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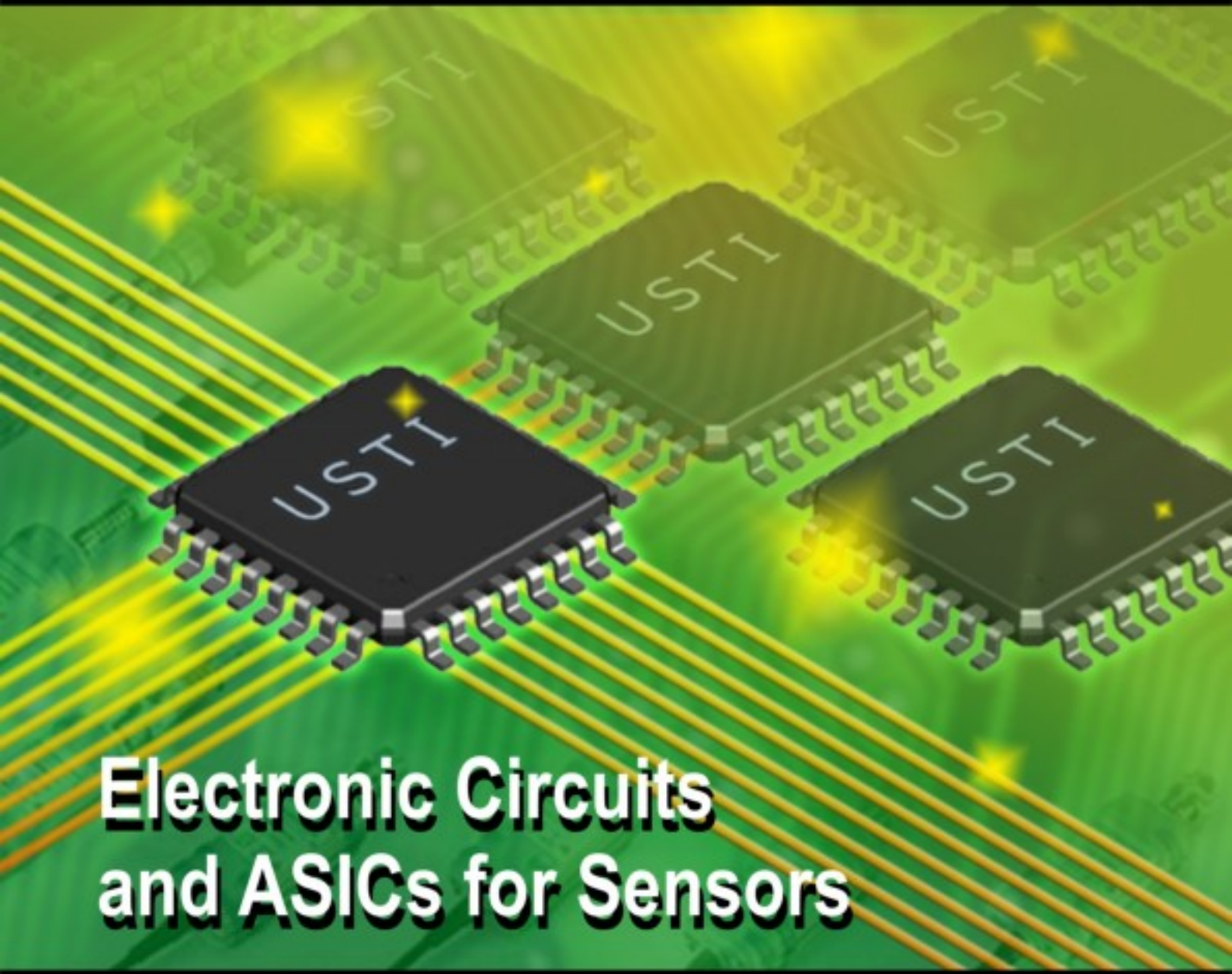

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Synthesis and Characterization of a Novel Ammonia Gas Sensor Based on PANI-PVA Blend Thin Films

