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The n-Bi_2S_3/p-PbS heterojunction for room temperature LPG sensors

R.D. Ladhe[a], P.K. Baviskar[b], S.M. Pawar[c], J.H. Kim[d], B.R. Sankapal[e,*]

[a] Department of Physics, School of Physical Sciences, North Maharashtra University, Jalgaon, 425001, India
[b] Advanced Physics Laboratory, Department of Physics, Savitribai Phule Pune University, Pune 411007, India
[c] Solar Cell Laboratory, LG Components R&D Center, 1271, Sa-Dong, Sanggrok-gu, Ansan-si, Gyeonggi-do 426-791, South Korea
[d] Department of Materials Science and Engineering, Chonnam National University, Gwangju 500-757, South Korea
[e] Nano Material and Device Laboratory, Department of Physics, Visvesvaraya National Institute of Technology, Nagpur 440010, India

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ABSTRACT

Heterojunction between bi-layer structured nanocrystalline films has been developed towards the liquefied petroleum gas (LPG) sensor at room temperature (27 °C) without post annealing treatment. These films consists of n-type Bi_2S_3 layer on fluorine doped tin oxide (FTO) coated glass substrate followed by deposition of p-type PbS layer to form heterojunction. However, simple and versatile successive ionic layer adsorption and reaction (SILAR) technique have been employed at room temperature (27 °C) to deposit the films. This technique involves ions as basic building blocks instead of atoms and hence growth rate can be controlled at ionic level. The completion of device was made by use of ohmic contacts using small drop of silver paste over p-PbS layer as a front contact and FTO coated glass substrate as a back contact. The device was kept overnight in order to dry the paste to ensure good contact. The formed heterojunction is porous with high surface area which enables enough space to adsorb and de-adsorb gas molecules easily and shows the gas response of 71% under the exposure of 1000 ppm concentration of LPG with 170 s and 300 s response and recovery time, respectively along with long term stability.

1. Introduction

The liquefied petroleum gas (LPG) is widely used as a fuel for domestic heating and industrial use to provide a clean source of energy for burning. However, content of LPG as butane and propane has potentially hazardous and high possibility towards accidental explosions even for small leakage. Hence, it is essential to develop the room temperature operated sensor in order to detect those hydrocarbon gases at earlier stage and perform active supression. This has stimulated the significant interest towards LPG detection based on metal oxide semiconductors in recent years. However, these sensors sense the gas species at only higher operating temperatures (150 °C–450 °C) [1–4] and with inferior sensitivity. Furthermore, higher operating temperature leads to an increase in the power consumption along with the stability issue. These are major disadvantages of commercially available LPG sensors and hence could not reached upto the depth demand by society. Beside; this conducting polymer is used as heteropartner with inorganic semiconductors has been found new class in gas sensing studies. Regarding this, an early studies showed that the chemically deposited n-TiO_2, n-CdS and electrochemically deposited n-CdSe, n-CdTe as a heteropartner with electrodeposited p-polyaniline for LPG detection at room temperature [5–8]. Nevertheless, the conducting polymer suffers through the processibility and stability problem due to its hygroscopic nature and thus it affects to the charge transfer phenomena.

Hence, the efforts have been putforth to develop the gas sensor which can operate at room temperature (27 °C) with reliable immovability along with low production cost. In this concern, the n-type Bi_2S_3 and p-type PbS were synthesized by using simple and low cost successive ionic layer adsorption and reaction (hereafter SILAR) technique at room temperature (27 °C). Both materials are nanocrystalline in nature with large surface-to-volume ratio resulting in the capability to react with the gas species and sense them readily; as the gas sensing performance strongly depends on material surface and interface. Furthermore, the semiconducting material such as n-type Bi_2S_3 was normally used in solar cell, gas sensor and supercapacitor application [9–11]. Besides this, PbS is p-type semiconducting material with potential application in IR-sensor and LPG sensor [12,13]. Also, the Bi_2S_3/PbS heterojunction was reported by Garcia et al. as a promising candidate for solar cell application [14].

* Corresponding author.
E-mail addresses: brsankapal@gmail.com, brsankapal@phy.vnit.ac.in (B.R. Sankapal).

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Herewith; till to date there is no attempt has been made on the facile synthesis of *n*-Bi_2S_3/*p*-PbS heterojunction towards room temperature (27 °C) LPG sensor. In this direction; the synthesis of Bi_2S_3 thin film on fluorine doped tin oxide coated glass substrate (hereafter FTO) followed by deposition PbS over Bi_2S_3 film was done by simple and inexpensive SILAR technique leads the formation of diffusion free heterojunction for sensing application at room temperature.

2. Experimental details

2.1. Synthesis of Bi_2S_3 thin film

In our previous report, the successive ionic layer adsorption and reaction (SILAR) technique was adopted for the synthesis of n-Bi_2S_3 on FTO coated glass substrate at room temperature (27 °C) [15]. In short, separately placed cationic and anionic aqueous precursor solutions as bismuth nitrate (30 mM) complexed using tri-ethanolamine (TEA) with the resultant pH ~ 10 and thioacetamide (100 mM) with pH ~ 13 adjusted by drop wise addition of dilute solution of hydrazine hydrate, respectively. The immersion time of substrate in an anionic and cationic solution was 15 s, and rinsing time in ion exchanged water was 10 s. Number of immersion cycles were optimized (45 cycles) to get uniform film with appropriate thickness. After deposition, the film was washed with double distilled water, dried in air and used as it is for characterization as well as for further deposition of p-PbS towards heterojunction formation.

