

# Study of room temperature LPG sensing behavior of polyaniline thin film synthesized by cost effective oxidative polymerization technique

Ravikiran B. Birajadar<sup>1,2</sup> · Deepak Upadhye<sup>2,3</sup> · Sandip Mahajan<sup>2,3</sup> · J. C. Vyas<sup>4</sup> · Ramphal Sharma<sup>2,3</sup>

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**Abstract** Polyaniline thin films doped with an inorganic acid were deposited on glass substrate using simple and cost effective oxidative polymerization technique. As-synthesized thin film of polyaniline was studied with different characterization techniques. The formation of polyaniline on glass substrate was confirmed by X-ray diffraction and UV spectroscopy. Surface morphological investigation was performed using scanning electron microscopy. Gas sensing behavior of polyaniline thin film was studied by I–V measurements before and after liquefied petroleum gas (LPG) exposure at room temperature, based on change in electrical resistance. The observed result shows polyaniline thin film sensor is efficient for LPG detection at room temperature.

## 1 Introduction

Liquefied petroleum gas (LPG) is a highly inflammable. It is widely used in industrial and domestic applications as a

fuel [1]. It is potentially hazardous because explosion accidents might be caused due to leakage. It has been reported that the sensible concentration of LPG leakage in air is very much greater than the lower explosive limit (LEL). There is a great demand and emerged challenges for gas sensors to monitor LPG for the purpose of control and safe applications in domestic and industrial area. Hence sensors are promising option to detect LPG under ambient conditions.

In this context gas sensors based on metal oxides such as SnO<sub>2</sub> [2], BaTiO<sub>3</sub>, WO<sub>3</sub> [3] and ZnO [4] have proved their excellence for detecting inflammable and toxic gases. However, it is noted that metal oxide gas sensors needs an elevated temperature (>400–450 °C) for its optimum operation [5]. Because of high operating temperature, metal oxide gas sensor requires an extra heating assembly with temperature controller system for its operation. This consumes the electricity and limits to miniaturize the device to make it portable for gas sensor application. Furthermore, gas sensor operation at elevated temperature causes gradual changes in properties of metal oxide semiconductor material itself, which influences the gas sensing properties of the device with time. To overcome these issues we are attempted to develop room temperature gas sensor based on conducting polymer.

Conducting polymers, which are stable, processible and have good mechanical properties leads to the possibility of new applications [6, 7]. Polyaniline is unique among the conducting polymer, doping of polyaniline with different acids viz. HCl, H<sub>2</sub>SO<sub>4</sub> etc. can vary its conductivity from insulator to conductor [8, 9]. The conducting polymers are advantageous as compared to the inorganic material in respect of their conjugated bond system [10], diversity, intrinsic conductivity, fast response, low cost, light weight, ease of synthesis, stability in air [11] and particularly their

✉ Ramphal Sharma  
rps.phy@gmail.com; ramphalsharma@yahoo.com

<sup>1</sup> Government Polytechnic, University Road,  
Pune 411016, MS, India

<sup>2</sup> Thin Film and Nanotechnology Laboratory, Department of  
Physics, Dr. Babasaheb Ambedkar Marathwada University,  
Aurangabad 431004, MS, India

<sup>3</sup> Department of Nanotechnology, Dr. Babasaheb Ambedkar  
Marathwada University, Aurangabad 431004, MS, India

<sup>4</sup> Technical Physics and Prototype Engineering Division,  
Bhabha Atomic Research Center,  
Trombay, Mumbai 400085, MS, India

sensitivity in gas sensor application at the room temperature [12].

As per best of our knowledge interaction of  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{H}_4$ ,  $\text{CO}_2$ ,  $\text{CO}$ , etc. with polyaniline thin film is reported in literature but effect of LPG exposure on polyaniline thin film is yet to be explored [13–16]. In present article, we have studied the effect of LPG exposure on polyaniline thin film at room temperature.

