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Preparation and characterization of Nanostructure Plasma PANI thin films

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Abstract: In this work, we have to prepared plasma polymerized aniline thin films. Plasma polymerization is a process of synthesis , in which crystal are changed in nanostructures. We have to monitor the growth rate of thin films with help of pulses and established an ideal condition. The characterization of PANI thin film was performed with the ultraviolet-visible spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) studies. The surface of the thin film possessed three-dimensional networks of the PANI belts as cauliflower like morphology with a diameter of 35-97 nm. In PANI prepared through chemical route, however no aniline seems to exist. The PANI films prepared by plasma polymerization are less crystalline compared by chemical route. PANI films prepared by plasma technique are however totally free from reagent chemicals. The sufficient sensitivity could be obtained for plasma prepared PANI sensors; there may be no need to go through cumbersome chemical route.

Keywords: Plasma polymer; thin Film; transparent thin films

1.INTRODUCTION

Plasma polymerization has been used to prepare films of a wide range of the conducting polymers including polyaniline (PANI) [1–8], polypyrrole [4], and polyacetylene [9], Among the reported advantages of plasma-polymerized materials are denseness and uniform but controllable film thickness, adhesion and conformability on various substrates [10] and further thermal and chemical inertness [5]. A wide range of volatile organic compounds can be used as the feed to a plasma reactor, but because no oxidants or solvents are involved, contamination of the film by extraneous species is eliminated in principle [11], Further and the polymerization process requires only a single step. The composition of a plasma-polymerized film can be tailored with the appropriate processing conditions, and the resulting material properties are often unique and unobtainable by wet synthetic methods [5]. Although the excited plasma species are mainly high-energy electrons that are relatively indiscriminate in rupturing chemical bonds, the substrate can be kept at the ambient temperature. [12]

Over all, plasma polymerization is an inexpensive processing route. PANI is the most highly conductive of all known polymers and has notably complex structure–property behavior involving four different oxidation states; the conducting form is stable in both air and water [13]. In situ doping with iodine vapour [3, 4, 6–8] can modify the conductivity of plasma-polymerized PANI; subsequent ion implantation of I^+ in PANI films has also been reported [14]. The protonic doping from acidic solutions is also well known. The morphology of a PANI film depends on the method of preparation [15], the substrate [7], and the deposition time [7]. On glass, plasma-polymerized PANI first forms irregular particles, then clusters, and finally a continuous film of irregular pentagons; in contrast, on a Pt substrate, the initial spongy, spherical particles grow into fibrils [7]. The range of applications for PANI films includes sensors [16], corrosion protection [2, 13], and electrochromic displays [13].

PANI can be synthesized by chemical, electrochemical, or plasma methods, and in each case, the composition, morphology, and physical properties of the resulting polymer are strongly dependent on the detailed reaction conditions.

Among the methods applied to characterize plasma polymerized aniline are IR spectroscopy [2, 3, 5–8, 14, 16], ultraviolet–visible (UV–Vis) spectroscopy [2, 8, 14], electron spin resonance [2], X-ray diffraction [3,4], thermal analysis, scanning electron microscopy (SEM) [2, 3, 6, 7, 14, 15], elemental composition by electron spectroscopy [3, 4, 6, 15], X-ray photoelectron spectroscopy [2,14], energy-dispersive spectroscopy/scanning electron microscopy [3], and the measurement of various electrical [2–7,14] and optical properties and also the contact angle [2,15].

PANI samples prepared by the wet-chemical or electrochemical oxidation of aniline have been examined by a similar range of dry ex situ methods. These include IR [17–19], UV–Vis [18–20], X-ray diffraction [19], ^{13}C-NMR [18], SEM [21], scanning tunneling microscopy [21], and atomic force microscopy [19],

Quantitative and qualitative wet analytical methods have also been applied to these polymers. Methods include gel permeation chromatography [19], solubility determination [17], and various electrochemical [13, 20–23] and spectro-electrochemical [23], techniques. Wet methods have seldom been used in characterizing plasma-polymerized materials. Although it is true that immersing a previously dry polymer film is likely to cause irreversible changes in its properties, invaluable information can be gained that permits a much more detailed comparison of materials made by different process routes. Not surprisingly, a direct comparison of materials made under different conditions is quite difficult.

