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NANOPOROUS ZINC TUNGSTATE HUMIDITY SENSOR

Anupam Kumar Tripathi* Narendra Kumar Pandey Vidhu Tripathi*****
**Department of Physics, Faculty of Engineering, University of Lucknow, Lucknow U.P. India.*
***Department of Physics, Lucknow university,Lucknow U.P. India.*
****Department of Physics BBD Engineering College Lucknow U.P. India.*

Abstract:
Various materials have been studied and used as sensing elements in humidity measurement applications [1-3]. Some metal oxides such as TiO_2, SnO_2, ZnO, Cr_2O_3 and WO_3 are semi-conducting materials among which WO_3 has been studied extensively because of its electro-chromic applications. Tungsten oxide and binary systems of tungsten oxide with other metal oxides are also being studied for their gas and humidity sensing applications. Sensors of great variety of application have been developed, numerous materials have been utilized for humidity sensing of which the metal oxides that are physically and chemically stable, have been extensively used at both room and elevated temperature [4-9]. This paper reports resistive type humidity sensing properties of composite powder of WO_3 and ZnO in the ratio of 4:1 and 2:1. Tungsten oxide powder has been obtained by oxidizing Tungsten powder (Lobachemie, 99% pure) at 600^0C. 500 mg of ZnO (qualigens, 99% pure) has been mixed with 2 gram and 1gm of WO_3. Pellets of these powder mixtures have been made at pressure of 3 tones. The pellets have been annealed at temperatures of 300^0C, 400^0C and 500^0C. Humidity sensing applications of pellets have been studied in a specially designed chamber [10, 11]. Standard solution of potassium sulphate has been used as humidifier and potassium hydroxide as de-humidifier. Variation in resistances has been noted using Sinometre (MΩ range, VC 9808). Relative humidity is measured using standard hygrometer (Huger, Germany).

Specific Sensitivity of the sensor is defined as the change in resistance (ΔR) of sensing element per unit change in relative humidity (RH %) per unit resistance, i.e.

$$\Delta S = \Delta R / R\ (\Delta\ RH\ \%) \quad \text{------} \quad (1)$$

Experimental procedure

The starting material is Tungsten powder. When tungsten powder is annealed at temperature 600^0C for three hours it gets converted into tungsten trioxide. Pressing powder WO_3, and ZnO taken in the weight percent ratio 4:1 and 2: 1, under a load of 3 tones up to half an hour, has prepared our sample. The pellet so formed has been annealed in an electric muffle furnace at temperature 300˚C, 400˚Cand 500˚C for three hours and after each time of annealing it has been exposed to humidity in the specially designed experimental setup. Relative humidity chamber consists of sample holder capable of holding the sample in the form of pellet. The sample pellet has been fitted in this holder and kept in the chamber. The holder carries two copper probes as well connected to a Sinometre used for electrical resistance measurement.

Results and Discussion

Resistance of the sample pellet has been measured after each time of annealing during controlled exposure to humidity in the range of 5% to 85%. Variation of resistance with change in relative humidity at temperatures 300°C, 400°C and 500°C of sample (WO_3 and ZnO) prepared in the ratio 4:1 and 2:1 is shown in figure 1 and 2 respectively which is divided into three sections a, b and c. Figure 1(a) shows the variation in resistance with relative humidity at 300^0C, the average sensitivity at this temperature is 0.02. Similarly figure 1(b) shows the same variation at 400^0C with same average sensitivity 0.02. Figure 1(c) shows the variation in resistance with relative humidity at 500^0C, having sensitivity 0.03. Thus we conclude that our results show better sensitivity at 500^0C as compared with 300^0C and 400^0 C. Thus we may predict that sensitivity increases with increasing annealing temperature. Figure 2(a) shows the variation in resistance with relative humidity at 300^0 C, at this temperature average sensitivity of the sample is 0.02. Figure 2(b) shows the variation in resistance with relative humudity at 400°C; at this temperature the average sensitivity of sample is same as that of sample at 300°C. Figure 2 (c) shows the variation in resistance with relative humidity Thus we conclude that our results show better sensitivity at 500^0C as compared with 300^0 C and 400^0 C. Thus we may predict that sensitivity increases with increasing annealing temperature. The decrease in resistance or increase in conductivity can be attributed to the mobility of the WO3 ions which are loosely attached to the Vander Wall's forces of attraction. This also proves the adsorption of the water molecules, which makes the material more p- type in nature i.e. the hole concentration is increased by donation of the lone pair from the conducting complex towards the WO3 water molecules [12].

