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p-PEDOT:PSS as a heterojunction partner with n-ZnO for detection of LPG at room temperature

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Investigation towards the performance of room temperature (27 °C) liquefied petroleum gas (LPG) sensor based on the heterojunction between p-PEDOT:PSS and n-type ZnO is reported. The junction was developed by using chemically deposited ZnO film on to fluorine doped tin oxide (FTO) coated glass substrate followed by coating of thin slurry layer of PEDOT:PSS by using spin coating technique. Both these methods are simple, inexpensive and suitable for large area applications. Different characterization techniques were used to characterize structural, surface morphological and compositional of the material deposited. LPG sensing behavior of the heterojunction was studied at room temperature along with the stability studies. At room temperature, the heterojunction showed 58.8% sensitivity upon exposure to 1000 ppm of LPG with good response and recovery time like 225 s and 190 s, respectively. Furthermore, the LPG sensor reported is cost-effective, user friendly, and easy to fabricate using low cost chemical methods at room temperature.

1. Introduction

Liquefied petroleum gas (LPG) is highly combustible, explosive, and toxic; hence there is a prevailing need to notice the leakage in its former stage and give the effective repression to shun any major accidents. Although, there is a development of scores of the semiconducting metal oxides towards sensor material including ZnO, Zn_2SnO_4 SnO_2, CdO and TiO_2 but suffer high operating temperatures (423–623 °C) and hence showed poor stability. In addition, high temperature is required for receiving the higher sensitivity value and thus increasing the power consumption [1–6]. In spite of the significant efforts, good sensors for LPG have not been found hitherto, the problem being of vital significance to industry as well as to the general public. Therefore, there is considerable interest in developing reliable and efficient LPG sensors having good sensitivity and hence many attempts were putforth by modifying structural parameters for the detection of LPG at very low concentration.

In recent years, heterojunction between n- and p-type semiconductors has been developed for various gases and showed cost effective tool towards detection of gases at low concentration with room temperature operation [7]. Usually, the detection mechanism of heterojunction gas sensor is based on changes in current flow across a rectifying junction and is distinct from that of single-phase semiconducting ceramic sensors. Mostly the accepted heterojunction based sensor is working on the principle of potential barrier height and the principle of formation of heterojunction barrier in the ambient air and their disruption on exposure to the LPG environment. The molecules of reducing gas (LPG) are responsible for the change in the potential barrier height and consequently, the current across the junction [8–12]. On the basis of this mechanism early study showed the LPG sensing performance of polyaniline based heterojunctions at room temperature. It has been well predictable that the conducting polymers are sensitive to environmental compositions. Beside this, some attempts have been made to fabricate the sensor with n-type CdS and CdTe, CdSe as a heterogeneous partner with p-type polyaniline and showed room temperature operation [8,13,14]. However, the use of Cd is toxic whereas polyaniline is moisture absorber (hygroscopic). Hence these materials are not useful for long term permanence and may affect for the use for wide application. Hence, there is a prevailing need for industrial production and environmental protection to replace toxic materials by less toxic alternative materials.

In this anxiety, the focus was made on the development of relevant sensing material with ground break through strategy to improve sensitivity, selectivity and stability. Among conducting polymers, (3,4-polyethylenedioxy-thiophene:poly (styrene sulfonic acid)) (PEDOT:PSS) has attracted a lot of attention in recent years due to its excellent properties such as long-term stability, high conductivity, optical transparency in its doped state, low

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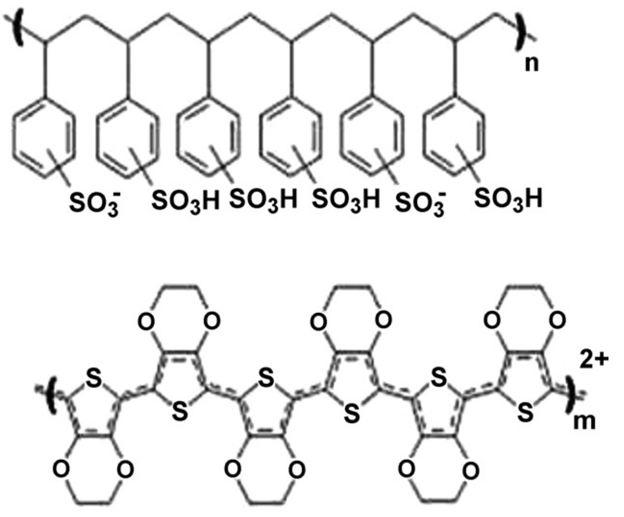

Fig. 1. The molecular structure of PEDOT:PSS.

band gap, and moderate redox potential. PEDOT:PSS is commonly accepted to be more environmentally stable than other conducting polymers such as polypyrrole and polyaniline. This feature of PEDOT:PSS is to formulate it proficient towards gas sensing applications [15]. To meet this demand, the synthesis of n-ZnO was performed with p-PEDOT:PSS as heterojunction partner to sense the LPG at room temperature.

