

Characterization and Humidity Sensing Application of WO₃-SnO₂ Nanocomposite

N. K. Pandey¹, Vandna Shakya², Suneet Mishra³

^{1, 2, 3}(Sensors and Materials Research Laboratory, Department of Physics, University of Lucknow, Lucknow, 226007, Uttar Pradesh, India)

Abstract: Studies on the sensitivity of the electrical resistance and fabrication process of SnO₂ doped WO₃ nanometer materials for sensing applications are reported in details. Other properties such as reproducibility, aging and hysteresis were also recorded and found satisfactory. The sensing mechanism was discussed based on their annealing temperature, composition, crystallite size, surface area and porosity of the sensing element. In general, at low humidity, surface area and water adsorption plays the dominant role, while at high humidity, mesopore volume and capillary condensation become important. At the annealing temperature 600°C, sample 3 weight % of SnO₂ doped WO₃ nanocomposites have been prepared through solid-state reaction route, shows average sensitivity of 18.61 MΩ/%RH in the 15%-95% RH range, lower hysteresis, less effect of ageing and high reproducibility. It was observed that as resistance of the pellets continuously decreased when relative humidity in the chamber was increased from 15% to 95%. As calculated from Scherer's formula, crystallite size for the sensing elements of SnO₂ doped WO₃ are in 11–234 nm range, respectively.

Keywords: Sensor, Humidity, Adsorption, Hysteresis, Porous.

I. Introduction

Ceramic humidity sensors, one of those based on porous and sintered metal oxides have been attracting attention due to their intrinsic characteristics, they are superior in reproducibility of the electrical properties, mechanical strength, chemical and physical stability. These materials possess a unique structure consisting of grains, grain boundary surfaces, and pores, which make them suitable for adsorption of water molecules because of the high surface exposure [1]. Among the metallic oxides, tungsten trioxide (WO₃), which is a great degree studied material for the development of solid-state devices based on pellet, thin and thick films. The most successful outcomes have been obtained in electrochromics [2, 3] and gas sensor fields. Teoh et al. prepared mesoporous WO₃ thin film exhibits regular pores with an average pore size of 5 nm and specific surface area of 151 m²/g [4]. Aihua Yan et al. have synthesized WO₃ nanowall using solvothermal [5]. Leng et al. prepared WO₃ nanofibers using an electrospinning method [6]. Liu et al. have synthesized tungsten oxide nanorods assembled microspheres by a facile hydrothermal process [7]. Zhou et al. highly ordered mesoporous tungsten oxides (WO₃) have been synthesized via the hard templating method using mesoporous silica as a hard template and phosphotungstic acid as a precursor [8]. Su et al. prepared WO₃ thick film using screen-printing method [9]. Tungsten trioxide (WO₃), is a wide band-gap n-type semiconductor, has been considered as a promising sensing material of solid-state semiconductor humidity sensor because of its excellent sensitivity and selectivity to satisfy several requirements to a wide range of applications: 1) sensitivity in a wide RH range, 2) rapid response to the variation of RH and good reproducibility of the electrical signal, 3) good mechanical properties and stability, 4) chemical and physical stability, 5) wide operating humidity range and low cost [1]. In ceramic oxide Water molecules are adsorbed to increase the conductivity of n-type ceramics and to decrease the conductivity of p-type ceramics [10, 11], because the conductivity is induced by the surface concentration of electrons, this sensing style is usually called "electronic type." The electrical behaviour of electronic-type sensors in the presence of water vapor a reaction takes place between the oxygen ions adsorbed on the surface of the semiconductor and the water molecule. Many attempts have been made to enhance the sensitivity of semiconductor humidity sensors, one of which involved the doping is an attractive and effective tool for improved different properties of humidity sensors [12, 13]. SnO₂ doped WO₃ alter various properties such as sensitivity, good reproducibility, exhibits different types of morphologies and have many applications.

Here we report the characterization and humidity sensing studies of both undoped and SnO₂ doped WO₃ nanocomposites prepared by solid state reaction route systematically, including the sensitivity, effect of aging, hysteresis and reproducibility. Herein, it has been shown that humidity sensor can be made from the binary system of SnO₂ doped WO₃.

