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Characterization of nanosized zinc oxide based ammonia gas sensor

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ABSTRACT

Nano-powders Zinc Oxides (ZnO) were synthesized using chemical bath deposition method. Powders were then used to make thick films on glass substrate by using standard screen printing technique. These films were dried and fired at 400^{0}C temperature for two hours in air atmosphere. The Morphological, Compositional and Structural properties of the ZnO thick films were performed by Scanning electron microscopy (SEM), Energy Dispersive Spectroscopy (EDAX) and XRD technique respectively. Chemical composition of nano ZnO film samples changes with firing temperature showing non-stoichiometric behaviours. XRD study indicated the formation of polycrystalline ZnO films with hexagonal wurtzite structure. I have explored NH_3 sensing properties of the nano powders ZnO thick films at 50 ^{0}C temperature.

Keywords: Nano-powders ZnO; gas sensitivity; NH_3

INTRODUCTION

Zinc Oxide is a wide-band gap semiconductor metal oxide with wide range of optical and electronic applications. ZnO is an n-type semiconductor of wurtizite structure with direct band gap of about 3.37eV at room temperature. Polycrystalline ZnO has found numerous applications such as related to surface acoustic wave devices, piezoelectric devices, varistors, planar optical waveguides, transparent electrodes, UV photo detectors, facial powders, gas sensors, etc. Out of these applications of ZnO, gas sensor devices have the sensitivity to various gases, high chemical stability, and suitability for doping, non-toxicity and low cost [1, 2].

Zinc oxide (ZnO) is a multi functional material with a wide range of applications. ZnO films have attracted considerable attention because they can be made to have high electrical conductivity, high infrared reflectance and high visible transmittance. Low resistive zinc oxide films have been achieved by doping with different group III elements like aluminium, boron, indium, gallium or with group VII elements like fluorine[(1)]. Many techniques including evaporation, chemical vapour deposition, spray pyrolysis, sputtering, etc can be employed to deposit these films [2, 3, 4, 5]. Due to the transparency in the visible range, high electrical stability, direct band gap (3.37 eV), absence of toxicity, abundance in nature, etc., ZnO is one of the versatile and technologically importance materials [6]. Controlled synthesis of semiconductor nanostructures in terms of size and shape has been strongly motivated and novel applications can be investigated dependent on their structural properties [7–10]. Among various semiconductor nanostructures, variety of nanostructures of ZnO has been investigated presenting it as richest family of nanostructures. It crystallizes in a wurtzite structure and exhibits n-type electrical conductivity [11]. ZnO nanomaterials with one-dimensional structure, such as nanowires or nanorods, are especially attractive due to their tunable electronic and opto-electronic properties, and the potential applications in the nanoscale electronic and opto-electronic devices [12].

Window layer [13], varistor [14], gas sensor [15-17], etc., are the reported applications. Researchers are now probing on this material as one of the alternative photoanode for dye-sensitized solar cells [18-20]. Zinc oxide has proven itself as one of the competitive and promising candidates to replace expensive materials like CdS, TiO2, GaN, SnO2, and In2O3 for applications such as solar cells [21], photocatalysis [22], ultraviolet laser [23, 24], transparent conductive oxides [25], spintronics [26], and gas sensors [27]. For gas sensor application, SnO_2 has been the most investigated material. However, ZnO is particularly applicable to gas sensors because of its typical properties such as resistivity control over the range 10^{-3} to 10^{-5} cm, high electrochemical stability, absence of toxicity, and abundance in nature [28].

Zinc Oxide nanostructures could be synthesized by several techniques such as vapor deposition, oxidation, sputtering, and pulse laser deposition.

Several deposition methods have been used to grow undoped and doped ZnO films such as Spray pyrolysis, evaporation, chemical vapour deposition, magnetron sputtering, pulsed laser deposition, sol-gel technique, screen printing technique [29].

The exposure of ammonia causes chronic lung disease, irritating and even burning the respiratory track, etc. Therefore all industries working on and for ammonia should have an alarm system detecting and warning for dangerous ammonia concentration. It is therefore, necessary to monitor ammonia gas and to develop the ammonia gas sensor.

The aim of present study is to prepare ZnO thick films of nano-powders by screen printing technique on glass substrate and to investigate their sensing properties for NH_3 gas.

MATERIALS AND METHODS

2.1 Synthesis of nano-powder ZnO.

Nano-powder ZnO were synthesized by CBD method on glass substrates at room temperature. The deposition procedure consists of preparation of 0.1 M solution of $ZnSO_4$ and 50% of NH_3 Solution (Fisher Scientific, reagent grade, without further purification). $ZnSO_4$ and NH_4OH precursors were used for the deposition of ZnO films. ZnO films had been deposited at room temperature and pH value is 12., as deposited films consists of zinc oxide and zinc hydroxide, these films were annealed in air at 200^0 C for 2 hours to get pure zinc oxide films then powder of ZnO were obtained from the films.

