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Volatile Organic Compounds Sensing Performance of ZnO Thick Film.

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ABSTRACT

Nanostructured zinc oxide thick film was prepared using ZnO nanoparticles. The nanoparticles were prepared from zinc acetate dihydrate and hexamethylenetetramine precursor. The structural studies showed that the synthesized ZnO nanoparticles were polycrystalline in nature with hexagonal wurtzite lattice structure. Scanning electron micrograph results revealed the formation of hexagonal shaped nanostructures. The room-temperature vapour sensing properties of ZnO thick film were studied toward various volatile organic compounds (VOC's) such as ammonia, acetaldehyde, acetone, xylene and ethanol. ZnO hexagonal shaped surface was highly sensitive towards 100 ppm of ammonia vapour.

Keywords: ZnO; Thick film; Solution growth; Ammonia.

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INTRODUCTION

ZnO is an n-type semiconductor with a direct band gap of 3.3 eV and large exciton binding energy of 60 meV [1] at room temperature. It has wide resistivity ranging from 10^{-4} to 10^{-12} Ωcm. It exhibits a high thermal stability (melting point 2248 K) [2], small electron affinity, good resistance against hydrogen plasma and chemical etching [3]. It also has a higher transmittance of 80 - 90% in the visible region and high absorbance in the UV range. Due to these properties, it is widely used in applications such as solar cells, optical devices, heat mirrors, UV detectors, transistors, memory devices, surface acoustic wave devices, etc. Owing to its good transmittance and low resistance along with its cost-effective nature makes it a valid substitute for ITO in TCO applications. Because of its chemical stability, it is used in gas sensing and solar cell applications. ZnO is also used as substrates or seed layers for epitaxial film growth owing to its good thermal conductivity. Since it possessesgood radiation hardness, it finds applications in high altitudes or space.

ZnO nano structures can be prepared in many ways like sputtering [4], spray pyrolysis method [5], sol-gel method [6], pulsed laser deposition [7], chemical vapour transport, MOCVD method and low temperature solvent growth method. Among these methods 'low temperature solution growth, method is broadly used for growing nano structures due to its large- scale production, low temperature (60 – 100^{o}C), less cost, high yield, controlled synthesis, etc. [8] Low temperature solution growth method is most suited for the starting materials which are wavering at higher temperatures and may undergo phase transformations below their melting point. Materials which are unstable at elevated temperatures and possess moderateto high solubility in the temperature range of 60 to100 °C in atmospheric pressure can be grown by low-temperature solution method. Properties of the samples prepared by solution growth method were affected by various parameters such as ion or molecule interactions between the solute and the solvent which is based on the solubility of substance, solvent concentration, pressure and temperature.

The low-temperature solution growth technique also allows to prepare different morphologies of the same material by altering the growth conditions or solvent. Being a low-temperature process it reduces the risk of major thermal shock to the samples during growth and as well as removal from the apparatus. Liew*et al*. [9] synthesized ZnO powders by solution growth method at low temperature and the solution grown ZnO contains Zn deficiency, rather than the O deficiency which is commonly observed. The cluster of nano rods to form flower shaped ZnO nano structures were synthesized by Wahab*et al*. [10] by the solution processusing zinc acetate dehydrate and sodium hydroxide at the low temperatures. Rout*et al*. [11] fabricated thick films using nano structures of ZnO, SnO_2 and In_2O_3 with ethylene glycol and studied their ammonia sensing properties, where all the films exhibited sensing response at elevated operating temperatures. Rao *et al*. [12] have reported the ZnO thick films synthesized using ZnO nano structures with deionized water and studied the response towards various gases like ammonia, carbonmonoxide, hydrogen, LPG, ethanol and acetone at room temperature. In this work, we have reported volatile organic compounds (VOCs) sensing characteristics of ZnO thick films synthesized from solution growth method using the precursor of zinc acetate dehydrate and hexa methylene tetramine (HMTA) with ethylene glycol as a binder.

