



EFFECT OF ANNEALING ON GAS SENSING PERFORMANCE OF NANOSTRUCTURED ZnO THICK FILM RESISTORS

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Abstract- ZnO nano-particles have been synthesized by simple chemical route using a starting solution consisting of zinc acetate and citric acid as a surfactant agent. The structural properties of the prepared ZnO nano-particles annealed at different temperatures have been characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses. The XRD patterns show ZnO-wurtzite phase in the nano-powders, and size of crystals increases by increasing the annealing temperatures. The TEM images show nano-particles as clusters with size in the range of 10-20 nm. Electron diffraction pattern of nano-powders annealed at 900°C temperature shows a well distribution of spherical particles due to the effect of citric acid as surfactant in chemical process. Thick films prepared by screen printing technique from zinc oxide nano-powders annealed at different temperatures (500–900 °C), characterized by SEM analysis and tested for various gases. The film prepared from ZnO powder annealed at 700°C shows the higher sensitivity to H₂S gas for 10 ppm gas concentration.

Index terms: ZnO nano-particles, annealing, TEM, thick films, gas sensor.

I. INTRODUCTION

Recently, synthesis of nano-particles with a uniform size and shape have shown interesting properties particularly nanocrystalline of metal oxides, due to its numerously important properties such as catalytic, electrical and optical properties. Among them, ZnO is one of candidate materials which have been attracting attention because of its wide band gap energy of about 3.36 eV. Therefore, ZnO is an important material for room temperature UV lasers and short-wavelength optoelectronic device [1, 2]. Furthermore, ZnO with its good electrical and optical properties can be used in many applications such as photoconductors, integrated sensors and transparent conducting oxide electrodes [3, 4]. Up to now, a number of chemical routes have been used to synthesize nanocrystalline ZnO powders such as hydrothermal method [5], simple chemical route [6], spray pyrolysis [7] and sol-gel method [8]. Among these methods, chemical route shows many advantages over other techniques such as its simplicity and low equipment cost.

However, synthesis of nano-particles of metal oxides at low cost in industrial scale is a challenge in material production. So, using the cheap materials, simple fabrication processes and suitable conditions of synthesis are the main requirement for this process. Therefore, the study of influence of various parameters such as initial solution combination, time and temperature of heat treatments, and type of surfactant is very important for nano-powders production.

The main purpose of the present research is to study the post-annealing temperature effect on structural, optical properties of ZnO nano powder and gas sensing performance of ZnO thick films synthesized by the simple chemical route.

II. EXPERIMENTAL PROCEDURE

a. Synthesis of ZnO nano-particles

ZnO nano-particles preparation by simple chemical route is summarized in a flow chart shown in figure 1. The precursor solution consisting of zinc acetate and citric acid dissolved in H₂O and methanol (1:1) separately with equal weight percentage is prepared and resulting mixture was stirred and dissolved at 60 °C for 30 min until a completely clear solution was obtained then pH of the solution was brought to 8.5 by drop wise addition of ammonium hydroxide solution (25%).

The reaction mixture was heated at 100°C for 24 h, and then allowed to cool to room temperature. The precipitate was poured out into a tube for centrifugal separating, washing, drying at 150°C for 3 h.

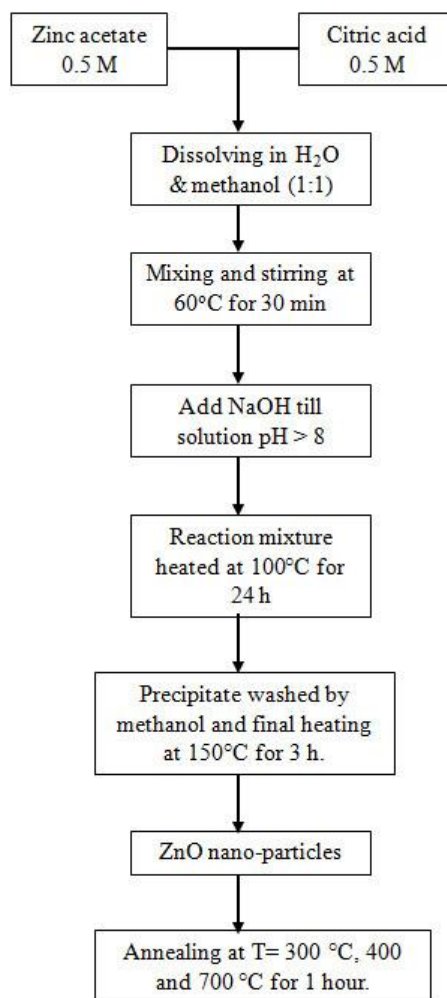


Figure 1. The flow chart of preparation of ZnO nano-particles by simple chemical route.

b. Post-annealing of ZnO nano-particles at different temperatures

The precursor powder, which has been prepared by grinding powder, was annealed at 500, 700 and 900 °C for 30 min (in air) in Muffle furnace and then cooled down to room temperature.

c. Preparation of ZnO thick films

The thixotropic paste was formed by mixing the synthesized material with solution of ethyl cellulose acetate as temporary binder with mixer of organic solvent such as butyl cellulose, butyl carbitol acetate and terpenol etc. The binder help to bind the material with glass plate .The ratio

of organic part to inorganic part is kept in range of 25:75 during formulating the paste. The thick film prepared by screen printing technique in which paste is robbed on screen printing machine. The uniform film is formed by applying uniform pressure. The film then fired at 550°C to remove organic material. The gas sensitivity is measured for various gases like ethanol, H₂S, NH₃, LPG, Cl₂, CO, CO₂, H₂ and O₂.

