Journal of Electron Devices, Vol. 10, 2011, pp. 433-437

© JED [ISSN: 1682 -3427]

Journal of Electron Devices
www.jeldev.org

TIN DIOXIDE/POLYPYRROLE MULTILAYER CHEMIRESISTOR AS A HYDROGEN SULFIDE GaS SENSOR

S.A. Waghuley
Department of Physics, Sant Gadge Baba Amravati University, Amravati-444602, INDIA.
sawaghuley@yahoo.co.in

Received 1/06/2011, accepted 5/06/2011, online 6/06/2011

Abstract

Tin dioxide (SnO_2)/Polypyrrole (PPy) multilayer thick film chemiresistor was prepared by screen-printing technique on glass substrate using Al_2O_3 as a base layer. SnO_2 was act as a sensing layer. The chemiresistor was used for investigating hydrogen sulfide (H_2S) gas at different ppm level at room temperature (303 K). The chemiresistor shows the response values (sensitivity) 0.15, 0.42 and 0.68 for 100, 300 and 700 ppm H_2S gas at room temperature. The resistance in presence of different concentration of H_2S gas of chemiresistor was found to be continuously decreases exponentially without saturation greater than 1000 ppm. The average resistance change per ppm of chemiresistor for H_2S gas was found to be 162.3×106 Ω/ppm at 303 K. The materials used for fabrication of chemiresistor were characterized through XRD and SEM.

Keywords: Tin dioxide, Polypyrrole, Hydrogen sulfide, Sensors

I. INTRODUCTION

Hydrogen sulfide (H_2S) gas is normally heavier than air, but when agitated, it can erupt from the confines of the pipe in levels of toxicity, which paralyze the lungs. Hydrogen sulfide is generated in the flow when sewage is allowed to stand for long period and become stagnant or septic. In these anaerobic conditions the sewage can contain up to 6000 parts per million. A gas sensor is a device, which detects the presence of different gases in an area, especially those gases that might be harmful to humans or animals. The development of gas sensor technology has received considerable attention in recent years for monitoring environmental pollution [1]. Tin dioxide (SnO_2) based chemiresistors have high gas sensing response as compare to the chemiresistors based on conducting polymers but they are operated at high temperature (>200 °C). Whereas conducting polymer-polypyrrole (PPy) based chemiresistors have shown better sensing response at room temperature.

Maekawa et al [2] first reported the enhanced sensitivity of SnO_2 with CuO dopant for H_2S gas detection. Subsequently several studies based on the CuO-SnO_2system have been reported using thick sintered pastes [3], Cu/SnO_2 bilayers [4], CuO-SnO_2 heterocontacts [5], and chemically fixed CuO on spin-coated SnO_2

films [6]. Chowdhuri et al [7] reported that the CuO nanoparticles on sputtered SnO_2 thin-film surface exhibit a fast response speed (~14 s) and recovery time (~61 s) for trace level (~20 ppm) H_2S gas detection.

A sensor device can keep to the actual limits depends on the overall performance of the chemical active layer. On the other hand, sensitive layers based on organic polymers inhibit many positive features and, consequently, are of wide interest and widely used in chemical gas sensors. The first disclosure of the gas sensitive properties of conducting polymers was made at a conference in 1983 [8]. This involved the use of filter paper impregnated with PPy, functioning as an ammonia gas sensor. The gas detention is based on fact that changes in the gaseous atmosphere after the properties of sensing layer in a characteristic way. In case of conductance sensors e.g. Metal Oxide (MOX) sensors, Conductive Polymer (CP) sensors, Ionic conductors etc. that are respond with changes in resistance/conductance, which is normally determined by 2-or 4-point resistance/conductance measurement.

In comparison with most of gas sensors, based usually on metal oxides and operated to high temperatures (>200°C), and less sensitive and selective for low gas concentration, many researchers [9-11] have developed conductive polymers for gas sensor applications, such as polypyrrole (PPy), polyaniline (PANI), polyacetylene (PAc), polythiophene (PTh) and their derivatives. The advantages of conducting polymer gas sensors are low cost, suitable for fabrication on various substrates, high sensitivity, short response time, good mechanical properties and room temperature operation [12, 13]. Conducting polymers are easy to be synthesized through chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerization or structural derivatives.

In the present work, SnO_2/PPy multilayer thick film chemiresistor was prepared by screen-printing technique on glass substrate using Al_2O_3 as a base layer. SnO_2 was act as a sensing layer (upper layer). The chemiresistor was used for investigating hydrogen sulfide (H_2S) gas at different ppm level at room temperature (303 K). The PPy was synthesized chemically using $FeCl_3$ as an oxidant.

