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Ammonia Gas Sensing Characteristics of Spin Coated Polyaniline Films

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ABSTRACT

The conductive layer of emeraldine base polyaniline (PANI) thin film coated on silicon has successfully tested for ammonia. The bulk PANI powder was synthesized by oxidative polymerization of aniline using ammonium peroxidisulfate in an acidic medium and dissolved in N-methyl pyrrolidone (NMP) for coating the thin film on Silicon using spin coater. FTIR, UVvisible, and SEM were used to characterize the PANI thin film. The electrical conductivity of the PANI films has been studied by measuring the change in electrical conductivity by Four Probe Set up on exposure to ammonia gas (NH_3) at different concentrations from 100 ppm to 500 ppm.

Indexing terms/Keywords

Conducting polymers; Polyaniline; Ammonia gas sensor; FTIR; UV; SEM.

Academic Discipline And Sub-Disciplines

Physics; Gas sensor

SUBJECT CLASSIFICATION

Spectroscopy; electrical properties

TYPE (METHOD/APPROACH)

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1. INTRODUCTION

The environmental importance is well understood and much research has been focused on the development of suitable gas sensitive materials like PANI, Polypyrrole, polythiophene etc. Among all these conducting polymers PANI has attracted greater attention due to its low density, better electrical conductivity and environmental stability [1]. The conducting polymer plays an important role in microelectronics and nanoelectronics applications such as sensors, organic

displays, TFTs, molecular recognition, energy storage, electromagnetic interference [2-5]. This can be of particularly importance as ammonia gas sensors are used in different applications such as industrial process, food technology, fertilizers, clinical diagnosis, farms and environmental pollution monitoring. Conducting polymers polypyrrole and PANI are widely investigated for NH_3 sensing [6]. The intrinsically conducting polymers are π-conjugated macromolecules which indicate the change in optical and electrical properties, after de-doped by some chemical agent. These property changes can be observed at ambient temperature, when they are exposed to lower concentrations of the chemicals, which make them attractive candidates for gas sensing elements [7]. PANI undergoes a non-redox reversible de-doping process based on simple acid base chemistry, making it possible to control over the properties like electrical conductivity, optical activity and sensor activity, and thus making it unique in the class of conjugated polymers [8]. The most common form of PANI is in green protonated emeraldine that has conductivity on a semiconductor level (of the order of 10^0 S cm^{-1}). This emeraldine base is of many orders higher in magnitude than that of common polymers $<10^{-9}$ S cm^{-1}) but lower than that of typical metals ($>10^4$ S cm^{-1}). Protonated PANI (e.g. PANI hydrochloride) gets converted to a non-conducting blue emeraldine base when treated with ammonium hydroxide. The polymerization of aniline is the simple method for the preparation of PANI. The efficient polymerization of aniline is achieved in an acidic medium, where aniline exists as an anilinium cation. A variety of organic and inorganic acids of different concentrations may be used in the synthesis of PANI; the resulting PANI, protonated with various acids, will have different solubility, conductivity and stability [9].

This paper reports the synthesis of polyaniline through the simple oxidative polymerization reaction as shown in Figure 1 and further fabrication of spin cast PANI films has been carried out using the synthesized PANI powder. The physiochemical characterization of PANI was performed and ammonia sensing behavior of synthesized PANI film was studied.

2. EXPERIMENTAL PROCEDURE

2.1 SYNTHESIS OF CONDUCTING POLYANILINE

The PANI synthesis is based on mixing aqueous solutions of aniline hydrochloride (C_6H_8CIN) and ammonium persulphate $(NH_4)_2S_2O_8$at ambient conditions, followed by the separation of PANI hydrochloride precipitate by filtration and drying. For this synthesis, we have selected hydrochloric acid in equimolar proportion to aniline i.e. aniline hydrochloride has been used as a monomer. The handling of solid aniline salt was preferred to liquid aniline from the point of view of toxicity hazards. Peroxydisulfate is the most commonly used oxidant, and its ammonium salt has been preferred because of its better solubility in water. The concentration of aniline hydrochloride was set to 0.2 M. The stoichiometric Peroxydisulfate/aniline ratio of 1:25 is optimized to obtain the best yield of PANI. The oxidative polymerization process is carried out by stirring the solution of Aniline hydrochloride and Ammonium peroxydisulfate dissolved in distilled water for an hour at room temperature and overnight aging. The PANI precipitate formed after overnight aging have been collected and washed thrice with 100ml portions of 0.2M HCl, and similarly with acetone. Washing the PANI precipitate with 0.2M HCl removes oxidant, residual monomer and its decomposition products. A final washing was done with acetone that removes low molecular weight organic intermediates and oligomers. It also prevents the aggregation of PANI precipitate during drying, and the product was obtained in a fine powder form. This synthesized greenish polyaniline (emeraldine) hydrochloride powder is then dried in air and stored in a container [9].