II. Sample Preparation and Experimental Process

The nanocomposite sample of WO₃-SnO₂ has been prepared through solid-state reaction route. 3% weight of SnO₂ powder (Loba Chemie, 99.99% pure) in WO₃ (Loba Chemie, 99.99% pure) have been mixed

uniformly and made fine by grinding in mortar with pestle for three hours. 10% weight of polyvinyl alcohol has been added as binder to increase the strength of the sample. The resultant powders have been pressed into pellet shape by uniaxially applying pressure of 267 M Pa in a hydraulic press machine (M.B. Instruments, Delhi, India) at room temperature. The pellet samples prepared are in disc shape having a diameter of 12 mm and thickness 2 mm. The pressed powder pellets have been sintered in air at temperatures 300⁰C-600⁰C for 3 hours in an electric muffle furnace (Ambassador, India) and slowly cooled to room temperature. After annealing 300⁰C-600⁰C, samples have been exposed to humidity in a specially designed humidity chamber. Fig. 1 shows schematic diagram of humidity sensing apparatus. Saturated salt solution of potassium sulfate has been used as humidifier and potassium hydroxide as de-humidifier. Inside the humidity chamber, a thermometer ($\pm 1^{\circ}\text{C}$) and standard hygrometer (digital, $\pm 1\%$ RH) are placed for the purpose of calibration. The electrical characteristic of the sensors were measured by a multifunctional digital multimeter ($\pm 0.001\ \text{M}\Omega$, VC-9808) at variant humidity environments. Copper electrodes have been used to measure the resistance of the pellets. The resistance of the pellet have been measured normal to the cylindrical surface of the pellets. For the study of ageing effect, the samples have again been exposed to humidity after six months. Samples of pure WO₃ have been labeled as “W” and samples of SnO₂ doped WO₃ as “WS”.

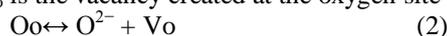
III. Principle of Operation of WO₃-SnO₂ Nanocomposite

As dry oxides of WO₃-SnO₂ nanocomposite are brought in contact with humid air, water molecules chemisorb on the available sites of the oxide surface. The adsorption of water molecules on the surface takes place via a dissociative chemisorption process which may be described in a two-step process as given below:

- (i) Water molecules adsorbed on grain surface react with the lattice A (A→W or Sn) as



Where O_o represents the lattice oxygen and V_o is the vacancy created at the oxygen site according to the reaction



- (ii) Doubly ionized oxygen, displaced from the lattice, reacts with the H⁺ coming from the dissociation of water molecules to form a hydroxyl group as



WO₃ and SnO₂ both have electron vacancies. Hence, because of this reaction, the electrons are accumulated at the WO₃/SnO₂ surface and, consequently, the resistance of the sensing element decreases with increase in relative humidity.

When another water molecule adsorbed through hydrogen bonding on the two neighboring hydroxyl groups due to which the top water molecule condensed cannot move freely (Fig.2) Thus this layer or the first physically-adsorbed layer is immobile and there are not hydrogen bonds formed between the water molecules in this layer. These two immobile layers cannot contribute to proton conducting activity, could provide electron tunneling between donor water sites [14, 15]. This mechanism is quite helpful for detecting low humidity levels, at which there is not effective protonic conduction. As water continues to condense on the surface of the ceramic, to form less ordered second physically adsorbed layer on top of the first physically adsorbed layer and protons may have more and more freedom to move inside the condensed water through the Grotthuss mechanism.

IV. Results and Discussion

4.1 Humidification Graphs

Fig. 3 and 4 are the humidification graphs for the sensing elements W and WS for the annealing temperatures 300⁰ C–600⁰ C in terms of resistance vs. relative humidity at a room temperature repeated over many cycles. Figs. 3 and 4 show large decrease in the values of the resistance for initial values of the relative humidity from 15%–40 % RH while in 40%–95% RH range the fall in resistance is slow. This phenomenon may be understood in the manner that electrons may be trapped by surface defects such as ionized oxygen vacancies and that these may be released when water molecules are adsorbed onto the defect sites and therefore resulting in a reduce of value of resistance of the n-type semiconductor at high humidity condition(>40% RH). On the other hand, low humidity(<40% RH) permits the electrons may be trapped by surface defects are released when water molecules are co-adsorbed onto the surface causing some of the oxygen ions to be desorbed and relatively high resistance is maintained.

Table I shows values of sensitivity for both sensing elements W and WS for annealing temperatures 300⁰ C–600⁰ C. From the Figs. 3 and 4, the values of sensitivity have been shown in two ranges of % RH, viz. 15%–40% RH and 40%–95% RH. As observed from Table I that in the humidity range 15%–40% RH and 40%–95% the average sensitivity for the sensing element W is lower compared to that of WS for all the annealing temperatures 300⁰ C–600⁰ C. From Fig.5 it is observed that as the annealing temperatures 300⁰C–600⁰C increases the sensitivity of both sample W (pure wo₃) and WS (SnO₂ doped WO₃) increases.