## 2 Experimental

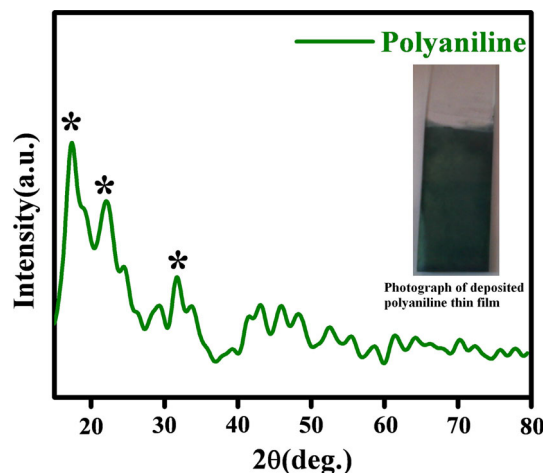
Oxidative polymerization technique was used to synthesize polyaniline thin film on glass substrate. 0.2 M aniline (distilled) was added in 1 M concentration of HCl solution with constant stirring at room temperature (29 °C). Then 0.25 M ammonium peroxydisulphate (APS) solution was prepared in aqueous medium. Prior to mixing, reactants were pre-cooled in an ice-bath container at  $4 \pm 2$  °C. Thereafter, 20 ml of APS was slowly added (drop wise) in 20 ml of as-prepared aniline solution with constant stirring at room temperature. Pre-cleaned glass substrate was inserted vertically in the mixed reactants for deposition of polyaniline film for 1 h [17].

The thickness of the as-deposited film was measured using gravimetric weight difference method and was found to be  $\sim 220$  nm. The as-deposited polyaniline thin film was studied using different characterization techniques. The structural study was performed through X-ray diffraction (XRD) using ‘Minislex model Rigaku’ having  $\text{CuK}\alpha_1$  radiations ( $\lambda = 1.5405$  Å). The optical study was done using UV–Vis (Perkin Elmer, Lambda-25) spectrophotometer in the wavelength range 300–900 nm. The surface morphological study was performed using scanning electron microscopy (SEM, JEOL). The gas sensing study of as synthesized polyaniline thin film carried in air and presence of LPG at room temperature by measuring (I–V) current–voltage characteristics. Data were recorded online using a computer interfaced with the system.

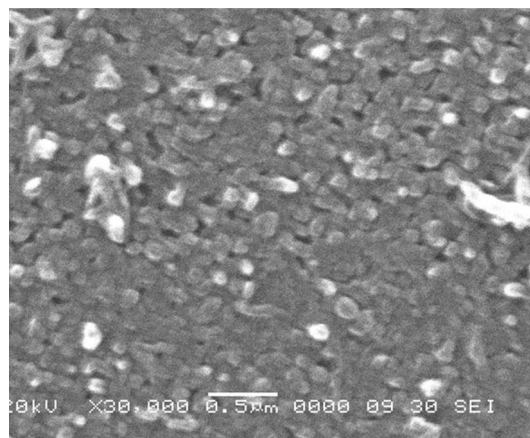
## 3 Results and discussion

### 3.1 Structural and surface morphological studies

Figure 1 shows the XRD pattern of polyaniline thin film deposited on glass substrate. The broad peaks between  $\sim 10^\circ$ – $35^\circ$  is observed and it is ascribed to the periodicity parallel and perpendicular to the polymer (PANI) chain [18, 19]. The low crystallinity of the polyaniline in the XRD pattern is due to the repetition of benzeoid and quinoid rings in polyaniline chains.



**Fig. 1** Representative XRD spectra of polyaniline thin film deposited on glass substrate

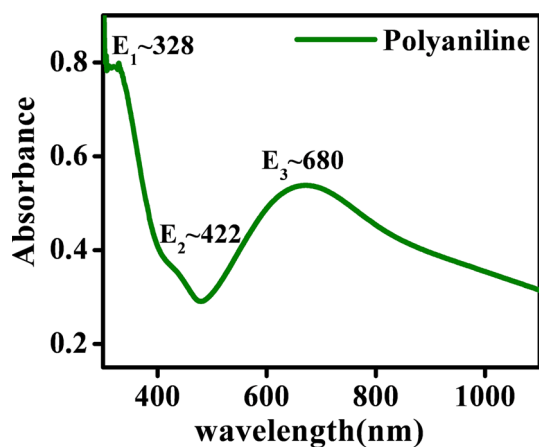


**Fig. 2** Representative SEM image of polyaniline thin film deposited on glass substrate

Figure 2 shows the SEM image of polyaniline thin film synthesized by Oxidative polymerization technique. It is observed polyaniline deposited on glass substrate have a porous and irregular granular morphology which are uniformly distributed over the entire glass substrate. It is evident from the literature that porous surface of film is essential for quick adsorption/de adsorption of gas which enhances response and recovery time.

