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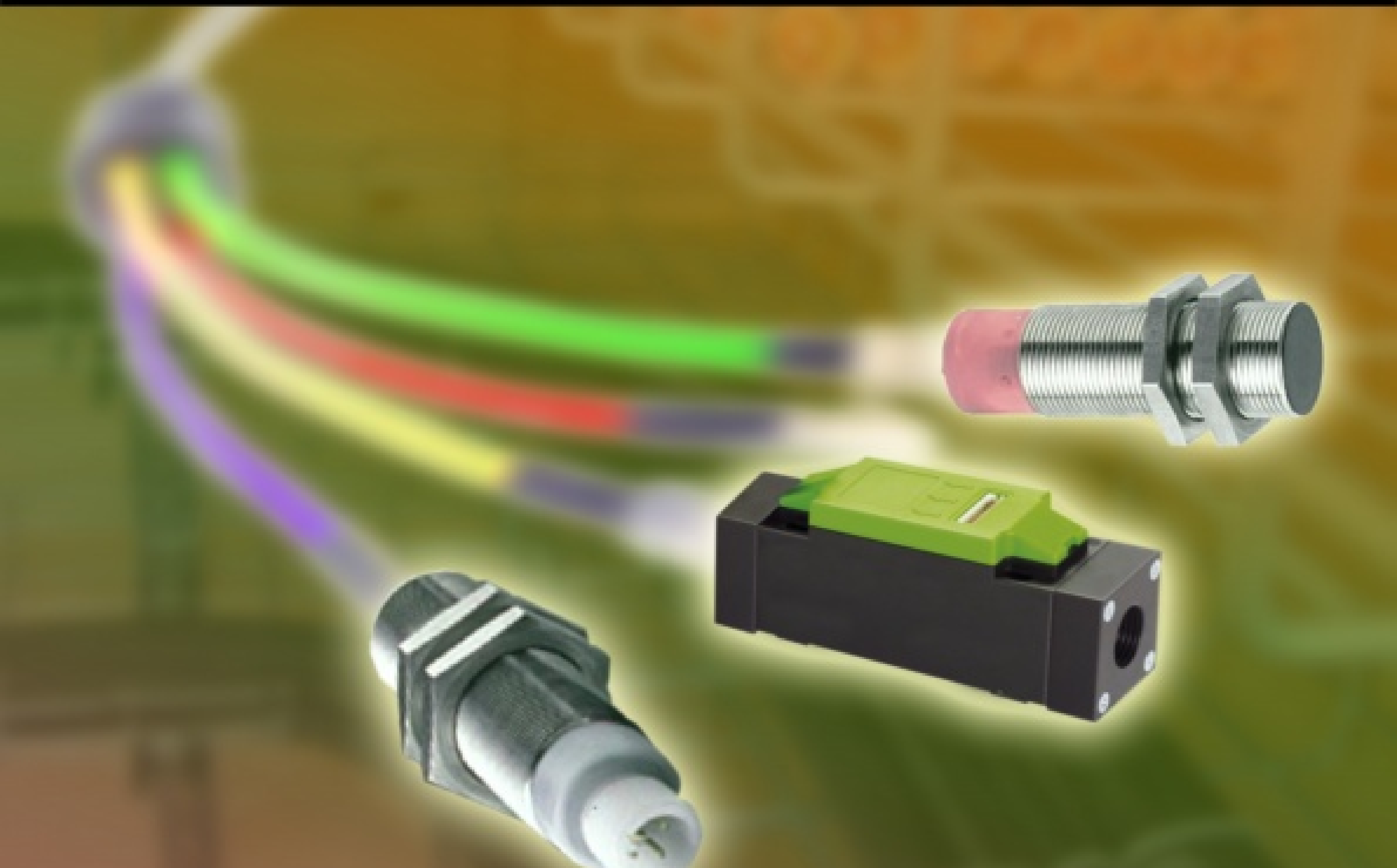

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Contents

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SnO_2/PPy Screen-Printed Multilayer CO_2 Gas Sensor

