RESEARCH ARTICLE

Preparation and Characterization of Polyaniline Thin Films for Sensor Applications

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Manuscript Details	ABSTRACT

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In the present article we report about preparation of Polyaniline thin films by using cost effective chemical route like solution polymerization reacting Ammonium per-oxi-disulphate (APS) $[(NH_4)_2S_2O_8]$, Hydrochloric acid [HCl] and Aniline $[C_6H_5NH_2]$ as the reactants at room temperature. These as deposited thin films have been characterized for physicochemical as well as optoelectronic properties using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray absorption spectra, optical absorption spectra and I-V characterizations. The compositional elemental analysis confirmed using the FTIR and EDAX reveals the expected elemental composition in polyaniline thin film. The morphological analysis by SEM images represents uneven distribution of grains all over the surface of the substrate. Optical absorption spectrum corresponds for exciton induced polaron charge transfer while the I-V characterization confirmed the conducting ohmic nature of the prepared polyaniline thin films. These films are tested for gas sensing applications.

Key words: thin films, polyaniline, FTIR, Exciton, physicochemical and optoelectronic

INTRODUCTION

Conducting polymers are a new class of sensing materials, which can be prepared by simple oxidative polymerization method. These polymers provide suitable structure for immobilization of ligands, enzymes and antibodies; therefore, their use in development of novel chemical and biological sensors has received considerable attention [Sadik and Wallace, 1993] Conducting polymer gas sensors commonly rely on conductivity changes that occur when they are exposed to certain gases [Brie et al., 1996]. The dc conductivity of polyaniline also depends on gas concentration, polyaniline containing nickel prepared by electrochemical oxidation [Krutovertsev et al., 1992]. In addition to ammonia gas, polyaniline based sensors can also detect H_2S, NO_x and SO_2 [Agbor et al., 1995]. Gas sensors based on conducting polymers are operated primarily by conductivity measurement techniques. There are

only very limited reports on conducting polymer optical gas sensors. However, the sensor response was slow and the total regeneration of the sensor was impossible. Conducting polymers are very promising gas sensing materials; however, their potential in analytical chemistry has not been fully utilized. Most gas sensors suffer from the problems of slow response time and regeneration difficulty. On the other hand new optical sensor has a rapid response to gas and regenerates easily, which is advantageous over the current polymer gas sensors based on electrical conductivity measurements.

Now days, most of the gas in our atmosphere is emitted direct or indirect by human activity and there are number of natural sources of gas on the earth [Connolly et al., 2005]. These high concentrations of gas in the surrounding form a threat to the human health. However; even below this limit hazardous gases are irritating to the respiratory system, skin and eyes. However, the presented method shows independence from environmental interference. The polyaniline films show significant changes upon exposure to gas at room temperature. This study demonstrates the optical property advantage of polyaniline over metal oxide. The method is based on the detection of a modulated signal caused by an absorbance variation. The interaction between the conducting polymer and gas molecules results in an increase or decrease of bipolaron densities inside the polymer band gap [Nicho et al., 2001].

MATERIAL AND METHODS

In solution growth technique**,** extreme cleanliness of the substrate is required, since the contaminated surface provides nucleation sites facilitating the growth, and resulting into non-uniform, porous and non-adherent film. All chemicals used for preparing polyaniline thin films were of A.R. grade as follows: Ammonium peroxidisulphate (APS) $[(NH_4)_2S_2O_8]$, Hydrochloric acid [HCl], and Aniline $[C_6H_5NH_2]$ as the reactants. For the deposition of polyaniline thin films, solutions of APS and Aniline were prepared separately using double distilled water. Thin film of polyaniline was prepared by solution polymerization method using HCl as dopent, ammonium peroxidisulphate (APS) as an oxidant and aniline as a monomer. Commercial glass slides supplied by Bluestar Company, Mumbai (India) were used as substrates for the deposition. Aniline was distilled under high pressure prior to use, the other chemicals were used as they received. Solution polymerization process proceeded as follow, 0.2 ml