2.2 Thick Film Preparation

ZnO thick films were prepared on alumina substrate by using standard screen-printing technique. The calcinated nanosized ZnO powder was crushed and mixed with glass frit and ethyl cellulose. The mixture was then mixed with butyl carbitol acetate to make the thixotropic paste. The paste was then screen printed on the alumina substrate. The films were dried under IR-lamp for 30 min and then fired at 400^0C for 2 hours.

2.3 Structural, Morphological and Gas sensing Studies.

The structural properties of ZnO films were investigated using X-ray diffraction analysis from 20-80^0 [Rigaku diffractometer (Miniflex Model, Rigaku, Japan) having CuKα, λ=0.1542 *nm* radiation] with 0.1^o/step (2θ) at the rate of 2 sec/step. The scanning electron microscopy (SEM- JOEL JED-2300) was employed to characterize the surface morphology. The Composition of ZnO thick film samples were analyzed by Energy Dispersive spectrometer (JOEL-JED 6360 LA). The thickness of the ZnO thick films was measured by using Taylor-Hobson (Taly-step UK) system. The thickness of the films was observed uniform in the range of 20µm to 22µm. The D.C. Resistance of the films was measured by using half bridge method in atmosphere at different temperatures. The gas sensing studies were carried out on a static gas sensing system under normal laboratory conditions. The gas response of thick films was studied in test assembly. The electrical resistances of thick film in air (*R*a) and in the presence of gas (*Rg*) were measured to evaluate the gas response (*S*) given by the relation,

$$S = \frac{Ra - Rg}{Ra} \quad (1)$$

Where Ra is the resistances of the thick film sample in air and Rg is the resistances of the thick film sample in gas atmosphere.

The ZnO thick films were characterized by X-ray diffraction technique from 20-80^o [diffractometer (Miniflex Model, Rigaku, Japan) with CuKα, λ = 0.1542 nm radiation] with a 0.1o/step (2θ) at the rate of 2 s/step. The average crystallite size was determined using Scherrer formula [30],

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (2)$$

Where
D = average crystalline grain size,
β = Full angular width of diffraction peak at the half maximum peak intensity (FWHM)
λ = wavelength of X-ray diffraction (1.542 Å)
θ = angle of diffraction

The surface morphology and chemical composition of the films were analyzed using a scanning electron microscope [SEM model JEOL 6300 (LA) Germany] coupled with an energy dispersive spectrometer (EDS JEOL, JED-2300, Germany).

RESULTS AND DISCUSSION

3.1 Composition of ZnO thick film

Table-1 shows the composition of the films fired at 400^{o}C. The EDX spectrum showed the presence of only Zn and Oxygen. From the analysis it was found that the ZnO films are nonstoichiometric. The deficiency or excess of any type of atom in the crystal results in a distorted band structure, with a corresponding increase in conductivity. Tin oxide looses oxygen on heating so that tin is then in excess. The oxygen, of course, evolves as an electrically neutral substance so that it is associated with each excess tin ion in the crystal; there will be two electrons that remain trapped in the solid material, thus leading to nonstoichiometry in the solid. This leads to the formation of the n-type semiconductor [31].

Table-1: Composition of the ZnO films at 400^{0}C firing temperature

Element	Mass %	At.%
O	14.85	40.89
Zn	85.15	59.11
Total	100	100

3.2 X-ray diffraction analysis

Fig. 1 shows X-ray diffraction patterns of nano- powder ZnO screen printed thick film deposited on glass substrate. XRD pattern show the different peaks of ZnO phases. It has been observed that [101] reflections corresponding to 2θ = 36.17^o is of maximum intensity for all film samples thereby a strong orientation with stacking of the plane along the c-axis, which indicates ZnO film had preferred orientation in the direction of [101] plane. The ZnO diffraction peaks for (100), (002), (101), (102), (110), (112) and (103) crystal orientation are identified. The standard interplaner spacing JCPDS data card Number 21-1486 matches with calculated values [32]. This clearly indicates that the structure of ZnO film is polycrystalline in nature. Besides except ZnO peaks, no other impurity peak is seen, suggesting formation of the single phasic ZnO.

