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Stability of CO2 gas sensor by doping nano ZnO in conducting polymer Polyaniline

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ABSTRACT
The conducting polymer polyaniline doped with nano ZnO and developed gas sensor by screen printing technique. Study of stability of CO_2 gas sensor studied at different concentration.Rate of change of resistance of the sensor with respect to time defines the stability of the sensor. A sensor should be more stable for its better response. The changes in the resistance for multilayer sensor 80ZnO:20PANI and pure samples were studied. 80ZnO:20PANI/PANI/Al_2O_3 multilayer is smaller and it is more porous and hence has greater surface area and therefore shows greater response to CO2 gas.It shows good stability than pure samples and dynamic response is also fast.It was also observed that resistance of multilayer sensor does not change drastically as that in case of pure samples. This shows that nano ZnO (nano metal oxide) doped multilayer sensor is more stable than other.

Keywords PANI; screen-printing technique; CO_2 gas sensor.

INTRODUCTION

It is well known that the sensing properties of ZnO-based material depend on its chemical and physical characteristics, which are strongly dependent on the preparation conditions, dopant and grain size.

This implies that the synthesis of the sensing material is a key step in the preparation of high-performance Metal oxide semiconductor (MOS) gas sensors. ZnO powders and films can be prepared by a variety of synthesis methods [1-4]. DC-electrical resistance of the films ZnO doped with PANi sensor was measured in presence of humidity and ZnO–5Al_2O_3 and ZnO–5Al_2O_3 sensors are found to be good sensing materials for humidity [5].

The present investigation mainly deals with the preparation of CO $_2$ gas sensor in ZnO doped Polyaniline. It was found that ZnO system with Polyaniline shows more sensitivity to 60 ppm of carbon dioxide gas concentration even at room temperature.

A gas sensor is a device, which detects the presence of different gases in an atmosphere, especially those gases that might be harmful to living animals. The design of gas sensor technology has received considerable attention in recent years for monitoring environmental pollution . Tin dioxide (ZnO) 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-Polyaniline (PANi) doped with metal oxides sensors have shown better sensing response at room temperature [6].

Chemical synthesis of CP is usually performed by such oxidants as $(NH_4)_2S_2O_8$ or $FeCl_3$ and is commonly used for the preparation of CP solutions, while electrochemical deposition is used mainly for deposition of CP films on conducting substrates. An advantage of this method is the possibility to control the film thickness by the charge passed through the electrochemical cell during the film growth. Other popular techniques for depositing thin films on various substrates are spin coating by a solution of a chemically synthesized CP, the deposition of one or more monomolecular layers of CP by Langmuir–Blodgett technique, or coating of substrates by bilayers of CP and opposed charged polymers by the layer-by-layer technique. CP's are multifunctional materials; it was not always possible to make a definite separation of their functions. Finally, the application of a combinatorial approach for synthesis and high-throughput screening of chemo-sensitive properties of CP is discussed., Polyaniline (PANI) is one such polymer whose synthesis does not require any special equipment or precautions. Conducting polymers generally show highly reversible redox behavior with a noticeable chemical memory and hence have been considered as prominent new materials for the fabrication of the devices like industrial sensors. The properties of conducting polymers depend strongly on the doping level, protonation level, ion size of dopant, and water content. Conducting PANI is prepared either by electrochemical oxidative polymerization or by the chemical oxidative polymerization method. The emeraldine base form of PANI is an electrical insulator consisting of two amine nitrogen atoms followed by two amine nitrogen atoms. PANI (emeraldine base) can be converted into a conducting form by two different doping processes: protonic acid doping and oxidative doping. Protonic acid doping of emeraldine base corresponds to the protonation of the amine nitrogen atoms in which there is no electron exchange. In oxidative doping, emeraldine salt is obtained from leucoemeraldine through electron exchanges. The mechanism causing the structural changes is mainly recognized to the presence of -NH group in the polymer backbone, whose protonation and deprotonation will bring about a change in the electrical conductivity as well as in the color of the polymer.

