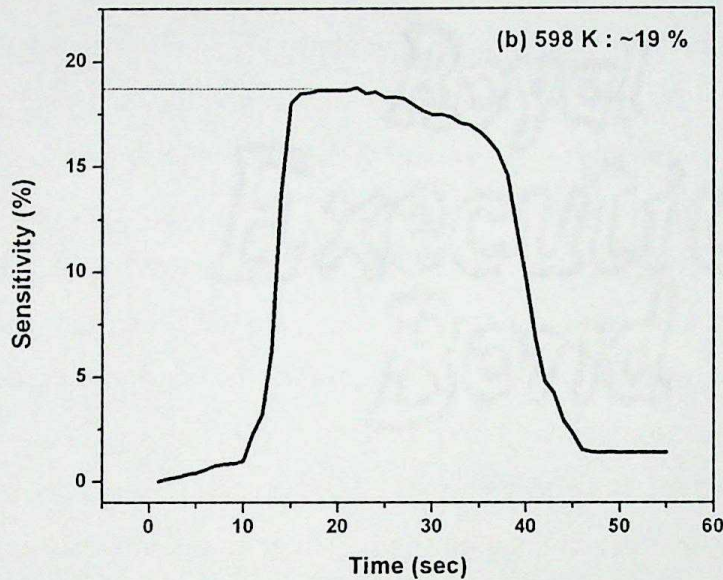


**Figure 5.3:** Typical plot of sensitivity as a function of time of ZnO film prepared at 598K core temperature for a 20ppm  $\text{H}_2\text{S}$  gas exposure and back.

Practically, the usefulness of the metal oxide semiconductor gas sensors is determined by the response time; which is the time required to reach 90% response signal. While sensor material should recover from the gas-surface reaction rapidly. This recovery time is defined as the time needed 90% of the original baseline signal. From Figure 5.5, comparison of response and recovery time of ZnO films prepared at different core temperatures under 20 ppm exposures to  $\text{H}_2\text{S}$  is possible. Figure shows that response times become shorter with increasing core temperature and becomes shortest at 598K and for core temperature  $\geq 598\text{K}$  response time again increases. No significant changes were observed in recovery time for the films prepared at core temperature  $\leq 598\text{K}$ ; while for film  $\leq 598\text{K}$  recovery time exhibits an increasing trend. Though, the film prepared at 598K shows an optimum  $\text{H}_2\text{S}$  sensing performance with optimum sensitivity accompanied by optimum transient characteristics.

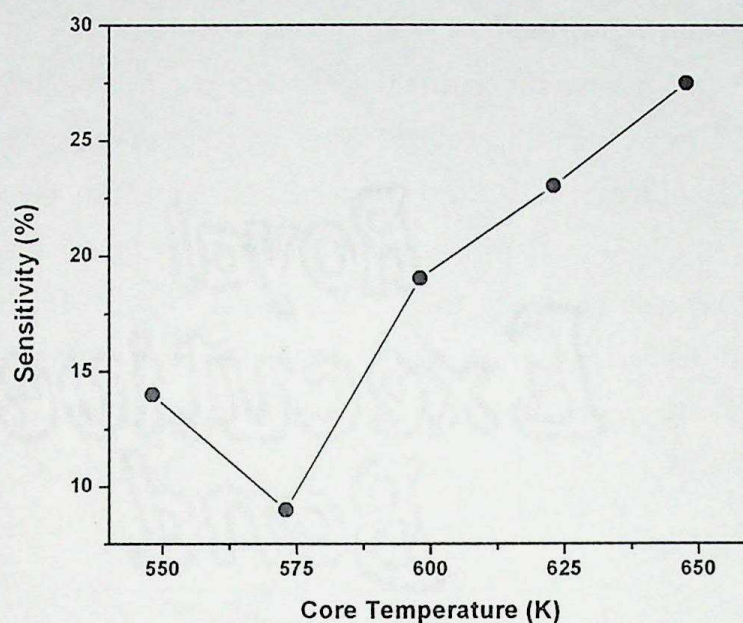


**Figure 5.4:** Variation of the ZnO film sensitivity towards  $H_2S$  gas as a function of core temperature.

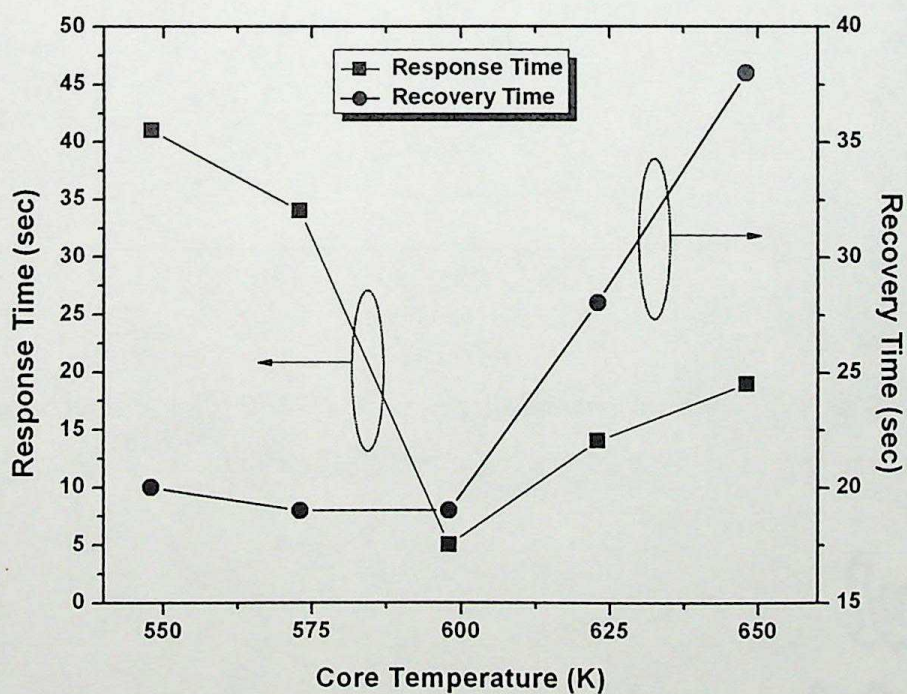


**Figure 5.5:** Response and recovery times for the ZnO thin films prepared at various core temperatures.

### 5.3.2 The H<sub>2</sub>S Sensing Properties of ZnO Thin Films Prepared At Different Substrate Temperatures

Figure 5.6 shows a typical transient sensitivity plot for the ZnO thin film prepared at 523K substrate temperature. The variation of sensitivity of ZnO films deposited at different substrate temperatures under 20 ppm H<sub>2</sub>S gas exposure and back at 573K is shown in figure 5.7. From the figure it is seen that the sensitivity increases gradually from about 14 to 20% when the sample growth temperature increases from 423 to 473K. However there is a drastic increase in sensitivity to ~76% for film deposited at 523K. This sudden high increase in sensitivity is attributable to a columnar growth of deposits.