2.2. Deposition of PbS over Bi_2S_3 thin film

The FTO substrate coated with Bi_2S_3 thin film was used to deposit PbS layer using SILAR technique. Lead acetate (100 mM) complexed with tri-ethanolamine and thioacetamide (100 mM) were used as anionic and cationic precursors, respectively. The immersion time was 20 s in anionic and cationic precursors with a rinsing time of 10 s in ion exchanged water. The immersion cycles were repeated for 30 times to cover the whole layer of Bi_2S_3 with PbS.

2.3. Characterizations

The crystalline phase and orientations of as deposited films were characterized by using X-ray diffractometer (Rigaku Miniflex diffractometer) with Cu$K\alpha_1$ radiations having the wavelength 1.5406 Å. The surface morphology and compositional analysis was examined by using scanning electron microscopy coupled with energy dispersive X-ray analysis unit (JSM- 6701F, JEOL, Japan). The current-voltage (I–V) characteristics were performed by Potentiostat/Galvanostat model Super-1000S SAP Instruments Pvt. Ltd. The wettability tests by contact angle measurements were performed by using Rame Hart measurement unit.

3. Results and discussion

3.1. Structural studies

The X-ray diffraction patterns of FTO/n-Bi_2S_3 and FTO/p-PbS films are depicted in Fig. 1a and 1b, respectively. From the appearance of the patterns, both the films exhibit the nanocrystalline nature. Tiny broad peaks at 2θ values of 16.2, 25.3, 32.6, 36.7, 47.1, 50.2, 60.5 and 64.6° corresponds to (014), (115), (212), (232), (0012), (181), (309) and (371) planes for n-Bi_2S_3 showing orthorhombic crystal structure are in good agreement with standard JCPDS data (card no.# 79-2384). p-PbS films shows small and

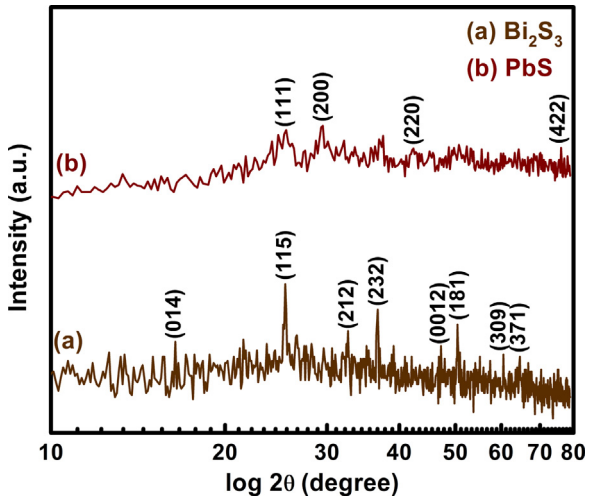

Fig. 1. The X- Ray diffraction patterns of (a) n-Bi_2S_3 and (b) p-PbS film on FTO coated glass substrate.

broad peaks at 2θ values of 25.9, 30.1, 43.1 and 76.1° corresponds to (111), (200), (220) and (422) planes showing cubic crystal structure (JCPDS card no.# 78-1901). The average crystalline size was calculated by using Debye Scherrer formula

$$t = \frac{k\lambda}{\beta \cos(\theta)}$$

where 't' is the average crystallite size, k is Scherrer constant, λ is the wavelength of X-ray used, 'β' is the FWHM and 'θ' is Bragg's angle. The average crystallite sizes were calculated from intense peak (115) of Bi_2S_3 and (200) of PbS using Scherrer formula and found to be 6 nm and 4 nm, respectively indicating their nanocrystalline nature.

3.2. Surface morphological studies and compositional analysis

Fig. 2a and b shows that the surface morphologies of n-Bi_2S_3 film on FTO coated glass substrate and p-PbS thin film on FTO/n-Bi_2S_3 substrates, respectively. The surface morphology of n-Bi_2S_3 shows the smooth and uniform nanostructured surface with particle size ranges between 10 and 30 nm. Surface morphology of p-PbS shows that the spherical particles with diameter less than 100 nm. These particles are formed due to aggregation of small size particles as evident by different dark and bright contrasts. From the careful observations, the small spacing at the grain boundaries separation is clearly distinguished resulting into formation of porous p-PbS structure. The porous nature of nanocrystalline p-PbS thin film and high surface to volume ratio would enhance the effective surface area which could enable the gas species to react easily with them. In other words, a well covered surface morphology of the first layer with an interconnected porous structure of the second layer allows an enough room for gas molecule to adsorb and de-adsorb easily at the heterojunction interface without causing any damage at the top layer. Inset image of Fig. 2c clearly demonstrates the interface between n-Bi_2S_3 and p-PbS layers.

Energy dispersive X-ray analysis is promising tool for quantitative and qualitative analysis. Since all the electromagnetic radiation can be classified on the basis of its wavelength and at the same time, preserve the thought of packets of energy called photons; wavelength and energy-dispersive techniques are measuring the same phenomenon. The equivalence is clear in Planck's equation: $\lambda = hc/E$. The rearrangement and substitution of appropriate values then yields $E = 1240/\lambda$. Where energy (E) is measured in kilo-electron volts (keV) and wavelength (λ) is measured in nanometer. The