

# Synthesis and Characterization of Nanocrystalline Zinc Oxide Thin Films for Ethanol Vapor Sensor

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## Abstract

ZnO nanoparticles as gas sensors have a property of changing the electrical conductivity of the sensing element on exposure to gas atmospheres. The number, density and size distribution of particles plays a key role in gas sensing applications. The gas sensing mechanism mainly depends upon the morphology, ion occupancy and the operating temperature, which helps in adsorbing the OH- groups on the surface of oxide materials. The ethanol vapor sensing measurements have been carried out on the ZnO pellet with silver pasted electrodes on both the ends. The change in electrical resistance was used as the measure of ethanol vapor response at different temperatures in the range of 25°C to 45°C at an interval of 5°C under an ethanol concentration of 25.02, 50.05, 75.08, 100.11 and 150.17 ppm. These results showed that the indium zinc oxide film based ethanol sensor has high response quick recovery time and selectivity to the ethanol vapor.

**Keywords:** ZnO; Nano particles; Ethanol gas sensor; X-RD; TEM

## Introduction

Zinc oxide (ZnO) nanoparticles have importance due to their vast area of applications, e.g., gas, chemical and bio-sensors, cosmetics, storage, optical and electrical devices, window materials for displays, solar cells, and drug-delivery [1-5]. ZnO is an attractive material for short-wavelength opto-electronic applications owing to its wide band gap 3.37 eV, large bond strength, and large exciton binding energy (60 MeV) at room temperature [6]. As a wide band gap material, In addition, due to its non-centrosymmetric crystallographic phase, ZnO shows the piezoelectric property [7,8], which is highly useful for the fabrication of devices, such as electromagnetic coupled sensors and actuators. ZnO have extensive applications in water purification [9]. ZnO is inexpensive n-type semiconductor [10]. Nanostructures made of ZnO have attracted significant attention due to their proposed applications in the low voltage and short-wavelength 368 nm electro-optical devices transparent ultraviolet UV protection films and gas sensors. Therefore, several new routes have been developed to synthesize ZnO-NPs, such as, sol-gel, sol-gel combustion, chemical precipitation [11,12], hydrothermal, solvothermal, chemical vapor deposition (CVD), a sonochemical method, and thermal oxidation [13-15]. Sol-gel method is widely adopted for the fabrication of transparent and conducting oxide due to its simplicity, safety, no need of costly vacuum system and hence cheap method for large area coating. Next, ethanol sensing property of ZnO sample (i.e. ZnO quantum dots embedded in PVP) has been examined by exploring the variation of sample resistance with time in presence of ethanol vapour [7]. Vapour sensing property of semiconductor is purely a surface phenomenon.

The main advantages of chemical sensors are their low price, small size, high sensitivity, and low power consumption. The use of nano-structured materials for the sensing device is envisaged to further improve the sensitivity of these devices. ZnO morphology could generate a large number of active centers that enhanced the ethanol gas response. Ethanol is one of the most commonly used and widespread alcohols, and thus there is a need to develop sensors for its detection. The most common application of ethanol sensors is as a breath analyzer, since the ethanol vapor inhuman breath is said to be correlated with the concentration in the blood. A semiconductor gas sensor possesses a property of changing the electrical conductivity of the sensing element

on exposure to different gas atmospheres. The gas sensing mechanism mainly depends upon the morphology, ion occupancy, the operating temperature, which helps in holding the OH groups on the surface of oxide materials. One of the requirements of the gas sensors is low power consumption, because the sensors need to work reliably and continuously. A low resistance material has lower driving power when it is used as a sensor. Appropriate donor doping can produce the electronic defects that increase the influence of oxygen partial pressure on the conductivity. The higher operating temperature (approximately 400°C) and poor sensitivity are some of the major concerns in using ZnO as sensing layer. The ZnO compound has been considered a potential gas detection device because it exhibits a good chemical sensitivity to different analyte gases, fast response time, and a shorter recovery time.

The optimum working temperature of semiconductor gas sensor depends upon the gas atmosphere and on the properties of the sensing material. Ethanol is one of the most commonly used and widespread alcohols, and thus there is a need to develop new generation sensors for its detection. The most common application of ethanol sensors is as a breath analyzer, since the ethanol vapors in human breath is said to be correlated with the concentration in the blood.

