6. Humidity Sensing Properties of Batio3 Doped Zno Thick Flims

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Abstract

In present study, $BaTiO_3$ doped ZnO nanoparticles was synthesized by a liquid phase 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 study of these nanocomposites sensing materials were done. Our result indicates that $BaTiO_3$ doped ZnO 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 ZB-1 decreases from 10^{11} Ω to 10^{6} Ω in comparison with the pristine materials. The similar change was also observed in sensitivity.

Key word: Nanoparticle of ZnO and $BaTiO_3$, Humidity sensor.

1. Introduction

Recently, Humidity sensor has achieve considerable attention driven by its applications in the various filed such as environment monitoring, industrial process control, and our daily life [1-5].As Barium titanate with a perovskite structure is widely used lead-free ceramic material and it has been broadly used for the humidity sensing application in the last century [6-8].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 SnO_2 , ZnO, WO_3, TiO_2, $BaTiO_3$ 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 [9].In present study, nanocomposites of $BaTiO_3$ and ZnO thick films were prepared by screen printing method and the humidity sensitive properties of the nanocomposites films.

2. Experimental

2.1 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.

2.2 Synthesis of Barium Titanate ($BaTiO_3$)

In preparation of barium titanate ($BaTiO_3$) 0.25 M $Ba(NO_3)_2$ solution and 0.25 M $TiO(NO_3)_2$ solution were dissolved in 2 N nitric acid solution in a beaker. About 0.6 M tartaric acid solution was then added to under constant magnetic string. The solution heated under continuous string to its boiling point until all the liquid evaporated. About 7 gm of ammonium nitrate was added towards the ends to avoid slurry formation. Brown fumes evolution takes places and fluffy mass were settled at the base of the beaker. The product is then dried in vacuum oven at 96 ^oC for 2 hrs. so that moisture will removed from the final product and we will get dry product. Then this dry product was crushed into fine powder and finally this fine nanopowder of $BaTiO_3$ was calcinated at temperature 800oC for 5 hrs. in the auto controlled muffle furnace to remove the impurity form the product will be completely removed and get a final product of $BaTiO_3$ nanoparticle.

2.3 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 $BaTiO_3$ and ZnO 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 $BaTiO_3$ and ZnO and it was screen printed on a glass substrate in the form of thick films and it was dried at 80-110^{o}C in oven for 1hrs. The dried films is fired at 500^{o}C 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.

3. Characterization Technique

3.1 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 [10].

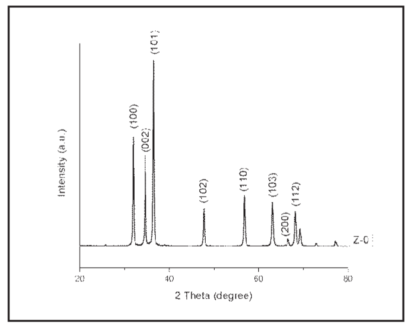

Figure 1: XRD of

Figure 2. shows the XRD pattern of pristine bariumtitanate (BaTiO3) nanostructure by liquid phase via sol-gel method calcinated at 800oC which is shows crystalline annealed with 2θ peak lying at (100), (110), (111), (200), (210),(211) and (220) planes. All the peaks match well with the standard provskitve type structure of barium titanate (BaTiO3) with lattice constant a = 3.992 Å, c = 4.036 Å

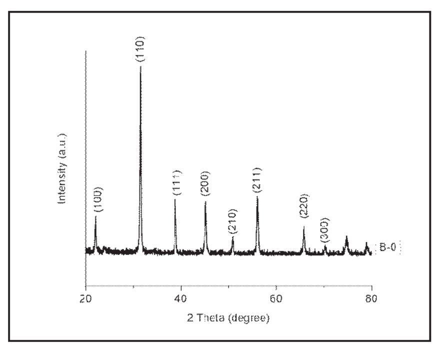

Figure 2: XRD of

[JCPDS card no1□□□1□□. All the peaks are perfectly match with pure BaTiO3 structure which indicates high purity of the obtained BaTiO3 nanoparticles. The average crystalline size was found to be 46.88 nm calculated by using Debey-Scherrer formula [11-13].

3.2 Field emission Scanning Electron Microscopy (FE-SEM)

Figure 3 decipts the FE-SEM micrograph of $BaTiO_3$ and ZnO nano composites thick films. The FE-SEM morphology shows the particles are small sized, almost spherical, rod like structure. The micrograph of ZB1 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 [14].

