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Aqueous chemical route deposition of nanocrystalline ZnO thin films as acetone sensor: Effect of molarity

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Abstract

Nanocrystalline ZnO thin films were deposited onto glass substrate using a simple and inexpensive aqueous chemical method at low temperature (90 °C). The concentration of precursor solution was varied in order to study its effect on structural, morphological, and gas response properties. Field-emission scanning electron microscopy (FESEM) images indicate the growth of ZnO with hexagonal shaped nanostructure. Further these films were used to explore gas response properties towards acetone, propanol and ethanol vapors. The sensor response was found to be decreased with increase in precursor concentration. The highest sensor response of 92% was observed towards acetone for the film deposited at 0.05 M at an operating temperature of 350 °C. The higher vapor response towards acetone is attributed to size and surface morphology of the film deposited at 0.05 M.

Keywords: Zinc oxide; Gas sensor; Aqueous chemical method

1. Introduction

Development in the industrialization and human life has created a need to detect and monitor the inflammable and toxic gases. Semiconductor sensor materials like ZnO, SnO_2, In_2O_3, Fe_2O_3,TiO_2, etc. [1–5] have been used to detect various toxic and inflammable gases. Among these semiconducting oxide materials, ZnO is a popular material for solid state gas sensors because of its versatile properties like chemical and thermal stability. Also it is an n-type semiconductor with large exciton binding energy of 60 MeV and band gap energy of 3.37 eV at room temperature. ZnO has been used as a sensor [6], photocatalyst [7], solar cell [8,9], transparent conductive coating [10], electro and photoluminescent material, etc. [11] ZnO gas sensors have been fabricated in various forms such as sintered pellets, thick films, thin films and heterojuctions [12–18]. ZnO is sensitive to numerous gases such as H_2, CO, and O_2 and has good stability but it has high working temperature, poor selectivity, and low response. Various attempts have been made to overcome these disadvantages; however still there are many critical limitations such as high working temperature and poor selectivity [19]. One dimensional nanostructures (nanorod, nanowires) of ZnO have gained significant research interest due to the high surface to volume ratio possessed by these nanostructures which makes them to be extremely sensitive even at low concentration of gases [20]. Aqueous chemical synthesis of nanostructure of ZnO is the most economical and energy efficient method and enables good morphological control of the nanostructure [21]. However, most of these gas sensors focus on C_2H_5OH [22], CO [23], NO_2 [24], and H_2 [25], and rare studies concern the acetone sensing characteristics. Acetone is generally used as a chemical reagent in industries and it easily evaporates at room temperature; continuous exposure to acetone may cause headache and fatigue to the workers [26,27]; therefore detection and measurement of acetone concentration in the work place is quite essential for our safety and health. Also as part of medical diagnostics of diabetes we should be able to know acetone concentration in the blood of a sick person. This is usually made with the help of paper indicators changing their color under contact with the urine of the sick man.

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This method has obvious shortcomings in the application; moreover, the constraint between concentrations of acetone in urine and blood is of a more complex character than the correlation of those parameters in expiration and in blood because the blood directly participates in the gas-exchange applications [28]. It is well known that the gas response properties of oxide materials are related to the surface morphology and are grain size dependent; therefore one can improve the response by controlling the grain size and surface morphology. In the present communication, we report the deposition of nanocrystalline ZnO thin films by a facile aqueous chemical method at low temperature and the effect of concentration of precursor solution on structural, morphological and gas response properties.

2. Experimental

All the reagents used in this work were of analytical reagent (AR) grade. Prior to the deposition of ZnO, the seed layer of ZnO was deposited on ultrasonically cleaned glass substrates. The seed solution was prepared similar to that reported elsewhere [29]. The seed layer facilitates the nucleation of ZnO which results in oriented growth of ZnO. The aqueous chemical growth process comprises two steps, the nucleation and growth. Creating the seed layer of ZnO plays an important role in the uniform growth of ZnO nanoparticles on the substrate. The seeding process also lowers the thermodynamic barrier by providing the nucleation sites and improves the aspect ratio of the synthesized nanocrystals. The precursors zinc acetate and hexamethylenetetramine serve as sources of zinc and hydroxyl ions respectively. The aqueous solution was prepared using zinc acetate and hexamethylenetetramine (HMT) in equimolar ratio and mixed in 160 ml solution and stirred for half an hour. Thin films were deposited at 90 °C. The molar concentration of zinc acetate and HMT was varied from 0.05 M to 0.2 M in steps of 0.05 M and accordingly films were denoted as Z0.05, Z0.10, Z0.15, and Z0.20. The structural characteristics of films were identified by the X-ray diffraction (XRD) technique using a Philips (PW 3710) diffractometer model with a Cu K_α ($\lambda = 1.54056$ A) target. The morphologies of the films were observed by field-emission scanning electron microscopy (FESEM) on a JEOL JEM-6700F microscope operating at 5 kV. The gas response properties of these thin film samples towards acetone (CH_3COCH_3), ethanol (C_2H_5OH), and propanol ($(CH_3)_2CHOH$) were studied in the temperature range 200–450 °C.

