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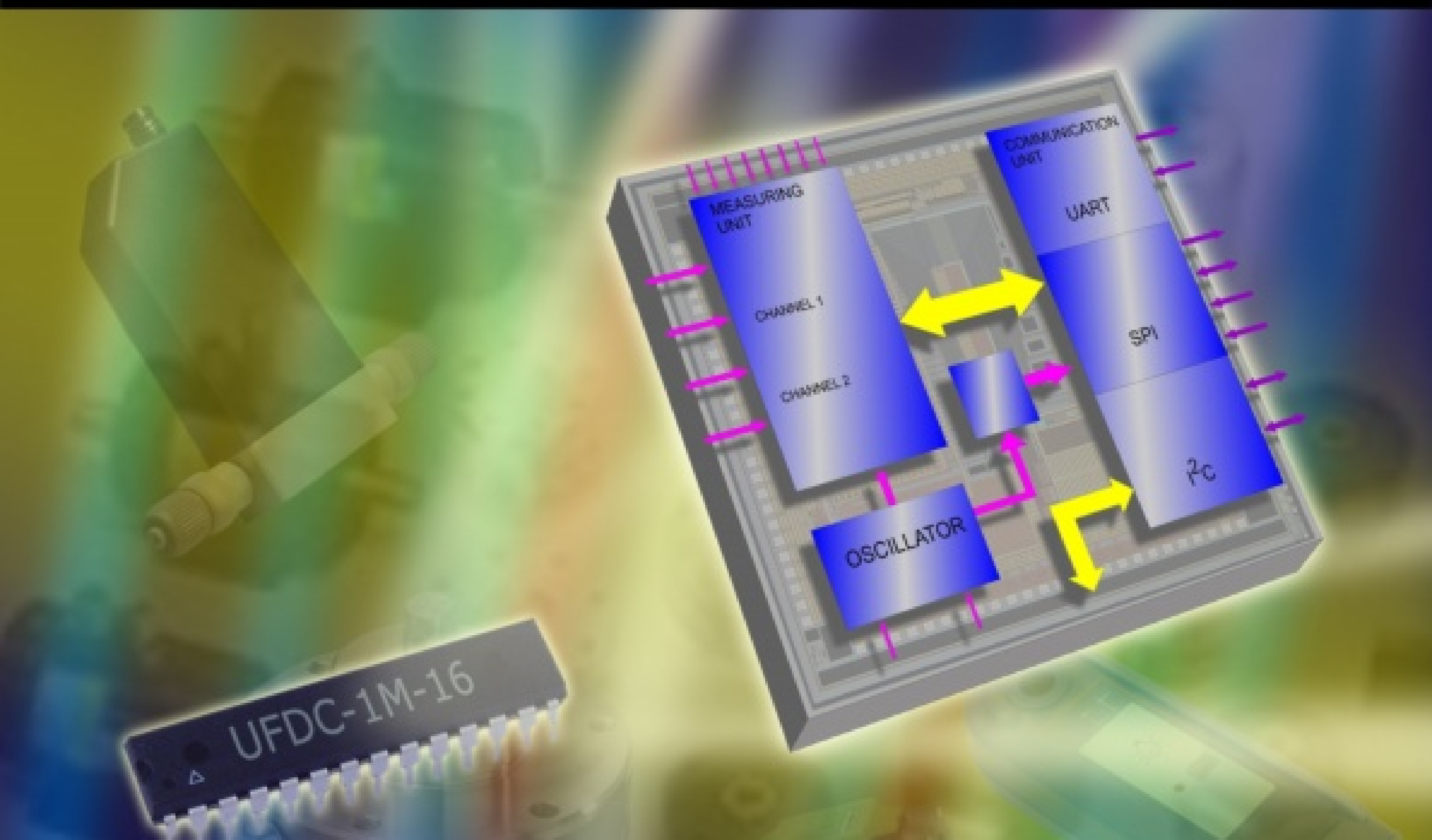

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Comparative Study of Moisture Sensing Properties of ZnO Nanomaterials through Hydroxide Route by Mixing Dropwise and Sudden

