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Exploitation of PANI based Metal Oxide (ZnO-SnO2) Thick Films Humidity Sensor[1]

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ABSTRACT

Polyaniline (PANI) based Metal oxide nanocomposite thick films were prepared by using the screen printing technique. The films were fired and optimized temperature of 60ºc for 30 minutes in an air atmosphere. In the present work, Polyaniline is prepared by polymerization of aniline under acidic conditions. Zinc Oxide (ZnO) nanoparticles and Tin Oxide (SnO2) prepared by the Precipitation method at room temperature. The films were showing a decrease in resistance with an increase in temperature indicating semiconducting behavior. It is observed that PANI doped Metal oxide nanocomposite sensor shows a high response and sensitivity with good repeatability as compared to that of pure PANI and Metal oxide nanoparticle. The crystallinity and the crystallite size were examined by X-Ray Diffraction technique (XRD), and Scanning Electron Microscopy (SEM). Also confirms that the properties of pure polyaniline can be improved by the synthesis of Polyaniline - Metal oxide nanocomposites

Keywords: *Polyaniline; Metal Oxides Nanocomposites; Humidity sensor; XRD; SEM*

INTRODUCTION

There is a growing demand for a sensing system that has high sensitivity, wide dynamic range, good stability, quick response, good reproducibility, simple structure and minimal cost. Metal oxide films sensitive to humidity have been reported earlier where sensing has been done using optical means. However, metal oxide humidity sensors depending upon measurements of electrical parameters require high temperature operation and consume significant amount of power. Humidity control and monitoring are of great interest to a wide area; these include moisture sensitive products, fresh and pack-age food, drug storage and environmental control for valuable Antiques or paintings etc. [1, 2]. Humidity sensors that are available in the market include dew point, infrared, catalytic and tin oxide-based sensors, which may be expensive, or require high temperature operation and consume significant amount of power and high cost of maintenance [3].Much research has been focused on the development of humidity sensitive material [4–6]. Among these are the investigation of using conducting polymers such as polyaniline, polypyrrole, and polythiophene for humidity and gas sensing [7–9]. Advantages with polymers as sensing materials are light weight, flexible, low cost and simple fabrication process [10]. Pure polymer, polymer blends and polymer–inorganic composites have also been studied for the purposes, resulting in different degree of advancements in this area [11–16].

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SYNTHESIS OF MATERIAL

A) Synthesis of Polyaniline (PANI): In general, it is synthesized using two major polymerization approaches: electronic and chemical polymerization. In the present work, polyaniline is synthesized by chemical polymerization method in which 0.2 M aniline hydrochloride is used as monomer unit. The synthesis is done by oxidative polymerization with 0.25 M ammonia peroxysulphate in aqueous medium. Both solution kept 1 hour at room temperature then mixed in beaker, briefly stirred. And left at rest to polymerize, next day, the pani precipitate was collected on a filter, washed with three 100 ml portion of 0.2 M HCL and similarly with acetone. Polyaniline hydrochloride powder was dried in air and then in vacuum at 60°C. Polyaniline prepared under these reaction and processing condition are further referred to as standard sample.

B) 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 nano powder of SnO_2 was calcinated at 600ºC up to 6 hours in the auto controlled muffle furnace (*Gayatri Scientific, Mumbai, India*.) so that the impurities from product will be completely removed.

C) Synthesis of Zinc Oxide (ZnO): It is prepared by the aqueous solution of zinc nitrate. And is prepared by dissolving 0. 2M of zinc nitrate hexahydrate in 100 ml of distilled water. To this aqueous zinc nitrate solution, 0.2 M sodium hydroxide is added and the reaction mixture was heated at 80°C along with stirring and the process is carried out for four hour after which the white precipitate was obtained. The formed oxide wet precipitate is centrifuged. Then the wet precipitate is washed with de-ionized water to remove impurity ions present in it and further heated in the oven at 150°C to dry the precipitate formed.

