INTERNATIONAL JOURNAL OF Electroactive Materials

Int. J. Electroactive Mater. **5 (2017) 6-12**
www.electroactmater.com

RECEIVED
14 July 2017

REVISED
15 July 2017

ACCEPTED FOR PUBLICATION
17 July 2017

PUBLISHED
25 October 2017

Liquefied Petroleum Gas Detection using SnO_2, PANI-SnO_2 and Ag-SnO_2 Composite Film Fabricated by Chemical Route

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ABSTRACT: In the present work, chemical route was used to deposit PANI and Ag doped SnO_2 thin films. After careful study, SnO_2 thin films with suitable growth conditions were selected for probing their response towards LPG. The prepared sensor structures, 1% PANI doped SnO_2 (SnO_2-PANI) based sensor was found to give high sensing response of about 67 towards concentration 1000 ppm of LPG gas at low temperature with response time (~ 1000 sec) and recovery time (~ 900 sec) time respectively. The structural, morphological and optical properties of the prepared sensor structures have been studied by X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FTIR) and Scanning Electron Microscope (SEM).
Keywords: Gas sensors, PANI and Ag doped SnO_2 Thin films, XRD, SEM.

1. Introduction

Liquefied petroleum gas (LPG) is widely used as fuel or source of energy for industries as well as households. It's highly flammable and explosive characteristics, poses a serious threat to mankind [1]. Due to the widespread use of LPG, fast and selective detection of LPG can prevent the occurrence of explosions. Metal oxides found potential application in the field of gas sensors. Among them, tin oxide (SnO_2) is the most preferred one [1].

SnO_2 is an n-type semiconductor with a wide bandgap (3.6 eV), which has been widely used as a gas sensing material because of its natural non-stoichiometry, low cost and high chemical stability. Its conductivity/receptivity is modified in the presence of different oxidizing as well as reducing gases [2-4]. This paper reports LPG detection using chemical route deposited SnO_2 thin films. Though SnO_2 thin films prepared by different techniques have been used extensively for sensing explosive and toxic gases such as H_2, CO_2, NO_2 and other hydrocarbons [5-9], not many articles appeared on detection of LPG using these the films [10].

Near room temperature, the oxygen vacancies are frozen and isothermal conductance change of a SnO_2 device are due to chemisorptions [11]. The electron concentration near the semiconductor surface varies with the density and occupancy of surface acceptors and donors. In a gas sensor, this density of surface states depends on surface reaction with ambient gases [11]. It has been shown that the gas sensing properties of tin oxide can be significantly improved by doping, such as PANI and Ag. Different types of specially designed materials have been intensely investigated in the past decade for gas sensing applications. Metal oxide semiconductor gas sensors have been used for domestic gas leak detectors in the house to produce an alarm at a given gas concentration [12-13].

In present work, an effort has been made to developed sensor structure based on, SnO_2 nanostructures doped with different catalysts (PANI and Ag) using the chemical route to detect 1000 ppm of LPG. Response and recovery characteristics of the films deposited at carefully chosen conditions are presented for LPG. The sensor has been fabricated by spin coating of nanoparticles colloidal solution onto a glass substrate having planer electrodes. The fabricated sensors have been exploited for the detection of LPG.

2. Experimental

2.1 Synthesis

SnO_2 nanostructures doped with PANI and Ag catalysts were prepared by a chemical route using $SnCl_4.5H_2O$, propenol and de-ionized water as precursors for SnO_2 fabrication. The preparation of PANI, Ag and SnO_2 nanoparticles have been mentioned elsewere [14-17]. The prepared nanoparticles (PANI and Ag) were doped into SnO_2 nanoparticle colloidal solution in the weight% of respectively SnO_2-PANI(1%); 7SnO_2-Ag(1%). SnO_2-PANI and SnO_2-Ag sol were used to deposit respective thin films on a glass substrate and planar electrode prepared on a glass substrate by using conducting silver paste.