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Abstract: In this paper we report comparative study of humidity sensing properties of ZnO nanomaterials synthesized through hydroxide route by dropwise and sudden methods. Sodium hydroxide is mixed with zinc sulphate solution at room temperature in the molar ratio 1: 2.2. It yields precipitate of zinc hydroxide. Precipitate is filtered out and washed with deionized water till the sodium ions are not completely removed and its subsequent calcinations give zinc oxide in powder form. We have used two methods such as Method 'A' and Method 'B'. Method 'A' stands for 'Drop wise' and method 'B' stands for 'Sudden'. For method 'A', sodium hydroxide has been mixed 'Drop wise' with zinc sulphate and for method 'B' it has been mixed 'Sudden' with zinc sulphate. For both methods, we get zinc hydroxide precipitate after 24 hours and its subsequent calcinations give zinc oxide nanomaterials in powder form. Pellets of these powders have been made and annealed for 3 hours at temperature 550°C in an electric furnace successively. After annealing, pellets are exposed to humidity and variations in resistances with the variations in humidity have been observed. SEM and XRD studies of samples have been done. *Copyright © 2007 IFSA.*

Keywords: Zinc oxide, moisture sensor, nano-size, electrical properties.

1. Introduction

Nanomaterials, due to high surface to volume ratios as compared with bulk materials, exhibit unique structure and properties. There are lot of methods for synthesis and characterization of nanomaterials [1-15]. ZnO has wide band gap of 3.37 eV and large exciton binding energy of 60 meV and reveals different type of morphologies such as nanorings, nanobelts, nanocombs, nanosheets, nanowires and which may be used in various applications [16-20].

In present paper we have made a comparative study of the humidity sensing properties of ZnO nanomaterials synthesized through hydroxide route by drop wise and sudden methods. SEM and XRD studies of samples have been done. Scanning Electron Micrographs obtained from Method ‘A’ show that the product consists of nanosheets with thickness around of 80-120nm and these obtained from Method ‘B’ show the nanorods with a length of around 250-350nm and average diameter between 40-50 nm. X-ray Diffraction patterns reveal that samples contain ZnO with slight impurities of sulphate hydrates.

2. Synthesis Method of ZnO Nanomaterial

ZnO is prepared by conventional precipitation method using sodium hydroxide and zinc sulphate. Calcinations of zinc hydroxide give zinc oxide in powder form. For the preparation of zinc hydroxide, sodium hydroxide has been mixed with zinc sulphate using two methods. For method ‘A’, sodium hydroxide has been mixed ‘Dropwise’ with zinc sulphate and for method ‘B’ it has been mixed ‘Sudden’ with the same. For both methods, we get zinc hydroxide precipitate after 24 hours continuous stirring and its heat treatment gives zinc oxide in powder form. These powders are mixed well with 10% glass powder. Addition of glass powder as a permanent binder during the process plays a major role in getting adhesion of the material for pellet formation. The pellets of these powders have been prepared using hydraulic pressing machine at normal pressure at room temperature. These pellets have been subjected for annealing at different temperatures.

3. Scanning Electron Micrograph and X-Ray Diffraction

The morphology of sensing material was investigated with a Scanning Electron Microscope (SEM, LEO-0430, Cambridge). Figures show the morphologies of sensing element in the form of ZnO films using sol-gel technique. Method ‘A’ gives ZnO nanomaterial in the form of nanosheets [21]. The product consists of nanosheets with thickness are around of 80-120nm as shown in Fig. 1. These nanosheets are obtained from ZnO film using sol-gel spin coating. Method ‘B’ gives ZnO nanomaterial in the form of nanorods [17]. The product consists of nanorods with a length of around 250-350nm and average diameter between 40-50nm as shown in Fig. 2. These nanorods are obtained from ZnO film using sol-gel spin coating.

Figs. 3 and 4 show X-ray Diffraction patterns of sensing materials in the form of ZnO powder for methods ‘A’ and ‘B’ at room temperature. X-ray Diffraction patterns show crystalline natures of ZnO nanomaterials. In both cases these patterns reveal that sample contains zinc oxide nanomaterials with slight impurity of sulphate hydrates.