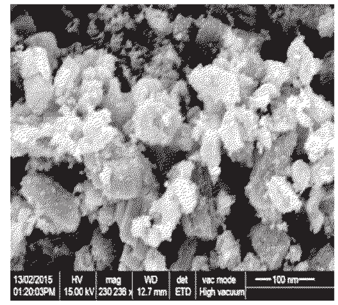

Figure 3: FE-Sem of sample ZB1

4. Results and Discussion

4.1 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 (4). A very small hysteresis present during increasing and decreasing cycle of relative humidity, where as a very significant average change observed in the value of resistance of sample, in the sample ZB1 (30ZnO – 70$BaTiO_3$) the change in value of resistance is from 10^{11} □ to 10^{6} □, 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 other samples. However, the sample ZB1 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.

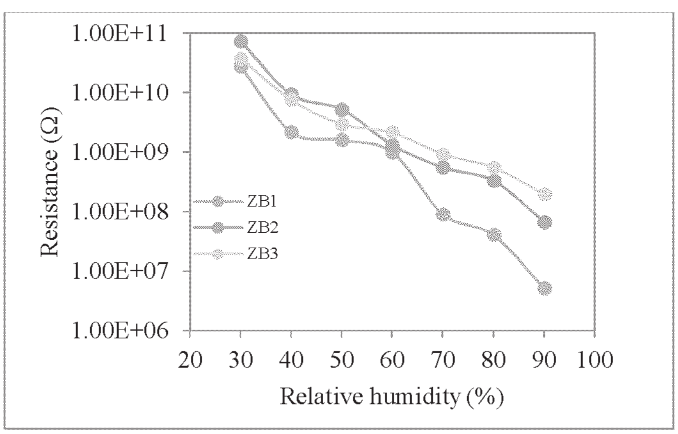

Figure 4: Hysteresis plot

4.2 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 (5). For higher RH the sensitivity is found to be higher in case of all samples of thick films. The sensitivity of ZB1 (30ZnO – 70$BaTiO_3$) is more than ZB2 (30ZnO – 50 $BaTiO_3$) and ZB3 (70ZnO – 30$BaTiO_3$) samples. The ZnO- $BaTiO_3$ composite sensors exhibits significantly higher sensitivity than sensor constructed from other metal oxide nanoparticles itself due to the formation of heterogeneous interface between them and more adsorption site was created to absorbed more water vapuors [15]. 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 [16]. Therefore, the sensitivity of the samples increases up to the particular limits and then remains constant for particular RH of all the samples. By addition of $BaTiO_3$ to ZnO nano-composites which shows that the sensitivity remains constant. As the change in conductivity is more in $BaTiO_3$ based ZnO nano composite samples the similar change is observed in sensitivity also. Hence, by the addition of BaTiO3 to the ZnO stabilized the sensitivity of all the samples.

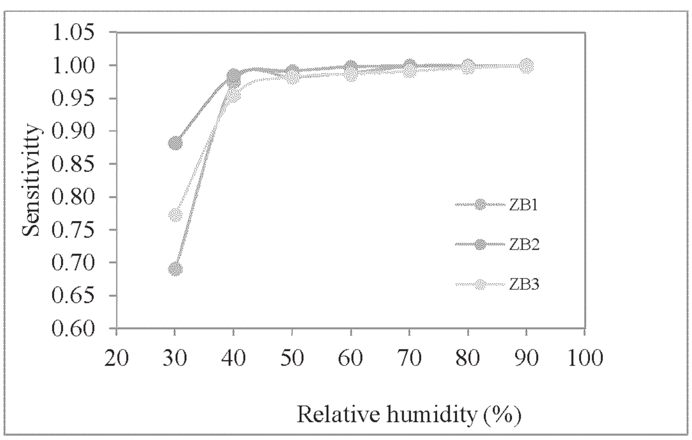

Figure 6: Graph of Relative humidity with Sensitivity.

5. Conclusion

Nanostructured ZnO and $BaTiO_3$ was successfully prepared via liquid phase method. Minimum crystallite size was found to be for ZnO is 37.32 nm and for $BaTiO_3$ is found to be

46.88 nm . Surface morphology of ZB1 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^{6} □ during increasing and decreasing cycles of relative humidity sample ZB1 (30ZnO – $70BaTiO_3$). 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 ZB1 is more sensitivity than other prepared samples.

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