MATERIALS AND METHODS

Preparation technique

The 0.1 M of zinc acetate dihydrate was dissolved in deionized water and stirred continuously for 1 h. The 0.1 M of hexamethylenetetramine (HMTA) was added to the solution as a solution stabilizer. After stirring for 1 h the solution was transferred into the container and sealed tightly. The sample kept undisturbed for 2 h at 80^{o}C in hot air oven. Then the precipitate was taken away and washed with the distilled water and dried in atmosphere.

The possible ZnO formation mechanism using solution growth method with HMTA$((CH_2)_6N_4)$ as a stabilizer is given below [13,14]:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 4NH_3 + 6HCHC0 \quad (1)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + 0H^- \quad (2)$$

$$Zn^{+2} + 4NH_3 \leftrightarrow Zn(NH)_4^{2+} \quad (3)$$

$$Zn^{+2}\ or\ Zn(NH)_4^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (4)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (5)$$

Characterization techniques

X-ray Diffractometer (Model X'PERT PAN analytical, The Netherlands) with Cu K_α source (λ=1.5408 Å) in the 2θ ranges from 30 to 60˚ with the scanning rate of 1˚min^{-1} was used to study the structural properties of the nanoparticles. Surface morphology of the ZnO powder prepared using solution growth method was studied using the Field Emission Scanning Electron Microscope (FE-SEM) (JEOL 6701F, Japan). The vapour sensing studies were carried out by employing an electrometer (Keithley, 6517A, USA). For sensing studies the synthesized ZnO powder was mixed with the ethylene glycol to make it as a paste. Then the paste was coated on to the cleaned glass substrates and dried at 80°C in the hot air oven for 1 h to obtain thick film. Further, ZnO thick film was tested with vapours like ammonia, acetaldehyde, acetone, ethanol and xylene at room temperature.

RESULTS AND DISCUSSION

Structural Studies

XRD pattern of solution grown ZnO nanoparticles is shown in Fig. 1. XRD pattern revealed that the prepared ZnO nanoparticles was polycrystalline and well matched with JCPDS card 36-1451- corresponding to hexagonal wurtzite structure. It exhibited a preferred orientation along (100) plane. Other peaks corresponding to (002), (101), (102) and (110) planes were also observed. No other peaks related to zinc acetate or zinc hydroxide were found. The peak of (100) plane indicated the lateral growth of the nanoparticles.
The crystallite size was calculated using the Scherer formula [15],

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (6)$$

where, λ= 1.54 Å, β is the full width at half maximum intensity, θ is the Bragg's angle. The calculated crystallite size was found to be 96 nm. The strain was calculated using the formula [15]

$$\varepsilon = \frac{\beta}{4\tan{(\theta)}} \qquad (7)$$

where, β is the full width at half maximum intensity, θ is the Bragg's angle. The calculated strain was found to be 1.23×10^{-3} due to which there was a shift in (100) peak position form 31.76º (bulk) to 32.45º (prepared).

Morphological studies

Fig. 2 shows the SEM image of ZnO nanoparticles in low and high magnifications. Formation of hexagonal nanoplates of various sizes can be noticed andalso they were separated from each other. This may be attributed to the effect of HMTA, which acts as a stabilizer and avoids the agglomeration of the ZnO precursor molecules through its chelating effects. The focused view is shown in Fig. 2(b) which revealed the formation of clear hexagonal plate like structure. The hexagonal structure is the most stable form for ZnO which is responsible for the formation of this structure [16].