2. Experimental details

For the synthesis of ZnO, zinc acetate $\{(CH_3{\cdot}COO)_2{\cdot}Zn{\cdot}2H_2O\}$ was purchased from Loba Chem. with 99.5% purity, hexamethylene tetramine (HMTA) $\{(CH_2)_6{\cdot}N_4\}$ was purchased from Glaxso Chem. with 99% purity and 25% ammonia (NH_3) as a complexing agent were used. The commercially available PEDOT:PSS (Clevios PH1000, HCD 08P062) was purchased from Baytron HC Starck's with 99% purity.

2.1. Synthesis of ZnO thin films

Synthesis of ZnO thin film was based on the immersion of the substrate in an alkaline bath containing complexed zinc salt at room temperature (27 °C). A precursor solution of zinc acetate $\{(CH_3{\cdot}COO)_2{\cdot}Zn{\cdot}2H_2O\}$, hexamethylene tetramine (HMTA) $\{(CH_2)_6{\cdot}N_4\}$ and 25% ammonia (NH_3) as a complexing agent was used as a deposition bath. The precursor was prepared by adding ammonia (25%) to the bath containing equimolar aqueous solutions (0.3 M) of zinc acetate and HMTA with constant stirring, which resulted in the formation of a white precipitate of $Zn(OH)_2$. This precipitate was dissolved by further addition of excess ammonia with a resultant pH ≈12.0. The solution was stirred for a few minute and then transferred into another beaker containing cleaned fluorine doped tin oxide (FTO) coated glass substrate placed horizontally at the bottom of the beaker at room temperature (27 °C) for the deposition of ZnO thin film. After the deposition, the substrate coated with films was taken out at suitable time intervals (10–50 h), washed with double distilled water and dried in air. The as-deposited films were annealed at 200 °C for 1 h in air to remove hydroxide phase and used for further characterizations as well as for coating of PEDOT:PSS (3,4 polyethylenedioxy-thiophene:poly (styrene sulfonic acid)) layer.

2.2. Synthesis of PEDOT:PSS on n-ZnO thin film

Fig. 1 shows the molecular structure of PEDOT:PSS in which the π-conjugated system is responsible for the hole transport in PEDOT:PSS. The different ratios of PEDOT:PSS:H_2O were used and optimized with respect to better coating of ZnO that corresponds to better LPG sensor properties. At each time, each volume was ultrasonicated for 1 h. We observed that the 1:1 ratio was optimal containing 50% water. This solution was coated on FTO/n-ZnO by using spin coating technique. For coating, the rate of the spin was 550 rpm for first 5 min in order to coat PEDOT:PSS layer on the particles of ZnO along with penetration of this layer inside the porous layer. This helps to cover most of the ZnO particles with PEDOT:PSS from top to bottom to get high surface area heterojunction. Then, the rate of spin was increased linearly for 1 min to achieve 4000 rpm and kept for next 5 min in order to dry the layer. After the coating, the film of FTO/ZnO/PEDOT:PSS was heated at 100 °C for 10 min in air.

2.3. Characterizations

The film was characterized by X-ray diffractometer (Ni-filtered X pert PRO Philips, Eindhoven, Netherlands) with Cu$K_{\alpha 1}$ target ($\lambda = 1.5406$ Å) in 2θ range from 30° to 80° in grazing incidence mode with angle 0.5°. The surface morphology was examined and composition analysis was done by using scanning electron microscopy coupled with energy dispersive X-ray analysis unit (JSM-6701F, JEOL, Japan). The chemical nature of n-ZnO and n-ZnO/p-PEDOT:PSS was examined by using model one FT-IR (Perkin-Elmer) spectrum. The current density–voltage (J–V) characteristics were performed by using Potentiostat/Galvanostat Model Super-1000S SAP Instruments Pvt. Ltd., Howrah, India.