aniline was added in 1 ml concentrated HCl solution with constant stirring at room temperature then 0.25 ml APS was prepared in an aqueous media, before mixing, these reactants were pre cooled in an ice bath container. Thereafter 20 ml APS was added slowly to the aniline solution with constant stirring at room temperature. Cleaned glass substrates were immersed in the reaction bath using substrate holder on completion of reaction one substrate was removed from the reaction bath which then washed with distilled water to remove the granules attached with the surface of the substrate, dried and preserved in dark desiccators. The reaction was carried for 5 h resulting in green color precipitate which confirms formation of polyaniline emeraldine salt.

The as-deposited polyaniline films were characterized for their physical and chemical properties by using following characterization techniques.

RESULT AND DISCUSSION
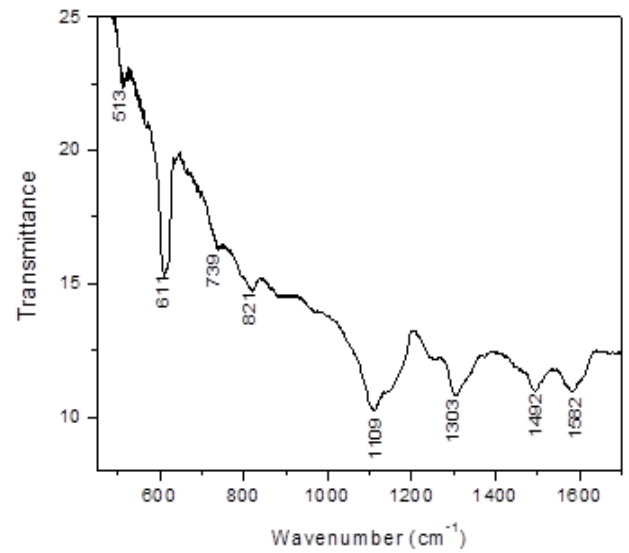
Growth of Polyaniline thin films

Aniline polymerization
The oxidative polymerization of aniline with APS in the presence of HCl shows an exothermic nature of the reaction which can be observed by monitoring the reaction temperature. Initial temperature of the reaction was $\sim 27^0C$ and the final temperature became $\sim 34^0C$. Increase in the temperature confirms the exothermic nature of the reaction. The acidity of the reaction bath increases continuously this may be attributed to increase in H^+ ion concentration in the reaction bath. Upon protonation the imine group of quinoid ring gets transformed into semiquinone radical cation. This leads to add H^+ ion to the reaction. This increase in H^+ ion concentration corresponds to decrease in pH of the reaction bath. Initial pH of the reaction bath was ~ 1.06 and at the completion of the reaction it became ~ 0.6. The stepwise decrease in pH indicates increase in doping level.