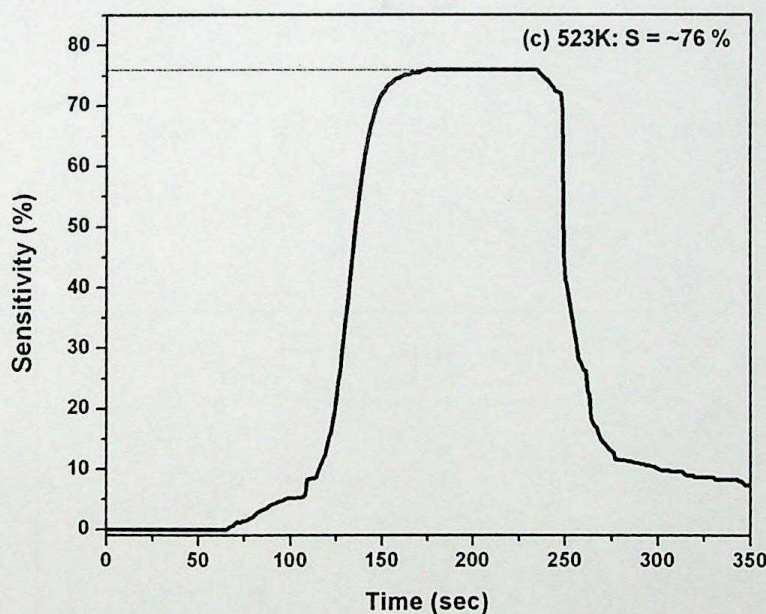


**Figure 5.6:** Typical transient sensitivity plot of ZnO film prepared at 523K substrate temperature for a 20ppm H<sub>2</sub>S gas exposure and back at 573K.

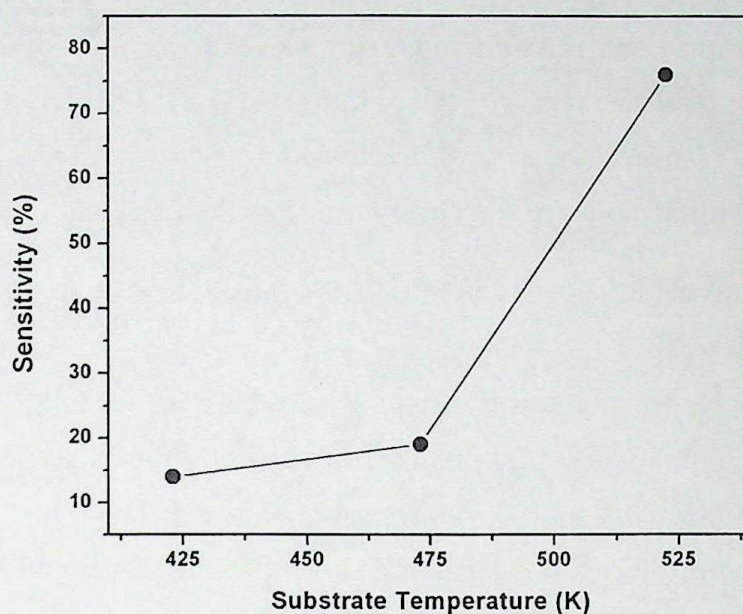


**Figure 5.7:** Variation of the ZnO film sensitivity towards  $H_2S$  gas as a function of substrate temperature.

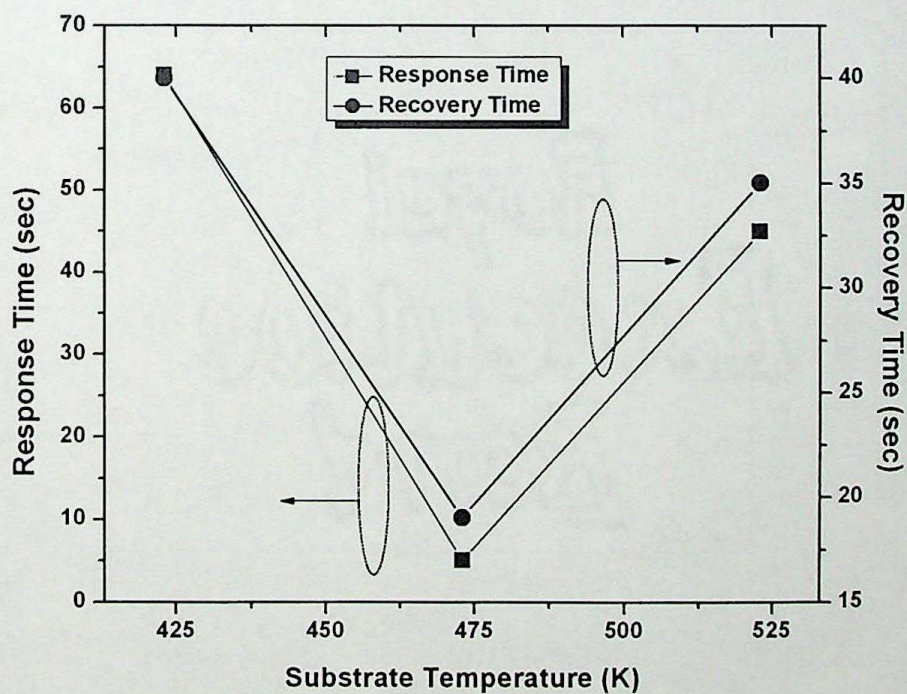


**Figure 5.8:** Response and recovery times (sec) for the ZnO thin films deposited at various substrate temperatures.

Further, the response and recovery times for the ZnO thin films deposited at various substrate temperatures are plotted in figure 5.8. It is observed that both the response and recovery times vary linearly with each other. All film possesses response time less than 65 sec and recovery time less than 40 sec.

### 5.3.3 The H<sub>2</sub>S Sensing Properties of ZnO Thin Films Prepared At Different Thicknesses

Figure 5.9 shows a typical transient sensitivity plot for the ZnO thin film with thickness 135 nm. The variation of sensitivity of ZnO films as a function of their thickness under 20 ppm H<sub>2</sub>S gas exposure and back at 573K is shown in figure 5.10. From the figure it is seen that the sensitivity increases gradually from about 11 to 20% when the film thickness decreases from 392 to 216 nm. However there is a drastic increase in sensitivity to ~66% when the film thickness decreases to 135 nm. This sudden high increase in sensitivity is attributable to smaller crystallite/grain size.

