INVESTIGATIONS ON ELECTRICAL APPLICATION, ACTIVATION ENERGY AND HUMIDITY/GAS SENSING STUDIES OF SYNTHESIZED AL DOPED ZNO NANOMATERIALS

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Abstract

In the present work, sol-gel method is used for obtaining synthesized Al doped ZnO nanocrystalline powders. In the experiments, zinc acetate ($Zn(CH_3COO)_2.2H_2O$) is used as starting material, methanol as organic solvent and mono ethanol ammine as surfactant. Aluminium sulphate is used for doping Al. All the sols were mixed in appropriate proportions so that there is 8% Al doping in ZnO. Prepared nanopowder was given pellet shape by applying pressure of 260 MPa. Pellets were annealed in air at different temperatures from 300ºC to 600ºC for 3 hours. Pellet samples made were categorized AZ-8 (8% Al doped in ZnO).

The activation energy values for sample AZ-8 from the Arrhenius plot is found to be 0.036 eV for temperature range 60°C to 140°C and 0.016 eV for temperature range 180°C to 200°C. This sensing element shows lower values of activation energies in the two regions indicating that this sensing element has lower operating temperatures and may be used at room temperature as well. A sudden increase in the current has been observed from the V-I characteristics graph of this sensing element.

The humidity sensing studies of these samples were also analyzed. The sample AZ-8 annealed at 600ºC is showing the best results with sensitivity of 23.60 MΩ/%RH. The crystallite size from XRD for the sensing element AZ-8 is in the 13-38 nm range. The average grain size as measured from SEM micrograph of this sensing element is found to be 95 nm suggesting agglomeration of the crystallites to form larger grains.

Keywords: Activation Energy, Doping, Sensing Element, Sol-gel, V-I Characteristics

1. INTRODUCTION

Analysis on electrical applications of the nanomaterials is very important as these nanomaterials are used in the development of the gas/humidity sensors. Activation energy gives us a deep understanding of the electrical properties of the nanomaterials. Zinc Oxide (ZnO) is one of the most important metal oxides having various applications in gas/humidity sensing [1-2]. ZnO is a very versatile II-VI compound semiconductor with a wide bandgap of about 3.3 eV. Need for gas/humidity measurement devices and control systems have increased in various industries like foodstuff, textile, sophisticated electronic devices production, etc. Gas/Humidity systems are also used in various scientific research laboratories worldwide. Numerous research labs all over the world are giving their best efforts to find excellent materials that show superb sensitivity, low hysteresis, and properties that are stable. Ceramic material based gas/humidity sensors based on porous and sintered oxides have attracted much attention due to their chemical and physical stability. ZnO is a versatile material having a wide band gap. It is a useful oxide because of its typical properties, e.g., direct band gap, transparency in the visible range, absence of toxicity, abundance in nature, high electrochemical stability [3]. Resistive or impedance type humidity sensors [4-5] are becoming more prevalent due to better quality. Zhang *et al.* studied humidity sensing properties of ZnO nanorod and nanowire films-coated quartz crystal microbalance (QCM). They found that the frequency shift of the ZnO nanostructures-coated QCM linearly decreased with increasing relative humidity over the range of 5%–97% RH [6]. Yawale *et al.* doped semiconducting materials SnO_2 and ZnO with TiO_2 and Al_2O_3 and screen printed them in the form of a film. DC-electrical resistance of the films was measured in the presence of humidity. They found SnO_2-5Al_2O_3 and ZnO-5Al_2O_3 to be good sensing materials for humidity. Rutile and hexagonal structures of SnO_2, ZnO and Al_2O_3 and their nanometer grain sizes have been found to be responsible for the formation of nanometer size pores, which ultimately adsorbed water. The adsorption of water (physisorbed water) on a hydroxylated surface causes electron injection [7]. Li *et al.* investigated the complex impedance spectra of the thin-film humidity sensors prepared using *in situ* synthesized inorganic/organic nanocomposites of sodium polystyrenesulfonate (NaPSS) and ZnO. The logarithm of the impedance of sensor based on composite film changed linearly by four orders of magnitude over the humidity range (11%–97% RH) [8]. Jeseentharani *et al.* investigated humidity sensing properties of the composites prepared by mixing 1:1 mole ratio of CuO-ZnO, CuO-NiO, and NiO-ZnO compound. The samples were sintered at 800°C for 5 h and then were subjected to resistance measurements as a function of relative humidity (RH) in the range of 5%–98% RH. Among the three composites, CuO-NiO compound possessed the highest humidity sensitivity. The response and recovery times of the CuO-NiO composites were 80 and 650 s, respectively [9]. Steele *et al.* fabricated capacitive humidity sensors using countersunk interdigitated electrodes coated with amorphous nanostructured TiO_2, SiO_2 and Al_2O_3 thin films grown by glancing angle deposition. The sensor utilizing TiO_2, exhibited the largest change in capacitance, increasing exponentially from ~1 nF to ~1 muF for an increase in relative humidity from 2% to 92% [10]. Doping is an attractive and effective method for manipulating different applications of semiconductors. Doped zinc oxide exhibits various properties, different types of morphologies and has many applications.