d. Characterization of powders

The X-ray diffraction (XRD) patterns of ZnO nano-particles prepared at various annealing temperatures were recorded by the D8 Advance Bruker system using CuK α radiation with 2θ in the range 20–80°. Transmission electron microscopy (TEM) micrographs and electron diffraction patterns of the prepared ZnO nano-particles were recorded by the Make Philips Model CM-200 (Specification: operating voltage 20-200 kV, resolution 2.4 Å. The required samples for TEM analysis was prepared by dispersing the ZnO nano-particles in ethanol using an ultrasonic bath. A drop of this dispersed suspension was put onto 200-mesh carbon coated Cu grid and then dried under UV lamp. Also, the optical absorption measurements of nano-particles in range of 200-700 nm were recorded using a UV–VIS spectrophotometer (Schimadzu-2450) for calculating optical band gap values. The surface morphology of thick films was analyzed by using a scanning electron microscope [SEM model JEOL 2300 Japan].

III. RESULTS AND DISCUSSION

a. XRD analysis

The XRD patterns of prepared ZnO nano-particles at different annealing temperatures are shown in figure 2. It is clear that the powder which is annealed at 500°C is slightly crystalline with a less intensity. Those annealed at 700 and 900 °C are well crystallized. All the diffraction peaks well matches with the standard JCPDS data of ZnO with card no. 36-1451. Also, the Bragg's peaks of the crystallized powders correspond to each sample agree well with the reflections of ZnO with a = 3.242 Å and c = 5.176 Å. The XRD patterns at all annealing temperatures show that the higher intensities of three basic peaks of the (1 0 0), (0 0 2), (1 0 1) and (1 1 0) planes are more than of other peaks.

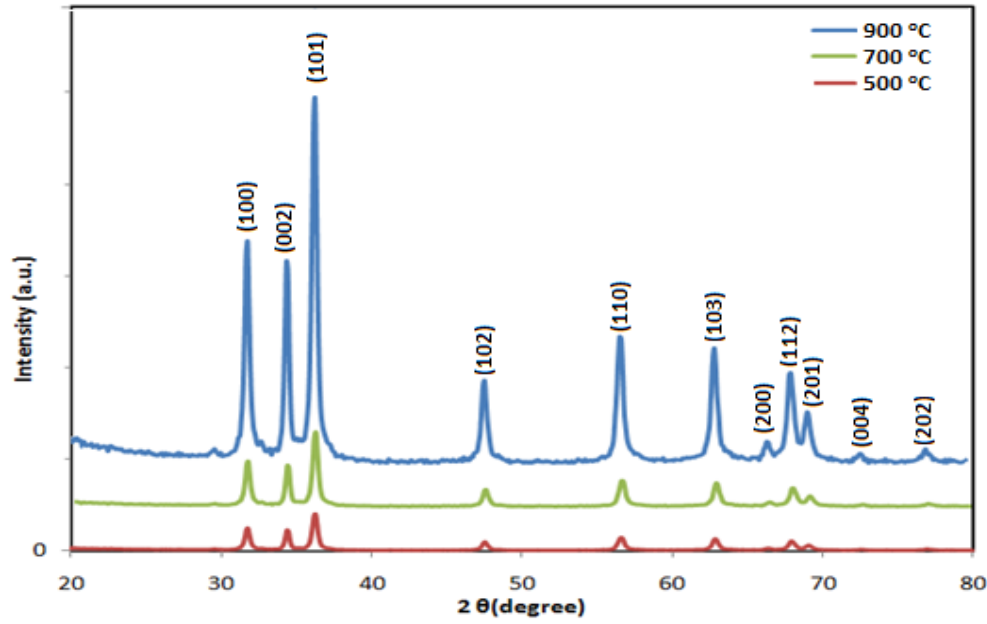


Figure 2. XRD pattern of ZnO powder at annealed at different temperature.

The area under the crystalline and amorphous portions was determined in arbitrary units and the degree of crystallinity (D_c) was calculated using the relation [9].

$$D_c = \frac{I_c}{I_c + I_a} \quad (1)$$

where I_a and I_c are the integrated intensity corresponding to amorphous and crystalline phases, respectively. Also, the grain size (t), interchain distance (r), interplanar distance (d) and distortion parameter (lattice strain) (g) were calculated as follows [9-11]:

$$t = \frac{0.9 \lambda}{\beta \cos \theta} \quad (2)$$

$$r = \frac{5}{8} \frac{\lambda}{\sin \theta} \quad (3)$$

$$d = \frac{\lambda}{2 \sin \theta} \quad (4)$$

$$g = \frac{\beta}{\tan \theta} \quad (5)$$

where t is the crystallite size, $\lambda = 1.542 \text{ \AA}$ (X-ray wavelength), and β is the peak FWHM in radian and θ is diffraction peak position. t , r and d are calculated with respect to the most intense

crystalline peak at the angular range of 36.2- 36.4°.

Table 1 shows the different XRD parameters for all the films. It can be seen that the percentage of crystallinity and grain size systematically increased with increase in annealing temperature. Similar reports of increase in crystallinity with different annealing temperature can be seen in literature [12]. Interplanar and interchain distances were marginally changed because the angle of the peak (θ) did not vary significantly. Also the lattice strain decreases with increase in annealing temperature.

