ISSN: 2277-9655
Impact Factor: 4.116
CODEN: IJESS7

IJESRT
INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

DOPED AND UNDOPED ZINC OXIDE AS HUMIDITY SENSOR

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DOI: 10.5281/zenodo.1135951

ABSTRACT

Present paper deals with a comparative performance of pure ZnO and Fe_2O_3-doped ZnO nanomaterials as humidity sensor. Fe_2O_3 doping was done for improvement of sensitivity. Characterizations of materials were done using SEM and XRD. SEM images show the surface morphology and X-ray diffraction reveals the crystallite size of sensing materials. The pellets were annealed at 500°C for 3 hours and thereafter humidity sensing studies were carried out. It was observed that as relative humidity (%RH) increases, there was decrease in the resistance of pellet for the entire range of %RH (relative humidity). Results were found reproducible for all the sensing elements. Maximum sensitivity was found to be 22.18 MΩ /%RH for Fe_2O_3-doped ZnO sensing elements.

KEYWORDS: Humidity; Pellets; Doped; Sensing Elements; Sensitivity.

I. INTRODUCTION

There is some content of water vapor present in the air around us, it is commonly known as humidity. It plays an important role in human life in many ways since water is present in all living organisms from simplest to the most complex living creature. Humidity drastically influences the life and the working efficiency. Nano materials can be developed from metals, ceramics, polymeric materials, or composite materials. ZnO nanostructures have been extensively investigated due to their potential applications in different type of electronic device [1-14]. In the present age, nonmaterial's due to their smaller particle size and larger surface area have great importance due to their remarkable properties in sensors, nano-devices, electronic and optoelectronic devices [15-24]. Jayanti *et al.* doped ZnO nanocrystals with impurities of Li, Na, Cu, Pr, and Mg under similar conditions by solid-state reaction method. Their study showed that undoped ZnO, Li and Na doped ZnO showed well-developed nanorods but Cu doped ZnO nanorods were not well-formed, rather they tended to form clusters [25]. Humidity and gas sensors are widely used in the entire world for specific purposes. These sensors are very important as these are used in various industrial areas as well as in scientific laboratories. Moisture is the water vapor content present in the air. It can make hot temperatures even more unbearable. Humidity is integral to both biological life and automated industrial processes. There is need to develop humidity sensors having applications based on specific needs and desired range. Research laboratories are making best efforts to find the suitable materials with better parameters like good sensitivity over large range of relative humidity, low hysteresis, low response and recovery time, and properties that are stable. For the development of nanodevices (or micro devices) with superb performance an in-depth knowledge of physical, chemical and structural properties of the metal oxide nonmaterial's is required. ZnO is a very versatile compound semiconductor with a band gap of about 3.3 eV. Numerous metal oxides (e.g., zinc oxide) have been analyzed for potential applications in the field of gas and humidity sensing [1-24]. The need for monitoring, measuring and controlling the relative humidity (RH) precisely has led to the development of variety of humidity sensors [26]. In ceramic sensors, sensitivity and response time are generally governed by the surface morphology; pore volume, shape and size distributions. Ceramic surface features show strong affinity for chemical and physical adsorption of water vapor molecules. Thus, porous metal oxides offer opportunity to develop humidity sensors with added advantage of their chemical and physical stability. Ceramic sensors are generally impedance or resistive type and are in vogue for their quality and low cost. Water adsorption mechanism leads to change in resistance of the oxide surface subsequent to exposure to humidity. Film or pellet sensors with nano-size grains and nano-porous structures offer high surface to volume ratio leading to efficient adsorption of water molecules and thus giving high sensitivity to these sensors. Yawale *et al.* fabricated

