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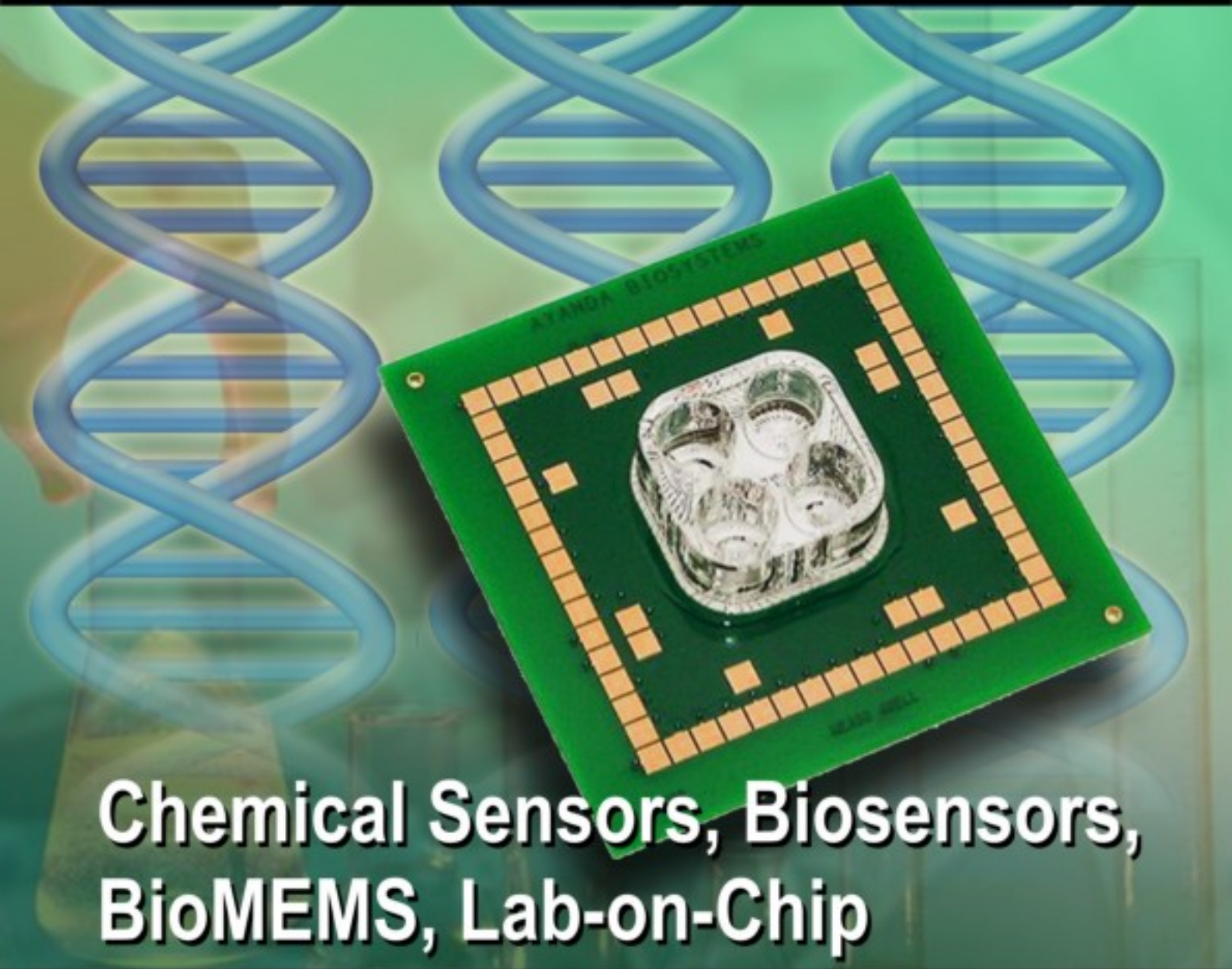