METHODOLOGY

Preparation of conducting Polymer Polyaniline:

In 100 ml solution of 0.4 M aniline in 1M sulfuric acid, 100 ml of 0.5 M solution of ammonium persulphate was added dropwise with constant stirring at room temperature at normal condition. After completion of the oxidant addition, stirring was continued for further 2 hours to insure completion of the reaction. During polymerization, the sequence of coloration of the reaction mixture was light blue, blue green and finally greenish black precipitate. This color indicates that the product was in conducting emeraldine salt form. The reaction mixture was kept overnight. Then it was filtered, washed with distilled water until the filtrate become colorless and finally with methanol to remove the impurities and oligomers.This Polyaniline is then used for active layers of Semiconductor Gas Sensors.

Sensor preparation:

ZnO and Al_2O_3 powders (AR grade) were calcinated at about 800 °C for 4-5 h and were crushed in mortal pestle to get fine powder of the samples. ZnO ,PANi were characterized by XRD. XRD patterns of the samples were obtained using Diffractometer system from GVISH, Amravati. The diffraction pattern was in the terms of 2θ at continuous scan type at step size = 0.015^0.

The ink or paste of the sample was prepared by using screen-printing (thick film technique) technique. The binder for screen-printing was prepared by thoroughly mixing 8 wt% butyl carbitol with 92 wt% ethyl cellulose. On chemically cleaned glass plate, paste of Al_2O_3 was screen printed and it was kept for 24 hr to dry it at room temperature and then heated at 140^0C for 2.5 h to remove the binder. The Al_2O_3 layer provides mechanical support as well as high thermal conductivity. Paste of ZnO and ZnO mixed in proper stiochometry was then screen printed on Al_2O_3 layer. Again plate was dried at room temperature for 24 h and binder was removed by heating it at 150^0C for 2.5 h. Finally PANi layer was deposited on ZnO doped with ZnO layer by screen printing, whole plate was dried and again binder was removed as above. Fabrication of multilayer sensor is shown in following fig. (1)

Finally on the top surface of the sensor, interdigited electrodes [26] were fabricated using conducting silver paste as shown in the Fig.1 (b). Thickness of ZnO doped with ZnO layer and PANi layers were recorded with the help digital micrometer (series 293, Japan) having resolution of $\pm$ 0.001 mm and were found to be 10 μm and 7 μm respectively. To measure the sensitivity, electrical resistance was measured with the help of voltage drop method, best one.

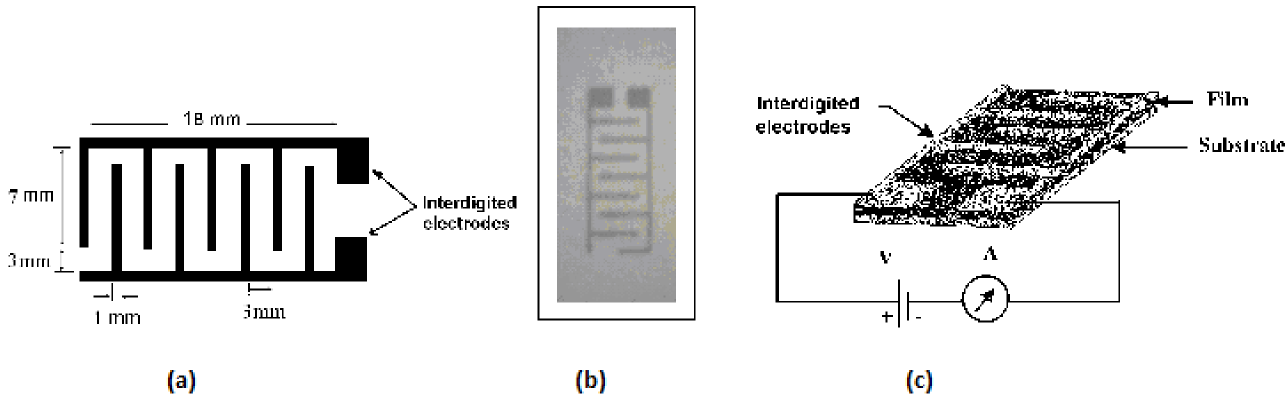

Fig.1:(a) Fabrication of interdigited Electrodes (b) Actual photograph of interdigited electrodes (c) Circuit of resistance measurement using interdigited electrodes.

