Studies on ZnO Nanomaterial For Gas Sensor Application

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Abstract: *Zinc is polycrystalline in nature, possessing hexagonal wurzite structure with (002) preffered oriented phase with a dominate peak at a Bragg angle around 34.2. Zinc oxide wide band gap 3.3 ev at room temperature. ZnO is colorless & transparent versatile material. It has good electrical & optical properties. ZnO nanomaterials are widely used to fabricate efficient gas sensors for the detection of various hazardous and toxic gases.*

Key Words: *Zinc oxide, Gas sensors, Sol gel method.*

1. INTRODUCTION:

Zinc oxide (ZnO) is an II-VI n-type semiconductor having a band gap of ~ 3.3 eV at room temperature, large exaction binding energy (60 meV) and optical transparency. It crystallizes in either a cubic zinc-blende or hexagonal wurtzite structure where each anion is surrounded by four cations at the corners of a tetrahedron, and vice versa. The Properties of ZnO with a direct band gap and high exaction binding energy are much higher than those of other widely used wide-band-gap materials, for example, ZnSe (20 meV) And GaN (21 meV) [1,2] Therefore, wide-band-gap properties ZnO enable it to become a potential material for short-wavelength optoelectronic devices, such as UV lasers, blue to UV light-emitting diodes and UV detector, which can be applied in high density data storage systems, solid-state lighting, secure communications and bio- detection [3,4].

1.1 Acetone Gas sensing Mechanism:

The sensing mechanism of the film to acetone may be described as follows. At first, oxygen is adsorbed on the zinc oxide surface when the film is heated in air. At lower temperatures, the surface reactions proceed too slowly to be useful. The adsorption of oxygen forms ionic species such as O^{2-}, O^{2-} and O^{-} which have acquired electrons from the conduction band and which desorbs from the surface at 80, 130 and 500 ^{0}C, respectively. So in the temperature range used, only O^{-} species which are the most stable ones will react with acetone. The reaction kinematics is as follows [5].

$$O_2 \text{ (gas)} \iff O_2 \text{ (absorbed)}$$
$$O_2 \text{ (absorbed)} + e^- \iff O_2^-$$
$$O_2^- + e^- \iff 2O^-$$

The reaction mechanism between acetone and ionic oxygen species may take place by two different ways having different rate constants (k) depending upon the temperature [6,7]

$$CH_3COCH_3 \text{ (gas)} + O^- \rightarrow CH_3CO + CH_2 + OH^- + e^-$$
$$k = 1.0 \times 10^{12} \exp(-21000/RT) \text{ [cm3/mol s]}$$
$$CH_3COCH_3 \text{ (gas)} + OH^- \rightarrow CH_3CHO + CH_3O^-$$
$$k = 2.0 \times 10^{12} \exp(-63000/RT) \text{ [cm3/mol s]}$$
$$CH_3CHO + O \text{ (bulk)} \rightarrow CH_3COOH + O \text{ (vacancies)}$$
$$CH_3COCH_3 \text{ (gas)} + O^- \rightarrow CH_3 + CO + CH_3O^- + e^-$$
$$k = 1.0 \times 10^{12} \exp(-42000/RT) \text{ [cm3/mol s]}$$
$$CH_3 + CO \rightarrow + CH_3 + CO$$
$$k = 2.0 \times 10^{11} \exp(-15000/RT) \text{ [1/s]}$$
$$CO + O^- \rightarrow CO_2 + e^-$$

2. EXPERIMENTAL :

The sol-gel method was developed in the 1960s mainly due to the need of new synthesis methods in the nuclear industry. A method was needed where dust was reduced (compared to the ceramic method) and which needed a lower sintering temperature. In addition, it should be possible to do the synthesis by remote control.

