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Zinc Oxide Nanostructure Thick Films as H_2S Gas Sensors at Room Temperature

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ABSTRACT

The ZnO nanostructures have been synthesized and studied as the sensing element for the detection of H_2S. The ZnO nanostructures were synthesized by hydrothermal method followed by sonication for different interval of time *i.e*. 30, 60, 90 and 120 min. By using screen printing method, thick films of synthesized ZnO nanostructure were deposited on glass substrate. Gas sensing properties of ZnO nanostructure thick films were studied for low concentration H_2S gas at room temperature. The effects of morphology of synthesized ZnO nanostructure on gas sensing properties were studied and discussed. ZnO nanostructure synthesized by this method can be used as a promising material for semiconductor gas sensor to detect poisonous gas like H_2S at room temperature with high sensitivity and selectivity.

Keywords: ZnO Nanostructure; Room Temperature Gas Sensor for H_2S

1. Introduction

Nanostructured materials such as WO_3, ZnO, SnO_2, and V_2O_5 have shown good sensing properties [1-7]. Among these nanostructure-semiconducting materials, ZnO has been studied extensively for gas sensing application. It has been proved that ZnO is a good gas sensitive material for detection of both reducing and oxidizing gases [8-16]. Various gases have been tested for ZnO nanostructure sensor studied including ethanol, acetone, NO_2, NH_3, H_2 and CO_2 and hydrogen [17-22].

H_2S is a toxic gas produced from the coal, oil and natural gas industries. In order to enhance the sensitivity and selectivity of H_2S, many attempts were made to systemize nanostructure ZnO with different morphologies [23-27]. However, there are very few reports on ZnO nanostructure based room temperature H_2S sensors.

In the present work, efforts were made to synthesize ZnO nanostructure with innovative morphology by hydrothermal route. The synthesized ZnO shows high sensitivity with fast response and recovery for low concentration of H_2S gas.

2. Experimental

2.1. Synthesis of ZnO Nanostructure

All chemicals were of analytical grade and used as purchased without further purification.

In present work, 5.2 g of Zinc acetate dehydrate was dissolved in 480 ml of distilled water. Subsequently, 20 ml of 2 M NaoH aqueous solution was introduced into the above aqueous solution drop by drop with constant stirring. The obtained mixture was kept at room temperature for 5 min. and transferred into 700 ml Teflon-lined stainless steel reactor (autoclave), maintained at temperature 120˚C. After 6 hr, allow it to cool to room temperature naturally and the resultant white solution were collected in a beaker. The obtained white solution were sonicated (Ultrasonic wave treatment) for different interval of time say 30, 60, 90 and 120 min with pulse rate 4 s and power 0.7 A. The resultant products were collected by centrifugation, washed several times with distilled water and ethanol, dried at temperature 70˚C for 3 hr. The obtained powder which was sonicated for 30, 60, 90 and 120 min were termed as 30 min ZnO, 60 min ZnO, 90 min ZnO and 120 min ZnO respectively.

2.2. Preparation of Thick Films

Thick films of synthesized nanostructure ZnO were prepared by using screen printing technique. In present process, thixotropic paste was formulated by mixing the synthesized ZnO powder with ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl

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cellulose, butyl carbitol acetate and turpineol. The ratio of ZnO to ethyl cellulose was kept at 95:05. The ratio of inorganic to organic part was kept as 75:25 in formulating the pastes. The thixotropic pastes were screen printed on a glass substrate in desired patterns. The films prepared were fired at 500˚C for 12 hr. Prepared thick films were called as pure ZnO thick films.

3. Materials Characterization

3.1. Thickness Measurement

Thickness of all ZnO thick films were measured by using technique "Marutek film Thickness Measurement System" with the help of provided equipment. The thicknesses of all films were observed in the range from 31 to 35 µm. Thick films of approximately uniform thicknesses were used for further characterization.

3.2. X-Ray Diffraction Studies

The crystallographic structure of the all synthesized ZnO nanostructure was characterized by powder X-ray diffraction (Philips X-ray diffractometer) with cu source and 2θ range of 20˚ - 80˚. **Figure 1** shows the XRD pattern of the 90 min ZnO nanostructure. The recorded XRD pattern confirmed that synthesized ZnO are high crystalline in nature. The corresponding X-ray diffraction peak for (100), (002), (101) and (102) planes confirm the formation of hexagonal wurtzite structure of ZnO (JCPDS card no. 36 - 1451)). Similarly, XRD pattern of 30 min ZnO, 60 min ZnO and 120 min ZnO shows similar result with different half width full maxima (not shown in this article).