2.2 DEPOSITION OF PANI FILM

The emeraldine base form of PANI was dissolved in N-methyl pyrrolidone (NMP) to make a viscous solution. By using this solution, the PANI film was deposited by spin coating technique on silicon substrate at 500 rpm for 20 second and at 1200 rpm for 50 second. Further, the electrical contacts were made on the polyaniline film by metal wire and silver paste [1].

2.3 GAS SENSING STUDY OF PANI FILM FOR AMMONIA

The ammonia sensing property of a polyaniline thin film was studied by using the gas sensor set up. The prepared PANI film was placed inside the gas testing chamber and closed airtight. The subsequent change in the resistivity of the film was measured by passing ammonia gas through the chamber at a fixed flow rate and the results are reported in terms of the change in the resistivity at a fixed rate [10].

SENSING ACTIVITY OF POLYANILINE

The normalized response (S) of a gas sensor may be calculated as the ratio of the change of resistivity due to exposure to the test gas to the resistivity of the sample in air.

$$S = (R_{gas} - R_{air}) / R_{air}$$

Where (R_{air}) is the resistance monitored in the air (in the absence of NH_3 gas), and (R_{gas}) is the resistance monitored in the presence of NH_3 gas [10].Gas monitoring application is classified by concentration range in parts per million(ppm) [11].

3. RESULTS AND DISCUSSION

The PANI powder was synthesized by oxidative polymerization and its thin film is formed by spin coating technique on silicon substrate. The prepared polyaniline thin films were analyzed by using Fourier Transform Infrared (FTIR) Spectroscopy and UV-Visible spectroscopic techniques. Ohmic behavior of PANI film was studied by using current-voltage

(I-V) characteristics. Surface morphology of the prepared PANI film was observed with Scanning Electron Microscopy (SEM).Further ammonia sensing behavior of PANI film was studied with gas sensing setup.

3.1 FTIR STUDIES

The IR spectrum of PANI deposited on Si-substrate is exhibited in Figure 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. The IR spectrum shows N-H stretching vibration band at 3557 cm^{-1}. The characteristic band appeared at 1583 cm^{-1} indicates nitrogen bond between benzoid and quinoid rings respectively. The band at 1668 cm^{-1} corresponds to C=C stretching. The peak at 1305 cm^{-1} is assigned to C-N stretching of tertiary aromatic amine. The peak at 815 cm^{-1} is due to an aromatic =C-H plane bending. [12-14].

3.2 UV-VISIBLE ANALYSIS OF PANI FILM

The Figure 3 shows UV spectra of PANI film measured by Chemto Spectra Scan UV2700. The peak at 320 nm is due to the excitation of benzoid rings in PANI, while a peak at 440 nm is attributed to exitonic transition of quinoid rings. The broad peak at 620 nm is related to the doping level and the formation of polarons of the conducting form together with extended tail nearly at 740 nm representing the conducting ES (Emeraldine Salt) state of Polyaniline, this confirms the formation of polyaniline film. [1, 8].

3.3 I-V CHARACTERISTICS OF PANI FILM

The I-V characteristic of polyaniline film was studied by measuring the voltage with varying current. Figure 4 shows I-V characteristics of PANI film. The nature of graph revels that the polyanilne film has an ohmic behavior [8, 10].

3.4 SEM ANALYSIS OF HCL DOPED PANI

The surface morphology of the HCl doped PANI film on silicon surface was studied by Scanning Electron Micrograph (SEM) (Figure 5). The synthesized film exhibits porous surfaces and are uniform in nature, which is one of the essential conditions for gas sensors. [3,8].