RESULT AND DISSCUSIONS

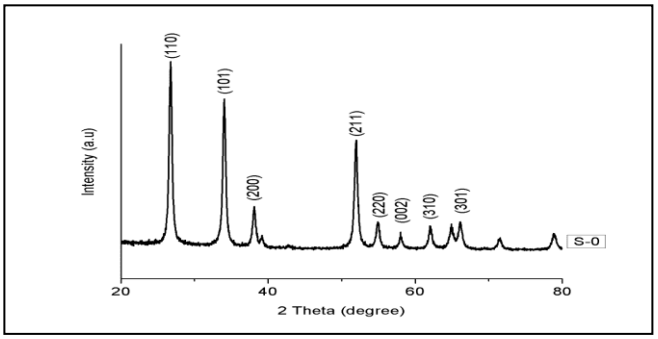

Fig .1. XRD of Pure SnO_2

XRD pattern of pristine Tin oxide (SnO_2) nanostructure synthesized by liquid phase method via chemical wet reaction method were calcinated at 800ºC as shown in figure 1. 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 ($V=72.24A^{o3}$). All the peaks are perfectly match with pure SnO_2 nanostructure, which indicates the high purity of obtained SnO_2 nanoparticles. The average crystalline size was found to be 26.31 nm calculated by using Debye-Scherer formula

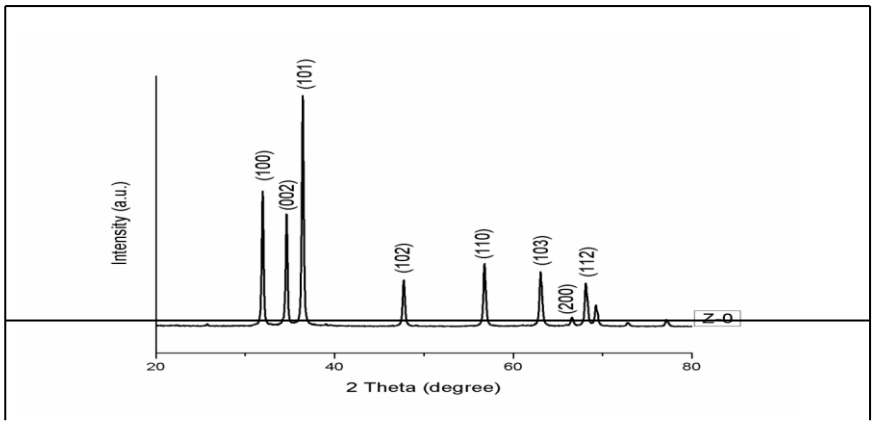

Fig. 2. XRD Pattern of ZnO

The XRD pattern of pristine zinc oxide (ZnO) nanostructure synthesized by liquid phase method via chemical wet reaction method were calcinated at 800^{o}C as shown in figure 2. The crystalline nature with 2θ peak lying at (100), (002), (101), (102), (110) and (103) planes. All the peaks match well the standard hexagonal wurtize structure of zinc oxide (ZnO) with lattice constants a = b = 0.3249 nm and c = 0.5206 nm. 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 36.48 nm calculated by Deye-Scherrer formula

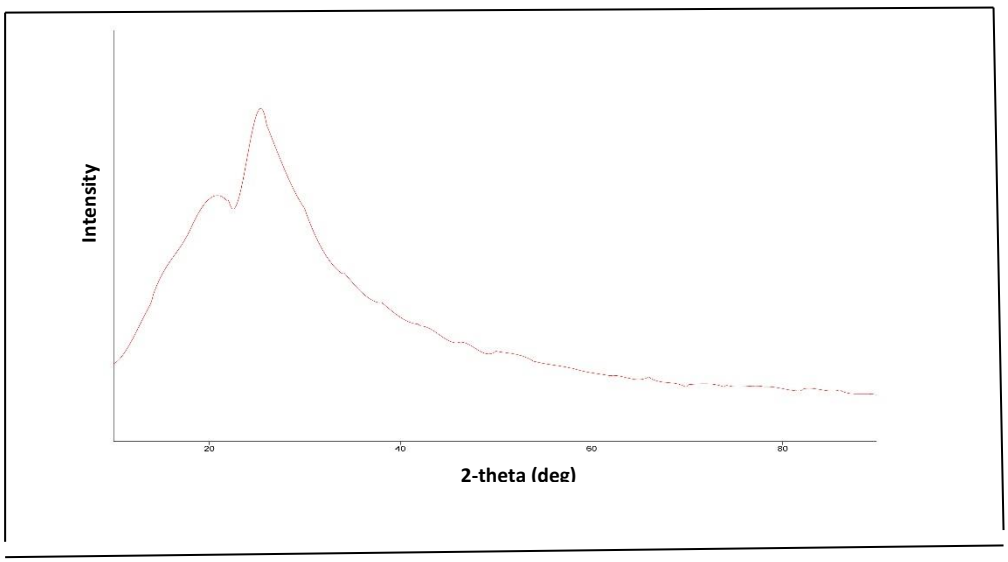

Fig. 3. XRD Pattern of Polyanalline (pani)

From the XRD pattern as shown in the fig. 3. It is found that the crystalline nature with 2θ peak lying at (011), (020), (200), planes and the crystallinity of Polyanalline was found to be 8 nm.