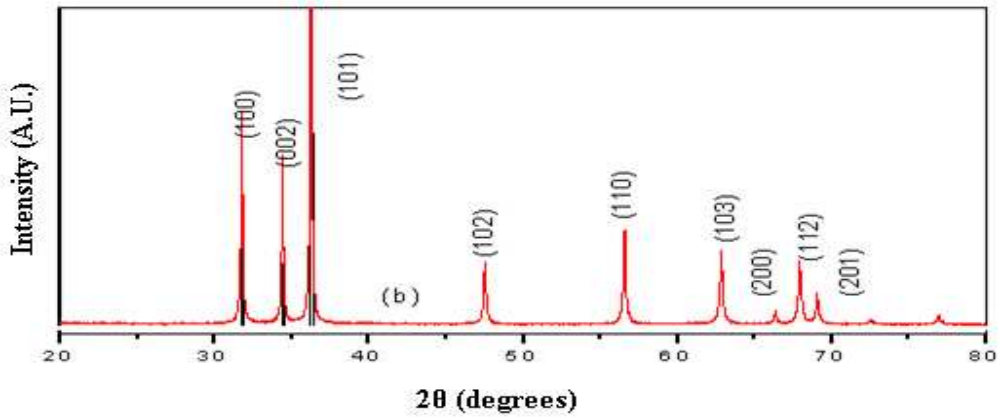

Fig.:1 X-ray Diffraction Pattern of ZnO Thick Film

The average crystallite size as per the calculations was found to be ~50-80 nm (±2 nm).

3.2 Scanning Electron Microscopy

The scanning electron microscopy is useful technique to observe surface morphology of deposited films. SEM images shows that the structure like porous and wafer type. This is because of porosity of the film as deposited at room temperature. Figure-2 shows SEM images of nanostructure ZnO thick film fired at 400^{o}Cin the air. Microstructural characterization was carried out by using scanning electron microscopy. SEM indicated rod type nanostructure with porosity. However some residual, intragranular porosity was seen. The film fired at 400^{o}C has good adhesion. Therefore it is used for gas sensing.

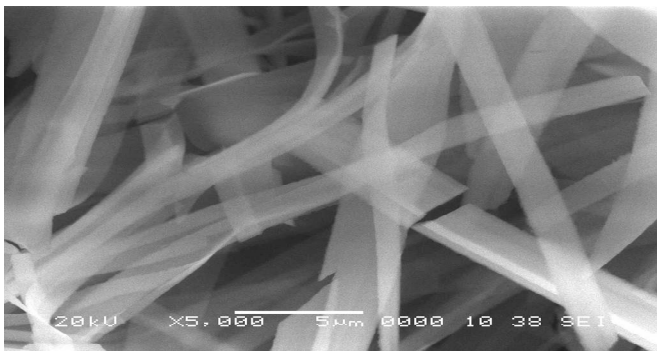

Fig.2: SEM micrograph of nano ZnO Thick Film

3.3 Gas Sensing Response

3.3.1. NH3 Gas Sensing

Figure-3 shows the variation of response of pure ZnO fired at 400^{o}C to 500 ppm NH3 gas with operating temperature. The gas response increases with temperature from 25 to 50^{0}C and then decreases with a further increase in temperature. The response of pure ZnO to NH_3 gas is 97.77 at 50^{0}C. In present work, every time prior to exposing the ZnO film to NH_3, it was allowed to stabilize at an operating temperature for 15 min and the stabilized resistance was taken as Ra. After exposing the film to the NH3 gas, the changed resistance was taken as Rg. NH3 is reducing gas. It reacts with surface oxygen ions of the film. Reduction of film increases the number of free carriers. Therefore resistance of the film decreases with reducing gases [33, 34, 35].

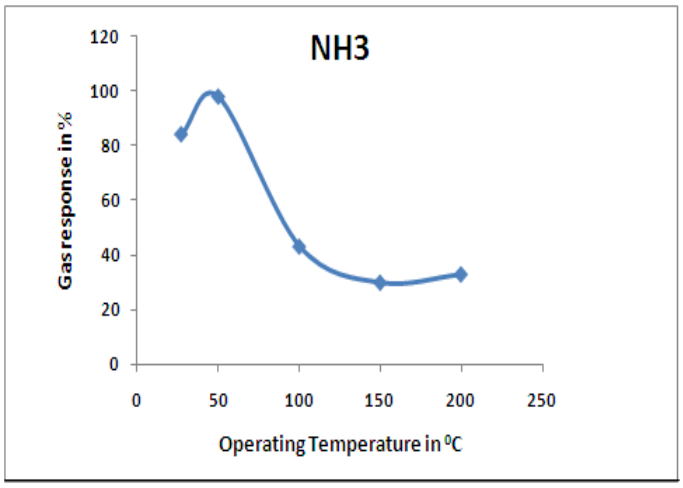

Fig.3. Variation of response with operating temperature for NH3 gas at 500 ppm

3.4.2. Gas Response and NH_3 Concentration

The variation of gas response of the ZnO film sample with NH3 gas concentration at 50°C temperature is represented in Figure-4. This film was exposed to different gas concentrations of NH3. The sensitivity values were observed to increase continuously with increasing the gas concentration up to 500 ppm.

