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Growth of ZnO Nanorods using Hydrothermal for Gas Sensing Application

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Abstract

In this paper; synthesis of ZnO nanorods by hydrothermal route with various parameters has been reported. C-axis oriented growth of nanorods and wurtzite (hexagonal) crystal structure is confirmed by XRD. The SEM images show oriented growth of nanorods with size of 200 nm to 500 nm. Effect of synthesis parameters such as concentration of precursors and temperature on growth of the ZnO nanorods has been discussed. Room temperature sensing of H_2S gas for 10 and 50 ppm has been studied. The ZnO nanorods show response and recovery times of 3-4 minutes and 1-2 hours, respectively.

Keywords: Room temperature gas sensor, ZnO nanorods, hydrothermal.

Introduction

Now days Metal Oxide based room temperature gas sensors have attracted great deal of attention due to simple circuitry and low power consumptions. Zinc Oxide is wide band gap semiconductor (Eg =3.4 eV) has been showing fascinating demand in technology due to its versatile properties. The nanostructures of Zinc Oxide (ZnO) have promising applications in TCO, self cleaning glasses, solar cells, smart windows, flexible electronic devices, piezoelectric sensors and photo-catalysis. Furthermore, various gas sensors based on ZnO (un-doped and doped) nanostructures have been studied to great extent, and the results reveal better sensitivity, selectivity, response and recovery times, in contrast to the SnO_2 based sensors. On the other hand, H_2S is one the toxic gas and shows hazardous effect on human health and environment. Hence its detection and monitoring is essential[1-6].

Methodology

ZnO nanorods were grown on glass substrates using hydrothermal route. The glass substrates were cleaned following a standard protocol. Prior to the hydrothermal synthesis, a seed layer was prepared on the pre-cleaned glass substrates. For this, seeding solution of 30 mM Zinc acetate ($Zn(O_2CCH_3)_2$ AR grade 99.50% purity, obtained from Thomas Baker) was prepared in ethanol. A few drops of the solution were spin coated onto the glass substrates, followed by annealing at 300 °C in a muffle furnace. These glass plates with ZnO seed layers were further used as substrates for hydrothermal synthesis. An aqueous solution of 100 mM Zinc Nitrate ($Zn(NO_3)_2$ 98.50% purity, Thomas Baker, Mumbai) and 100 mM Hexamethylenetetramine (HMT) ($C_6H_{12}N_4$) (AR grade, 99% purity, Merck Specialities) was used. The hydrothermal reaction was carried out at 85°C for 8 hrs. The glass substrate with the deposited film was washed with distilled water and annealed at 400 °C for 3 hours.

Results and Discussion

The as-synthesized samples were characterized using XRD (Bruker Advance D8) and Scanning Electron Microscope (JEOL JSM-6360A) in order to reveal the structural and morphological properties. The H_2S gas sensing studies were carried out in indigenously designed and commissioned gas sensing set up. For gas sensing, Au contacts were made with mesh mask using PVD (Physical Vapor Deposition) technique. and resistance of the samples was tested for 10 ppm and 50 ppm gas concentrations at room temperature. Figure 1 shows a XRD pattern of the ZnO nanorods film. The appearance of an intense direction peak indexed to the (002) crystalline plane of wurtzite ZnO confirms highly C-axis oriented growth of the synthesized ZnO film. (JCPDF no. 36-1451). Furthermore, using Scherer's formula, we have estimated the garin size, which is found to be ~ 200 nm.