2.4. Volume measurements

Before the measurement, valve II was closed; the space in the glass dome (27 L) was evacuated by using the vacuum pump in order to remove any residual gas or air in the dome. Fresh air was admitted into the dome through the two way valve (valve III) and then valve III was kept closed. Prior to the measurement, the double distilled water used in the glass bottle was saturated with gas to be measured in order to avoid the possibility of dissolution of the inserted gas. When valve I was opened, valve II was kept closed, the gas from the cylinder was filled in the empty space of the glass bottle which was observed online by the displacement of an equivalent volume of water (the level was raised) in the liquid level monitor. Then valve I was kept closed and valve II was opened slowly for a short time. When the desired volume of the gas was injected inside the dome (which was monitored online by observing the decrease in the water level in the liquid level monitor) valve II was kept closed and current–voltage measurements were noted. For the next measurement, the dome was again evacuated; fresh air was admitted inside the dome and the above procedure was repeated. The schematic set-up used is shown in Fig. 2. The gas concentration is measured in terms of vol.% and can be converted into ppm by using following relation,

$$\text{Gas concentration (ppm)} = \frac{\text{Known volume of gas}}{\text{Volume of chamber}}$$

2.5. Gas sensing properties of n-ZnO/p-PEDOT:PSS heterojunction

The gas sensing properties of n-ZnO/p-PEDOT:PSS (3,4 polyethylenedioxy-thiophene:poly (styrene sulfonic acid)) heterojunction were studied by using a lab-made gas sensor unit described elsewhere [16]. The forward biased current density–voltage (J–V) characteristics of the junction, before and after exposure to gas environment were measured at room temperature in a voltage range of 0–3 V. The electrical current of n-ZnO/p-PEDOT:PSS heterojunction in air (I_a) and in the presence of gas (I_g) was measured. The gas sensitivity (S%) was calculated by using the following relation

$$S\% = \frac{I_a - I_g}{I_a} \times 100$$

The response and recovery time of the junction were determined at fixed voltage by measuring the change in current.

3. Results and discussion

3.1. Structural characterizations

X-ray diffraction pattern of the chemically deposited ZnO film on fluorine doped tin oxide (FTO) coated glass substrate is shown in Fig. 3a with removed background peaks of FTO substrate. Film shows a pure ZnO phase with a wurtzite crystal structure (JCPDS card no. 36-1451). This supports the complete removal of the $Zn(OH)_2$ phase and its conversion to pure ZnO after annealing in air at 200 °C. The mean values of $a = 3.22$ Å, $c = 5.20$ Å are in a good accord with the reported values. Fig. 3b shows that the X-ray diffraction pattern of ultra thin layer of PEDOT:PSS on FTO/ZnO. Unchanged structural behavior with no identification of any sharp peak for PEDOT:PSS layer gives clear evidence of amorphous nature of polymer and/or due to ultrathin thickness of polymer on ZnO. The intense peaks of ZnO along (1 0 0), (0 0 2) and (1 0 1) remain unaltered with slight diminished intensities. Some low intense peaks are disappeared in ZnO/PEDOT layer since the X-ray diffraction pattern was taken with grazing incidence mode with incident angle of 0.5° to see the effect of only PEDOT:PSS ultrathin layer on ZnO. Hence, structural contribution towards ZnO in ZnO/PEDOT:PSS layer is less as compared to ZnO layer.