2. SAMPLE PREPARATION AND EXPERIMENTAL PROCESS

The samples of synthesized Al doped ZnO nanomaterials were prepared through chemical reaction route. In the present work, sol-gel method is used for obtaining synthesized Al doped ZnO nanocrystalline powders. In the experiments, zinc acetate ($Zn(CH_3COO)_2.2H_2O$) is used as starting material, methanol as organic solvent and mono ethanol ammine as surfactant. Aluminium sulphate is used for doping Al. All the sols were mixed in appropriate proportions so that there is 8% Al doping in ZnO. Prepared nanopowder was given pellet shape by applying pressure of 260 MPa in a hydraulic pressure machine at room temperature. Pellet samples prepared were in the disc shape having a diameter of 12 mm and thickness 2 mm. Pellets were annealed in air at different temperatures from 300°C to 600°C for 3 hours in an electric muffle furnace. Pellet samples made were labeled AZ-8 (8% Al doped in ZnO). After annealing, samples were analyzed for electrical applications, activation energy and also for humidity/gas sensing studies.

3. ACTIVATION ENERGY

For an n-type semiconductor, the variation of resistance with temperature is given by the relation:

$$\sigma = \sigma_o e^{-E/kt} \quad (1)$$

Here, $\sigma_o = 2\mu e[2\pi m^* (kT/\hbar 2)]^{3/2}$, E is the activation energy of electronic transport, m* is the effective mass, μe is the mobility of electron, e = electronic charge, k = Boltzmann's constant, $\hbar = h/2\pi$, where h is the Planck's constant. Equation (1) in terms of resistance may be written as

$$R = R_o e^{-E/kt} \quad (2)$$

$$\ln (R) = \ln(R_o) - E/kT \quad (3)$$

From the slope of the plot log(R) versus $1/T$ values of activation energy for electronic transport may be calculated. Fig. 4 shows graph between log(R) and $1000/T$. The activation energy values for sample AZ-8 from the Arrhenius plot is found to be 0.036 eV for temperature range 60°C to 140°C and 0.016 eV for temperature range 180°C to 200°C, indicating that there are two different inter-band transitions for electrons. Sample of Al doped ZnO nanomaterial shows lower values of activation energies in the two regions indicating that this sensing element has lower operating temperatures and may be used at room temperature as well. Figure 1 shows Arrhenius Graph for Activation Energy for sample AZ-8.