II. EXPERIMENTAL

AR grade chemicals (SnO_2, pyrrole monomer, $FeCl_3$, Al_2O_3) were used in the present study. Pyrrole monomer was used as received. The chemical synthesis of PPy was carried out according to the reference [14]. SnO_2 powder and Al_2O_3 powder were calcined at 800°C for 4-5h. Fine powder of SnO_2 and Al_2O_3 were formed in agate and mortar. The chemiresistor was prepared by screen-printing technique and details are given elsewhere [15]. The materials were characterized by X-ray (XRD) and scanning electron microscopic (SEM) techniques. The X-ray diffraction pattern of powders was recorded on a Phillips-1730 (PANalytical) X-ray diffractometer using Cu K$\propto$ radiation (λ = 1.54 Å). The diffractogram was in terms of 2θ in the range 10°–99°. The morphology of powders was investigated by using JEOL-JSM (Model-5200) SEM instrument. The resistance of chemiresistor was measured at room temperature for different concentration of H_2S gas. The sensitivity was determined according to reference [15].

III. RESULTS AND DISCUSSION

Figure 1 (a) and (b) shows XRD pattern of SnO_2 and PPy. From Figure 1 (a), it is observed that XRD pattern contain 8-10

peaks. These are prominent peaks of SnO_2. The (h k l) values are obtained by using 2θ and d-values from XRD pattern. SnO_2 has one stable state called as cassiterite. From Figure 1 (b), PPy is mainly amorphous in nature. A broad peak is observed at about 2θ =12°, which is characteristic peak of amorphous PPy. However the peak obtained at 26° matches [16] with d-value (3.38Å) of $FeCl_3$. The average grain size, determined from XRD pattern using Scherrer formula [14] of these materials, is about 120 nm for SnO_2 and 73 nm for PPy respectively.

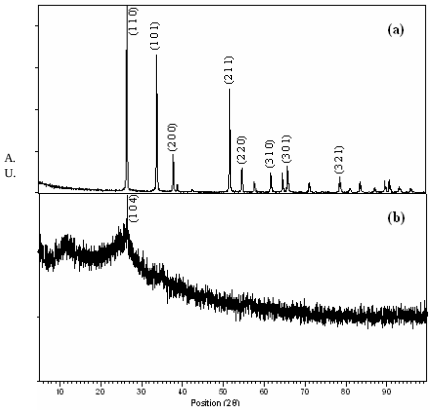

Fig. 1. XRD (a) SnO_2 calcined at 800°C for 4-5h and (b) Chemically synthesized PPy.

The surface morphology of PPy and SnO_2 materials was analyzed by SEM and the pictures are shown in Figure 2 (a) and (b). In Figure 2 (a), more amorphous nature of PPy seen in the SEM pictures is reflected in the XRD also. The partly crystalline behavior is also seen from the micropictures as in XRD. The phases so obtained are due to $FeCl_3$ that remained as a dopant in PPy. It is observed that the PPy shows non-uniform voids, bigger patches and flat patches in the micrograph. The voids are seen randomly and the size varies from ~ 20 nm to 200 μm. Thus the morphology of PPy is strongly dependent on the Py/$FeCl_3$ weight ratio that was used in the chemical polymerization and also on the preparation method. This may be due to solvent polarity [17].

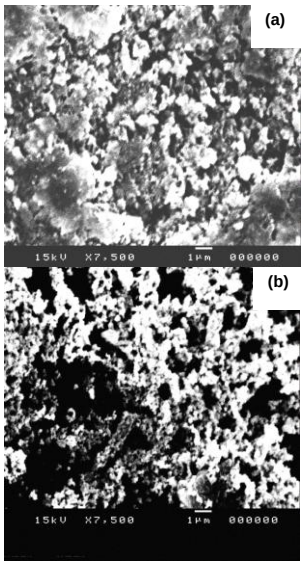

Fig. 2. SEM pictures of PPy (a) and SnO_2 (b).

Figure 2 (b) shows the randomly distributed SnO_2 grains, calcined at 800°C for 4-5 h with larger size and shape distribution. The large number of grains which leading to high porosity and large effective surface area available for adsorption of gas species. The non-uniform voids, bigger and flat patches also seen in the SnO_2 micrograph. The size of voids varies from ~10 nm to 400 μm and pore size varies from ~50 nm to 10 μm. The average grain size seen from micrograph varies from ~100 nm to 500 nm.The sensitivity is the device characteristics of percepting a variation in electrical property of the sensing material under gas exposure and it can be defined as in Eq. (1)

$$\left.\begin{aligned} S &= \frac{R_g - R_a}{R_a} \text{ if } R_g > R_a \\ S &= \frac{R_a - R_g}{R_a} \text{ if } R_g < R_a \end{aligned}\right\} \quad (1)$$

where R_a is the resistance of sensor in air and R_g is the resistance in presence of gas, respectively.