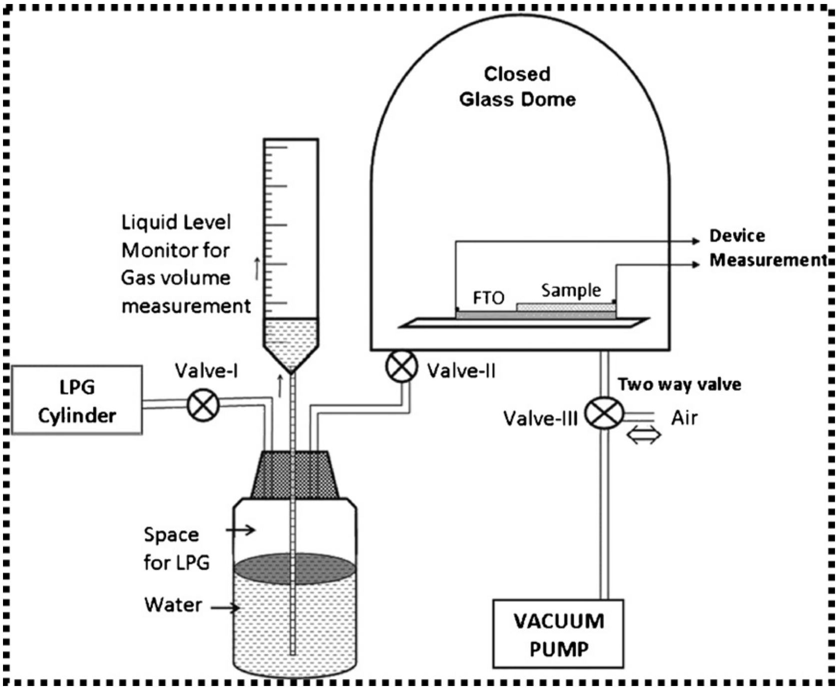

Fig. 2. The schematic setup of the gas sensor assembly with LPG volume measurement unit.

3.2. *Surface morphological and compositional analysis*

Fig. 4a shows the surface morphology of the bare n-ZnO thin film having crystallites with different morphologies with size ranges from few hundred nanometers to a few micrometers. The random shape of crystallites facilitates high surface area of n-ZnO which is necessary to get larger heterojunction area. Appearance of black blurred image of n-ZnO in contrast to white n-ZnO crystals (Fig. 4b) gives the clear evidence of coverage of p-PEDOT:PSS layer on n-ZnO. The entire cross section image of FTO/n-ZnO/p-PEDOT:PSS layer is as shown in Fig. 4c. The thin layer of p-PEDOT:PSS on the top of n-ZnO is clearly visible with penetration of thin blackish slurry towards the bottom of the film with covering of the n-ZnO crystallites (shown by dotted line). This clearly demonstrates filling and coverage of n-ZnO by p-PEDOT:PSS from top to bottom. The average thicknesses of the n-ZnO/p-PEDOT:PSS film is about 28 μm with p-PEDOT:PSS layer is about 200 nm (±5%) calculated from weight difference method. In order to minimize the error, large surface film area was selected. These data were also compared with thickness observed by cross-sectional SEM image. From energy dispersive X-ray analysis (EDAX), the content of Zn, O, and Sn was observed in n-ZnO as shown in Fig. 5a. Zn, O, Sn, C and S are observed in EDAX pattern of p-PEDOT:PSS layer on n-ZnO depicted in Fig. 5b. The inclusion of Zn and O is from n-ZnO whereas C and S were observed from sulphonated p-PEDOT:PSS layer on n-ZnO. Appearance of Sn is due to used substrate fluorine doped tin oxide (FTO) coated glass as shown in Fig. 5a and b. A similar type result was reported by Wang et al. for PEDOT layer on TiO_2 [15].

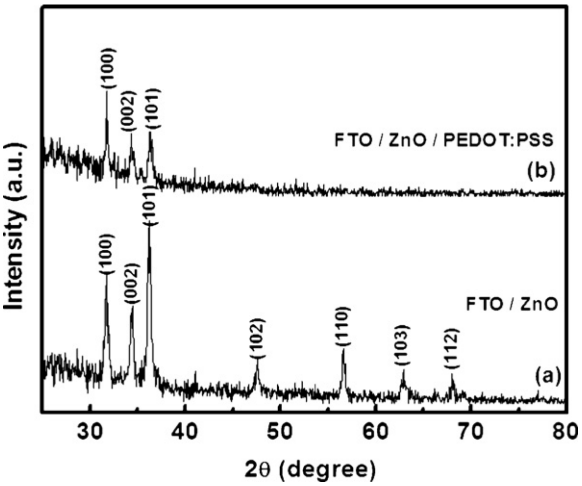

Fig. 3. The X-ray diffraction patterns of (a) FTO/n-ZnO and (b) FTO/n-ZnO/p-PEDOT:PSS film on glass substrate.

