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Ethanol Sensor Based on Dip Coated ZnO Thick Films

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Abstract: Gas monitoring devices consisting of metal oxide thin films have been very widely applied as chemical sensors. They find profound use towards detection of toxic pollutant gases and organic vapors. They provide beneficiary merits as large scale commercial sensors owing to their low price, small size, high sensitivity and consume very low power. Ethanol is one of the most commonly and extensively used alcohol, both in the fields of research and industrial applications. There is an imminent need to develop sensors for its detection with very sensitivity. In this study, Zinc oxide nanoparticles were prepared by a suitable soft chemical method. ZnO thick films were prepared from these nanoparticles by dip coating method. ZnO thick films are coated on an Alumina substrate and the sensor is tested for ethanol for 50 ppm at various temperatures. The sensor was found to operate with maximum efficiency at an optimum temperature of 350°C.

Key words: ZnO thick films, ZnO nanoparticles, dip coating, ethanol sensor, gas sensor

INTRODUCTION

Zinc oxide has been extensively studied in many fields includes catalysts, optoelectronics and photochemistry in semiconductor devices etc. Zinc oxide is also the most researched material in the family of metal oxides for numerous applications, for many decades now, varying from gas sensing, solar cell, display screen, photocell electrode to UV-light emitting applications. Zinc oxide (ZnO) is an environmentally benevolent material and finds extensive use as traditional inorganic UV-absorbing materials and cosmetics. They are also applied as optoelectronic materials for solar cells, light emitting diodes and gas sensors (Gopel *et al*., 1991a, b). It has also been found to act as a catalyst during the synthesis of methanol and phosphor (Newbury *et al*., 1995). Wurtzite type ZnO is a wide band-gap semiconductor (3.37 eV) with a large exciton-binding energy. It poses as an attractive material towards sensing applications due to its unique properties, such as optical transparency, electric conductivity, piezoelectricity and near-UV emission. The physical and physiochemical properties of ZnO crystals are determined by critical growth related parameters such as size and morphology. One-dimensional (1D) ZnO materials can be grown by various methods. (Shimizu and Egashira, 2001; Williams and Pratt, 2000). Researchers have been able to synthesis ZnO nanorods very effectively, in basic solution systems at low temperatures and under hydrothermal conditions (Rao and Rao, 1999).

Metal oxides have been extensively used as sensing materials to sense toxic and hazardous gases (Lin *et al*., 1994, Kadu *et al*., 2009). ZnO proves to be more useful in the nanoregime with its more benevolent properties. Various sensors have been materialised based on ZnO nanoparticles. Gas sensors for detecting PPM levels of CH_4, CO have been reported (Jones *et al*., 1984). Very recently research works depict the use of ZnO nanoparticles to be used in dye sensitized solar cells (Liu *et al*., 2011). The band gap of ZnO nanoparticles can be modified very easily while synthesizing them by means of controlling the morphology or the particles or by varying the annealing temperature. ZnO nanoparticles have been synthesized with very high band gap energies of 3.35, 3.29 and 3.25 eV corresponding to the violet blue region of the electromagnetic spectrum (Rusdi *et al*., 2011). Many biosensors have also been developed based on ZnO's owing to its bio compatibility, selectivity and highly modifiable reactive sensing mechanisms towards various biological agents. Both enzymatic and non-enzymatic bio sensors have been developed for determining glucose (Kong *et al*., 2009), penicillin (Ibupoto *et al*., 2011) etc.

It is very essential to provide sub micrometric level control of the length of the nanorods to achieve a range smaller than the wavelength of visible light for

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applications towards synthesis of optically transparent materials, like ZnO-polymer composite films which can be used as a component of recording media. ZnO thin films have been prepared by different types of thin film deposition techniques. Techniques like pulsed-laser deposition (Franklin *et al*., 2011), RF magnetron sputtering (Carcia *et al*., 2003; Youssef *et al*., 2009), chemical vapour deposition (Kim *et al*., 2010), spray pyrolysis (Tewari and Bhattacharjee, 2011), chemical bath deposition (Khallaf *et al*., 2009) and the sol-gel process (Ilican *et al*., 2008; Khan *et al*., 2011) have been reported by the research community.

