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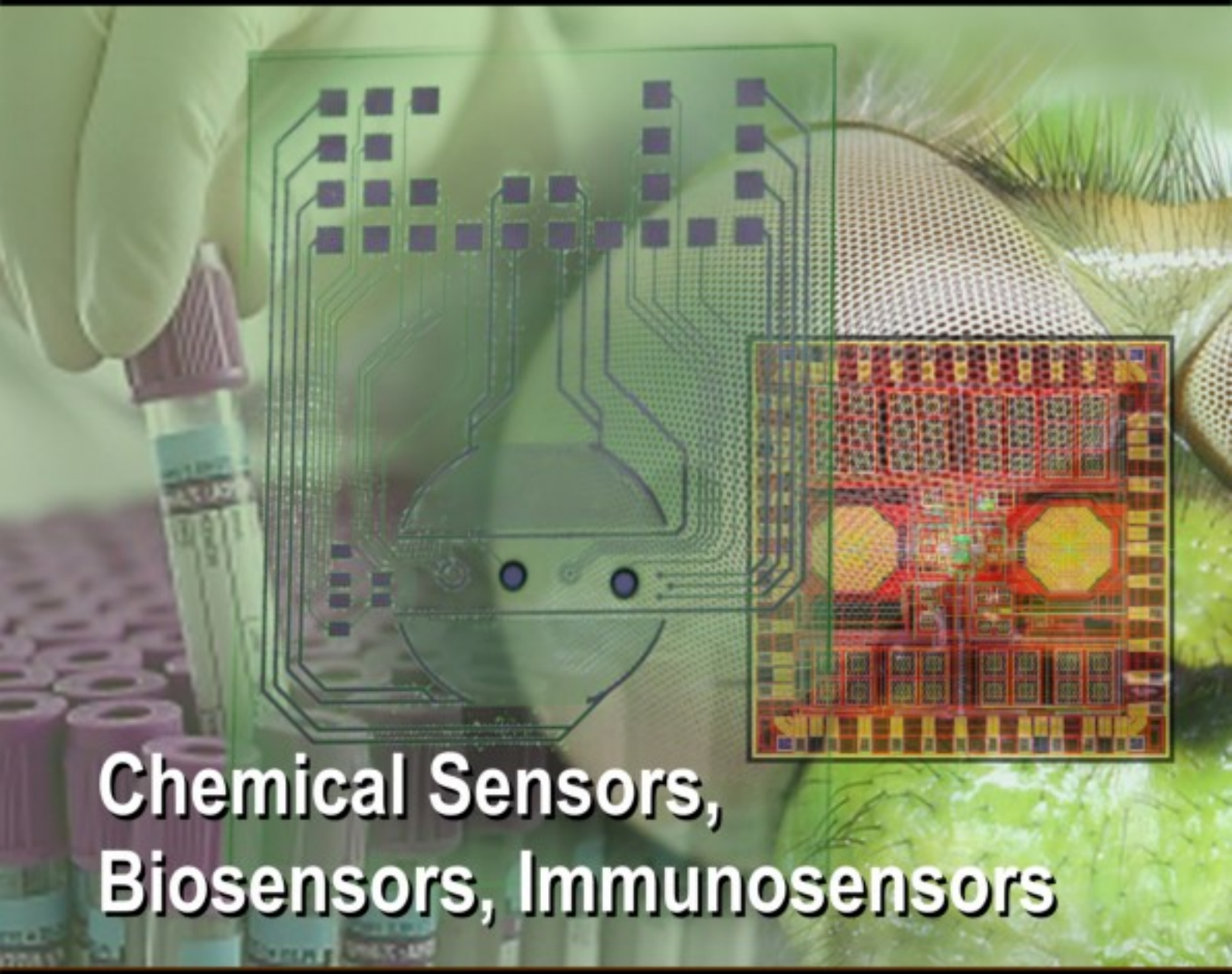

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Ammonia Gas Sensing Characteristics of Chemically Synthesized Polyaniline Matrix