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Metal Oxides Doped PPY-PVA Blend Thin Films Based Gas Sensor

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Abstract: Synthesis of metal oxides doped polypyrrole–polyvinyl alcohol blend thin films by in situ chemical oxidative polymerization, using microwave oven on glass substrate for development of Ammonia and Trimethyl ammine hazardous gas sensor. The all experimental process carried out at room temperature(304 k).These polymer materials were characterized by Chemical analyses, spectral studies (UV-visible and IR) and conductivity measurement by four –probe technique . The surface morphology as observed in the SEM image was observed to be uniformly covering the entire substrate surface. The sensor was used for different concentration (ppm) of TMA and Ammonia gas investigation at room temperature (304 k). This study found to possess improved electrical, mechanical and environmental stability metal oxides doped PPY-PVA films. *Copyright © 2009 IFSA.*

Keywords: Polymer blend, Thin film, Ammonia, TMA-Gas sensor, Polypyrrole, Metal oxides polyvinyl alcohol

1. Introduction

Research interest in the development of conducting polymers such as polyaniline, polypyrrole, polythiophene, polyphenylene, etc. has increased tremendously because of the versatility of their applications [1]. In this technique, a host of insulating polymers, namely, poly(vinylalcohol), poly(styrenesulphonate), polycarbonate, poly(methyl methacrylate), polyimide, *etc*., have been combined with a number of conducting polymers such as polypyrrole, polyaniline, polythiophene, *etc*., in aqueous or organic medium to produce conducting polymer composites which will have the

conducting properties of the conducting polymer with some of the superior mechanical properties of the host insulating polymer [2-3]. Attempts have been made to produce composites or blends of conducting polymer films with some insulating polymer in order to overcome the drawbacks such as poor process ability and the lack of essential mechanical properties exhibited by these polymers. Blending insulating polymers is an attractive route to improve their mechanical properties without loosing their conductivity. [4]

Recently, this principle has been behind a series of studies that introduced a new family of materials, designated as organic compound-doped metals. The methodology of their preparation enables one to incorporate small or large(polymeric) organic molecules within metals, thus creating a new family of metal matrix composites [4-5]. The methodology of preparation of those metal matrix composites involves metal synthesis by chemical reduction of a metal cation in the presence of the selected organic molecule. The composite is obtained in a powder form, which can be hot pressed to create films.[6]

Special attention has been devoted in the present investigation development of entrapment of polymers because intimate polymer –metals dopant composites represent novel materials, which, to the best of gas sensor at room temperature operation which is inexpensive and can be used for detection of TMA (Trimethyl ammine) gases at lower concentration 5 ppm-800 ppm or above level with best response and recovery time and environmental stability.

2. Experimental

2.1. Chemical Used for Synthesis

All chemical used were analytical reagent (AR) grade for synthesis of metal oxides doped PPY-PVA thin films. Pyrrole was distilled twice before use (99 %) Rankem and polyvinyl alcohol with an average degree of polymerization (mw.14,000.quiligen fine–chem., India). All process was carried out in double distilled conductivity water. Anhydrous ferric chloride (Spectro chem), hydrochloric acids (qualigen fine –chem. India). Metal oxides TiO_2, ZnO and SnO_2Qualigen fine – chem, (India).

2.2. Synthesis of Metal Oxides Doped PPY-PVA Blend Thin Films

We have synthesized metal oxides doped PPY-PVA blend thin films at room temperature on glass substrate by using chemical oxidative polymerization method using microwave oven technique. The pyrrole (monomer) was double distilled prior to use. The glass substrates were cleaned using chromic acids solution, followed by rinsing with double distilled conductivity water. Initially we have optimized the molar concentration of monomer (pyrrole), primary dopant (HCL), polymer additive matrix (PVA), and oxidant ($FeCl_3$) as follows. The polyvinyl alcohol dissolved in conductivity water with constant stirring then optimize molar concentration of pyrrole (monomer 0.5 M), primary dopant (HCL–1M), PVA additive (25 mg), Oxidant ($FeCl_3$-0.5M), and metal oxides TiO_2, ZnO and SnO_2 (0.02 M).