Fig. 1 shows plot of thickness verses deposition time. The steps involved in the oxidative polymerization of aniline are as follows: When the reactants were mixed, within few minutes the induction of film in the form of layer starts on substrate. The time required for such induction is called as induction period. Induction of layer starts with nucleation at a point on the substrate around which then further growth of film occurs. This structural enhancement proceeds with increase in protonation of acid which causes increase in chain
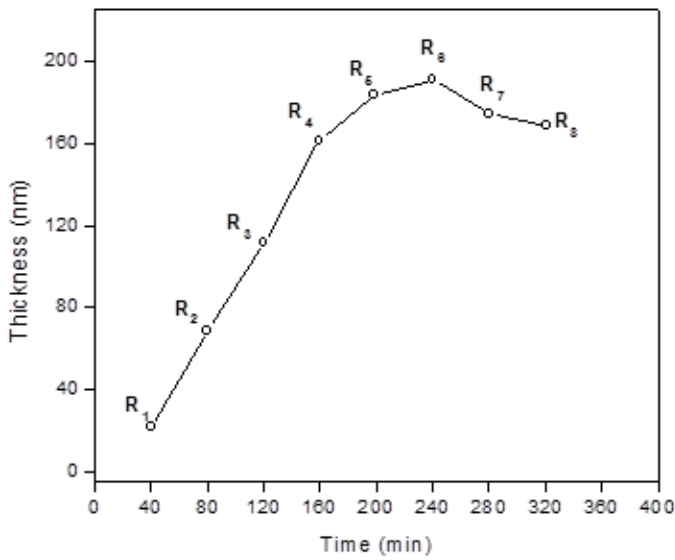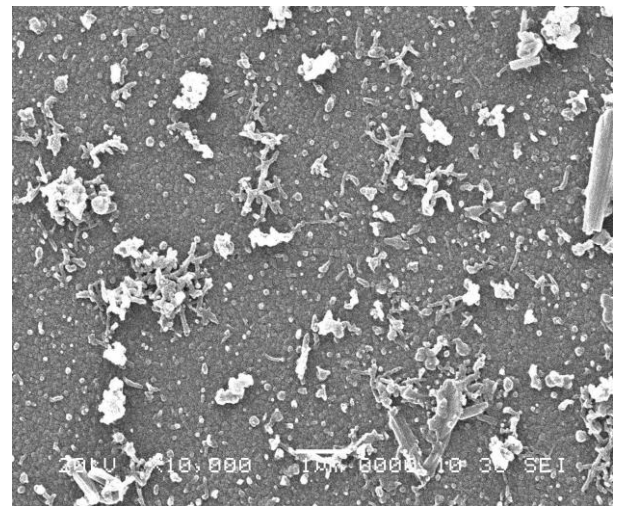
Fig. 1 : Plot of thin film thickness verses thin films deposition time.
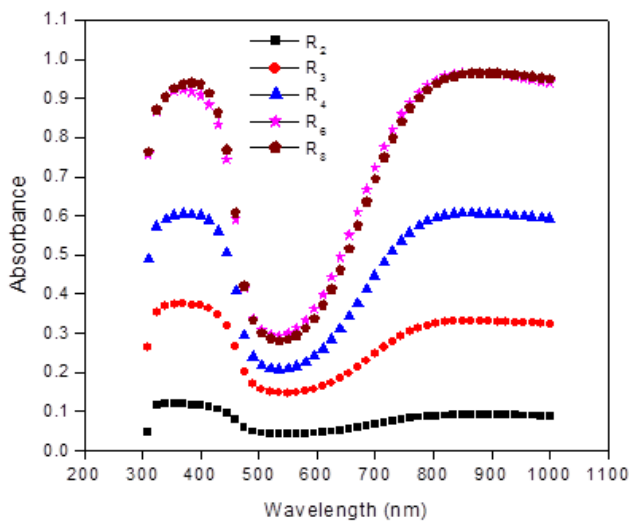

Fig 2: FTIR spectra obtained from polyaniline powder.
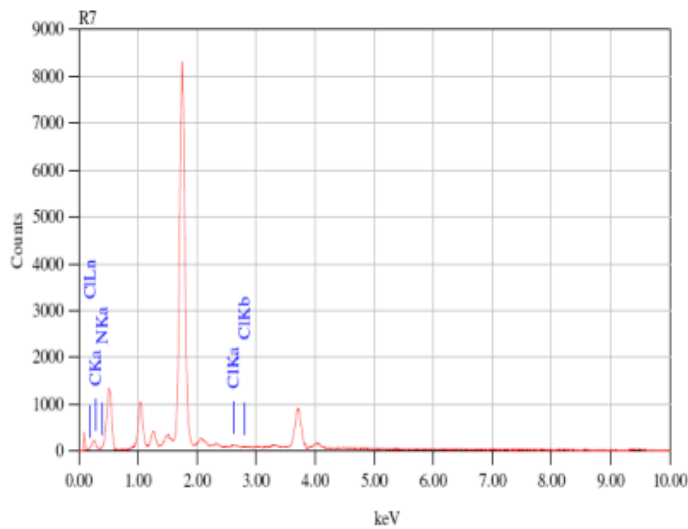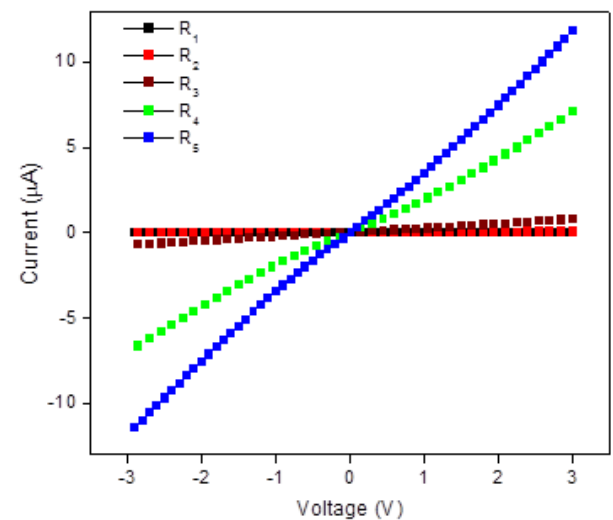

