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Aqueous Chemical Method Synthesis of Hexagonal Nanostructured ZnO: Effect of Ag Doping on Ethanol Vapor Response Property

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Abstract - Undoped and Ag doped ZnO thin films with various Ag doping concentrations (1 to 3 at.%) were prepared by aqueous chemical method. The structural and gas sensing properties of the films were carried out. XRD patterns show hexagonal structure of the ZnO with reduced in (002) intensities after Ag doping. The 2 at % Ag doped ZnO sample shows highest gas response towards 100 ppm ethanol at low operating temperature with fast response of 8s and recovery time of 23 s as compared with undoped ZnO thin film. The results demonstrated that Ag doped ZnO sensor could be a good choice for ethanol gas sensing.

Keywords: Ag doped zinc oxide; Gas sensor; aqueous chemical route;

I. INTRODUCTION

Zinc oxide (ZnO) is an interesting *n*-type semiconductor which is chemically and thermally stable and having wurtzite structure with large-band gap energy of 3.37 eV. The gas sensors based on ZnO have been fabricated by various techniques, such as chemical vapour deposition [1], thermal evaporation [2], spray pyrolysis [3], hydrothermal method [4], etc. Among them the aqueous chemical method is a unique technique which offers a relatively facile and versatile method for the large-scale synthesis of nanostructures that are exceptionally long in length, uniform in diameter, large in surface area; especially diversify in composition [5]. The solution-based aqueous chemical method offers a simple and low cost route for large area thin film coating method and proved as an alternative to high temperature thermal deposition techniques [6]. Moreover, it has the advantage of fabricating thin films with a small grain size and a large surface area, useful for gas sensing applications. However, the response of ZnO based materials, especially to some chemically reduced gases, such as ethanol, acetone, etc. is observed at high working temperature of 400–500ºC. Therefore, there is an obligatory need of making effort to improve their gas sensing property at low temperature. Of the available solutions, doping is an important and effective way to improve the properties of semiconductor gas sensors. The dopant acts as a catalyst, produces structural change, which enhances the gas sensing properties [7-8]. The gas sensing properties are related to some critical factors, such as the surface state, morphology, surface to volume ratio and active centers of the material.

In this study, undoped ZnO and Ag doped ZnO thin films with various Ag concentrations were synthesized using an aqueous chemical method. The effect of Ag doping on the structural and the ethanol sensing properties of ZnO thin films is investigated.

II. EXPERIMENTAL DETAILS

2.1. Synthesis method

The undoped and Ag doped ZnO thin films were deposited using the aqueous chemical method. Prior to dipping into the seed solution the glass substrates were cleaned ultrasonically by a freshly prepared dilute hydrochloric acid, distilled water and further these substrates were dried at room temperature. The detailed procedure of formation of seed solution has been described earlier report [9]. The seeded substrate was further used to deposit the material in present study. The equimolar solution was prepared by using zinc acetate and Hexamethylenetetramine (HMTA) 0.025M (equal molar) powder and they were dissolved in a 160 ml of double distilled water. The precursor solutions were added with vigorous stirring for 30 min and it was refluxed at 95ºC for optimum time. The concentration of Ag was varied from 0 to 3 at.% with a step of 1 and accordingly the samples were denoted as S1, S2, S3, and S4 respectively.

2.2. Experimental measurement

The structural characteristics of undoped and Ag doped ZnO nanostructured thin films were identified from X-ray diffraction (XRD) technique using Philips (PW 3710) diffractometer model with a Cu Kα (λ=1.54 Å) target. The gas response properties of these nanostructured thin film samples were studied towards ethanol, acetone, LPG and NH3 in the temperature range of 200-450°C.