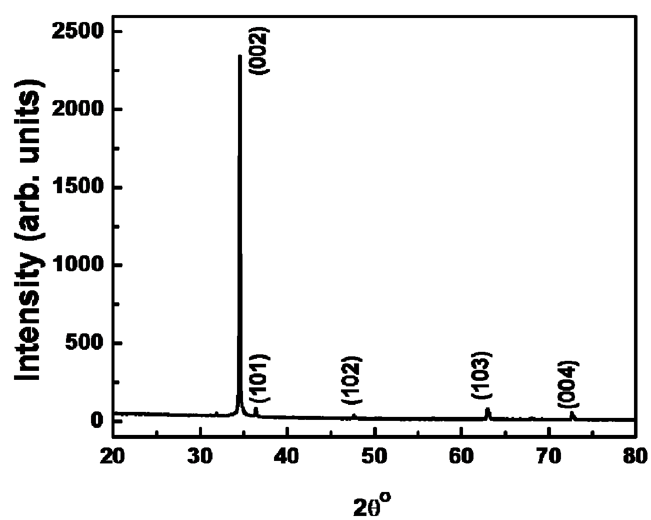

Figure-1
XRD of ZnO nanorods Film

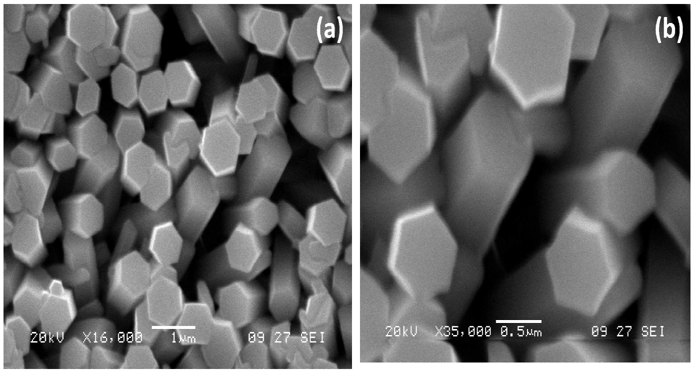

Figure-2
(a) and (b): SEM micrographs of ZnO Thin Film

The SEM micrographs (figure 2(a) and (b)) of the hydrothermally synthesized ZnO thin film depict vertically aligned growth of ZnO nanorods under the prevailing experimental conditions, with average size of 200 nm. A careful observation of the SEM image recorded at higher magnification (Figure-2(b)) reveals presence of tiny pores on the nanorods, which are beneficial for the sensing activity. These pores are expected to increase the effective surface area for gas adsorption and thus enhance the sensing activity.

The room temperature gas sensing properties of the ZnO nanorods thin film towards H_2S gas entity are shown in the following figures. The figures 3(a) and 3 (b) depict the response time of the senor exposed to 10 and 50 ppm H_2S concentration, respectively. The resistance of the film shows rapid variation upon exposure to the gas and the response time is estimated to be 2-3 minutes. However the film takes relatively larger time to recover its initial resistance upon withdrawal of the gas from the chamber. The measurements were repeated at least for two samples synthesized under same experimental conditions and were found to be quite reproducible.

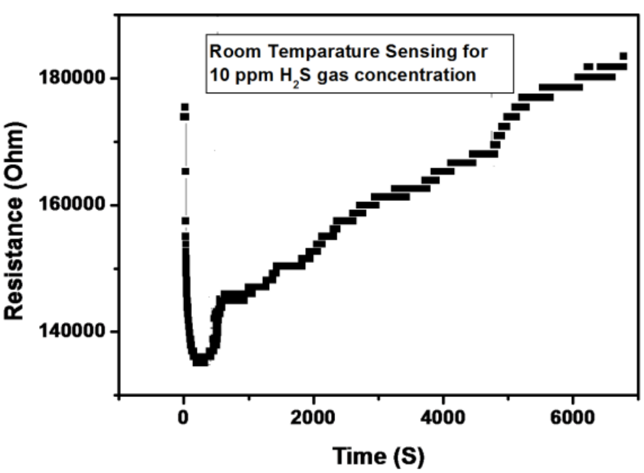

Figure-3(a)
Room temperature sensing of ZnO film for 10 ppm H_2S gas concentration

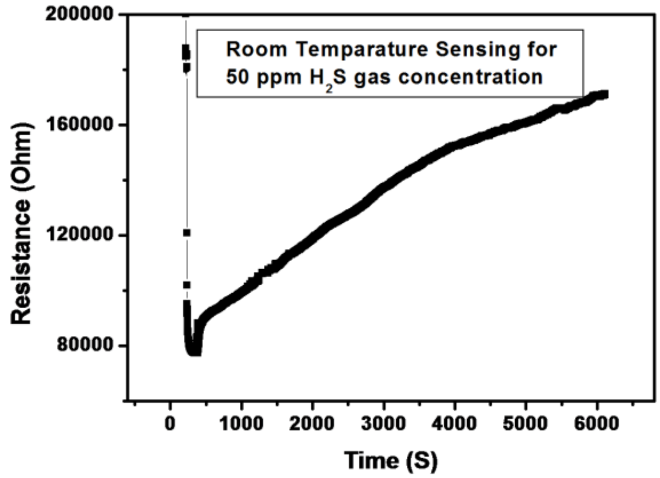

Figure-3(b)
Room temperature sensing of ZnO film for 50 ppm H_2S gas concentration