### 3.2 Optical studies

Figure 3 represents the optical absorption spectrum of polyaniline thin film deposited on glass substrate. The spectrum of polyaniline shows three fundamental characteristics peaks at  $\sim 328$ ,  $\sim 422$  and  $\sim 680$  nm (broad). The absorption peak present at  $\sim 322$  nm is ascribed to the  $\pi$ – $\pi^*$  transitions of benzenoid ring while the peaks at  $\sim 422$

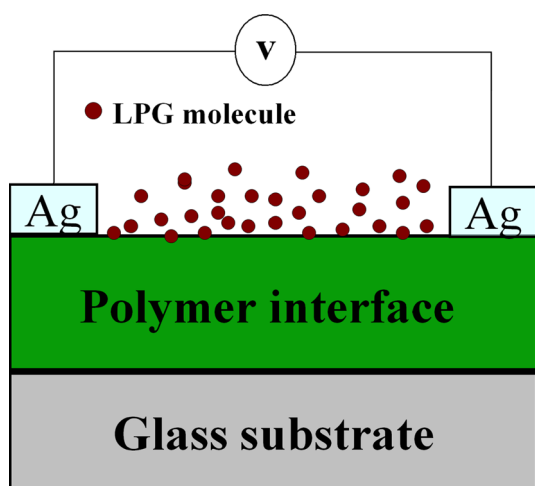


**Fig. 3** Representative optical absorbance spectrum of polyaniline thin film deposited on glass substrate

and ~680 nm are attributed to the polaron-  $\pi$  transitions [20]. However, ~422 and ~680 nm peaks represent the polaron formation in HCl doped polyaniline [17, 21].

### 3.3 Gas sensing studies

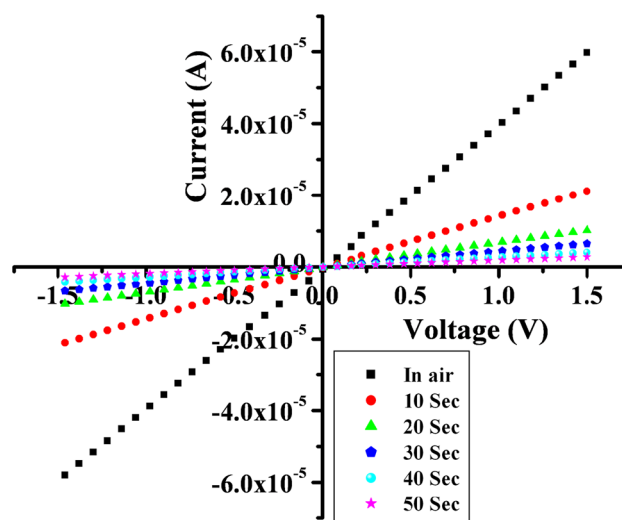
The LPG gas sensing study of HCl doped polyaniline thin film was performed at room temperature by measuring I–V characteristics in air and LPG. Initially the sample of polyaniline was taken having the dimensions  $1 \times 1 \text{ cm}^2$ . Silver contacts were created by Hind Hivac vacuum coating unit on above polyaniline thin film sample. Two leads were taken out for the electrical measurement, whole sensor device configuration represented in Fig. 4. Before exposing to LPG gas, the polyaniline thin film was allowed to stable for more than 30 min and the stabilized resistance was taken as the resistance in air ( $R_a$ ). Known concentration of LPG (100–600 ppm) was injected into the test



