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Development of ZnO/Ag Nanocomposite Film for Gas Sensing Application

DEEPAK DAVIS and SHEELA SINGH*

Department of Physics & Nanotechnology, SRM University, Kattankulathur, Chennai-603 203, India

*Corresponding author: E-mail: sheela2k5@gmail.com

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The sol-gel technique was used to prepare zinc oxide nanoparticles doped with silver ions. The sample phase and microstructure were characterized by different techniques such as X-ray diffraction, field emission scanning electron microscopy, also absorption and metal composition were finding by UV-visible spectra, EDAX, respectively. In this paper, we tried with ZnO/Ag nanocomposite with pH 9 and varying the composition of silver ions. X-ray diffraction study showed that increasing in intensity of silver with the silver concentration, which indicates the formation of ZnO/Ag composite. The prepared sample maintains the good morphology and microstructure of pure ZnO. Sensing results showing that ZnO/Ag nanocomposite shows better sensing properties. 5 wt % $AgNO_3$ and 0.5 g of ZnO with adding 1 mol $NaBH_4$ in 5 mL of ZnO/Ag composite (pH 9) were giving better sensing output. The fabricated device showed that high sensor response of 72 % at 1000 ppm and the low detection limit is 5 ppm.

Keywords: ZnO/Ag nanocomposite, Gas sensing, Thin film, Nanoparticle, Sol-gel.

INTRODUCTION

An inorganic compound like zinc oxide (ZnO) is widely used as an additive into numerous materials like plastics, ceramics, glass, *etc*. [1]. It is also using in emerging applications for energy saving in transparent electrodes as in liquid crystal displays and reducing agent of heat in a light emitting diode (LED) [2]. Now a day, due to increasing the global warming effects of various toxic and flammable gasses has been motivated to make accurate and low-power consuming also reliable detection to monitoring number of gases [3]. Acetylene is the most pollutant with around 3300 °C flammability and toxicity. Acetylene is widely used as a fuel or has been a raw material in various chemical and mechanical industries [4]. Sometimes it may leak and create massive explosions, therefore, reliable C_2H_2 sensors are being sought for the safety issues [5]. The number of research results show the limitations, such as complex synthesis roots, high operating temperature, limits of detection and gas selectivity, are still ongoing research [6]. The continued development of various nanostructured metal oxides, like ZnO, has been attracted immense interest for sensor applications due to the favourable properties for the fabrication of various sensors such as low sensor response, poor selectivity and working temperature limit is higher for its practical applications [7]. Gas sensor performances are greatly influenced by the shape and size of the sensing nanomaterials. When the adding micrometer-scale and nanometer-scale building blocks in the 3D architectures help to induce and introduced a variety of novel properties including the structure features, specific surface area is higher and porosity and it will improve the accessibility of test gasses [8]. Recently, Zhang *et al.* [9] and Lao *et al.* [10] were improved the sensing properties of C_2H_2 through the synthesis of ZnO nanostructures at high temperature and it shows surface area is increased, mass transport is easier and stability is higher than other nanostructures. The aim of this work is to study the C_2H_2 sensing properties based on prepared ZnO/Ag nanocomposite.

EXPERIMENTAL

The experiment work was divided into two steps, first, the preparation of ZnO nanoparticle and second step the synthesized ZnO will be added into silver nitrate solution to get silver nanoparticle. The reducer solution was used in the experiment is $NaBH_4$.

Synthesis of ZnO nanoparticle: In this process, 2 mol of $Zn(CH_3COO)_2{\cdot}2H_2O$ (zinc acetate dihydrate extra pure - Sisco Research Laboratories Pvt. Ltd.) and 1 mol of NaOH (RANKEM Research Laboratories Pvt. Ltd.) were dissolved in isopropyl alcohol (Sisco Research Laboratories Pvt. Ltd.) under magnetic stirring for 30 min. Then, a few drops of ammonia solution (Sisco Research Laboratories Pvt. Ltd.) was added to the mixer to obtain the level of pH is 9. Then mixer is heated on a hot plate at 100-200 °C for 3 h to get a sol-gel foam, after that using muffle furnace for 5 h at the temperature of 200 °C. Followed by natural cooling to room temperature, washing and drying [11].

Synthesis of ZnO/Ag nanocomposite: For the preparation of ZnO/Ag composite, 0.5 g of purely synthesized ZnO nanoparticle and 3 weight percentage of $AgNO_3$ (extra pure - Sisco Research Laboratories Pvt. Ltd.) (with respect to the ZnO) were dissolved in 20 mL of deionized water *via* sonication in the presence of $NaBH_4$. In the same way the different ZnO/Ag composites were synthesized by varying the silver content at 3 wt %, 5 wt % and 7 wt % with respect to ZnO.