Fig. 3: EDAX spectra of HCl doped polyaniline.

Fig. 4: SEM image of the thin films

Fig. 5: The optical absorbance spectra obtained from polyaniline thin film.

Fig. 6: I–V characteristics obtained from polyaniline thin films.

length and number of oxidized state sites. The process continues till it reaches a maximum thickness called as critical thickness (T_c). Film at this stage is dense, rigid forming highly open structure containing large fraction of pores leading to inhomogeneous or multilayered structure. After attaining T_c, partial decrease in thickness is observed this may be attributed to depletion of either oxidant or monomer or both. The time at which depletion occurs is called as depletion period. Here we found the critical thickness as 191.1 nm for R_6 sample. Further increase in deposition time shows slight decrease in thickness, which may be attributed to increase in rate of dissolution than the rate of deposition after attaining the critical thickness (T_c).

Compositional Analysis
Infrared spectra

Fourier-transform infra-red (FTIR) spectrum of the green polyaniline powder was conducted, which was collected and filtered after the polymerization process was over. Fig. 2 shows the FTIR spectra of polyaniline powder. The peak at 1582 cm^{-1} is related to C = C stretching deformation of quinoid (Q) ring, 1492 cm^{-1} corresponds for C = C stretching of benzenoid (B) ring, 1303 cm^{-1} due to the carbon nitrogen (C–N) stretching of secondary aromatic amine, 1109 cm^{-1} shows B–NH$^+$ = Q stretching, 821 cm^{-1} is attributed to aromatic C–H out of plane deformation vibration of 1,4-disubstituted benzene ring, 611 cm^{-1} indicate C–S stretching vibration [Macdiarmid et. al., 1987], 513 cm^{-1} is assigned for – SO$_3$H group absorption spectra. Existence of all these bonds confirms the presence of functional group which are basic contain of the reactants used in the reaction.

EDAX Spectra

Polyaniline thin film deposited on silicon was used for compositional analysis. Fig. 3 shows energy dispersive X-ray (EDAX) spectra of the HCl doped polyaniline, which shows chlorine (Cl), carbon (C), and nitrogen (N) elements present in the sample. Carbon (C) and nitrogen (N) come from polymer shell while presence of chlorine (Cl) confirms HCl doping. Peak at ~1.8 KeV indicates Silicon substrate.

Morphological Analysis
SEM

The surface morphology of as-deposited Polyaniline thin films is observed by scanning electron microscopy (SEM) technique. Fig. 4 shows the SEM image of the sample. It can be seen that the granules are unevenly distributed over the entire substrate surface.

