



Water Vapour Sensing Properties Of Znobased SnO₂doped Nano Composite Thick Film and Its Characterization

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Abstract:

In this paper ZnO and SnO₂ nanoparticles was synthesized by a liquid phase method. Structural and compositional characterizations have been studied by using X-ray powder diffraction (XRD). Sensing material was made in the form of thick film. Surface morphologies of the samples were analysed using Field Emission Scanning Electron Microscopy (FE-SEM). Humidity sensing investigations of these sensing materials were studied. Our result indicates that ZnObased SnO₂doped in form of thick film was most sensitive for humidity in comparison to pristine material under similar conditions. The hysteresis plot between increasing and decreasing the RH range of 30–90% Rh and vice versa. The resistance of sample wasdecreases 10¹⁰ Ω to 10⁷Ω in comparison with the pristine materials of sample ZS-5. The similar change was also observed in sensitivity and conductivity also. The results were re- producible up to ± 77% after 2 months of observations.

Keywords: Humidity Sensing, ZnO, SnO₂ nano particle.

Introduction:

Recently, the thick film technology is the most widely used technology for the humidity sensor fabrications. This technology has no difficulty in matching the packaging. It is believed to be one of the main driving forces for the future development of thick film sensors in various field [1]. Among these humidity sensors, resistive humidity sensors are widely manufactured and applied because of their suitable linearity, high response, suitable working stability, relatively simple structure, and low cost [2]. The metal oxide based electrochemical approaches are more attractive due to unaffected experimental procedures, having fast response time and good stability to build portable sensors. ZnO, SnO₂, WO₃, CuO, In₂O₃ and TiO₂ metal oxide gas sensors are extensively in

use [3-5]. Among these, ZnO based sensors are striking due to their wide band gap, excellent electrical properties, good chemical and thermal stability under standard operating environments. ZnO has gained attention as favourable sensor material for detection of watervapours [6]. Also, SnO₂ has recently become viewed as a potential humidity-sensing material owing to its wide band gap, relatively simple structure, suitable selectivity, and low cost [7,8]. As the flexibility, ZnO and SnO₂ are the best materials and the most thoroughly researched n-type semiconductors. The applications that can use these materials are gas sensors, humidity sensor [9].

Experimental:**Synthesis of zinc oxide (ZnO):**

In preparation Zinc Oxide (ZnO) 0.2M Zinc Acetate dehydrates was dissolved in 100 ml deionised water was ground for 15 min and then mixed with 0.02 M solution of NaOH with the help of glass rod. After the mixing the solution was kept under constant magnetic stirring for 15 min. and then again it was ground for 30 min. The white precipitate product was formed at the bottom and abundant liquid was discarded. The product was washed with the deionized water and methanol to remove by products and then filtered. The obtain precipitate was kept in a vacuum oven at 80 °C for 4 hrs. so the moisture will remove from the final product and we will get dry product. Then this dry product was crushed into a fine powder by using grinding machine and finally this fine nano-powder of ZnO was calcinated at temperature 800 °C for 6 hrs. in the auto-controlled muffle furnace so that the impurities from product will be completely removed and get a final product of ZnO nanoparticles.

Synthesis of tin oxide (SnO₂):

In preparation of SnO₂, 0.1 M of stannous chloride dehydrate (SnCl₂.2H₂O) was prepared. After complete dissolution, about 4 ml ammonia solution is added to above aqueous solution with magnetic stirring. Stirring is continued for 20 minutes. White gel precipitate is immediately formed. It is allowed to settle for 12 hrs. Then it is filtered and washed with water 2-3 times by using deionized water. The obtain precipitate

were mixed with 0.27 g carbon black powder. The obtained mixer is kept in vacuum oven at 70 °C for 24 hours so that the mixer gets completely in to dried powder. Then this dry product was crushed into a fine powder by grinder. Now obtained product of fine nanopowder of SnO₂ was calcinated at 700°C up to 6 hours in the auto-controlled muffle furnace so that the impurities from product will be completely removed.