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Abstract: The polyaniline - polyvinyl alcohol blend films were synthesized by oxidative polymerization using chemical synthesis route. The polyaniline films were synthesized using optimized concentration of monomer aniline, hydrochloric acid as a dopant using ammonium peroxy-disulphate as an oxidant and insulating addative matrix polyvinyl alcohol on glass substrate for development of ammonia sensor. The formation of PANI- PVA blend films show good uniform surface morphology at 10°c temperature, maintained at constant temperature bath .The synthesized PANI-PVA blend thin films were characterized by analyzing UV-Visible and FTIR spectra. The SEM study ensures that the thin films are uniform and porous in nature. The I-V characterization shows ohmic behaviour and also determines conductivity of the films. The response time of PANI-PVA blend thin films show that excellent behavior for 50-800ppm and higher range of ammonia gas. This study reveals that PANI-PVA blend thin films provide a polymer matrix with very good mechanical strength, environmental stability, uniformity in surface, porous morphology and high conductivity, which are suitable for ammonia gas sensing. *Copyright © 2008 IFSA.*

Keywords: Polymer blend, Thin film, Conducting polymer, Ammonia gas sensor, Polyaniline, Polyvinyl alcohol

1. Introduction

It was ages ago when all carbon based polymers were rigidly treated as insulators. In 1960s it was discovered that some conductive polymers and their derivatives undergo transition from insulator to semiconductor when doped with a weak oxidizing agent or reducing agent. One of such class of materials is polyaniline and its derivatives which are extensively exploited for research purposes (1, 2). However poor solubility and process ability limits the applications of polyaniline. (3, 4).

In order to overcome this problem various attempts have been made to blend polyaniline with insulating polymer that have good mechanical strength (2, 3). Polymer blend or composites are attractive because of their ability to form new materials with enhanced properties by combination of properties of the individuals. Development of new materials through polymer blending has become an important activity with increasing interest over a past one decade. This method allows tailoring of the product properties in a way that is more economical than the costly synthesis of new homopolymer. Because most polymers are thermodynamically immiscible, melt mixing of two polymers will often yield a two – phase system with coarse morphology leading to a high interfacial tension and poor interphase adhesion. Interfacial tension between the blend components makes it difficult to generate polymer blend having a desired degree of dispersion of random polymer mixtures (4, 5). To avoid this difficulty just mentioned a polymer blend which is a suspension of polymer matrix of water soluble polymer like polyvinyl alcohol can be useful.

The PANI-PVA blend thin films have been prepared successfully by chemical oxidative polymerization technique. The UV-visible, FTIR and SEM study gives idea about uniformity, porosity and surface morphology of the films. Finally, the films were exposed to ammonia gas with different concentrations ranging from 50 - 800 ppm and higher using computer controlled gas sensing characterization system to study sensing characteristics of the films.

2. Experimental

2.1. Materials

All the chemicals and solvents used were dried and purified by standard methods. Analytical grade aniline (Rankem ,Ranbaxy New Delhi) was purified by distillation under reduced pressure in presence of zinc dust prior to use and PVA powder with an average degree of polymerization (MW - 1400) (qualigen fine – chem. Indian). All processes were carried out in double distilled conductivity water. Ammonium per – oxodisulphate (APS), Hydrochloric acid (HCL) (SD - fine chem) and Ammonia were also of (SD – fine chem) analytical grade.

2.2. Preparation of PANI -PVA Blend Thin Films

The PANI-PVA blend films are synthesized by chemical oxidative polymerization. The aniline monomers were double distilled prior to used for formation of blend thin film. Different concentration of monomer – dpoant - oxidant - additive (insulating matrix PVA) were used as given in Table 1.

The preparations were carried out at 10 ºC temperature using constant temperature bath. The total volume of suspension homogeneous solution was 10 ml. The thin films deposited on glass substrate to get uniform PANI-PVA blend films.

Table 1. Different concentration of monomer – dpoant - oxidant - additive**.**

Synthesis of PANI-PVA Blend films	Monomer (Aniline)	Dopant HCL	Additive PVA	Oxidant APS	Surface Morphology
D1	0.4 M	1 M	25 mg	0.5 M	Non-uniform
D2	0.4 M	1 M	50 mg	0.5 M	Uniform
D3	0.4 M	1 M	75 mg	0.5 M	Uniform
D4	0.4 M	1 M	100 mg	0.5 M	Uniform
D5	0.4 M	1 M	125 mg	0.5 M	Non-uniform
D6	0.4 M	1 M	150 mg	0.5 M	Non-uniform

3. Results and Discussion

The synthesized PANI-PVA blend films were characterized by following techniques.