I. PREPARATION OF PANI THIN FILMS

The polyaniline thin films have been prepared by an inductively coupled pulsed-plasma reactor. Independently of the pulsing of the RF plasma, the monomer injector also operates in a pulsed manner; the RF frequency is much greater than that of the injector, so each burst of injected aniline is exposed to a plasma reactor environment that is effectively steady. The pulsed-plasma reactor system having monomer injection system with custom-built automotive fuel injector, a syringe containing liquid monomer under pressure, and an oscilloscope to provide a timing pulse to control the injection of vapourized monomer (Fig. 3.1). When a pulse of the monomer entered the evacuated reactor, most of the liquid immediately vapourized by flash boiling; any remaining liquid disintegrated into droplets that were collected by mesh separators placed about 2 cm from the injector nozzle. The aniline was injected in 10-ms pulses until the pressure in the reactor reached the desired value at 40 Pa. All the depositions were performed with a static fill of vapour, electrical pulses used to introduce monomer vapour and form the thin films.

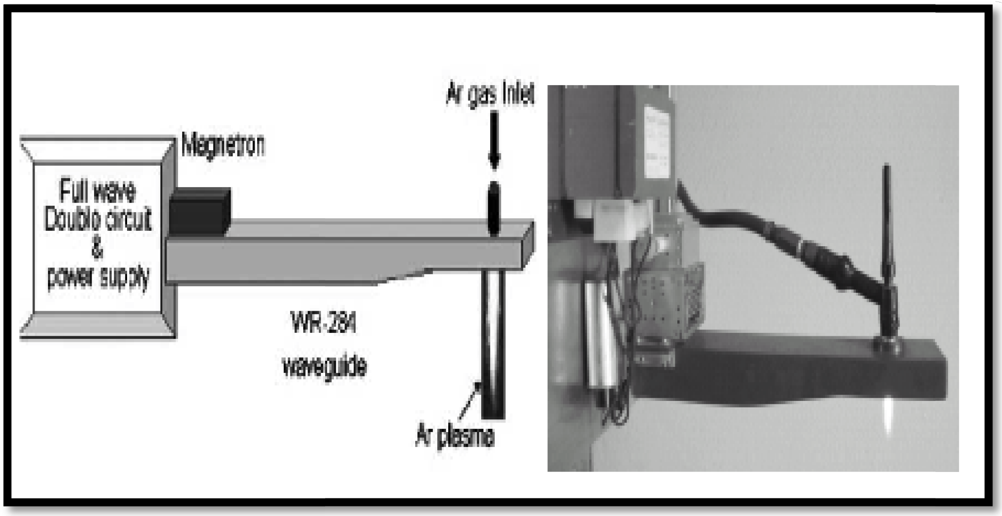

Fig.3.1. A typical picture of plasma polymerization unit.

II. EQUIPMENT DETAILS:

A thermocouple gauge and a capacitance manometer were with the system for the monitoring of the reactor pressure. The manometer was used to calibrate the thermocouple gauge in the absence of plasma and was removed during film deposition; by itself, a thermocouple gauge cannot provide absolute pressures, but the plasma does not affect it. Calibration runs were performed in triplicate from 0 to 1000 m Torr for air, aniline vapour, and a mixture of aniline vapour and hydrogen. When enough monomer had been injected into the reactor to reach the desired deposition pressure, the plasma was repetitively activated through the discharge of a 1.8-μF capacitor initially held at 23 kV, the RF coil excitation being with a damped sinusoid of 290 kHz and a decay time constant of 10 μs. After 10 such plasma shots, the reactor was evacuated completely and refilled with fresh monomer vapour. One hundred plasma pulses were used to grow most PANI samples. The substrate holder could be positioned at various distances from the RF coil. The substrates included glass plates, indium tin oxide (ITO) glass, and glass microscope slides; in some runs, the choice of the substrate was dictated by the characterization method that was to be used. The reagent-grade aniline monomer was purified by triple distillation over zinc granules and then stored in a dark bottle under nitrogen. [13].

III. RESULTS AND DISCUSSION:

The average deposition rate obtained for different plasma processes and number of pulses involved to prepare a film is discussed as in the following.

2.4.1 Film deposition rate:

Variations in the film thickness can provide a direct measure of the net growth rate under different conditions. As per **Table.3**.1 the profilometer data can directly be correlated with the pressure in the reactor and the number of plasma pulses, but the growth dynamics is complex. The average growth rate increases with higher pressure for a fixed number of plasma pulses, but at pressures of 27 or 40 Pa, the average rate decreases as the number of pulses is raised from 50 to 100. The drop is more pronounced at higher pressure. At 13 Pa, however, the deposition rate increases if more pulses are used. Different mechanisms of polymerization or film growth may be rate-controlling under different conditions [29]. And there may be a critical film thickness at which the growth rate slows down.