3. Result and discussion

3.1. Structural study

Fig.1. shows the X-ray diffraction patterns of Z0.05, Z0.10, Z0.15 and Z0.20. All the diffraction peaks can be indexed to hexagonal ZnO with *d*-spacing and lattice constant values in good agreement with those in the standard JCPDF (79-2205) for ZnO. XRD study shows formation of highly oriented peak along (0 0 2) plane with no other peaks corresponding to impurity phase. The crystallite size was determined from full width at half maximum (FWHM) for the most intense (002) peak, which was obtained by slow step scanning around that peak at 0.2 °/min based on Scherrer's formula [30]

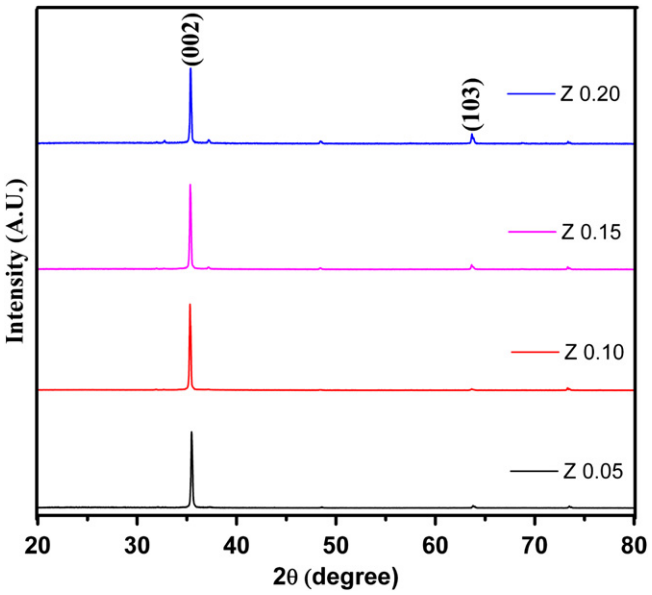

Fig. 1. XRD pattern of the different as-deposited ZnO films.

$$D = \frac{0.9\lambda}{\beta\ Cos\ \theta} \quad (1)$$

where 'β' is FWHM (in radians), 'θ' the angle of reflection and 'λ' the wavelength of X-ray radiation used. The crystallite size was found to be increased from 45 to 55 nm with increase in the concentration of precursor solution from 0.05 to 0.20 M.

3.2. Morphological study

Typical field-emission scanning electron microscopy (FESEM) images of ZnO nanocrystals are shown in Fig. 2. Uniform and evenly distributed growths of ZnO nanocrytals with hexagonal shape were observed. The grain size is found to increase with increase in concentration of the solution. As the concentration of precursor solution increases the number of metal nuclei centers available for deposition increases and due to this the film formed at 0.20 M concentration is denser and more clustered as compared to others.

3.3. Gas response properties

The gas response properties of thin film samples were studied using the commercial gas sensing setup reported elsewhere [31]. The gas response measurements were taken during cooling of the sample in the temperature range 200–450 °C after being heated to sufficiently high