Sensing studies

The sensing mechanism of ZnO thick film sensors can be explained as follows: when ZnO film (n-type) was exposed to the atmosphere, oxygen molecules in the atmosphere were adsorbed on to the surface of the film due to which the free electrons were removed from the conduction band of ZnO [5].

$$O_2 + e^-_{ZnO\ surface} \longrightarrow O^-_{2(ads)} \quad (8)$$

This resulted in an increase in the surface resistance of the film and the steady state resistance was obtained which was fixed as the base line resistance (R_a) for sensing measurements. When the film was exposed to reducing vapours like ammonia, acetone, xylene, etc., the adsorbed oxygen will react with the reducing vapour and liberated the adsorbed electrons, which in-turn reduced the resistance of the film and attained to a steady state value. This value was fixed as the resistance in gas atmosphere (R_g). Hence, the response of the film towards the particular vapour was calculated using the equation [5],

$$S = \frac{R_a}{R_g} \quad (9)$$

where, R_a is the resistance of the film in air and R_g is the resistance of the film in gas atmosphere. The responses of the thick film towards 100 ppm of ammonia, xylene, acetaldehyde, acetone and ethanol vapours is shown in Fig. 3. This study revealed the better sensing response of ZnO thick film towards ammonia vapour.

The sensing mechanism towards ammonia vapour is given below [17]:

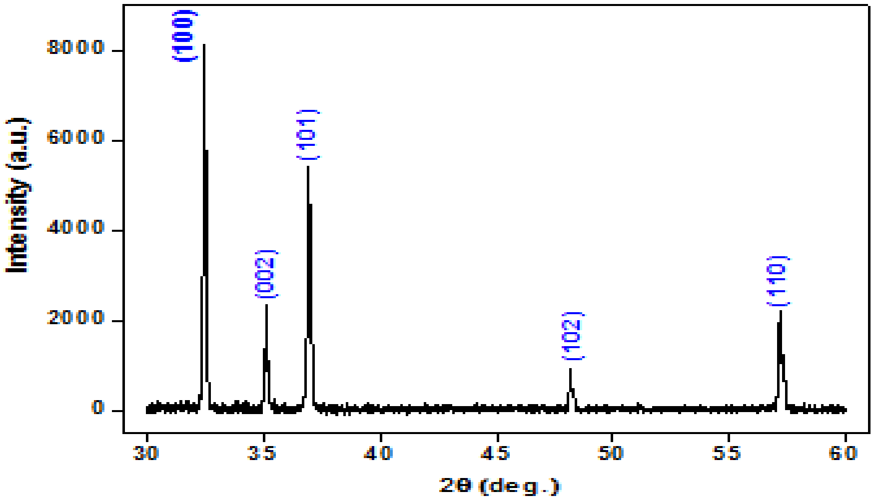
$$4NH_3 + 3O^-_{2\,(ZnO\ Surface)} \rightarrow 2N_2 + 6H_2O + 6e^- \quad (10)$$

The response of the ZnO thick film towards various concentrations of ammonia like 5, 10, 30, 50 and 100 ppm is shown in Fig. 4 and the transient graph for 100 ppm representing the base line and gas resistance is shown in Fig. 5. The response and recovery time towards 100 ppm of ammonia were found to be 31 and 13 s respectively. The presence of hexagonal plate like morphology with the larger surface area and porous surface might have enhanced the VOC sensing response of ZnO thick film at the room temperature. A comparison of the sensing response of the present ZnO thick film with the results available in the literature is given in Table. 1. This comparison obviously highlights the better sensitivity of the ZnO thick film towards ammonia that too at room temperature.

Table 1 Comparison of the performance of the present thick film sensors with the literature.

Sl. No.	Gas	Operating temperature K	Concentration ppm	Response	Ref.
1	Ammonia	300	30	46	Present work
2	Ammonia	300	30	35	[12]
3	Ethanol	673	100	38.4	[18]
4	Ethanol	673	750	25	[19]
5	Formaldehyde	483	10	237	[20]

Figure 1: XRD pattern of ZnO nanoparticles.