SnO_2/ZnO with TiO_2/Al_2O_3 films and measured DC-electrical resistance of the films. SnO_2-$5Al_2O_3$ and ZnO-$5Al_2O_3$ proved to be better humidity sensing materials. Rutile and hexagonal structures of SnO_2, ZnO and Al_2O_3 and their nano-meter grain size formed nano-sized pores that adsorbed water [27]. Li *et al.* investigated humidity sensors prepared using synthesized inorganic/organic nanocomposites of sodium polystyrenesulfonate and ZnO. Sensor performance based on composite film changed by four orders of magnitude over the humidity range 11–97% RH [28]. The humidity sensing properties of mesoporous ZnO-SiO_2 composites synthesized by sol-gel methods with different Si/Zn molar ratios were investigated by Yuan et. al [29]. Introduction of ZnO improved humidity sensitivity of composite in the range of 11% to 95% RH and the sample with a Si/Zn ratio of 1:1 showed promising results. Sensor resistance changed 4 times in 11%-95% RH range. Sensor showed response and recovery time of about 50 s and 100 s, respectively. Spin-coated nanorod thin film humidity sensors of aluminum doped zinc oxide were prepared by Sin *et al*. With increase in doping concentration, length of nanorods increased. Sensor that contained 0.6 at% aluminum doped in ZnO exhibited highest sensitivity in 40%–90% RH humidity range [30]. Jeseentharani *et al. tested* composites of CuO-ZnO, CuO-NiO and NiO-ZnO for humidity sensing in the range of 5%–98% RH. CuO-NiO compound showed the maximum sensitivity. Response and recovery times of CuO-NiO composites were 80 s and 650 s, respectively [31]. ZnO-In_2O_3 thin film humidity sensors were fabricated by radio-frequency layer by layer sputtering of ZnO and In_2O_3 precursors. Sample fabricated by applying ZnO two times and In_2O_3 one time showed the best results as total resistance changed by 4 orders in 11%-95% RH range [32]. Yongsheng *et al.* prepared ZnO nanorod and nanobelt films on the Si substrates with comb type Pt electrodes by the vapor-phase transport method. They found that at room temperature, resistance changed by more than four and two orders of magnitude when ZnO nanobelt and nanorod devices were exposed respectively to a moisture pulse of 97% relative humidity [33].

II. EXPERIMENTAL PROCESS

Solid-state reaction route was adopted to fabricate pellets from nonmaterial samples of undoped ZnO and Fe_2O_3-doped ZnO. 10% by weight of glass powder (binder) was added to undoped ZnO and Fe_2O_3-doped ZnO nonmaterial. Mixtures were grinded separately till uniformity was achieved. Samples with 0.2%, 0.6%, 0.8% and 1.0% of Fe_2O_3 doped in ZnO were labeled as FZ-0.2, FZ-0.6, FZ-0.8 and FZ-1, respectively. Powders were pressed at room temperature into disc shaped pellets under 260 M Pa pressure by a hydraulic pressure machine. Thickness of samples was kept 2 mm and diameter 4 mm. Pellet sample of undoped ZnO was also fabricated for comparison purpose. Pellets were annealed in air at 500°C for 3 hours. The developed pellets were analyzed for humidity sensing studies.

III. SEM AND XRD STUDIES

Using scanning electron microscope [LEO-430, Cambridge, England] study of surface morphology of the samples was carried out. From the SEM micrographs it became clear that a network of pores is formed. SEM micrographs show porous structure and small crystallites without inside pores but many inter grain pores. These pores are expected to provide sites for humidity adsorption. Higher porosity increases surface to volume ratio of the materials and therefore, helps in getting good sensitivity. The average grain size for FZ-1 samples measured from SEM micrographs was found to be 102 nm.

The crystallinity, structural phases and the gross crystal structure of the as synthesized nonmaterial's were investigated by powder X-Ray diffract meter XPERT PRO-Analytical XRD system (Netherlands). The crystallite sizes were found to be in the range 94-150 nm range from XRD studies. Wavelength of CuKα source used is 1.54060 Å. X-ray patterns for FZ-1 nonmaterial sample have been analyzed. The average crystallite size of the sample was calculated using Scherrer's formula (given below).

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Here, D = crystallite size, K = fixed number of 0.9, λ = X-ray wavelength, θ = Bragg angle, B = full width at half maximum of the peak.

IV. EXPERIMENTAL

For studying humidity sensing applications, humidity control chamber was used. The change in values of resistance was recorded corresponding to the change in humidity level. The pellets (after annealing) were inserted in a humidity control chamber. Copper electrodes were used for measuring resistance normal to the pellet's cross-section. Surface contact area of all sensing elements with electrodes was 113.11 mm^2 and the cylindrical surface area that was exposed to the humidity in the chamber was also 113.11 mm^2. Calibration of the chamber was done by a standard hygrometer (Huger, Germany, ±1% RH) and a thermometer (±1°C). A multi-meter (±0.001 MΩ, model: VC-9808) recorded variation in resistance with change in %RH. Ageing and reproducibility studies were done by repeating the process after six months. To check stability, samples were exposed to chamber humidity at fixed values of % RH, and resistance was recorded as a function of time. The stability was within ±4%. Standard solution of potassium sulphate has been used as a humidifier and potassium hydroxide as a de-humidifier. Sensitivity values of the sensing elements were also recorded with the variation in the humidity level. All the experimental measurements were performed at room temperature.