3.1. UV-Visible Spectra

The UV-Visible absorption spectra of PANI-PVA films were recorded in air backgrounds on glass deposited thin films using UV - Visible 1601 Shimadzu - spectrophotometer in the range of 200- 1100 nm. The PANI-PVA blend thin films show three peaks at 292nm, 380nm and 809 nm respectively. The first peak was due to $n \rightarrow \pi^*$ transition at 292 nm. The second peak for $\pi \rightarrow \pi^*$ transition at 380 nm corresponds to benzenoid , rings while the sharp groove at 440 nm can be assigned to the localized polarons which are characteristic of protonated PANI-PVA film with the extended tail at 800 nm. Third peak represents the conducting emerald salt form of polymer for all samples. This spectrum suggest that the composite band compact coil structure as described previously for polyailine,(2,3) in Fig 1.

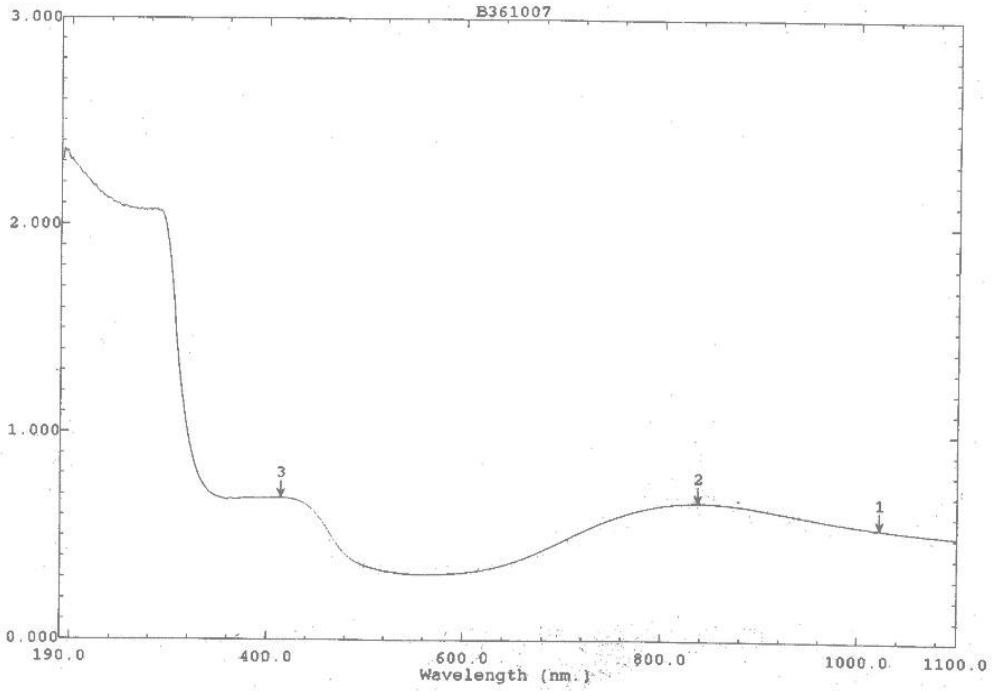

Fig. 1. UV-Visible spectrum of PANI-PVA blend thin film.

3.2. FTIR Spectra

The FTIR- spectrum of PANI-PVA films were recorded in the range of 400-4000 cm^{-1} as shown in Fig-2. The point at which absorption occurs indicates the type of functional group present in the polymer. The strong and broad band at intermolecular 3300-3650 cm^{-1} indicates the presence of strong hydrogen bonded O-H strech and suggest the formation of polyvinyl alcohol.

The alcohol also gives sharp and strong band due to C-O, C-N stretching in the range of 1200 - 1265 cm^{-1}. The N-H stretching appears at 3444 cm^{-1} and 2945 cm^{-1} stretching for C-H aromatic stretching. It can be seen that quinoid or benzonid ring stretching overtone band appear at 1480 cm^{-1} 1670 cm^{-1}. The C-H plane and out of plane bending vibration appear at 1055 cm^{-1}. These entire characteristic bands confirm the presence of conducting PANI-PVA blend thin films.