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Abstract: Tin dioxide (SnO_2) plays a dominant role in solid state gas sensors and exhibit sensitivity towards oxidizing and reducing gases by a variation of its electrical properties. The electrical conducting polymer-polypyrrole (PPy) has high anisotropy of electrical conduction and used as a gas sensor. SnO_2/PPy multilayer, pure SnO_2, pure PPy sensors were prepared by screen-printing method on Al_2O_3 layer followed by glass substrate. The sensors were used for different concentration (ppm) of CO_2 gas investigation at room temperature (303 K). The sensitivity of SnO_2/PPy multilayer sensor was found to be higher, compared with pure SnO_2 and pure PPy sensors. The multilayer sensor exhibited improved stability. The response and recovery time of multilayer sensor were found to be ~2 min and ~10 min respectively. *Copyright © 2007 IFSA.*

Keywords: Tin dioxide, Polypyrrole, Multilayer sensor, CO_2

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1. Introduction

Carbon dioxide (CO_2) is one of the most common greenhouse gases and is a primary component among corrosive gas species and affects corrosion rate of equipment used in chemical processing. There is essential need to control it. The control of CO_2 gas also plays an important role in agricultural sector [1, 2]. Literature survey reveals that SnO_2 is a promising material, used in different gas sensors. The reaction of SnO_2 in air with different test gases is relatively extensively studied. Generally CO, CH_4 and NO_x are the most used gases to characterize the performance of sensor, because of their different sensing mechanisms [3]. CO and CH_4 introduce electrons in the conduction band (decrease sensor resistance) by reacting with the SnO_2 surface, whereas NO_x removes electrons and increase sensor resistance [4].

SnO_2 based gas sensors are sensitive only at high temperature (>200^0C), and less sensitive and selective for low gas concentration. Many researchers [5, 6] have developed conductive polymers for gas sensor applications, such as polyacetylene (PAc), polypyrrole (PPy), and polyaniline (PANI). The advantages of conducting polymers gas sensor are low cost, suitable for fabrication on various substrates, and near room temperature operation [7, 8]. PPy is highly sensitive to gases but it shows saturation effect at higher concentration of gases [9]. Zheng Jiao *et al* [10] reported that SnO_2/Fe_2O_3 multilayer thin film exhibited improved selectivity and stability, but slightly reduced sensitivity, compared with SnO_2 and Fe_2O_3 thin films.

The aim of this work is to study CO_2 gas sensing properties of SnO_2/PPy multilayer sensor, prepared by screen-printing method on Al_2O_3 layer followed by glass substrate. SnO_2 and PPy powder samples were analyzed by XRD.

2. Experimental

SnO_2 powder (AR grade) and Al_2O_3 powder (AR grade) were calcined at 800^0C for 4h. Fine powder of SnO_2 and Al_2O_3 were formed in agate and mortar. PPy in powder form was prepared by using 4.290-weight ratio of pyrrole monomer to oxidant ($FeCl_3$) and methanol as a solvent. The reaction was carried out by procedure reported in reference [11]. The SnO_2 and PPy powder samples were characterized by XRD. The XRD pattern of powder samples was recorded on Philips-1730 (PANalytical) X-ray diffractometer using CuKα radiation (λ =1.54 Å). The diffractogram was in the term of 2θ in the range 5- 99^0.

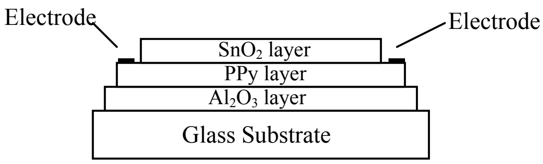

Fig. 1. The structure of SnO_2/PPy multilayer sensor.