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Abstract: In present investigations polyaniline matrix was synthesized by oxidative polymerization (chemically synthesized). The polyaniline matrix was prepared on Si- substrate. The active layer of PANI as a sensor was fabricated with the help of spin-coating technique. The structural insight into the synthesized polyaniline matrix was sought by Fourier Transform Infrared (FTIR) spectroscopy. The mechanism of formation of polyaniline was also confirmed by UV spectroscopy. The electrical conductivity was measured by four probe method at room temperature. Ammonia gas sensing characteristics of the synthesized polyaniline matrix was studied by measuring the change in electrical resistance on exposure to ammonia gas at different concentrations from 100 to 500 ppm. The polyaniline matrix exhibits excellent sensing behavior for ammonia gas. *Copyright © 2010 IFSA.*

Keywords: Polyaniline, Oxidative polymerization, Ammonia sensor, Matrix

1. Introduction

Extensive research has been carried out in the field of development of gas sensors using conducting polymers like polyaniline (PANI), polypyrrole (Ppy), polythiophene, etc [1-6]. Among these conducting polymers PANI has attracted greater attention because of its low density, good electrical conductivity and environmental stability. An important feature of PANI is that, it can occur in several redox forms. This property provides a basis for the development of sensors for controlling both donor

and acceptor gases. Polyaniline was found to be a suitable material for gases such as ammonia because of its higher sensitivity and shorter response time.

Conducting polymers such as polypyrrole, polyaniline, polythiophene, and their derivatives have been investigated for gas sensing applications for more than 20 years. Gas sensors based on conducting polymers have many features such as their higher sensitivity on changes of electrical or optical properties when exposed to various types of gases or liquids. The sensor prepared by conducting polymer is superior to its metal oxides counterpart due to its superior properties like high sensitivities, short response time, and room temperature operation. In contrast, metal oxides generally operate at elevated temperatures around 300 ^{o}C [7, 8]. Conducting polymers can be easily synthesized through chemical synthesis processes; this fact motivates successful designs of different types of sensors based on conducting polymers.

From the last decade, conducting polymers, such as polyaniline (PANI) and their derivatives have attracted considerable attention due to the wide variety of technological importance. The unique electrical, optical and chemical properties offer these materials to be used in gas sensing, anticorrosion surface coatings [9, 10], electromagnetic shielding [11], rechargeable polymeric batteries [12], photovoltaic's [13], polymer sensor and actuators etc. Moreover, properties of conducting polymers are originated from their highly regulated molecular and morphological structures. The electrical conductivity, appearance, and morphology of conducting polymers are affected by the conditions of polymerization [14, 15]

An advantage of the polyaniline thin film as a material for active layer in sensor is that, their conductivity changes significantly in the presence of analyte gases at room temperature. This fact, promises successful designs of different types of sensor transducers based on conducting polymer like polyaniline [16]. The polyaniline with their unique structural and electrical properties provide a special case of conjugated polymers. From the sensor point of view a very important feature of polyaniline is that, it can occur in several redox forms. This property provides a basis for the development of sensors [17, 18]. Gas monitoring applications are classified by concentration range in parts per million (ppm). Various toxic gases like carbon monoxide (CO), chlorine (Cl), nitrogen oxide (NO_2), ammonia (NH_3) are hazardous if these gases are present above threshold level in the environment [19, 20].

The present investigation deals with the synthesis of PANI matrix by oxidative polymerization technique. The active layer of PANI as a sensor was fabricated with the help of spin-coating technique. The physiochemical characterization of PANI was performed and ammonia sensing characteristics of synthesized PANI matrix was studied.

2. Experimental

2.1. Synthesis of Polyaniline (PANI) by Oxidative Polymerization

Polyaniline the environmentally stable polymer was prepared in our laboratory by chemical synthesis route .The polyaniline was synthesized by oxidative polymerization of aniline hydrochloride using ammonium per sulfate as an oxidant.

