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Fabrication and performance of polypyrrole (Ppy)/TiO_2 heterojunction for room temperature operated LPG sensor

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ABSTRACT

In this paper, we report on the fabrication and performance of room temperature operated liquefied petroleum gas (LPG) sensor based on polypyrrole/TiO_2 (Ppy/TiO_2) heterojunction. Ppy/TiO_2 heterojunction was prepared by sequencial depositing TiO_2 film by chemical bath deposition and Ppy film by electrodeposition method. Ppy and TiO_2 films were characterized using X-ray diffraction (XRD), scanning electron microscope (SEM), FTIR and thermo-emf techniques. The XRD study revealed amorphous and nanocrystalline natures for Ppy and TiO_2 films, respectively. The SEMs of Ppy and TiO_2 films showed cauliflower-like and densely compact morphologies respectively. Maximum gas response of 55% was observed for Ppy/TiO_2 heterojunction at 1040 ppm of LPG. Relative humidity affected the gas sensing performance of heterojunction. Good stability, fast response and recovery times indicate that Ppy/TiO_2 heterojunction is a one of the candidate for room temperature LPG detection.

1. Introduction

Semiconductor–metal oxide based gas sensors have been widely studied in which the principle of gas detection is based on the change in resistance of semiconductor by interaction with gas molecules at high operating temperature [1]. Semiconductor metal oxide based gas sensors have been used to detect most of reducing gases. But the main disadvantage is that their high operating temperature which results in increased power consumption [1–4]. The new alternative to this is nothing but the development of room temperature heterojunction gas sensor. Heterojunction gas sensor consists of two semiconducting materials in contact, and active region is the interface between them, which behaves like a p–n junction.

Now a day's conducting polymers have emerged as the sensitive materials for gas sensing applications due to advantages such as easy synthesis and room temperature operation [5]. Devices based on conducting polymers have potential application for sensing vapors of variety of gases [6]. Recently heterojunctions such as Bi_2S_3/CuSCN [7], polyaniline/TiO_2 [8], polyaniline/CdTe [9] and polyaniline/PbS [10] have been developed as room temperature LPG sensors.

For the fabrication of heterojunction sensor, the metal oxide (SnO_2, CdO, ZnO, TiO_2) and polymer materials (polyaniline, polypyrrole) are used. Among them, TiO_2 is the potential metal oxide candidate for the heterojunction because of its low cost, stable phase, desirable sensitivity, high chemical stability, ability to doping, nontoxicity, abundance in nature. TiO_2 nanoparticles show a hydrophobic nature. It forms highly compact and smooth film [6].

The TiO_2 based polymer heterojunction such as polyaniline/TiO_2 [8] is used for LPG sensor however polyaniline is not stable in the environment. Due to poor stability and less sensitivity of polyaniline, a new approach is needed to increase the sensitivity and stability. Instead of polyaniline, polypyrrole is one of best alternative for good environmental stability, conductivity and sensitivity of heterojunction as room temperature LPG sensors.

In the present work, we report the fabrication of Ppy/TiO_2 heterojunction with good rectifying ratio by adopting a simple and an inexpensive chemical route. The nanocrystalline TiO_2 thin film was deposited on stainless steel substrate by chemical bath deposition method, followed by Ppy film by electrodeposition method. These films were characterized using different techniques. Sensing performance at different concentrations of LPG (260–1040 ppm) was studied at room temperature (300 K) in forward bias condition at different humidity levels.

2. Experimental details

2.1. Chemical deposition of TiO_2 thin film

Chemical bath deposition method (CBD) is used for the deposition of TiO_2 thin films [8]. Chemical bath consists of 0.1 M $TiCl_3$ and

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30% ammonia solutions. The pH value of solution bath was adjusted to 2.0 ± 0.1 with adding ammonia solution drop by drop. Precleaned stainless steel substrate was dipped in bath and bath was kept at 343 K for 3 h to deposit titanium hydroxide onto stainless steel substrate. The terminated thickness, at which the highest amount of $Ti(OH)_2$ film is deposited on the substrate, is 0.50 μm after this thickness film gets pill up due to the overgrowth of $Ti(OH)_2$ material further the film is air annealed at temp 673 K for 2 h to form TiO_2. This film has used for further characterization.

2.2. Electrochemical deposition of polypyrrole (Ppy)

To carry out the electrodeposition of Ppy film, a scanning potentiostat (EG &G Princeton Applied Research Model 263A) is used. The three electrode system consisting of graphite electrode as a counter electrode, saturated calomel electrode (SCE) as a reference electrode and TiO_2 deposited on stainless steel substrate as a working electrode was used. The graphite electrode is used as counter electrode, because it is chemically inert, unreactive and a low cost material. A solution consisting of 0.5 M sulphuric acid and 0.1 M pyrrole monomer solution was used for deposition of Ppy film. The pH of solution was 3 ± 0.1. Ppy film was deposited potentiodynamically onto previously deposited, 0.50 μm thick TiO_2 film in the potential window of 0 to +1 V/SCE. In order to optimize Ppy film thickness of 0.40 μm, five cycles were taken at the scan rate of 50 mV/s. After five cycles Ppy film gets pill up from stainless steel substrate due to overgrowth of material. The optimized thickness and ideality junction factor for TiO2 and Ppy shown in Table 1.