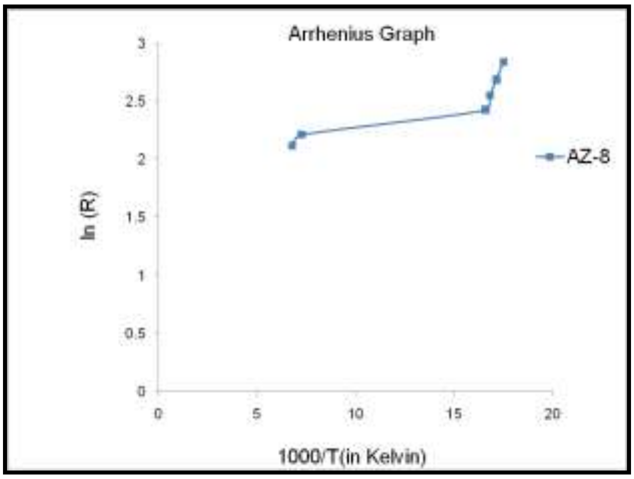

Fig.1 Arrhenius Graph for Activation Energy for sample AZ-8.

4. V-I CHARACTERISTICS ANALYSIS

From the V-I characteristics graph of the sample AZ-8, a sudden increase in the current has been observed. This sudden increase in current is due to the release of large number of electrons in the semiconducting material which is known as breakdown phenomenon. Figure 2 shows V-I characteristics graph for sample AZ-8. A sufficiently strong electric field enables tunneling of electrons from the valence to the conduction band of a semiconductor leading to a large number of free charge carriers. This sudden generation of carriers rapidly increases the current.

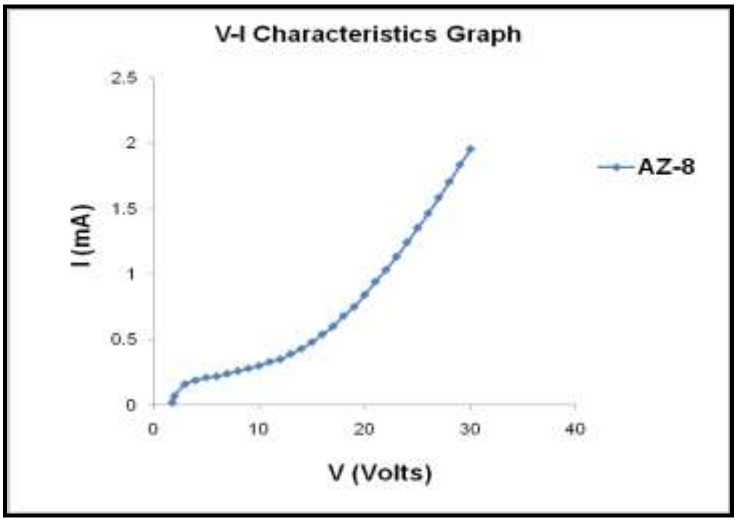

Fig.2 V-I Characteristics Graph for sample AZ-8.

5. SCANNING ELECTRON MICROSCOPE (SEM) STUDY

The study of the surface morphology of sample AZ-8 annealed at 600°C was carried out using SEM (LEO-430, Cambridge, England). Micrographs showed grains of ZnO scattered throughout the whole substrate forming a network of pores and flakes. These pores were expected to provide sites for humidity/gas adsorption. SEM micrograph for the sample AZ-8 annealed at 600°C is shown in Figure 3. The SEM micrograph of this sensing element shows great clustering and agglomeration of large number of crystallites. The average grain size calculated from SEM micrograph for this sensing element is 95 nm.

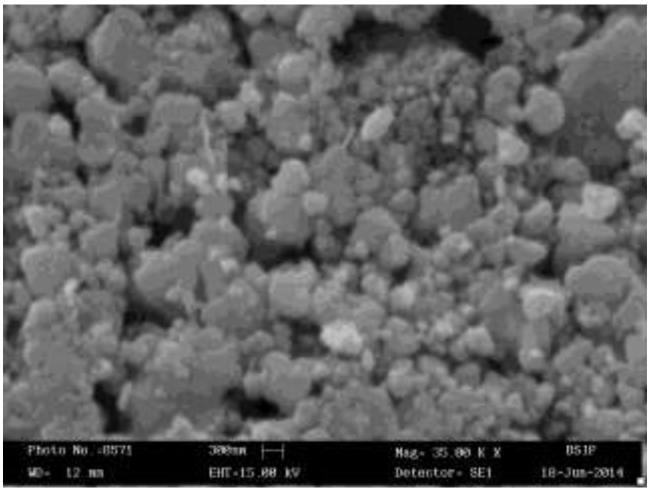

Fig.3 SEM of sample AZ-8 annealed at 600°C.