Fig. 1 indicates the oxidation of aniline hydrochloride with ammonium per sulfate. In this process aniline hydrochloride (2.59 gm) and ammonium per sulfate (5.71 gm) was dissolved in 50 ml distilled water separately. Then both the solutions were mixed to initiate process of polymerization. As the polymerization of aniline is an exothermic reaction, temperature rises with the progress of polymerization. After stirring for 1 hour, the solution was kept to rest over a night. The precipitate was filtered and washed with 1M HCl; followed by further washing with deionized water. The resulted

emeraldine salt was subsequently treated with NH_4OH (1M) to make it emeraldine base, which showed better solubility in an appropriate solvent. This precipitate was washed with water and acetone and dried for 6 hour [21]

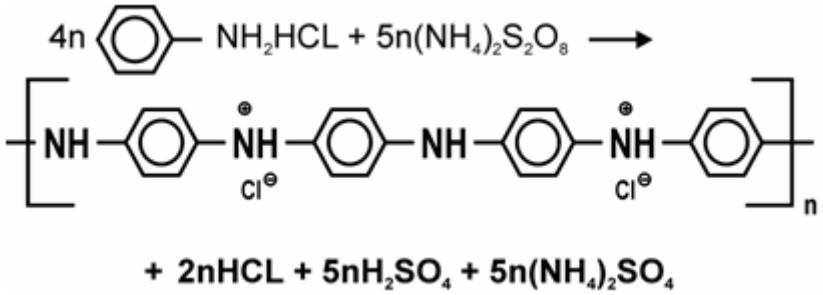

Fig. 1. Oxidation of aniline hydrochloride with ammonium peroxidisulphate yields polyanilineю

2.2. Formation of Film on Si Substrate

For the formation of PANI film the silicon substrate with silver pasted electrodes was used [11]. The NMP (n-methylpyrrolidone) was used as a solvent to prepare a paste of synthesized PANI powder. This paste was applied on substrate so as to form a PANI film by spin coating technique. Initially the speed of spin machine was kept at the 500 rpm for 20 second and 1200 rpm for 50 second [22]. The prepared PANI film was further used as an active layer for ammonia sensor.

3. Results and Discussion

The polyaniline was synthesized by oxidative polymerization and its matrix was formed by spin coating techniques on Si substrate. The polyaniline matrix was subjected to spectral and electrical characterization. Further its ammonia sensing characteristics was studied.

4. Fourier Transform Infrared Spectroscopy (FTIR) Analysis of PANI Matrix

The FTIR spectrum of polyaniline matrix is shown in Fig. 2.

This study is useful to determine the chain orientation, structure of polymer and also used to elucidate mechanism of polymerization. The FTIR analysis was done by Nicolet 380 spectrophotometer in our laboratory. This IR spectroscopic characterization shows following bands at 2950 cm^{-1}(-NH-),1350 cm^{-1}(-C-N) and 1600-1420cm^{-1} (C=C of phenyl ring).The peak at 1500 cm^{-1} may be due to Benzenoid ring. This shows very good agreement with earlier reported results [23].

5. UV-Visible Analysis of PANI Film

The UV –Visible absorption spectrum of the synthesized PANI matrix at room temperature is shown in Fig. 3.