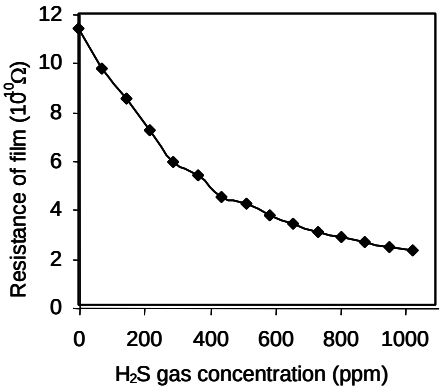

Fig. 3.Variation of resistance of chemiresistor with H_2S gas concentration at 303K.

The resistance in presence of different concentration of H_2S gas of chemiresistor (fig.3) is found to be exponentially decreases without saturation greater than 1000 ppm.

The chemiresistor exhibits a fast response speed (~6 s) and recovery time (~34 s) for 200 ppm concentration of H_2S gas.
The sensitivity of chemiresistor is calculated using Eq. (1) for different concentration of H2S gas at 303 K and shown in Fig. 4. The sensitivity is found to be increases exponentially with concentration of H2S gas. The maximum value of sensitivity is 0.78 for 900 ppm H_2S gas. The average resistance change per ppm of H_2S gas at 303 K is 162.3×106 Ω/ppm at 303 K.

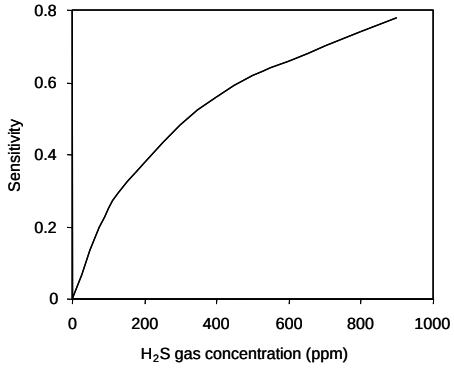

Fig.4. Sensitivity of chemiresistor with different concentrations of H_2S gas at 303K.

In case of reducing gas, the adsorption of oxygen on the surface extracts conduction electrons from the near surface region forming an electron depleted surface layer, which results in an electric field and a potential barrier associated with this electric field [18]. The model of intergrain potential barrier is as shown in Fig. 5.

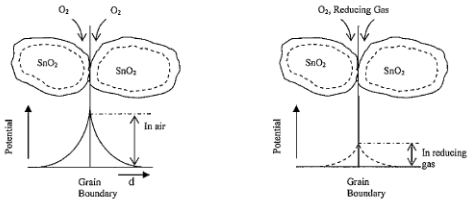

Fig. 5. Model of intergrain potential barrier.

The potential barrier is depending upon the concentration of adsorbed oxygen. When reducing gas H_2S adsorbed on the SnO2 surface then adsorbed oxygen is consumed by reacting with H_2S gas, and the entrapped electrons are returned to the SnO_2 grains resulting in a decrease of the potential barrier and the resistance [19,20].

IV. CONCLUSION

The screen-printing technique is the simplest technique for the preparation of SnO2 based chemiresister. The middle layer in chemiresistor of chemically synthesized PPy may be acting as a stabilized current conduction layer. The Al_2O_3 may provide the mechanical support to the chemiresistor. The resistance in the presence of different concentration of H_2S gas of chemiresistor is found to be continuously decreases without saturation greater than 1000 ppm exponentially. Hence sensitivity is exponentially increases. XRD study revels that the SnO_2 has one stable state called as cassiterite and the PPy is mainly amorphous in nature. The average grain size, determined from XRD pattern of these materials, are about 120 nm for SnO_2 and 73 nm for PPy respectively. In the surface morphology of PPy, it is observed that the PPy shows non-uniform voids, bigger patches and flat patches in the micrograph. The voids are seen randomly and the size varies from ~ 20 nm to 200 μm. The SEM picture of SnO_2 shows the randomly distributed SnO_2 grains

with larger size and shape. The large number of grains which leading to high porosity and large effective surface area available for adsorption of gas species. The non-uniform voids, bigger and flat patches also seen in the SnO2 micrograph. The size of voids varies from ~10 nm to 400 μm and pore size varies from ~50 nm to 10 μm. The average grain size seen from micrograph varies from ~100 nm to 500 nm. The gas sensing mechanism is explained on the basis of model of intergrain potential barrier. The potential barrier is depending upon the concentration of adsorbed oxygen. When reducing gas H_2S adsorbed on the SnO_2 surface then adsorbed oxygen is consumed by reacting with H_2S gas, and the entrapped electrons are returned to the SnO_2 grains resulting in a decrease of the potential barrier and the resistance.