A suitable combination which shows good response to Ammonia and TMA gas has been selected further synthesis and characterization. The glass substrate was submerged the (20 ml) of suspension homogeneous solution reaction mixture in closed vessel at room temperature to get uniform metal oxides doped PPY-PVA blend thin films.

2.3. Characterization

The structural and morphological characterization of metal oxides doped PPY-PVA blend thin films was performed UV-visible and FTIR by UV-visible. The UV-visible and FTIR spectra of all polymer samples were recorded at room temperature in Dimethyl sulphoxide (DMSO) solvent. The surface morphology was characterized by using scanning electron microscopy (SEM) at different magnification range by (JEOL-JSM-6360 A). Synthesized Metal oxides doped PPY-PVA films were subjected to the Ammonia and TMA gas at room temperature by using indigenously developed computer controlled gas sensor system and electrical conductivity (I-V characteristics) of the films was recorded using four probe- methods computer control system.

3. Results and Discussions

The synthesized metal oxides doped PPY-PVA blend thin films characterized by following analysis.

3.1. UV-Visible Spectra

The UV-Visible absorption spectra of the polymer films were recorded by dissolving the polymer film in Dimethyl Sulfoxide (DMSO) solvent and the absorption spectra of, metal oxides TiO_2, ZnO and SnO_2 doped PPY- PVA Fig. 3.1 (a). The band observed at 260-290 nm for samples corresponds to π -π * transition of in metal oxides PPY-PVA films. The bands appear at the 380-395 nm is due to n-π * in metal oxides PPY-PVA film due to lone pair on nitrogen in pyrrole ring ,which is inter charge transfer band associated of benzenoid to quinoid ring .The transitions of quinone-imine groups, together with the extending tail at 990-1100 nm. The conducting emeraldine salt (E S) phase in the polymer is identified by broad peak at 960 nm. Thus from the UV-visible spectroscopic measurements it was observed that the polymer is composed of mixed phase i.e. conducting and insulating of the polymer. All these UV –visible spectral data clear that in these synthesized metal oxides doped PPY-PVA formation take place.

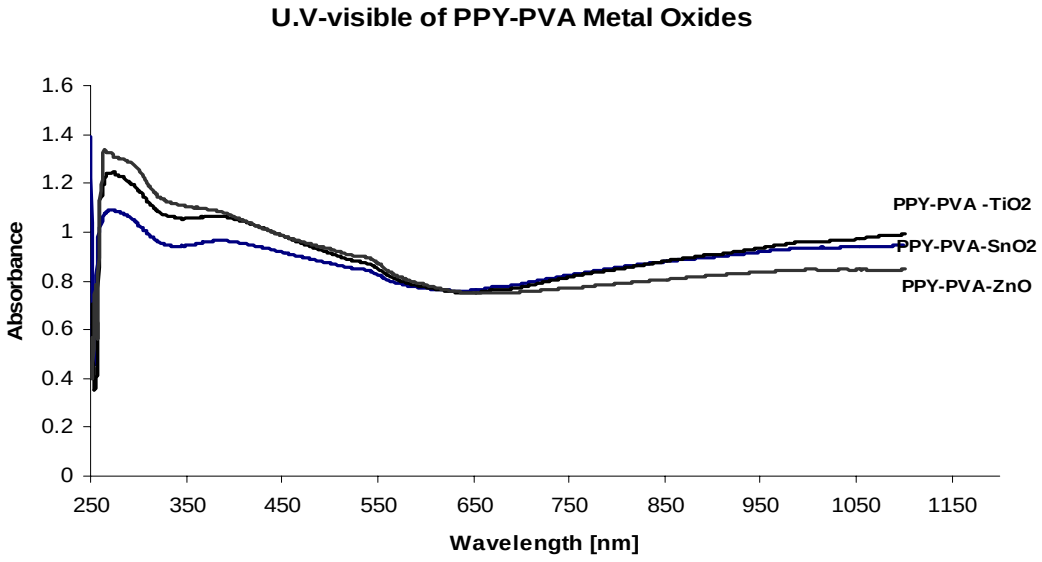


Fig. 3.1. UV- Visible Spectra of metal oxides doped PPY-PVA Blend films.