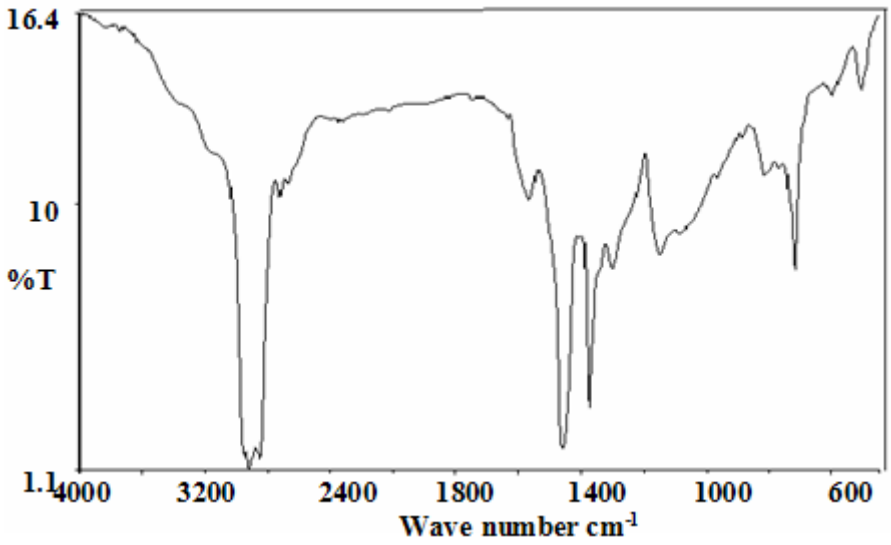

Fig. 2. FTIR spectrum of PANI matrix.

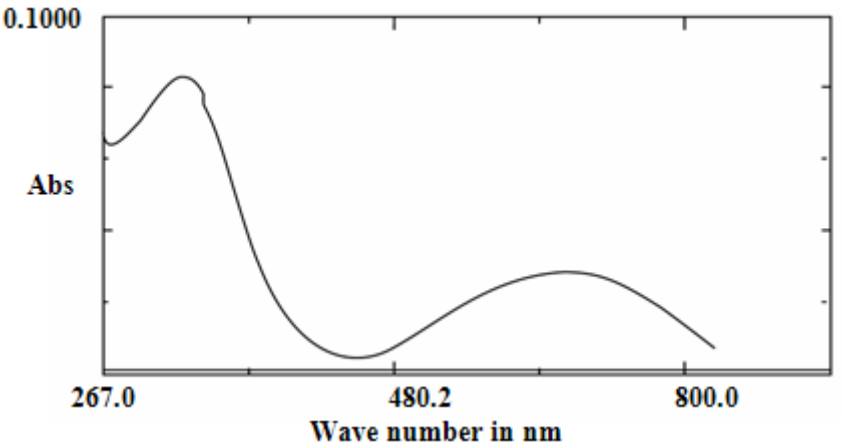

Fig. 3. UV-VIS spectra of Polyaniline matrix.

The peak at 300 nm corresponds to the π-π* transition of the benzenoid ring, while the sharp trough at 440 nm can be assigned to the localized polaron which are characteristics of the protonated Polyaniline, together with extended tail nearly at 720 nm representing the conducting ES state of Polyaniline. This confirms the formation of polyaniline matrix.

6. I-V Characteristics of PANI Film

The I-V characteristics of the PANI film was studied by indigenously developed I-V measurement system. A linear relationship of I-V curve (Fig. 4) confirms the ohmic behavior of the matrix [19].

7. SEM Analysis of HCl doped PANI

The surface morphology of the HCl doped PANI was studied by Scanning Electron Micrograph (SEM). The SEM image of HCl doped PANI matrix is as shown in Fig. 5.

