# Electrical and Humidity Sensing Properties of Porous Zn Doped $Wo_3$ Ceramic Nanomaterials

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***Abstract*-In humidity sensors, ceramic nanometre materials have attracted great attention due to their high surface area and high porosity. The paper proposes a novel resistive humidity sensor based on Zn doped $WO_3$ obtained through solid- state reaction route. The pellet was made under a pressure of 267 M Pa and it was annealed at 300, 400, 500 and 600$^0$C for 3 hrs successively. After each annealing the resistance of pellet changes depends on the amount of adsorbed water vapour. It is observed that as relative humidity (% RH) increases, there is a decrease in the resistance for the entire range of humidity from 15 % to 95 %. At the annealing temperature 600□C, sample 1.5 weight % of Zn doped $WO_3$ nanocomposites shows average sensitivity in the 15%-95% RH range, lower hysteresis, less effect of ageing , response and recovery times were also recorded and found satisfactory. In general, surface area and water adsorption plays the major role, at low humidity while at high humidity, mesopore volume and capillary condensation become important. X-ray diffractometry (XRD) and scanning electron microscopy (SEM) shows the structure and morphology of the pellets.**

*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]. Tungsten trioxide ($WO_3$), which is a wide band-gap n-type semiconductor with $d^0$ configuration, has been considered as a promising sensing material of solid-state semiconductor humidity sensor because free electrons originating from oxygen vacancies contribute to electronic conductivity. All tungsten atoms at the surface change their valence state when the surface $W^{5+}$ sites react with the oxidizing atmosphere of air, leading presumably to a formation of the $W^{6+}$-OH bonds in a humid ambiance . Due to surface reactivity with moisture and porous microstructure of a ceramic $WO_3$ are used for sensing purpose. To enhance the sensitivity of semiconductor humidity sensors, doping is an attractive and effective tool for improved different properties of humidity sensors [2, 3]. ZnO doped $WO_3$ alter various properties such as sensitivity, good reproducibility, exhibits different types of morphologies and have many applications. In the present research paper, the investigation on ZnO doped $WO_3$ nanomaterial, operating in the dc mode as humidity sensor, is reported.

## II. EXPERIMENTAL

The nanocomposite sample of $WO_3$-ZnO was prepared through solid-state reaction route. The starting material is $WO_3$ (Loba Chemie, 99.99% pure). 1.5 weight % (sample WZ-1.5) of ZnO powder (Loba Chemie, 99.9%) has been added to $WO_3$. 10% weight of polyvinyl alcohol was added as binder to increase the strength of the sample. Mixed powder was grinded to uniformity for three hours. The resultant powder was 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. After sintering, each sensing sample was placed in a same humidity chamber and its sensing outputs were obtained under different humidity levels. Inside the humidity chamber, a thermometer (±1°C) and standard hygrometer (Huger, Germany, ±1% RH) are placed for the purpose of calibration. Variation in resistance has been recorded with change in relative humidity. Relative humidity has been measured using the standard hygrometer. Variation in resistance of the pellets has been recorded using a resistance meter (Sino meter, ±1 MΩ, model: VC-9808). Copper electrode has been used to measure the resistance of the pellets. The resistance of the pellets has been measured normal to the cross-section of the pellets. To see the effect of aging, the sensing properties of these elements have been examined again in the humidity control chamber after four and eight months. The response and recovery time for the sensing elements are also observed.

## III. PRINCIPLE OF OPERATION OF WO3-ZNO NANOCOMPOSITE

As dry oxides of $WO_3$-ZnO 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 Zn) as

$$H_2O + Oo + A \leftrightarrow 2OH\text{–}A + Vo + 2e^- \qquad (1)$$

Where Oo represents the lattice oxygen and Vo is the vacancy created at the oxygen site according to the reaction:

$$Oo \leftrightarrow O^{2-} + Vo \qquad (2)$$

(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:

$$H^+ + O^{2-} \leftrightarrow OH^- \qquad (3)$$

$WO_3$ and ZnO both have electron vacancies. Hence, because of this reaction, the electrons are accumulated at the $WO_3$/ZnO surface and, consequently, the resistance of the sensing element decreases with increase in relative humidity.