The domain size of the crystal can be estimated from the full width at half maximum (FWHM) of the peaks by means of the Scherrer formula,

$$D = \frac{K\lambda}{\beta \sin\theta}$$

where λ is the wavelength of incident beam (1.5406 Å), β is the FWHM of the peak in radians, θ is the diffraction angle and K is Scherrer constant. The average crystallite size was calculated from (101) peak of 90 min ZnO is found to be 17 nm.

3.3. Transmission Electron Microscope

By using Transmission Electron Microscope (TEM), the morphology and structure of the synthesized powders were investigated. TEM images show that the synthesized ZnO consists of flower like structure. **Figure 2(c)** shows the ZnO sonicated for 90 min, shows that the crystallite size is very less as compared to the other ZnO sonicated for different time interval (**Figures 2(a)**, **(b)** and **(d)**).

4. Gas Sensing Properties

The gas response of the sensor was defied as the ratio of the change in conductance of a sample upon exposure to the target gas to the original conductance in air. **Figure 3** shows the gas responses of ZnO thick films to 25 ppm H_2S at operating temperature. This high response of ZnO thick film to H_2S may be due to the interaction of ZnO with H_2S, forming ZnS [28]. ZnS exhibits higher elec-

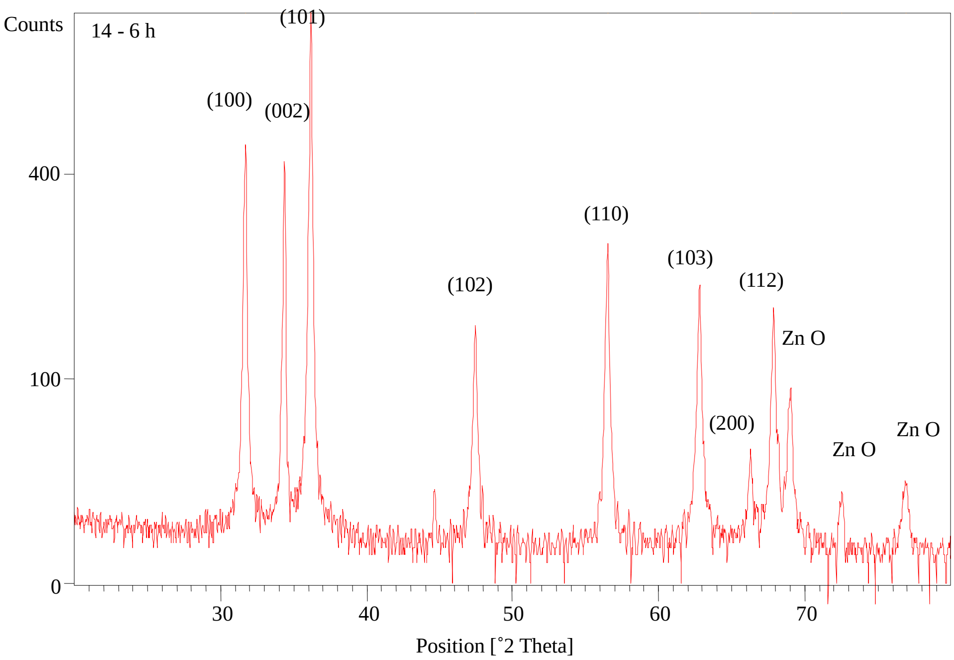

Figure 1. Powder XRD pattern of 90 min ZnO nanostructure synthesized by hydrothermal route.