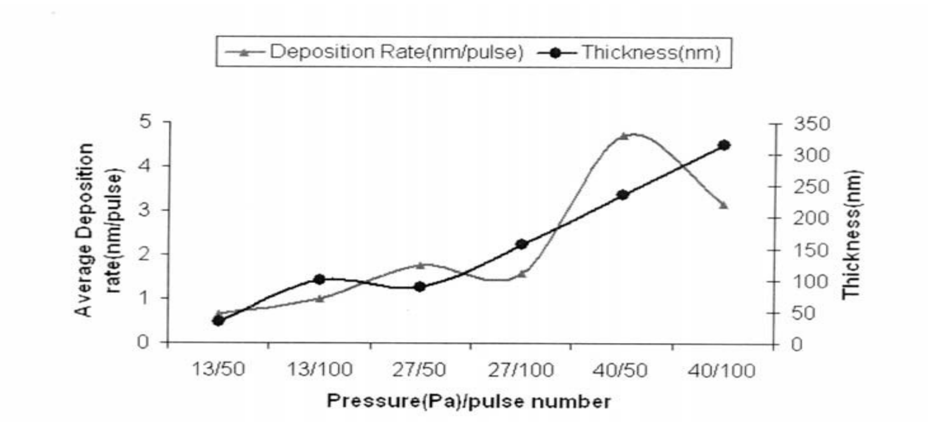

TABLE 3.1

Film Thickness and Average Deposition Rate of PANI

Sl. No.	**Experimental condition**	**Thickness (nm)**	**Average deposition rate (nm/pulse)**
1.	13 Pa, 50 plasma pulses	32.8	0.66
2.	13 Pa, 100 plasma pulses	98.8	0.99
3.	27 Pa, 50 plasma pulses	88.6	1.77
4.	27 Pa, 100 plasma pulses	157	1.57
5.	40 Pa, 50 plasma pulses	236	4.72

6.	40 Pa, 100 plasma pulses	314	3.15

2.5 Characterization of PANI film:

The prepared PANI thin films were characterized by using UV-Vis, FTIR, XRD and SEM. An Ocean Optics HR 4000 High Resolution Spectrophotometer recorded the UV-Vis spectra of the films. For FTIR measurements the films were grown on glass microscope slides and then were scraped off and pressed into KBr pellets. The spectra were recorded between 4000 and 400 cm^{-1} with a Perkin Elmer BX FTIR microscope (Shelton, CT); an averaging of 64 scans was done to minimize noise. The XRD spectra of the material were obtained by using powder XRD system Model PAN analytical X'Pert Pro having $CuK_{\alpha1}$ X-ray source of wavelength 1.5406 Å. The sample morphology and surface uniformity were assessed microscopically with SEM (S-570, Hitachi, San Jose, CA) in the secondary electron mode. Finally the results obtained for the present PANI samples have been compared with those available for PANI samples prepared by chemical methods.

2.5.1 UV-Vis spectra:

The UV-Vis spectrum of the PANI thin film grown on glass substrate (Fig.3.2) shows an absorption peak in the UV range at 328 nm and another in visible at 560 nm. These are characteristic peaks of undoped PANI. The peak at 328nm corresponds to π-π excitations of amine nitrogen of the benzenoid segments and that at 560 nm to imine nitrogen of the quinoid segments of PANI respectively [25]. The observed UV-Vis spectra thus support the formation of PANI through plasma polymerization.

However, in the Fig 3.3 spectrum of PANI samples obtained through wet chemical method [26] the above two peaks were at 328 nm and 635 nm respectively. There was further an additional third peak at 268 nm, which was associated to change transfer process.