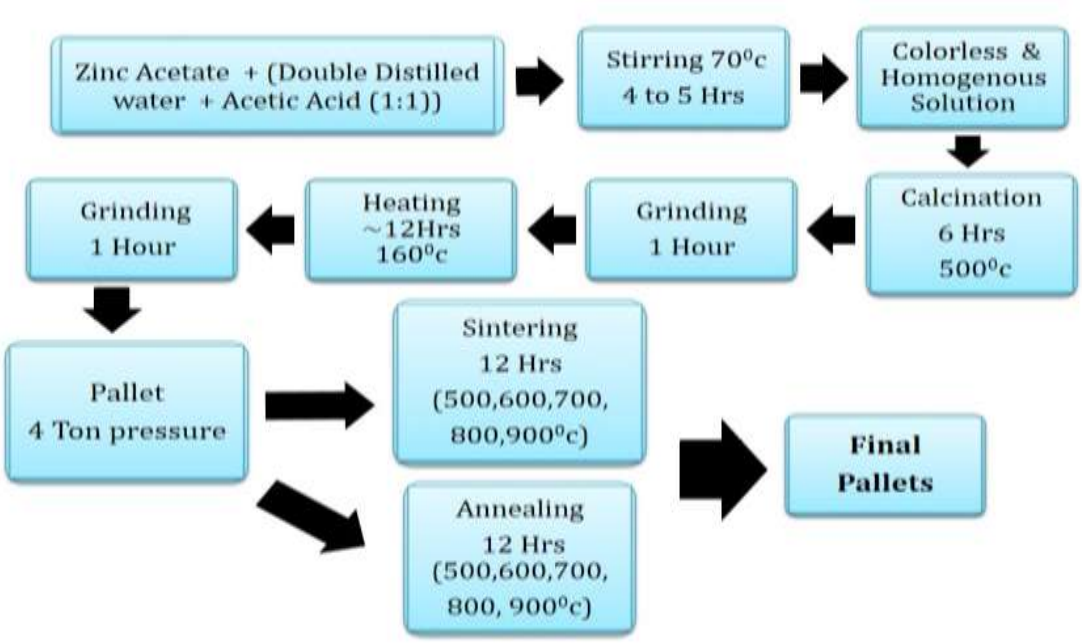

Fig.1 Sol Gel Method

3. RESULTS:

ZnO samples were prepared in polycrystalline form using modified sol-gel method employing acetate precursor route [8]. Initially, stoichiometric proportion of $Zn(CH_3COO)_2 \cdot H2O$ was dissolved in acetic acid and double distilled water (DDW) in 1:1 volume ratio resulting in 0.4M solution at 90 °C. After condensation and gelation, the solution was dried in air at 150 °C and the product powder was calcined at 400 °C for 6 hour. After the grinding of the well calcined powder of ZnO, the final product was pelletized followed by final sintering at 500 °C - 900 °C in air for 6 hour. Hereafter, ZnO nanostructured samples will be referred as Z5, Z6, Z7, Z8 and Z9, respectively, for 500 °C - 900 °C sintering temperatures. All the samples were characterized for their structural and microstructural properties using X-ray diffraction (XRD: Model: PANalytical PW3040/60 X'pert PRO), transmission electron microscopy (TEM: Model: JEOL, JEM 2100).

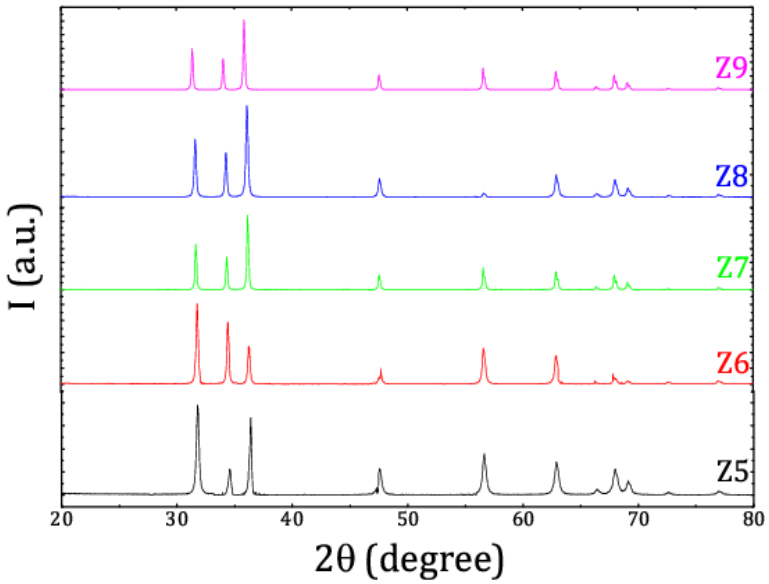

Fig. 2 XRD patterns of ZnO samples sintered at various temperatures

XRD was performed at room temperature. Figure 2 shows the XRD pattern of all the ZnO samples understudy. All the samples show single phasic nature without any detectable impurities within the measurement range studied.