With the help of particle size analyzer (Brookhaven 90 Plus) find out that pH 9 particle size is 30 nm to 100 nm and it is the better size for the gas sensing application. The sensor devices were fabricated by depositing the materials onto 2 mm × 2 mm glass substrates *via* spin coating. Then with the help of high vacuum physical vapour deposition (Vacuum Technique Pvt. Ltd-Bangalore) the gold electrode deposited on the surface of ZnO/Ag thin film. Sensing of gas is measurements on the fabricated sensors by carried out in an open air environment between 25 and 300 °C. The device is attached to a ceramic heater to supply the temperature. The Keithley 4200 characterization system was used for data collection and measurements. Sensor response was calculated as:

$$S = (Rg - Ra)/Ra \times 100$$

where Ra and Rg are the resistances of the device in the presence of air and carrier gasses.

RESULTS AND DISCUSSION

UV-visible absorption (LAB INDIA Instruments Pvt. Ltd, U.V 3000+ Model) were recorded (Fig. 1) the absorption spectrum of the prepared samples of ZnO (pH 9). Zinc oxide has large direct band gap energy of about 3.4 eV at room temperature. The obtained blue shift and red shift is 202 and 278 nm, respectively.

Field emission scanning electron microscopy (FESEM) (JSM-6500F) image (Fig. 2) shows that 1.5-2.0 µm microsphere-like hexagonal structures of ZnO. After the addition of silver nanoparticle into the synthesized ZnO nanoparticle clearly observed that randomly oriented nanosphere was formed with

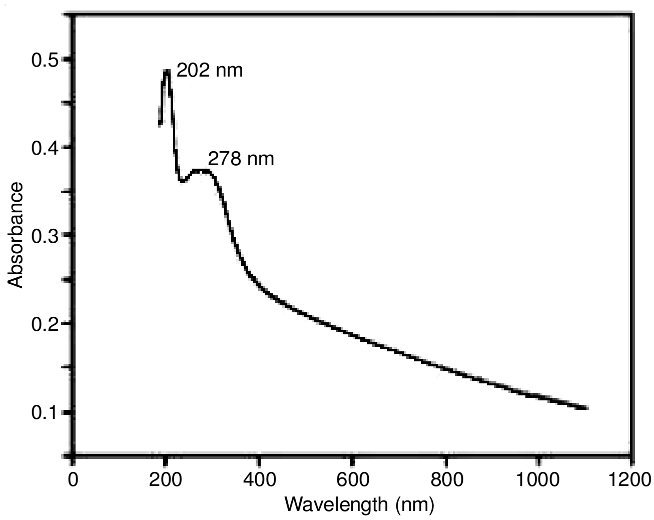

Fig. 1. UV-visible spectra of ZnO sample at pH 9

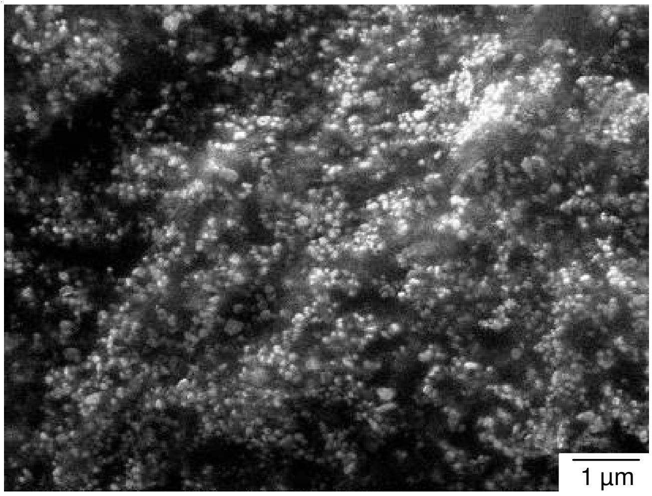

Fig. 2. FESEM image of ZnO sample at pH 9

reduction of the size of an average diameter of 30-100 nm. In the composite (Fig. 3), the presence of Ag was not clearly observed by FESEM, may be caused by the low content of silver nanoparticles. When the addition of $NaBH_4$ the size of the particle is reducing compared to without addition of $NaBH_4$.

The typical EDAX (Fig. 4) shows that the spectrum of ZnO/Ag sample. The peak of Zn, O and Ag in EDAX indicates that the thin films are made up of zinc, oxygen and silver, which confirms the presence of Ag in the film for acetylene sensor studies.