2.2 Thin film deposition technique

A thin film of the sample was prepared by a spin coating method on taking glass substrate. For this purpose, the synthesized powder was dissolved in isopropyl alcohol and then it was sonicated for 30-40 min. The sonicated solution was stirred at 100 °C for 6 h to obtain the solution. This solution was used for fabrication of thin film using spin coating method. The resulting thin film was dried at 120 °C for 10 min after deposition of each layer of the prepared solution using spin coating. This drying procedure stabilizes the thin film.

Further, the thin film was annealed at 200 °C which converts the thin film as sensing material. The film was almost uniform and the thickness of the film was found 0.4 μm measured by Accurion variable angle spectroscopic ellipsometer (Nanofilm EP3 Imaging). Further, we took the silver paste and deposited it on opposite sides of the film for signal registering. Two parallel Ag electrodes were inserted on top of the film. The resistance was measured using Keithley Electrometer [Model: 6517B]. Sensing film with silver contact was used for LPG sensing.

3. Results and discussion

3.1 Scanning Electron Microscopy

Fig. 1(a), 1(b) and 1(c) show Scanning Electron Micrographs of a thin film of PANI, SnO_2 and SnO_2-PANI at different scales of 5 μm and 10 μm. The SEM images reveal that prepared film has clusters of crystallites over the entire surface of the material. The porosity of the material is an imperative parameter regarding gas sensing point of view as the film has a number of active sites. A close look at scanning electron micrographs reveals that the material is porous in nature, therefore; the prepared film absorbs more gas through the surface which causes changes in the resistance of the sensing film. The average size of pores nanocomposite SnO_2-PANI was found to be 5 μm.