2.3. Characterization techniques

The structural characterization of polypyrrole and TiO_2 thin films were carried out by analyzing X-ray diffraction (XRD) patterns obtained with CrK_α radiation from a Philips X-ray diffractometer model PW-1710 in the span of angle 10–100°. Surface morphology of the films was studied with JEOL JSM model 6360. The optical absorption study was carried out within a wavelength range 350–850 nm using a UV-1800 SHIMADZU spectrophotometer, with glass substrate as a reference. The FT-IR spectra of the films were recorded in the spectral range of 350–4000 cm^{-1} using Perkin Elmer spectrophotometer. The tin contacts were made using vacuum coating unit manufactured by HIND HIGHVAC before conductivity measurement. The type of electrical conductivity was determined from thermo-emf measurement.

2.4. Polypyrrole/TiO_2 heterojunction for LPG gas sensor

The schematic diagram of the Ppy/TiO_2 heterojunction is illustrated in Fig. 1(a). Fig. 1(b) shows the actual photograph of Ppy/TiO_2 heterojunction LPG sensor. Top contact to Ppy is made using tin (Sn) metal before gas sensing (*I–V*) measurement. The current-voltage (*I–V*) characteristics before and after exposure of LPG were recorded in a forward bias region 0 to +0.6 V in LPG concentration range of 260 to 1040 ppm. From the *I–V* characteristics, voltage corresponding to the maximum current change occurred was noted. Using the following relation the gas response was calculated:

$$S(\%) = \frac{\Delta I}{I_a} \times 100 \quad (1)$$

where ΔI is the change in current upon exposure to the gas, and I_a is the current in the air.

The experiment was carried out at room temperature and at relative humidity of 35%. Effect of relative humidity on heterojunction was studied in humidity chamber. The Ppy/TiO_2 heterojunction was kept in humidity chamber at different relative humidities and *I–V* characteristics were recorded.

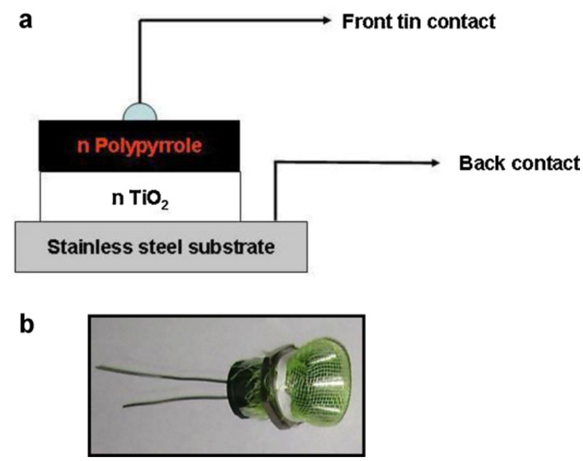

Fig. 1. (a) The schematic of Ppy/TiO_2 heterojunction and (b) photograph of Ppy/TiO_2 heterojunction sensor device.

3. Results and discussion

3.1. Characterization of polypyrrole and TiO_2 films

3.1.1. Structural studies

The XRD patterns of Ppy and TiO_2 thin films on stainless steel substrate are shown in Fig. 2(a and b). The XRD pattern of Ppy declares the absence of any sharp diffraction line, indicating that the deposited material is amorphous. Similar result was reported by Dubal et al. [11]. Also Palaniappan and Manisankar [12] reported the similar structural property of Ppy synthesized by greener mechanochemical route. The XRD pattern of TiO_2 exhibited some broad peaks which are assigned to (1 1 0), (1 0 1), (1 1 1) and (2 1 0) planes. The observed '*d*' values are in good agreement with standard '*d*' values (JCPDS card no. 82-0514). These peaks confirmed the formation of TiO_2 with kestrite structure [8,13]. The grain size was estimated to be 70 nm for (1 1 0) plane. We have not included the XRD pattern of heterojunction in the figure as no peaks corresponding to TiO_2 are observable. The peaks marked by 'star' are due to the contribution from stainless steel substrate.

3.1.2. Surface morphological studies

The morphologies of TiO_2 and Ppy thin films were analyzed using a SEM and are presented in Fig. 3(a and b) at X 5000

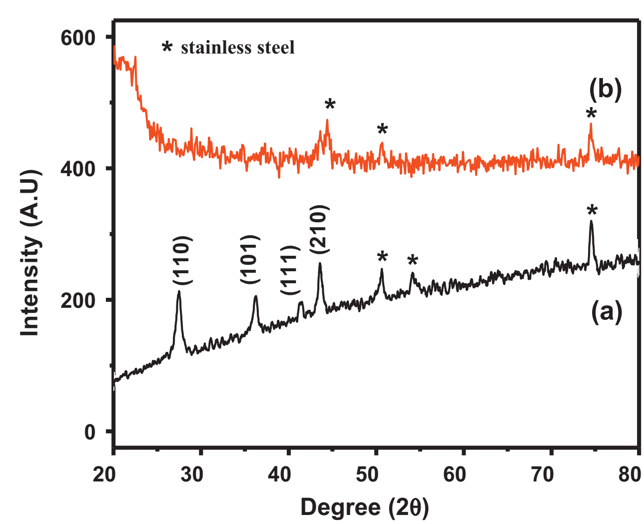

Fig. 2. The XRD patterns of (a) TiO_2 and (b) Ppy thin films onto stainless steel substrate.