Table 1. The XRD parameters and mean grain size at different annealing temperatures.

Annealing temp. (°C)	Peak angle θ (degree)	Degree of crystallinity D_c (%)	Grain size t (nm)	Interplanar distance d (Å)	Interchain distance r (Å)	Lattice strain g (%)
500	18.2	62.30	16	2.4684	0.7845	0.23
700	18.2	73.22	18	2.4702	0.8127	0.20
900	18.2	96.59	21	2.4728	0.8454	0.13

b. TEM analysis

The TEM micrographs of the ZnO powders annealed at different temperatures are shown in figure 3. The TEM images confirm the nanometric size of the particles in the range of 8, 14 and 18 nm depending on the annealing temperature 500, 700 and 900°C respectively. Figure 3(a) exhibits nano-sized ZnO particles inside a dark background due to the organic additives maintenance, i.e. citric acid, in the powder. By increasing the annealing temperatures nano-particles are observed well, as shown in figure 3(b)–(c). In addition, the morphology of ZnO nano-particles strongly depends on the annealing temperatures, so that in higher temperatures, especially in $T = 900^\circ\text{C}$, the size of nano-particles is increased, as shown in figure 3(c). The TEM micrograph of powders also shows a well distribution of nano-particles in powders.

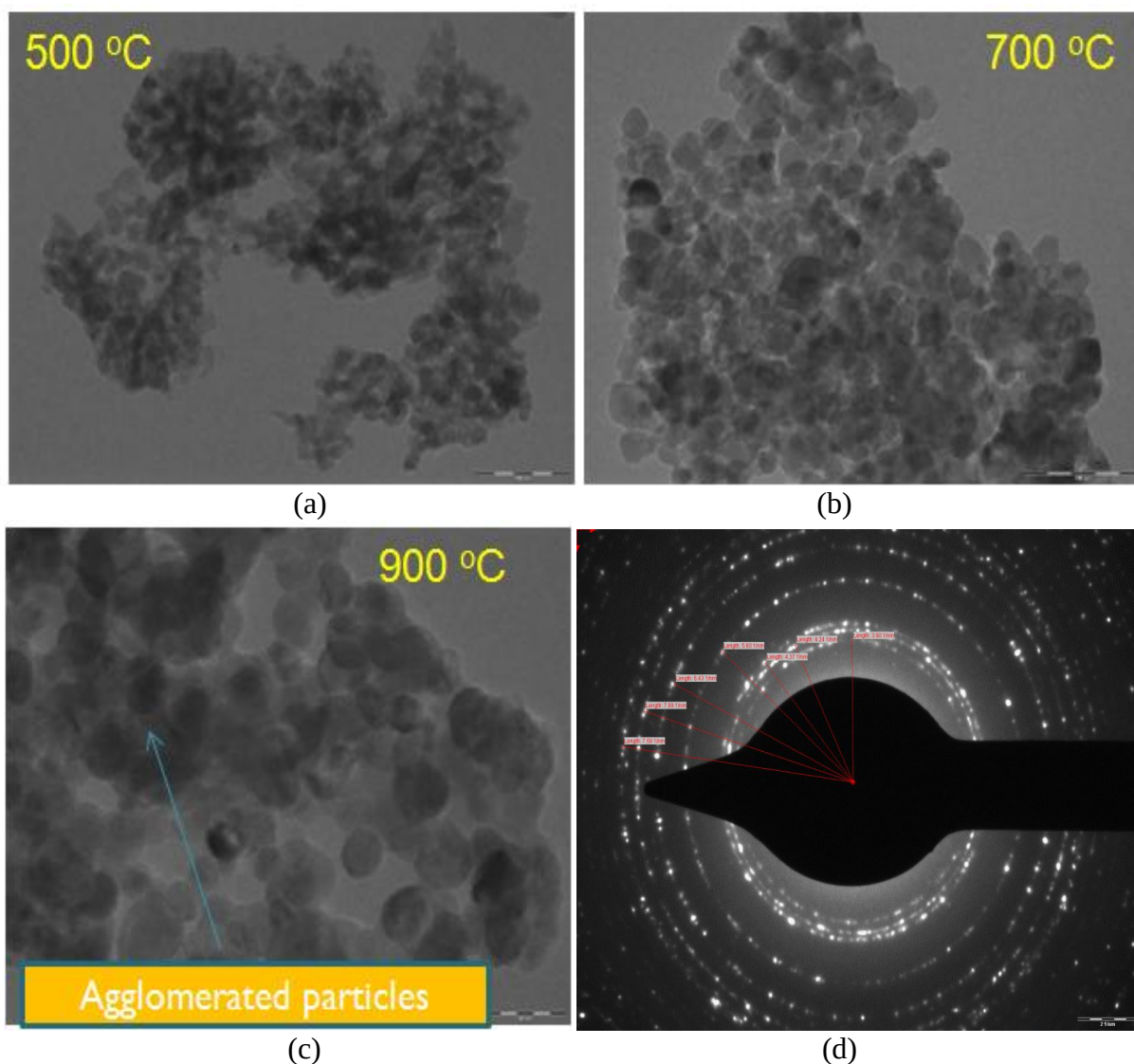


Figure 3. TEM images of ZnO powder annealed at different temperatures (a-c) and typical SAED pattern of sample annealed at 900°C (d).