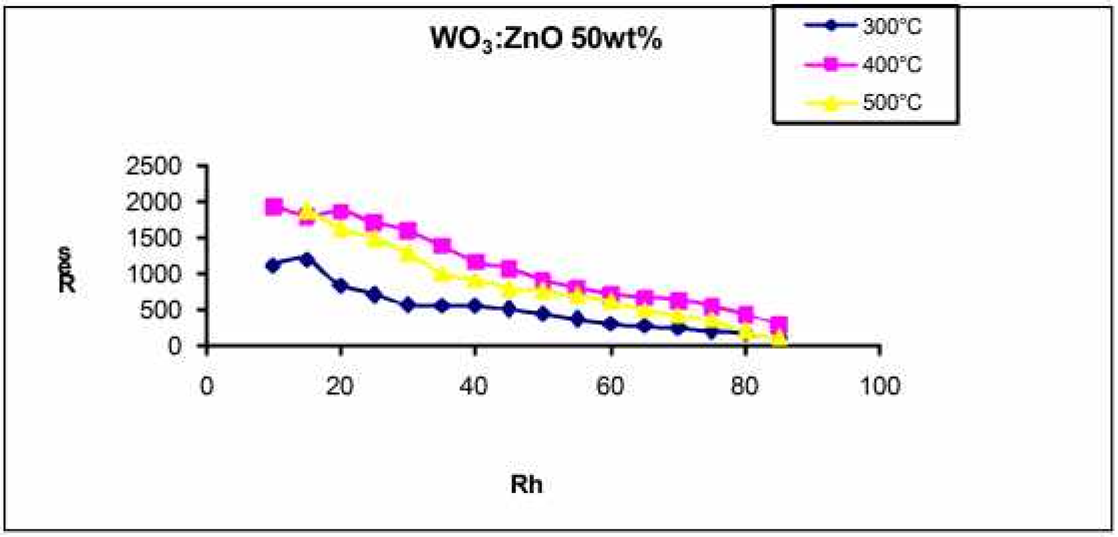

Figure 1- Plot of Resistance with temperatures for WO_3: ZnO (50 wt %)

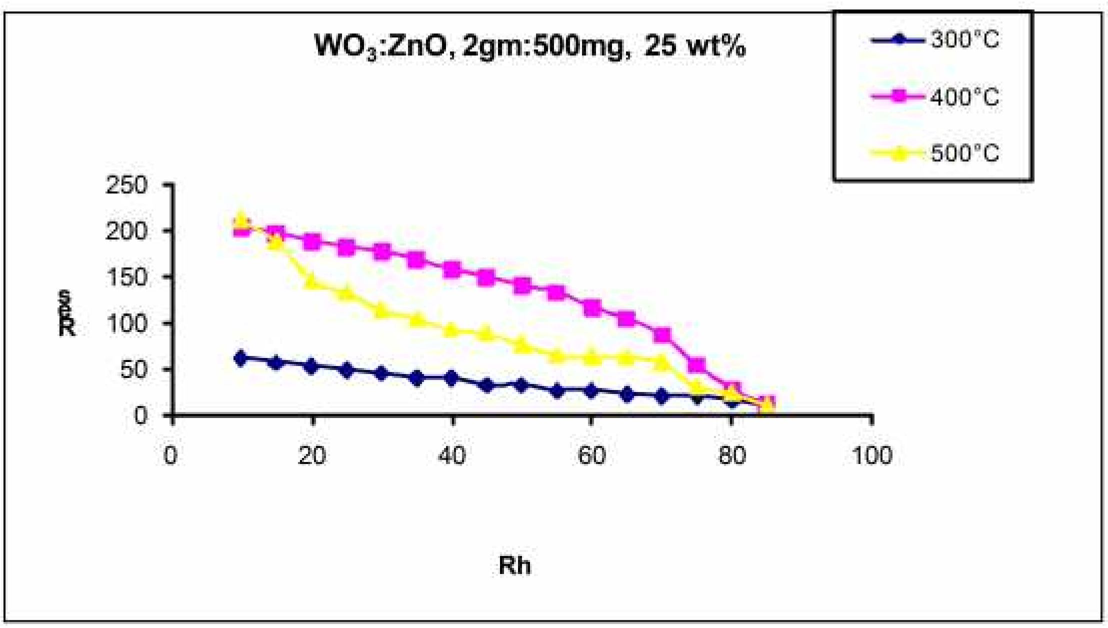

Figure 2- Plot of Resistance with temperatures for WO3: ZnO (25 wt %)

Study of Surface morphology

Scanning Electron Microscopy

Figure 3 and 4 shows the SEM images of sample formed in ratio of 4:1 and 2:1 respectively of WO_3: ZnO annealed at 500°C. Figure 3 shows particles of WO_3 are uniformly distributed, agglomerated and approximately of same size. Our pellet has a uniform granular morphology.

It is observed by comparing both images that grains of WO3 - ZnO composites are arranged in manner and porosity of sample is larger for composition 2:1. Thus effective surface area was expected to increase which enhances the optimum sensing to gas & humidity by adsorption of oxygen atoms at higher temperature.