Here the sensitivity of humidity sensor is defined as the change in resistance (ΔR) of sensing element per unit change in RH (ΔRH %). For calculation of average sensitivity, the humidity from 15% to 95% RH 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

$$\text{Sensitivity} = [(\Delta R) / (\Delta\% \text{ RH})] \quad (4)$$

4.2 Humidification and Desiccation Graphs (Hysteresis)

Metal oxide and binary systems of metal oxides have higher surface sites available for the adsorption and co-adsorb of water molecules on the surface of sample between the humidification process and the desiccation process. To determine the hysteresis effect in the sensing elements, first of all the humidity has been increased from 15% RH to 95% RH and then cycled down to 15% RH in the humidity chamber and the values of resistance of the sensing elements recorded with the variation of % RH. Figs.6 and 7 show the hysteresis graphs for the sensing elements W and WS, respectively, for annealing temperature 600⁰ C. The phenomenon of hysteresis may be understood in the manners that due to the adsorption of water on the surface of the sensing elements a chemisorbed layer form. This chemisorbed layer, once formed is not further affected by exposure to or removal of humidity, it can be thermally desorbed only. Hence in the decreasing cycle of % RH, the initially adsorbed water is not removed fully leading to hysteresis. The value of Hysteresis for the sensing elements W and WS are 0.10% and 2.68% for annealing temperatures, 600⁰ C respectively.

4.3 Ageing Effect

Ageing is a significant problem in sensing devices based on metal oxides [16, 17]. To see the aging effect, after humidification and desiccation the sensing elements have been kept in laboratory environment and their humidity sensing characteristics regularly monitored. The sensing properties of the same sample W and WS for annealing temperature 600⁰C have been examined again in the humidity control chamber after two and four months and variation of resistance with % RH recorded. The variation of resistance of the sensing elements W and WS with change in % RH after two and four months have been shown in Figs. 8 and 9. From the Fig.8 the value of the average sensitivity of the sample W after two and four months is 7.46 M Ω /%RH and 4.85 M Ω /%RH for the annealing temperature 600⁰C. From Fig.9 the average sensitivity of the sample WS in the range of 15%–95% RH after two and four months is 15.27 M Ω /%RH and 11.26 M Ω /%RH for the annealing temperature 600⁰C. It is found that both sample W and WS became less sensitive after two and four months.

Ageing effect present in ceramic humidity sensor may be due either to prolonged exposure of surface to high humidity, adsorption of contaminants preferentially on the cation sites, loss of surface cations due to vaporization, solubility and diffusion, or annealing to a less reactive structure, migration of cations away from the surface due to thermal diffusion.

4.4 X-Ray Diffraction (XRD) Analysis

XRD has been studied using XPERT PRO-Analytical XRD system (Netherlands). The wavelength of the source CuK α used is 1.54060 Å. Fig.10 shows the XRD pattern of sample WS for annealing temperature 600⁰C prepared at room temperature. The average crystalline size of the samples has been calculated using Debye Scherer's formula:

$$D = K\lambda / \beta \text{Cos}\theta, \quad (5)$$

Where D is the crystallite size, K is the fixed number of 0.9, λ is the X-ray wavelength, θ is the Bragg angle and β is the full width at half maximum of the peak. The crystallite size calculated from Scherer's formula for the sample WS is found to be 11-234 nm. The properly indexed XRD pattern shows formation of tetragonal tin tungsten oxide structure along with WO₃ and SnO₂ peaks.