The typical selected area electron diffraction (SAED) pattern of nano-particles in powder sample annealed at 900 °C temperature is shown in figure 3(d). The electron diffraction patterns of nano-particles represent a collection of halo-rings and discrete spots, and confirm poly-crystalline structure of the prepared nano-particles. Seven fringe patterns corresponding to planes: (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) are consistent with the peaks observed in XRD patterns. The ring to the centre distance of each ring is measured as 3.90, 4.23, 4.37, 5.60, 6.43, 7.09 and 7.58 nm and expressed in terms of nm^{-1} . The reciprocal of these values gives the interplanar distance d [13]. Details are given in table 2.

Table 2: *d* values obtained from XRD and TEM.

Reported <i>d</i> values (Å)	X-ray diffraction (XRD) <i>d</i> values (Å)	Electron diffraction (TEM)		Planes (<i>hkl</i>)
		Reciprocal of <i>d</i> values δ_{hkl} (nm^{-1})	<i>d</i> values d_{hkl} Å	
2.8143	2.8117	3.90	2.5641	(1 0 0)
2.6033	2.6049	4.24	2.3640	(0 0 2)
2.4759	2.4728	4.37	2.2883	(1 0 1)
1.9111	1.9088	5.60	1.7857	(1 0 2)
1.6247	1.6248	6.43	1.5552	(1 1 0)
1.4771	1.4764	7.09	1.4104	(1 0 3)
1.3582	1.3775	7.58	1.3192	(1 1 2)

c. SEM analysis

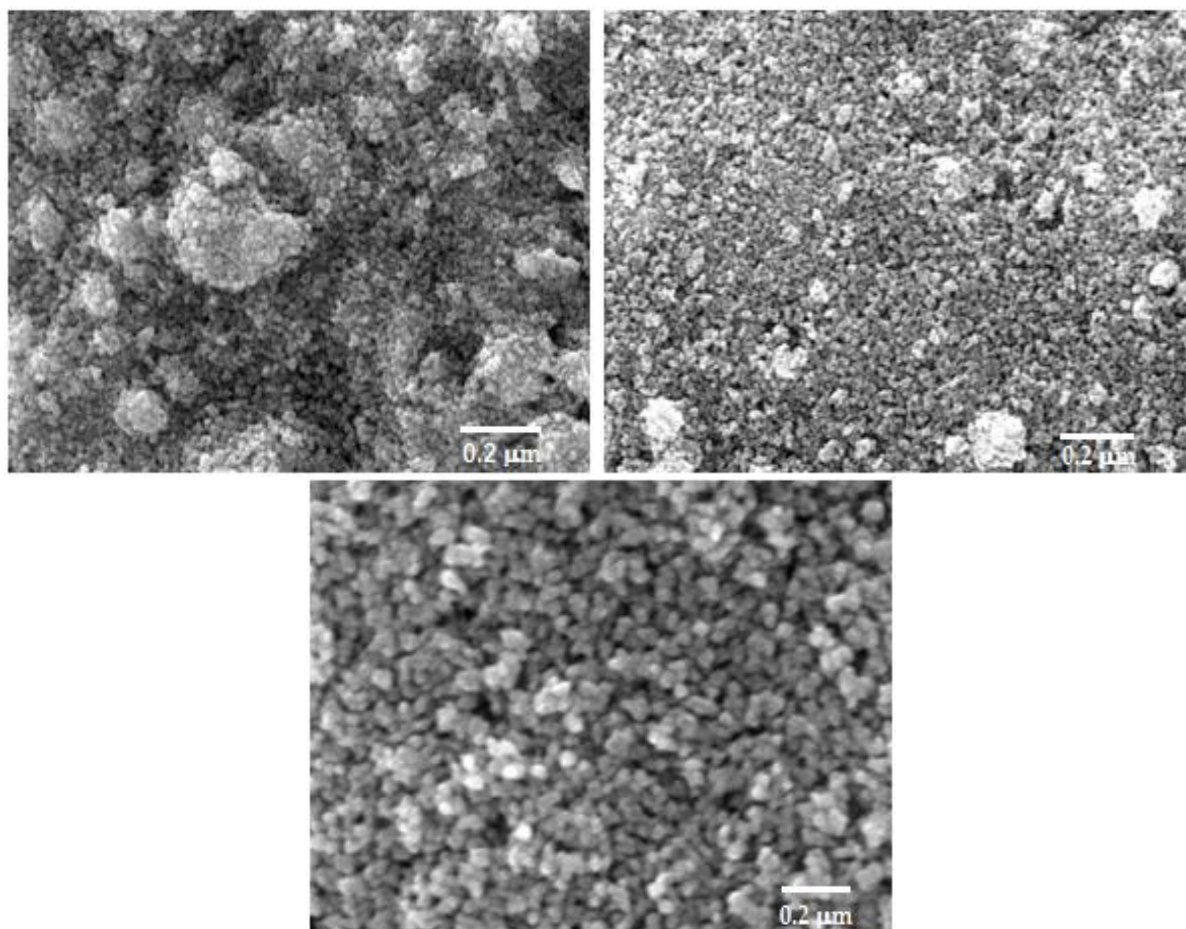


Figure 4. SEM photographs of ZnO thick films at annealing temperature (a) 500°C, (b) 700°C and (c) 900°C.

