Application of V₂O₅-ZnO Nanocomposite for Humidity Sensing Studies

Narendra Kumar Pandey, Abhishek Panwar, Suneet Kumar Misra*

Sensors and Materials Research Laboratory, Department of Physics, University of Lucknow, Lucknow, India

Email address:

suneetm31@gmail.com (S. K. Misra)

*Corresponding author

To cite this article:

Narendra Kumar Pandey, Abhishek Panwar, Suneet Kumar Misra. Application of V₂O₅-ZnO Nanocomposite for Humidity Sensing Studies. *International Journal of Materials Science and Applications*. Vol. 6, No. 3, 2017, pp. 119-125. doi: 10.11648/j.ijmsa.20170603.12

Received: March 15, 2017; Accepted: March 29, 2017; Published: April 14, 2017

Abstract: Paper reports humidity sensing studies of V₂O₅-ZnO nanomaterial. When sample of V₂O₅-ZnO annealed at 500°C was exposed to increasing humidity, resistance decreased. Aging over six months was within ±6% for ZnO and ±2% for V₂O₅-ZnO; hysteresis was within ±6% for both ZnO and V₂O₅-ZnO sensing elements. Grain size for pure ZnO was 620 nm, and 400 nm for V₂O₅-ZnO nanomaterial. XRD suggested a distribution of crystallite size. For ZnO-V₂O₅, distribution in the crystallites size was as wide as 130% compared to only 20% for ZnO. Sensitivity of ZnO-V₂O₅ nanomaterial was 500% more compared to ZnO sample.

Keywords: ZnO, V₂O₅, Humidity, Sensor, Annealed

1. Introduction

Humidity can be defined as water vapor content present in the air. Moisture is also related to the word humidity. It can raise the atmospheric temperature to a great extent. Humidity is an important aspect for both biological life and automated industrial processes. Hence, it's monitoring, detection and control under different working conditions is also important. The need for monitoring, measuring and controlling the relative humidity (RH) precisely has led to the development of variety of humidity sensors [1-7]. 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.

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.

Properties like direct band-gap, least toxicity, transparency in the visible range, easy availability, inexpensive, high electrochemical and mechanical stability and resistivity control over wide range 10⁻³-10⁵Ωcm makes ZnO a versatile material. Inorganic compound Vanadium oxide (V₂O₅) is both an amphoteric oxide and an oxidizing agent. From the industrial perspective, it is the most important compound of vanadium, being principal precursor to alloys of vanadium and is a widely used as an industrial catalyst [8]. Doping is an effective method to manipulate applications of semiconductors. Doped metal oxides manifest different types of morphologies leading to various properties, and so find many additional applications. Various preparation methods offer the possibility of preparing numerous potential compounds, which enable the synthesis and foundation for nanostructure sensitive films and condensed pellets [9-10].

Yawale *et al.* fabricated SnO₂/ZnO with TiO₂/Al₂O₃ films and measured DC-electrical resistance of the films. SnO₂-5Al₂O₃ and ZnO-5Al₂O₃ 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 [11]. 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 [12]. 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.* [13]. 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 aluminium doped zinc oxide were prepared by Sin *et al.* With increase in doping concentration, length of nanorods increased. Sensor that contained 0.6 at% aluminium doped in ZnO exhibited highest sensitivity in 40%–90% RH humidity range [14]. 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 [15]. $\text{ZnO-In}_2\text{O}_3$ 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 [16]. 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 [17]. 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 [18]. Pandey *et al.* studied moisture sensing application of Cu_2O doped ZnO nanocomposites [19] as well as Ag-WO_3 nanocomposites [20]. While in the former they reported that the sample with 20% Cu_2O -80% ZnO showed best results with sensitivity of 4.78 $\text{M}\Omega/\%\text{RH}$ for annealing temperature of 400°C, in the latter case, the sample with 4 weight% of Ag in WO_3 showed best result with a sensitivity of 2.38 $\text{M}\Omega/\%\text{RH}$ for annealing temperature of 700°C. In the present work, the sensing element V_2O_5 doped ZnO annealed at 500°C showed best results with sensitivity approximately 350% higher than Cu doped ZnO and approximately 700% times greater than Ag doped ZnO . $\text{V}_2\text{O}_5\text{-ZnO}$ system exhibits multifunctional properties. Single phase $\text{V}_2\text{O}_5\text{-ZnO}$ is considered as diluted magnetic semiconductor (DMS) material. Multi-phase $\text{ZnO-V}_2\text{O}_5$ manifests varistor like

properties. While varistor properties are generally due to greater metal ions but in $\text{ZnO-V}_2\text{O}_5$ smaller vanadium ion is responsible [21].