Acknowledgement

The author is very much thankful to Head, Department of Physics, Sant Gadge Baba Amravati University, Amravati, for providing internet facility and also thankful to Director, Govt Vidarbha Institute of Science & Humanities, Amravati for providing necessary facility at the time of his research work.

References

[1] B. Ding, M. Wang, J. Yu and G. Sun, "Gas sensors based on electrospun nanofibers", Sensors, **9** (2009) 1609.

[2] T. Maekawa, J. Tamaki, N. Miura, and N. Yamazoe, "Sensing behavior of CuO-loaded SnO_2 element for H_2S detection", Chem. Lett., (1991) 575.

[3] V. Lantto, P. Romppainen, T. S. Rantala, and S. Leppavuori, "Equilibrium and non-equilibrium conductance response of sintered SnO_2 samples to H_2S", Sens. Actuators B **4** (1991) 451.

[4] L. Jianping, W. Yue, G. Xiaoguang, M. Quing, W. Li and H. Jinghong, "H_2S sensing properties of the SnO_2-based thin films", Sens. Actuators B **65** (2000) 111.

[5] R.B. Vasiliev, M.N. Rumyantseva, S.E. Podguzova, A.S. Ryzhikov, L.I. Ryabova, A.M. Gaskov, "Effect of interdiffusion on electrical and gas sensor properties of CuO/SnO_2 heterostructure", Mater.Sci. Eng. B**57** (1999) 241.

[6] D. J. Yoo, J. Tamaki, S. J. Park, N. Miura and N. Yamazoe, "Copper Oxide-Loaded Tin Dioxide Thin Film for Detection of DiluteHydrogen Sulfide", Jpn. J. Appl. Phys. **34** (1995) 455

[7] A. Chowdhuri, V. Gupta, K. Sreenivas, R. Kumar, S. Mozumdar and P. K. Patanjali, "Response speed of SnO_2-based H_2S gas sensors with CuO nanoparticles", Applied Physics Letters 84, 2004.

[8] C. Nylabder, M. Armgrath and I. Lundstrom, "An ammonia detector based on a conducting polymer", Proc. Int. Meeting on Chem. Sens., Fukuoka, Japan. (1983),.203.

[9] N. Nath and A.Q. Contractor, "A study of polypyrrole films formed at the liquid|vapor interface", J. of Electroanalytical Chemistry **571** (2004) 55.

[10] F. Selampenar, L. Toppare, U. Akbulut, T. Yalcin and S. Suzer, A "Conducting Composite of Polypyrrole; II As a Gas Sensor", Synthetic Metals **68** (1996) 10.

[11] D.M. Liu, J. Aguilar-Hernandez, K. Potje-Kamloth and H.D. Liess, "A new carbon monoxide sensor using a polypyrrole film grown on an interdigital-capacitor substrate", Sens. Actuators B **41** (1997) 203.

[12] M. Matsuguchi, K. Tamai and Y. Sakai, "SO_2 Gas Sensors using Polymers with Different Amino Groups", Sens. Actuators B **77** (2001) 363.

[13] G. Harsanyi, "A Review of Present uses and Future Possibilities", Sensor Review **20** (2000) 98.

[14] S.A. Waghuley, S.M. Yenorkar, S.S. Yawale and S.P. Yawale, "Application of chemically synthesized conducting polymer-polypyrrole as a carbon dioxide gas sensor", Sens. Actuators B **128** (2008) 366.

[15] S.A. Waghuley, S.M. Yenorkar, S.S. Yawale and S.P. Yawale, SnO_2/PPy "Screen-Printed Multilayer CO_2 GaS Sensor,Sens". Transducers **79** (2007) 1180.

[16] JCPDS data file no. 790205, (1997).

[17] X. Chen, J. Devaux, J.P. Issi and D. Billaud, "Chemically oxidized polypyrrole: Influence of the experimental conditions on its electrical conductivity and morphology", Polym. Eng. Sci. **35** (1995) 642.

[18] M. Batzill and U. Diebold, "The Surface and Material Science of Tin Oxide", Progress in Surface Science **79** (2005) 47.

[19] J. Liu, X. Huang, G. Ye, W. Liu, Z. Jiao, w. Chao, Z. Zhou and Z. Yu," H_2S Detection Sensing Characteristic of CuO/SnO_2 Sensor", Sensors **3** (2003) 110.

[20] S.A. Waghuley, "Gas Sensitive Electrical Conduction of Polypyrrole Modified SnO_2-Al_2O3 Sensors", Ph.D. Thesis, (Sant Gadge Baba Amravati Univ., Amravati., India 2008).