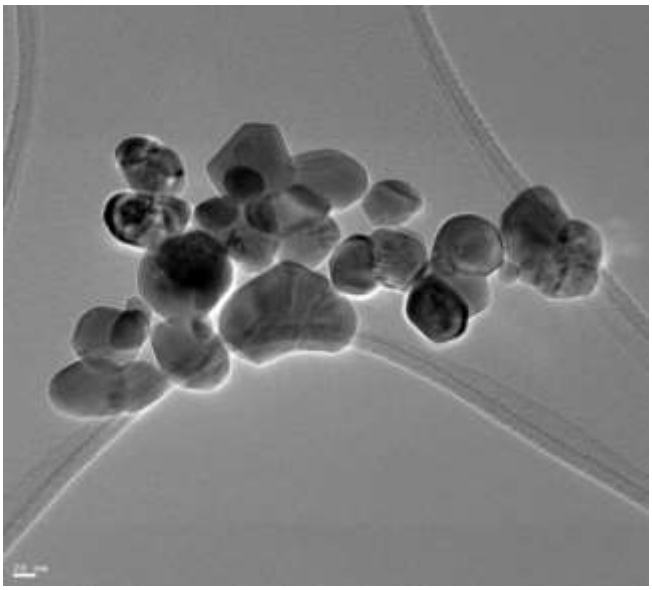

Fig. 3: Typical TEM image of ZnO sample sintered at 900ºC

TEM measurements were carried out at room temperature for all the ZnO samples. Figure 3 shows typical TEM images of ZnO samples sintered at 900ºC. It is clear from the image that ZnO sample possesses nanostructured particle formation having the size in the range of 100-300nm. In addition, particles are in spherical shape with clear crystallographic orientations throughout the sample studied.

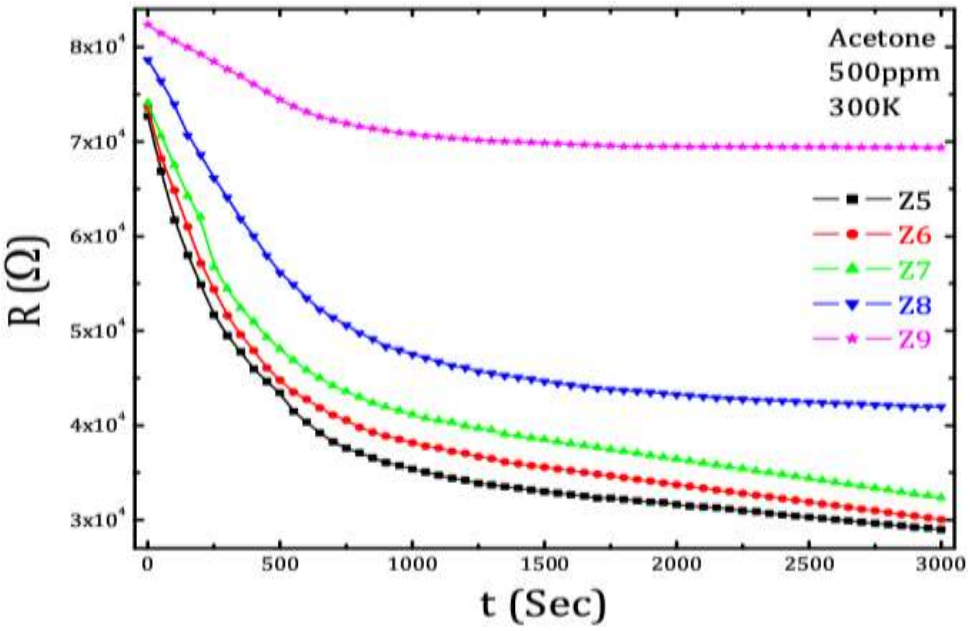

Fig.4: Variation in surface resistance of nanostructured ZnO samples sintered at various temperatures

Figure 4 shows the variation in surface resistance of all the nanostructured ZnO samples sintered at various temperatures, measured after 50sec up to 3000sec, in the presence of acetone gas once filled in the chamber with 500ppm pressure. It can be seen from figure 4 that with increase in sintering temperature, the surface resistance increases, throughout the time measured. The variation in resistance behavior with time can be distinguished into two active regions – (i) higher slope (dR/dt) of lower time scale region below 500sec and (ii) comparatively lower slope of higher time scale region above 500sec. These observations indicate that particle morphology as well as defect density play an important role in sensing the acetone gas for the presently studied nanostructured ZnO samples.