3.5 AMMONIA GAS SENSING BEHAVIOUR OF POLYANILINE FILM

The ammonia gas sensing behaviour of polyaniline film was studied under static gas chamber by indigenously developed system. The sensing element was kept on Four-Probe assembly inside the gas chamber. The known volume and concentration of ammonia gas was introduced in the chamber which allows polyaniline to interact with ammonia gas of desire concentration. The corresponding change in surface resistance of polyaniline film was recorded as a function of time [1, 15]. Polyaniline is a polymer, which shows a reversible acid/base doping process. In the acid doped or emeraldine salt (ES) state of polyaniline is conductive, while in the emeraldine base (EB) or dedoped state of polyaniline is insulating. The emeraldine salt on treatment with base (ammonia vapors) can be converted to emeraldine base, which on reaction with acid (HCl vapors) gets reconverted to emeraldine salt. Thus it shows that these two states are interconvertable as shown in the following Figure 6 [16]. The change of resistance of polyaniline film when it is exposed to ammonia gas is demonstrated in terms of $\Delta R \setminus R_0$ (%), where R_0 is the initial resistance of the polyaniline film and R is the change of resistance of the film 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 film when it was exposed to ammonia gas as shown in Figure 7 [1]. When polyaniline interacts with ammonia, the following reversible reaction occurs.

$$PAH^{+} + NH_3 \leftrightarrow PA + NH_4^{+} \qquad (1)$$

Where, PA and PAH^{+} are the initial undoped repeated block and proton-doped repeated block of polyaniline chains respectively. In the presence of ammonia, this reaction goes predominantly towards the right, as NH_3 molecule take up protons from the polyaniline, and forming energetically more favourable ammonium NH_4^{+}. It is the PANI de-doping (de-protonation) reaction. But in the air (with no ammonia) the above reaction (1) begins towards left. Ammonium de-composes into ammonia and protons which being added to PANI molecules, restore the initial level of doping. In this way reversibility of the ammonia on PANI occurs [17]. Thus when ammonia interacts with polyaniline, two competing processes of proton gain (by ammonia and by PANI) occurs. The probabilities of the two processes are more or less the same because the heat of ammonia adsorption onto polyaniline is low. The results revealed that ammonia gets adsorbed onto polyaniline film. It shows maximum responses at higher concentrations of ammonia because the number of molecules striking over the polymer increases as the concentration increases from 100 ppm to 500 ppm [1, 15].

4. CONCLUSION

In the present work the conducting polyaniline was successfully synthesized by oxidative polymerization method at room temperature. The spin coating technique was used to deposit an active layer of a polyaniline on Silicon substrate. Chemically deposited PANI single film was employed as sensing element to detect NH_3 molecules. 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-

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Visible analysis of PANI film confirms the ES state of polyaniline. The PANI film shows excellent response to ammonia gas. The PANI film is used as a sensing material for development of a sensitive ammonia gas sensor based on a simple and low cost sensor electrode model. The detection sensitivity of the sensor was calculated by the surface resistance as a function of the concentration of ammonia gas under the ambient conditions. It was observed that the resistance of electro active polymer PANI film increases with increase in concentration of ammonia.