Thin films consist of various ranges of ZnO/Ag distributed randomly, it offers the more surface area ineffective to enable effective adsorption-desorption of the oxygen. The porous nature of the film increases the pore of oxygen adsorption and it would increase the oxidative/reductive nature of the film. The structural changes and identification in phases of the deposited ZnO/Ag thin films were studied with the help of X-ray diffraction (X-Pert Powder XRD System, Spectris Technologies Pvt. Ltd). The diffracting angle (2θ) was recorded in between 20 and 80 and the XRD patterns (Fig. 5) were shows for all the samples. a - f shows the XRD patterns for all the thin films on deposited at 45 °C to the glass substrates. The XRD patterns revealed that the deposited films are hexagonal Wurtzite in nature with mixed phases of Ag and ZnO. The peaks of diffraction corresponding to ZnO and Ag can identify by JCPDS data card nos. 36-1451 and 45-1027, respectively. The peaks of diffraction are (002), (100), (101), (102), (112), (200) and (004) in the XRD patterns correspond to the hexagonal Wurtzite ZnO phase, but the diffraction peak, (200) at 2θ = 44.04 stems from Ag. Other peaks were not observed in the XRD patterns of ZnO/Ag thin films. The peak intensity if silver was increase slowly with respect to the concentration of silver, it shows that formation of the ZnO/Ag composite. Moreover, the peak position of the (002) plane was shifted to the lower 2θ angle with respect to the increasing Ag content. This shift may have occurred by the difference in radii of ion (*i.e.*, Zn = 0.65 Å and Ag = 1.02 Å).

Gas sensing properties study: 5 wt % $AgNO_3$ and 0.5 g of ZnO *via* spin coated with adding 1 M $NaBH_4$ in 5 mL of ZnO/Ag composite will less particle size compared to other. So that 5 wt % load sample selected for gas sensing studies.

