Nanostructured polyaniline thin films prepared by plasma polymerization at atmospheric pressure

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ABSTRACT

Plasma polymerization technique includes plasma (state) polymerization which is one of the most powerful methods for surface modification of polymeric materials. Plasma polymerized organic thin films have received a great deal of interest because of their unique characteristics such as: pinhole-free, structurally cross-linked, insoluble and highly adhered. In this work, nanostructures polyaniline (PANI) thin films were prepared by dielectric barrier discharge plasma jet polymerization technique. The dielectric barrier discharge plasma jet local mead for plasma polymerization. The effects of substrate position, working gas flow rate and annealing temperature on thin films properties were studied. The characterization of prepare PANI thin films were performed with the ultraviolet-visible spectroscopy (UV-VIS), Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD) and atomic force microscope (AFM). The AFM images show that the surface of the PANI thin films consist of grains with average grain size about 100 nm. Electrical and optical properties reveal the conductivity of the PANi thin films at room temperature are nearly 0.68×10^{-4} S.cm^{-1} and the band gap with range of 2 to 2.7 eV depending on prepared conditions. This inexpensive process which is friendly for environment affords a new technique in the field of conducting polymers for coating large substrate areas.

Keywords: Plasma polymerization, non-thermal plasma jet.

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INTRODUCTION

Plasma polymerization can be defined as 'the formation of polymeric materials under the influence of plasma' (Yasuda, 1985). Solid deposits from organic compounds formed in a plasma early as in 1874 (de Wilde, 1874; Thenard and Hebd, 1874). Systematic investigation of plasma polymerization started only in the 1960's (Goodman, 1960; Stuart, 1963; Bradley and Hammes, 1963) following the rapid advancement of polymer science in those years (Yasuda, 1985; d'Agostino, 1990). Over the past two decades, the advantages of plasma polymerization have been fully recognized; today, plasma polymerization is accepted as an important process for the formation of entirely new materials, and as a valuable technique to modify the surfaces of polymers or of other materials. Advantages of plasma polymerization include the fact that pinhole free, conformal thin films can be deposited on most substrates, using a relatively simple one-step coating procedure (Rinsch et al., 1996).

Additionally, a wide range of compounds can be chosen as a monomer for plasma polymerization, even saturated hydrocarbons, providing a great diversity of possible surface modifications. The conducting polymers have been found suitable for microelectronic device fabrication due to their excellent electric characteristics and ease of processability. Among these polymers, polyaniline (PANI) has emerged as a promising candidate with great potential for practical uses such as in light emitting diodes, transparent electrodes, electromagnetic radiation shielding, corrosion protection of metals, gas and humidity sensing, battery applications and many more (Chakane et al., 2002). Nanoparticles have become an interesting topic among the various science fields due to the unique properties of the material at very small particle size. There is no strict dividing line between nanoparticles and non-nanoparticles. The size at which materials display different properties to the bulk material is material
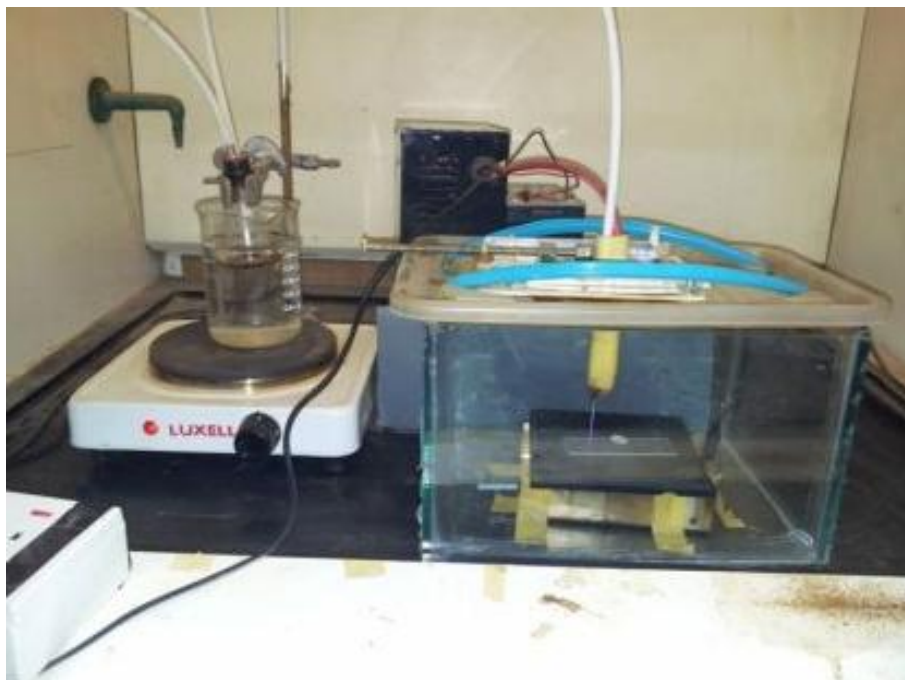
Figure 1. Schematic diagram for non-equilibrium atmospheric pressure plasma polymerization experimental set-up.