2. Experimental Process

2.1. Fabrication of Sensing Elements

Solid-state reaction route was adopted to fabricate nanocomposite samples of $\text{V}_2\text{O}_5\text{-ZnO}$. ZnO and V_2O_5 by different weight% were mixed. 10% by weight of glass powder (binder) was added. Mixtures were grinded separately till uniformity was achieved. Samples with 0.2%, 0.5%, 0.8%, 1.0% and 1.2% of V_2O_5 in ZnO were labeled VZ-0.2, VZ-0.5, VZ-0.8, VZ-1 and VZ-1.2, respectively. Powders were pressed at room temperature into disc shaped pellets under 260 MPa pressure. Thickness of samples was kept 2 mm and diameter 4 mm. Pellet sample of pure ZnO was also fabricated for comparison purpose. Pellets were annealed in air at 500°C for 3 hours.

2.2. Apparatus for Characterization: SEM and XRD Studies

Study of surface morphology of the samples was carried out using scanning electron microscope [LEO-430, Cambridge, England]. Figure 1 and Figure 2 show micrographs of pure ZnO and $\text{ZnO-V}_2\text{O}_5$ nanocomposite samples respectively.

Figure 1. Scanning electron micrograph of sample pure ZnO .

Figure 2. Scanning electron micrograph of sample VZ-1.

Micrographs show ZnO scattered throughout the whole substrate forming a network of voids and pores. SEM micrographs would reveal 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 measured from SEM micrographs is 620 nm for sample of pure ZnO and 400 nm for ZnO-V₂O₅ nanocomposite sample.

Figure 3. XRD of pure ZnO.

Figure 4. XRD of sample VZ-1.

The crystallinity, structural phases and the gross crystal structure of the as synthesized nanocomposite materials were investigated by powder X-Ray diffractometer XPERT PRO-Analytical XRD system (Netherlands). Wavelength of CuK α source used is 1.54060 Å. X-ray patterns for pure ZnO and ZnO-V₂O₅ samples are shown in Figure 3 and Figure 4 respectively. The diffraction peaks were well defined. The XRD shapes of different composition looked similar. Patterns

show extent of crystallization. Scherrer's formula (given below) was used to find average crystallite size of the sample.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

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.

2.3. Measurement Conditions

Post annealing, samples were inserted in a humidity chamber shown in Figure 5.

Figure 5. Humidity Sensing System.

Copper electrode was used to measure resistance normal to the cross-section of the pellet. Given the high resistivity of the materials under consideration, the potential inaccuracy due to contact resistance was assumed negligible. Standard solution of potassium sulphate was used as humidifier and potassium hydroxide as de-humidifier. Surface contact area of all sensing elements with electrodes was 113.11 mm² and the cylindrical surface area that was exposed to the humidity in the chamber was also 113.11 mm². Calibration of the chamber was done by a standard hygrometer (Huger, Germany, $\pm 1\%$ RH) and a thermometer ($\pm 1^\circ\text{C}$). A multi-meter ($\pm 0.001 \text{ M}\Omega$, model: VC-9808) recorded variation in resistance with change in %RH. Aging 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 $\pm 3\%$.

3. Sensing Principle

Either ionic or electronic type mechanism is responsible for the conduction mechanism in the sensors based on the ceramic materials. Electrons are donated by the water molecules in the electronic type mechanism. 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 may occur. 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. V_2O_5 nanoparticles doped in ZnO enhance the adsorption and desorption rates of the water molecules and hence helps in increasing the sensitivity of the material. In chemisorption, molecules are adsorbed on the surface by valence bonds and only form monolayer adsorption. Chemisorption is a kind of adsorption which involves a chemical reaction between the surface and adsorbate. New chemical bonds are generated at the adsorbate and the substrate surface creates new type of electronic bonds. The layer formed due to chemisorption process is known as chemisorbed layer. 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. When moisture comes in contact with V_2O_5 -ZnO nanocomposite, water molecules irreversibly chemisorb on oxide surface [18]. Chemisorbed layer can be thermally desorbed by increasing temperature.