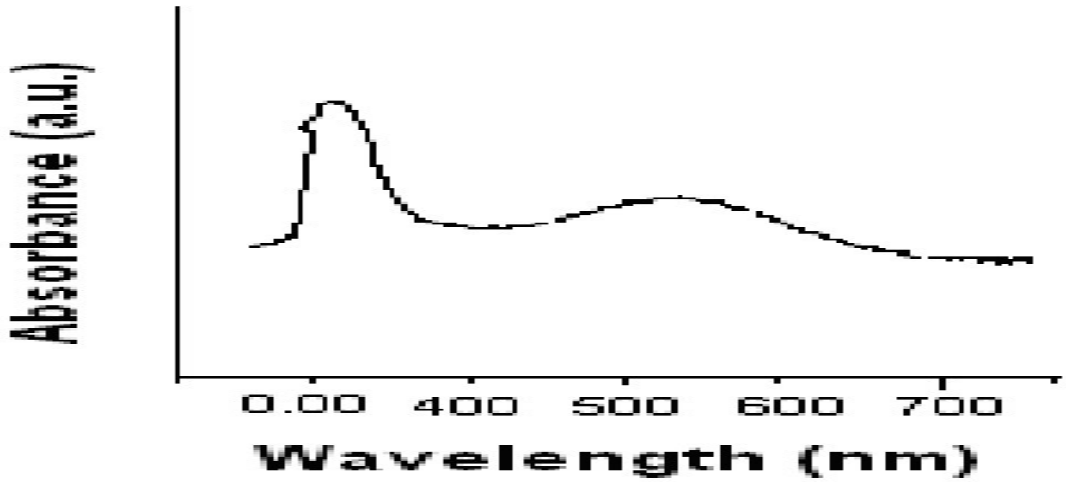

Fig 3.2: Uv-Vis spectrum of the PANI thin film.

2.5.2 FTIR spectra:

FTIR spectra **(Fig.3.4)** indicates not only that the chemical bonding in plasma-polymerized aniline differs from that of the monomer but also that the molecular structure of the deposited film is a strong function of distance (z) from the RF coil in the plasma reactor. The strong z dependence of FTIR spectra and thus of chemical composition and structure of plasma-polymerized materials has long been known [27,28],The films whose FTIR spectra are shown in **Figure 3.4** were grown on glass slides placed 16, 24, 32, and 40 cm from the center of the coil, under otherwise identical conditions (40 Pa and 100 plasma pulses). For an easy comparison, the spectrum of the aniline monomer is also shown in **Figure 3.4.** But it should be noted that the intensities of all five spectra are in arbitrary units and therefore are not directly comparable. The spectra for Z=40 cm is well marked and explained in the text.

We can determine the effect of the axial position (z) on the chemical functionality of the films by first identifying bands that are common to all four of the PANI spectra and then focusing on features that are significantly different. The common bands include those near 3338 cm^{-1}, indicative of a secondary amine; those at 698 cm^{-1} and 756 cm^{-1}, indicative of deformation in a mono-substituted benzene ring; and those at 439 and 541 cm^{-1}, indicative of deformation of substituted benzene. However, the spectrum for the 40-cm film shows a clearer evidence for aromaticity than any of the others. The I. R. bands near 1027, 1069, 1156, 1182, 1448, 1492, 1539, and 1599 cm^{-1} are present in the spectra for different Z- films but are considerably sharper for the Z=40 cm film; and further all are consistent with aromaticity. A comparison of the FTIR spectrum of Fig. 3.4 for plasma polymerized aniline with the FTIR spectrum of PANI prepared through chemical route [Fig 3.4] shows that there is a unique band at 3024 cm^{-1} in Fig. 3.4 which is totally absent in Fig. 3.5. This shows that during plasma polymerization some aniline monomer or its oligimers remain in the PANI film prepared. This band is more significantly seen in film prepared for low Z values, and seems to be due to aniline or its oligimers.

The spectra for films grown closer to the RF coil (smaller Z) have a prominent band in the region from 1673 to 1684 cm^{-1}, which shows frequencies that are associated with C=O stretching of a ketone created due to oxygen left in the reactor after pump down, Such a band may also be assume to C=C band of quinoid ring. The C=C bond of benzenoid rings has clearly been observed at 1492 cm^{-1}. The relative intensity of this band decreases as the axial distance increases. These observations are consistent with those obtained by other workers regarding the plasma polymerization of aniline [2, 6–8] and fluorinated monomers [27, 29]. It is believed that free radicals are trapped in the as-grown film in concentrations that increase with the field strength; it is however not clear whether these highly energetic species react in situ with residual oxygen left in the reactor after pump down or whether subsequent exposure to atmospheric concentrations of oxygen is required. It may be relevant that films handled initial way to low Z but grown at Z=40 cm do not show any carbonyl band in FTIR. The model of electron temperature profiles developed earlier by Shepsis [24] predicts that the plasma electrons should be most energetic in the vicinity of the RF coil and that their temperature should decrease with the axial distance away from it.