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FIGURE/CAPTIONS

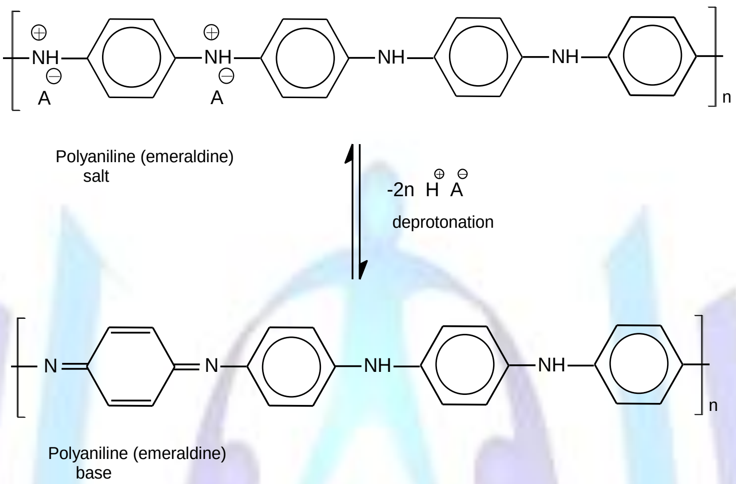

Fig. 1 Oxidative Polymerization of PANI

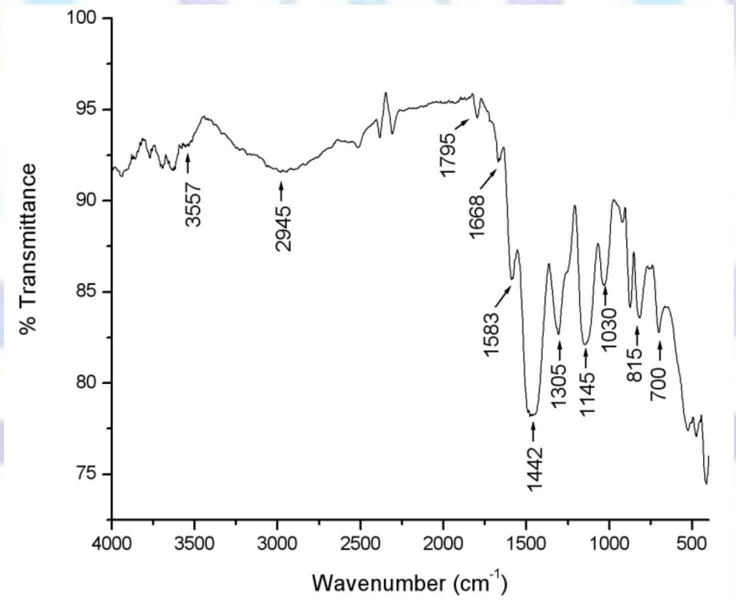

Fig. 2 FTIR spectra of PANI

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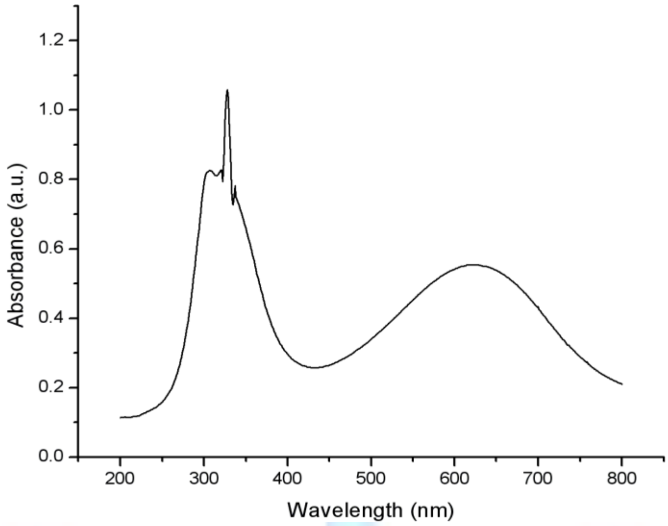