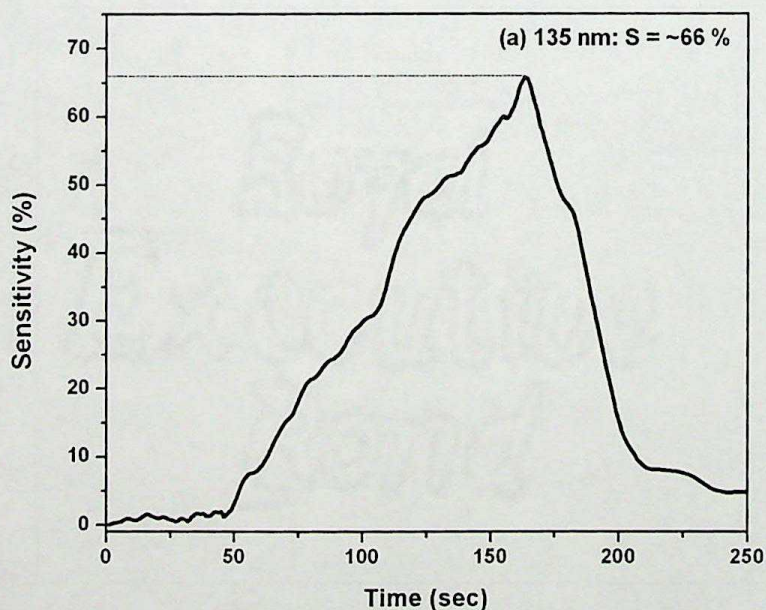


**Figure 5.9:** Typical transient sensitivity plot of ZnO film of 135nm thickness for a 20ppm H<sub>2</sub>S gas exposure and back at 573K.

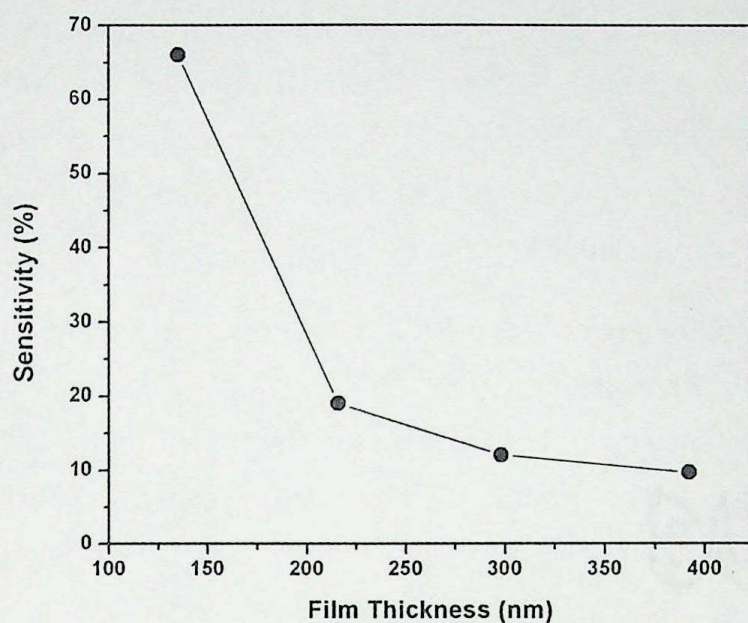


**Figure 5.10:** Variation of the ZnO film sensitivity towards  $H_2S$  gas as a function of film thickness.

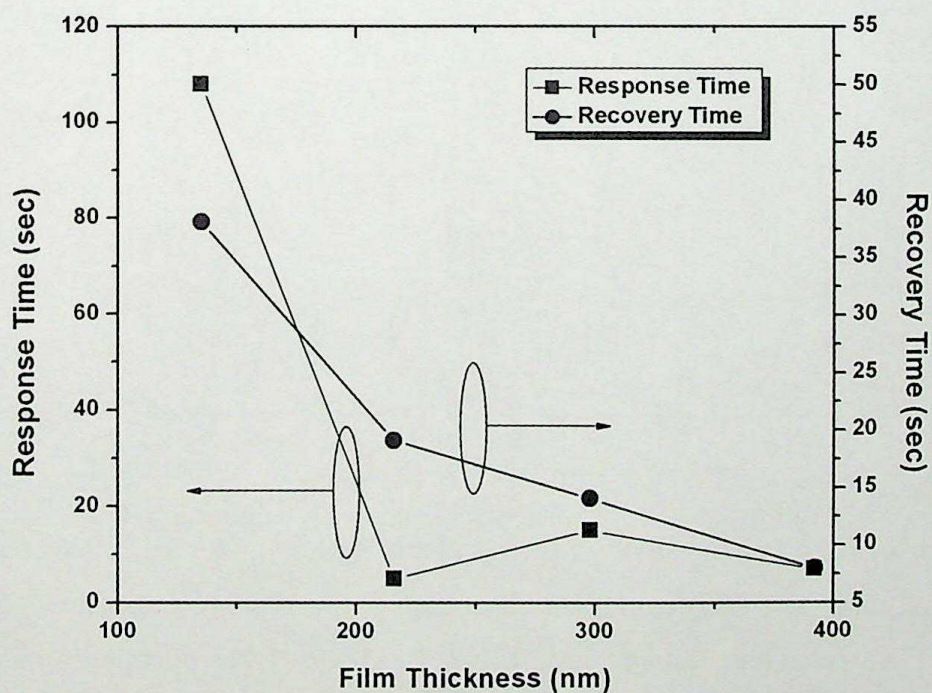


**Figure 5.11:** Response and recovery times for the ZnO thin films deposited at various thicknesses.

Further, the response and recovery times for the ZnO thin films as a function of film thickness are plotted in figure 5.11. It is seen that the response and recovery times decreases with increase in film thickness. The 135 nm thick film shows takes large time  $\sim 110$  sec to response towards 20 ppm  $H_2S$  and also recovers very slowly ( $\sim 80$  sec). Further for film thickness  $\geq 216$  nm, there is no significant variation in response time.

#### 5.3.4 The $H_2S$ Sensing Properties of ZnO Thin Films Prepared By Layer By Layer (LBL) Deposition

Figure 5.12 shows a typical transient sensitivity plots for the ZnO thin film with a single layer and four layers. The variation of sensitivity of ZnO films as a function of number of ZnO film layers under 20 ppm  $H_2S$  gas exposure and back at 573K is shown in figure 5.13. From the figure it is seen that the sensitivity decreases gradually from about 19 to 15% when the number of ZnO layers increases from 1 to 2. However, there is slight increase of sensitivity (17%) for 4 layer ZnO sample. Thus it is clear that there is no drastic change observed in sensitivity of ZnO films when the samples were prepared by layer by layer route.