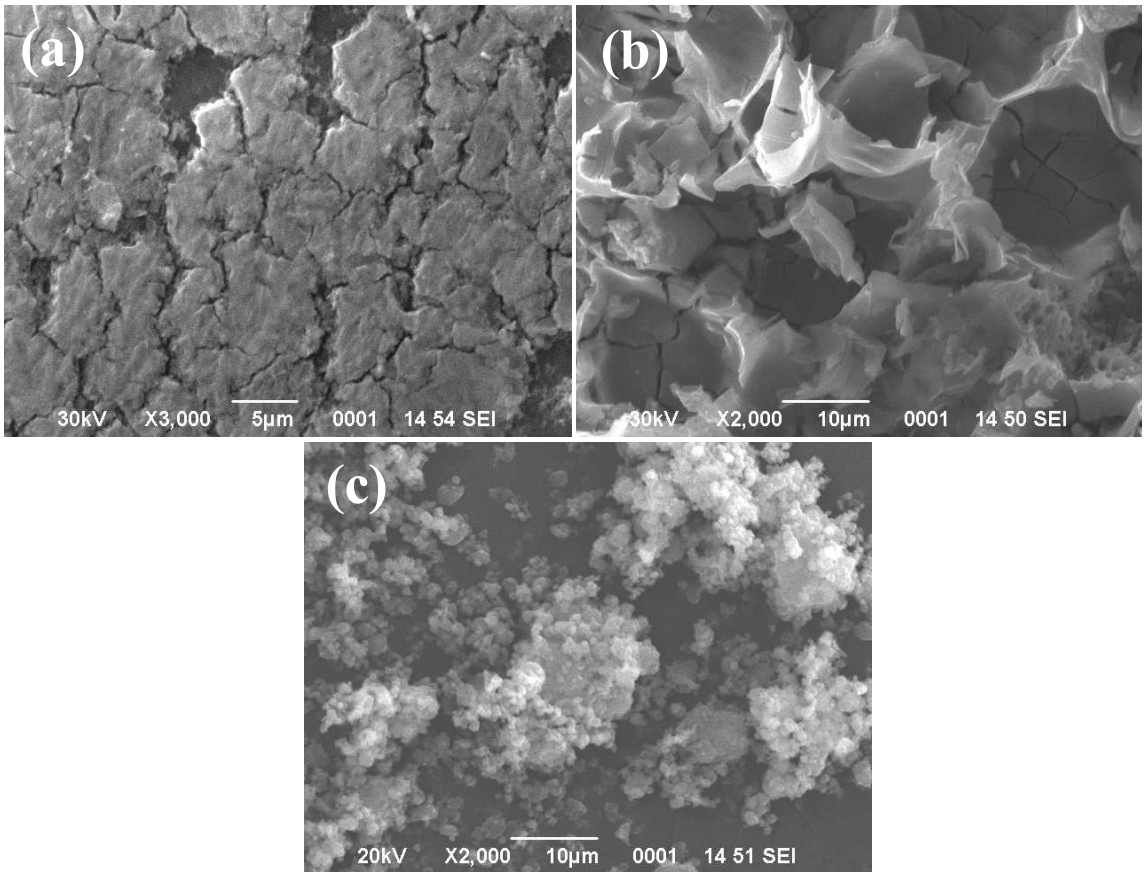

Figure 1: Scanning electron micrographs of thin film of (a) PANI at 5 μm scale (b) SnO_2 at 10 μm scale and (c) SnO_2-PANI at 10 μm scale

3.2 X-Ray Diffraction

X-Ray diffractions show the extent of crystallization of the sample. The average crystallite size (D) of the sensing material can be calculated by the Debye-Scherer's formula, which is given as [18];

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

where K= 0.94 is Scherer's coefficient, which depends on the shape of the crystallite and the type of defects present, λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the diffraction peak and θ is the angle of diffraction. **Fig. 2** shows the XRD patterns of samples prepared at room temperature shows that the synthesized material is pure and less crystalline.

Fig. 2a show the XRD pattern of the SnO_2 thin film prepared at room temperature and reveals that the sensing material consists of only two peaks. Broad and well-defined reflections corresponding to (110), (101), (200), (211) and (220) planes of SnO_2 were observed at 26.52º, 33.96º, 38.17º, 51.87º and 54.91º respectively for the deposited SnO_2 thin film and are in good agreement with the corresponding values reported for the rutile structure of SnO_2 [19].

Fig. 2b shows the XRD diffraction pattern of PANI. The two diffraction peaks around 20º and 25º for PANI should be assigned to the scattering from the periodicity perpendicular to PANI chains. The average value of crystallite size of SnO_2 calculated from Scherer's formula is found to be 18 nm. The SnO_2 thin film having 18 nm crystallite sizes provide a large surface to volume ratio hence the ability for exposure of gas through the surface of the thin film increases which enhance the sensitivity of the gas sensor.

3.3 Fourier Transform infrared spectroscopy

Fig. 3 show the FTIR spectrum of the obtained SnO_2-PANI hybrid composite material using KBr pellets were recorded in the range 400-4000 cm^{-1}. The SnO_2-PANI spectrum show characteristic peaks attributed to the N-H starching vibration of amines absorption at 1572 cm^{-1}, the starching vibration of CN^+ and C-N at 1471 and 1292 cm^{-1}, the absorption band at 1121 and 801 cm^{-1} are attributed to the aromatic C-H bending in the plane and out-of-plane aromatic ring [20-21]. The absorption peaks at 559 and 811 cm^{-1} correspond to Sn-OH and Sn-O-Sn respectively [22]. The above-absorbed absorption characteristics conform the formation of SnO_2-PANI.