Among the preparation techniques of ZnO films, the sol-gel process offers a very effective method of preparing a customised area of coating of ZnO thin films at low cost for various sensing applications. Various factors affect the gas sensing properties of a thin film coated sensor. Apart from the intrinsic factors of materials, extrinsic factors like grain size and operating temperature play a crucial role in determining the sensitivity and the range of detectable PPM levels of the gas. Zinc oxide is n-type semiconductor material and exhibits high electron mobility. Semiconducting thin films have good sensing characteristics towards gases. This technique has been explored and many sensors have been developed (Siyama *et al*., 1962). Typical working temperatures for ZnO based gas sensors are between 200 and 450°C. Higher working temperature would change the surface morphology and microstructure of thin films, over time, leading to reduction in stability and sensitivity of the coated film (Mitra *et al*., 1998; Yoshino *et al*., 2000). This critical factor demands a scientific investigation and innovation to develop zinc oxide sensors with high sensitivity at optimum working temperature. Another basic requirement of gas sensors is low power consumption as these sensors would be required work continuously and should be highly reliable too. It is preferable to use a low resistance material which requires lower driving power when it is used as a sensor. A significant resistance change in the sensing material, when exposed to gas at PPM levels is again very crucial. This change then can be translated towards change sensors output voltage drop. Higher change in resistance per change in exposed gas levels results in a higher sensitivity. This work reports on ZnO film based gas sensors fabricated by deposition of ZnO thin film by dip coating method using copper as the electrode. Atomic force microscopy, UV-Vis spectra analysis, X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques were used to characterize the structural properties and chemical composition of ZnO gas sensing thin films which were deposited on alumina (Al_2O_3) substrate.

MATERIALS AND METHODS

Preparation of zinc oxide particles: A stock solution 0.2 M zinc sulfate ($ZnSO_4$) of pH = 5.3 and an alkali solution of 4.0 M sodium hydroxide (NaOH) of pH = 13.8 were prepared by dissolution of zinc sulfate heptahydrate ($ZnSO_4.7H_2O$, 99.5%) and NaOH with double distilled Millipore water. The reactions were performed with continuously stirring the stock solution of ZnSO4 along with the highly base solution of NaOH and double distilled millipore water. It has been reported that a highly basic condition is better suited for the direct synthesis of wurtzite type ZnO crystals (Kawano and Imai, 2008). So, the pH of the mixture solution was continuously monitored using a digital pH meter until a pH of 13 was obtained. After the mixing of the solutions, the mixture was placed in a hot plate at 110°C for 2 h to enable precipitation. The precipitated products were centrifuged, washed with double distilled millipore water and later dried at 400°C for 1 h. The procedure was repeated several times with different ratios of the solutions. It was observed using characterization techniques that the shape and size of obtained nanoparticles was dependent on the ratios of solutions, the mixing procedure of the solutions and annealing temperatures.

Preparation of zinc oxide thick films: Zinc oxide films can be produced by using several methods, like spin coating, dip coating, Pulsed laser vapor deposition, physical vapor deposition and chemical vapor deposition. Dip coating method is easier to implement at laboratory level facilities with a more uniform and even deposition to form thick films. Zinc oxide nanopowder was mixed with PVA (polyvinyl alcohol) to form a fine paste. The paste was coated onto an alumina tube on which two copper wires had been pre soldered at each end. The alumina tube was chosen as the substrate owing to its inertness to the ZnO coating and its mechanical and thermal durability to withstand high temperatures within the range used for this sensing application. The dimensions of the alumina tube used were about 1.8 cm in length, 1.6 mm in internal diameter and 2 mm in external diameter. The alumina substrate was pretreated with moderately concentrated HCl and HNO_3 and then washed with distilled water in order to remove any contaminants present on the surface of the tube. The gas sensors were calcined at 600°C for 1 h to improve stability and repeatability. This treatment enables the decomposition of PVA and increases the contact strength of oxide grain substantially in the final sensor element to the desirable limit.

Sensor setup: The experimental set up used to test the gas sensor is shown in the Fig. 1. The experiment setup consists of Gas testing chamber, heater, temperature controller, electro meter and thermocouple.