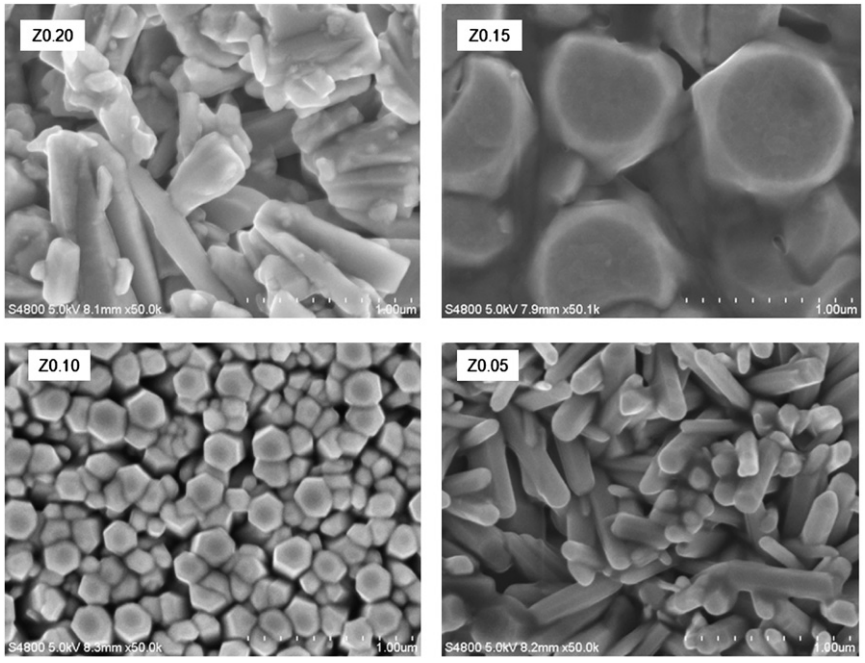

Fig. 2. FESEM micrographs of the different as-deposited ZnO films.

temperature to attain stability, thereby securing a good reproducibility of the response temperature characteristics. We have used the two probe technique for gas response measurement with conducting silver paste to make Ohmic contacts on the films. A known amount of gas was injected in the gas sensing system and the change in resistance of the sensor was measured. The gas response (S%) is calculated using

$$S(\%) = \frac{(R_a - R_g)}{R_a} \times 100 \quad (2)$$

where R_a is the resistance of the film in air and R_g is the resistance of the film after the gas exposure.

Fig. 3 shows variation in response with operating temperature for sample Z0.05 at 2000 ppm of acetone, ethanol and propanol. The response increases with the operating temperature, attains maximum value at a particular temperature and then decreases with a further rise in operating temperature in case of all gases. The sensor exhibited highest response to acetone as compared to other gases at 350 °C with response value of 92%, where it exhibited response of 66% and 71% to ethanol and propanol respectively. The sensor showed maximum response of 80% and 72% to ethanol and propanol at 300 °C and 275 °C respectively. Previously Comini et al. [32] and Shen et al. [33] reported maximum response to acetone at an operating temperature of 400 °C for nanocrystalline ZnO thin films; thus by employing the aqueous chemical route for deposition we succeeded in decreasing the operating temperature by 50 °C. At low temperature, the response is restricted by the rate of chemical reaction; however at higher temperature the rate of diffusion of gas

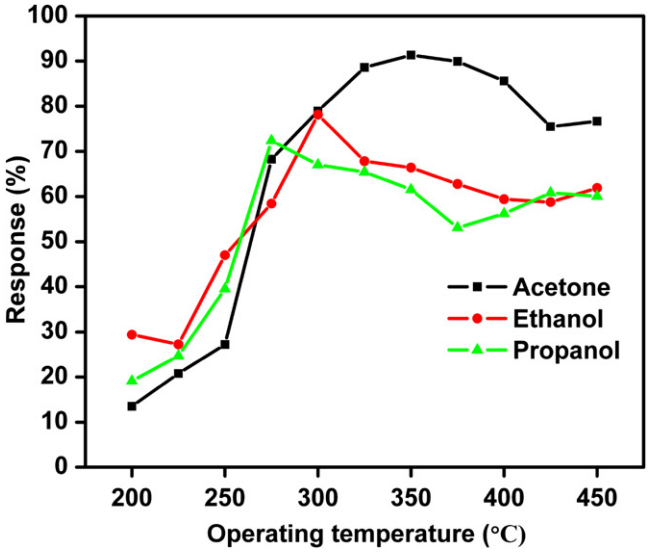

Fig. 3. Plot of the response versus operating temperature for Z0.05 towards different test gases at 2000 ppm concentration.

molecule controls the response. At the optimum temperature, the rates of chemical reaction and diffusion of gas molecules become equal and the sensor exhibits maximum response [34]. Thus, by selecting the particular operating temperature, one can employ the same sensor for detection of different gases. Different gases have different energies for adsorption, desorption and reaction on the metal oxide surface, and therefore the response at different temperatures would depend on the gas being sensed. Acetone is further used to study the response characteristics of different samples of ZnO.

The response as a function of operating temperature for different ZnO samples towards acetone is shown in Fig.4. One can easily notice that the optimum operating temperature for each sample is different and is the lowest for Z0.05. The effect of precursor concentration on response properties is significant as observed in the surface morphological properties. The smaller crystallite size and large surface area exhibited by Z0.05 provides more surface states for adsorption of oxygen and interface for reaction of adsorbed oxygen species with acetone molecules and hence Z0.05 shows the highest response to acetone as compared to others.