3.2. FTIR Analysis of Synthesized Metal Oxides Doped PPY –PVA Blend Thin Film

The Infrared spectra of metal oxides doped PPY- PVA Blend films are appear dissolved in DMSO solvent.. The FTIR spectrum of synthesized metal oxides doped PPY-PVA Blend thin film is shown in Fig. 3.2. The bands related to N–H stretching of an aromatic amine (> NH stretching) normally appear in the region between 3100 and 3600 cm-^{1}[6]. A broad band near at 3444 cm^{-1} for metal oxides doped PPY-PVA film, the same time NH region also shows dependence of the doping anion. Anion which typically forms hydrogen bond with amine group shows variations in the intensity and shape of the NH band, which indicates that the doping is higher in the sample .The band appear at 2900 and 3000 cm^{-1} due to CH_3 and CH_2 (C-H stretching). The two bands observed in the 1410 – 1440 cm─1 regions are related to the stretching of the C–N bonds of the benzonic and quinonic rings, respectively and are present due to the conducting state of the polymer [5].The intensity of these bands illustrates an idea of the oxidation state of PPY. When they appear unequal intensities, PPY is in the emeraldine base form. The bands corresponding to quinoid (N=Q=N) and benzenoid (N–B–N) ring stretching modes were observed at 1666 cm^{-1}for (C=N) Stretching and 1439 cm^{-1} for (C-N), respectively. We attributed the shoulder bands at 1033 cm^{-1} as the asymmetric and symmetric C-O stretching vibrations of polyvinyl group, and peaks at 707 cm^{-1}assigned to C-H bending. All these characteristic bands confirm the presence of conducting emeraldine salt phase of the polymer of metal oxides TiO_2, ZnO and SnO_2 doped PPY-PVA Blend material functional group.