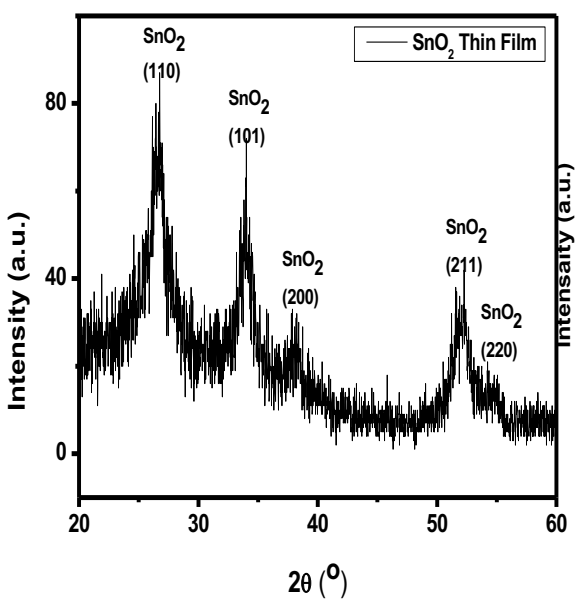

Figure 2a: X-Ray Diffraction of synthesized SnO_2

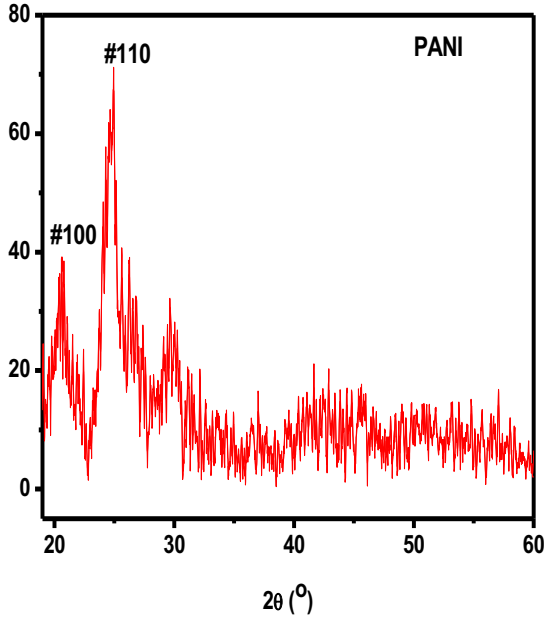

Figure 2b: X-Ray Diffraction of synthesized PANI

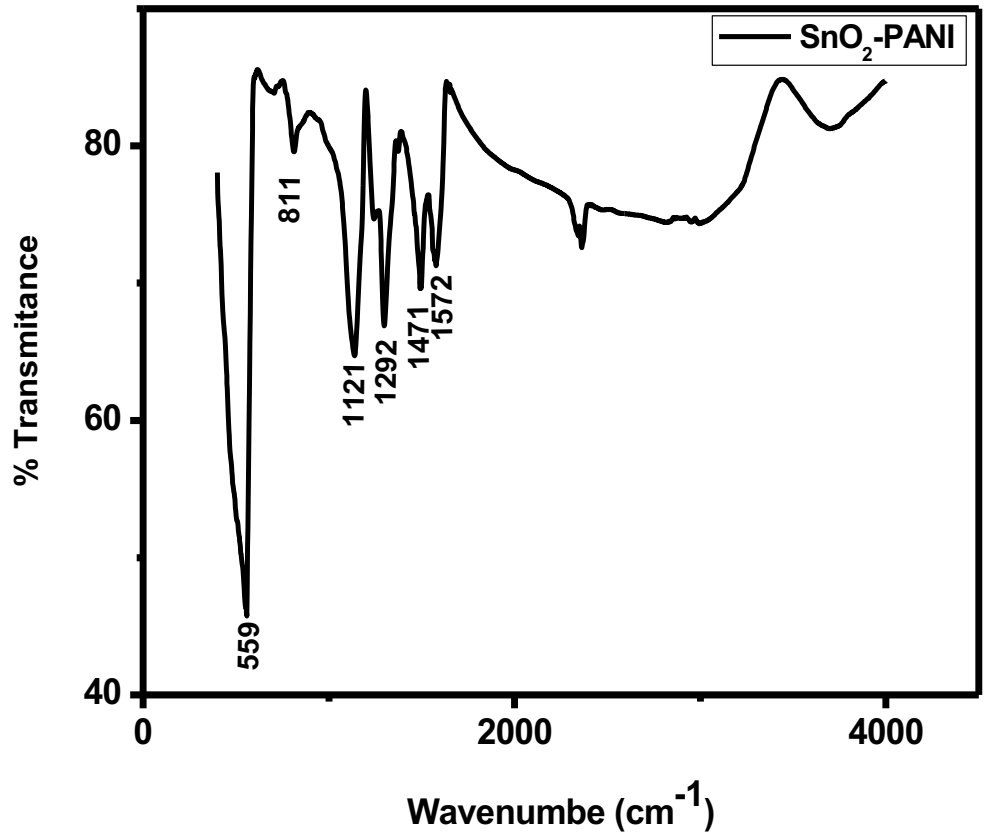

Figure 3: FTIR spectra of SnO_2-PANI

3.4 Gas Sensing Measurements

The schematic diagram of LPG sensing set-up is shown in **Fig. 4(a)**. The sensing film with silver electrodes was placed inside the glass chamber having two knobs. One knob is associated with the concentration measuring system (gas inlet) and other is an outlet knob for releasing the gas. Concentration measuring system is shown in **Fig. 4(b)**, which consists of a glass bottle containing double distilled water, which is saturated with LPG, in order to avoid the possibility of dissolution of inserted gas. At the top of the bottle, the measuring tube (pipette) is connected by a vacuum seal. The cock I is connected to the LPG cylinder and cock II is connected to the inlet of the gas chamber.

When the cock I is opened, the LPG from the cylinder is filled in the glass bottle and an equivalent amount of water is displaced in the measuring pipette. When the cock II is opened, the desired amount of gas e.g. 1, 2, 3, 4, 5 Vol.% and onwards is entered in the gas chamber. Before passing the LPG in the chamber, the gas chamber with a resistance measuring holder was stabilized for 10-20 minutes.

For studying the gas sensing properties, gas dilution system shown in **Fig. 4** and the sensing film with silver contacts was used for measurements of LPG sensing properties. The change in sensor resistance was recorded in the presence of different concentrations of LPG with the help of Keithley electrometer (6517B) interfaced with a computer. The stabilized resistance of the film was taken as stabilized resistance in the presence of air (R_a). Now, this was exposed with LPG and variations in electrical resistance with the time for different Vol % of LPG were recorded by using Keithley electrometer (Model: 6517B).

Sensitivity of the LPG sensor is defined as the change in resistance in the presence of gas (R_g) to the resistance in presence of air (R_a) that is given as

$$S = \frac{R_a}{R_g} \tag{2}$$

Percentage sensor response for the sensing material is defined as

$$\%SR = \frac{[R_a - R_g]}{R_g} \quad (3)$$

where R_a and R_g are mentioned as above.