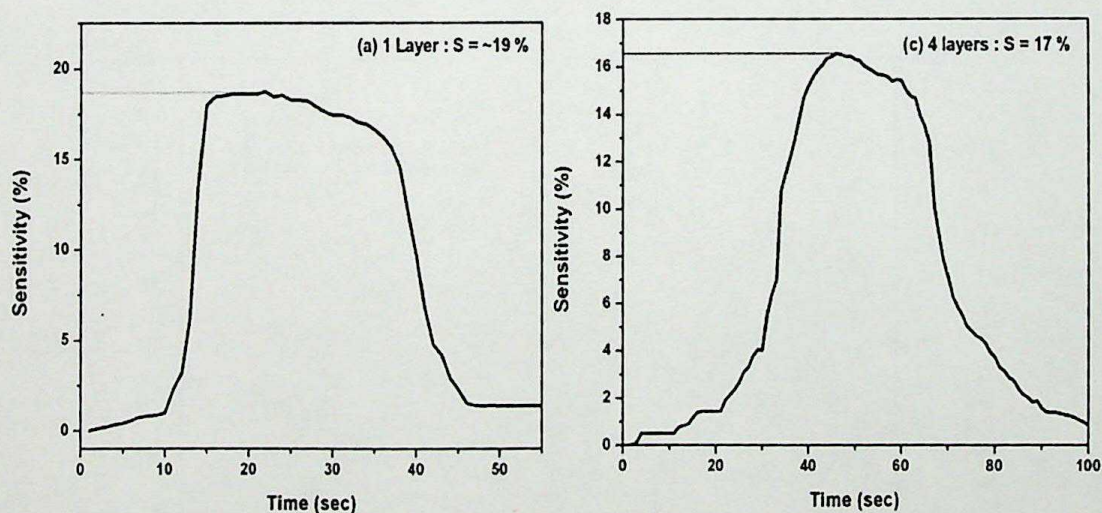


**Figure 5.12:** Plot of transient sensitivity plot of ZnO film with (a) 1 layer and (b) 4 layers, for a 20ppm  $H_2S$  gas exposure and back at operating temperature of 573K.

The response and recovery times for the ZnO samples as a function of number of ZnO film layers are plotted in figure 5.14. It is seen that the response and recovery time increases with increase in number of ZnO thin film layers.