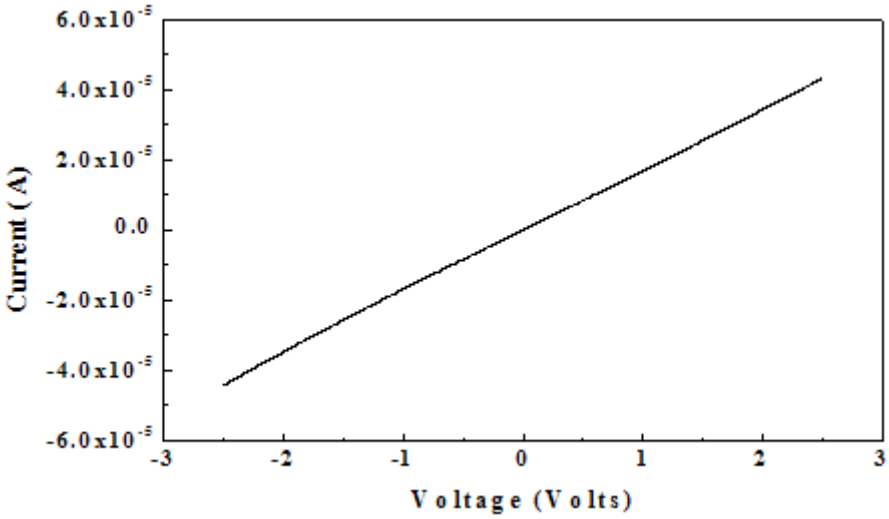

Fig. 4. I-V Charactristics of PANI matrix.

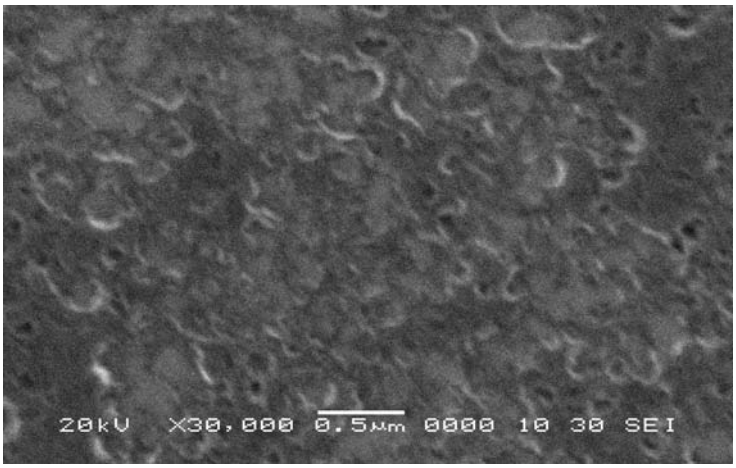

Fig. 5. SEM image of HCl doped polyaniline matrix.

The synthesized matrix exhibits uniform, porous, and granular surface morphology, which is suitable for gas sensing applications [5, 24].

8. Ammonia Gas Characteristics of Polyaniline Matrix

The ammonia gas sensing characteristics of polyaniline matrix was studied under static gas chamber by indigenously developed system. The sensing element was kept on Four-Probe assembly in the gas chamber. The known volume and concentration of ammonia gas was introduced in the chamber which allows polyaniline matrix to interact with ammonia gas of desire concentration. The corresponding change in surface resistance of polyaniline matrix was recorded as a function of time.

One of the possible mechanisms of interaction of PANI with ammonia is can be explained as illustrated in Fig. 6.

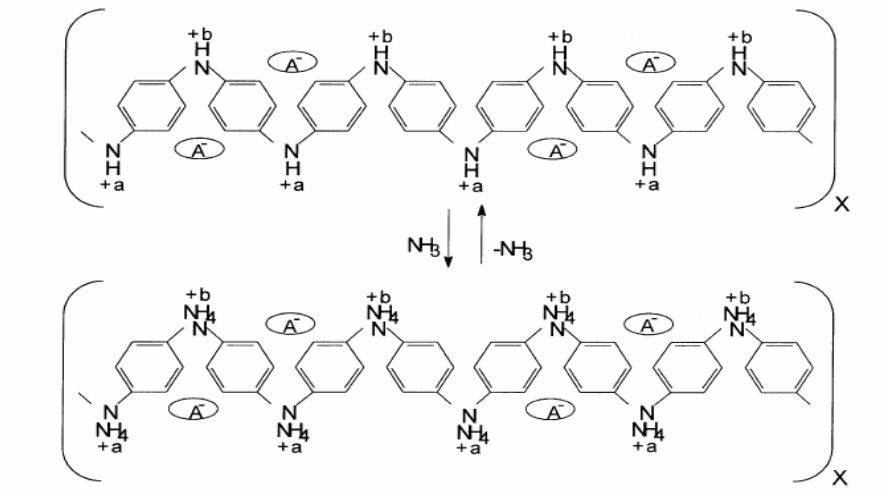

Fig. 6. Mechanism of interaction between PANI and NH_3.