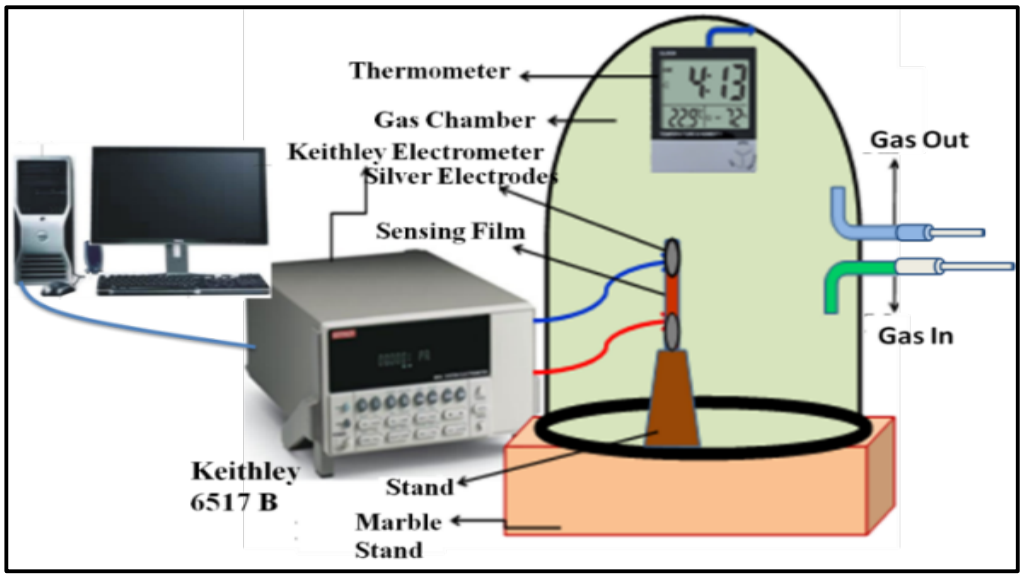

Figure 4(a): Sensitivity measuring Set-up

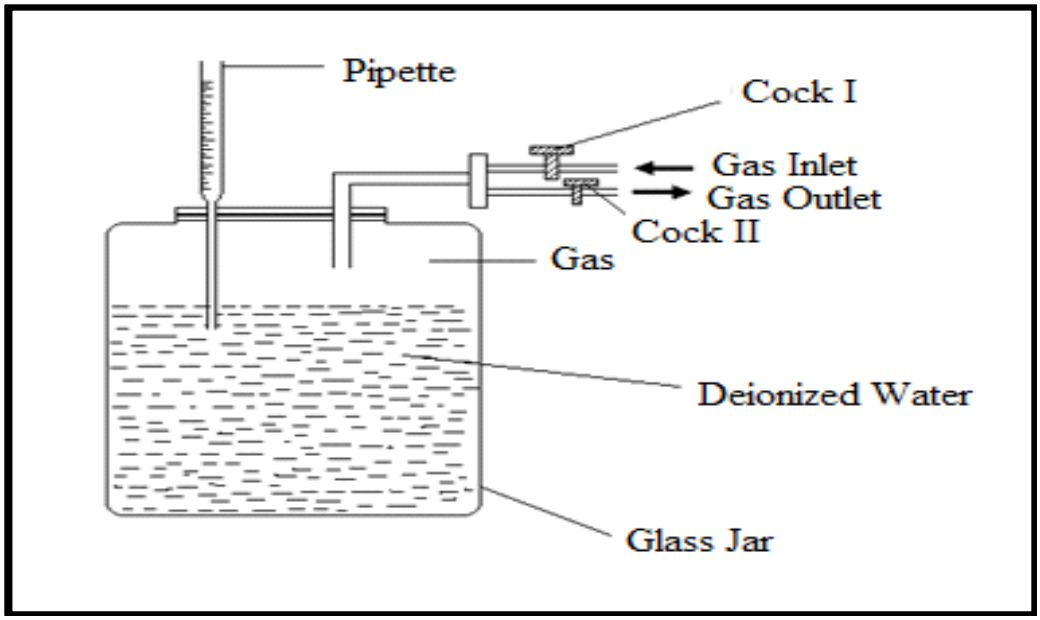

Figure 4(b): Concentration measuring system

Fig. 5 illustrates variations in resistance of the film with time after exposure to 1000 ppm of LPG at low temperature (160 ^{o}C). The sensing response of bare SnO_2 thin film for 1000 ppm of LPG purge in chamber shows small variation in resistance with time after exposure and inset figure shows the resistance decreases after exposing gas. The sensing response for SnO_2-Ag(1%) doped thin film at 1000 ppm of LPG exhibits improved response. Further, the sensing response for SnO_2-PANI(1%) thin film at 1000 ppm of LPG shows that resistance decreases sharply with time after exposure up to 3000 s and has better sensitivity.