## IV. RESULTS AND DISCUSSION

Variation in resistance with the change in % RH for WZ-1.5 sensing elements is shown in Figure. 1 for the humidification process. The decrease in resistance with increase in the % RH is observed for all the sensing elements. Penetrated water molecules can promote the decrease in the barrier heights of grain boundary potential barriers exponentially and therefore some slight decrease of grain boundary barriers height on relative humidity can cause strong decrease of resistance (or increase of conductance).These graphs also shows that from 15 to 40% RH there is a rapid change in resistance while in 40 to 95% RH range the variation of resistance is comparatively slow which means in 15 to 40% RH range sensitivity of the sample is high whereas in 40 to 95% RH range sensitivity is comparatively low. 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

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

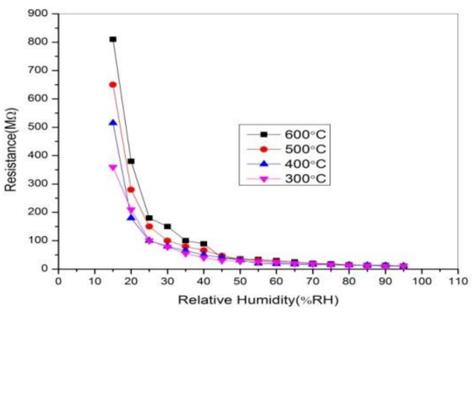


Fig.1 Humidification graph for sample WZ-1.5 at different annealing temperature.

To observe hysteresis, the variation in resistance for both increasing and decreasing cycles has been measured. All the sensing elements show small hysteresis. However, the lowest hysteresis is observed for the sensing element WZ-1.5 at annealing temperature $600^0$C. Fig. 2 shows the hysteresis graph for the sensing element WZ-1.5 at annealing temperature $600^0$C. The sensitivity values are also observed for the WZ-1.5 sensing elements annealed at different temperatures from 300°C to 600°C
temperature range. The results generally show that the sensitivity value increases with the increase in the annealing temperature. The best sensitivity value is 10 MΩ/% RH for the WZ-1.5 sample annealed at 600 °C.

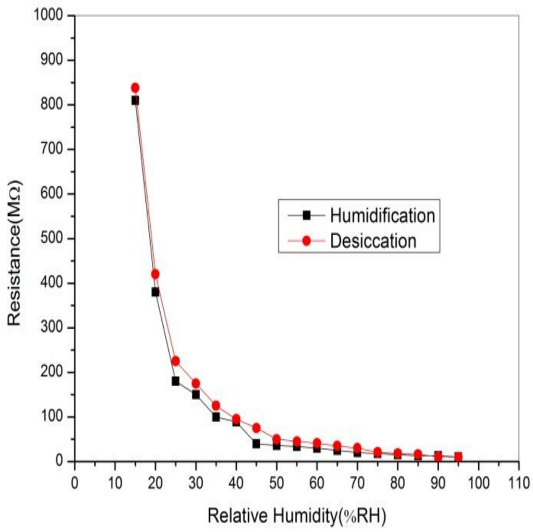


Fig. 2 Hysteresis graph for sensing sample WZ-1.5 for annealing temperature $600^0$C.

Ageing is a significant problem in sensing devices based on metal oxides [4]. 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. From the Fig.3 the value of the average sensitivity of the sample WZ-1.5 after four and eight months is 7 MΩ/%RH and 5.87 MΩ/%RH for the annealing temperature 600°C.

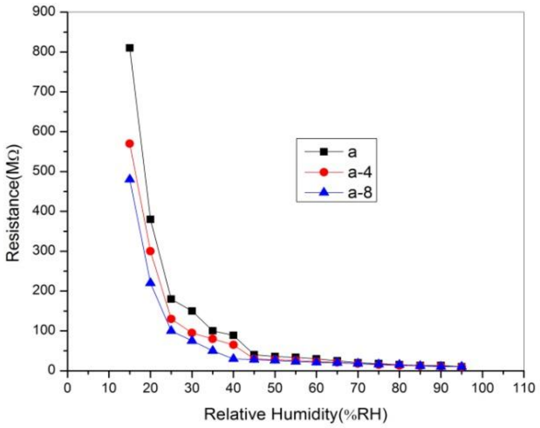


Fig. 3 Ageing graph for sensing sample WZ-1.5 for annealing temperature $600^0$C; a: initial humidification cycle of % RH; a-4: humidification cycle of % RH after four months; a-8: humidification cycle of %RH after eight months.