Figure 4 consists of SEM images representing surface morphology of the ZnO thick films with different annealing temperature. It is seen that the particle microstructure of these films quite similar except for increases in particle size. The average particle sizes obtained from the SEM images are 10-20 nm. It is found that the ZnO thick films have relatively porous morphology. The SEM images reveal the increase of average particle size with increasing annealing temperature, up to an approximate average particle size of 20 nm at 900°C. However, as determined from XRD data, the average grain size ranged from 10-20 nm, which was substantially smaller than the 10-20 nm dimensions of grains observed in SEM.

III. GAS SENSING PERFORMANCE OF ZnO THICK FILMS

The gas sensing study was initiated with a view to study the gas sensing performance of ZnO thick films annealed at different temperature. As the gas sensors are based on resistive material used in the form of thick film, an electrical characterization is related to the resistance measurements at various operating temperatures in different gaseous environments (ppm level of H₂S, CO₂, NH₃, CO, H₂, Cl₂, O₂, Ethanol vapor and LPG in normal atmospheric conditions). The semiconductor sensors are based on an interaction between the metal oxide semiconductor and the gas ambient which produces a change in the conductivity of semiconductor. It is known [14-19] for many years that the adsorption-dependent electrical properties of metal oxide semiconductors are often sensitive to many gaseous ambient. This phenomenon is the basis of present study.

The main characterization is the optimization of operating temperature of film sample for test gases. On the basis of measured data, the sensitivity and selectivity of thick film sensor for gas concentration in the range from 10-100 ppm in air ambient condition are calculated.

a. Sensitivity of ZnO thick films to H₂S gas with operating temperature

For comparison, the H₂S sensing properties of the ZnO thick films at different annealing temperature were also studied under identical experimental conditions. The annealing temperature is an important parameter for gas sensing materials and in designing of sensors. The sensing materials have to be annealed at various temperatures to achieve crystallization and structural evolution. A sufficient degree of crystallinity is required to attain the desired electronic

properties necessary for gas sensor application. The dependence of the sensitivity of the ZnO thick films to 10 ppm of H_2S at annealing temperature 500°C, 700°C and 900°C on the operating temperature is shown in figure 5. The sensitivity is found to be maximum when the annealing temperature was 700°C. The annealing in air renders more oxygen vacancy generation, which enhances the gas sensitivity. It is observed that the sensitivity increases 50°C to 200°C and then decreases with the further increase in the operating temperature. It showed the maximum sensitivity of 123, 376 and 95 to 10 ppm of H_2S at annealing temperatures 500°C, 700°C and 900°C respectively.

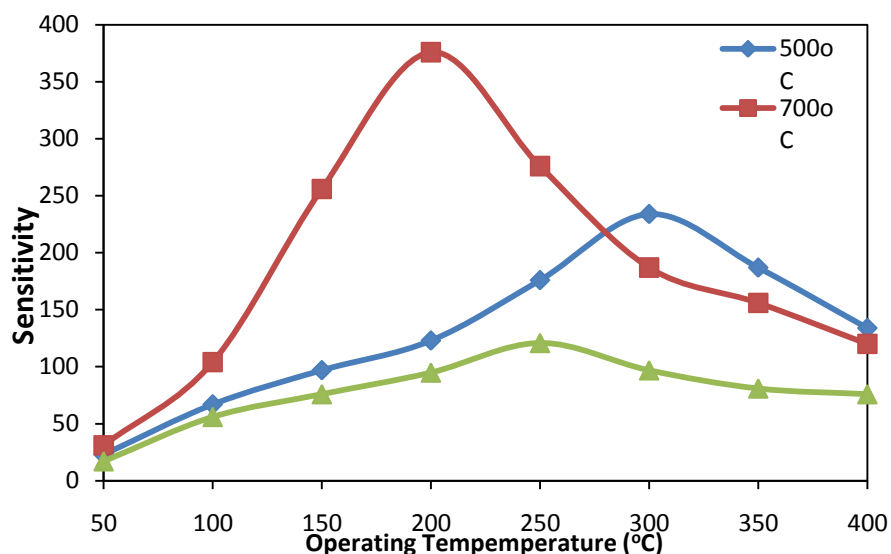


Figure 5. Effect of annealing temperature on the sensitivity of ZnO thick films to 10 ppm of H_2S gas.

b. Variation in sensitivity with H_2S gas concentration

The dependence of the sensitivity of ZnO thick films on the H_2S concentration at an operating temperature 200°C is shown in figure 6. It is observed that the sensitivity increases linearly as the H_2S concentration increases from 1 to 10 ppm and then decreases with further increase in the H_2S concentration. The linear relationship between the sensitivity and the H_2S concentration at low concentrations may be attributed to the availability of sufficient number of sensing sites on the film to act upon the H_2S . The low gas concentration implies a lower surface coverage of gas molecules, resulting into lower surface reaction between the surface adsorbed oxygen species and the gas molecules. The increase in the gas concentration increases the surface reaction due to a large surface coverage. Further increase in the surface reaction will be gradual when saturation of

the surface coverage of gas molecules is reached. Thus, the maximum sensitivity was obtained at an operating temperature of 200°C for the exposure of 10 ppm of H₂S. ZnO thick films are able to detect up to 1 ppm for H₂S with reasonable sensitivity at an operating temperature 200°C. The linearity of the sensitivity in the low H₂S concentration range (1-10 ppm) suggests that ZnO thick film sensors can be reliably used to monitor the concentration of H₂S over this range.