V. FIGURES AND TABLES

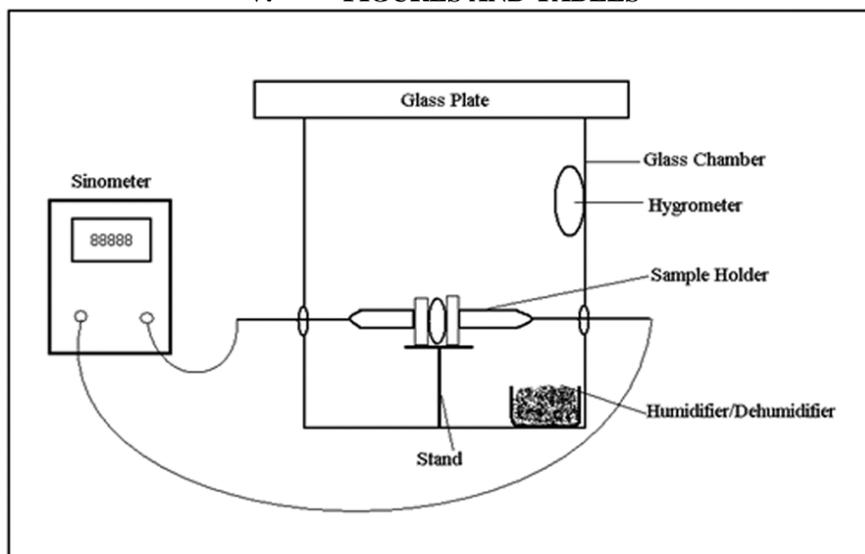


Fig. 1. Schematic diagram of humidity sensing apparatus.

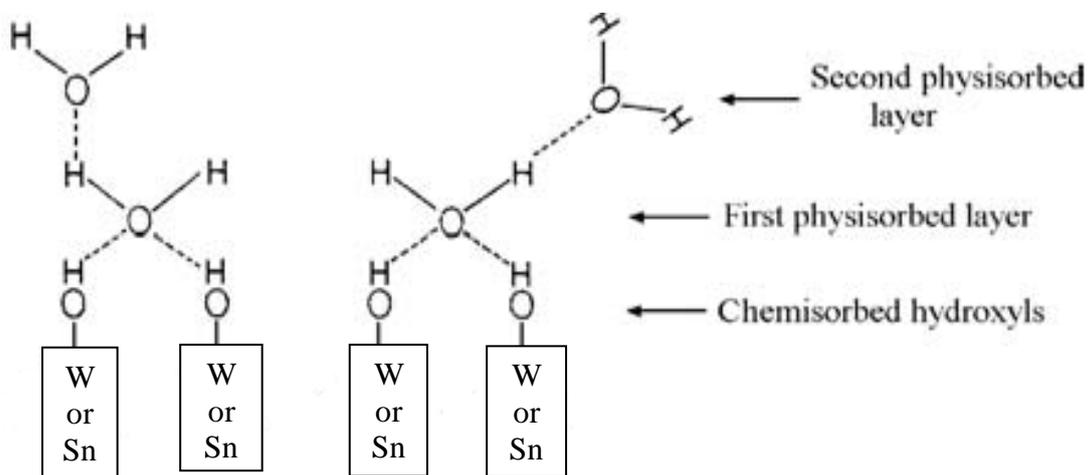


Fig. 2. Sensing mechanism of solid state humidity sensor.

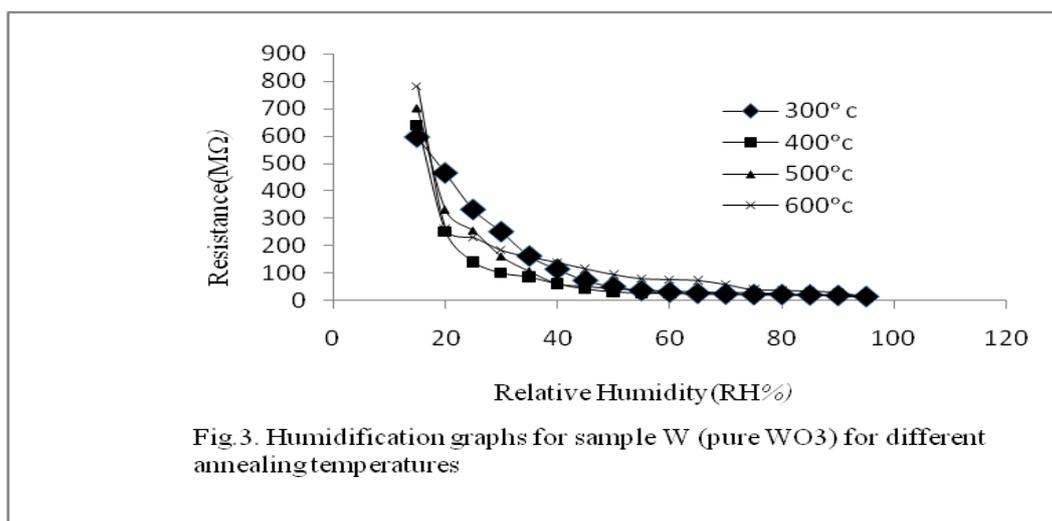


Fig. 3. Humidification graphs for sample W (pure WO_3) for different annealing temperatures