6. X-RAY DIFFRACTION ANALYSIS

X-Ray diffraction was studied using XPERT PRO-Analytical XRD system (Netherlands). The wavelength of the CuK_α source used was 1.54060Å. Figure 4 shows X-ray pattern for the sensing element AZ-8 annealed at 600°C. The average crystallite size of the sample was calculated using Scherrer's formula. The crystallite size for AZ-8 annealed at 600°C calculated from Scherrer's formula is in the 13-38 nm range.

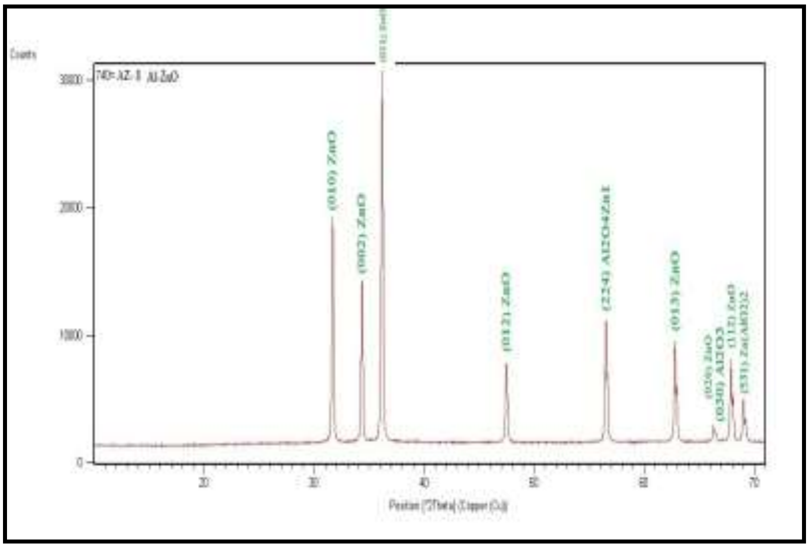

Fig.4 XRD of sample AZ-8 annealed at 600°C.

7. HUMIDITY/GAS SENSING INVESTIGATIONS:

Variation in resistance with the change in % RH for AZ-8 sensing elements is shown in Figure 5 for the humidification process. A continuous decrease in resistance with increase in the % RH is observed for all the sensing elements. As semiconducting dry oxide of ZnO nanomaterials is brought in contact with humid air, water molecules chemisorb on the available sites of the oxide surface leading to accumulation of electrons at the surface of ZnO. This causes resistance of the sensing element to decrease with increase in % RH. Sensing element AZ-8 annealed at 600°C shows low hysteresis value within acceptable limits. The sensitivity value increases with the increase in the annealing temperature. The best sensitivity value is 23.60 MΩ/%RH for the sample AZ-8 annealed at 600°C. The response and recovery time of this sensing element is found to be 78 seconds and 218 seconds, respectively. Figure 6 shows the sensitivity vs. temperature graphs for all the AZ-8 sensing elements annealed at different temperatures from 300°C to 600°C. Due to the excellent electrical properties and enhanced adsorption capability of the synthesized nanomaterials AZ-8 it can prove to be an excellent gas sensor for various gases.

A polynomial of sixth degree (given below) fitted to the curve of resistance versus %RH (Relative Humidity) graph of the sensing element AZ-8 annealed at 600°C.

$$y = -2\times10^{-07}x^6 + 5\times10^{-05}x^5 - 0.005x^4 + 0.331x^3 - 9.330x^2 + 77.77x + 1940 \quad (4)$$

Here, x= %RH (Relative Humidity) and y= Resistance in MΩ

Moreover, it is also found that a polynomial of third degree (given below) fitted to the curve of sensitivity versus temperature graph of the sensing element AZ-8.