Fig. 7 shows the ammonia gas sensing characteristic of polyaniline matrix. The change of resistance of polyaniline matrix when it is exposed to ammonia gas is demonstrated interms of ΔR \ R0 (%) where R0 is the initial resistance of the polyaniline matrix and R is the change of resistance of the matrix when it is exposed to ammonia gas. The concentration of ammonia gas was varied from 100 ppm to 500 ppm. We observed increase in the resistance of polyaniline matrix when it was exposed to ammonia gas. The nitrogen atom of the ammonia molecule is responsible for coordinating with the dopants proton enabling its sensing characteristics. The nitrogen-free doublet of ammonia molecules can establish a coordinate bonding with the free atomic orbital of the dopants proton [25]. This reaction leads to the deprotonation of polyaniline nitrogen atoms, supporting the disappearance of charge carriers which causes increase in electrical resistance. When polyaniline interacts with ammonia, the following reversible reaction occurs.

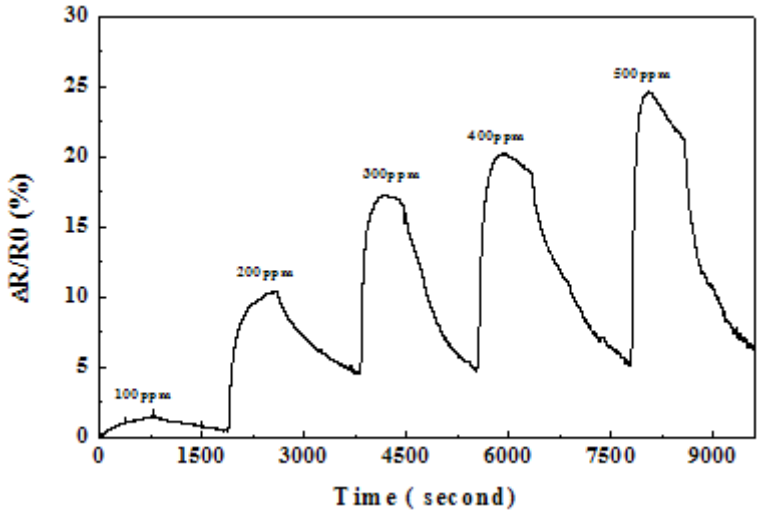

Fig. 7. Ammonia gas sensing characteristics of PANI matrix.

$$PANIH+ + NH_3 \leftrightarrow PANI + NH_4+$$

In the presence of ammonia this reaction goes predominantly towards the right, as NH_3 molecules up protons from the polyaniline, thus forming energetically more favorable NH_4+. In fact, in this case we

are dealing with chemical bonding [20]. This confirms the fact that the process of ammonium ion (NH4+) formation is accompanied by an energy gain because it has a more stable tetrahedral configuration. On the other hand, the reverse process (gaining protons by PANI) is also energetically favorable. Its nitrogen atoms have sp_2 hybridized electron orbital so formation of a third bond with a hydrogen atom is accompanied by a lowering of the total energy of the polymer chain. Thus when ammonia interacts with polyaniline, two competing processes of proton gain (by ammonia and by PANI) occur. Since the heat of ammonia adsorption onto polyaniline is low the probabilities of the two processes are more or less the same. The result is that ammonia gets adsorbed onto polyaniline matrix.

9. Conclusions

In the present work the conducting polyaniline was synthesized at room temperature by oxidative polymerization method. The spin coating technique was used to deposit an active layer of a polyaniline matrix on Si substrate. The FTIR spectra confirms the polymer formation by showing the -N-H-, -C-N- and C=C bonds in the backbone of polymer chain. The UV-Visible analysis of PANI matrix confirms the ES state of polyaniline. The PANI matrix shows excellent response to ammonia gas at ambient conditions. It was observed that the resistance of electroactive polymer PANI matrix increases with increase in concentration of ammonia.

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