3.3. *Study of Fourier transform infrared (FT-IR) spectrum for n-ZnO and n-ZnO-p-PEDOT:PSS*

The chemical nature of n-ZnO and n-ZnO-p-PEDOT:PSS was studied by Fourier transform infrared (FT-IR) spectrum. It is the characteristic of a particular compound providing information about its functional groups, molecular geometry and inter/intra molecular interactions. FT-IR spectrum for ZnO in the wave number range between 450 and 4000 cm^{-1} is as shown in Fig. 6a. The FT-IR spectrum of ZnO presented the bands at 2922.97 cm^{-1} occurs because of the Nujol source used and the absorption bond due to O–H stretching of hydroxyl group centered at 1154.07 cm^{-1}. The bond at 2727.97 cm^{-1} is attributed to the stretching vibration of C–H bond of the organic compound. The absorption bond appearing in the spectrum at 722.14 cm^{-1} is attributed to the O–R ($R = CH_3$, CH_5, CH_7, etc.) groups linked to Zn or actually the presence of C=C aromatic hydrocarbon and out of plane ring bending vibration rather than C–H out of plane bending. In this spectrum, the absorbance bond is situated at 564 cm^{-1} which is due to the Zn–O bond.

Fig. 6b shows that the FT-IR spectrum for n-ZnO/p-PEDOT:PSS in the wave number range between 450 and 4000 cm^{-1}. The FT-IR spectrum of ZnO/PEDOT:PSS presented the bands 3465.17 occurs due to the Nujol source. The absorption bonds due to C–H stretching of alkenes group centered at 2925.97 cm^{-1}. The bond 2065.37 cm^{-1} due to the weak overtone band can be assigned substitution of ring.

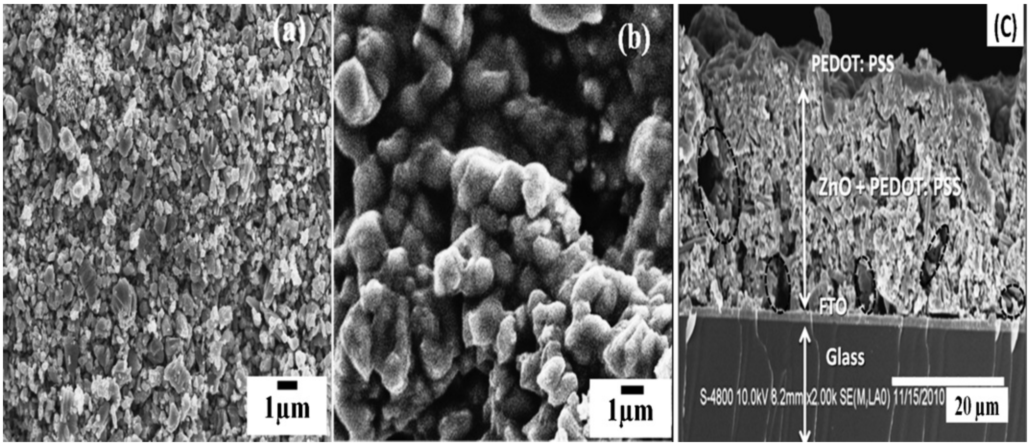

Fig. 4. The scanning electron micrographs of (a) n-ZnO film on FTO coated glass substrate and (b) FTO/n-ZnO/p-PEDOT:PSS. (c) Cross section view FTO/n-ZnO/p-PEDOT:PSS of film.

In addition to the aromatic band due to extended resonance the polar character of C=C double bond at about 1636.15 in five member ether group. The bond at 1462.62 and 721.98 is attributed due to the presence of C=C aromatic hydrocarbon and out of plane ring bending vibration rather than C–H out of plane bending in ZnO. The absorbance bond which appears in the spectrum at 1372.96 and 1201.48 due to the asymmetric stretching of S=O and symmetric stretching of S=O respectively, indicates the presence of sulfur from sulphonated PEDOT:PSS layer.