4. Results and Discussion

Variation in resistance with change in %RH for V_2O_5 -ZnO and pure ZnO samples for annealing temperature 500°C are plotted in Figure 6.

Figure 6. Resistance Vs% RH graph for samples for annealing temperature 500°C .

A decrease in resistance is noticed with increase in the % RH for all samples VZ-0.0, VZ-0.2, VZ-0.5, VZ-0.8, VZ-1.0 and VZ-1.2. Fall is sharp for initial range of 35%-55% RH and gradual for 55%-95% RH range. Table 1 shows values of sensitivity for these samples; column I show sensitivity for sample of pure ZnO. Column Ia indicates sensitivity for an initial increasing cycle, column Ib shows the sensitivity for decreasing cycle and Ic shows sensitivity value after six months for the sample of pure ZnO. Similarly, values of sensitivity for samples VZ-0.2, VZ-0.5, VZ-0.8, VZ-1.0 and VZ-1.2 are shown in Table 1.

Table 1. Sensitivity of Samples ($M\Omega/\%RH$).

I			II			III			IV			V		
Sample Pure ZnO			Sample VZ-0.2			Sample VZ-0.5			Sample VZ-0.8			Sample VZ-1.0		
a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
2.65	2.95	2.51	9.58	9.4	9.15	11.66	14.05	11.21	17.01	15.33	17.36	16.88	18.71	16.63

^aincreasing cycle of relative humidity, ^bdecreasing cycle of relative humidity, ^cincreasing cycle after six months

Here, sensitivity of humidity sensor is defined as the change in resistance (ΔR) of sensing element per unit change in relative humidity ($\Delta RH\%$). For calculation of sensitivity, the humidity has been divided in equal intervals of 5% RH each. Difference in the value of the resistance for each of this interval has been calculated and then divided by 5. The average has been taken for all these calculated values. Formula for calculation of sensitivity of the sensing elements may be written as given below:

$$\text{Sensitivity} = (\Delta R)/(\Delta \%RH) \quad (2)$$

With increase in doping percentage of V_2O_5 in ZnO the sensitivity of the pellet samples increased from 2.65

$M\Omega/\%RH$ for pure ZnO to 16.88 $M\Omega/\%RH$ for 1% V_2O_5 doped ZnO.

Change in lattice parameters depends on ionic radius of doping atom. Doped atoms may substitute the Zn ion in the lattice. Use of additives arrests grain growth. When additive ions are smaller in size they comfortably take lattice sites. V^{5+} ions having much smaller size (63 pm) than Zn^{2+} (88 pm) are expected to take lattice site. Therefore, it is reasonable to suggest that most of V^{5+} takes lattice site. Ionic size of V^{2+} is 93 pm. In ZnO, due to charge matching, Zn^{2+} ions in lattice are generally substituted by 2^+ oxidation state. For vanadium doping, ionic radius of V^{2+} ($0.93 \text{ \AA}$) ion is larger than Zn^{2+} ($0.88 \text{ \AA}$) ion. If V^{2+} ion substitutes Zn^{2+} ion in lattice then the

ionic radii mismatch may cause change in lattice parameter. Some V²⁺ ions do substitute the Zn²⁺ ions in ZnO lattice leading to agglomeration and subsequent growth in grain size [15-16]. This causes distribution of grain size leading to creation of more voids and porosity. Higher porosity increases surface to volume ratio. In this process, more surface area of sensing element gets exposed leading to more adsorption. This increases sensitivity. V₂O₅ behaves as acceptor impurity in n-type ZnO; hence, its presence in ZnO can modify electrical properties of ZnO and change the electrical response of ZnO [5].

In case of pure ZnO sample there is distribution in size of crystallites. Minimum crystallite size is 447 nm at θ value of 31.82 and maximum 534 nm at θ value of 66.41. In case of ZnO-V₂O₅ nanocomposite a wide distribution in the size of crystallites is noticed. Minimum crystallite size occurring at θ value of 76.98 is 260 nm and maximum crystallite size occurring at θ value of 66.41 is 598 nm. Thus, in case of ZnO-V₂O₅ nanocomposite, distribution in the crystallites size is as wide as 130% as compared to 20% in the case of pure ZnO sample. Hence, addition of V₂O₅ increases distribution of crystallite size. Addition of V₂O₅ also reduces average crystallite size. Average crystallite size for pure ZnO sample is 486 nm that reduces to 394 nm for ZnO-V₂O₅ nanocomposite.