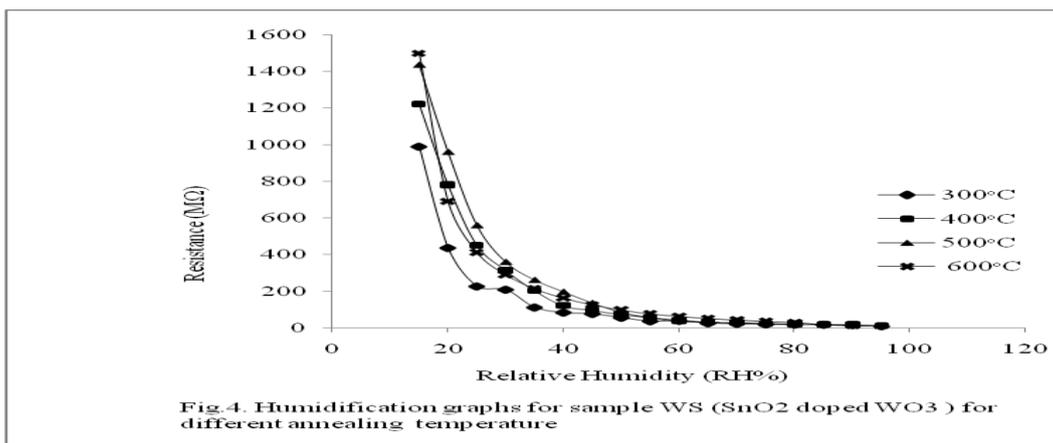


Fig.4. Humidification graphs for sample WS (SnO_2 doped WO_3) for different annealing temperature