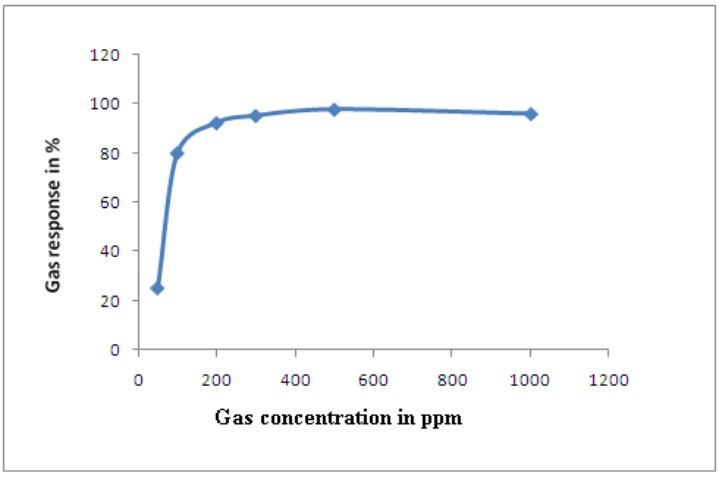

Fig.4. Variation of gas response with gas concentration

3.4.3. Selectivity for NH3 against Other Gases

It is observed from Figure-5 that the ZnO sample shows maximum response to NH3 (500 ppm) at 50°C. Sample showed highest selectivity for NH3 against all other tested gases viz: NO_2, LPG. Ethanol vapours, CO_2, H_2S.

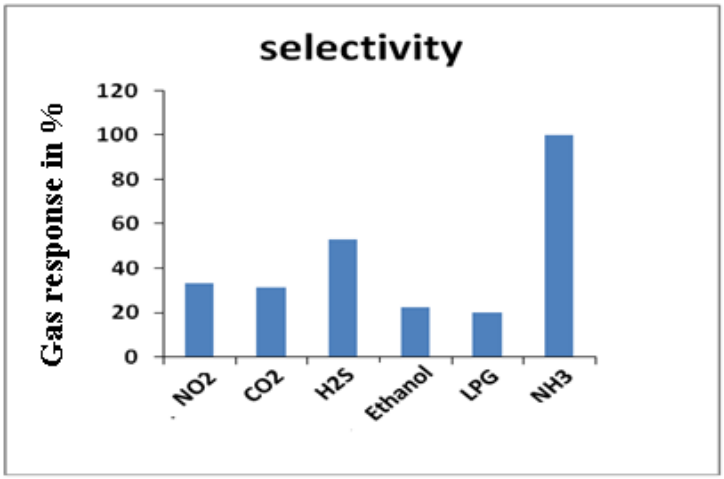

Fig. 5 Selectivity of ZnO sample for various gases

3.4.4. Response and Recovery Time

The response and recovery times of ZnO film sample are represented in Figure-6. The response was quick (~ 14 s) to 500 ppm of NH3 while the recovery was fast (~ 25 s). The quick response may be due to faster oxidation of gas. Its high volatility explains its quick response and fast recovery to its initial chemical status.

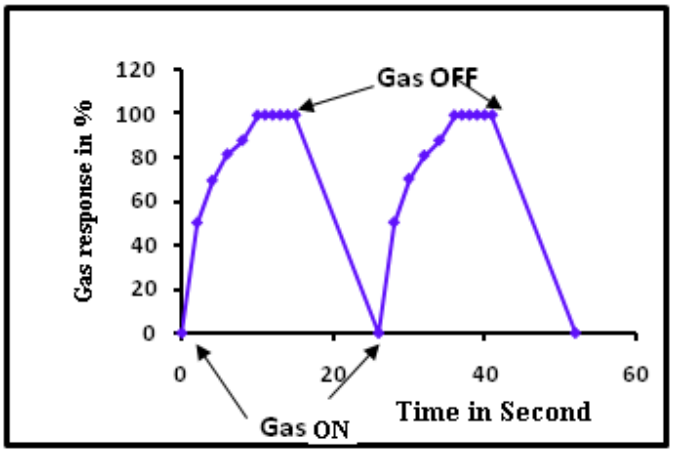

Fig. 6 Response and recovery of ZnO sample

CONCLUSION

This work demonstrated the successful synthesiz of Nano-powders Zinc Oxides (ZnO) using chemical bath deposition. Obtained powders were then used to make thick films on glass substrate by using standard screen printing technique. Nano powders ZnO screen printed thick film shows good adhesive to glass substrate employing a simple, inexpensive method and capability of the ZnO films for NH3 gas sensing. The film fired at 400ºC exhibited good sensing performance to NH3 at 50 ^{0}C temperature.

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