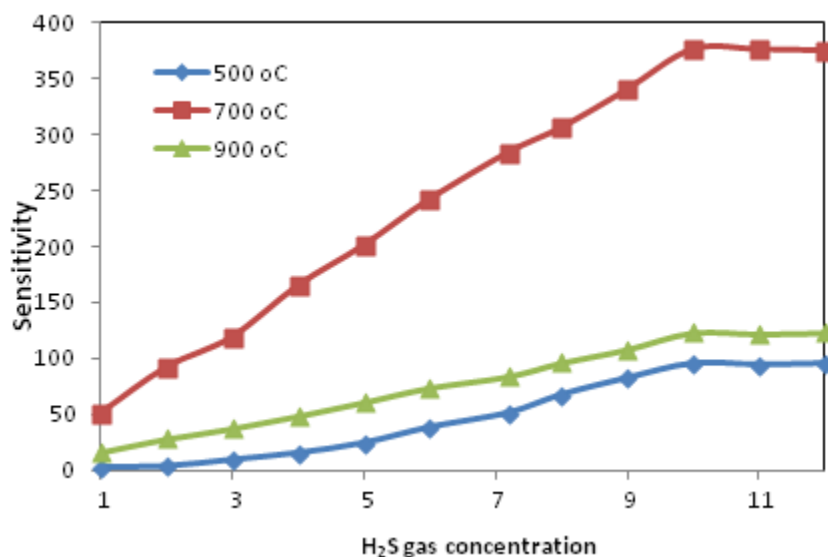


Figure 6. Dependence of the sensitivity of ZnO thick films on the H₂S concentration at 200°C

c. Selectivity of ZnO thick films for various gases

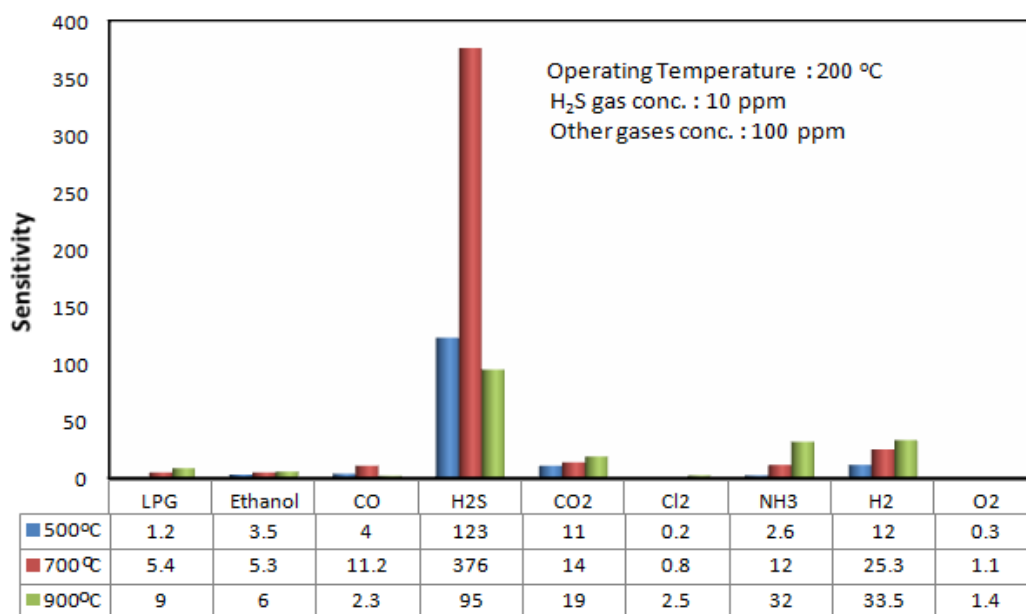


Figure 7. Selectivity of ZnO thick films for various gases.

It is observed from figure 7 that ZnO thick films gives maximum sensitivity to H₂S (10 ppm) at 200°C. The films showed highest selectivity for H₂S against all other tested gases: NH₃, LPG, Cl₂, CO, CO₂, O₂, H₂ and ethanol. The selectivity also increases with annealing temperature.

d. Response time and recovery time

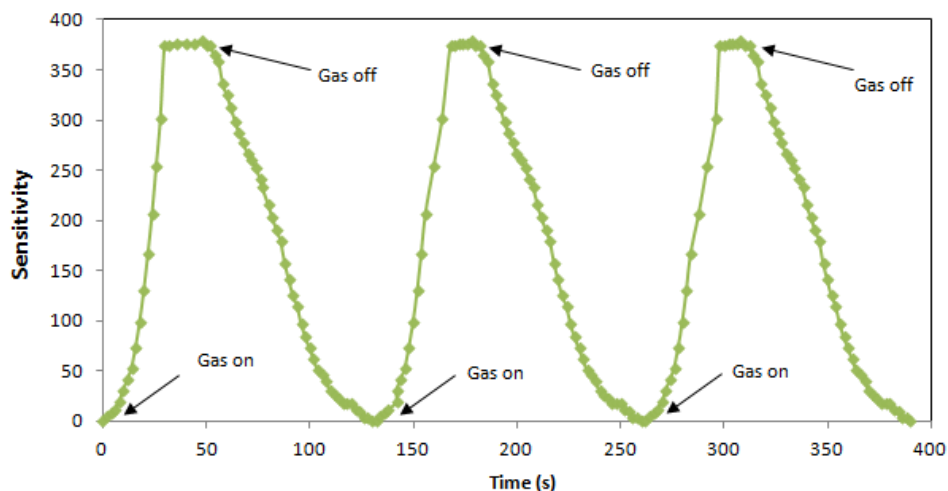


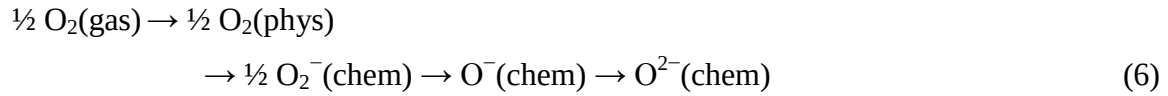
Figure 8. Response and recovery of ZnO thick films.