## Experimental measurements

Nanocrystalline (NC) ZnO thin films was grown by sol-gel process [16,17]. Zinc acetate was dissolved in 100 ml zinc acetate as precursor [Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O]. The pH value of the solution was between 3.7 and 4.0. The mixture was heated at 80°C under continuous stirring for 3 h after which precipitate occurred. Then the solution is left for 30 minutes which results in the formation of white bulky solution. The

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solution is then washed 8–10 times with distilled water and filtered in a filter paper. The residue obtained is put for drying in oven at a temperature of about 95°C for 8 hr. The precipitates were recovered, thoroughly rinsed in distilled water followed by drying wafer at 100°C and subsequent annealing at 100°C, 200°C, 300°C and 400°C for one hour to optimize temperature suitable for good quality ZnO films. Finally the sensing response of nanorods with nanoparticles of zinc oxide to ethanol at different temperatures has also been compared.

Ten coatings were done to obtain the optimum thickness of the film needed for characterization. The spherical zinc oxide nanoparticles were produced using different concentration of zinc acetate which was used as the zinc source by simple sol gel method which is short time process and cost effective [18]. The film thickness was 250 nm, 256 nm and 334 nm by ellipsometric investigations. The structural, morphological and optical properties of these particles were characterized by XRD, TEM and UV-VIS techniques (Figure 1).

Zinc oxide crystallizes in a wurtzite structure with alternating planes of tetrahedral coordinated  $Zn^{2+}$  and  $O^{2-}$  bonded alternately along c-axis of hexagonal unit cell with  $a_0=0.3250$  nm and  $c_0=0.5207$  nm. The cause for the natural N-type nature of ZnO is due to the sensitiveness of ZnO lattice constants to the presence of structural point defects (vacancies and interstitials) and extended defects (threading/planar dislocations) that are commonly found in ZnO resulting in a non-stoichiometric compound  $Zn_{1+d}O$  with an excess zinc.

The end product was pale white precipitate. The calcinated powders are studied using different characterization techniques. Confirmation of pure ZnO phase is verified by XRD analysis.

## Results and Discussion

### XRD pattern

Synthesized NC-ZnO particles are analyzed on the basis of their crystallinity, crystallite size, band gap and structural properties. X-Ray Diffraction pattern (Figure 2) is used to calculate crystallite size and variation in band gap. Unique characteristic X-ray diffraction pattern of each crystalline solid gives the designation of “fingerprint technique” to XRD for its identification. The XRD of the annealed film shows the peaks corresponding to ZnO, confirming that the Zn film has been completely oxidized to form ZnO.

The XRD pattern consists of a single (002) peak which occurred due to ZnO crystals and grows along the c-axis. High purity and crystallinity of the prepared ZnO NPs confirms the sturdy and clear peak. For other

impurities no characteristic peak was accessible [19]. The deviation of the lattice parameters is caused may be due to presence of various point defects such as zinc antisites, oxygen vacancies, and extended defects, such as threading dislocation. With increasing calcinations temperature peak height increases and FWHM decreases as result diffraction peaks become stronger and sharper, thereby indicating that the crystal quality has been improved and the size of particles become bigger [20-24]. Moreover, all diffraction peaks of the product show stronger peak intensities, indicating that the obtained ZnO nanoparticles have high crystallinity.