The binder for screen-printing was prepared by thoroughly mixed 8 wt% butyl carbitol with 92wt% ethyl cellulose. Multilayer sensor was prepared in three steps. In first step, paste of Al_2O_3 powder was prepared and screen-printed onto a chemically cleaned glass substrate. The glass plate then dried at room temperature for 24h and heated at 150^0C for 2h. The Al_2O_3 layer mainly provides the high thermal conductivity and mechanical support. In second, paste of PPy powder was screen printed onto Al_2O_3 layer, and dried at room temperature for 24h and heated at 150^0C for 3h, so that removed the volatile organic solvent. In third step, paste of SnO_2 powder, screen printed onto PPy layer and dried at room temperature for 24h, heated at 200^0C for 3h. For resistance measurement, electrical contacts of silver paint were deposited on adjacent sides of PPy layer. The structure of SnO_2/PPy multilayer sensor is shown in fig. 1. Thickness of PPy layer and SnO_2 layer was measured by Digimatic Outside Micrometer (series-293, Japan) having resolution ± 0.001mm and found to be 9 μm and 11μm. The electrical resistance was measured by using voltage drop method adopted by Yawale *et al* [12].

3. Results and Discussion

3.1. XRD analysis

Figure 2 (a) and (b) shows XRD pattern of SnO_2 and PPy. From Figure 2 (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 or rutile. From Figure 2 (b), PPy is mainly amorphous in nature. A broad peak is observed at about $2\theta = 12^0$, which is characteristic peak of amorphous PPy. However the peak obtained at 26^0 matches with d-value (3.38Å) of $FeCl_3$. The average grain size, determined from XRD pattern using Scherrer formula [13] of these materials, is about 60 nm for SnO_2 and 73 nm for PPy respectively.

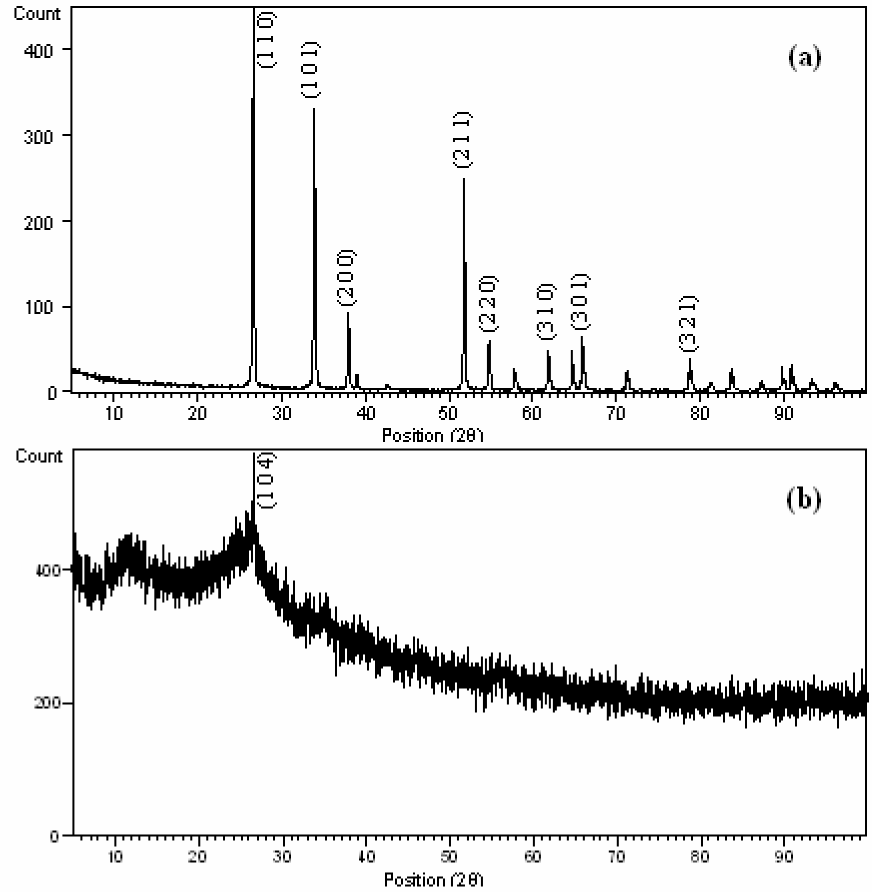

Fig. 2. XRD (a) SnO_2 calcined at 800^0C for 4h and (b) Chemically synthesized PPy.