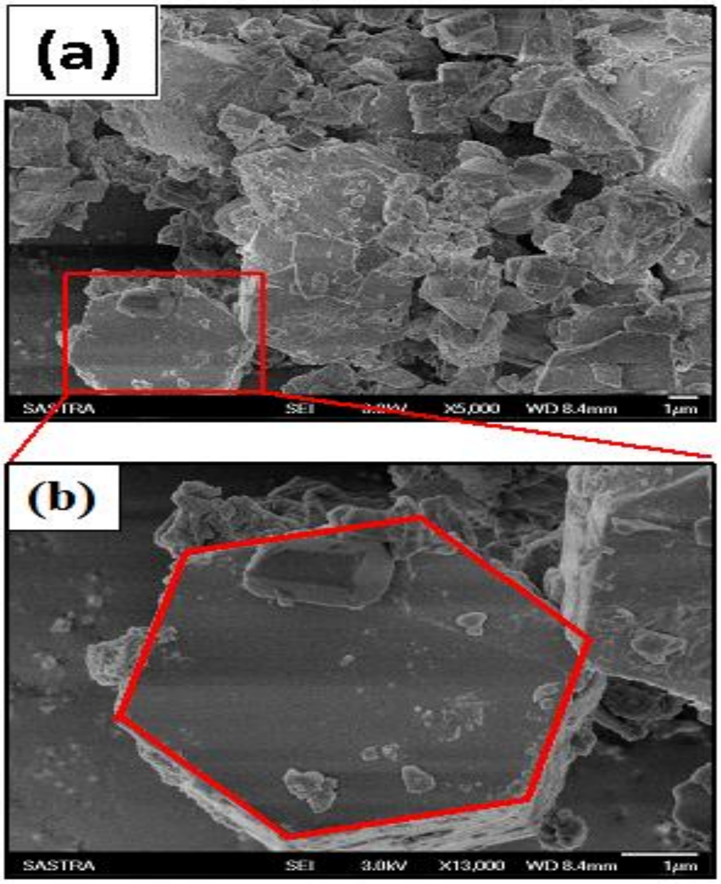


Figure 2: SE micrograph of (a) ZnO nanoparticles and (b) focused view of the hexagonal plate.

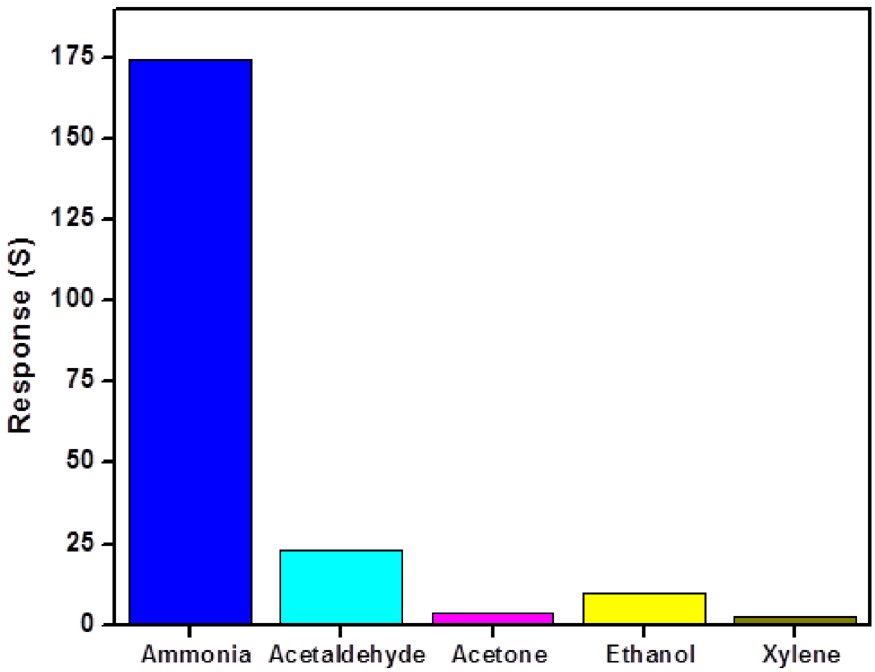


Figure 3: Room temperature response of the ZnO thick film towards 100 ppm of various VOCs.

