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Synthesis and Humidity Sensing Investigations of Nanostructured Zno Doped Sno2 Thick Films

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Abstract:

In present study, ZnO and SnO2 nanoparticles was synthesized by a chemical precipitation method. Structural and compositional characterizations have been studied from X-ray powder diffraction (XRD). Surface morphologies of the samples were analyzed using Field Emission Scanning electron microscopy (FE-SEM) for thick flim of different molecular weight ratio. Further, humidity sensing investigations of these nanocomposites sensing materials were done. Our result indicates that ZnO doped SnO2 in form of thick film for different molecular weight ratio was most sensitive for humidity in comparison to pristine materials under same conditions. The hysteresis plot between increasing and decreasing the RH range of 30–90% and vice versa. The samples resistance of sample ZS-3 decreases from 1011 Ω to 105 Ω in comparison with the pristine materials. The similar change was also observed in sensitivity. Activation energy measured from Arrhenius plot of conductivity at different RH and found to be 1.7010-3 eV respectively. The results were re- producible up to ± 77% after 2 months of observations.

Key words: ZnO, SnO2 nanocomposites, Humidity sensor.

Introduction

Recently, the development in humidity sensor has receives much more attention due to the necessity of controlling and monitoring environment in many varrious fields like industrial and domestic part [1-3]. Semiconducting oxides based humidity sensors has many advantages when compared to other types of humidity sensors, such as low cost, simple construction, small size etc in operating the environment. The metal oxide such as SnO2 , ZnO, WO3, TiO2, BaTiO3 etc the change in electrical conductivity depends upon the composition of the gas/humidity surrounding them. Therefore, they are used as popular and useful sensing materials for making inexpensive gas sensing devices [4]. The nanocomposites of ZnO and SnO2 seem to be one of the most promising metal oxide semiconductor for gas/ vapours/ humidity sensing. It has been observed that these nanostructure materials are more perceptive due to their high surface volume ratio, large band gap energy and have more chemically active [5-7].

In present study, nanocomposites of ZnO and SnO_2 thick films were prepared by screen printing method and the humidity sensitive properties of the nanocomposites films were investigated and compared with those of the pure films. The variation of resistance was studied as a function of relative humidity.

Experimental

Synthesis of zinc oxide (ZnO):

ZnO Nanoparticle were synthesized by solid state reaction method, using Zinc acetate dehydrate $Zn(O_2CCH_3)_2(H_2O)_2$, sodium hydroxide as starting materials . 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. The mixed and the solution were 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. Then abundant liquid was removed and the product was washed several times with the deionized water and methanol to remove by products. The final products was then filtered and it was kept in a vacuum oven at 80 ^oC for 4 hrs. so the moisture will removed from the final product. Then this dry product was calcinated at temperature 800 ^oC for 6 hrs. in the auto controlled muffle furnace (Gayatri Scientific, Mumbai, India.) so that the impurities from product will be completely removed and get a final product of ZnO nanoparticles.

Synthesis of tin oxide (SnO_2) :

In preparation of SnO_2 nanoparticle the Stannous chloride dehydrates ($SnCl_2.2H_2O$), Ammonia solution and deionized water were used as starting materials. Initially, 2 g (0.1 M) of stannous chloride dehydrate ($SnCl_2.2H_2O$) is dissolved in 100 ml water. 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 (charcoal activated). The obtained mixer is kept in vacuum oven at 70 ºC for 24 hours so that the mixer gets completely in to dried powder. Then this dry product was crushed into a find powder by grinder. Now obtained product of fine nanopowder of SnO_2 was calcinated at 700^oC up to 6 hours in the auto controlled muffle furnace (Gayatri Scientific, Mumbai, India.) so that the impurities from product will be completely removed.

Preparation of thick films :

The thick film were prepared by screen printing technique on a glass substrate. 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 SnO_2 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 SnO_2 and it was screen printed on a glass substrate in the form of thick films and it was dried at 80-110^oC in oven for 1hrs. The dried films is fired at 500^oC for 25 min in muffle furnace (Kumar make Mumbai), to remove organic impurities form the sensor material. For the surface conductance measurement the electrodes of silver paint were formed on adjacent sides of the films.

Characterization Technique

X-Ray Diffraction (XRD)

The XRD pattern pure zinc oxide (ZnO) synthesized nanostructure in figure (1). The crystalline nature with 2θ peak lying at (100), (002), (101), (102), (110) and (103) planes. All the peaks match are perfectly with the standard hexagonal wurtize structure of zinc oxide (ZnO) with lattice constants a = b = 0.3249 nm and c = 0.5206 nm [JCPDS card no. 36-1451] and 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 [8].