dependent and can certainly be claimed for many materials much larger in size than 100 nm (Polymer Composites as Construction Materials, 2009). An example of a material that behaves differently in the bulk form than the nano form is Iron. In the bulk form, the element is stable, but in the nano form it is highly flammable in an oxygen environment. Nanoparticles offer the benefit of needed properties that can be easily added to another bulk material. We have successfully prepared nanostructures polyaniline (PANI) thin films by dielectric barrier discharge plasma jet polymerization technique, with high voltage of sinusoidal shape of 7.5 kV and frequency of 28 kHz peak to peak. In this article, the effects of substrate position with different gas flow and annealing temperature on thin films properties and the characterization of prepare PANI thin films, will be described, with the ultraviolet-visible spectroscopy (UV-VIS), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and atomic force microscope (AFM), and electrical and optical properties study.

EXPERIMENTAL

Preparation of PANI thin film

PANI thin films were prepared by dielectric barrier discharge plasma jet. The films were deposited on glass substrates. The glass substrates were cut into standard sizes of 10 × 10 mm, and then cleaned with acetone under ultrasonic condition prior to the plasma polymerization. Pure aniline monomer was obtained from the Chemical Department and used as the organic precursor. The schematic diagram for the non-equilibrium atmospheric pressure plasma of then films deposit by plasma polymerization is shown in Figure 1. Gas mixture consisted of 1, 2 and 5 L/min of Ar as the working gas and the admixed monomer gas, which was vaporized by passing the Ar tube through the aniline vessel. This mixture was allowed to flow in through the inlet pipe, and the plasma was ignited by using an electric source at a fixed frequency of 28.0 kHz. The plasma was generated downstream to the substrate which was positioned along different distance from the pipe end. The film deposition was carried out for 5 min under various conditions of carrier gas flow rate.

Characterization

PANI thin film was characterized with the UV-Vis, FTIR and AFM measurements. UV-Vis spectra was recorded by a double-beam UV-VIS-NIR 210A. Spectrophotometer was used to measure the transmittance and absorption of PANI films deposited in the range of 200 to 1200 nm. The FT-IR spectra were recorded by using KBr and testing all samples by Shimadzu Co. FT-IR 8000 series Fourier transform, infrared spectrophotometer from wavelength range of 400 to 4000 cm^{-1} under identical conditions. FAM was studied on the using a AA3000 Scanning Probe

Table 1. Optical energy gap with different parameters.

Sample	Gas flow (L/min)	Distance (cm)	Thicknesses (nm)	Annealing temperature (ºC)	Energy gap (eV)
A	1	1	261	100	2.5
B	2	1	235	100	2.57
C	2	1	244	28	2.7
D	5	1	239	100	2.65
E	2	2	312	100	2.2

Table 2. The experimental condition for the preparation of polyaniline thin films by plasma polymerization.