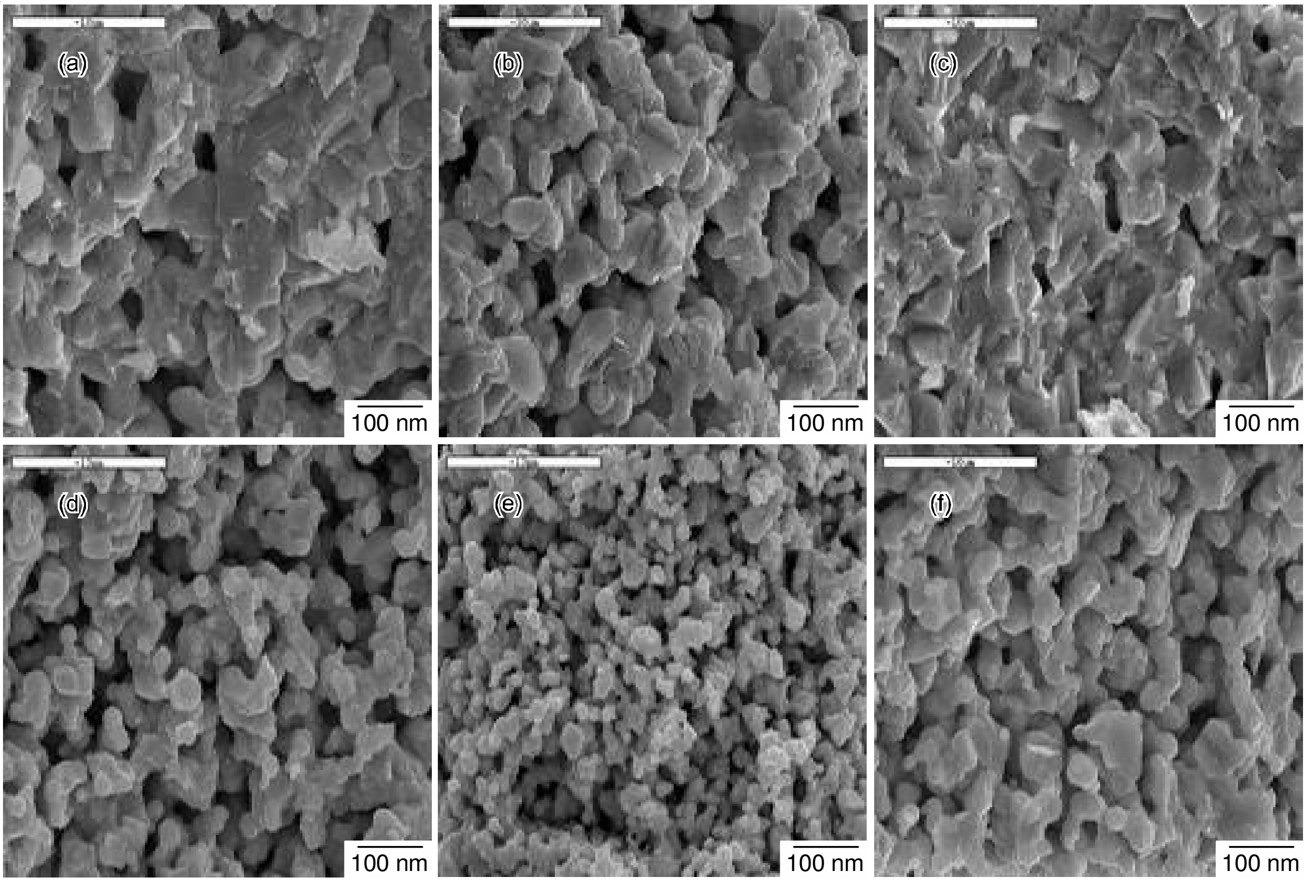

Fig. 3. ZnO/Ag nanocomposite in thin film mode (a): 3 wt % $AgNO_3$ and 0.5 g of ZnO *via* spin coated without adding $NaBH_4$, (b): 5 wt % $AgNO_3$ and 0.5 g of ZnO *via* spin coated without adding $NaBH_4$, (c): 7 wt % $AgNO_3$ and 0.5 g of ZnO *via* spin coated without adding $NaBH_4$ (d): 3 wt % $AgNO_3$ and 0.5 g of ZnO *via* spin coated with adding 1 M $NaBH_4$ in 5 mL of ZnO/Ag composite, (e): 5 wt % $AgNO_3$ and 0.5 g of ZnO *via* spin coated with adding 1 M $NaBH_4$ in 5 mL of ZnO/Ag composite, (f): 7 wt % $AgNO_3$ and 0.5 g of ZnO *via* spin coated with adding 1 M $NaBH_4$ in 5 mL of ZnO/Ag composite

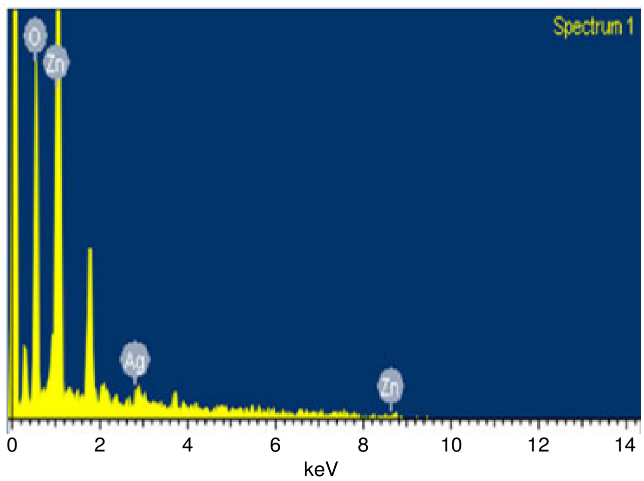

Fig. 4. EDAX spectrum of ZnO/Ag film

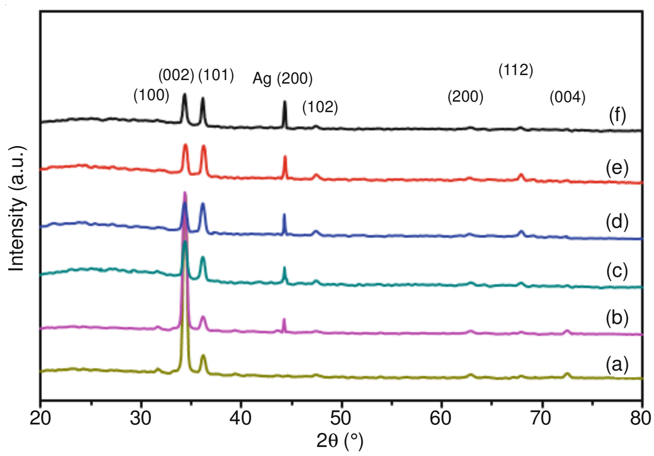

Fig. 5. XRD for thin-film ZnO/Ag composite (pH 9) (a): 3 wt % $AgNO_3$ and 0.5 g of ZnO *via* spin coated without adding $NaBH_4$, (b): 5 wt % $AgNO_3$ and 0.5 g of ZnO *via* spin coated without adding $NaBH_4$, (c): 7 wt % $AgNO_3$ and 0.5 g of ZnO *via* spin coated without adding $NaBH_4$ (d): 3 wt % $AgNO_3$ and 0.5 g of ZnO *via* spin coated with adding 1 M $NaBH_4$ in 5 mL of ZnO/Ag composite, (e): 5 wt % $AgNO_3$ and 0.5 g of ZnO *via* spin coated with adding 1 M $NaBH_4$ in 5 mL of ZnO/Ag composite, (f): 7 wt % $AgNO_3$ and 0.5 g of ZnO *via* spin coated with adding 1 M $NaBH_4$ in 5mL of ZnO/Ag composite