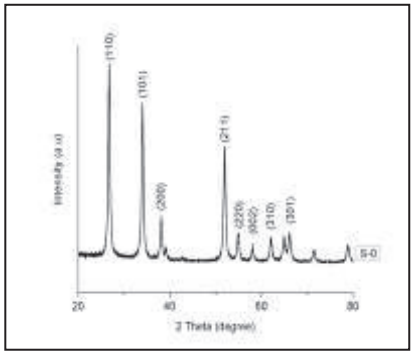

Figure. 1

The XRD pattern pure SnO_2 nanostructure is as shown in figure (2). 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 SnO_2. All the peaks match well with the standard tetragonal structure of SnO_2 with lattice constant a = 4.723 nm and c = 3.238 nm and its unit cell volume (V=72.24A^{o3}) with JCPDS card no. 71-0652. The average crystalline size was found to be 23.19 nm [9].

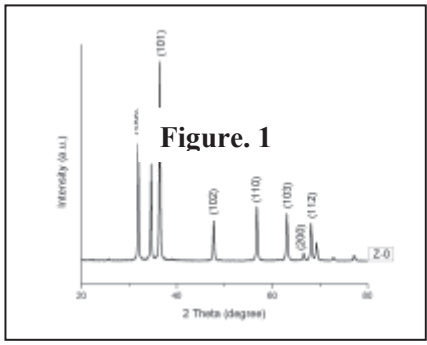

Figure. 2

The observes peaks are the mixed combination of ZnO and SnO_2 semiconducting metal oxides as shown in figure (3). In these case from crystal quantization plot mostly the peaks about (90%) corresponds to ZnO nanomaterial and very few about (10%) corresponds to SnO_2 nanomaterials. The XRD pattern of the sample such as ZS-1, ZS-3,and ZS-5shows crystalline nature and crystalline planes are obtained due to ZnO and SnO_2 both. The average crystalline size is obtained by using scherrer formula and has been found to be 36.42 nm, 28.33 nm, 42.5 nm respectively.

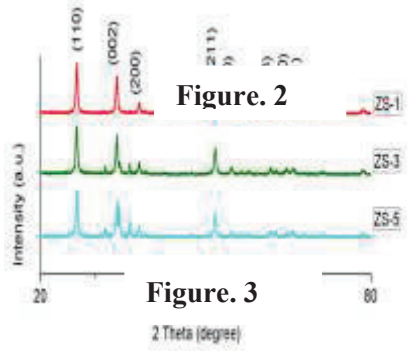

Figure. 3

Field emission Scanning Electron Microscopy (FE-SEM)

Figure (4a, 4b and 4c) decipts the FE-SEM micrograph of pristine SnO_2 and ZnO nano composites thick films. The FE-SEM morphology shows the particles are small sized, almost spherical, rod like structure. The micrograph of ZS-3 reveals that they possess the grain size of nanometre order and shows nonporous 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 [10].

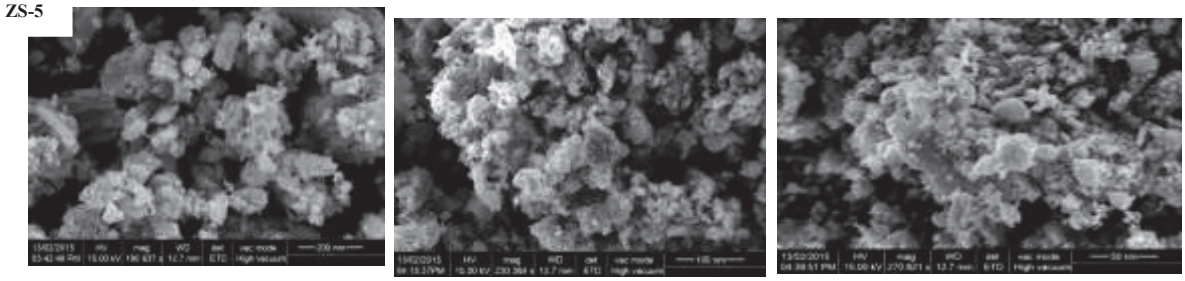

Figure. 4(c)

Figure. 4 (a) **Figure. 4 (b)**

4. Results and Discussion

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 at constant temperature as shown in the figure (5). A very small hysteresis present during forward and reverse cycle of relative humidity, where as a very significant average change observed in the value of resistance of sample, in the sample ZS-3 (30ZnO - 70SnO_2) the change in value of resistance is from 10^{11} □ to 10^5 □, these is a remarkable change in the value of resistance.