V. RESULTS AND DISCUSSION

A. Sensitivity (Humidity Sensing)

Sensitivity of humidity sensor is defined as the change in resistance (ΔR) of sensing element per unit change in relative humidity (Δ%RH). Sensitivity of the sensing elements is given below:

$$\text{Sensitivity} = (\Delta R)/(\Delta\%RH)$$

Variation in resistance with change in %RH for Fe_2O_3-doped ZnO samples for annealing temperature 500˚C were analyzed. Figure 1 shows variations in resistance with change in %RH for Fe_2O_3-doped ZnO samples annealed at 500˚C. It was found that a decrease in resistance is noticed with increase in the % RH for all sensing elements. The sensitivity was found to be 22.18 MΩ /%RH for Fe_2O_3-doped ZnO sensing elements. Fe_2O_3-doped ZnO sensing elements showed better sensitivity as compared to undoped ZnO sensing elements. The sensing elements has relatively low adsorption capacity for moisture and hence low sensitivity due to uniform distribution of grains, less formation of voids; lower inter-connected voids or capillaries which are important conditions for adsorption of water molecules in the sample. It is possible that multiplicative effect of two or more parameters of nanomaterial may cause higher sensitivity. The mechanism by which a metal atom interacts with the surface of a metal oxide is varied and complex, it is not easy to establish the exact single parameter affecting the sensitivity. Higher porosity increases surface to volume ratio and enhances diffusion rate of water into or out-of the porous structure. This causes sensitivity to increase. At high relative humidity, liquid water condenses in capillary nano-pores, forming a liquid like layer. Resistance may also decrease due to change of grain boundary barrier height in ceramics. Adsorption of water molecules at metal oxide surface penetrated inside the sample decreases height of potential barrier at grain surfaces and also at surface of necks between metal oxide grains. Thus, size of depletion regions in the vicinity of necks in electric field direction gets lowered and conductance increases. The initial chemisorptions on the surface of sensing elements cause hysteresis. It can be minimized through the process of thermal desorption only. To estimate hysteresis, chamber humidity was scaled up from 35% RH to 95% RH and then cycled down to 35% RH. Samples show tolerable hysteresis values.

B. Sensing principle (for humidity sensing)

Electrons are donated by the water molecules in the electronic type mechanism. Either ionic or electronic type mechanism is responsible for the conduction mechanism in the sensors based on the ceramic materials. These water molecules get chemisorbed and hence in this way the electronic conductivity gets increased or decreased. This conductivity actually depends on the fact whether the material is p-type or n-type semiconductor. If the mechanism is ionic type then the impedance of the sensor decreases with increase in the value of RH (relative humidity) due to the formation of the physisorbed layer and condensation of the water molecules in the capillary on the material‘s surface. As soon as the nanomaterials developed from the ZnO come in contact with humid air, the chemisorption process starts and the water molecules chemisorb on the available sites of the material surface. Firstly, the chemisorbed layer is formed due to the dissociative chemisorption process and thereafter the physisorbed layer is formed. The electrons are accumulated at the surface of ZnO and consequently, the resistance of the sensing element decreases with increase in relative humidity. Physisorption is also known as physical adsorption. It is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption. For physisorption water molecules can form multilayer adsorption. The layers formed due to physisorption process are known as physisorbed layers. Physisorbed layers are easily desorbed but chemisorbed layer can be thermally desorbed only. In case of physisorption typical binding energy is about 10-100 meV while that in case of chemisorption typical binding energy is in the range of 1-10 eV. So, the energy required for the removal of physisorbed layer is very less as compared to the energy required for the removal of chemisorbed layer.