Fig. 3 UV-VIS Absorption Spectra of PANI

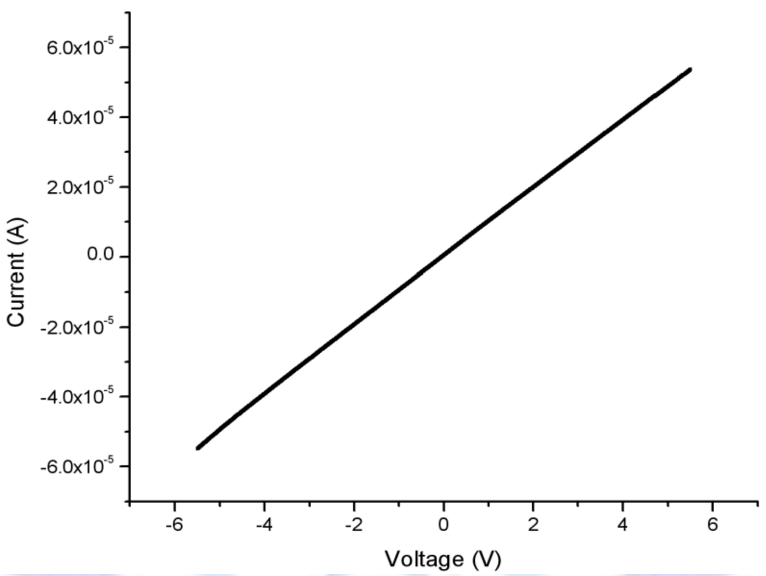

Fig. 4 I-V Characteristics of PANI Film

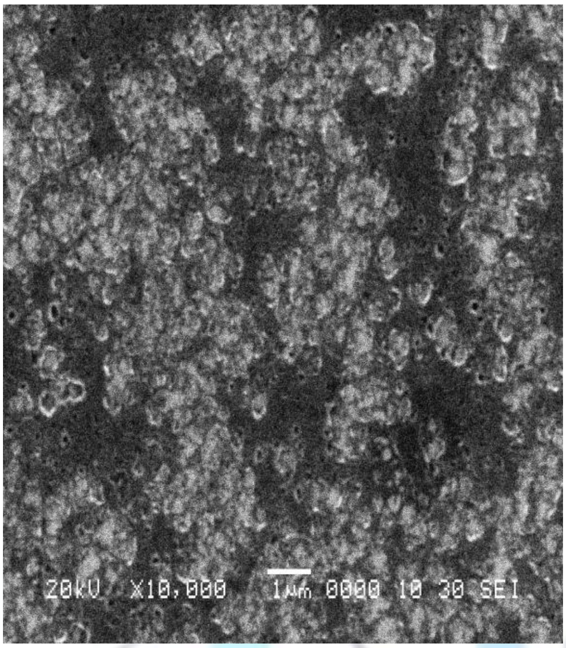

Fig. 5 SEM Image of HCl Doped PANI Film

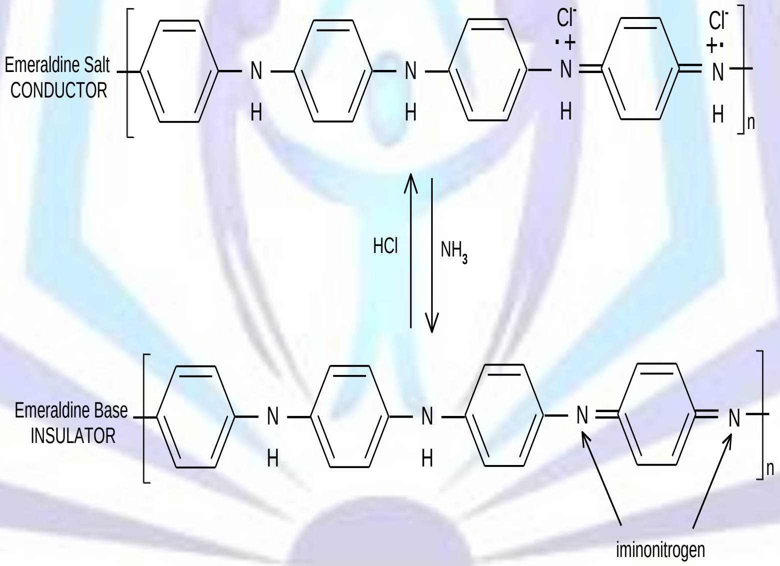

Fig. 6 Inter-Convertible States of Polyaniline.

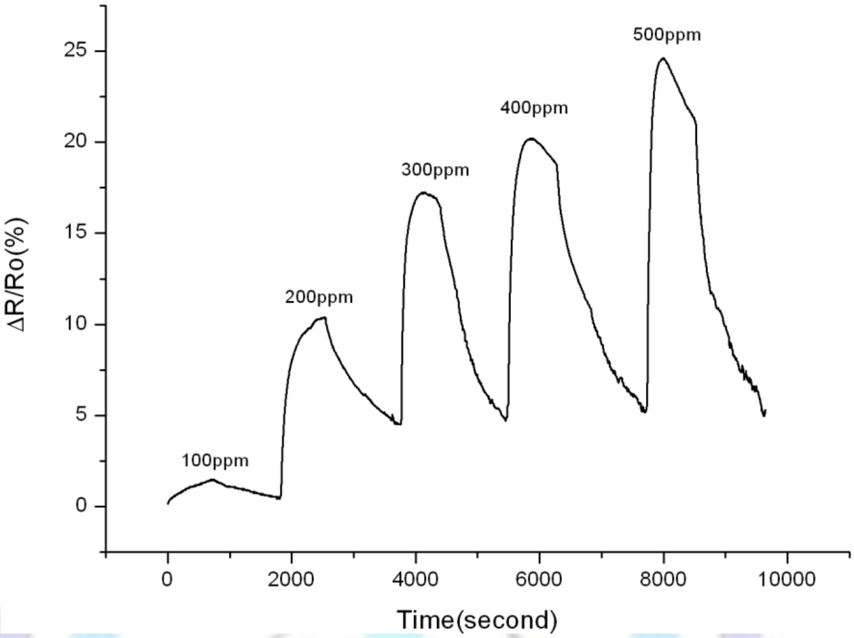

Fig. 7 Ammonia Gas Sensing behaviour of PANI Film

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Author' biography with Photo

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