**Fig. 4** Schematic representation of sensor device

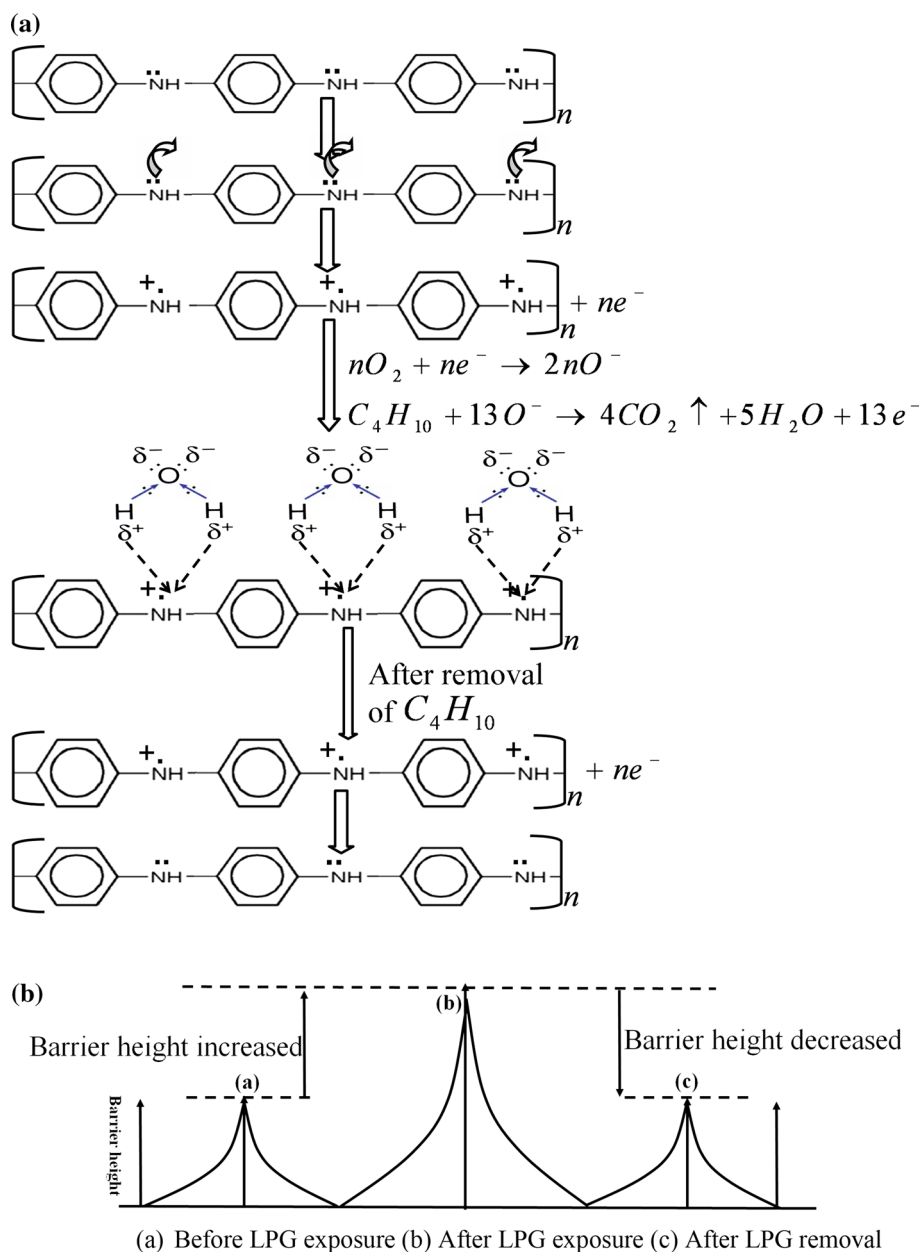
chamber with the help of micro-syringe. After the exposure to the LPG the film resistance was measured with an interval of 10 s until it reaches the steady state value. The response of a sensor was calculated from the change in the resistance of film with time of exposure of LPG at room temperature. The gas response was monitored in terms of the normalized resistance ( $R_g/R_a$ ), where  $R_g$  is the resistance of the sensor in presence of LPG gas and  $R_a$  is the resistance of the sensor in air atmosphere.

Figure 5 shows I–V characteristics of polyaniline thin film at room temperature. We found maximum response for 300 ppm of LPG exposed to polyaniline thin film. It is observed that the resistance of the polyaniline film increases on LPG (~300 ppm) exposure and the current drops drastically [22]. This type of behavior of polyaniline thin film is reported for  $\text{NH}_3$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{NO}_2$  gases [23–28]. It is well known fact that polyaniline emeraldine salt is more conducting than emeraldine base. After doping with HCl acid emeraldine base is converted into emeraldine salt which is green (photograph of deposited polyaniline thin film shown in inset of Fig. 1). However in present case it might be possible that when polyaniline sample interact with LPG, electron is liberated from lone pair of each nitrogen (N) atom from polymer chain. These electrons reduce the oxygen molecules in air to  $\text{O}^-$ . This  $\text{O}^-$  ion oxidizes butane ( $\text{C}_4\text{H}_{10}$ ) present in LPG to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$  with liberation of an electron. As in  $\text{H}_2\text{O}$ , oxygen is more electronegative it attracts the bonding pair of OH bond towards itself giving net partial negative charge ( $\delta^-$ ) on O atom and positive charge ( $\delta^+$ ) on each H atom. These polarized  $\text{H}_2\text{O}$  molecules are attracted towards the electronegative nitrogen atom of polyaniline giving partial polar bond between H and N as shown in Fig. 6a. As a



**Fig. 5** I–V characteristics of polyaniline thin film recorded at room temperature in air and 300 ppm concentration of LPG

**Fig. 6** **a** LPG sensing mechanism of polyaniline thin film deposited on glass substrate. **b** Schematic representation of variation in barrier height across polyaniline thin film in air, in LPG atmosphere and after removal of LPG