Sample	Flow-rate (L/min)	Distance (cm)	Annealing temperature (°C)	Deposition rate (nm/s)
A	1	1	100	0.87
B	2	1	100	0.78
C	2	1	28	0.81
D	5	1	100	0.80
E	2	2	100	1.04

Microscope SPM, tip NSC35/AIBS.

DC conductivity measurements

The DC electrical conductivity was measured as a function of temperature for PANI films over the range of 300 to 423 K by using the electrical circuit. The measurements were done using sensitive digital electrometer type keithley (616) and electrical oven.

RESULTS AND DISCUSSION

In order to study the influence of variables of annealing and flow rate and the distance, we observe Table 1. This table shows the experimental condition for the preparation of five polyaniline thin films by plasma preparation. Films A, B, and D were prepared to study the effect of gas flow rate on the polyaniline thin films chemical composition, while films B and E were prepared to study the effect of the substrate distance from plasma torch end on polyaniline prepared thin film chemical composition. Also, this table shows the effectiveness of annealing of films deposition rate which is slightly affected by varying the gas flow rate and substrate distance from plasma torch end.

In Table 2, samples B and E show that when the distance increases, deposition rate is increased. Samples B and C show that deposition rate decreases at annealing increase. Table 3 and Figure 2a, b, c, d and e, show the FTIR spectra for the five prepared thin films. From these FTIR spectra, there are common band and peaks as shown in Table 3.

Table 3 shows some vibration bands at 3445, 2981.88, 1492.314, 1292.90 and 1125.68, etc. These values are characteristic of polyaniline chain and are in agreement with theoretical predictions (Kostić et al., 1992). And, the band 1125 cm^{-1} is considered to be a measure of the degree of electron delocalization and therefore it is the characteristic peak of PANI conductivity (Huang et al., 2003). On comparing the thin films prepared at different gas flow rate, it is evident that there is no major effect of gas flow rate on thin films chemical composition, except the peak at 1400 to 1480 cm^{-1} and the peak at 1600 to 1500 cm^{-1} which is absent at the FTIR spectra of sample (A), and is however present in other samples spectra. Also, the FTIR spectra for samples prepared at different distance from the plasma torch end show no difference in these spectra except the peak at 1598.88 cm^{-1} is more intense and more broaden for sample C which was prepared at distances of 1 and 2 cm and gas flow rate of 2 L/min. Also, the peak at 1400 and 1100 cm^{-1} is absent at the FTIR spectra of sample E. However, some shifting in position is observed, which might be due to different polymeric matrix of the synthesized PANI.

The prepared thin films show light green colors which indicate that the films belong to the emeraldine base polyaniline form, so this is a conductive polymer. Emeraldine base is also regarded as the most useful form of PANI due to its high stability and the fact that electrically properties of PANI can be optimized by doping the emeraldine form.

The optical energy gap values (E_g) for PANI films as shown in Table 1 have been determined. A plot of $(\alpha h v)^2$ versus hv for PANI films with different flow distance, annealing temperatures, and thicknesses is shown in Figure 3a to e.

The plot is linear indicating the direct band gap nature of the films. Extrapolation of the line to the hv axis gives the band gap. The value of the optical energy gap increases with the increasing of flow rate for samples A,

Table 3. FT-IR data of PANI.