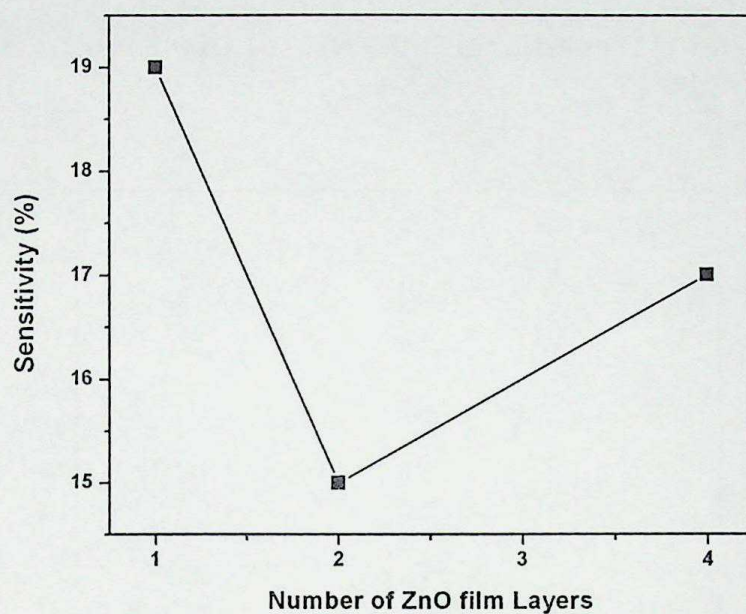


**Figure 5.13:** Variation of the ZnO film sensitivity towards  $H_2S$  gas as a function of number of thin film layers.

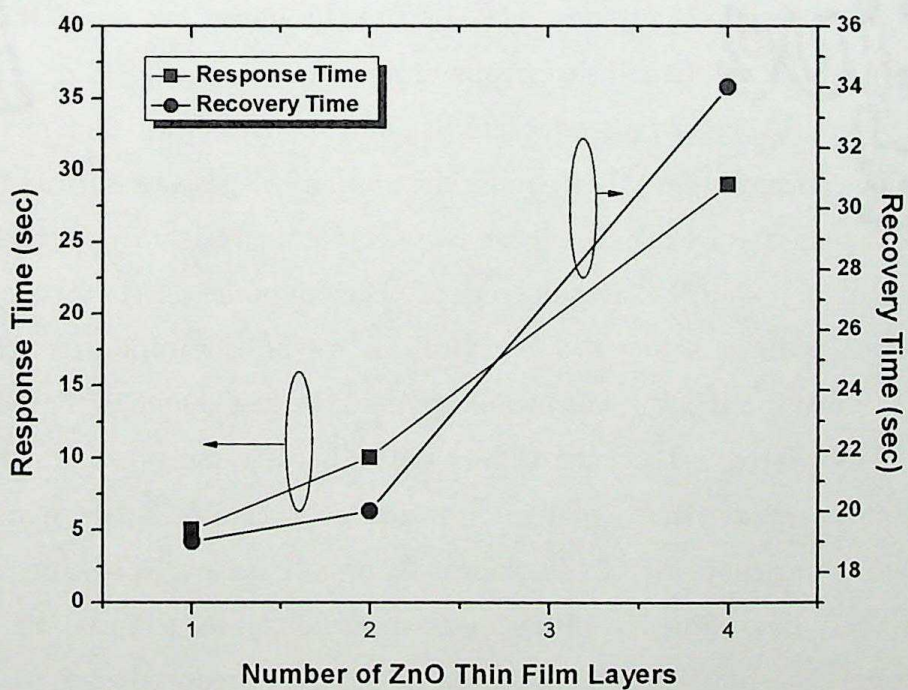


**Figure 5.14:** Response and recovery times for various number of ZnO film layers

### 5.3.5 The H<sub>2</sub>S Sensing Properties of ZnO: Cu (CZO) Thin Films

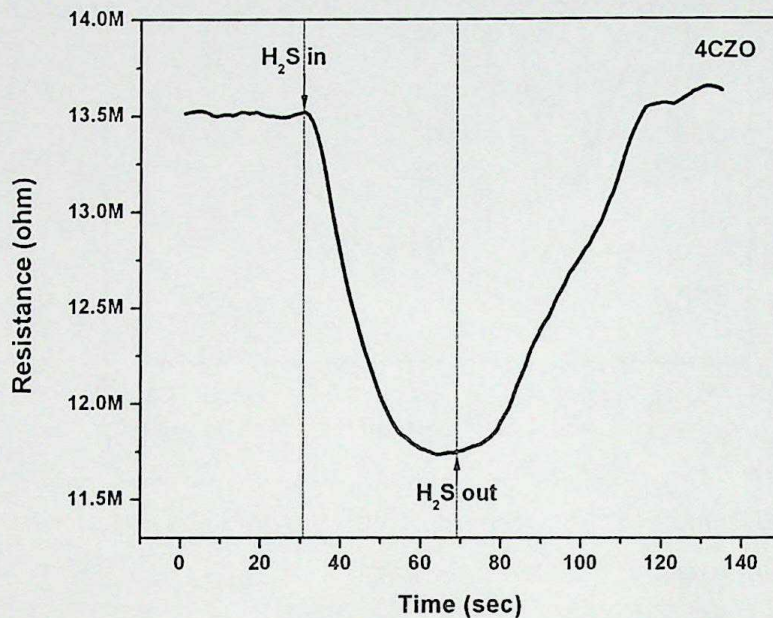


**Figure 5.15:** Transient response of the 4 at% Cu doped ZnO film (4CZO) to a 20ppm H<sub>2</sub>S gas exposure and back at operating temperature of 523K.

Figure 5.15 displays a typical transient response of ZnO: Cu film at 4 at % Cu doping concentration (4CZO) under the 20ppm H<sub>2</sub>S gas exposure and back at operating temperature of 523K. It can be seen that the resistance decreases with injection of 20 ppm H<sub>2</sub>S. The characteristic behavior of the resistance decrease of the sensor upon detecting H<sub>2</sub>S is typical for n-type semiconductor oxide gas sensors. When the H<sub>2</sub>S gas was introduced into the test chamber, the resistance of the sensor decreased and soon afterwards it became saturated. When the gas was removed, the resistance of the sensor increased. Figure 5.16 presents typical sensitivity transient of the 4CZO sensor to 20 ppm H<sub>2</sub>S gas at 523K. The response and recovery time (time for 90% of resistance change) for H<sub>2</sub>S gas /air mixture for 20 ppm concentration at 523K is about 9 and 24 sec respectively.

The Variation of the CZO films sensitivity as a function of Cu doping concentration, towards 20ppm H<sub>2</sub>S gas at 523K is represented in figure 5.17. It is seen that sensitivity increases from 11 to 28 % as the Cu doping concentration in

ZnO increases from 1 to 4 at %. The maximum sensitivity for 4CZO film is may be due to decreased grain size.

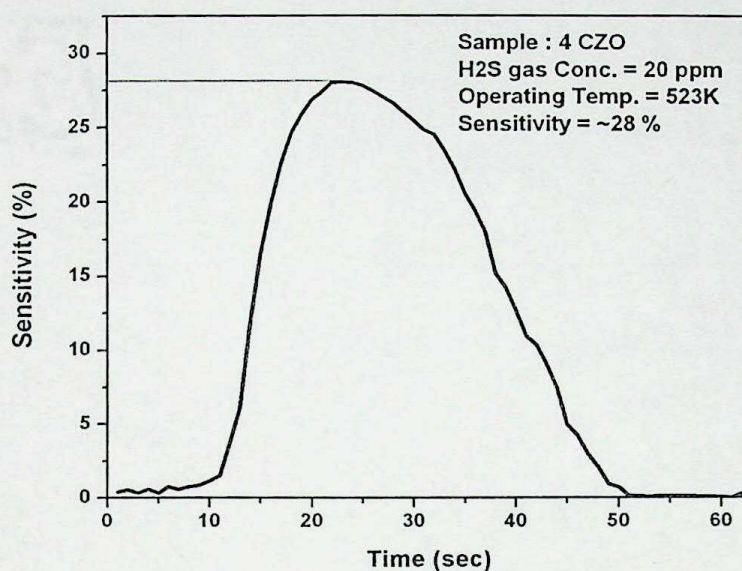


**Figure 5.16:** Typical sensitivity transient of ZnO: Cu film at 4 at % Cu doping concentration ( 4CZO), for a 20ppm H<sub>2</sub>S gas exposure and back at operating temperature of 523K.

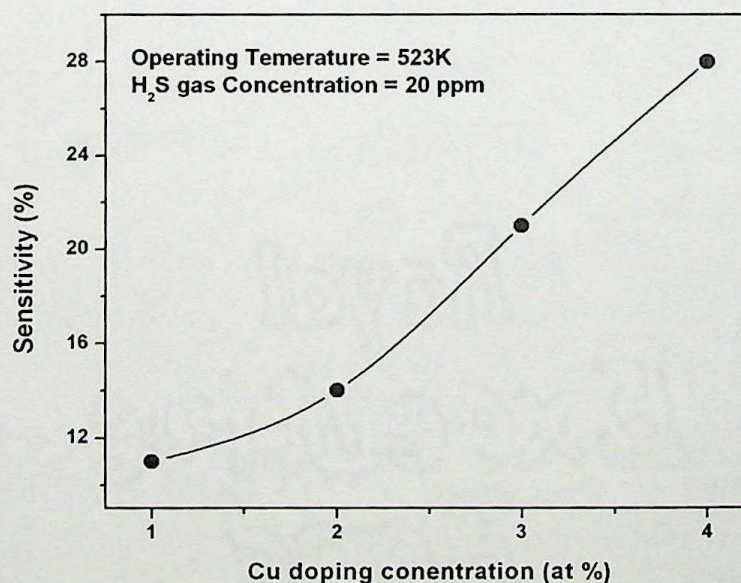


**Figure 5.17:** Variation of the ZnO: Cu (CZO) film sensitivity as a function of Cu doping concentration, towards 20ppm H<sub>2</sub>S gas and at operating temperature 523K.

The comparison of response and recovery time of ZnO films prepared at different Cu doping concentrations, under 20 ppm exposures to H<sub>2</sub>S and back at 523K, is shown in figure 5.18. All films showed response time less than 18 sec and recovery time less than 30 sec. Though, the 4CZO film shows an optimum H<sub>2</sub>S sensing performance with optimum sensitivity accompanied by optimum transient characteristics.