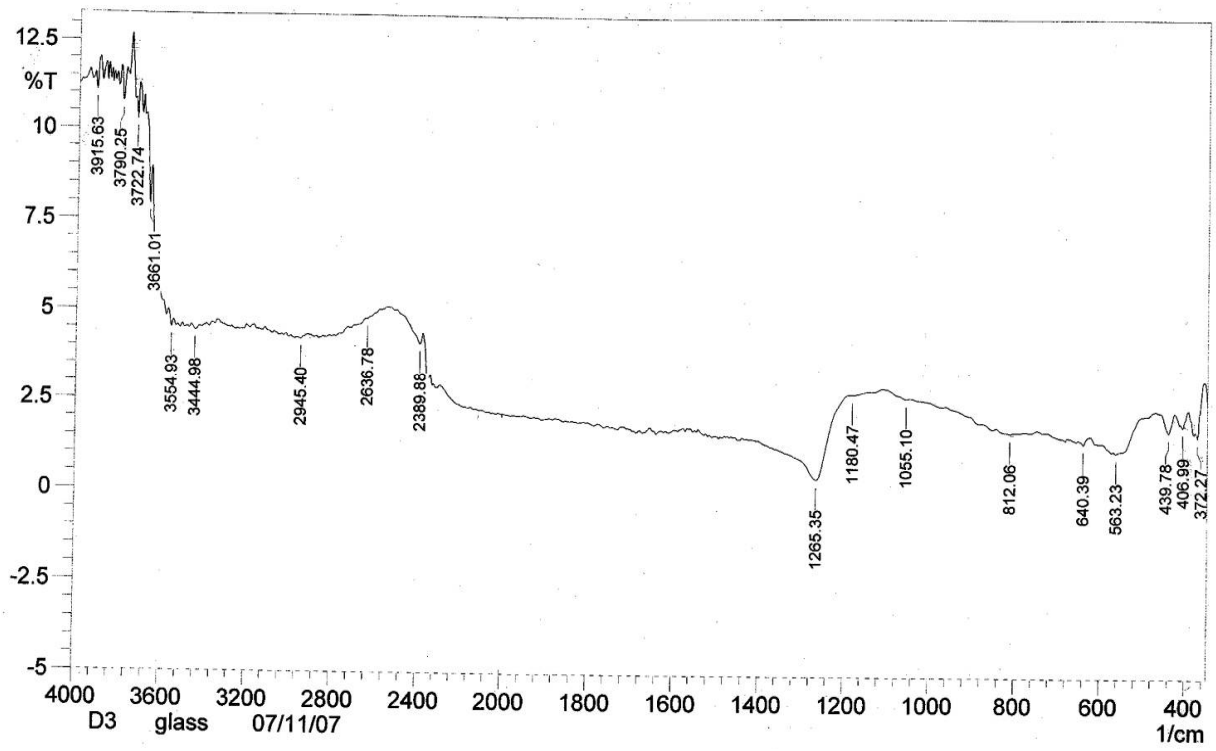

Fig. 2. FTIR for PANI-PVA blend film.

3.3. SEM Study

The surface morphology of synthesized PANI-PVA film was studied by scanning electron microscope (SEM) The micrograph of PANI - PVA film for optimized concentration of monomer, dopant, oxidant and additive as shown in Fig. 3. Granular and porous surface morphology with very excellent uniformity and adhesivity was observed which is suitable for sensor applications. The comparative SEM study of polyaniline and PANI- PVA blend thin film shows that the PANI-PVA thin film has the similar morphology that is porosity, uniformity and granular in nature of that of polyaniline thin films shown in Fig. 3 (a,b,c and d).