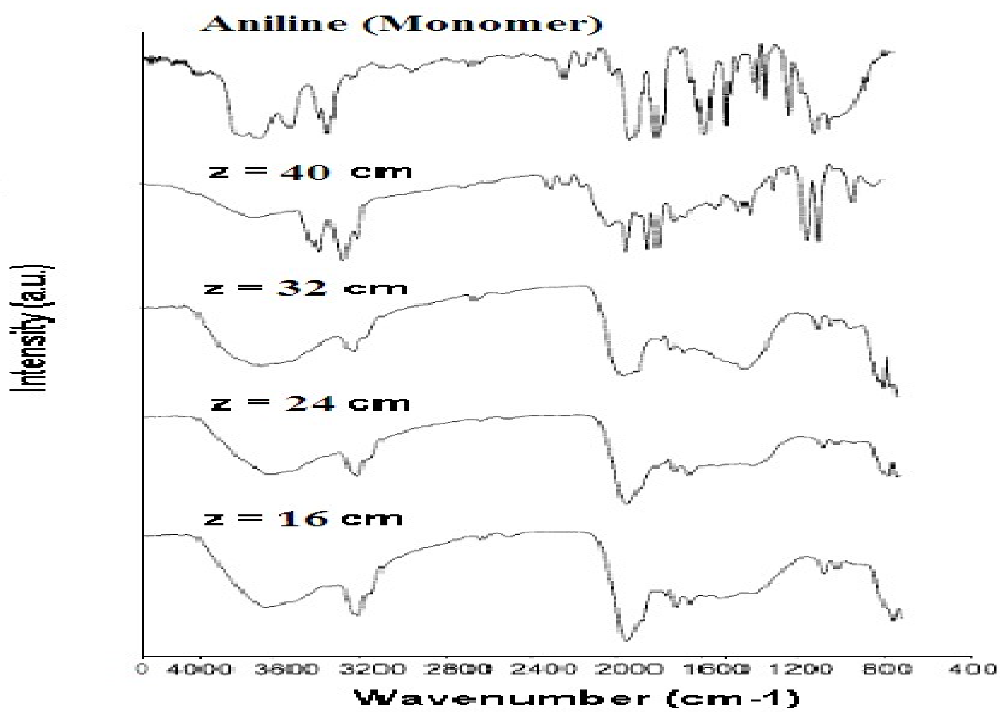

Figure 3.4 FTIR spectra of aniline monomer and plasma polymerized aniline films deposited on ITO substrates at various distances from the center of the RF coil. The reactor pressure was 40 Pa, and there were 100 plasma pulses.

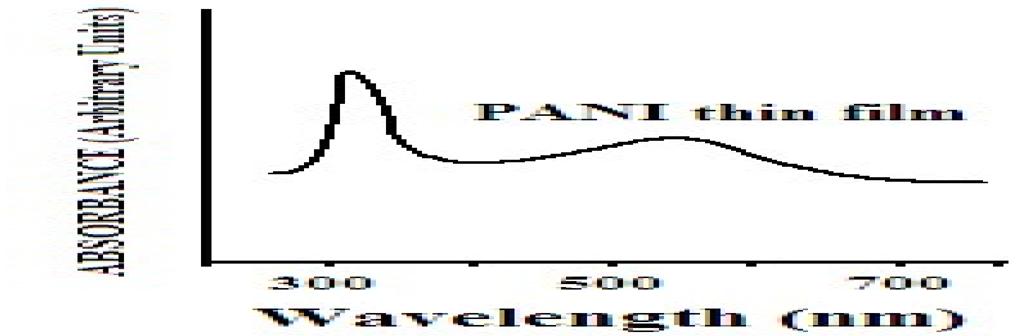

Figure 3.2. UV-Vis spectrum of the PANI thin film.

2.5.3 XRD Spectra:

The XRD of the PANI thin films prepared by plasma technique clearly shows their amorphous nature and gives unresolved crystalline peaks in the 15º-30° region of 2θ (Fig. 3.6).The XRD spectra of PANI prepared by chemical route are further shown in Fig. 3.7. These spectra show resolved broad band in 7º-30º region of 2 θ. A comparision of XRD spectra of Fig. 3.5 and 3.6 shows that PANI crystallites are of smaller size ($<10^{-6}$ cm) in plasma polymerized films. The XRD peaks for PANI prepared by chemical route do exhibit some resolved structure for 2θ from 7º to 30º, indicating that in such PANI samples the crystallites are of somewhat bigger size, due to enough crystallization in the process of preparation.