The initial resistance of the unreacted ZnO film, before exposing it to ethanol was measured and recorded. Adequate quantity of the analyte gas (ethanol) is injected to the test chamber. The gas inlet is monitored to result in the desired concentration level in air (ppm). The substrate is heated to the desired of temperature of 350°C to enable the effective reaction of the analyte gas with the thick film of ZnO. The temperature in the chamber is maintained constant by a closed loop control system employing a thermocouple, temperature controller and heater. The resistance of the coated ZnO film is expected to change as it reacts with the ethanol and is subsequently measured and recorded. Change in resistance of the film is measured and recorded with respect of time until a steady state value is obtained. The chamber is then purged with air and then vented out. This allows the sensor to reach its initial (unexposed) value of the resistance before the next iteration of the experiment is carried on. The experiment is repeated for different temperatures and the response is recorded.

The sensitivity of the sensing material is highly dependent on the temperature. The sensor exhibits maximum sensitivity for sensing various gases at different temperatures. In this work, sensing characteristics of a thick film ZnO film as an ethanol sensor was studied at various temperatures to achieve an optimum temperature for maximum sensitivity. Sensitivity of the sensor varies as a function of temperature. Analyte gas concentration and the temperature at which the sensor exhibits maximum sensitivity are carefully recorded.

The response and recovery times of a sensor towards an analyte gas are very important parameters that decide the utility of the sensor. Response time is the time taken by the sensor for attaining steady state resistance from its initial resistance value in clean air, after exposing it to the mixture of air along with the desired ppm levels of ethanol. Recovery time is the time taken for the complete recovery of resistance of the sensor to initial value in air when it is exposed to clean air after exposure to the air containing the analyte gas. As in the case of response time of a sensor towards an analyte gas differs depending upon the sensor material and operating temperature.

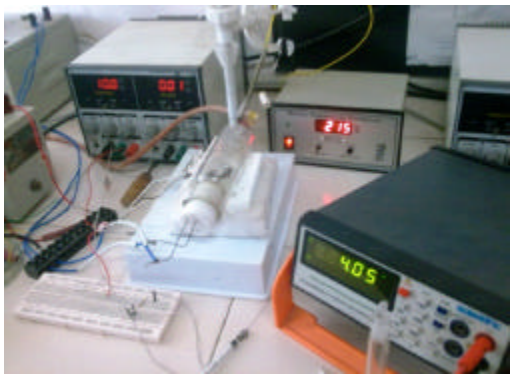

Fig. 1: Temperature controlled gas sensing setup

RESULTS AND DISCUSSION

XRD of ZnO nanoparticles: XRD patterns of ZnO nanopowder samples synthesized by addition of zinc sulphate with NaOH are shown in Fig. 2. Three diffraction peaks which correspond to the polycrystalline hexagonal wurtzite structure, (1 0 0) (0 0 2) (1 0 1) and a weak peak associated with cubic zinc sulphate were observed. Samples correlate with and could be identified to be tetragonal ZnO from JCPDS reference data (JCPDS 36-1451).

The crystal size of the nanoparticles were calculated from Scherrer formula and were found to be 69 nm:

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

As per Bragg's law:

$$n\lambda = 2d \sin\theta$$

Where:

n = Order of the diffraction
d = Distance between the atomic planes
θ = Angle of incidence