RESULTS AND DISCUSSION

1. *XRD Analysis:*

XRD of PANi and 80ZnO:20ZnO [fig.2 (a) and (b)] showed that Polyaniline is amorphous in nature. A broad peak at 2θ = 26^0 was observed which gives the evidence for amorphous nature of Polyaniline. Broad peak is the characteristic of amorphous nature of Polyaniline and it is due to the scattering from PANi chains at the inter-planar spacing [28]. The average crystalline size of PANi was calculated by using Scherrer's formula given by equation (1),

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

Where, D is the crystalline size, K is the shape factor and β is the full width at half maximum of diffraction angle in radians. The average crystallite size of PANi was found to be 101 nm.

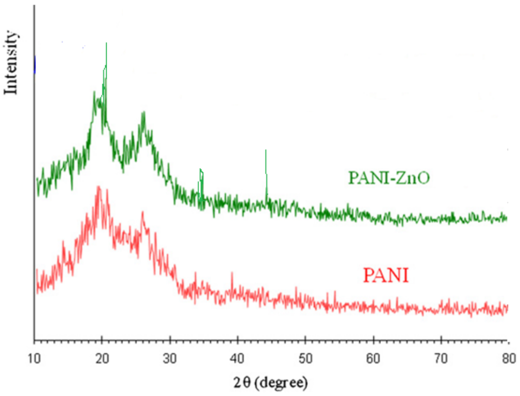

Fig.2: XRD of PANI and PANI-ZnO

2. FTIR and SEM

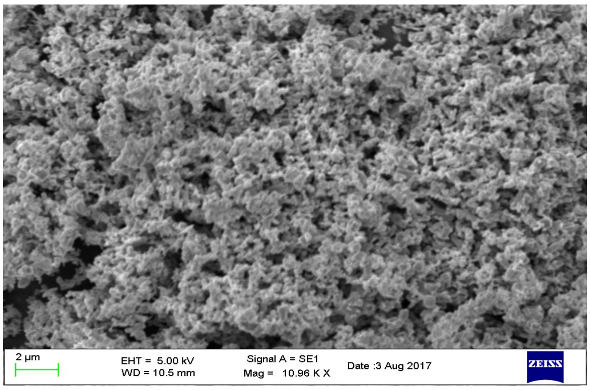

Fig. 3:The SEM were studied at Department of Physics at Rashtrasant Tukdoji Maharaj Nagpur University ,Nagpur.

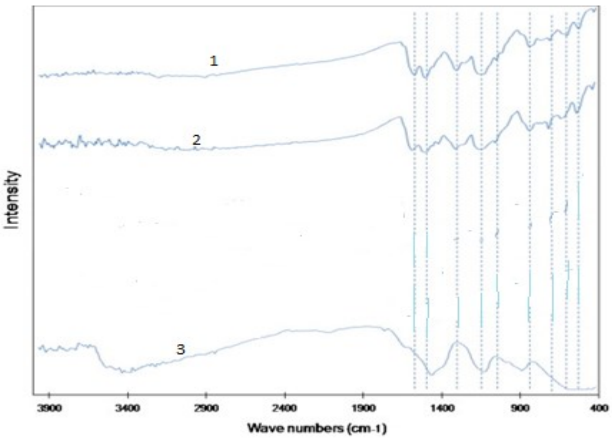

Fig. 4: FTIR pattern of (1) PANI, (2) PANI–ZnO nanocomposites and (3) ZnO nano particles.