In all the samples hysteresis is present which shows processes of regeneration is slower as compare to the samples. On the other hand a sample 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. However, the sample ZS-3 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.

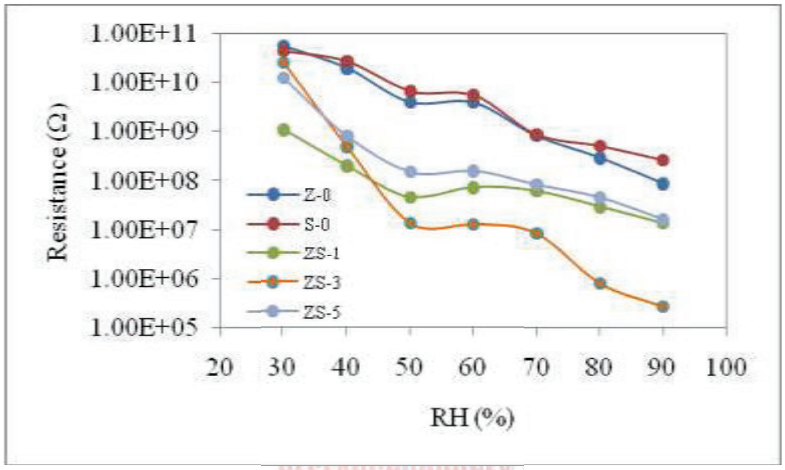

Figure 5: Hysteresis plot.

Sensitivity

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 (6). For higher RH the sensitivity is found to be higher in case of all samples of thick films. The sensitivity of ZS-3 (30ZnO-70SnO_2) is more than ZS-1(10ZnO-90SnO_2) and ZS-5 (50ZnO-50SnO_2) samples and also from the pristine samples S-0 and Z-0. The ZnO-SnO_2 composite sensors exhibits significantly higher sensitivity than sensor constructed specially from ZnO and SnO_2 nanoparticles itself due to the formation of heterogeneous interface between them and more adsorption site was created to absorbed more water vapuors [11]. 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. Initially, at low humidity levels the adsorbed water molecules get ionized on the surface and the hydronium ions are produced by the assistance of high electric charge density in the neighbourhood of the hydroxyl (OH-) sites resulting in the protonic conduction to the adjacent sites [12]. The change in conductivity is more in ZS-3 nano-composite the similar change is observed in sensitivity also and hence ZnO-SnO_2 based nano-composites sensors exhibit significantly higher sensitivity than other samples.

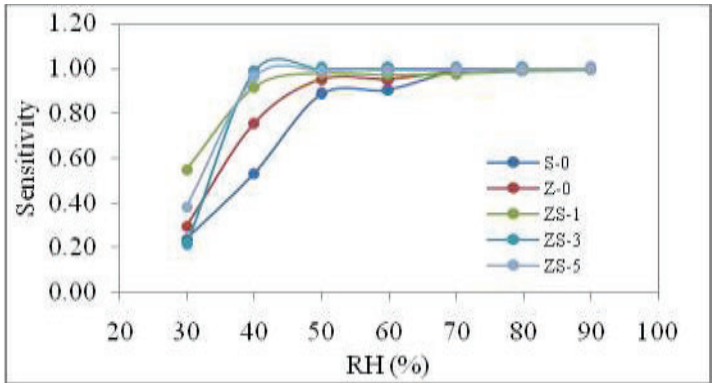

Figure 6: Variation of Relative Humidity with Sensitivity.

Activation Energy

The Arrhenius plot for all the samples found to be linear and by using Arrhenius equation;

□□□□□□□ 1

The activation energy □E For all the samples the activation is found to be quite reasonable for the electrical conduction the values of activation energy for the pristine SnO_2 and ZnO which is much more smaller at constant different RH. This shows that the smaller amount of energy is required for the conduction of electrons due to absorption of water molecules there by increasing the number of donor electron [13]. The activation energy of sample ZS-3 was found to be 1.70x 10^{-3} eV.

Conclusion

Nanostructured ZnO and SnO_2 was successfully prepared via chemical precipitation method. Minimum crystallite size was found to be for ZnO is 37.32 nm and for SnO_2 it is found to be 23.19 nm . Surface morphology of ZS-3 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 plot shows very significant average change in the value of the resistance from 10^{11} □ to 10^{5} □ during forward and reversed cycles of sample ZS-3(30ZnO-70SnO_2). 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. Amongst all the prepared samples ZS-3 is more sensitivity than other prepared samples. Activation energy measured and found to be 1.7010^{-3}eV respectively. This nanocomposites carries a good scope for the development of moisture sensor in the range of relative humidity 30% to 90% RH.

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