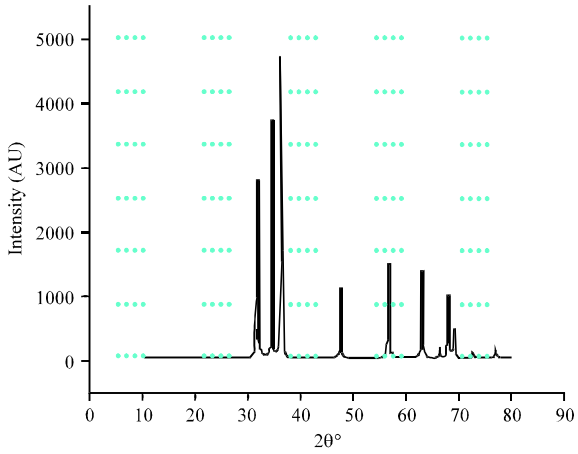

Fig. 2: XRD characterization of dip coated ZnO thick film

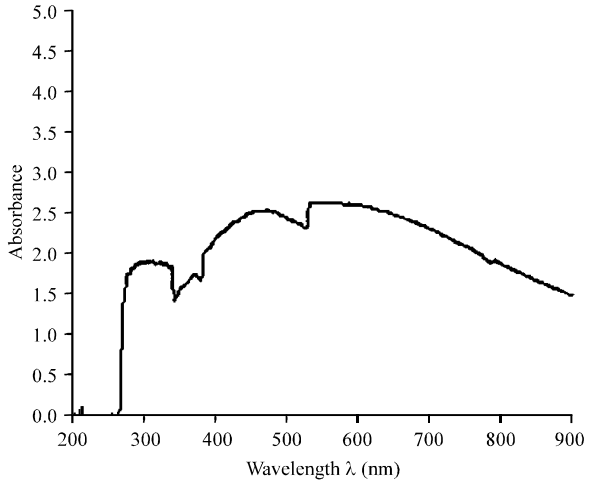

Fig. 3: UV-Vis characterization of dip coated ZnO thick film

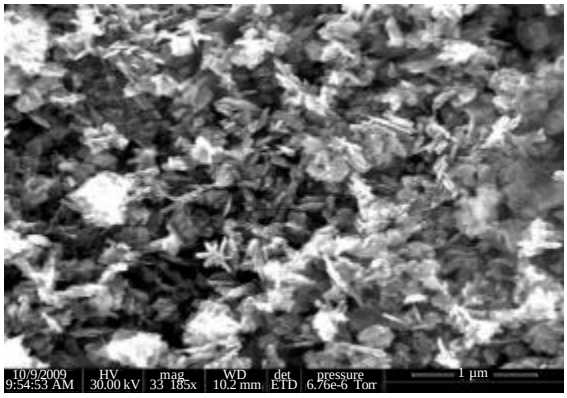

Fig. 4: SEM image of zinc oxide nanoparticles at µm scale

UV-Vis characterization: The UV-Vis spectra of ZnO thin films dip coated on a glass substrate are shown in Fig. 3. The absorption onset of ZnO thin film is at 341 nm. The peak at 341 nm shows the characteristic electron transition of ZnO. Figure 3 represents the plot of the UV absorbance at 341 nm as a function of the layer.

Scanning electron microscopy: Scanning Electron Microscopy (SEM) image revealed well coated surfaces of metal zinc oxide prepared by dip coating. After annealing at 500°C, the film was observed to be more homogeneous in composition and morphology.

Figure 4 shows the SEM images of the nanopowder ZnO. It is clearly seen that the ZnO particles are mostly of nanorods in morphology with nanoflowers also present. It is also highly evident that even though a thick film was deposited, it consisted of particles of nanometers in

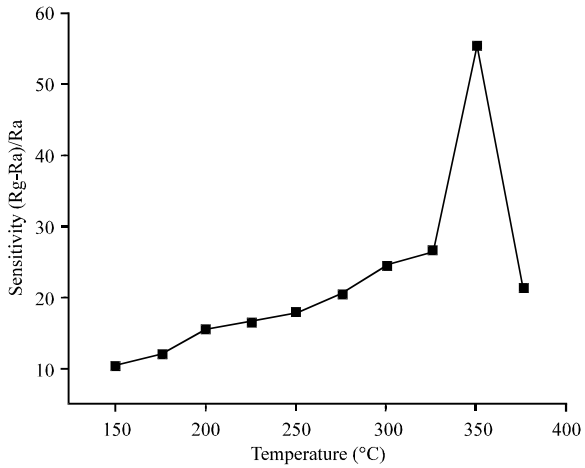

Fig. 5: Sensitivity of the sensor towards enthanol at different temperatures

dimensions. More efforts are in progress to effectively control the morphology of the nanoparticles, to a controlled shape and size to achieve a better selectivity and sensitivity of the sensor. Modified approaches are underway to achieve these criteria.

Sensitivity: Ethanol gas sensing properties of zinc oxide thin films were studied in the temperature interval between 150 and 400°C. Below 350°C the sensitivity was observed to be highly in appreciable. The sensitivity was found to increase rapidly and then falls down as temperature increases. At 350°C, sensitivity of the sensor towards ethanol was approximately 30% more than at both higher and lower temperatures. After 350°C again the sensitivity decreases. So from the above experiments it is concluded that the ethanol sensor based zinc oxide films coated on the alumina substrate gave very good sensitivity at 350°C. Hence, the optimum temperature for the operation for this sensor was at 350°C. The graph plotted in Fig. 5, shows the sensitivity of zinc oxide film towards ethanol at different temperatures.