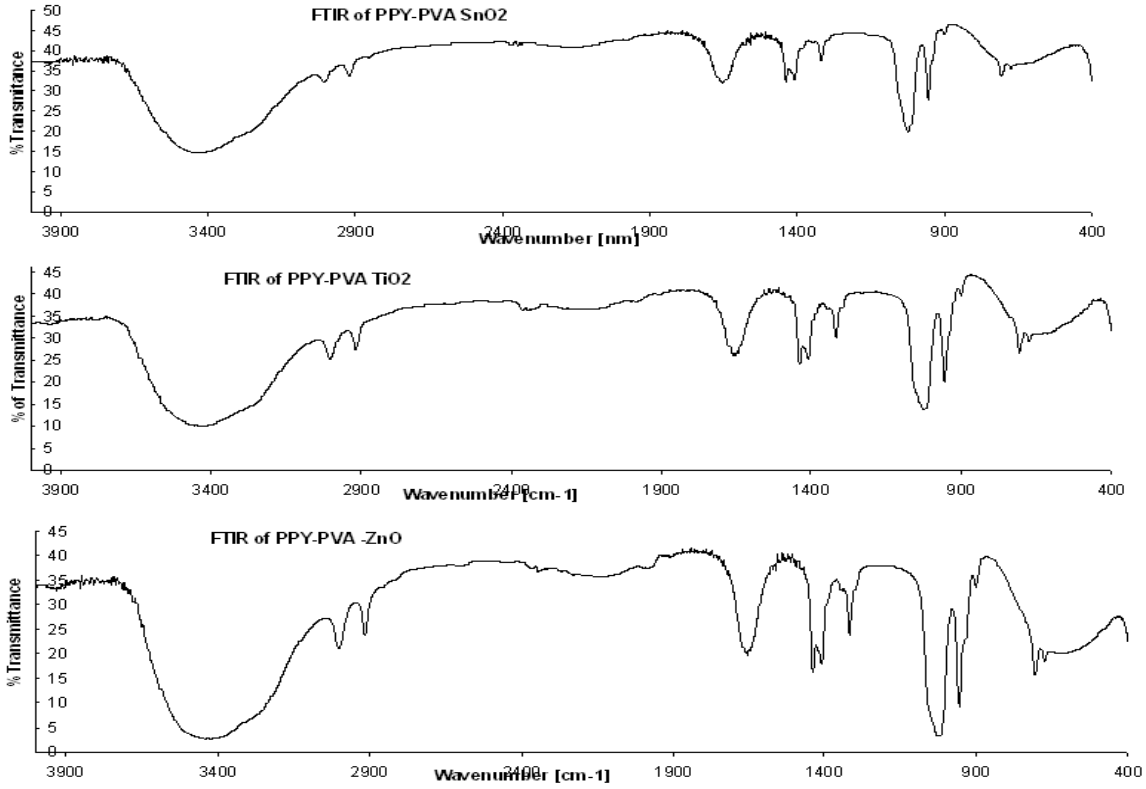
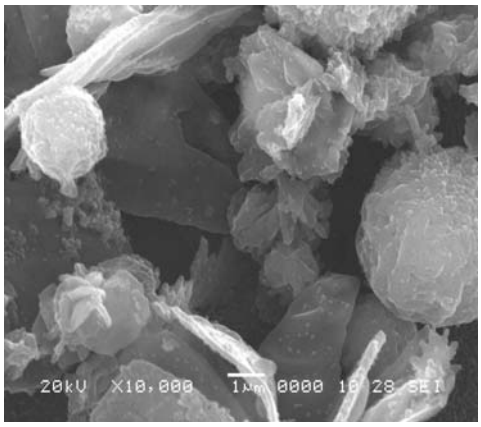


Fig. 3.2. FTIR Spectra of metal oxides doped PPY-PVA Blend films: (a) PPY,(b) PPY- PVA Blend.

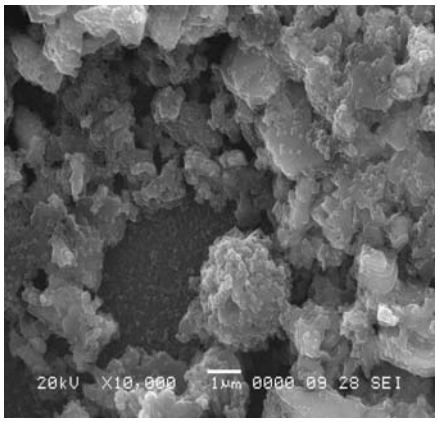
3.3. Morphology of the Metal Oxides Doped PPY –PVA Blend Film

Scanning Electron Microscopy is used to study of surface structure (morphology) of polymer. The object of electron microscopy is to observe the relationship between adjacent particles and small group of particles. The surface morphology of the synthesized metal oxides doped PPY-PVA Blend thin

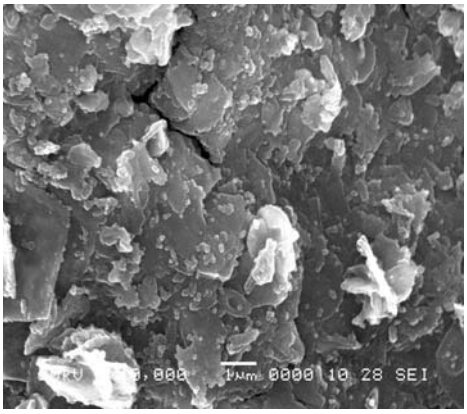
films was studied by using scanning electron microscope (SEM) are shown in Fig. 3.3. We have observed better porous, granular and globular surface morphology with very good uniformity and adhesiveness for synthesized film samples suitable for sensor application.