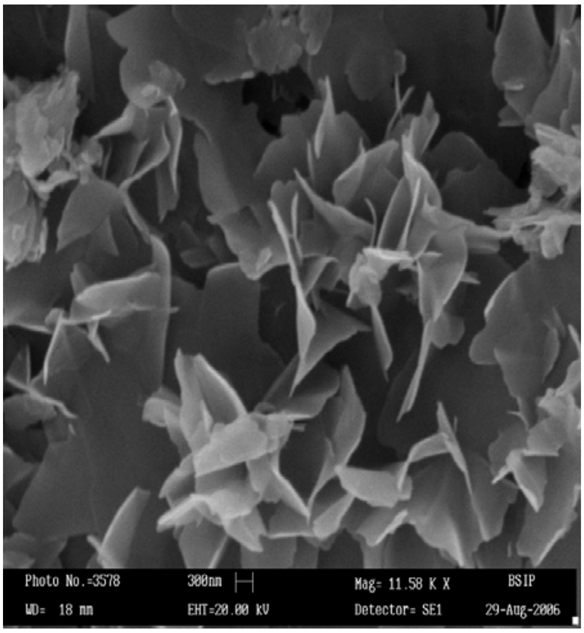

Fig. 1. Scanning Electron Micrograph of ZnO Film using sol-gel technique on nanoscale for method 'A'.

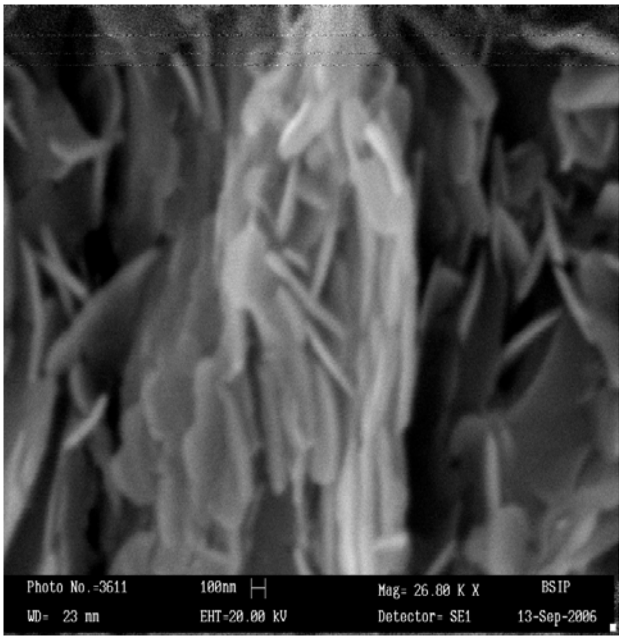

Fig. 2. Scanning Electron Micrograph of ZnO Film using sol-gel technique on nanoscale for method 'B'.

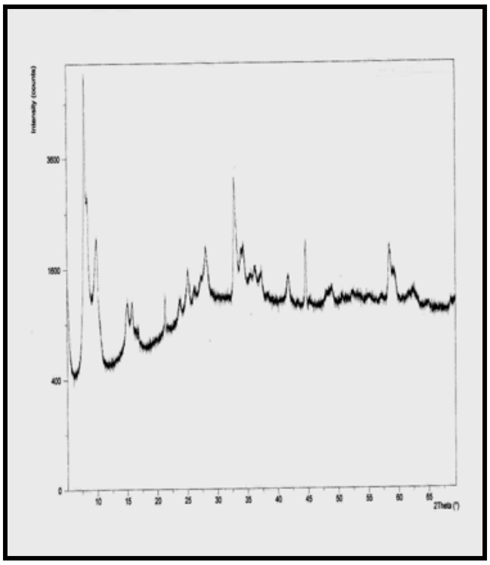

Fig. 3. X-ray Diffraction of sensing material in the form of ZnO powder for method 'A'.

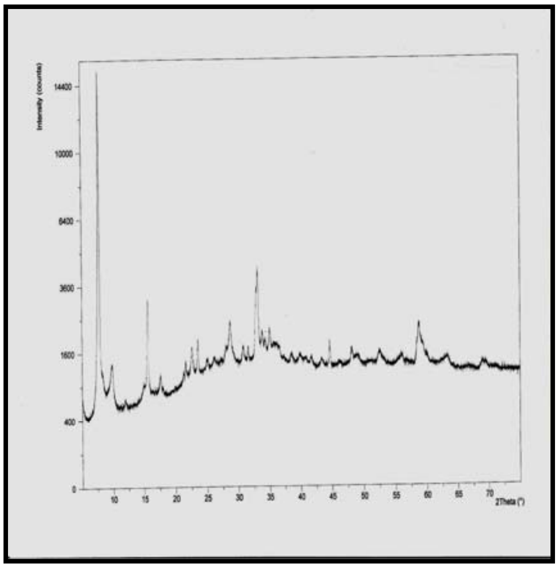

Fig. 4. X-ray Diffraction of sensing material in the form of ZnO powder for method 'B'.