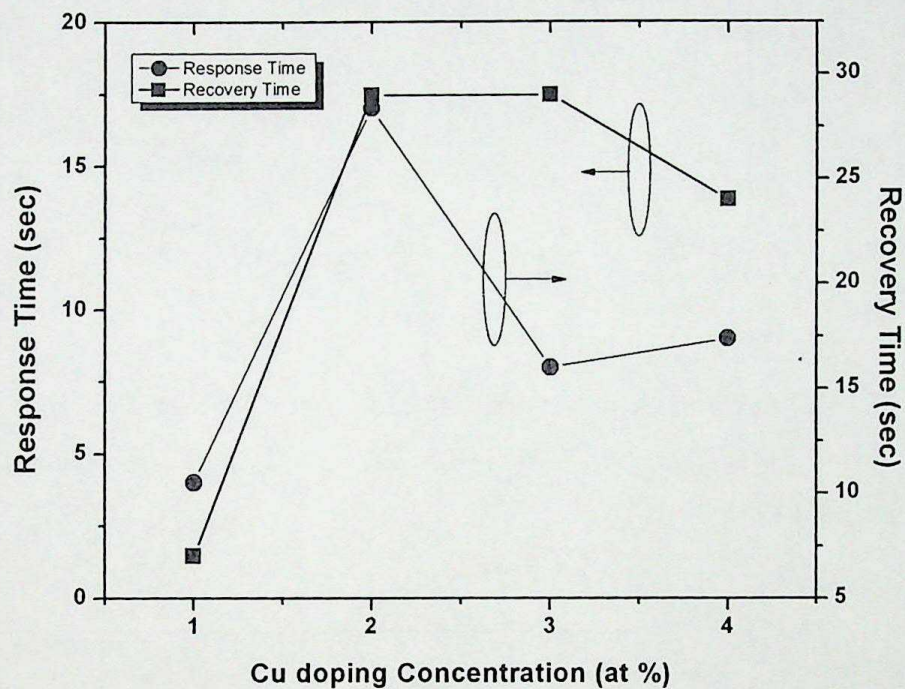


**Figure 5.18:** Response and recovery times for the ZnO: Cu (CZO) thin films deposited at various Cu doping concentrations.

Sensitivity of a 4CZO thin film to 20 ppm H<sub>2</sub>S gas from 423 to 573K is shown in Figure 5.19 and it can be seen that the sensitivity increases with increasing operating temperature and attains a maximum at 523K. However for further increase in operating temperature sensitivity decreases. At 523K working temperature, the 4CZO film shows a maximum sensitivity ~ 28 %. It is interesting to note that even at 423K; the film shows about 12 % response towards H<sub>2</sub>S.

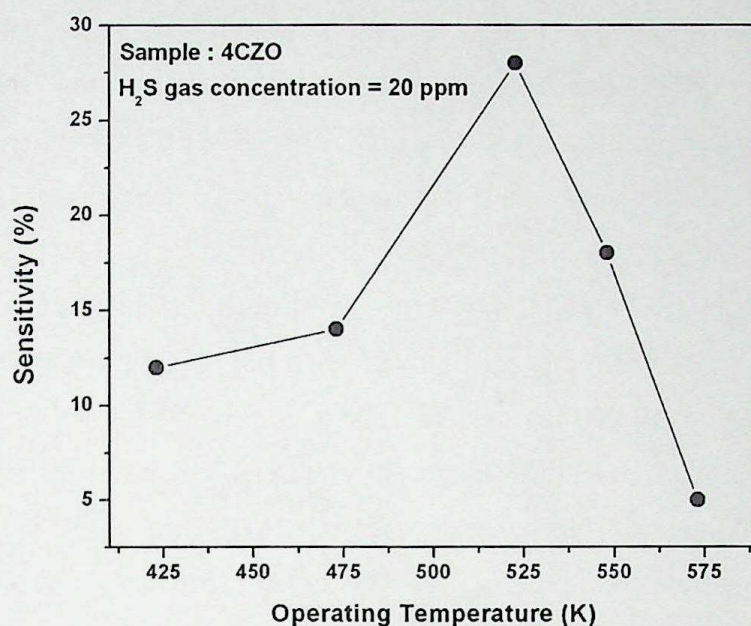


*Figure 5.19: Variation of sensitivity of ZnO film doped with 4 at % Cu (i. e. 4CZO) towards 20 ppm H<sub>2</sub>S gas as a function of operating temperature.*

### 5.3.6 The H<sub>2</sub>S Sensing Properties of ZnO: Sn (SZO) Thin Films

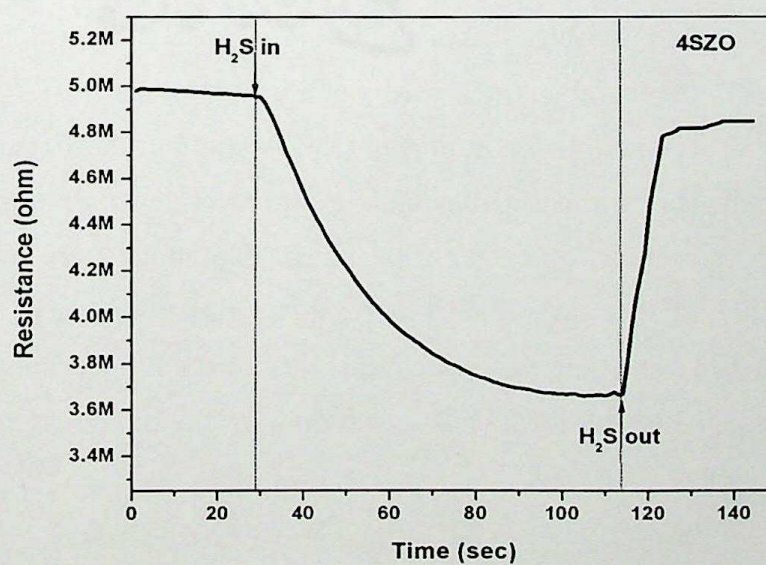
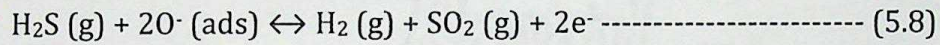
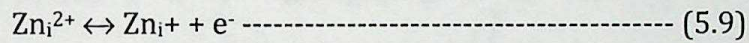


*Figure 5.20: Transient response of the 4SZO film to a 20ppm H<sub>2</sub>S gas exposure and back at operating temperature of 473K.*

Figure 5.20 represents the change in resistance of 4SZO sample as a function of exposure time to 20 ppm H<sub>2</sub>S and subsequent exhaust of H<sub>2</sub>S gas at 473K. The ZnO: Sn resistive sensors are highly resistive at room temperature due to the lower carrier concentrations and adsorption of atmospheric oxygen on the film surface that develops a potential barrier ( $\phi_b$ ) to charge transport. Even at working temperatures below 473K, the response of the films to reducing H<sub>2</sub>S gas is limited by the rate of the chemical reaction; since the gas molecules do not have sufficient thermal energy to react with the surface adsorbed oxygen species. However, at 473K the thermal energy acquired by ZnO: Sn thin film resistors is high enough to reduce the potential barrier ( $\phi_b$ ) and H<sub>2</sub>S reacts to the film surface to inject the electrons into conduction band so as to raise the electron concentration substantially [22]. This in turn leads to a decrease in film resistance. The reaction involved in H<sub>2</sub>S sensing [23] is,

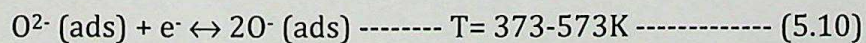


Moreover, in accordance with the Dayan et al. the intrinsic defects on the ZnO surface can ionize and contribute electrons to decrease in the resistance of sensor [24].