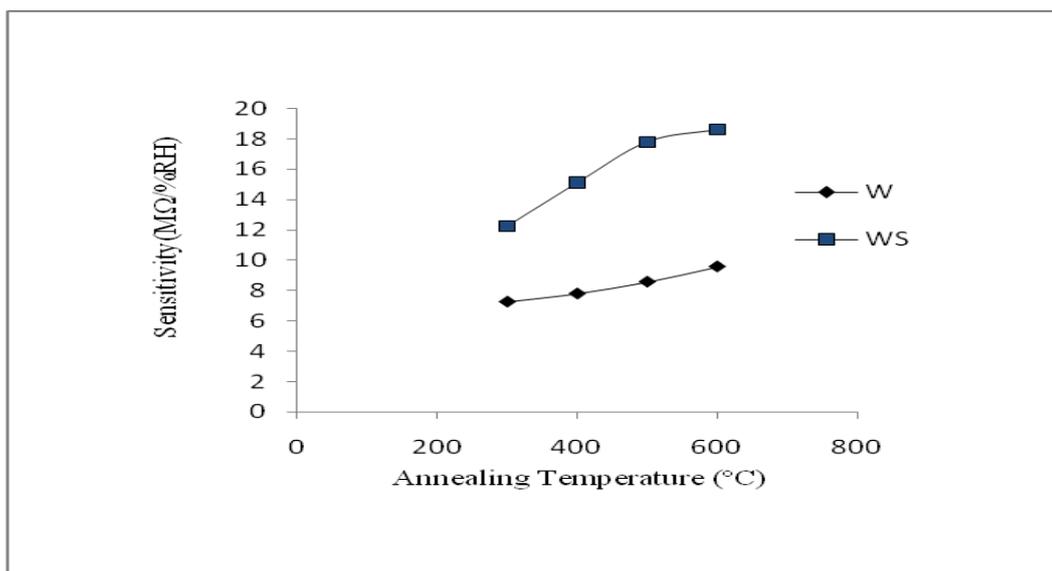
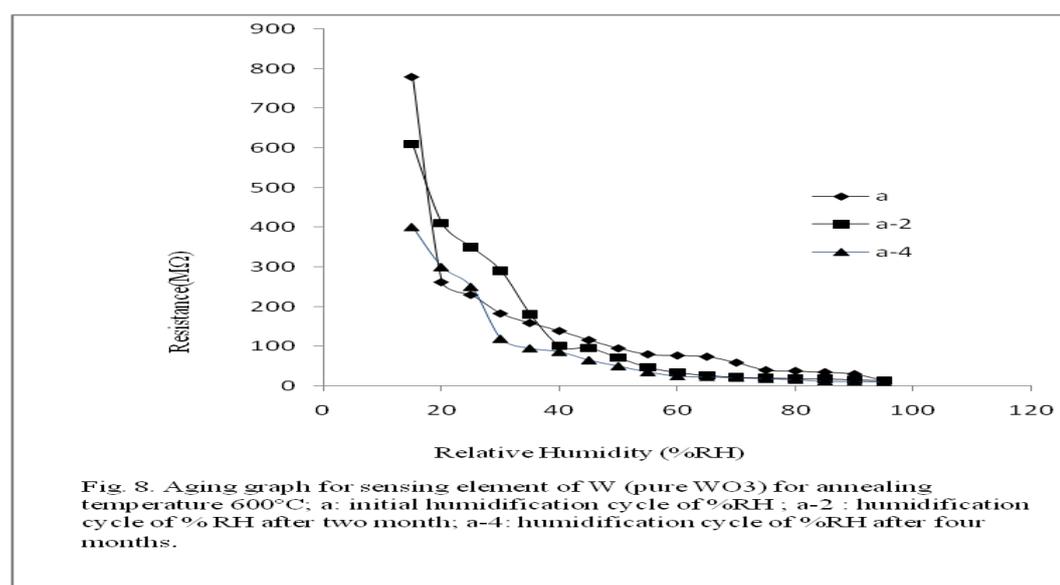
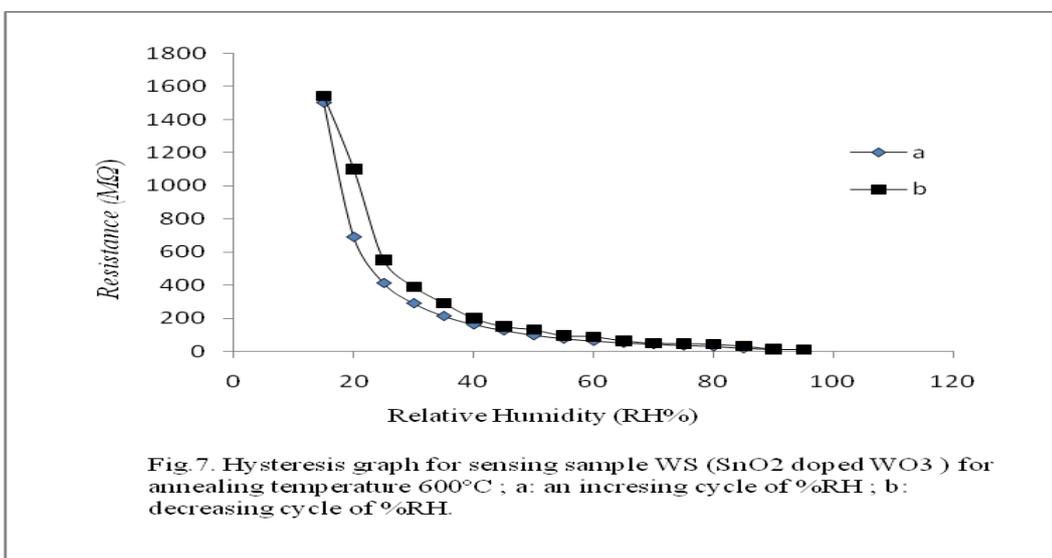
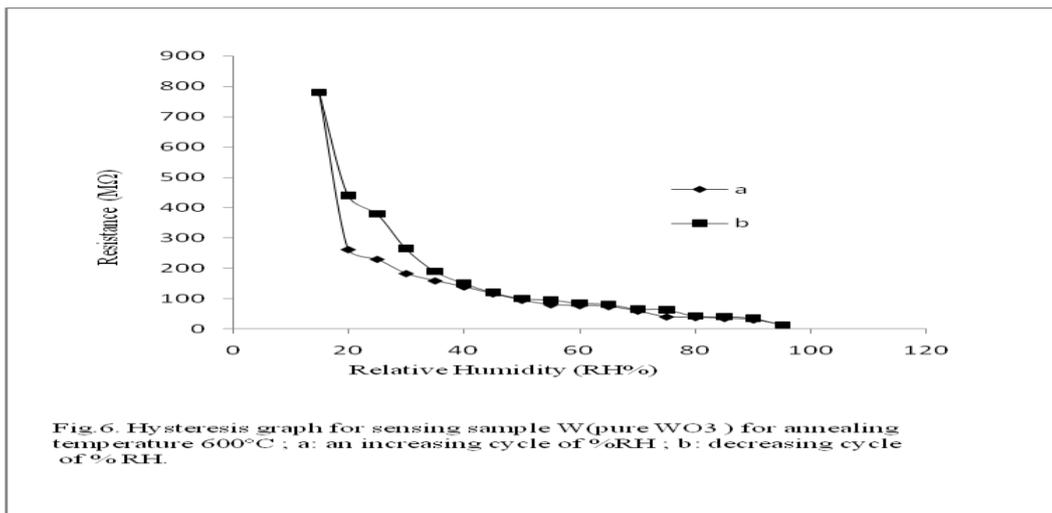