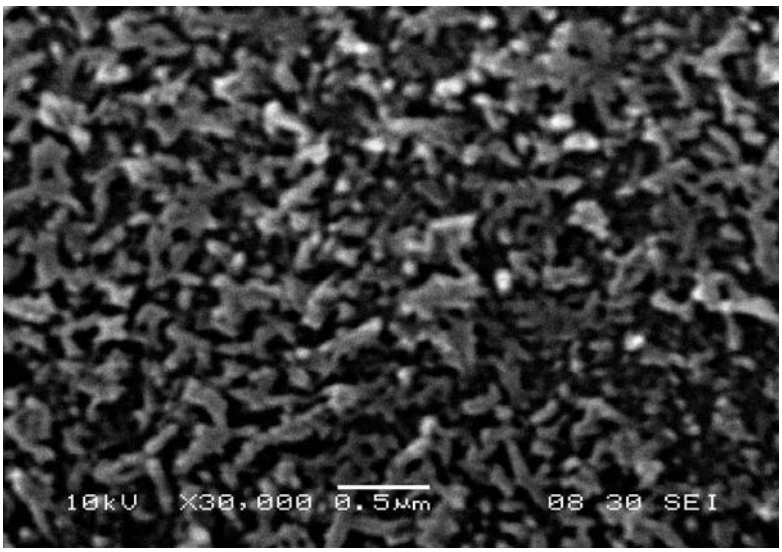

Fig. 3(a). PANI film Micrograph.

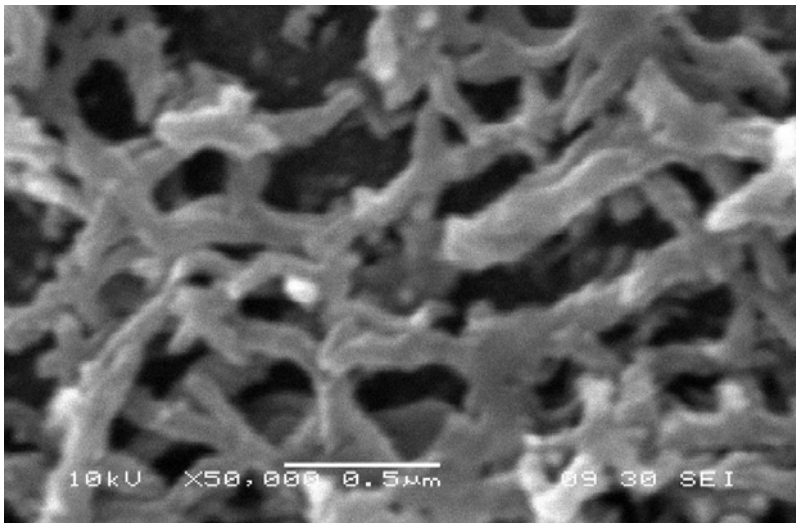

Fig. 3(b). PANI film Micrograph.

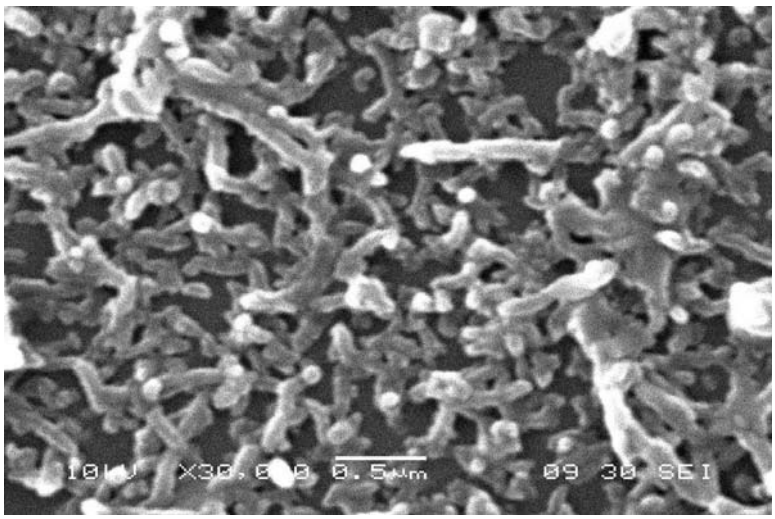

Fig. 3(c).PANI-PVA film Micrograph.

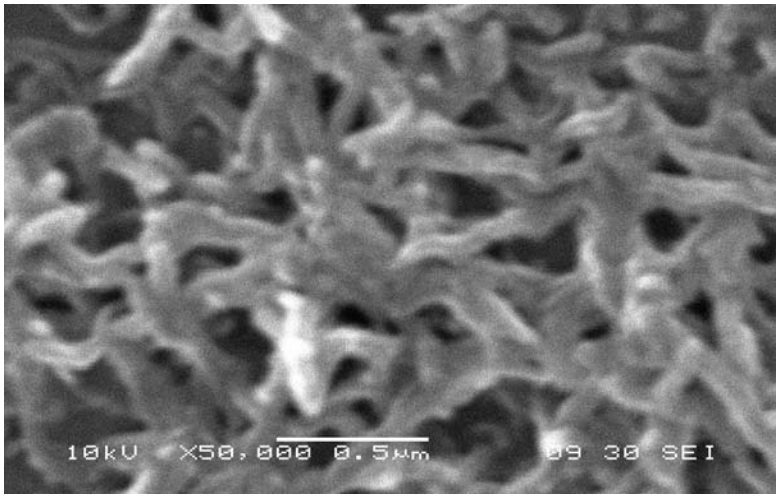

Fig. 3(d). PANI-PVA film Micrograph.