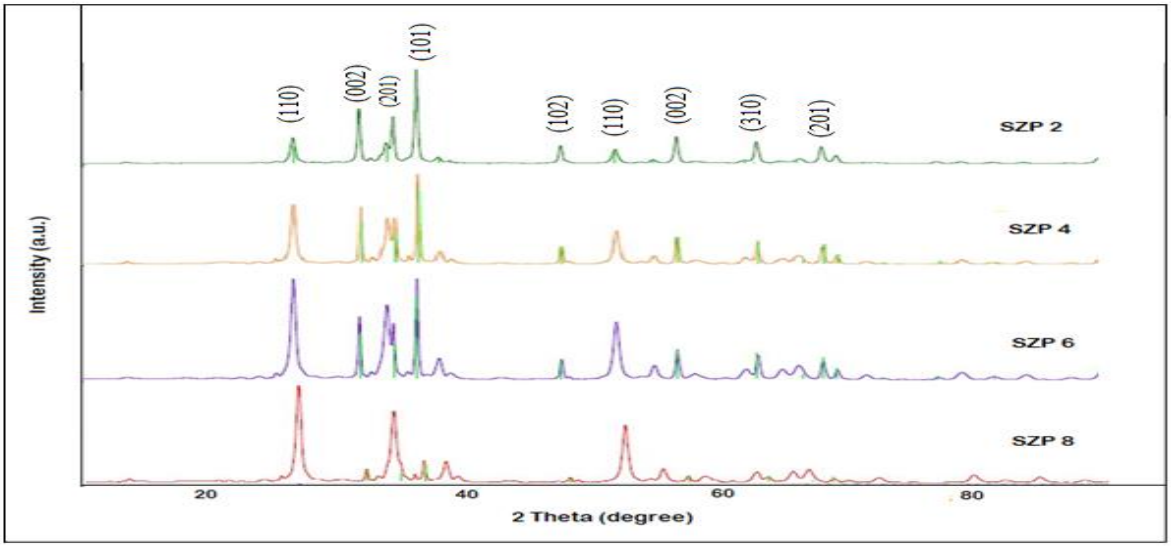

Fig. 4. XRD Pattern of Polyaniline (PANI) Doped Metal Oxide Nanocomposites

Figure. 4. shows the XRD pattern of nanocomposite of Series (SZP) having four samples SZP-2(20SnO_2 - 70ZnO - 10 PANI), SZP-4 (40SnO_2-50ZnO-10PANI), SZP-6 (60SnO_2 - 30Zn -10PANI), and SZP-8 (80SnO_2 -10ZnO-10PANI). It is observed that from XRD pattern for SZP-4 sample shows crystalline nature with 2θ peaks lying at (110), (002), (201), (101), (102), (110) and (002) (310) and (201) planes. The observes peaks are the mixed combination of ZnO and SnO_2 semiconducting metal oxides and Polyanilne (PANI). It is seen from crystal quantization plot, that more peaks about are corresponds to SnO_2 nanomaterial and very few about of them are corresponds to ZnO and polyaniline (PANI) nanomaterials. For the XRD pattern of the sample such as SZP-8, SZP-6, SZP-2 also shows crystalline nature and crystalline planes are obtained due to ZnO, SnO2, and polyaniline. The average crystalline size is obtained by using Scherrer formula and has been found to be 38.44 nm, 29.33 nm, 52.58 nm, 61.26 nm, for sample SZP-2, SZP-4, SZP-6, and SZP-8 respectively.