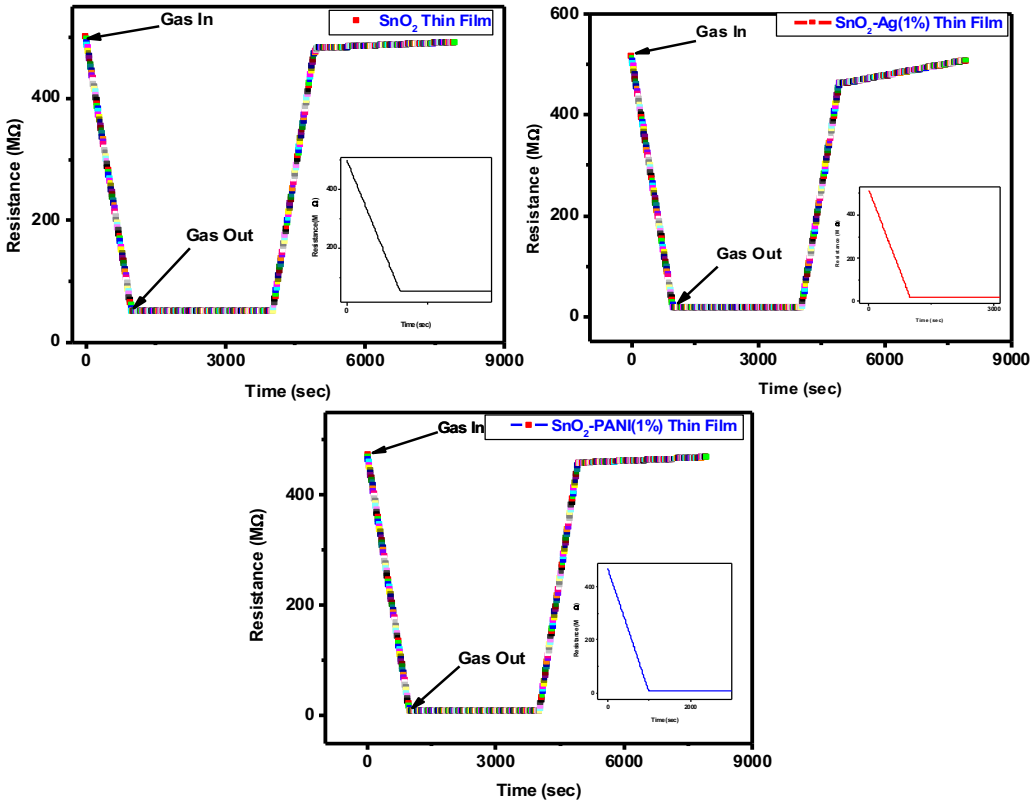

Figure 5: Variations in resistance of SnO_2, SnO_2-Ag and SnO_2-PANI thin film with time after exposing 1000 ppm of LPG

Fig. 6 exhibits the variations of average sensitivity with a concentration of LPG and it was found that as the concentration of LPG (ppm) increases, the average sensitivity of sensor increases linearly up to ppm of LPG later it increases slowly. The linear increment of the sensitivity of the sensor is a significant factor for device fabrication. The maximum sensitivity was obtained for 1000 ppm of LPG and was found to be ~ 67.

The gas sensing mechanism of SnO_2 thin film based sensor belongs to a surface controlled type, i.e. resistance change is controlled by surface area and the amount of chemisorbed oxygen. LPG consists of CH_4, C_3H_8 and some hydrocarbons. In each composition, the reducing hydrogen species are bound to carbon atom, therefore, LPG dissociates into the reactive reducing components hardly on the surface of the sensing element. As LPG is exposed to sensing element, the conductivity increases due to adsorption of oxide and capture more electrons that contribute to reducing in the current.

It was observed that as the concentration of LPG increases, the average sensitivity increases linearly in the beginning and later it becomes saturated. The linear relationship between sensitivity and gas concentration may be attributed to the availability of a sufficient number of sensing sites on the film to act upon the LPG. The low concentration implies a lower surface coverage of gas molecules, resulting in a lower surface reaction between the surface adsorbed oxygen species and the gas molecules. The increase in LPG concentration increases the surface reaction due to a large surface coverage. Further increase in the LPG concentration does not increase the surface reaction and eventually, saturation takes place.

Thus, the maximum sensitivity was obtained at a higher concentration of LPG i.e. 1000 ppm. The linearity of average sensitivity for the LPG suggests that the SnO_2-PANI composite film can be reliably used to monitor the LPG over this range of concentration as the lower explosive limit (LEL) for LPG is 4.0 Vol. % (1000 ppm) [23] therefore, response is measured up to 4.0 Vol. % in order to detect the LPG below LEL for safety requirement.