Optical analysis

Fig. 5 shows the optical absorbance spectra for polyaniline samples. Two peaks are observed in figure at ~ 400 nm (~ 3.1eV) and at ~ 830 nm (~ 1.5 eV). These peaks can be interpreted as excitation to the polaron band [Bhadra et al., 2009]. Peak at 1.5 eV (830 nm) indicates the transition from the valence band to the hole polaron called as polaron band which is a strong transition. The other peak at 3.1eV (400 nm) indicates the transition from polaron band to the conduction band. Polaron can be considered as a type of electronic defect that occurs with π orbital of the polymer backbone which produces molecular asymmetry responsible for high conductivity of the doped polyaniline. From graph, the flat breadth observed in every sample may be related to variation in the order of quinoid and benzenoid ring and the molecular conformation. The intraband absorption is due to excitation of polaron. As the thickness of the sample is increased there is increase in corresponding absorbance this may caused by molecular symmetry variation. The increase in thickness gives rise to asymmetric molecularity, dense surface and inhomogeneous morphology. Even it is seen that the optical band gap energy decreases from 2.57 eV to 2.51 eV with the increase in thickness from 21.3 nm to 191.1 nm. Decrease in the energy band gap may be attributed to variation in the structural morphology with increase in thickness [Yadav et al., 2008]. Increase in thickness shows blue shift in band gap energy (E_g) which may be related to structural morphology dependant energy band gap.

Electrical analysis

The electrical transport was checked with the help of I–V characteristic which was conducted for all samples using two probe method. Silver paste was used for making ohmic contacts. Fig. 6 shows I–V Characteristics for all samples. The linear nature of the graph shows ohmic behavior of the Ag/polyaniline junction. From the I–V plot resistance (R) of each sample was calculated which was further used for calculating conductivity (σ) [Huang et al., 1997]. Conductivity of the polyaniline sample found to be increasing with increase in thickness of the sample. For sample R2, the conductivity (σ) was 1.48×10^{-2} (Ω-cm^{-1}) and it increased to 6.66×10^{-2} (Ω-cm^{-1}) for sample R6 (of critical thickness). In emeraldine salt, polarons were found to be charge carrier which occurs by electron-phonon interaction. The density of charge carrier (polarons) may be increased by varying the doping level which also enhances the conductivity of polyaniline emeraldine salt. The doping is achieved by protonation of backbone nitrogen site of polyaniline.

The charge transfer is introduced through oxidation of aniline in which the total number of electron in the film remains same but the vacancies are created in film. The chemical structure of polyaniline has three benzene ring separated by amine (- NH -) group and one quinoid ring separated by imine (-N =) group. The quinoid ring has two pair of carbon atom and a double band with nitrogen atom with four π electrons. Upon protonation the imine group gets transformed to semiquinone radical cation state. This cation is more localized with degradation generating polarons. The protonation leads to increase H^+ ion concentration so numbers of holes are increased in the imine group which surround quinoid ring. This addition of holes creates charge localization in the valence band of polyaniline. Increase in doping level increases number of valence band charges resulting significant change in significant change in molecular orbital and band structure. The double bond in imine reorganizes changing the quinoid configuration as three carbon atom with six π electrons. So this change in geometry weakening the double bond between nitrogen and quinoid ring. This would increase the charge carrier density and strength of interaction between carrier states.

Gas Sensing Study

Gas detection testing was carried out Polyaniline film is inserted vertically in the gas chamber and change in characteristic of the film was detected. It is observed that the absorbance of the film increases when gas is purged in the chamber, indicating the adsorption and surface reaction occurred between gas molecules and polyaniline. The sensitivity of the sensor is defined by using (standard) relation, $S=(A_g-A_a)/A_a$ where A_g and A_a are the absorptions of films in gas and in air, respectively. The sensitivity of the sensor increases with increase in gas concentration. The response time and recovery time of the sensor are moderate.

CONCLUSION AND SUGGESTIONS

In the present article polyaniline thin films have been synthesized using user friendly cost effective solution polymerization techniques at room temperature. These thin films studied for physicochemical as well as optoelectronic properties for testing the sensor applicability of these materials. The peaks observed in FTIR spectra and an elemental composition in EDAX confirms expected ingredients in thin films. Optical absorption spectra represents exciton induced bipolaron transitions while electrical properties studied shows conducting nature of the thin films. The sensor properties reveal that these polyaniline thin films can be used as sensor materials.

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