However, the factor by which the resistance changes due to H<sub>2</sub>S exposure; differs from sample to sample. This is due to the intrinsic electrical properties of AZO thin films; that depend on the growth (substrate) temperature.

On the other hand, H<sub>2</sub>S is removed (H<sub>2</sub>S out) molecular oxygen from the surrounding adsorbs on the ZnO: Sn surface that raises ZnO: Sn film resistance by entrapping the conduction band electrons. The depletion layers formed on the surface of ZnO: Sn film after sufficient oxygen adsorption decreases carrier concentration and hence increases the resistance of the film sensor. In this, the oxygen is adsorbed in the form of O<sup>2-</sup> depending on the operating temperature [25].



The Variation of the film resistance as a function of time is used to evaluate sensitivity (S) for ZnO: Sn films. The H<sub>2</sub>S sensitivities of ZnO: Sn films deposited at different Sn concentrations evaluated using eq. (6.7), for 20 ppm H<sub>2</sub>S gas exposure and at 473K operating temperature are measured as a function

of time. Figure 5.21 shows the variation of sensitivity with Sn doping concentrations in ZnO. From figure it is observed that sensitivity of ZnO: Sn films increases with increase in Sn doping concentration. Under 20 ppm H<sub>2</sub>S exposure at 473K, the 1, 2, 3 and 4 at% Sn doped ZnO samples exhibits about 19, 20, 22 and 27% sensitivity. The increasing sensitivity of SZO films with increasing Sn concentration may be attributed to the declining crystallinity of the SZO films.

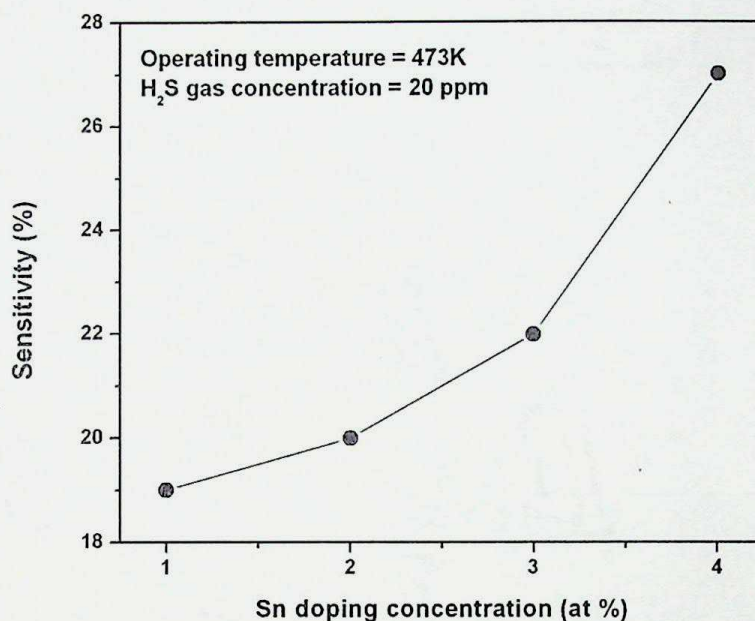


**Figure 5.21:** Variation of the ZnO: Sn (SZO) film sensitivity as a function of Sn doping concentration, towards 20ppm H<sub>2</sub>S gas and at operating temperature 473K.

The response and recovery time of ZnO: Sn films prepared at different Cu doping concentrations, under 20 ppm exposures to H<sub>2</sub>S and back at 473K, are shown in figure 5.22. All films showed response time less than 46 sec and recovery time less than 22 sec. Though, the 4SZO film shows an optimum H<sub>2</sub>S sensing performance with optimum sensitivity accompanied by optimum transient characteristics.

Moreover, the optimum 4SZO sample is used to find out the optimum operating temperature for H<sub>2</sub>S detection. The sensitivity of 4SZO sample was measured for 20 ppm H<sub>2</sub>S gas at various operating temperatures ranging from 423K to 573K at step of 50K. Typical sensitivity transient plots of 4SZO films for 20ppm H<sub>2</sub>S gas exposure and back at 473 and 423K are represented in figure

5.23. The 4SZO thin film shows a maximum sensitivity of 27% at 473K and about 17% at 423K. However, the sensor sensitivity decreases with the increasing operating temperature and at 573K sensitivity of 23% exhibited by 4SZO sample. The variation of sensitivity of 4SZO sample with operating temperature is represented in figure 5.24.

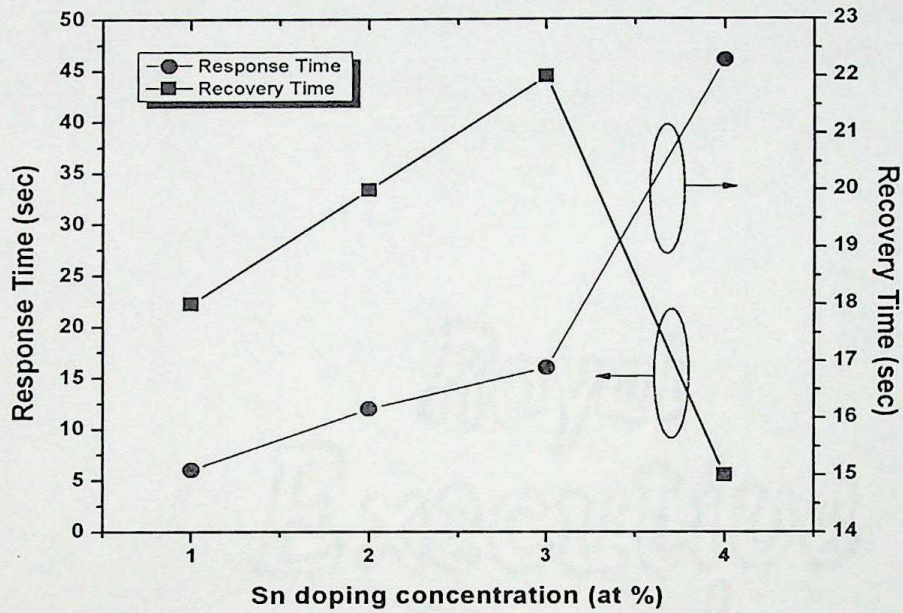


**Figure 5.22:** Response and recovery times for the ZnO: Sn (SZO) thin films deposited at various Sn doping concentrations.