4. Principle of Operation

Ceramic humidity sensors show chemical resistance [22-24]. Conductivity of such sensing materials varies with amount of water adsorbed by it. This principle is employed for the measurement of humidity in resistive type humidity sensors. This type of sensor can be subdivided into ionic type and electronic type humidity sensor depending upon their conduction mechanism. These sensors mostly work at low temperature. The change in impedance of porous ceramics at different environmental humidity values is related to the water adsorption mechanism on the oxide surface [24]. At low humidities, conduction is due to proton hopping between hydroxyl ion on the first layer of chemisorbed water, while at higher humidities, protons hop between physisorbed molecules with a

Grotthuss chain reaction mechanism [25]. The morphology of the sensing element influences water vapours adsorption and desorption. The condensation of water vapours occurs as a result of capillary action. The behavior of this condensation is a function of ceramic pore size and its distribution. Therefore, in this case as humidity inside the chamber increases, adsorption of water vapor increases, consequently, resistance of sensor decreases.

5. Experimental Procedure

A controlled humidity chamber has been designed [26]. Potassium hydroxide is used as dehumidifier and potassium sulphate is used as humidifier. Variations in resistance have been noted by using a digital multimeter of MΩ (VC 9808, India). Relative humidity is measured using standard hygrometer associated with thermometer (Huger, Germany). The humidifier/dehumidifier is kept in a dish over a stand. In the process the temperature of the chamber remains same throughout the experiment. The chamber is then dehumidified up to 10% RH by using the dehumidifier potassium hydroxide. The least count of hygrometer used here is 1% RH and that of the thermometer 1°C. Pellet of ZnO powder with 10% glass powder as binder has been made by using hydraulic pressing machine. This pellet has been put within a conductivity-measuring holder and then it is exposed to humidity inside a specially designed controlled humidity chamber. It has been observed that as Relative Humidity (RH %) inside the chamber increases, resistance of pellet decreases for the entire range of humidity for both methods. Further the pellet which acts as sensor material has been annealed for 3 hours at temperatures 150°C, 300°C, 450°C and 550°C in an electric furnace successively. After each and every time of annealing, the pellet is exposed to humidity and variations in resistance with humidity have been observed. But here we are reporting only the data of sensing element annealed at 550°C for making a comparative study.

Sensitivity of humidity sensor has been defined as the change in resistance (ΔR) of sensing element per unit change in relative humidity (RH %) and calculated by this formula as given below -

$$S = \frac{\Delta R}{\Delta RH\%} \ M\,\Omega\,/RH\% \quad . \tag{1}$$

6. Results and Discussion

Variations in resistance with the variations in relative humidity for the sensing element of zinc oxide prepared through hydroxide route using two methods have been plotted in Fig. 5 The plots for sensor annealed at 550ºC show similar nature but show different sensitivities for both methods.

For method 'A' curve for annealing temperature θ = 550˚C shows that as relative humidity increases, resistance decreases sharply up to 50%RH and shows highest average sensitivity (8.8 MΩ /RH%) in this range, then it decreases less rapidly up to 95%RH and shows least average sensitivity (1.9 MΩ/RH%) in this range. Its average sensitivity is 5.35 MΩ/RH% over the entire range of RH% i.e. from 10% to 95%.

For method 'B' curve annealing temperature θ = 550˚C shows that as RH increases, resistance decreases sharply up to 75%RH and shows highest average sensitivity (10.26 MΩ /RH%) in this range, then it decreases less rapidly up to 95%RH and shows lesser average sensitivity (4.25 MΩ /RH%) as relative humidity increases. Its average sensitivity is 7.25 MΩ /RH% over the entire range of R.H. i.e. from 10% to 95%.

Variations in resistance with the variations in annealing temperature have been plotted for the sensing elements for both methods as shown in Fig. 6. It is observed that as annealing temperature increases resistance of the material decreases [27].