The response and recovery of ZnO thick films annealed at 700°C are represented in figure 8. The response was quick (~30 s) even to a trace amount (10 ppm) of H₂S gas, while the recovery was fast (~76 s). The quick response may be due to faster oxidation of gas. The negligible quantity of the surface reaction product and its high volatility explains its quick response and fast recovery to its initial chemical status. These results indicate that the ZnO prepared by spray pyrolysis method is a suitable material for the fabrication of the H₂S sensor. A number of experiments have been carried out to measure the sensitivity as a function of the operating temperature. All the time the sensitivity of the sensor element has approximately constant values, indicating the repeatability of the sensor.

e. H₂S-sensing mechanism

According to the present understanding on the response of semiconductor gas sensors, the change in the electrical resistance is closely related to the chemical properties of the surface oxygen. In the aerial atmosphere where the partial pressure of oxygen is taken as constant, oxygen is adsorbed on ZnO surfaces in different forms depending on the temperature, usually

from physisorption to chemisorption (including entering the crystal lattice), that is, from molecular form to dissociative form as temperature increases.



These oxygen adsorbates (O_2^- , O^- and O^{2-}) on the surface of n-type ZnO can induce an electron-depleted surface region, resulting in the increase in surface potential barrier and electrical resistance, as depicted schematically in figure 9 (a). Upon exposures to reducing gases like H_2S , the surface oxygen is consumed due to the chemical reaction (figure 9 (b)), donating a few electrons back and thus leading to the decrease in potential barrier (figure 9 (c)) and then also in electrical resistance, where the concentration of surface oxygen shifts from the steady-state value in air to a new steady value, depending monotonically on the concentration of the reducing gas. The chemical adsorption of oxygen and its reaction with reducing gases underlie the sensing mechanism of ZnO nano-particles toward H_2S gases.

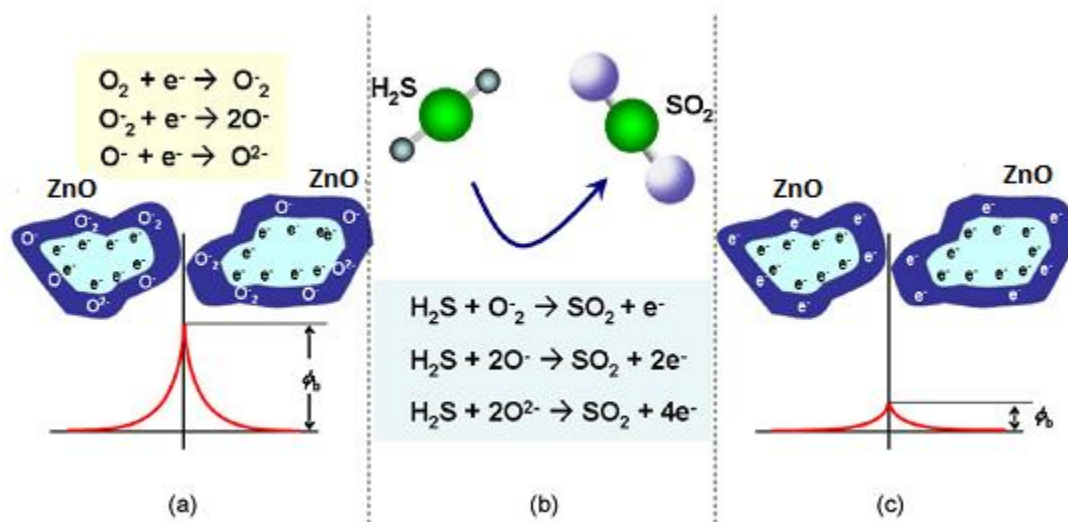
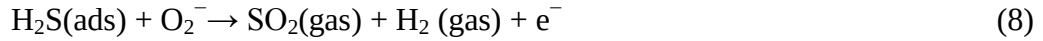


Figure 9. Schematic drawing of chemical reactions on ZnO surface underlying H_2S -sensing mechanism of ZnO nano-particles, where Φ_b denotes the potential barrier.

Let us first consider that the surface oxygen chemisorption is dominated by only one species, assuming meanwhile that H_2S adsorbed on the surface will entirely participate in the reaction.