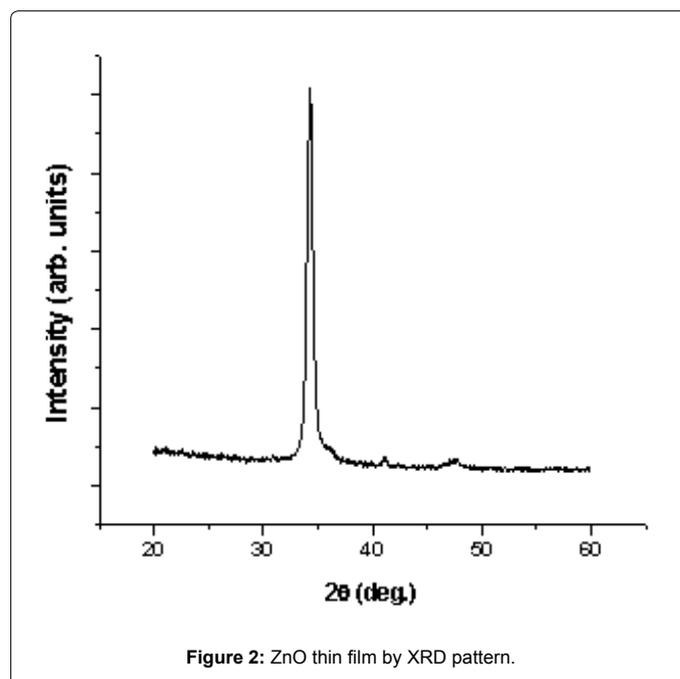
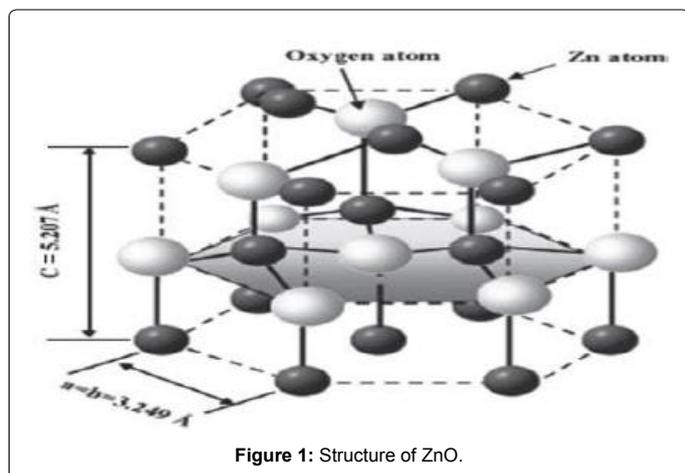
### EDX and UV-VIS spectra

The EDX of the ZnO sample was done by the SEM machine. The EDX reveals that the required phase has present. Both Zinc (Zn) and Oxygen (O) is present in the sample. Again the graph shows the presence of ZnO nanoparticles. This is due to the substrate over which it was held to do the SEM characterization. Energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample.

The size of the ZnO nanoparticles plays an important role in changing the entire properties. Thus, size evolution of semiconducting nanoparticles becomes very essential to explore the properties of the materials. UV-visible absorption spectroscopy is widely being used technique to examine the optical properties of nanosized particles. The absorption spectrum of ZnO nanopowder is shown in Figure 3. It exhibits a strong absorption band at about 355 nm. An excitonic absorption peak is found at about 258 nm due to the ZnO nanoparticles which lie much below the band gap wavelength of 358 nm.

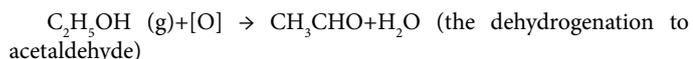
### Resistance vs. time of EtOH sensor

The gas sensing mechanisms normally accepted for semiconductor sensors assume that the oxygen adsorbed on the surface of the oxide removes some of the electronic density and thus decreases the material's conductivity. When reduction gas molecules come into contact with this surface, they may interact with this oxygen, leading to an



inverse charge transference [20]. Upon the return of the electrons to the conduction band, conductivity increases. This utilizes the gas-induced resistance variations in potential barrier height at grain boundaries (i.e. changes in thickness of the space charge layer) to detect ethanol vapors in air (Figure 4).

The change in electrical resistance was used as the measure of ethanol vapor response at different temperatures in the range of 25°C to 45°C at an interval of 5°C under an ethanol concentration of 25, 50, 75, 100 and 150 µL. The possibility of a reaction of ethanol with the ZnO nanoparticles sensing layers can be explained as two oxidation states [21-22]:



in which [O] represents the surface oxygen ions.