Sensitivity of the sensor is calculated from the formulae:

$$S = \frac{|Rg - Ra|}{Ra}$$

where, 'Ra' is the resistance of the ZnO film when exposed to air; 'Rg' is the resistance of the ZnO film when exposed to ethanol gas.

Response time: In the case of gas detection sensors, the response time is defined as the time taken to achieve 90%

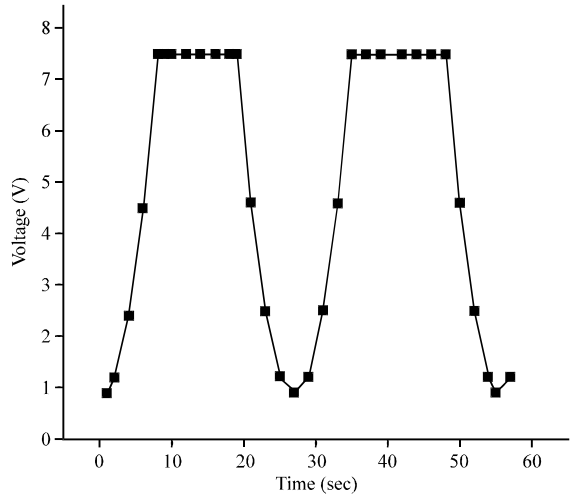

Fig. 6: Response time analysis of the sensor for consecutive trials

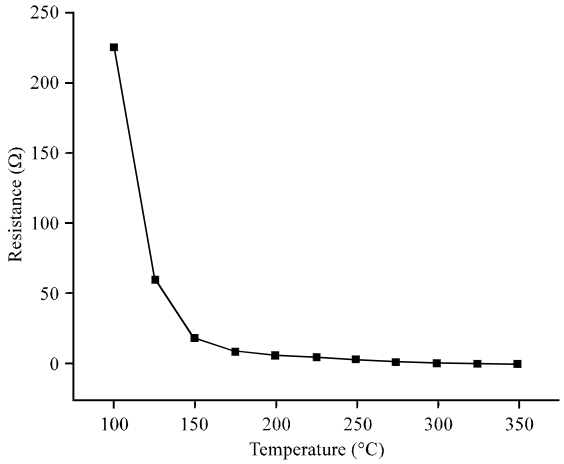

Fig. 7: Change in output resistance of the ZnO thick film at various temperatures

of the final change in resistance following a step change in gas concentration applied to the sensor.

The temperature of the sensor was increased to and maintained at 350°C. The resistance of the sensor was measured. Then 50 ppm of ethanol was injected in to test chamber and the sensor responds to the ethanol slowly and the resultant sensor output increases. The sensor output was allowed to reach a maximum and a steady state. Then the chamber was flushed with air and vented. The decrease in the sensor output was monitored till it reached the initial value. Again the ethanol was injected in to the chamber. This procedure was repeated a number of cycles until a regularized sensor output versus time pattern were achieved as shown in the Fig. 6. It can be inferred from the graph that the response time of the sensor to be about 5 sec. The entire experiment was conducted at a constant temperature of 350°C.

Temperature vs. resistance: Figure 7 shows the relation between the resistance and temperature of the sensor.

It can be observed from the graph that the response of the sensor decreases in terms resistance variation as temperature increases but attains a constant value around 10 Ω at 350°C.

The sensor output can be formulated with the following relation between voltage applied, voltage output and the load resistance of the measurement circuit:

$$R_g = R_L \frac{V_{in}}{V_{out}} - 1$$

where, 'R_L' is load resistance, 'V_{in}' is the input voltage supplied to the circuit and 'V_{out}' is the sensor output.

CONCLUSION

Zinc oxide nanoparticles were prepared by using suitable soft-chemical method and the particles were characterized by using different characterization techniques. Sensing film was coated on the alumina substrate using dip coating method. Gas sensor was tested for ethanol gas. Gas sensing properties of 50 ppm of ethanol at different temperatures were calculated. It was found experimentally that ZnO nanoparticle plays important role in enhancing the sensitivity of the sensor. The optimum working temperature for the zinc oxide based gas sensor operation was identified. In the case of ethanol gas the sensitivity is maximum at 350°C rather than in remaining temperatures.

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