(a) [TiO_2 -PPY-PVA Film]



(b) [SnO_2 -PPY-PVA Film]



(c) [ZnO -PPY-PVA Film]

Fig. 3.3. Metal oxides PPY-PVA film Micrograph.

3.4. Conductivity Measurement

The electrical conductivity of metal oxides doped PPY-PVA Blend thin film was measured by an indigenously developed computer controlled conductivity measurement system using four- probe method at room temperature. Further increase of the particles (above the percolation threshold) in the blends results in improvement of the conducting network and hence enhance the conductivity of the blend increases by dopant of metal oxide TiO_2, ZnO and SnO_2 doped PPY-PVA blend thin film. It is interesting to notice that, despite the insertion of metal oxide dopant and insulating PVA, the DC conductivity of the PPY-PVA blends increases is found to be significantly higher than the PPY–PVA Films at room temperature.

3.5. I-V Measurement

The I-V characterization measurement of Metal oxides doped PPY-PVA film was recorded by an indigenously developed computer controlled I-V measurement system using four- probe method at

room temperature. The current–voltage (I-V) characteristics of the synthesized metal oxides doped PPY –PVA Blend thin films were studied to ensure an ohmic behavior of the films. A linear relationship of the I-V characteristics shown in Fig. 3.5.

Table 3.4. Conductivity measurement of Metal oxides PPY-PVA Blend films.

Sample	Amount of metal oxides	DC Conductivity (S/cm)
PPY-PVA		0.1816×10^{-5}
PPY-PVA-(ZnO**)**	0.02M	0.3425×10^{-5}
PPY-PVA-(SnO_2**)**	0.02M	0.6013×10^{-5}
PPY-PVA-(TiO_2**)**	0.02M	0.7182×10^{-5}