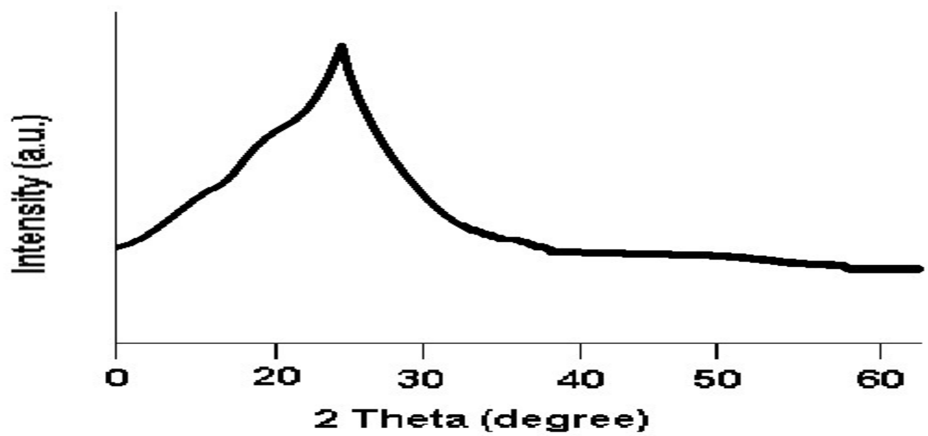

Figure 3.5 XRD spectra of polyaniline thin film prepared by plasma polymerization technique at 40-Pa reactor pressure

2.5.4 SEM:

SEM images show that the morphology plasma polymerization of the PANI thin film and as per Fig.3.8 **e**xhibit smooth texture in films. So a films prepared through chemical route are concerned, the SEM images were not much different from Fig. 3.8.

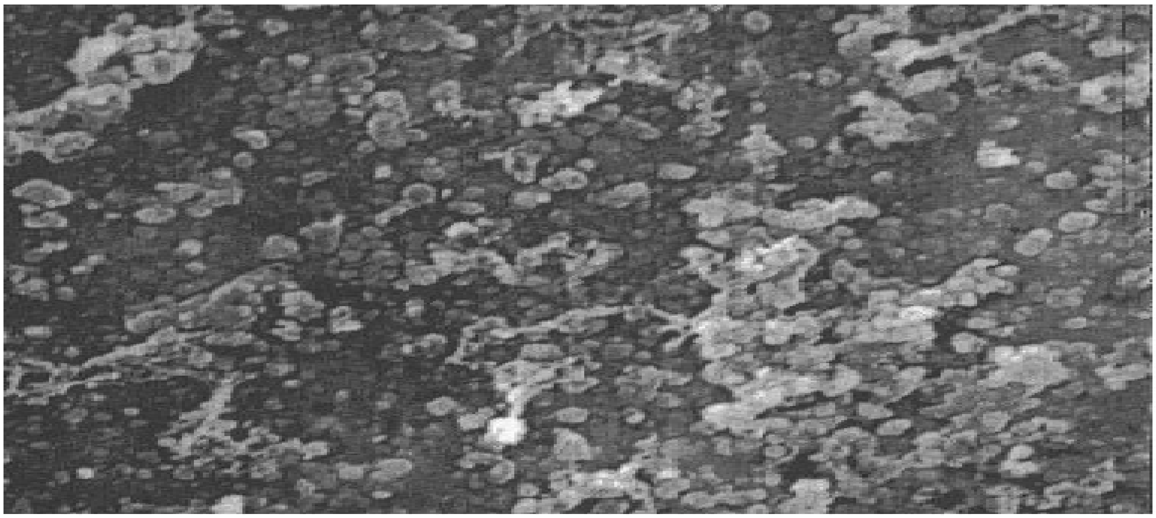

Figure 3.8: SEM micrographs of PANI deposited on glass substrate 40-Pa reactor pressure and 50 plasma pulses

IV. CONCLUSIONS

UV-Vis, FTIR, and XRD spectra of plasma-polymerized films clearly indicate the existence of polyaniline. Some aniline monomer, oligimer content seems to exist in plasma prepared PANI. In PANI prepared through chemical route, however no aniline seems to exist. The PANI films prepared by plasma polymerization are less crystalline compared by chemical route. PANI films prepared by plasma technique are however totally free from reagent chemicals. Thus if, as given in next chapters, sufficient sensitivity could be obtained for plasma prepared PANI sensors, there may be no need to go through cumbersome chemical route.

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