Humidity Sensing Properties of ZnO/SnO_2 Doped $BaTiO_3$ Screen Printed Thick Film Sensor

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Abstract

In this paper ZnO and $BaTiO_3$ nanoparticles was synthesized by a chemical precipitation method. Structural and compositional characterizations have been done by X-ray powder diffraction (XRD). Sensing material was made in the form of thick film. Surface morphologies of the samples were analyzed using Field Emission Scanning electron microscopy (FE-SEM) for thick film of different molecular weight ratio annealed at 600°C. Further, Water vapour or humidity sensing investigations of these sensing materials were done. Our result indicate that ZnO/SnO_2 doped $BaTiO_3$ in form of thick film for different molecular weight ratio was most sensitive for humidity in comparison to pristine material under same conditions. The hysteresis plot between increasing and decreasing the RH range of 30–90% Rh and voice versa. The samples resistance of sample BZ-2 decreases 10^{10} Ω to 10^{6} Ω in comparison with the pristine materials. The similar change was also observed in sensitivity. The results were re- producible up to ± 77% after 2 months of observations.

Key words: *ZnO,SnO_2, $BaTiO_3$ nanocomposites, Humidity sensor.*

Introduction

Humidity, the concentration of water molecules in air, affects various materials used in daily life and industrial processing of drugs, beverages, food, electronic goods etc. High and low humidity affects human beings adversely. Excessive high humidity causes corrosion in metallic components and failure of electronic as well as optical devices [1,2].Semiconducting oxides based humidity sensors has various 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/humidity sensing devices [3].

In present study, nanocomposites of ZnO , and $BaTiO_3$based 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 ^{o}C for 4 hrs. so the moisture will removed from the final product. Then this dry product was calcinated at temperature 800 ^{o}C 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, 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°C 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 $BaTiO_3$**

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 °C 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 800°C 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.

- **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. 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 25 min in muffle furnace (Kumar make Mumbai), so that all the organic materials (in the form of binders) 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 15 min for drying the silver paint.

- **Characterization**

The XRD pattern of nanocomposites of samples SZB-2 (20 SnO_2 - 70 ZnO -10 $BaTiO_3$), SZB-4 (40 SnO_2 - 50 ZnO -10 $BaTiO_3$), and SZB-6 (60 SnO_2 - 30 ZnO -10 $BaTiO_3$).

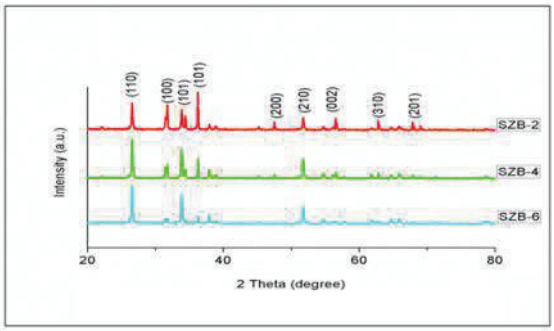

fig.: 1

In this it is observed that from XRD pattern for the sample SZB-2 (20 SnO_2 - 70 ZnO -10 $BaTiO_3$) shows the crystalline nature with 2θ peaks lying at (110), (100), (101), (101), (200), (210), (002), (310) and (201) planes. The observed peaks are the combination of SnO_2, ZnO and $BaTiO_3$ metal oxide. By using crystalline quantization plot, these more peaks about (45%) corresponds to SnO_2, (33%) corresponds to the ZnO and about (22%) peaks corresponds to the $BaTiO_3$ nanomaterials. It is observed from crystalline quantization plot, mostly peaks about 45% corresponds to the ZnO, about 33% corresponds to the SnO_2 and about 22% corresponds to the $BaTiO_3$nanomaterials. For the other XRD pattern of sample such as SZB-4 and ZSB-6 also shows the crystalline nature and crystalline planes are obtained from SnO_2, ZnO and $BaTiO_3$. The peaks intensity of $BaTiO_3$ peaks is found to be very less because of constant mole% of $BaTiO_3$and it is very less as compared to the other onces. The average crystalline size is obtained by using Scherrer formula and it has been found to be 92.88 nm, 63.75nm, and 56.64 nm for the sample SZB-2, SZB-4 and SZB-6 respectively. Hence, all the nonmaterials are found to be in the purely crystalline form.