Reversibility of experimental results for sensing elements annealed at θ = 550˚C for both methods have also been studied. Curve 'a' represents the values of resistances when %RH increases and curve 'b' represents the values of resistances when %RH decreases. Method 'B' gives good reversibility as compared to method 'A'. It also shows good reversibility over entire region of RH. This shows that at annealing temperature 550˚C, adsorption and desorption powers of sensing material are approximately same. Reversibility of resistances with %RH for method B is plotted as shown in Fig. 7.

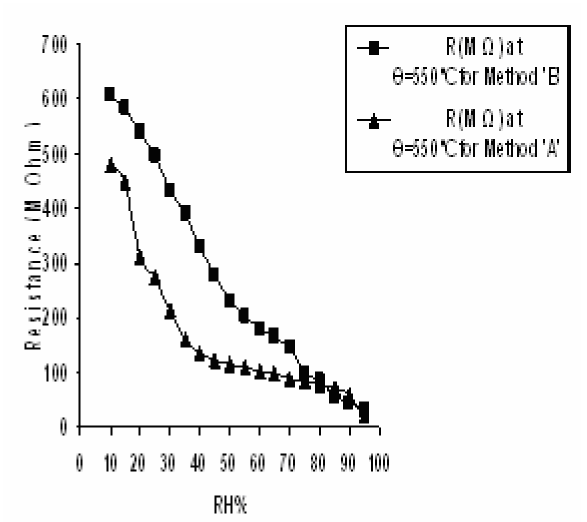

Fig.5. Variations in resistance with the variations in relative humidity for the sensing elements of zinc oxide prepared through hydroxide route for method 'A' & method 'B'.

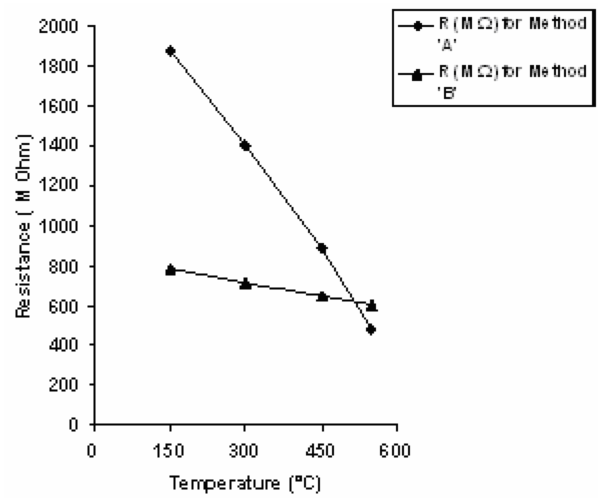

Fig.6. Variations in resistance with the variations in annealing temperature have been plotted for the sensing elements for method 'A' & method 'B'.

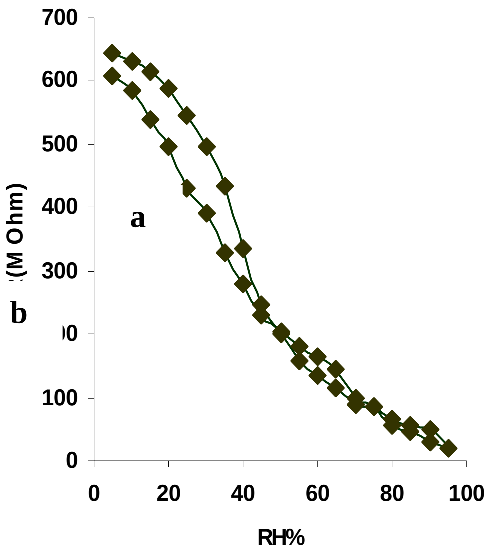

Fig.7. Reversibility of experimental results of resistances R (MΩ) for method 'B'.

7. Conclusion

Highest value of sensitivity is obtained for method 'B' as compared to method 'A'. Method 'B' gives highest average sensitivity 10.26 MΩ / RH% up to 75% RH. Its average sensitivity is 7.25 MΩ / RH% over the entire range of RH% that is from 10% to 95%. We conclude that for synthesis of ZnO nanomaterial, sudden mixing is the better method in order to obtain high sensitivity and better performance. Thus the humidity sensor reported here based on electrical resistance is robust, cost effective and user friendly and can be used for measuring a wide range of relative humidity.

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