The time taken to accomplish 90% of the initial total resistance variation is defined as response/recovery time during the humidification and desiccation processes the response time and recovery time for the best sample i.e. WZ-1.5 annealed at $600^0$C are 100 seconds and 780 seconds respectively. Since desorption is an endothermic process, it takes longer time to desorb the water vapor; therefore, the recovery time is always greater than the response time.

## V. X-RAY DIFFRACTION (XRD) ANALYSIS

X-Ray diffraction was studied using XPERT PRO-Analytical XRD system (Netherlands). The wavelength of the CuK source used was 1.54060Å. Figure. 4 shows X-ray pattern for the sensing element WZ-1.5 annealed at 600 °C. The average crystallite size of the sample was calculated using Scherrer's formula.The crystallite size calculated from Scherer's formula for the sample WZ-1.5 is found to be 16-94 nm.

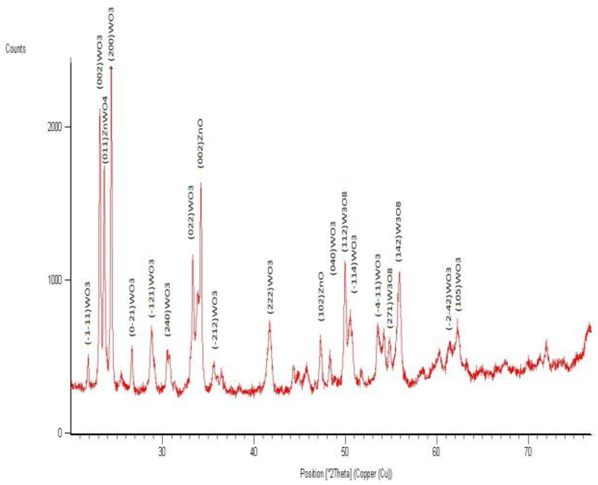


Fig. 4 XRD pattern for sensing element of ZnO doped $WO_3$ (sample WZ-1.5) for annealing temperature 600°C.

## VI. SCANNING ELECTRON MICROSCOPE STUDY

The study of the surface morphology of sample WZ-1.5 annealed at 600 °C was carried out using SEM (LEO-430, Cambridge, England).Scanning micrographs of WZ-1.5 show fig.5, the presence of capillary pores that are expected to provide sites used for sensing mechanism. The average grain sizes for the sensing elements WZ-1.5 calculated from SEM micrographs are 200 nm. The SEM micrograph of this sensing element shows clustering and agglomeration of large number of crystallites thus, more of the surface areas of the sensing elements are exposed leading to more adsorption of water molecules. Thus sensitivity of the sensing elements increases.

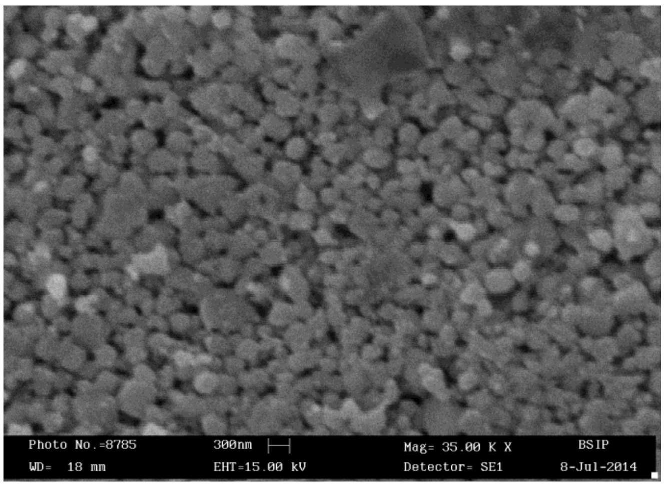


Fig 5. SEM micrograph of sensing sample WZ-1.5 for annealing temperature $600^0$C.

## VII. CONCLUSION

The Sensing element WZ-1.5 showed a better response, annealed at 600°C with average sensitivity of 10 MΩ/%RH in the 15%–95% RH range, lower hysteresis, less effect of ageing and higher reproducibility. XRD pattern for sample WZ-1.5 show the monoclinic structure of $WO_3$ with space group P21/n and show the hexagonal structure of ZnO with space group P63mc .Hence our studies suggest that, ZnO-$WO_3$ composite can be a promising material for high performance humidity sensing applications.

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