3.4. *LPG sensing mechanism of n-ZnO/p-PEDOT:PSS heterojunction*

The completion of the device was made by employing the ohmic contacts with small spot of silver paste 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 ohmic contact [17]. The schematic representation of FTO/n-ZnO/p-PEDOT:PSS/Ag is depicted in the inset of Fig. 7. The current–voltage (*J–V*) characteristics obtained from FTO/n-ZnO/p-PEDOT:PSS/Ag layer is depicted in Fig. 7 with a positive voltage at the silver electrode and a negative voltage at the FTO electrode. The characteristic curve shows Schottky diode like behavior. Initially, we examined the individual sensing properties of FTO/n-ZnO and FTO/p-PEDOT:PSS layers towards the LPG environment with reference to air. The stable nature of the current density–voltage (*J–V*) characteristics before and after LPG exposure clearly shows the non-sensing behaviors of FTO/n-ZnO and FTO/p-PEDOT:PSS films at room temperature as depicted in the inset of Fig. 8. The interface between n-ZnO/p-PEDOT:PSS structure with high surface area due to porous network was exposed to LPG environment which enables the gas species to enter and react at the interface. Fig. 8 shows the typical current density–voltage measurement curves under forward biased condition in the presence of ambient air (a) and under environment of various concentrations of LPG (b–f) from 400 to 1200 ppm. As the junction was exposed to LPG, the forward biased current was linearly decreased up to certain limit. From *J–V* characteristics, the maximum change in the current was observed for 1000 ppm concentration of LPG. For further increase in LPG concentration to 1200 ppm, the sudden increase in the current was observed. The gas response (%) at various concentrations of LPG was calculated at fixed voltage value of 2.3 V and is shown in Fig. 8. The gas response was increased continuously from 40 to 58.8% with increase in the gas concentration in the range 400 and attained the maximum at 1000 ppm. The increase in the gas response value was observed because of the decrease in forward current with increase in gas concentration. This was mainly attributed to the decrease in the charge carriers with increase in the depletion layer width and thus, the increase in height of potential barrier. Similar results are reported in n-TiO$_2$/p-polyaniline heterojunction [14,18]. At 1200 ppm of LPG; the sensitivity was decreased drastically since the effect of active area was diminished due to saturation of LPG molecule at the interface. Another way at lower gas concentrations (<1000 ppm LPG), the unimolecular layer of gas molecules would be expected to form on the interface, which would interact with the interface more actively giving larger sensitivity. Above the 1000 ppm level of LPG, a decrease in the sensitivity value is observed which may be due to the formation of multilayers of gas molecules at the interface of the junction and slowing down of the reaction rate between gas molecule and interface of junction. This may be due to the adsorbed gas molecules at the interface which lead to an increase in the forward resistance of the junction or an increase in the potential barrier height at the interface and hence, thereafter the decrease in sensitivity towards LPG.

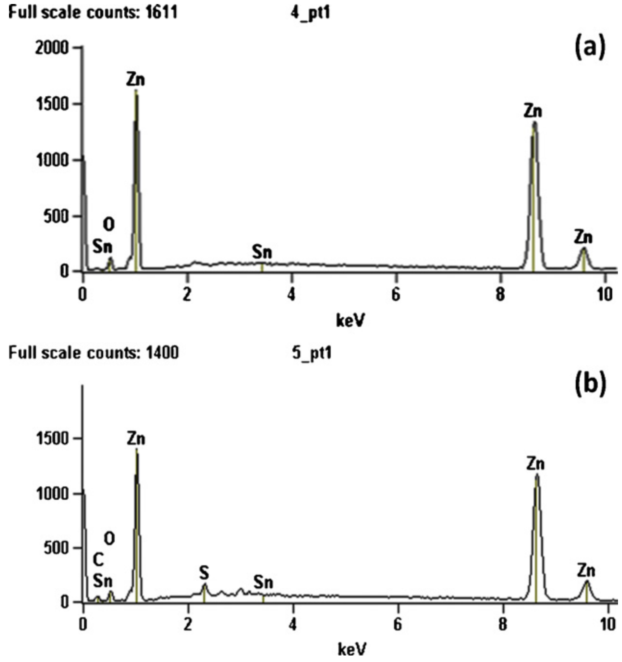

Fig. 5. The elemental analysis of (a) n-ZnO/FTO and (b) FTO/n-ZnO/p-PEDOT:PSS heterojunction film.