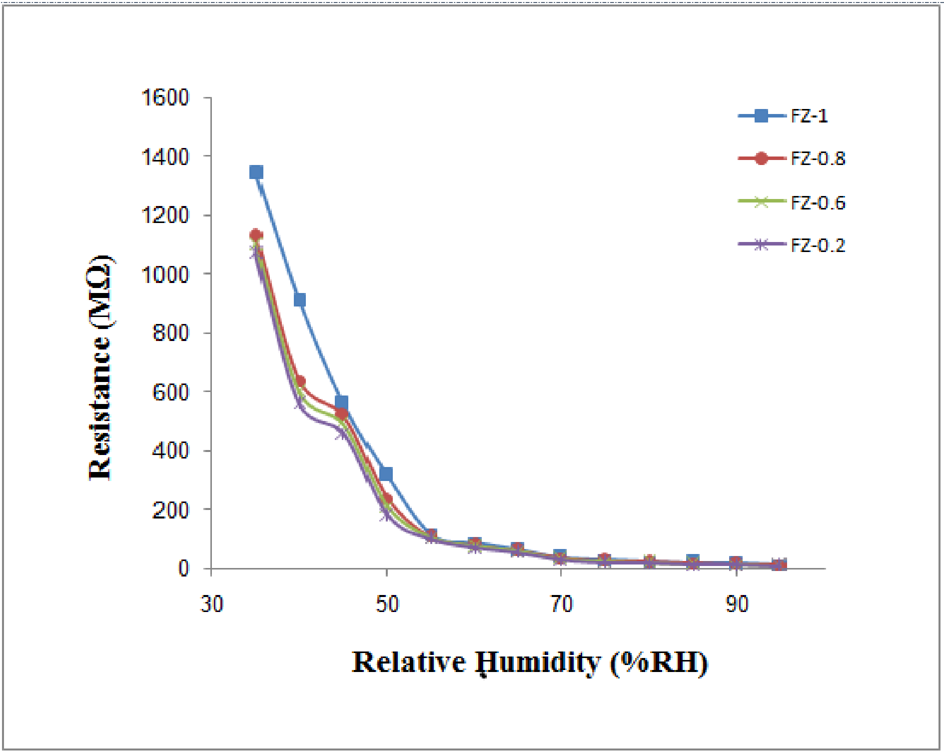

Fig.1. Variation of resistance with change in %RH for the sensing elements FZ-1 for different doping percentages and annealed at 500°C

C. Hysteresis And Aging Effect

Figure 2 shows hysteresis behavior of sample FZ-1 annealed at 500°C for humidity sensing studies. Hysteresis is also an important aspect as far as sensor is concerned. In the present research work all sensing elements have acceptable hysteresis values. Hysteresis was found to decrease with increase in the annealing temperature for all the Fe_2O_3-doped ZnO sensing elements for humidity sensing studies. Figure 3 shows ageing effect behavior of sample FZ-1 annealed at 500°C for humidity sensing studies. For analysing the effect of ageing, sensing properties of these elements were examined again in the humidity control chamber after six months and variation of resistance with change in humidity level was recorded. Variation of resistance of all the sensing elements with change in humidity concentration after six months was analyzed. For all the sensing elements annealed at 500°C, values were generally repeatable within ±6.00% in the 35% RH to 95% RH range after six months. Sensitivity values were reproducible within ±5.72% for samples FZ-1 for humidity sensing studies. Hence, good reproducibility has been achieved for sample FZ-1 as compared to sample undoped ZnO sample.