III. RESULTS AND DISCUSSION

3.1. XRD analysis

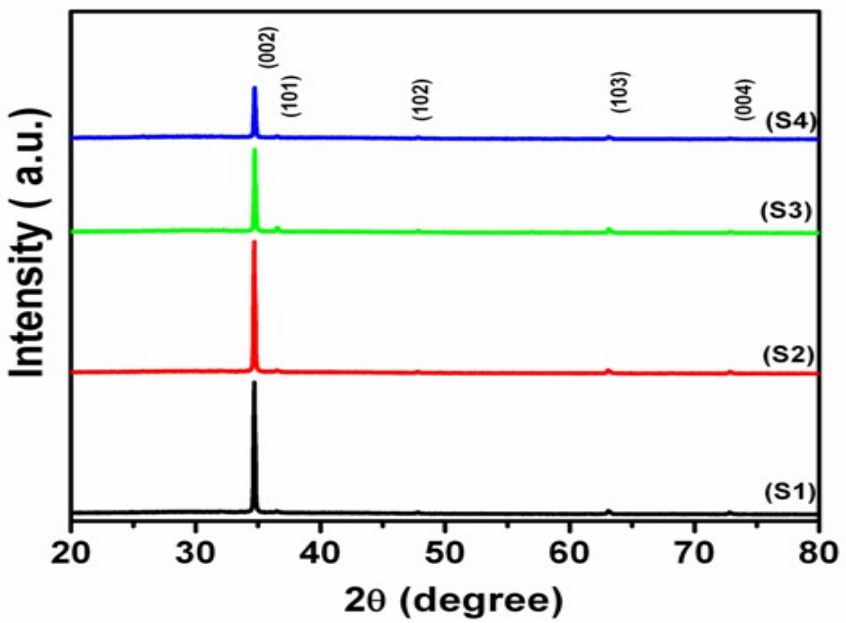

Figure 1: XRD patterns for undoped and Ag doped ZnO samples.

Fig. 1 shows the typical XRD patterns for undoped and Ag doped ZnO thin films. The diffraction peaks match well with the standard JCPDS (card No. 36-1451) for the hexagonal wurtzite structure. The (002) peak is the most prominent peak observed in the XRD of ZnO films. Other planes such as (101), (102), (103), (004), etc. are observed with low relative intensities. With increase in Ag concentration, it is observed that, the intensity of peak corresponding to (002) reflection plane is reduced which indicates the formation of the Ag doped ZnO. The average crystallite size (D) was calculated using the Scherrer equation as follows;

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad \text{……..……. (1)}$$

Where, λ, β and θ are the X-ray wavelength, the full width at half maximum (FWHM) of the diffraction peak and the Bragg's diffraction angle, respectively. The crystallite size was found to be in the range of 60 to 95 nm. The ionic radii of Ag^{+} and Zn^{+2} are 1.02A˚and 0.65A˚respectively. It may be considered that, the substitution of Zn^{+2} by larger ionic radius of Ag ions produces crystal defects and charge imbalance in ZnO structure [10-11]. The average crystallite size varied with increase in Ag concentration which is clearly seen through broadening and lowering of intensity of the intense peak (002).