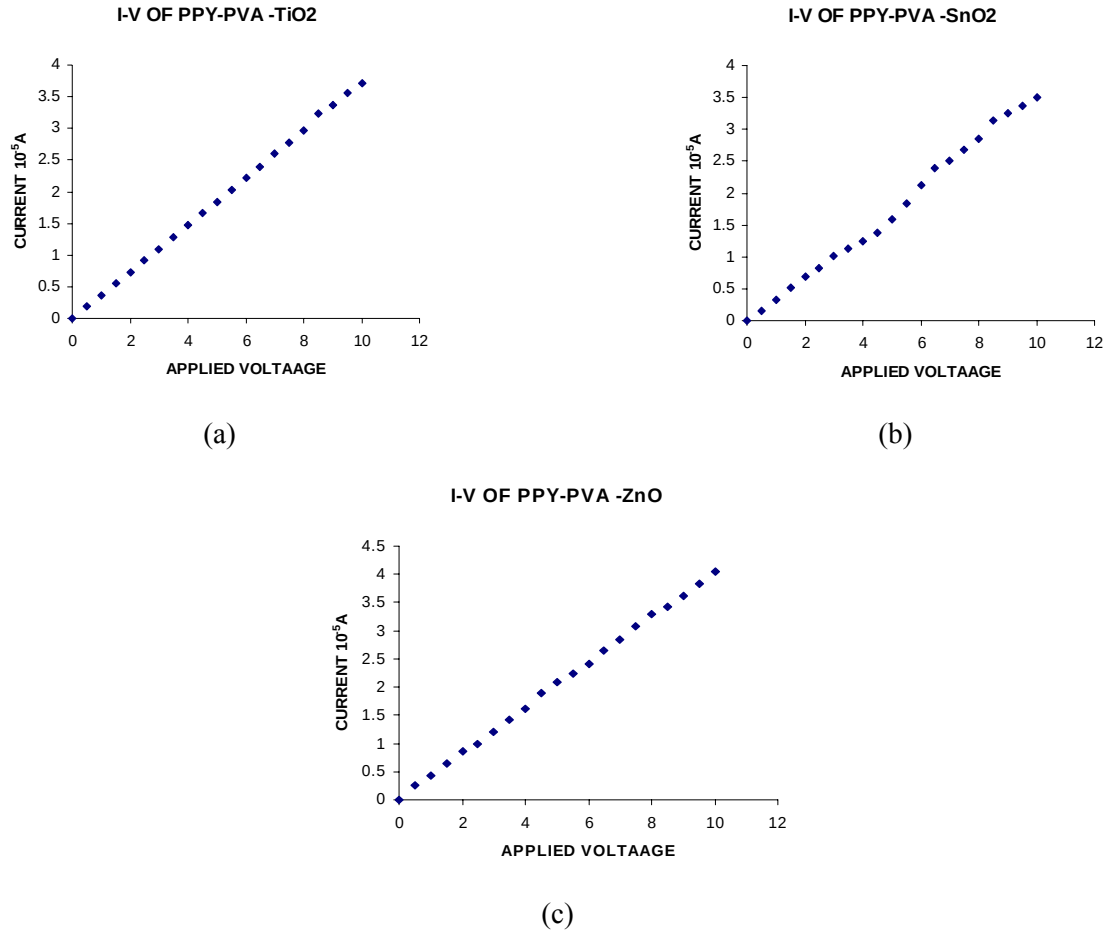


Fig. 3.5. I-V Characteristics of metal oxides PPY-PVA Blend thin films.

3.6. TMA and Ammonia Gas Sensing Characteristics

To observe the TMA and ammonia gas-sensing characteristics of the synthesized metal oxides doped PPY –PVA Blend thin films at room temperature, we have used the Four-probe technique of resistivity measurement, where four electrical contacts were made on the doped PPY-PVA film. This film was enclosed in indigenously designed and fabricated a gas chamber. The synthesized PPY-PVA films were exposed to TMA and ammonia gas for 5 minutes. The recovery time was measured by exposing

the film to the air for 5 minutes. The change in resistivity of the film was measured at an interval of 10 s. All the sample films show response to the ammonia and TMA gases vapor. We have explored the ammonia and TMA gas-sensing curves of metal oxides doped PPY–PVA at different concentrations of ammonia gas 5 ppm to 800 ppm. It was observed that the resistivity of the PPY-PVA Blend thin film increases in the presence of ammonia and TMA gases and after a few minutes becomes saturated and the resistivity decreases steadily to a minimum value, when the ammonia and TMA gas was removed however, a drift from its original value was observed.. Extensive studies of the gas-sensing properties of conducting polymers show that when these polymers are exposed to electron-donating gases such as ammonia and TMA, if the gases are absorbed, the polymers exhibit an increase in resistance it can be seen from the figures, the conductivities of polymers show marked changes when exposed to NH_3 gas. The change in conductivity of polymers can be attributed to the different nature of both dopant anions and NH_3 gas. Dopant anions have different sizes and to NH_3 vapors can differently diffuse in Polymer matrix.

The relationship between change in resistivity and time of the synthesized metal oxides doped PPY-PVA Blend film when exposed to different concentration of TMA and ammonia gas are shown in (Fig. 3.6.)