It was reported that the lesser particle size gives more sensing results according to the temperature level of sensing [3]. The sensing mechanism of gas in the ZnO-based sensor can be explained by the help of adsorption/desorption reactions between the chemisorbed oxygen anions (O^{-}_{ads}) on the ZnO surface and the target gas molecules, which depend on the operating temperature [1]. The operating temperature is varying within 25–300 °C for 100 ppm acetylene. The significant increase in the magnitudes of response was observed in the ZnO/Ag composites. The maximum value was obtained is 200 °C for the 5 wt % ZnO/Ag, it shows that the temperature for optimum operating is 200 °C (Fig. 6). Generally, the chemisorbed oxygen ions are formed a potential barrier to prevent movement of the C_2H_2 molecules on the ZnO surface at lower temperatures from reacting side. Fig. 7 shows the response against the C_2H_2 concentration of 5 wt % ZnO/Ag at the temperature level of 200 °C. It shows that 5 wt % ZnO/Ag is detected C_2H_2 as low as 5 ppm while maintaining and showing good linearity for all of the gas concentrations (5-1000 ppm).

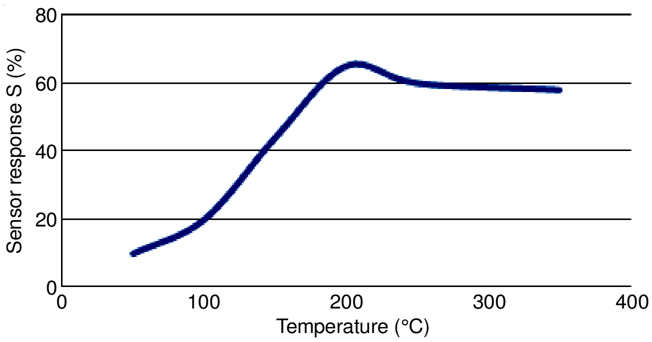

Fig. 6. Response to operating temperature to 100 ppm C_2H_2

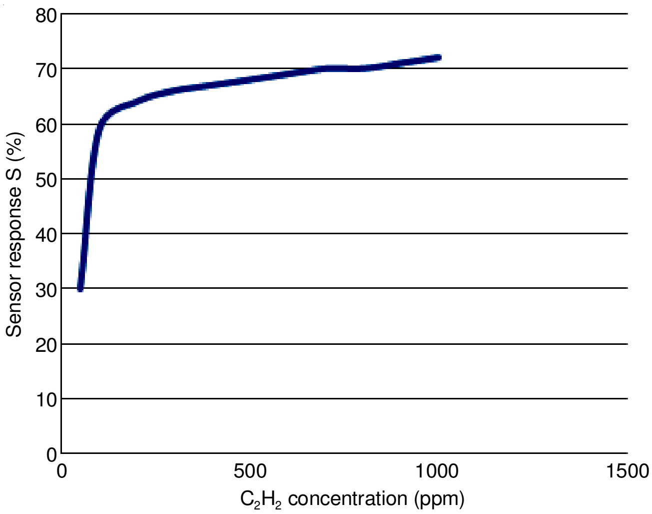

Fig. 7. Response against C_2H_2 concentration of 5 wt % ZnO/Ag at 200 °C

Conclusion

The sol-gel method is used to synthesized ZnO and adding Ag to the sample to form composites. It has been successfully synthesized. 5 wt % $AgNO_3$ and 0.5 g of ZnO with adding 1 mol $NaBH_4$ in 5 mL to form ZnO/Ag composite (pH 9) were giving better sensing output. The average particle size is 30-100 nm and it was calcined at 200 °C for 5 h. It should be efficient for the detection of acetylene at 200 °C. The fabricated device showed that high sensor response of 72 % at 1000 ppm and the low detection limit is 5 ppm. This fabricated sensor is satisfying the low cost- as well as the high-efficiency parameter for high pollutant gas like acetylene.

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