The gas sensing of highly oriented ZnO nanorods were studied for H_2S gas sensing at room temperature. Figure 3a and 3b shows response behavior for 10 ppm and 50 ppm H_2S gas concentrations. Gas sensitivity of the films were calculated by standard formula i.e. ratio of resistance of the film in air (Ra) to resistance of the film in H_2S gas (Rg). Response time for 10 ppm gas concentration was found 150 seconds where as recovery time was slower (5000 seconds) due to operation of sensor at room temperature and presence of humidity (R_H 40 %) in atmosphere. For 50 ppm, response time was 280 seconds and recovery of 5500 seconds. Sensitivity for the 10 ppm and 50 ppm were 1.28 and 2.33 respectively.

Discussion: Growth of the ZnO nanorods by hydrothermal growth has been reported by several authors; it is discussed that generally ZnO grows along c- axis in the form of rods and wires. There are several reports on ZnO nanorods and nanowires used for various gas sensing such as; Lupon O. et al. reported ZnO nanorods for hydrogen sensing. T. Gao et al. have reported ZnO nanorods for ethanol gas sensing at 1000 ppm level. K. Mirabbaszadeh et al. have reported ZnO nanorods for ethanol gas sensing for 5000 ppm at 300 ^{o}C operating temperature. ZnO Nanowires are also extensively explored for the gas sensing. Lupon O. et al. reported ZnO nanorods for hydrogen ultrafast sensing at room temperature[7-12].

Gas sensing mechanism is not precisely well understood; but the most accepted mechanism is as given below. When oxygen molecules are adsorbed on the surface of n type metal oxide wide band gap semiconductor, electrons can be transferred to gas molecules from metal oxide due to lower occupied molecular orbit (LUMO) of Oxygen lies below the Fermi level of the n type metal oxide. This is resulted in to the formation of electron depletion region on the surfaces of the grains and formation of oxygen ions on the surface. Formation of depletion region results to increase the resistance of the film. Further, when any reducing species such as H_2S interact with these oxygen ions thereby delocalization of electrons from the oxygen species takes place and hence increases in the conductivity of the metal oxide[11-14].

Conclusion

In the present study, room temperature H_2S gas sensing for lower concentrations has been observed for the highly orientated Zinc Oxide nanorods with pores. To improve response and recovery time higher operating temperatures sensing is needed. Also effect of porosity on enhanced sensing and effect of catalyst for improvement in sensitivity and selectivity will be explore in the further study.

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References

1. Liu Bin et al., *Journal of the American Chemical Society* **125,** 4430, **(2003)**
2. Lee Yiling et al., *Journal of the American Ceramic Society,* **92(9),** 1940, **(2009)**
3. Elen Ken et al., *Nanotechnology,* **20,** 055608, **(2009)**
4. Wang Caihong et al., *Sensors and Actuators B: Chemical,* **113,** 320, **(2006)**
5. Dhobale Sandip et al, *Science of Advanced Materials,* **4(4),** 4, **(2012)**
6. Kolhe, Rangnath K., et al., *Physics and Technology of Sensors (ISPTS), 2012 1st International Symposium on*. IEEE, **(2012)**
7. Lupan Oleg, Guangyu Chai and Lee Chow, *Microelectronics Journal,* **38(12),** 1211-1216, **(2006)**
8. T. Gao and T.H. Wang, *Applied Physics A,* **80(7),** 1451-1454 **(2005)**
9. Mirabbaszadeh K. and M. Mehrabian, Synthesis and properties of ZnO nanorods as ethanol gas sensors, *Physica Scripta,* **85(3)**, 035701 **(2012)**
10. Lupan O., et al., *Sensors and Actuators B: Chemical,* **144(1),** 56-66 **(2010)**
11. Batzill Matthias and Ulrike Diebold, *Progress in surface science,* **79(2),** 47-154, **(2005)**
12. Barsan Nicolae and Udo Weimar, *Journal of Electroceramics,* **7(3),** 143-167, **(2001)**
13. Comini E., et al. *Applied Physics Letters,* **81(10),** 1869-1871 **(2002)**
14. Wang, Chengxiang, et al., *Sensors,* **10(3),** 2088-2106, **(2010)**