When the dominating species that is O_2^- , the equation describing its interaction with H_2S on ZnO surface can be written as



Application of the mass action law to (5) and (6) gives

$$[H_2S(ads)] = K_{H_2S} P_{H_2S} \quad (9)$$

$$\begin{aligned} [e^-] &= K_1 [H_2S(ads)] [O_2^-] [SO_2]^{-1} [H_2]^{-1} \\ &= K_1 K_{H_2S} P_{H_2S} [O_2^-] [SO_2]^{-1} [H_2]^{-1} \end{aligned} \quad (10)$$

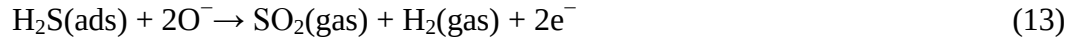
where K_{H_2S} and K_1 are the equilibrium constants of (7) and (8), P_{H_2S} is the concentration of H_2S gas in air, and the brackets mean the concentration per unit area. The electrical resistance (R_g) is inversely proportional to $[e^-]$ so that we obtain

$$R_g \propto (K_1 K_{H_2S} P_{H_2S})^{-1} [O_2^-]^{-1} [SO_2] [H_2] \quad (11)$$

Inserting this into (8) where R_a is irrelevant to P_{H_2S} gives the response

$$S = R_a/R_g \propto P_{H_2S} \quad (12)$$

Similarly, when the dominating species that participating in the reaction is O^- , we obtain

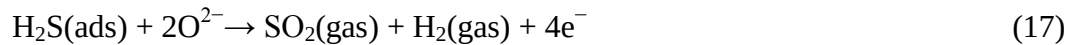


$$[e^-]^2 = K_2 K_{H_2S} P_{H_2S} [O^-]^2 [SO_2]^{-1} [H_2]^{-1} \quad (14)$$

$$R_g \propto (K_2 K_{H_2S} P_{H_2S})^{-0.5} [O^-]^{-1} [SO_2]^{0.5} [H_2]^{0.5} \quad (15)$$

$$S = R_a/R_g \propto P_{H_2S}^{0.5} \quad (16)$$

When the dominating species that participating in the reaction is O^{2-} , we obtain



$$[e^-]^4 = K_3 K_{H_2S} P_{H_2S} [O^{2-}]^2 [SO_2]^{-1} [H_2]^{-1} \quad (18)$$

$$R_g \propto (K_3 K_{H_2S} P_{H_2S})^{-0.25} [O^{2-}]^{-0.5} [SO_2]^{0.25} [H_2]^{0.25} \quad (19)$$

$$S = R_a/R_g \propto P_{H_2S}^{0.5} \quad (20)$$

where K_2 and K_3 are the equilibrium constants of (13) and (17).

Therefore, the dependence of the response on gas concentration can be characterized by the power law

$$S \propto P_{H_2S}^m \quad (21)$$

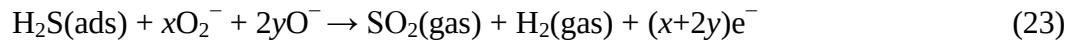
where the power law exponent m takes the value of 1, 0.5 or 0.25 respectively depending on the species of chemisorbed (ionisorbed) oxygen (O_2^- , O^- and O^{2-} correspondingly) and thus on the temperature.

Here, it is interesting to compare the value of m obtained from experiment results ($m = 0.6$) with that from theoretical analysis, that is

$$0.5 < (m = 0.6) < 1 \quad (22)$$

This relation indicates that at 200 °C, the oxygen chemisorption on ZnO surfaces might be dominated by O_2^- and O^- simultaneously, which is in accordance to the TPD, FTIR and EPR studies conducted on ZnO surfaces [20,21] indicating that the molecular form (O_2^-) dominates below 200 °C, and above this temperature the ionic species dominate, predominately as O^- below 400 °C and O^{2-} above 400 °C, which is then directly incorporated into the lattice above 600 °C.

Furthermore, the proportions of O_2^- and O^- involved here could be calculated through the reaction expressed by:



where x and y are the proportions of O_2^- and O^- respectively so that $x + y = 1$.

At this time, application of the mass action law to (21) gives:

$$[e^-]^{1/1+y} = K_4 K_{H_2S} P_{H_2S} [O_2^-]^x [O^-]^{2y} [SO_2]^{-1} [H_2]^{-1} \quad (24)$$

and we obtain:

$$R_g \propto (K_4 K_{H_2S} P_{H_2S})^{-1/1+y} [O_2^-]^{-x/1+y} [O^-]^{-2y/1+y} [SO_2]^{1/1+y} [H_2]^{1/1+y} \quad (25)$$

$$S = R_a/R_g \propto P_{H_2S}^{1/1+y} \quad (26)$$

where K_4 is the equilibrium constant of (21). Inserting the value of $m = 0.6$ into (24) leads to:

$$x = 1/3 \quad (27)$$

$$y = 2/3 \quad (28)$$

The important implication of (27) and (28) is that, at 200 °C, oxygen might be ionisorbed on ZnO surfaces predominantly as O_2^- and O^- with the proportion ratio of 1:2, which needs to be demonstrated by further spectroscopy study.

The above discussion suggests that the power law exponent is characteristic of the surface reaction and thus specific to the kind of target gas as well as the temperature which determines the dominating species of oxygen adsorbates and the proportion they account for. Obviously, for a specific target gas like H_2S , the value of the power law exponent merely depends on the operation temperature. This explains well why the same power law exponent value at 200 °C has

been observed for the sensor samples prepared from three different kinds of ZnO nano-particles toward H₂S gas in the range 10–100 ppm.

V. CONCLUSIONS

The ZnO nano-particles were synthesized successfully by simple chemical route accompanied by citric acid as a surfactant. From XRD and SEM analysis, it is confirmed that grain size systematically increased with increase in annealing temperature. The TEM images confirm the nanometric size of the particles in the range of 8, 14 and 18 nm depending on the annealing temperature 500, 700 and 900°C respectively. The maximum sensitivity was obtained at an operating temperature of 200°C for the exposure of 10 ppm of H₂S over other gases with quick response (30 s) and fast recovery (76 s) for ZnO thick film prepared from powder annealed at 700 °C.

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