IV. GAS RESPONSE STUDIES

4.1. Effect of operating temperature

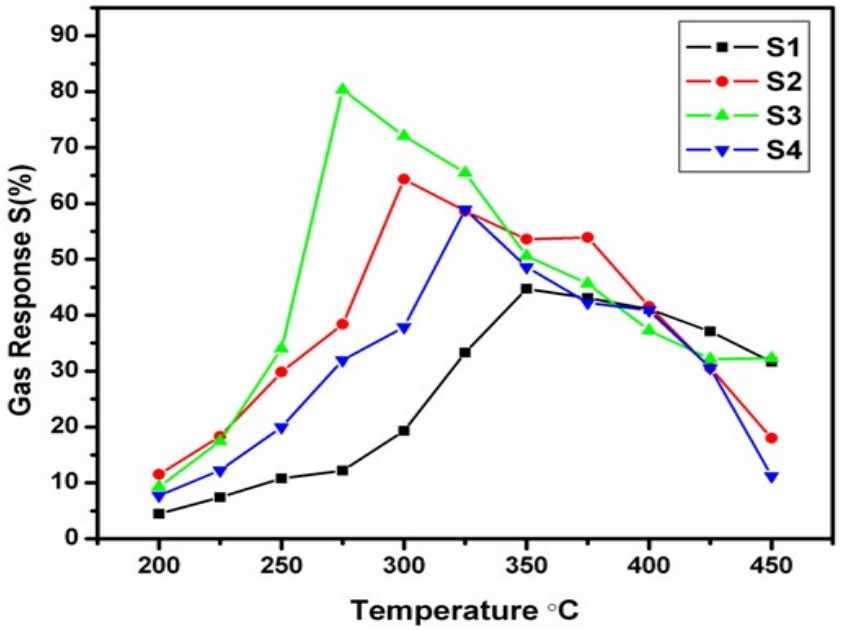

Figure 2: The gas response as a function of operating temperature for undoped and Ag doped

The gas response properties of thin film samples were studied using the gas sensing set up as described in earlier report [12]. Fig.2 shows the relationship between operating temperature and gas response of undoped and Ag doped ZnO sensors at 2000 ppm ethanol vapor. For each sample the response towards ethanol increased with operating temperature, reaching its maximum and then decreased rapidly with the increase in operating temperature. This behavior is mainly due to the influence of operating temperature on the amount of absorbed oxygen species on the surface of ZnO film [13]. At low temperature the amount of absorbed oxygen species is low so the sensor response exhibited is consequently small while at very high temperature the progressive desorption of the previously adsorbed oxygen species occurs and hence the sensor response decreases [14]. The S3 sample showed maximum response of 81% at low operating temperature of 275ºC, which is highest as compare to all the other samples S1 (44% at 350°C), S2 (64% at 300°C), and S4 (58% at 325°C), respectively. When the optimum amount of Ag (S3) is incorporated on the surface of the ZnO film, Ag or Ag_2O species would be distributed uniformly throughout the surface of the film. When the amount of Ag or Ag_2O on the surface of the film is less than the optimum. The 2at.% Ag doped ZnO (S3) exhibited maximum response of 81% at an operating temperature of 275°C. The S3 sensor exhibited high response and low operating temperature as compared to S1, S2 and S4 sensors. Thus S3 sample has proved to be the potential candidate for ethanol detection with high response and relatively moderate operating temperature.

4.2. Effect of gas concentration

The response of S3 sample as function of concentration for various test gases at 275 °C is shown in Fig. 3 the sensitivity values were observed to increase with increase the gas concentration up to 2000 ppm. From the above graph, it is clear that the sensitivity towards ethanol increased linearly with increase in gas concentration upto 500 ppm. Above 500 ppm the increase in sensitivity is slow and it almost saturates at 2000 ppm.