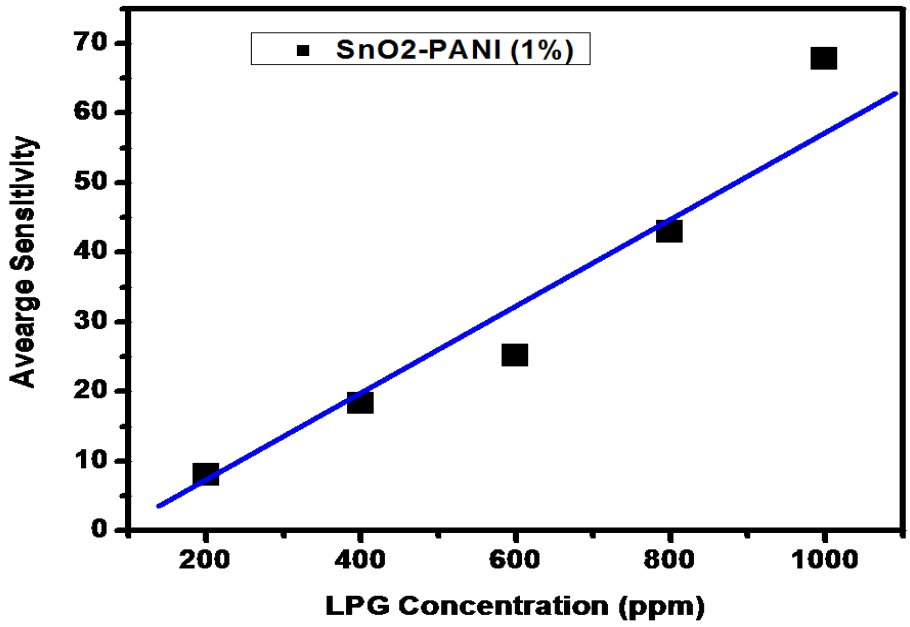

Figure 6: Variations of average sensitivity of SnO_2-PANI thin film in presence of LPG

The LPG sensing mechanism is based on the changes in the resistance of the tin oxide thick film. The oxygen adsorbed on the surface of the film influences the resistance of the tin oxide based sensor. Initially, oxygen from the atmosphere adsorbs on the surface of the film and extracts electrons from its conduction bands to form O_2^- species on the surface, consequently resistance increases. After that an equilibrium state is achieved between oxygen of SnO_2 and atmospheric oxygen and the value is stabilized.

$O_2(\text{gas}) \leftrightarrow O_2(\text{ads})$ (Thin Film Surface)

$O_2(\text{gas}) + e^- \leftrightarrow O_2^-$ (Thin Film Surface)

When the thin film is exposed to LPG, it reacts with the chemisorbed oxygen. On interaction with hydrocarbons (C_nH_{2n+2}) of LPG, the adsorbed oxygen is removed, forming gaseous species and water vapor. Consequently, the resistance changes, which is due to the change in the width of depletion layer after exposure to LPG. The overall reaction of LPG with the chemisorbed oxygen may takes place as shown below [24]:

$$C_nH_{2n+2} + O_2^- \rightarrow C_nH_{2n}O + H_2O + e^- \quad (4)$$

Where, C_nH_{2n+2} represent the various hydrocarbons. Due to the liberation of the electrons the resistance of the sensing film decreases drastically in the beginning due to rapid adsorption, afterwards it decreases slowly and finally becomes saturated. When the flow of LPG is stopped for the study of recovery characteristics, the oxygen molecules in air will be adsorbed on the surface of film, and the capture of electrons through the process indicated in equation, will increase the sensor resistance. As the sensing mechanism is based on the chemisorptions reaction that take place at the surface of the film, so increasing specific surface area of the sensitive material leads to more sites for the adsorption of the target gas. Larger the ability of the surface to receive the target gas, larger may be the change in resistance of the sensor, and hence, improvement in the sensing response of the device.

4. Conclusions

In this work, LPG sensors operating at low temperature were fabricated using SnO_2-PANI (1%) thin film sensor structures. The maximum sensing response of about 67 was obtained at low temperature towards 1000 ppm of LPG for 1% PANI doped sensor structure with a response and recovery times of 1000 sec and 900 sec respectively.

Acknowledgement

Dr. Rakesh Kumar Sonker acknowledges the financial support provided by the Science and Engineering Research Board, India, under the DST, SERB-National Post-Doctoral Fellowship (File No. PDF/2016/002827).

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