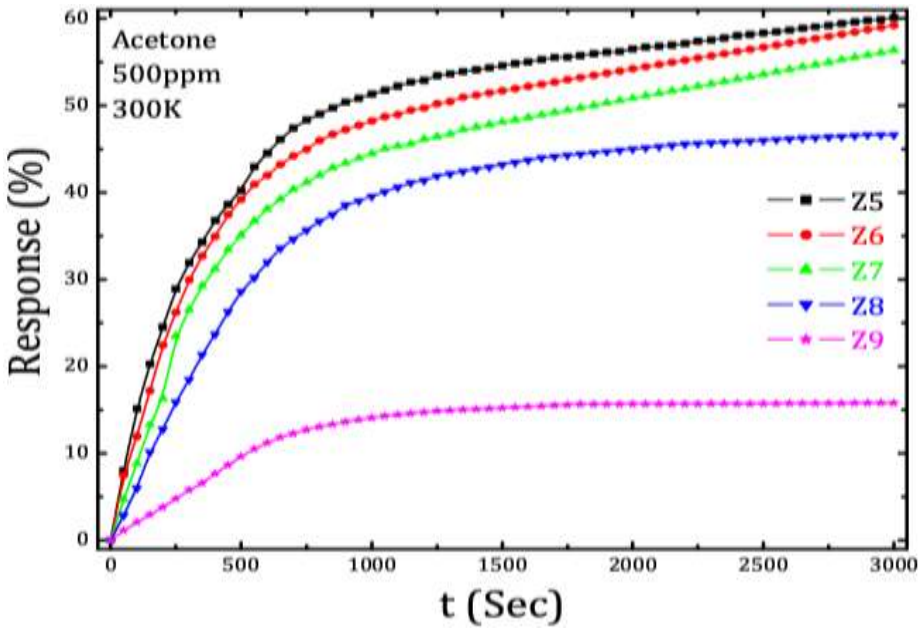

Fig.5: Time dependent variation in nanostructured ZnO samples sintered at various temperatures

To understand the time dependent variation in the gas sensing response of the presently studied nanostructured ZnO samples sintered at various temperatures, the gas sensing response was calculated using the formula: Response (%) = [{(R_a – R_g) / R_a} × 100], where R_a and R_g are the values of resistance measured in air and under exposed acetone gas[9]. Figure 5 shows the variation in gas sensing response with time for all the nanostructured ZnO samples understudy. It can be seen that below 500 sec, almost all the nanostructured sensors exhibit sharp increase in sensing response which is due to the large reaction rate of acetone traces with the largely available oxygen species on the surfaces of the ZnO particles. At higher time scale, above 500 sec, the reaction between the acetone traces and oxygen species gets reduced due to reduced number of oxygen species on the surface and reaction becomes almost saturated.

4. CONCLUSION:

XRD measurements reveal the single phase nature of the samples while Rietveld analysis of the XRD results justifies the hexagonal wurtzite structure of the samples understudy having $P6_3mc$ space group (no. 186). The crystallite size (CS) increases from 36.44nm (Z5) to 46.48nm (Z9), calculated using the Scherer's formula. TEM image carried out at room temperature suggests the spherical shape of the particles. Clear crystallographic orientations can be seen from the TEM image obtained. The variation in surface resistance in air has been discussed in detail on the basis of sintering temperature effect and defect density exists. Time dependent variation in the surface resistance for all the nanostructured samples and their gas sensing response, calculated, have been understood on the basis of adsorption of oxygen species, reaction between the acetone traces – oxygen species and particle morphology (including boundary density and surface area available) in detail.

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