As V₂O₅ is doped in ZnO, an evolution in distribution of crystallite size is noticed. Grain size distribution is noticeably influenced by addition of V₂O₅ in ZnO. With increase in doping of V₂O₅ in ZnO, more pores and voids are created due to drift of V⁵⁺ ions in oxygen vacancies of ZnO during annealing process. Pure ZnO sample 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. Sensing element of ZnO-V₂O₅ nanocomposite has higher void concentration and distribution of grain size. This synergy creates affinity towards moisture and thus higher conductivity. It is possible that multiplicative effect of two or more parameters of nanocomposite 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. Sample without V₂O₅ may have more grains per unit area of the surface, yet the range of crystallite or grain size distribution is so narrow and limited that the surface of the composite appears smooth and therefore does not provide required porosity as adsorption sites.

Sensing element V₂O₅-ZnO shows high value of sensitivity for the initial range of 35 to 55% RH and a low value of sensitivity for range 55-95% RH. Variation of resistance with change in% RH in the range 10%-35% RH was not regular and repeatable and so it is not reported. The increase in the conductivity of the sample with relative humidity in the lower range (<55% RH) is due to adsorption of the water molecules on pellet surface with capillary nano-pores. 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 (>55% RH),

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.

Figure 7 shows hysteresis graph for sample VZ-1; the process of humidification and dehumidification together for VZ-1.

Figure 7. Hysteresis graph behaviour for sample VZ-1 for annealing temperature 500°C.

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. Minimum hysteresis recorded for samples VZ-0.0, VZ-0.2, VZ-0.5, VZ-0.8 and VZ-1.0 were ± 5.26 , ± 4.62 , ± 17.61 , ± 6.00 ± 5.50 and ± 9.50 , respectively. Figure 8 shows aging graph for the sample VZ-1. The graph shows an initial humidification process as well as humidification process after six months. Sensor performance may significantly be impacted due to aging factor.

Figure 8. Aging graph for sample VZ-1 for annealing temperature 500°C, a. Initial increasing cycle and b. increasing cycle after six months.

Aging of sensors based on metal oxides is a significant retrograde. Data were found to be generally reproducible over

different operation cycles. Sensitivity values were reproducible within $\pm 5.28\%$, $\pm 4.48\%$, $\pm 3.85\%$, $\pm 2.05\%$, $\pm 1.48\%$ and 2.95% for samples VZ-0.0, VZ-0.2, VZ-0.5, VZ-0.8, VZ-1.0 and VZ-1.2, respectively. As it is evident aging% decreased with increase in doping percentage of V_2O_5 in ZnO [32]. Sample VZ-1.0 manifests reproducibility within $\pm 2.0\%$ which is quite high for sensors based on metal oxides. Figure 9 shows graph between sensitivity and % of V_2O_5 in ZnO for humidification, dehumidification and humidification after six months. The value of sensitivity increased with increase in % of V_2O_5 in ZnO up to 1% and after that the sensitivity did not increase. Thus the sensitivity is the maximum for VZ-1.0. The hysteresis is low for this sample at ± 5.50 and the aging is only ± 2.0 .

Figure 9. Variation of sensitivity with change in % of V_2O_5 in ZnO for increasing humidity, decreasing humidity and increasing humidity after six months.

5. Conclusions

Sample VZ-1 shows best sensitivity of $16.88 \text{ M}\Omega/\%RH$. For this sample, hysteresis is within $\pm 6\%$ and reproducibility within $\pm 2\%$ in 35-95% RH range. As doping percentage of V_2O_5 is increased in ZnO aging gets reduced from ± 5.28 to $\pm 1.48\%$. Grain size for sample of pure ZnO is 620 nm and for V_2O_5 -ZnO nanocomposite the grain size is 400 nm. As V_2O_5 is doped in ZnO there is an evolution in the distribution of crystallite size. Range of crystallite size for pure ZnO is 447-534 nm and for ZnO- V_2O_5 nanocomposite it is 260-598 nm. For ZnO- V_2O_5 nanocomposite the distribution in the size of crystallites is as wide as 130% as compared to only 20% in the case of pure ZnO sample. This result in the increase in sensitivity of ZnO- V_2O_5 nanocomposite by more than 500% compared to the pure ZnO sample.

Acknowledgments

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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