Fig. 5. Average sensitivity versus annealing temperature for the humidity range of 15%–95% RH; W: for sensing element of pure WO_3 ; WS: for sensing element of SnO_2 doped WO_3 .

TABLE I
Average Sensitivity of Samples W and WS for Different Annealing Temperatures in Two Separate Ranges of Relative Humidity, Viz 15%–40% RH and 40%–95% RH

Annealing temperature	% range of relative humidity	Sensitivity ($M\Omega/\%RH$)	
		W	WS
300°C	15-40%RH	19.32	18.24
	40-95%RH	01.81	1.34
400°C	15-40%RH	23.12	44.0
	40-95%RH	0.85	1.98
500°C	15-40%RH	25.56	49.56
	40-95%RH	0.87	3.38
600°C	15-40%RH	25.64	53.52
	40-95%RH	2.27	2.74



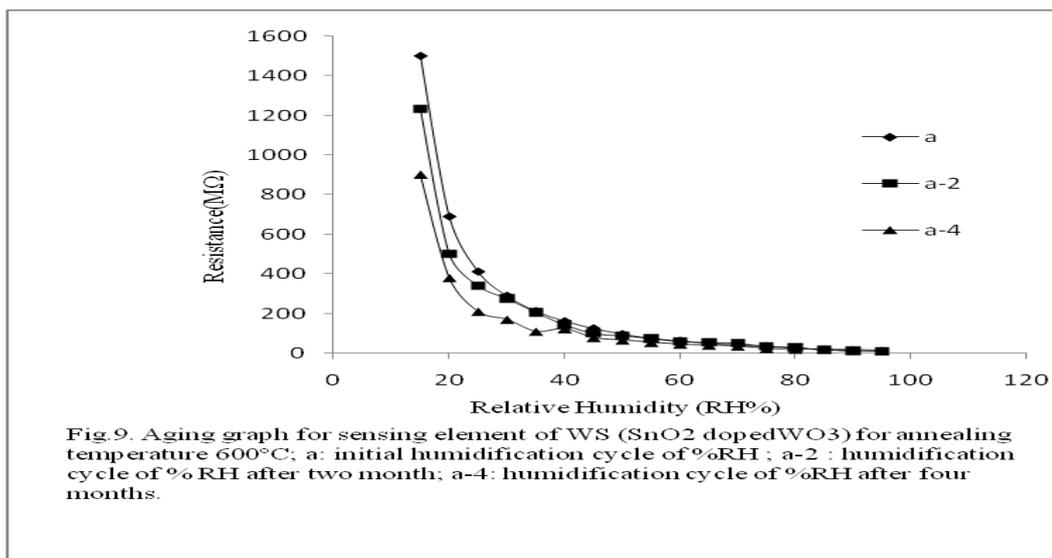


Fig.9. Aging graph for sensing element of WS (SnO_2 doped WO_3) for annealing temperature $600^\circ C$; a: initial humidification cycle of %RH; a-2 : humidification cycle of %RH after two month; a-4: humidification cycle of %RH after four months.