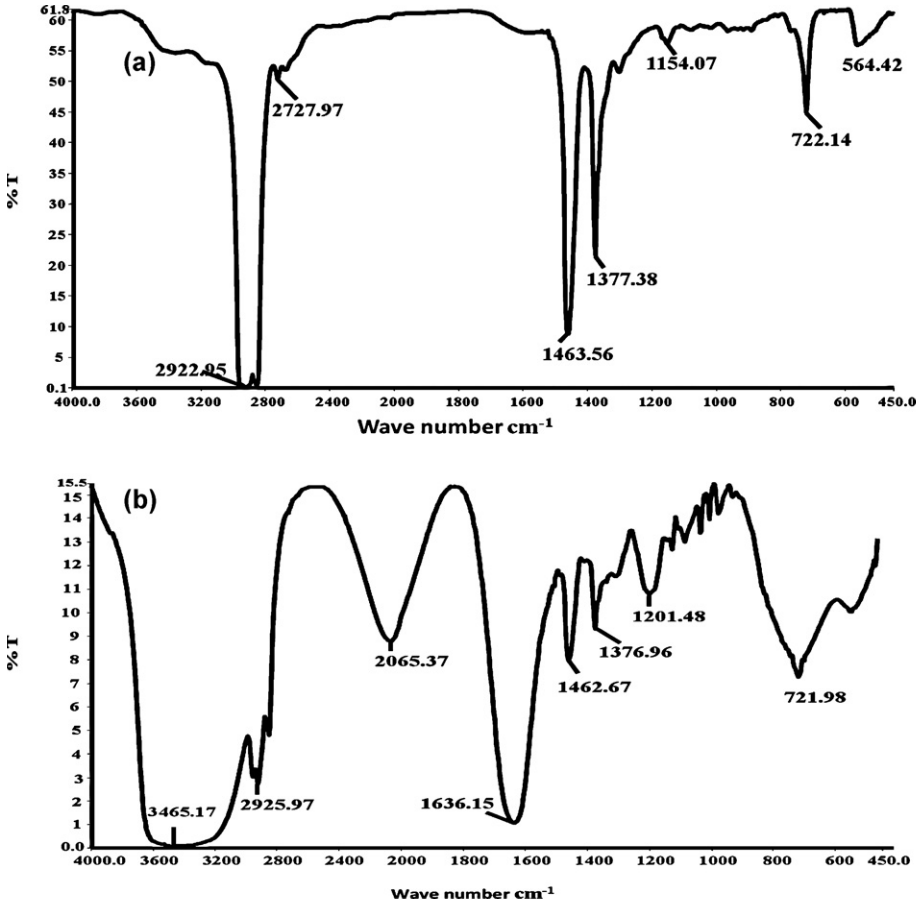

Fig. 6. Study of Fourier transform infrared (FT-IR) spectrum of (a) n-ZnO and (b) n-ZnO/p-PEDOT:PSS.

The stability of heterojunction sensor material was measured for 12 days at an interval of 2 days as shown in the inset of Fig. 9. Initially, heterojunction gas sensor showed relatively high sensitivity (58.8%), however it dropped to 55% and the stable sensitivity was obtained thereafter. In the initial stage, we believe that the heterojunction may undergo interface modification during operation and then it reaches to steady state indicating the stability of the heterojunction. Fig. 10 shows that the response and recovery time which were measured by using forward biased current density–voltage measurement. This was measured at constant voltage of 2.3 V with 1000 ppm of LPG concentration. When LPG was exposed (ON-State) the response of the device goes to 58.8% within

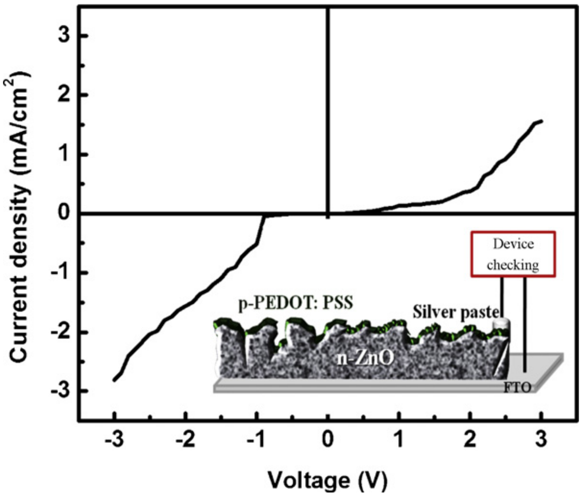

Fig. 7. The current density–voltage (*J*–*V*) plot of n-ZnO/p-PEDOT:PSS heterojunction. Inset shows the schematic representation of FTO/n-ZnO/p-PEDOT:PSS/Ag heterojunction.