Fig. 5 shows the response for different ZnO samples as a function of acetone concentration at 350 °C. The response increases linearly as concentration of acetone increases from 100 to 1000 ppm. The slope of all the graphs decreases with concentration which is due to occurrence of saturation in the response. With a small concentration of gas, exposed on a fixed surface area of a sample, there is a lower coverage of vapor molecules on the surface and hence lesser surface reaction occurred. An increase in vapor concentration increases the surface reaction due to a larger surface coverage. Beyond a certain concentration the increase in surface reaction will be gradual, where the saturation point on the coverage of molecules is reached and we observe constant response above a certain concentration.

The graph of the thickness of ZnO film against the molar concentration of the precursor is shown in Fig. 6. It is observed that film thickness increases with an increase in the molar concentration of the aqueous solution; however the response decreases with increase in thickness of a thin film ZnO sample. The transient response characteristics of various ZnO samples exposed to 2000 ppm of acetone at their respective optimum operating temperatures are shown in Fig. 7. In these measurements, sensors response as a function of time was measured. From the figure it is obvious that as we go from Z0.05 to Z0.20, sensor response is found to decrease significantly, which is attributed to the change in morphology and enhancement in crystallite size of the sample. In case of Z0.05 the number of active adsorption sites for oxygen is high as compared to Z0.10, Z0.15 and Z0.20. The adsorption of oxygen on the surface increases the resistance of the sensor material due to transport of electrons from conduction band to adsorbed oxygen which results in increase in gas response. The response and recovery times are one of the important parameters used to exemplify the sensor performance. The response time is the period in which the sensor resistance change reaches 90% of the steady value. The recovery time is defined as the time for the resistance to recover 90% of the total variation when the test gas is removed. The response time of 7 s, 11 s, 21 s, and 32 s was

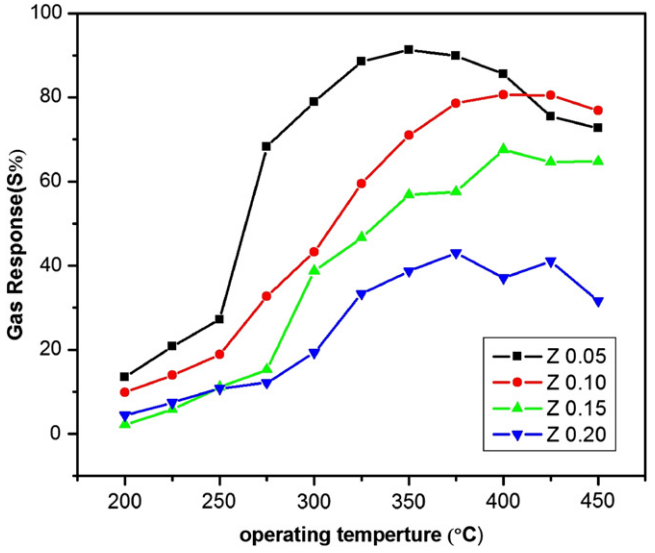

Fig. 4. Response as a function of operating temperature for different ZnO samples towards 2000 ppm of acetone.

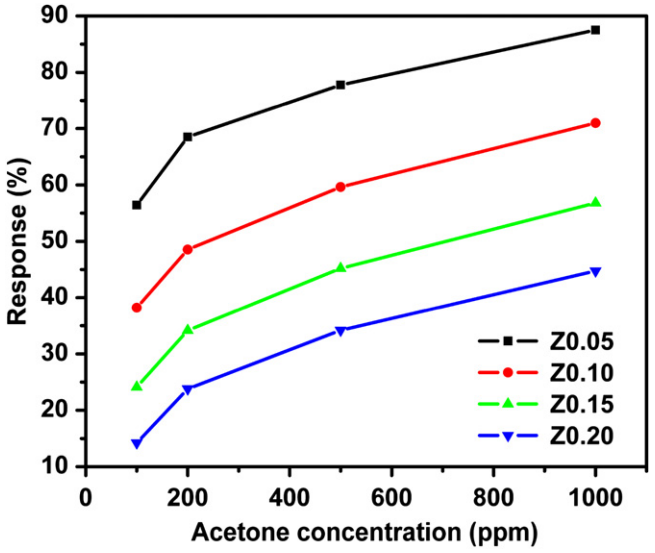

Fig. 5. Plot of response verses acetone concentration for different ZnO samples.