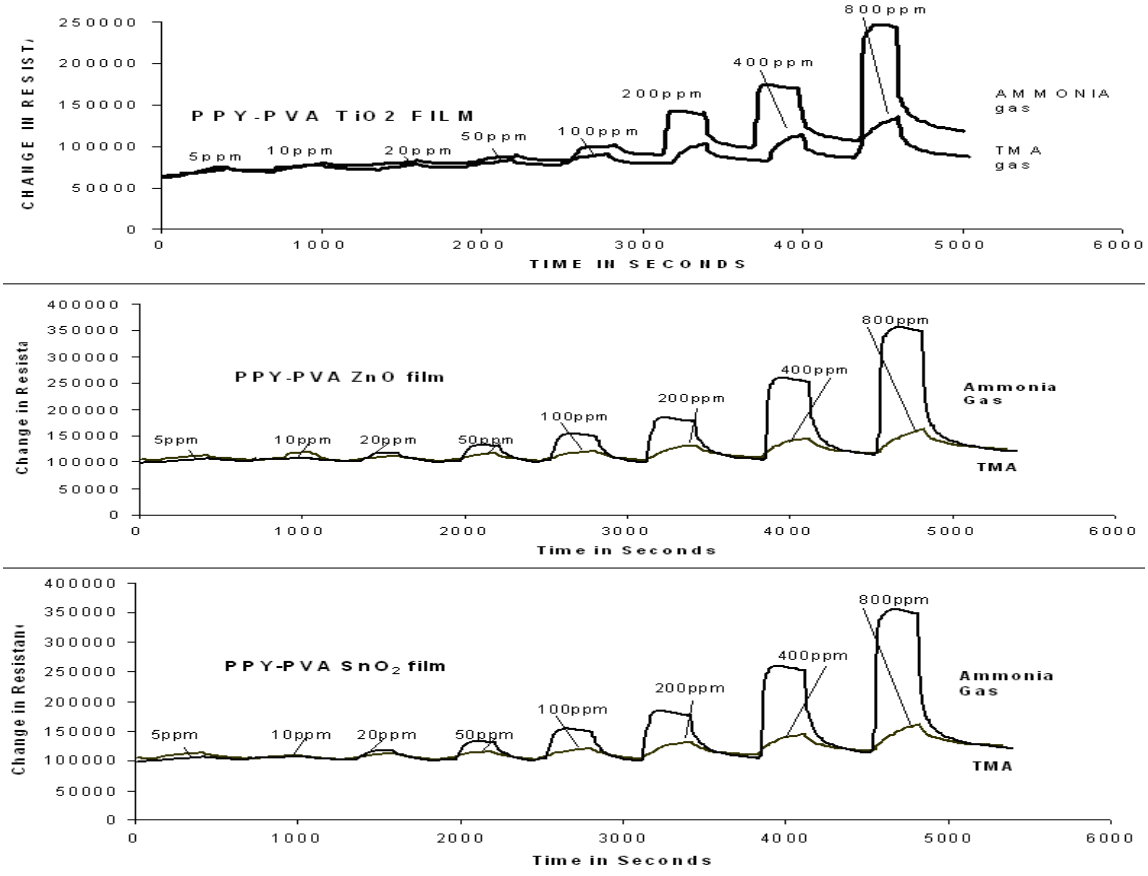


Fig. 3.6. Metal oxides doped PPY-PVA A) Ammonia and B) TMA gas sensing Response from 5-800ppm.

4. Conclusions

1. In this present investigation, we have successfully synthesized metal oxides dopant TiO2, ZnO and SnO_2 doped PPY-PVA Blend thin films by using microwave oven techniques on glass substrate.

2. The synthesized film studies their structural characterization by using UV–visible and FTIR-Spectroscopy.
3. The uniform surface morphology for better sensitivity of metal oxides doped PPY-PVA films by SEM study.
4. The metal oxides doped PPY-PVA Blend thin films have ohmic behaviour confirm by I-V Characteristics study.
5. The TiO_2 doped metal oxide PPY-PVA Blend thin show good response and recovery tine at 5-ppm lower level ammonia and TMA gas vapours than SnO_2 and ZnO doped metal oxides PPY-PVA films.
6. Hence from present study we are concluded that synthesized TiO_2 doped metal oxide PPY-PVA blend thin film ,more environmental ,thermal stability and good response to lower level ppm of gases at room temperature and this work are applicable for environmental pollution monitoring .

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Guide for Contributors

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