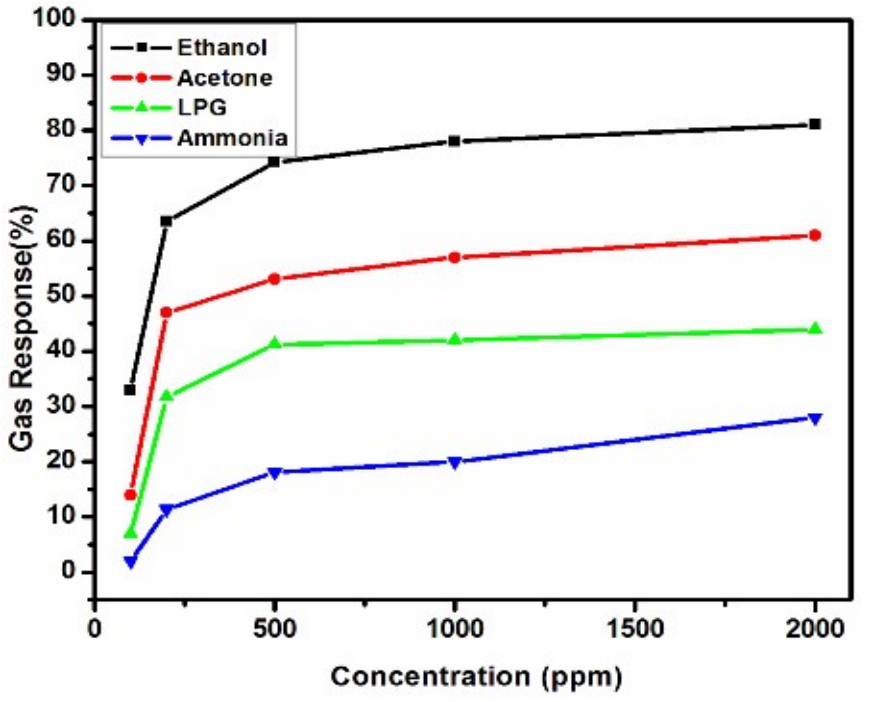

Figure 3: Plot of response versus concentration for various test gases for S3 sample.

At lower gas concentrations, the uni-molecular layer of gas molecules would be formed on the surface of the sensor which could interact more actively giving larger response. At the higher gas concentrations, the multilayer of gas molecules may formed that would result into saturation in response beyond 500 ppm [15-17]. The silver species catalyses the reaction promoting the rapid electron transfers between the adsorbate and substrate.

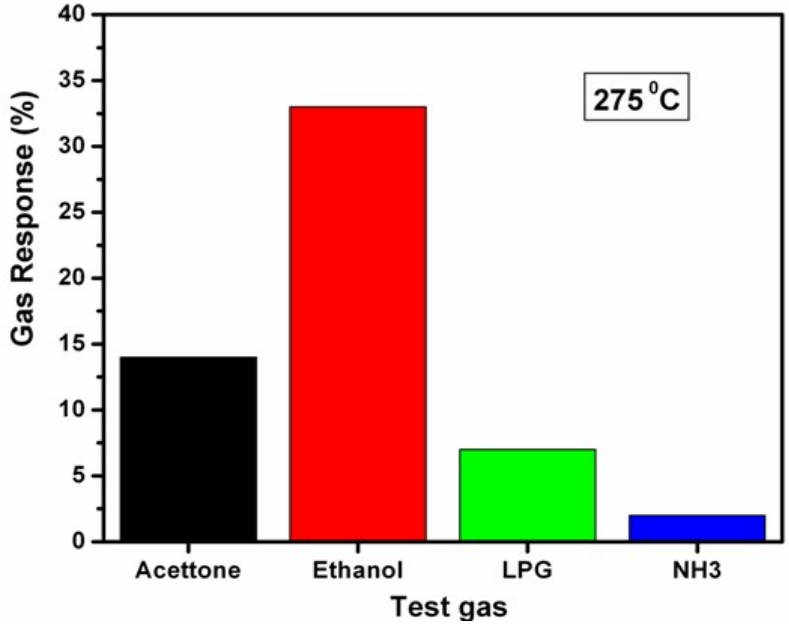

Figure 4: The gas response for S3 sample towards various test gases at 100 ppm.

Furthermore, Fig. 4 show that the gas response of S3 was tested towards 100 ppm different gases like ethanol, acetone, LPG, NH_3 at optimal operating temperature 275°C. The gas sensing properties of S3 sample

exhibited gas response of 33, 14, 7 and 2 % towards ethanol, acetone, LPG and NH_3, respectively. The S3 sensors show maximum selectivity for ethanol among all the tested gases.

4.3 Response and recovery time

The transient response characteristics of all the samples exposed to 100 ppm ethanol at an operating temperature of 275ºC are shown in Fig.5 in these measurements gas was introduced into the sealed glass tube and sensors resistivity was measured in air and in the presence of ethanol gas. The sensors response as a function of time was measured. From figure it is obvious that, as we go from S1 to S4 the sensor response is found to enhance significantly, which is attributed to the change in morphology and reduction in crystallite size of the sample with doping, which facilitates the adsorption of oxygen significantly. In case of S3, the number of active adsorption sites for oxygen is high as compared to S1, S2 and S3. It reveals that doping Ag promoted the gas response; improved the response and recovery characteristics of S3 at 275ºC