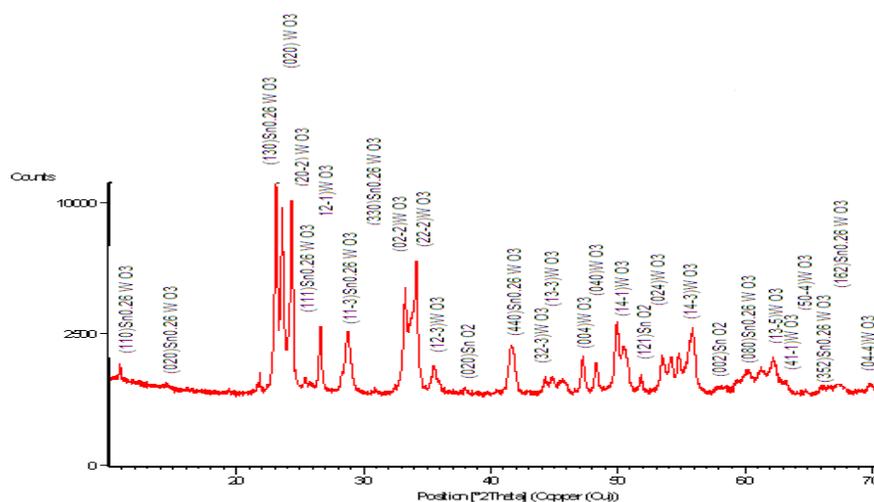


Fig. 10. XRD pattern for sensing element of SnO_2 doped WO_3 (sample WS) for annealing temperature $600^\circ C$.

VI. Conclusion

In summary, WO_3-SnO_2 nanoparticles were prepared through solid-state reaction route. The effect of relative humidity on resistance of sensing element was studied in the humidity range of 15% to 95% RH. Results revealed that relative humidity increases there is decrease in the resistance of the sensing elements. The results confirmed that the value of sensitivity increase with increase in annealing temperature $300^\circ C-600^\circ C$ both for the Sensing element of SnO_2 doped WO_3 and pure WO_3 . The Sensing element of SnO_2 doped WO_3 showed a better response, annealed at $600^\circ C$ with average sensitivity of $18.61 M\Omega/\%RH$ in the 15%–95% RH range, lower hysteresis, less effect of ageing and higher reproducibility. The minimum crystallite size calculated from Scherer formula is found to be in 11 nm which has good sensing properties for water vapour adsorption. Thus WO_3-SnO_2 nanocomposite carries a good scope for the development of humidity sensor for the range of relative humidity from 15 to 95 % RH.

Acknowledgements

The authors would like to thank the Geological Survey of India, Lucknow, India, for providing the XRD facility.

References

Journal Papers:

- [1] MARIO PELINO AND CARLO CANTALINI, *Active and Passive Elec. Comp.*, 1994, Vol.16, pp. 69-87.
- [2] K. Bange, T. Gambke, *Adv. Mater.* 2 (1990) 10.
- [3] P.V. Ashrit, G. Bader, Vo-Van Truong, *Thin Solid Films* 320 (1998) 324.
- [4] L. G. Teoh,^a I. M. Hung,^a J. Shieh,^b W. H. Lai,^a and M. H. Hona,^z, *Electrochemical and Solid-State Letters*, **6** (8) G108-G111 (2003).
- [5] Aihua Yana, Changsheng Xie, Dawen Zeng, Shuizhou Cai, Huayao Li *Journal of Alloys and Compounds* 495 (2010) 88–92.
- [6] Ji-yan Leng , Xiu-juan Xu , Ning Lv , Hui-tao Fan , Tong Zhang *Journal of Colloid and Interface Science* 356 (2011) 54–57.
- [7] Zhifu Liu, Masashio Miyauchi, Toshinari Yamazaki, Yanbai Shen, *Sensors and Actuators B* 140 (2009) 514–519.
- [8] Liang Zhou , Qijun Ren , Xufeng Zhou , Jiawei Tang , Zhanghai Chen , *Chengzhong Microporous and Mesoporous Materials* 109 (2008) 248–257.
- [9] P.-G. Su ^{a,*}, Wu Ren-Jang ^b, Nieh Fang-Pei ^c, *Talanta* 59 (2003) 667- 672
- [10] J. F. Boyle and K. A. Jones, *J. Electronic Mater.* 6, 717 (1977)
- [11] G. N. Avani and L. Nanis, *Sens. Actuators B* 2, 201 (1981).
- [12] Barakat, M. A.; Hayes, G.; Shah, S. I. J. *Nanosci. Nanotech.* , **2005**, 5, 759.
- [13] Su, P. G.; Wang, C. P.; *Sens. Actuators B*, **2008**, 129, 538.
- [14] V. K. Khanna and R. K. Nahar, *J. Phys. D: Appl. Phys.* 19, L141 (1986).
- [15] Y. Yeh, T. Tseng, and D. Chang, *J. Am. Ceram. Soc.* 72, 1472(1989).
- [16] E. Traversa, *Sens. Act. B*, pp. 135–156, 1995.
- [17] Y. Shimizu, M. Shimabukuro, H. Arai, and T. Seiyama, *Chem. Lett.*, vol. 14, no. 7, pp. 917–920, 1985.