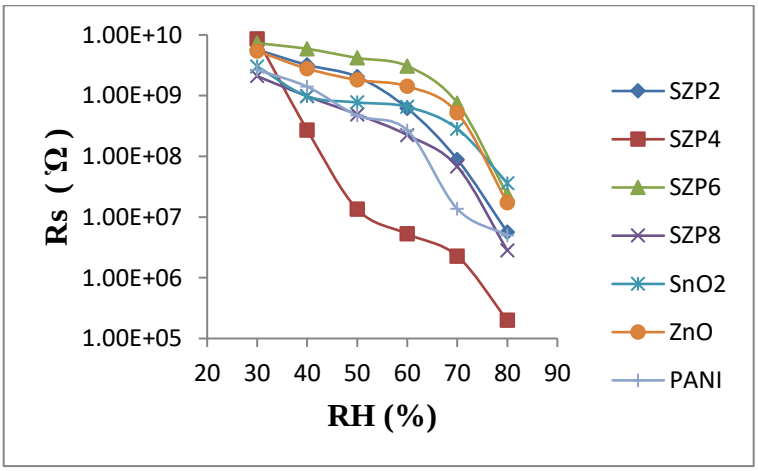

Fig. 5. Hysteresis plot

Hysteresis plot shows the variation between resistances of sample with respect to the relative humidity in increasing and decreasing order from 30 to 80 % RH as shown in the fig. 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 SZP-4 (40SnO_2-50ZnO -10PANI) the change in value of resistance is near about from 10^{10} □ to 10^5 □, these is a remarkable change in the value of resistance.

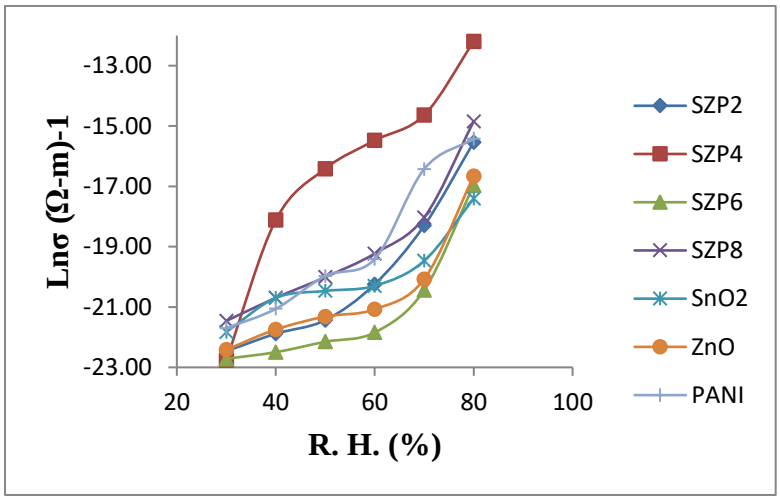

Fig. 6. Variation of Conductivity with Relative Humidity

It is observed that in fig .6. The conductivity increases perfectly linearly with relative humidity from 30 to 80 % RH and decreasing relatively on same path from 80 to 30 % RH. In this case also the conductivity increases with increase in temperature and it is highest at temperature 80°C and lowest at temperature 30°C. the conductivity difference between temperature 30°C and other ones minimizes and the conductivity curves are not seen mixed so as seen in the group of sample. This behavior is obtained due to the addition of small amount of PANI in the SnO_2 and ZnO. Hence the stability, linearity and equality are obtained in the samples