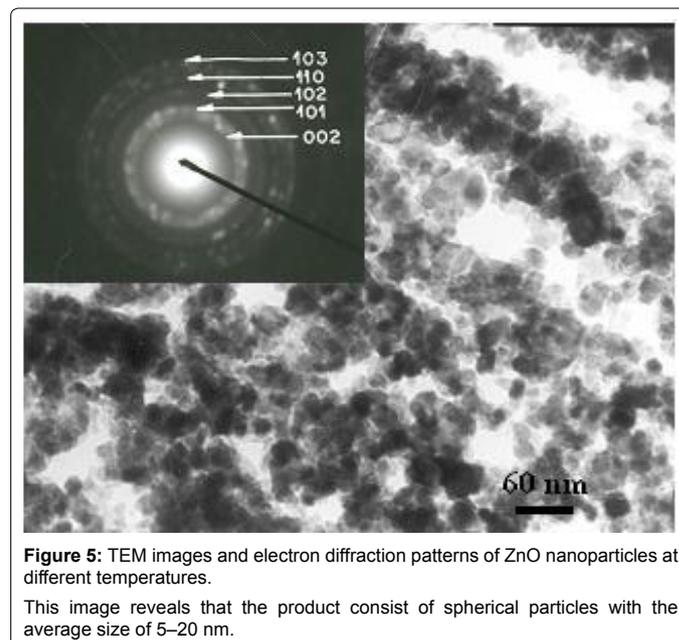
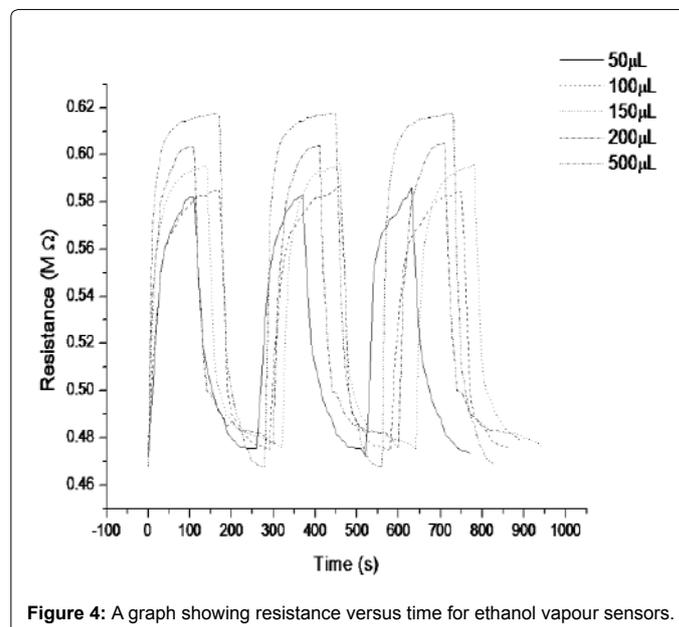
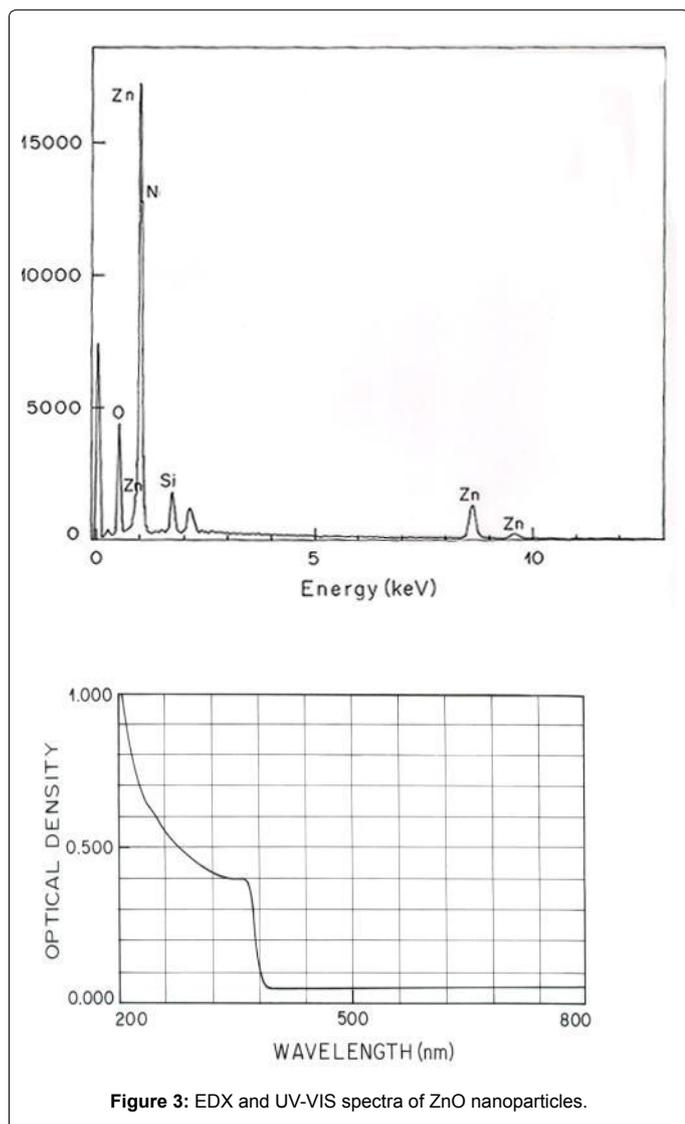
The first reaction is a process initiating the oxidation by the dehydrogenation to CH<sub>3</sub>CHO intermediate, and the second reaction