Result and Discursion

- **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 fig. 2. 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 SBZ 2 (20 SnO_2- 70 ZnO-10 $BaTiO_3$) the change in value of resistance is from 10^{10} Ω to 10^6 Ω, these is a very remarkable change in the observed in the value of resistance. In all the prepared sample the hysteresis is present which shows processes of regeneration is quite slower as compare to the other samples. Apart from these 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 SBZ 2 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.

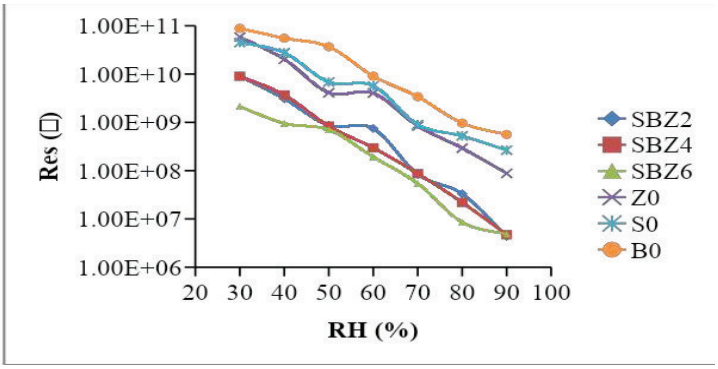

Fig.: 2

- **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 fig. 3. For higher RH the sensitivity is found to be higher in case of all samples of thick films. The sensitivity of SBZ-2 (20 SnO_2- 70 ZnO-10 $BaTiO_3$) is more than SBZ-4, SBZ-6, and samples and also from the pristine samples S-0, Z-0 and B-0. By addition of $BaTiO_3$ to ZnO-SnO_2 nano-composites which shows that the sensitivity remains constant. As previously stated that the change in conductivity is more in $BaTiO_3$ based ZnO-SnO_2nano composite samples the similar change is observed in sensitivity also. Hence, by the addition of $BaTiO_3$ to the pristine ZnO and SnO_2 stabilized the sensitivity of all the samples. The (ZnO-SnO2-$BaTiO_3$) composite sensors exhibits significantly higher sensitivity than sensor constructed specially from ZnO, SnO_2 and $BaTiO_3$ nanoparticles itself due to the formation of heterogeneous interface between them and more adsorption site was created to absorbed more water vapuors [4-5]. 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.

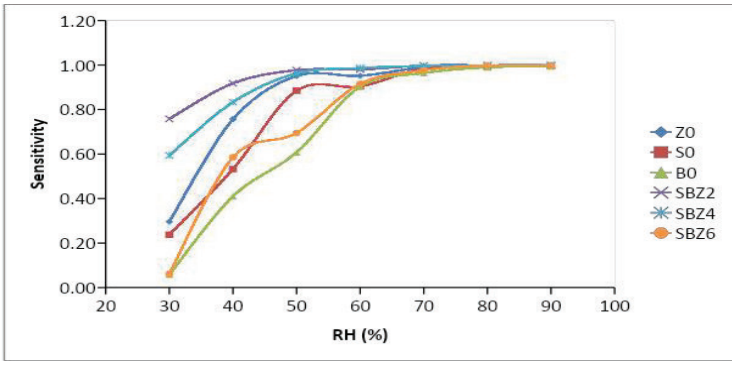

Fig.: 3

Conclusion

Nanostructured ZnO, SnO_2 and $BaTiO_3$ was successfully prepared via chemical precipitation method. Minimum crystallite size was found to be for ZnO is 37.32 nm, SnO2 it is 23.19 nm and for BaTiO3is . Surface morphology of SBZ-2 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^{10} Ω to 10^6 Ω during forward and reversed cycles of sample SBZ-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 SBZ-2 is more

sensitivity than other prepared samples.. This nano composites carries a good scope for the development of moisture sensor in the range of relative humidity 30% to 90% RH.

References

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