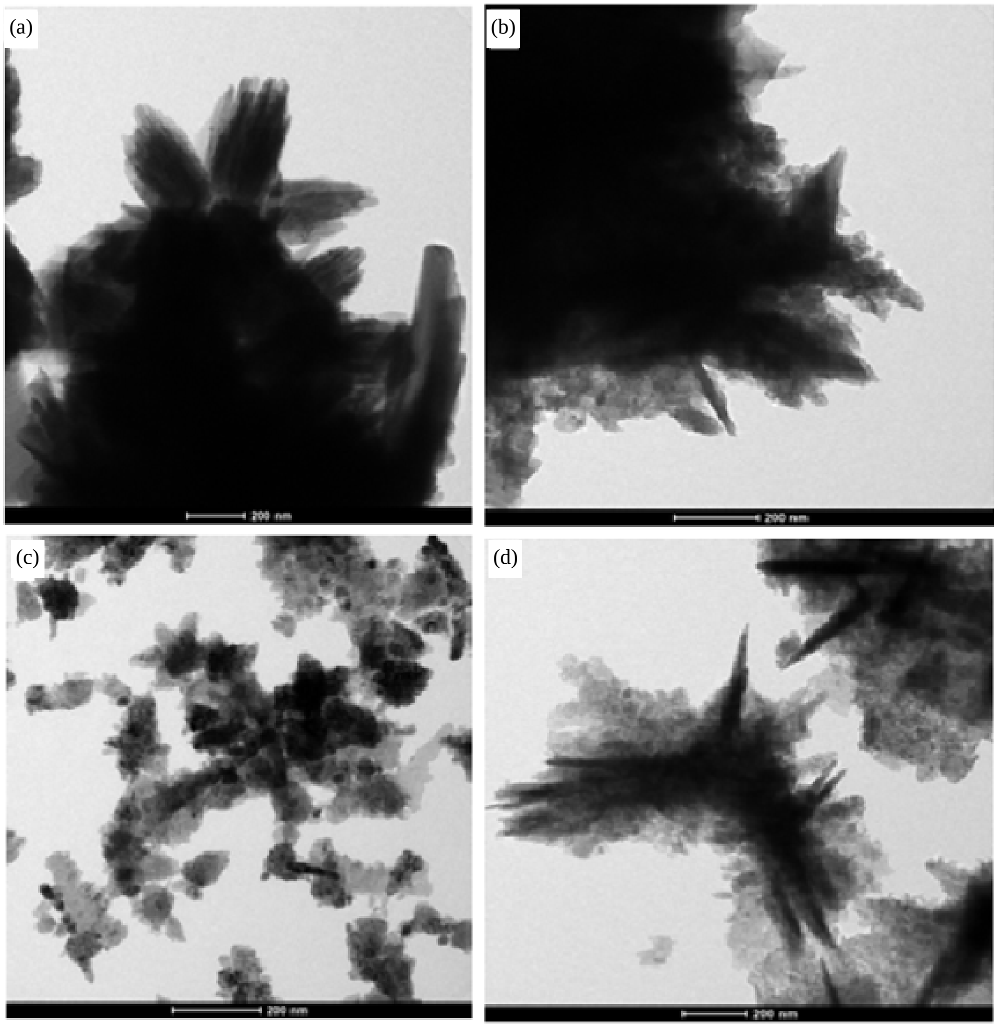

Figure 2. TEM image (a) 30 min ZnO; (b) 60 min ZnO; (c) 90 min ZnO; (d) 120 min ZnO.

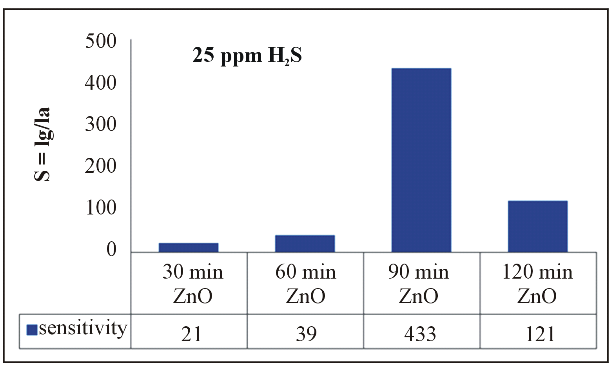

Figure 3. Gas responses of ZnO nanostructure thick films.

tronic conductivity as compared to ZnO.

Figure 3 also indicates that 90 min ZnO have maximum gas response (433) whereas 30 min ZnO has minimum gas response (21) to low concentration H_2S. The higher response of 90 min ZnO nanostructure upon exposure to H_2S may be attributed to the decrease in concentration of oxygen adsorbents (O_{ad}^{2-}) and a resulting increase in concentration of electron.

The gas response was mainly dependent upon two factors. The first was the amount of active sites for oxygen and the reducing gases on the surface of the sensor materials. It is seen form TEM images (**Figure 2(c)**) that the surface of 90 min ZnO rougher than that of other thick films. The surfaces of 90 min ZnO contain more active sites than of other thick films. This could explain why the response of 90 min ZnO thick films was higher than other thick films.

5. Conclusion

In summary, sensors were fabricated with ZnO nanostructures, which were synthesized by a hydrothermal method followed by sonication, and their gas sensing properties were measured. The results demonstrated that 90 min ZnO is very sensitive to low concentration H_2S. Such nanomaterials with innovative structure can be used for gas sensors to monitor hazards gas like H_2S.

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