is initiated by the dehydration to C<sub>2</sub>H<sub>4</sub>. But the selectivity for the two reactions is initiated by the acid-base properties of the oxide surface. This behavior of the sensors is attributed to the increase of concentration of oxygen species on the surface by replacing adsorbed hydroxyl groups and conversion of adsorbed oxygen species by following reactions: O<sub>2</sub>(gas) → O<sub>2</sub>(ads) → 2O<sup>-</sup>(ads) → 2O<sub>2</sub><sup>-</sup>

### TEM analysis

Transmission electron microscope examination can yield the information like topography, morphology, composition as well as crystallographic information's (Figure 5).

In TEM there is no change in the refractive index of the medium when the illumination beam is deflected, the vacuum in the lens is the same as the vacuum in the column.



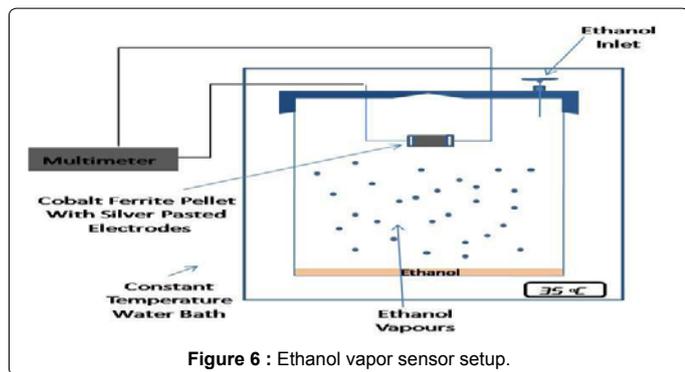


Figure 6 : Ethanol vapor sensor setup.

### Analysis of ethanol vapour

The entire setup for measuring sensitivity of the ethanol vapour sensor is shown in Figure 6. The resistance of the sensor is measured, with respect to time upto the saturation of the sensor to the gas, and then the air was allowed into the chamber. The resistance measurement of the sensor is continued up to the complete recovery of the sensor resistance to the air ambient value. The measurement was repeated for number of cycles to determine the cyclic nature of the sensor. The resistance of the sensor is measured for different temperatures in the range of 25°C to 45°C at an interval of 5°C under an ethanol concentration of 25.02, 50.05, 75.08, 100.11 and 150.17 ppm. in ethanol vapor-air ambient. Gas response (S) is defined as the ratio of the change in resistance of the sensor on exposure to the target gas to the original resistance in air.

### Conclusion

In this study, the structures and sensing properties of ZnO nanoparticles thin films as an ethanol vapor gas sensor obtained by characterization were investigated. XRD, TEM, EDX and UV visible characterization reveals surface morphology and particles size of ZnO nanoparticles. The film exhibited good sensitivity to the ethanol vapors with quick response-recovery characteristics, and it was found that the sensitivity and selectivity is increased ZnO nanoparticles seems to be a promising semiconducting material for the detection of ethanol vapor. The change in electrical resistance was used as the measure of ethanol vapor response at different temperatures in the range of 25°C to 45°C at an interval of 5°C under an ethanol concentration of 25, 50, 75, 100 and 150 µl. These results showed that the indium zinc oxide film based ethanol sensor has high response quick recovery time and selectivity to the ethanol vapor.

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