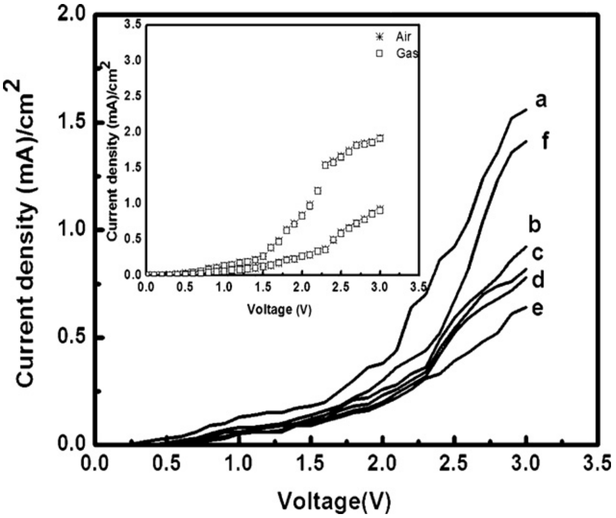

Fig. 8. Forward biased current density–voltage (*J*–*V*) characteristics of n-ZnO/p-PEDOT:PSS heterojunction at various concentrations of LPG (a) air, (b) 400 ppm, (c) 500 ppm, (d) 800 ppm, (e) 1000 ppm and (f) 1200 ppm. Inset shows the individual sensing properties of FTO/n-ZnO and FTO/p-PEDOT:PSS were performed towards air and LPG environment.

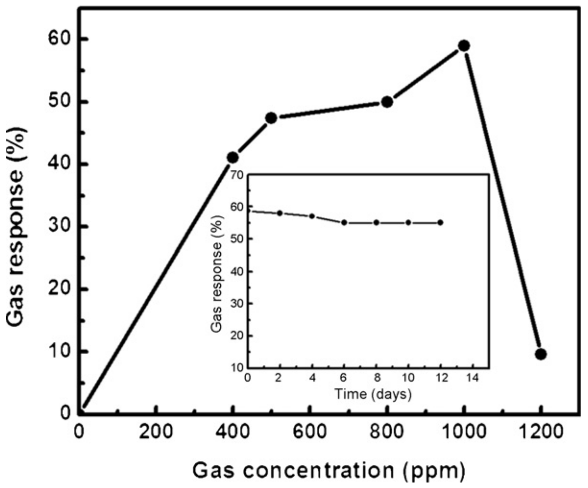

Fig. 9. The plot of variation in gas response (%) vs. gas concentration (ppm) of n-ZnO/p-PEDOT:PSS heterojunction and inset shows the gas response vs. time (days) at fixed voltage of 2.3 V at 1000 ppm of LPG concentration.

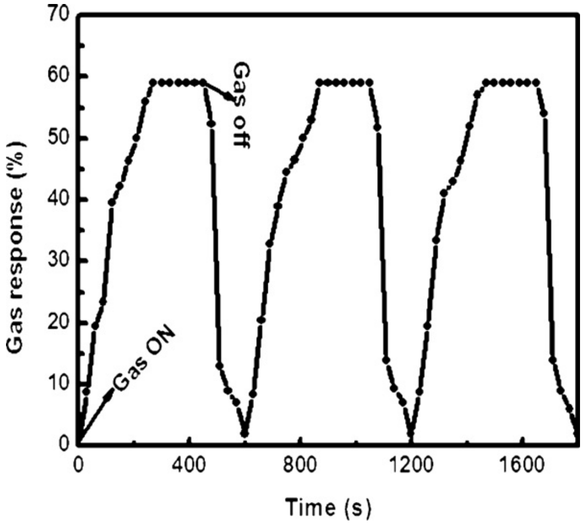

Fig. 10. The plot of repeatability test as gas response (%) vs. time (s) of the n-ZnO/p-PEDOT:PSS heterojunction at a fixed voltage of 2.3 V with 1000 ppm of LPG concentration.

225 s and attained a maximum value. When LPG was stopped (OFF-State), the recovery time was found to be 190 s. Higher value of response time may be due to the possibility of the penetration of gas molecules towards interior of the film up to the bottom and thus, leading to generation of charge carriers at the interface from top to bottom with slower rate. Similar behavior was observed for higher value of recovery time in reverse manner. The observed values of response and recovery time are little high and hence efforts are in progress.

4. Conclusions

The film of n-ZnO/p-PEDOT:PSS (3,4 polyethylenedioxythiophene:poly (styrene sulfonic acid)) was successfully deposited by using simple and inexpensive chemical methods at room temperature to form a good heterojunction. The individual layers were non-sensitive whereas junction was sensitive to liquefied petroleum gas (LPG) environment at room temperature. The remarkable sensitivity of 58.8% at 1000 ppm level of LPG was achieved using simple methods at room temperature with stability for more than 10 days. Furthermore, the response and recovery time were still high (225 s and 190 s) and detailed studies are in progress to lower down these values.

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