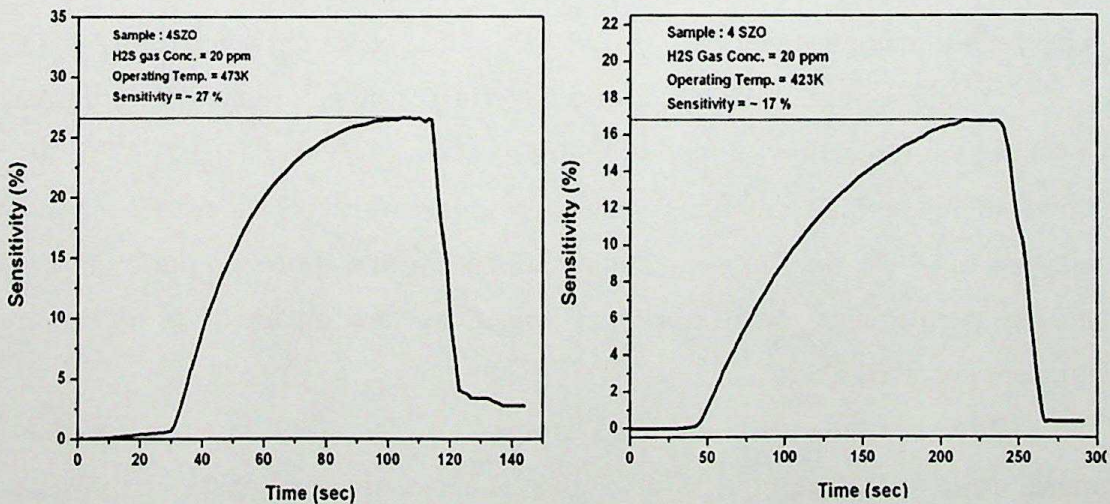


**Figure 5.23:** Plot of Sensitivity as a function of time of 4 at % Sn doped ZnO film for a 20ppm H<sub>2</sub>S gas exposure and back at operating temperature of (a) 473K and (b) 423K.

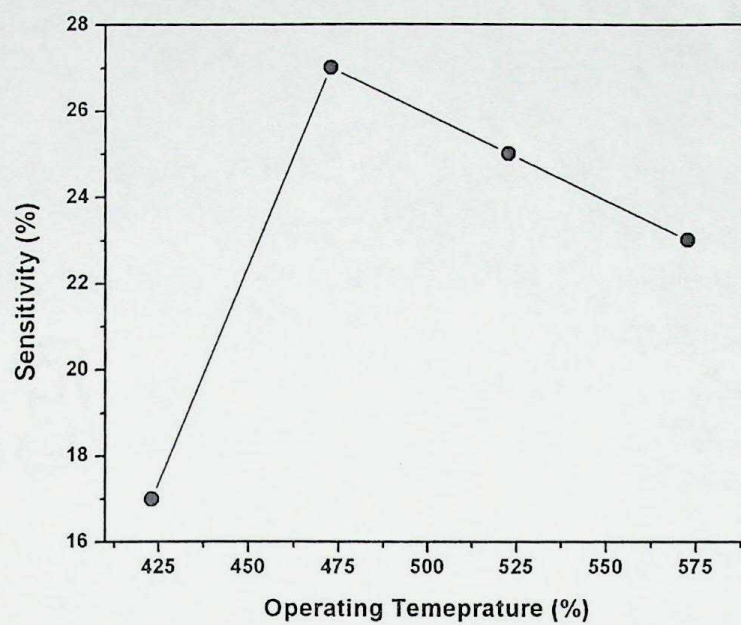


**Figure 5.24:** Variation of sensitivity of 4SZO sample towards 20 ppm H<sub>2</sub>S gas as a function of operating temperature.

## References:

1. N. H. Al-Hardan, M. J. Abdullah, A. Abdul Aziz, H. Ahmad, L. Y. Low, *Vacuum* 85 (2010) 101-105.
2. D. Stirling, *the Sulfur Problem: Cleaning Up Industrial Feedstocks*, The Royal Society of Chemistry, 2000.
3. Dorman D C , Brennenman K A , Struve M F , Miller K L, James R A, Marshall M W, et al. *Teratology* 22 (2000) 71.
4. H<sub>2</sub>S fact sheet, Michigan Department of Environmental Quality Water Bureau Drinking Water and Environmental Health Section 525 West Allegan, 127 (1978) 368.
5. C. Wang, X. Chu, M. Wu, *Sens. Actuators B* 113 (2006) 320–323.
6. S. Kar, B. N. Pal, S. Chaudhuri, D. Chakravorty, *J. Phys. Chem. B* 110 (2006) 4605.
7. L. Liao, H. B. Lu, J. C. Li, H. He, D. F. Wang, D. J. Fu, C. Liu, *J. Phys. Chem. C* 111 (2007) 1900-1903.
8. C. Li, Z. S. Yu, S. M. Fang, H. X. Wang, Y. H. Gui, J. Q. Xu, R. F. Chen, *Chinese Chemical Letters* 19 (2008) 599–603.
9. N. Zhang, Ke Yu, Q. Li, Z. Q. Zhu, Q. Wan, *J. Appl. Phys.* 103 (2008) 104305 (6pp).
10. D. Calestani, M. Zha, R. Mosca, A. Zappettini, M. C. Carotta, V. Di Natale, L. Zanolini, *Sens. Actuators B* 144 (2010) 472–478.
11. C. M. Ghimbeu, J. Schoonman, M. Lumberras, M. Siadat, *Appl. Surf. Sci.* 253 (2007) 7483–7489.
12. S. S. Badadhe, I. S. Mulla, *Sens. Actuators B* 143 (2009) 164–170.
13. P. Mitra, A. P. Chatterjee and H. S. Maiti, *Mater. Lett.* 35 (1998) 33.
14. N.J. Dayan, S.R. Sainkar, R.N. Karekar, R.C. Aiyer, *Thin Solid Films*, 325 (1998) 254
15. K. Arshak and I. Gaidan, *Mater. Sci. Eng. B*, 118 (2005) 44
16. H. Windischmann, P. Mark, *J. Electrochem. Soc.* 126 (1979) 627.
17. S. Kar, B. N. Pal, S. Chaudhuri, D. Chakravorty, *J. Phys. Chem. B* 110 (2006) 4605.
18. N. J. Dayan, S. R. Sainkar, R. N. Karekar, R. C. Aiyer, *Thin Solid Films* 325 (1998) 254.
19. K. Arshak, I. Gaidan, *Mater. Sci. Eng. B* 118 (2005) 44.