The Polyaniline powders prepared were analyzed by FTIR. FTIR spectra showed the main characteristic peaks at 759cm−1 corresponding to C-N bond, 1265 cm−1 corresponding to C-H deformation,1513 cm−1 and 1449 cm−1 corresponding to the fundamental vibrations of Polyaniline . The peaks at 1640 cm−1 corresponding to C=C. The peak at 3401 cm−1 corresponds to the N-H bond . These peaks were observed in the present work for preparations using $FeCl_3$ as oxidants and various dopants such as ZnO and ZnO. This is confirmed the formation of Polyaniline[12]

3. Sensitivity of sensor:

The sensitivity of the sensor is given by equation (2),

$$S = \left(\frac{R_{air} - R_{gas}}{R_{air}}\right) = \left(\frac{\Delta R}{R_{air}}\right) \quad (2)$$

Where, R_{air} and R_{gas} are the resistances of sensors in air and gas respectively.

From Fig. (5), multilayer structure of the sensor shows more sensitivity to CO_2 gas than that for pure ZnO and pure ZnO. Resistance of multilayer sensor was found to be decreasing with increase of CO_2 gas concentration and thereby sensitivity was increasing[10]. Maximum sensitivity was recorded for multilayer sensor at 80 ppm concentration of CO_2.

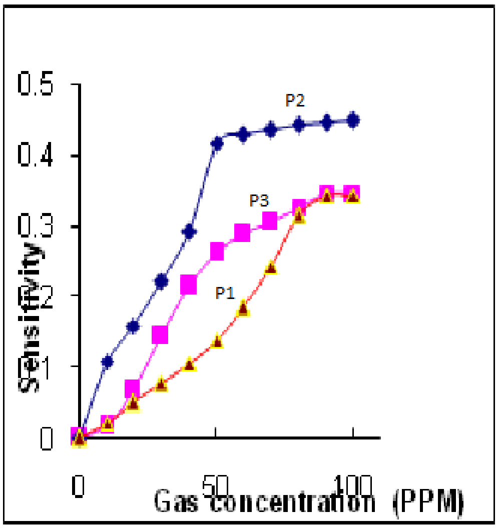

Fig. 5: Variation of sensitivity with of CO_2 gas concentration at room temperature.

Table. 1:Sample Codes:

Sr. No.	Pure	Codes
1	ZnO	P1
2	PANI-ZnO(nano)	P2
3	PANI	P3

4. Stability of sensor:

Rate of change of resistance of the sensor with respect to time defines the stability of the sensor. A sensor should be more stable for its better response. The changes in the resistance for multilayer sensor (80ZnO:20ZnO)[13-14] and pure samples are shown in the fig. (7).

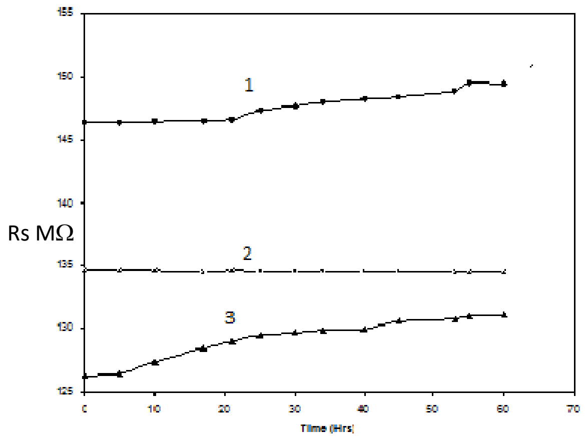

Fig. (7) Stability of the sensor (1) PANI, (2) PANI–ZnO nanocomposites and (3) ZnO nano particles.

From fig. (7), it is observed that resistance of multilayer sensor does not change drastically as that in case of pure samples. This shows that multilayer sensor is more stable than other.

CONCLUSION

From XRD, it is concluded that the crystallite size of 80ZnO:20ZnO/PANi/Al_2O_3 multilayer is smaller and it is more porus and hence has greater surface area and therefore shows greater response to CO_2 gas. SEM analysis confirmed the surface morphology.Screen printing technique is the easiest for the preparation of sensor. 80ZnO:20ZnO/PANi/Al_2O_3 multilayer sensor shows good stability than pure samples and dynamic response is also fast.

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