$$y = 7\times10^{-07}x^3 - 0.001x^2 + 0.490x - 61.72 \quad (5)$$

Here, x= Temperature and y= Sensitivity in MΩ/%RH

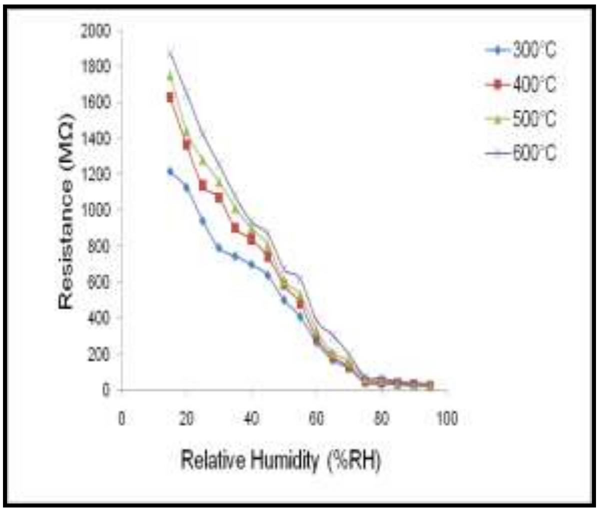

Fig.5 Variation of resistance with change in % RH for the sensing elements AZ-8 annealed at different temperatures for humidification process.

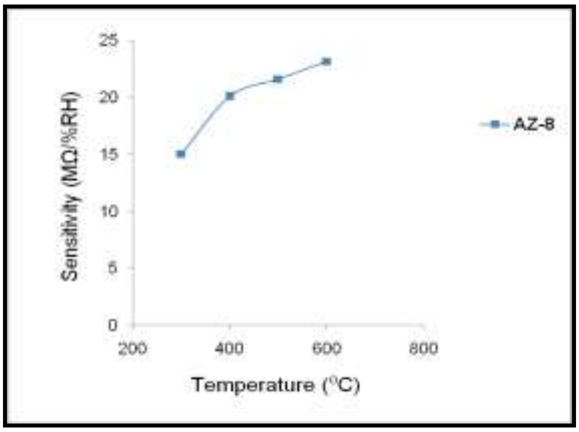

Fig.6 Variation of Sensitivity with Temperature for the sensing elements AZ-8 annealed at different temperatures for humidification processes.

8. RESULTS AND DISCUSSION

The values of activation energies for sample AZ-8 indicate the presence of two different inter-band transitions for electrons. From the lower values of activation energies for sample AZ-8 it is clear that this sensing element has lower operating temperatures and may be used at room temperature as well. A sudden increase in the current has been observed from the V-I characteristics graph of the sample AZ-8. This sudden increase in current is due to the release of large number of electrons in the semiconducting material which is known as breakdown phenomenon. A continuous decrease in resistance with increase in the % RH is observed for all the sensing elements. As semiconducting dry oxide of ZnO nanomaterials is brought in contact with humid air, water molecules chemisorb on the available sites of the oxide surface leading to accumulation of electrons at the surface of ZnO. This causes resistance of the sensing element to decrease with increase in % RH. Moreover, the synthesized nanomaterials AZ-8 can prove to be an excellent gas sensor for various gases due to its excellent electrical properties and enhanced adsorption capability.

CONCLUSION

The activation energy values for sample AZ-8 from the Arrhenius plot is found to be 0.036 eV for temperature range 60°C to 140°C and 0.016 eV for temperature range 180°C to 200°C. From the V-I characteristics graph of the sample AZ-8, a sudden increase in the current has been observed. Sensing element AZ-8 annealed at 600°C proves to be the best sensing element with sensitivity of 23.60 MΩ/%RH. Sensing element AZ-8 manifests lower hysteresis, less effect of ageing and higher reproducibility. The response and recovery time of this sensing element is found to be 78 seconds and 218 seconds, respectively. XRD pattern shows peaks of cubic gahnite and hexagonal corundum. As calculated from Scherrer's formula the crystallite size for this sensing element is in the 13-38 nm range and according to SEM micrograph average grain size is 95 nm.

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