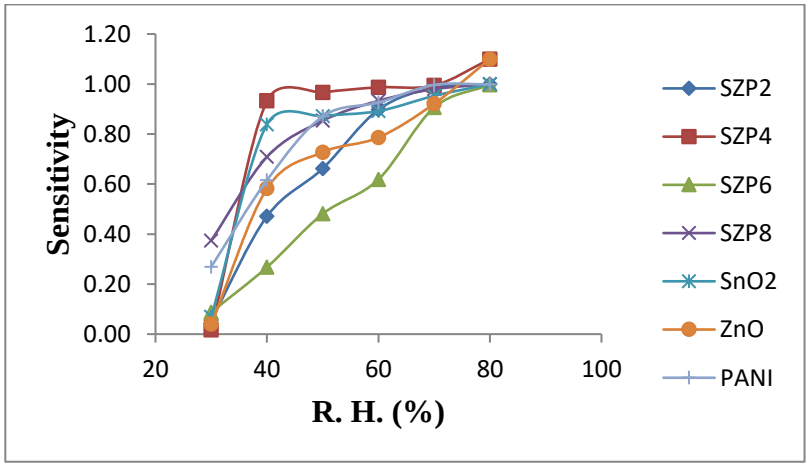

Fig. 7. Variation of Sensitivity with Relative Humidity

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. 7. For higher RH, the

sensitivity is found to be higher in case of all samples of thick films. The sensitivity of SZP-4 (40 SnO_2 -50 ZnO - 10PANI) is more than SZP-2, SZP-6, and SZP-8 samples and also from the pristine samples S-0 , Z-0 and P-0. The (SnO_2-ZnO-PANI) composite sensors exhibits significantly higher sensitivity than sensor constructed specially from SnO_2 , ZnO nanoparticles and PANI itself due to the formation of heterogeneous interface between them and more adsorption site was created to absorbed more water vapours.

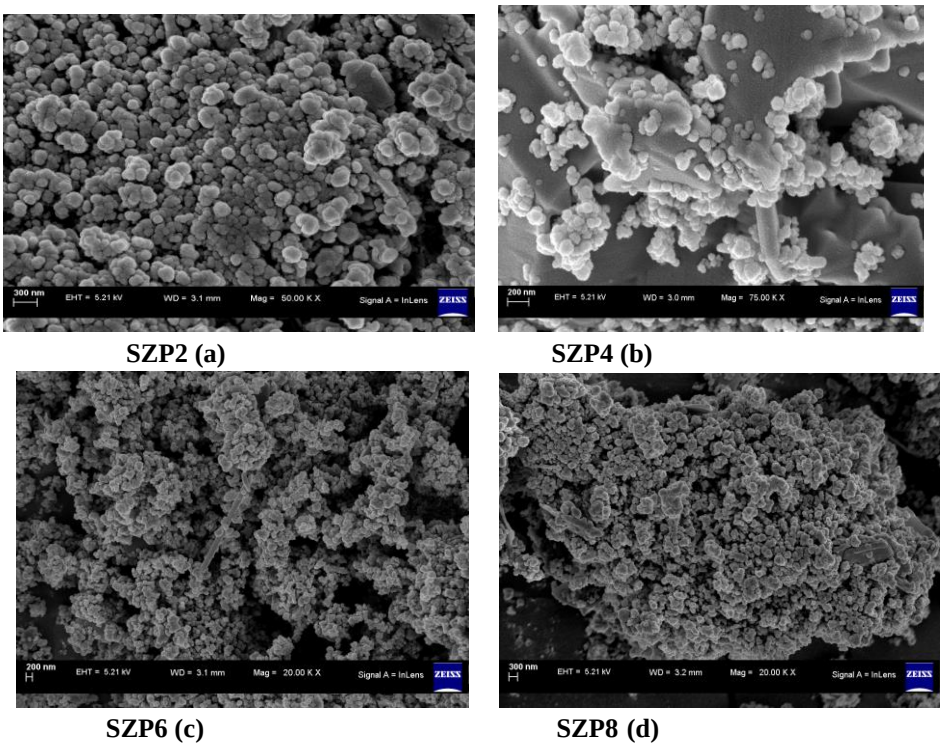

Fig. 8. FESEM Image of PANI Doped Metal Oxide Nanocomposites

The FE-SEM morphology of nanocomposites shows the particles are small sized, almost spherical, rod like structure. The micrograph of SZP-4 (figure.8.(b).) One can see that nanocrystalline and porous SnO_2, ZnO, is formed on the surface of SZP4 . Each grain seems to be like a bead of different shape and reveals that they possess the grain size of nanometer 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.

CONCLUSIONS

Nanostructured SnO_2, ZnO, was successfully prepared via chemical precipitation method and PANI with IUPAC polymerization technique. Minimum crystallite size was found to be for SnO_2 (S0) is 26.31 nm and ZnO (Z0) is 36.48 nm. The Hysteresis plot shows very significant average change in the value of the resistance from near about $10^{10}\Omega$ to $10^5\Omega$ during forward and reversed cycles of sample SZP-4(40 SnO_2 -50 ZnO-10PANI). 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 SZP-4 is more sensitivity than other prepared composite samples. The FESEM Morphology reveals that SnO2, ZnO was uniformly mixed within the PANI matrix. The nanocomposites could be good material for detection humidity at room temperature.

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