Preparation of thick films:

The thick film was prepared by using screen printing. Initially, for the screen printing the thixotropic paste was formulated by mixing the sintered fine powder of pure and composite nano powder of ZnO and BaTiO₃ in different molecular weight ratios, a with a solution of ethyl cellulose (as 10% temporary binder) in a mixture of organic solvent such as butyl cellulose, butyl carbitol acetate and turpineol. The ratio of inorganic to organic part was kept as 75:25 in formulating the paste. The paste of pure and composite materials of ZnO and BaTiO₃ and it was screen printed on a glass substrate in the form of thick films. The prepared films were dried at 80-110°C in oven for 1hrs then the dried films are kept for fired at 500°C for 20 min in muffle furnace so that all the organic and organic impurities can be evaporated form the sensor material. For the surface conductance measurement, the electrodes of silver paint were formed on adjacent sides of the films and again, the films were subjected to heating at 80°C for 20 min for drying the silver paint.

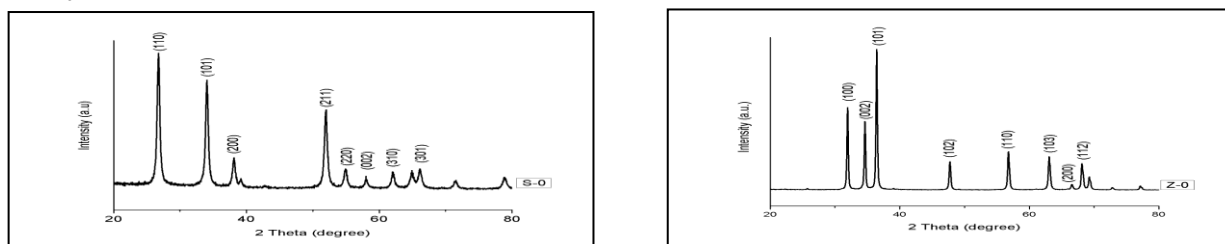
Characterization:**X-Ray Diffraction:**

Figure (1). X-Ray Diffraction of (a) ZnO and (b) SnO₂

The XRD pattern of pristine zinc oxide (ZnO) nanostructure synthesized by liquid phase method via solid state method calcinated at 800°C as shown in figure (1)(a). The crystalline nature with 2θ peak lying at (100), (002), (101), (102), (110) and (103) planes. All the peaks match well the standard hexagonal wurtzite structure of zinc oxide (ZnO) with lattice constants $a = b = 0.3249$ nm and $c = 0.5206$ nm [JCPDS card no. 36-1451]. All the peaks are perfectly match with pure ZnO structure, which indicates the high purity of the obtained ZnO nanoparticle. The average crystalline size was found to be 37.32 nm calculated by Deye-Scherrer formula [10]. Figure (1)(b). shows the XRD pattern of pristine stannic oxide (SnO₂) nanostructure synthesized by liquid phase via co-precipitation method

calcinated at 400°C it is clearly observed that the highest intensity peak is obtained at (110) crystal planes and other peaks lying at (101), (200), (211), (220) and (002) of SnO₂. All the peaks match well with the standard tetragonal structure of SnO₂ with lattice constant $a = 4.723$ nm and $c = 3.238$ nm and its unit cell volume ($V=72.24A^{03}$) with JCPDS card no. 71-0652. All the peaks are perfectly match with pure SnO₂ nanostructure, which indicates the high purity of obtained SnO₂nanoparticles. The average crystalline size was found to be 23.19 nm calculated by using Debye-Scherer formula [11].

FE-SEM:

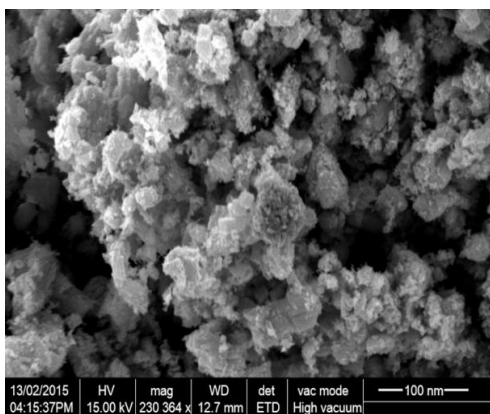


Figure (2). FE-SEM of nanocomposite

Figure (2) shows the FE-SEM morphology of composite thick film, it shows the particles are small sized, almost spherical, rod like structure. The micrograph reveals that they possess the grain size of nanometre order and shows nano porous

structure. It means that the structure is likely to facilitate the adsorption and condensation processes of water molecules because of the capillary pore and having large surface area. This porosity leads to an effective response and recovery towards humidity