3.4. I-V Characteristics

The synthesized PANI – PVA films with optimized concentration of monomer, dopant, oxidant and additive were subjected to I - V characterization to study the ohmic behavior of the films. A linear relationship of the I - V characteristics are observed (Fig -4) reveals that the PANI-PVA film has an ohmic behavior. This characteristic gives the thin film has conductivity in microamperes.

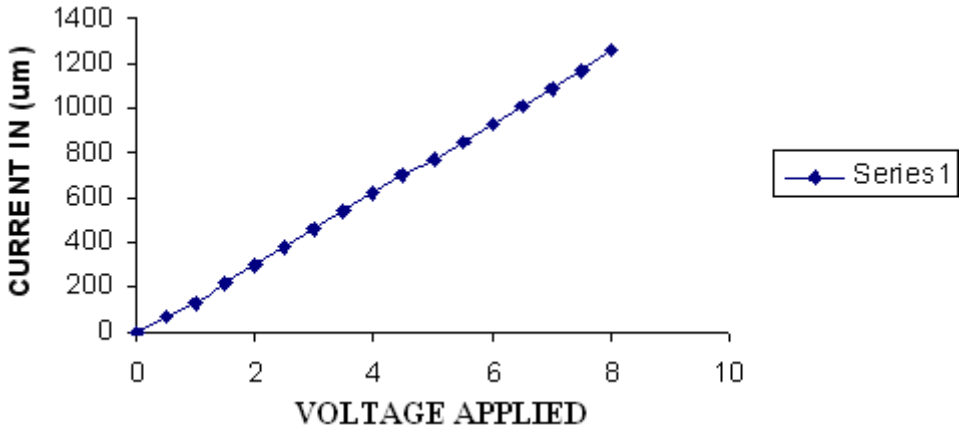

Fig. 4. I-V Characteristics of PANI-PVA Film.

3.5. Ammonia Gas Sensing Behaviour

Sensing behavior of synthesized PANI-PVA film for ammonia gas was studied at room temperature 27^0C.by using indigenously developed computer controlled gas sensing system. The increase resistance of the film was measured when the synthesized PANI - PVA film exposed to ammonia gas 1) Liner regression analysis; 2) Repeatability; 3) Sensitivity of film.

Initially the films were allowed to saturate for 1-2 hours before exposing to ammonia gas. The PANI-PVA film first exposed to 5 minutes to predefined concentration of ammonia gas. Then it was exposed

to air to recover initial resistance for 5 minutes the same process was repeated for various ppm concentration of ammonia gas. Interaction of ammonia with PANI-PVA film found to increase the resistance and on exposure to air reverse phenomenon was observed. The change in resistance measured by four probe method when exposed to ammonia gas with different concentrations from 50-800 ppm. Initially 50 ppm ammonia gas was passed through the gas chamber on which the resistance increased and on air exposure the resistance decreased which ensuresthe gas sensing behaviour of the thin film. The barrier height increases with adsorbed gas concentration. The change in resistance is found to be linearly proportional to the ammonia concentration shown in (Fig. 5).