3.2. Sensitivity Measurement

The sensitivity is defined as

$$S = \frac{Rg - Ra}{Ra} = \frac{\Delta R}{Ra}, \quad (1)$$

where Ra and Rg are the resistance of sensor in air and the CO_2 gas respectively.

The resistance of SnO_2/PPy multilayer, pure SnO_2 and pure PPy sensors is increases with CO_2 gas concentration. The relationship between sensitivity and CO_2 gas concentration for SnO_2/PPy multilayer, pure SnO_2 and pure PPy sensors at room temperature (303 K) displays in Figure 3. SnO_2/PPy multilayer sensor shows a high sensitivity to CO_2 gas, compared with pure SnO_2 and pure PPy sensors. SnO_2/PPy multilayer sensor exhibits a good dependence on CO_2 gas concentration up to 1100 ppm, where it reaches a saturation level. With a fixed surface area, a lower gas concentration implies a lower coverage of gas molecules on the surface. An increase in the gas concentration raises the surface coverage eventually leading to saturation level, thus determining the upper limit of detection.

3.3. Dynamic Response

The dynamic response of SnO_2/PPy multilayer sensor for 100 ppm, 300 ppm and 500 ppm CO_2 gas concentration at room temperature is shown in Figure 4. The response (τ_{res}) and recovery (τ_{rec}) time are two important parameters to characterize a sensor. The response time is defined as the time taken to reach 90% of the response when ppm of gas is changed. The recovery time is defined as the time taken to reach 90% of the recovery when gas is turned off. It is clearly shows that the response is fast (~ 2min), but to recover the sensor takes longer time (~ 10min). For a breath analysis sensor that requires high sensitivity and fast response, the slow recovery may not pose any practical challenge.

3.4. Stability

Stability is defined as the change of sensor resistance with time. The resistance change of SnO_2/PPy multilayer sensor in air is compared with that of pure SnO_2 sensor displays in Table 1. The resistance of SnO_2/PPy multilayer sensor is stable after 41h, while resistance of pure SnO_2 sensor continues to change even after 53 h. In other words, stability of the SnO_2/PPy multilayer sensor is better than that of pure SnO_2 sensor.

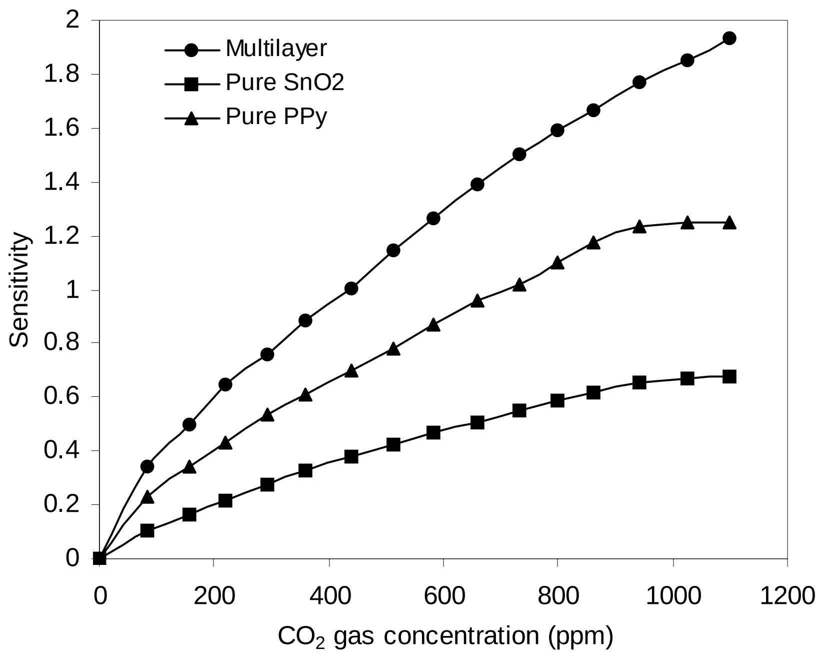

Fig. 3. Sensitivity of SnO_2/PPy multilayer, pure SnO_2 and pure PPy sensors as a function of CO_2 gas concentration at room temperature.