Hysteresis plot:

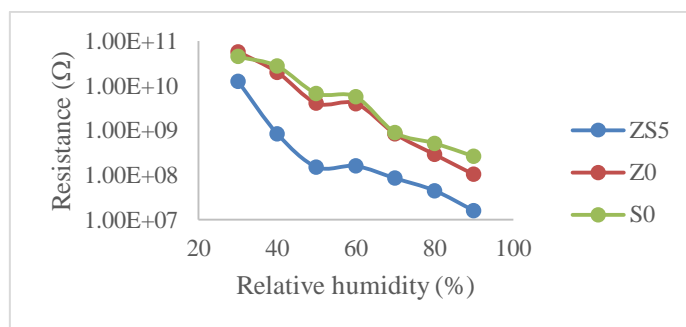


Figure (3). Hysteresis plot

Hysteresis plot shows the variation between resistances of sample with respect to the relative humidity in increasing and decreasing order from 30 to 90 % RH as shown in the figure (3). A very significant and small hysteresis present during forward and reverse cycle of relative humidity, where as a very significant average change was observed in the value of resistance of sample the change in value of resistance is from $10^{10}\Omega$ to $10^7\Omega$, these is a very remarkable change in the observed in the value of resistance of composite sample ZS5. In all the prepared sample the hysteresis is present which shows processes

of regeneration is quite slower as compare to the pristine samples [12]. Apart from these a sample ZS5 (40 SnO₂- 60 ZnO) shows comparable decrease in resistance with an increase in % RH which indicates that the conduction occurred at the grain surface by release of electron from the water molecule as compare to the pristine material. However, the sample shows the remarkable change in the resistance values in between the humidity range 30-90 % RH and possessed a high sensitivity factor due to large surface area and porosity in the form of thick films

Sensitivity:

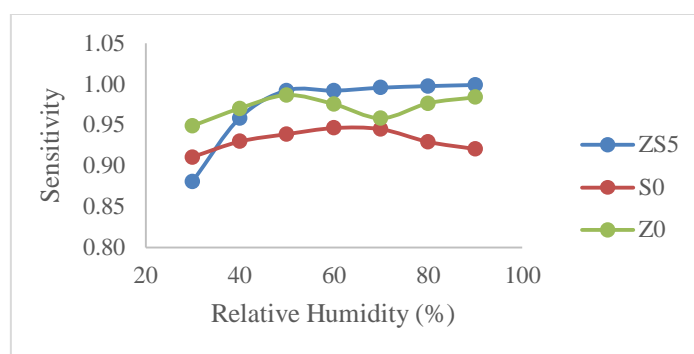


Figure (4) Sensitivity curve

In the above samples the sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant as shown in figure (4). For higher RH the sensitivity is found to be higher in case of all samples of thick films. The sensitivity of ZS5 (40 SnO₂-60 ZnO) is more than pristine samples. By addition SnO₂ to ZnO as a nano-composites which shows that the sensitivity remains constant. As the change in conductivity is more in ZnO-SnO₂ nano composite samples the similar change is observed in sensitivity also. Hence, by the addition of SnO₂ to the pristine ZnO stabilized the sensitivity of all the samples. The nano composite sensors

exhibit significantly higher sensitivity than sensor constructed specially from pure ZnO, nanoparticles itself due to the formation of heterogeneous interface between them and more adsorption site was created to absorb more water vapours [13, 14]. The fall in resistance is mainly due to the increased amount of conduction electron or charge carrier upon adsorption of water vapours by the surface layer of the thick films.

Conclusion:

Nanostructured ZnO and SnO₂ was successfully synthesised via chemical precipitation method. Minimum crystallite size was found to be for ZnO is 37.32 nm, and for SnO₂ it is 23.19 nm. Surface

morphology of composite material shows that most particles are spherical in shape leaving more space as pores and hence it was most sensitive among all the prepared samples. The Hysteresis curve shows very significant average change in the value of the resistance from $10^{10}\ \Omega$ to $10^7\ \Omega$ during forward and reversed cycles of sample ZS5 rather than pristine material. The sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant. As compare to the pristine the nano composite of ZS5 (40 SnO₂- 60 ZnO)sample is more sensitivity. This nano composite carries a good scope for the development of moisture sensor in the range of relative humidity 30% to 90% RH.

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