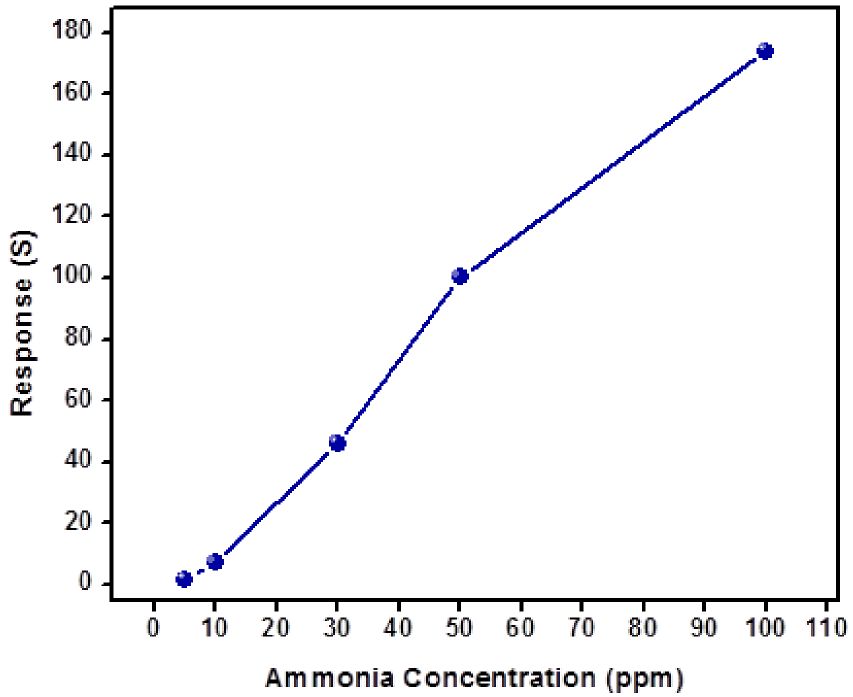


Figure 4: Response of the ZnO thick film towards various concentrations of ammonia

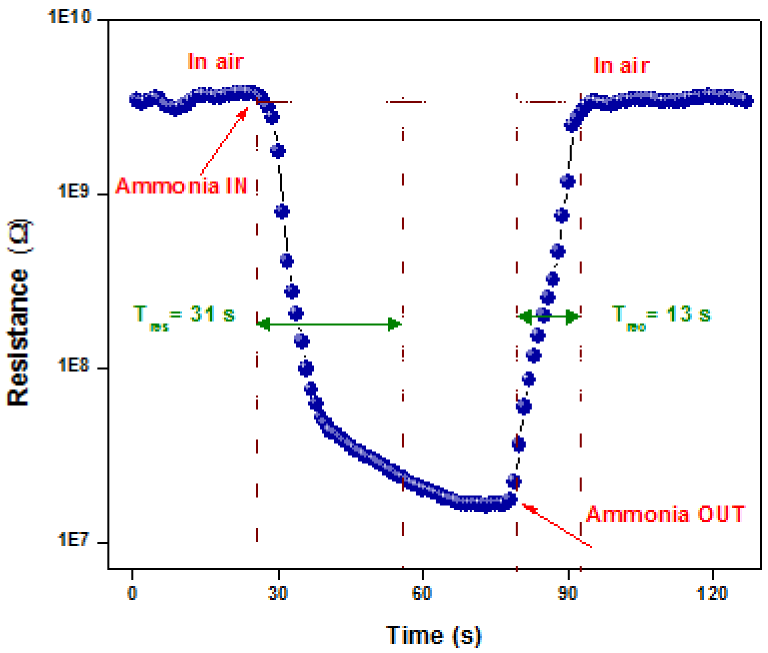


Figure 5: Transient response of ZnO thick film towards 100 ppm of ammonia vapour at the room temperature

CONCLUSION

Zinc oxide nanostructure was successfully synthesized using the solution growth method. XRD pattern revealed the formation of polycrystalline ZnO film with a preferred orientation in the (100) plane. SEM images revealed the presence of hexagonal shaped grains as it is the stable structure of ZnO. Porous morphology was obtained because of the chelating effect of HMTA. The prepared thick film was highly selective to ammonia and the sensing response was mainly attributed to the surface morphology of ZnO thick film.

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