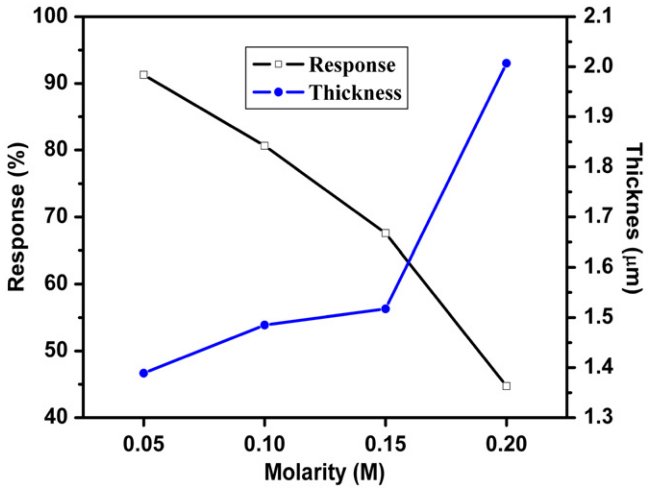

Fig. 6. Plot of film thickness and response as a function of molarity of the solution.

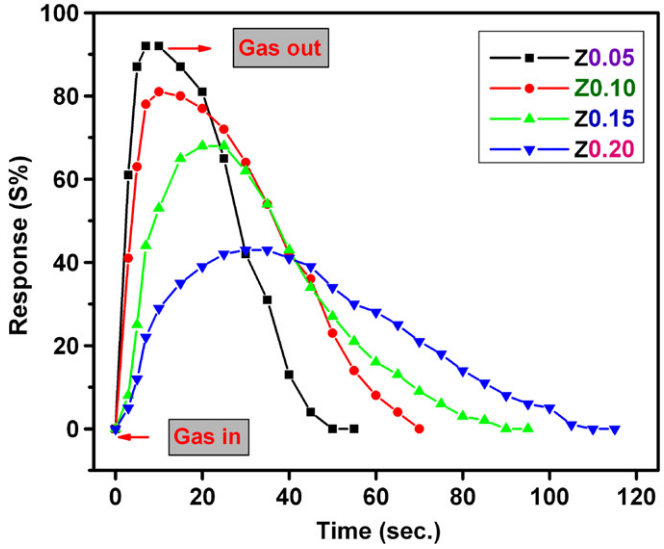

Fig. 7. Transient response characteristics of different ZnO samples towards 2000 ppm of acetone at their respective optimum operating temperatures.

observed for Z0.05, Z0.10, Z0.15 and Z0.20; with recovery time of 52 s, 68 s, 90 s, and 109 s respectively. The faster response and recovery in case of Z0.05 is attributed to the small crystallite size and highly porous nature exhibited by it. Fast and easier gas diffusion to grain boundaries would enable the gas to be oxidized immediately, giving faster response. The gas sensing mechanism of ZnO-based sensors belongs to surface controlled type in which change in resistance occurs due to adsorption of oxygen, and test gases, and subsequent reaction between them [35]. In the presence of air atmosphere, oxygen species are adsorbed on the surface of ZnO, which generates chemisorbed oxygen species (O_2^-,O^{2-},and O^-) and thus the resistance of ZnO will increase due to extraction of electrons from the conduction band. When sensors are exposed to air, the surface of the ZnO nanorods adsorbs atmospheric oxygen on the film surface. This adsorbed oxygen captures electrons from the conduction band of the ZnO and becomes oxygen ions (O^- or O_2^-). The reaction mechanism is as follows [36]:

$$O_{2(ad)} + 2e^- \rightarrow 2O_{(ads)}$$

This forms depletion layer on the surface of ZnO nanostructures, causing reduced carrier concentration. Therefore, resistance of ZnO in ambient air is higher than that in vacuum. The introduction of acetone vapor on the surface of ZnO causes adsorption and reaction between adsorbed oxygen and molecules of acetone. The electrons are released back to the conduction band which causes the decrease in resistance of the material. The overall reaction of acetone molecules with adsorbed oxygen can be explained as follows [37]:

$$CH_3COCH_3 + 8O^-_{(ads)} \rightarrow 3CO_2 + 3H_2O + 8e^- \quad (3)$$

As products of the reaction are CO_2 and H_2O, they can be easily desorbed from the surface and reproducible response–recovery characteristics are achieved without any difficulty.

4. Conclusions

In summary, thin films of nanocrystalline ZnO with hexagonal morphology were successfully deposited by an aqueous chemical route. Structural study revealed formation of nanocrystalline ZnO with predominant orientation along the (002) plane. Structural, morphological and gas response properties were strongly influenced by concentration of precursor solution. The results demonstrated that the ZnO sensor deposited at 0.05 M concentration exhibited excellent acetone response with small response and recovery time as compared with the sensors deposited at other concentrations. In conclusion, the aqueous chemical route proved its versatility in yielding nanocrystlline thin film which can stand as reliable sensor elements in acetone sensing applications.

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