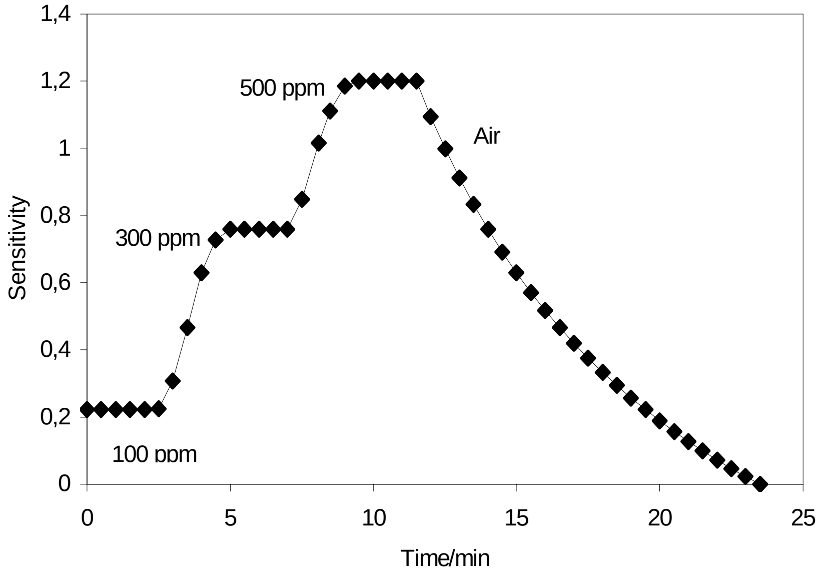

Fig. 4. Dynamic response of SnO_2/PPy multilayer sensor for 100, 300 and 500 ppm CO_2 gas concentration at room temperature

Table 1. The resistance change of SnO_2/PPy multilayer and pure SnO_2 sensor in air.

Time	0	5 h	10 h	21 h	29 h	37 h	41 h	45 h	49 h	53 h
R_M (10^3 MΩ)	277	114	250	263	357	333	312	312	312	312
R_S (MΩ)	104	177	660	569	109	100	421	168	102	67

R_M = resistance of SnO_2/PPy multilayer sensor; R_S = resistance of pure SnO_2 sensor

There may be a possibility of current conduction part (PPy layer) and the gas sensitive part (SnO_2 layer) for obtaining better stability of SnO_2/PPy multilayer sensor. The current conduction part needs to be stable for long time. PPy is suitable for this purpose because of its current conduction stability [14]. The sensitive part needs to interact with selective gas.

The possible mechanism for CO_2 gas detection in SnO_2 material is based on reactions that occur at the sensor surface, resulting in a change in concentration of adsorbed oxygen. At lower temperature (<150^{0}C), oxygen adsorption at the surface is mainly in the form of O_2^-. Oxygen ions adsorb onto the surface of material removes electrons from the bulk and create a potential barrier that limits electron movement and resistivity. When exposed to an oxidizing gas such as CO_2 then it is chemisorbed on bridging oxygen atoms with the formation of a surface carbonate [15], subsequently increasing the barrier height and the resistivity. In case of PPy, response of sensor to CO_2 gas is due to small kinetic diameter of CO_2 molecule (0.33nm) [16]. The CO_2 molecule may form weak bond with π-electron of PPy surface, which results in a decrease of conductivity or an increase in sensor resistance [17].

4. Conclusions

From these studies the following conclusion can be drawn.
1. Screen-printing method is a simplest method for preparation of multilayer sensor.
2. Multilayer sensor gave high sensitivity to CO_2 gas, compared with pure SnO_2 and pure PPy sensors.

3. Multilayer sensor showed better stability than pure SnO_2 sensor.
4. Dynamic response of multilayer sensor showed ~ 2 min response time and ~ 10 min recovery time.

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Sensors & Transducers Journal (ISSN 1726- 5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually.

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