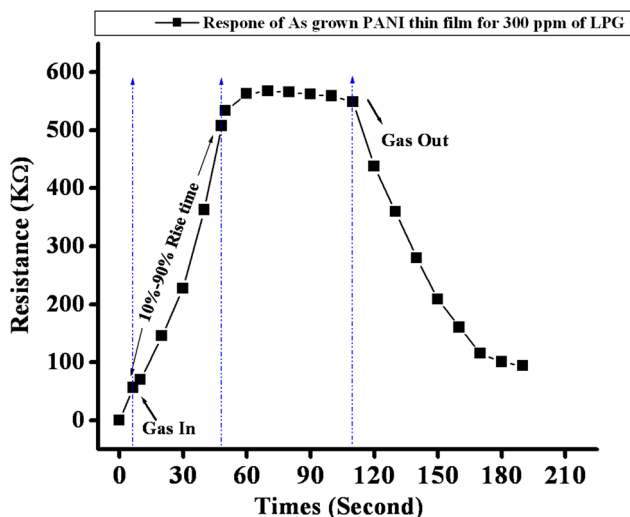


result of this partial bonding between H and N increases the inter chain distance in polyaniline structure. Due to this swelling behavior, it affects the electron hopping between adjacent chains and increases the barrier height across polyaniline thin film as shown in Fig. 6b. At this point emeraldine salt is converted into emeraldine base. After removal of LPG from the test chamber, liberated electrons of polyaniline regained from the oxidation of butane converts again emeraldine base into emeraldine salt which means sensor has recovered. This whole sensing mechanism is explained diagrammatically in Fig. 6.

The another possible reason for increase in resistance of polyaniline thin film after interaction of LPG is that, the

length of backbone is an integral characteristic that determines the physical properties of a polymer chain. The length of polymer chain or number of monomers in a polymer affects the different physical properties of the polymer. As the chain length increases, melting point, boiling point and viscosity increases with decrease in mobility. This change in resistance is attributed to the fact that when LPG interacts with polyaniline thin film, the mobility decreases and resistance across the sample increases.

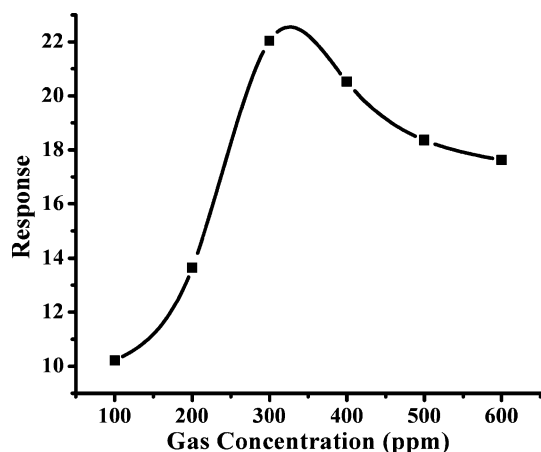
Figure 7 shows the variation in resistance of polyaniline thin film in LPG atmosphere with time. It is observed from graph as the LPG injected in test chamber the magnitude of



**Fig. 7** Variation in resistance of polyaniline thin film as function of time in presence of 300 ppm LPG

resistance increases and reaches to steady state due to conversion of polyaniline emeraldine salt to emeraldine base as discussed above. We have also estimated the response speed by considering the 10–90 % of rise time and recovery time, which is found to be  $\sim 42$  and  $\sim 80$  s respectively. This whole mechanism indicates polyaniline thin film exhibits excellent sensing behavior to LPG at room temperature.

The variation in response of the polyaniline thin film as a function of LPG gas concentration at room temperature is shown in Fig. 8. The plot shows the inverted bell shape structure. It is observed that response increases with increase in gas concentration from 100 to 300 ppm and then decreases further with increase in gas concentration. The low gas concentration implies a lower surface coverage by the gas molecule which tends to lower surface reaction



**Fig. 8** Response of polyaniline thin film towards different gas concentrations (100–600 ppm) of LPG

between film and target gas molecules. The increase in gas concentration increases the surface reaction due to larger surface coverage. Further increase in gas concentration does not increase the surface reaction and finally saturates the surface; therefore response decreases with further increase in gas concentration [29].

## 4 Conclusions

In the present work polyaniline thin films were synthesized by simple cost effective Oxidative polymerization technique on glass substrate. The XRD spectra show the amorphous nature of polyaniline thin film on glass substrate. SEM study shows that polyaniline thin films prepared by present method are porous in nature with granular structure. Due to porous structure polyaniline thin film shows an excellent response to LPG gas at room temperature. It was observed that resistance across polyaniline thin film increases with LPG interaction. The polyaniline thin film exhibits excellent response and recovery behaviors.

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