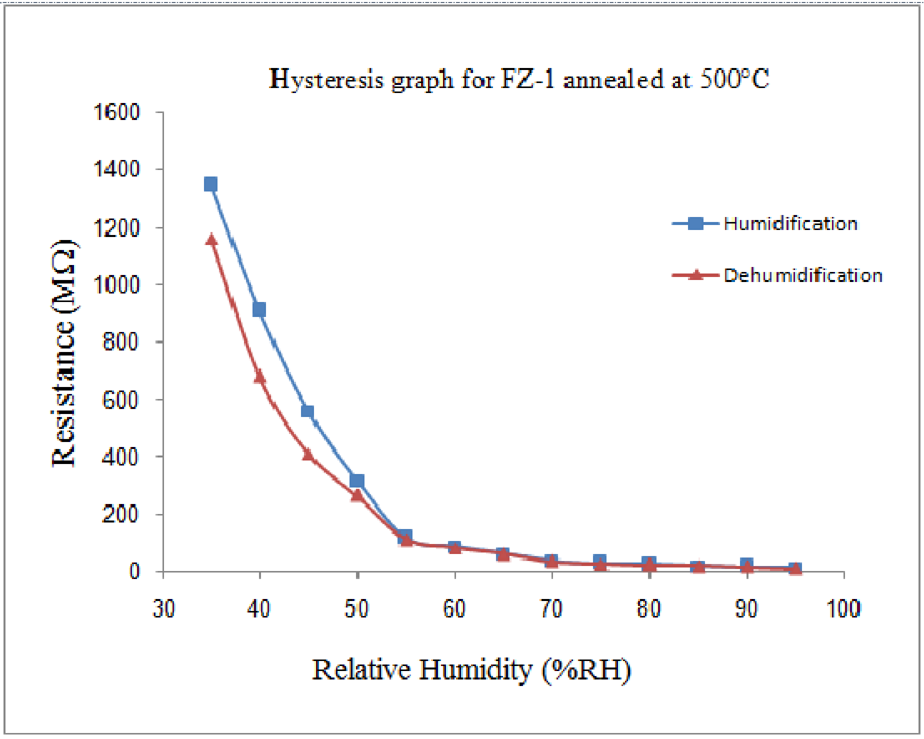

Fig.2. Hysteresis behavior of sample FZ-1 annealed at 500°C.

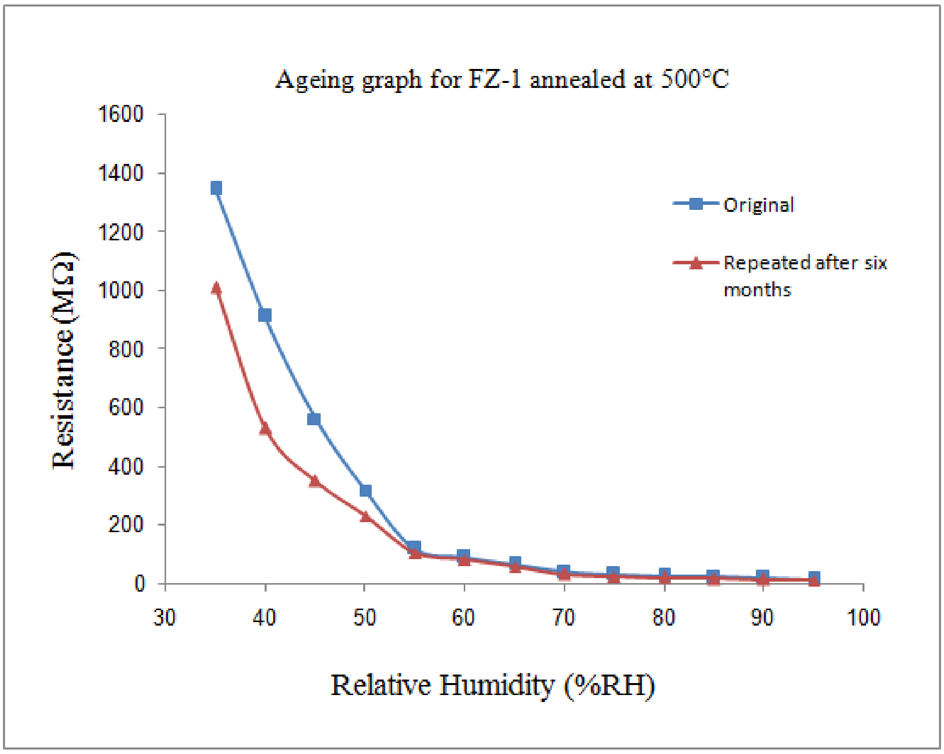

Fig.3. Aging effect behavior of sample FZ-1 annealed at 500°C.

VI. CONCLUSIONS

The Fe_2O_3-doped ZnO samples showed better sensitivity as compared to undoped ZnO nonmaterial's for humidity sensing studies. The sensors developed from Fe_2O_3-doped ZnO nonmaterial's annealed at 500°C showed the best sensing behaviours for humidity sensing studies with sensitivity 22.18 MΩ /%RH. The sensing elements developed from Fe_2O_3-doped ZnO nonmaterial's annealed at 500°C, has properties like low effect of ageing, low hysteresis and high reproducibility. Therefore, Fe_2O_3-doped ZnO sensors, annealed at 500°C, proved to be promising practical humidity sensors.

VII. ACKNOWLEDGEMENTS

Authors would like to thank the University Grants Commission, India, for providing the Financial Support for carrying out the research work through Major Research Project Grant [(File No. 42-788-2013 (SR)].

Mr. Suneet Kumar Misra would also like to thank the University Grants Commission, India, for providing UGC-BSR (Basic Scientific Research) fellowship for carrying out the research work

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CITE AN ARTICLE

Panwar, A., Pandey, N. K., & Misra, S. K. (n.d.). DOPED AND UNDOPED ZINC OXIDE AS HUMIDITY SENSOR. *INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY, 7*(1), 179-185.