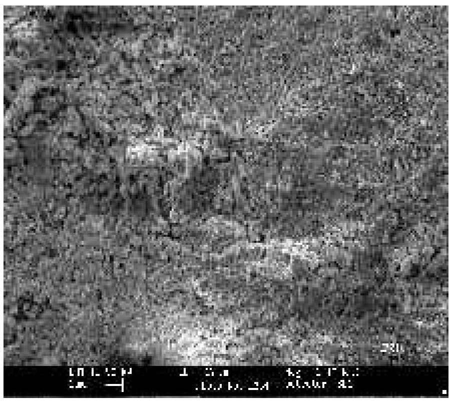

Figure 3

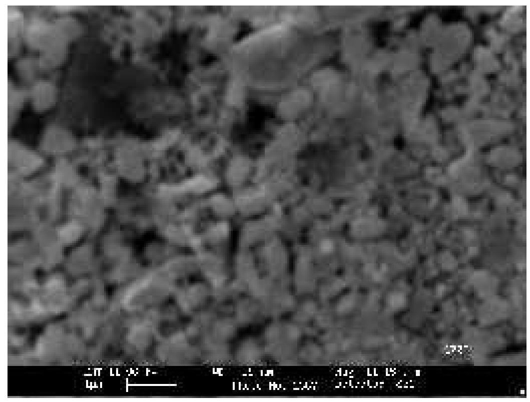

Figure 4

X- Ray Diffraction

We have characterized our sensing element on account of X-ray Diffraction by X-pert PRO XRD system (Netherland). From XRD it reveals that both the materials i.e. ZnO and WO_3 have been mixed and made a new sensing element known as Zinc tungstate. It can be shown in figure that most of the peaks are of Zinc tungstate. All the diffraction peaks at different d-spaces can be indexed as Zinc tungstate ($ZnWO_4$) phase (010, 100, 011, 111, 202, 031, and -212). After refinement, the lattice constants are a = 4.6926Å, b = 5.7213Å and c = 4.9281Å, which are very close to the reported values for $ZnWO_4$ (JCPDS Card No. 01-088-0251). No evidence of impurities can be found in the XRD pattern.With the help of Scherer's formula we have calculated the particles size which reveals that particles are of nano sized having range 22 nm (minimum) to 108 nm (maximum).

XRD image of sensing element

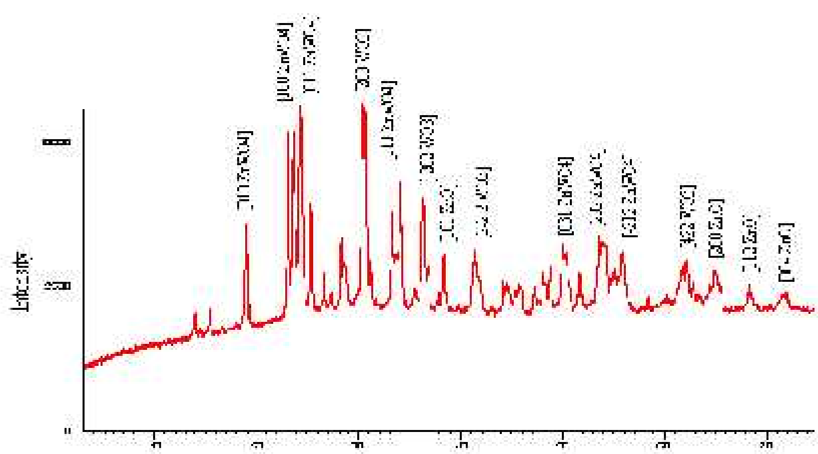

Figure 5

X-Ray Diffraction Analysis: The powder product has been analyzed by X-ray diffraction (XRD) on an X-Ray diffractometer Xpert PRO-Analytical, (Netherland) using CuKα radiation (wavelength λ = 1.54060). Figure 5 shows the XRD patterns of WO_3 sensing material at room temperature. All the diffraction peaks at different d-spaces can be indexed as Zinc-tungstate ($ZnWO_4$) phase (010, 100, 011, 111, 202, 031, and -212). After refinement, the lattice constants are a = 4.6926Å, b = 5.7213Å and c = 4.9281Å, which are very close to the reported values for $ZnWO_4$ (JCPDS Card, No. 01-088-0251). No evidence of impurities can be found in the XRD patterns.

Conclusion

Consequently we may also predict that average sensitivity is mainly the function of annealing temperature, larger variations in composition do not play major role in the sensing mechanism because our sensing element is quite good for humidity sensing. In this paper WO_3- ZnO (mixed to form nano sized Zinc tungstate) composite has been investigated for its humidity sensing characteristics. The sensing element annealed at 500 ^{0}C shows good sensing properties for water vapour. Nearly all the sensing elements have shown similar trend i.e. at minimum RH%, resistance is maximum and at maximum RH%, resistance is minimum. Thus the humidity sensor reported in this paper is easy to fabricate, cheap, friendly for users and sensitive to the entire range of RH. This may also be applicable for commercial production.

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