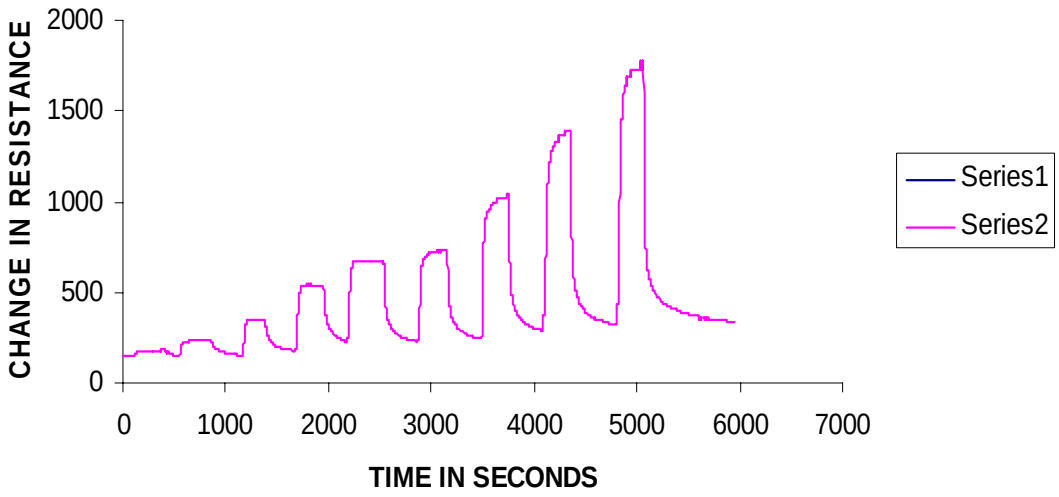

Fig. 5. Ammonia gas exposed at various conc. from 50-800 ppm.

3.6. Sensing Mechanism

The UV-Visible absorbance at 800nm confirms that the film is totally protonated. The protonation reaction with using the HA type acid can be expressed by reaction 1:

$$PA + HA \text{ -}\rightarrow PAH^{+} + A^{-}, \quad (1)$$

where PA and PAH^{+} denotes the repeating block of polymer chain before and after protonation (red- ox reaction) respectively. During the protonation PANI - PVA molecule gains proton, creating energetically more favorable N^{+}- H chemical bond. The N^{+}- H bond forms positive charge centers which enhances the P-type semiconductor characteristic in contact with a reducing gas (NH_3, H_2S). The protonated form of PANI - PVA is susceptible to the red -ox reaction.

$$PAH^{+} + NH_3 \rightarrow PA + NH_4^{+} \quad (2)$$

In the presence of ammonia the reaction shifts toward the right side. The NH_3 molecule reaching the surface of PANI-PVA blend thin films react with N-H group of polymer chain and gain their energetically more favorable proton forming ammonium ($NH4^{+}$) ions near the acid radical. Above reaction shows the de-protonation of PANI – PVA thin film to the emeralidine base form (EB). The air exposure of film causes the reaction (2) to go to the left side. The ammonium NH_4^{+} ions decomposed into ammonia (NH_3) which is volatile and proton which is absorbed by PANI-PVA blend thin film recover the initial stage of doping emeralidine salts. Hence reversibility and regeneration of sensor is achieved. (7-8)

4. Conclusions

The PANI -PVA blend films have been successfully synthesized by oxidative chemical polymerization of monomers, dopant, oxidant and additive PVA matrix co-optimized for excellent PANI - PVA films on glass substrate. The UV-Visible and FTIR study confirm formation of PANI - PVA blend films on glass substrate. The SEM studies show uniform, granular and porous surface morphology which is suitable for gas sensing application. The response of PANI - PVA blend film (50-800 ppm) above range of ammonia gas concentration reveals that it has a good potential to be used as a novel ammonia gas sensor.

Acknowledgment

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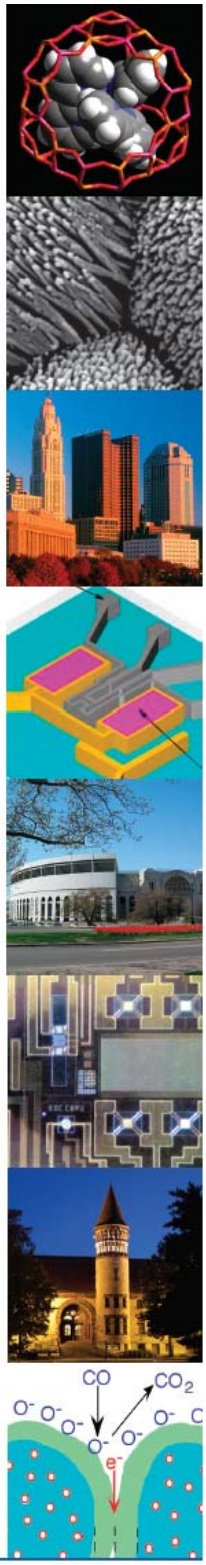

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