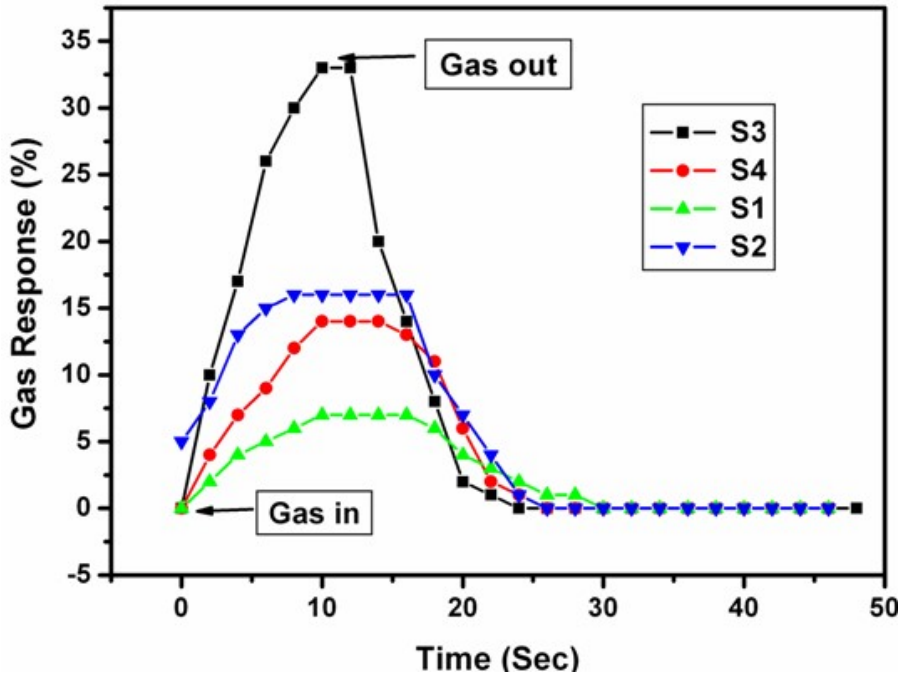

Figure 5: The plot of response and recovery time for S3 sample towards 100 ppm ethanol.

The S3 sample exhibited response and recovery time of 8s and 23s respectively for 100 ppm of ethanol. The faster response and recovery time for S3 might be due to the high reactivity of ethanol vapor with adsorbed oxygen in the presence of Ag sites on the surface of the sensor and also to the highly porous nature of the sensor. Fast and easier gas diffusion to grain boundaries would enable the gas to be oxidized immediately, giving fast response.

4.5. Gas sensing mechanism

ZnO nanostructure sensor are exposed to air, oxygen molecules can be adsorbed on the surface and form O^-, O_2^- and O^{2-} by capturing free electrons from the conduction band as a high resistance in air. When the nanostructured surface is exposed to reducing gas (such as ethanol) at appropriate temperature, ethanol may react with the surface oxygen species. Thus, the electrons trapped by O^- are released to the ZnO nanostructure. The reaction leads to a reduced resistance of ZnO nanostructure. The ethanol sensing mechanism of this ZnO based gas sensor can be summarized as follows [18-19]:

$$CH_3CH_2OH_{ads} + 6O^-_{ads} \rightarrow 2CO_2 + 3H_2O + 6e^- \quad \text{..... (2)}$$

As far as the effect of Ag doping on the gas sensing performances of ZnO can be explained by the defect chemistry model of acceptor-doped ZnO suggested by Fukui and Nakane [19]. On the other hand, Ag

doped ZnO nanostructure has large surface-to-volume ratio and a high density of active adsorption sites, which results the sample of 2at.% Ag doped ZnO has a relatively higher response than undoped ZnO.

V. CONCLUSIONS

Undoped and Ag doped ZnO thin films were prepared using a simple aqueous chemical method. XRD patterns of the samples showed that the formation of hexagonal wurtzite structure which reveal variation in (002) peak intensities with Ag doping. It was found that, the 2 at.% Ag doped ZnO film exhibited improved response to ethanol. The response and recovery times (8s, 23s) towards 100 ppm of ethanol were observed for the sample with the 2 at.% Ag doping at 275°C indicating promising material for ethanol detection.

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