Bond range (cm^{-1})	Observed peaks position for all sample (cm^{-1})					Expected vibrations
	A	B	C	D	E	
3100-3500	3407.98	3464.92	3440	3309.9	3425.3	N-H stretching
2923	2945.1	2945.1	2920	2927.7	2974	C-H stretching of aromatic ring
1600-1500	1679, 1508	1598.88, 1508	1629, 1384	1627.8	1625.88, 1514	C=C stretching of quinoid ring (N=Q=N)
1400-1480	0	1458	1421	1421.4	0	C=C stretching vibration of benzenoid ring (N-B-N)
1300-1200	0	1367, 1244	1384.7	1380.9	1265.2	C-N stretching of primary aromatic amines
1100	1035	1105.14	1153.3	1027.9	0	C-H bending vibration
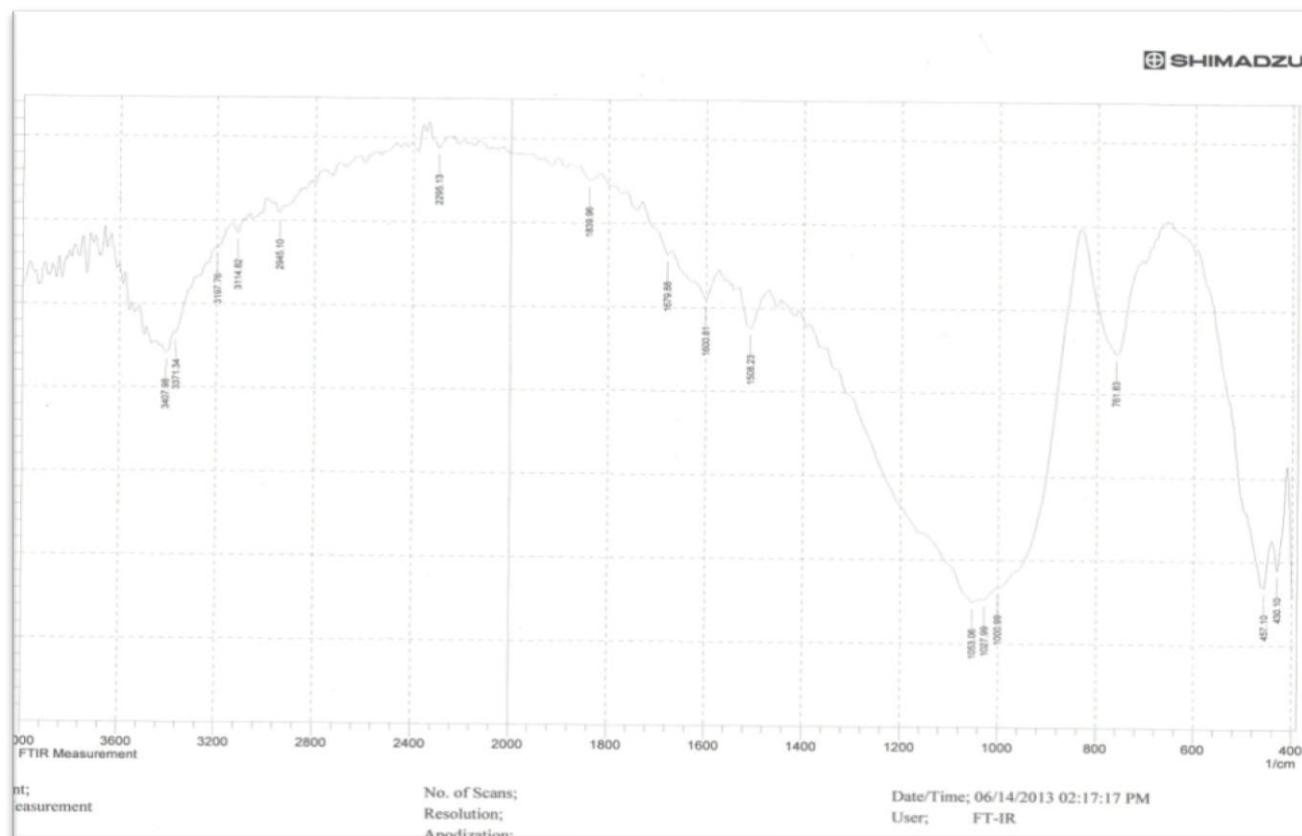
Figure 2a. FTIR spectra for polyaniline thin films prepared by non-thermal low temperature plasma jet.
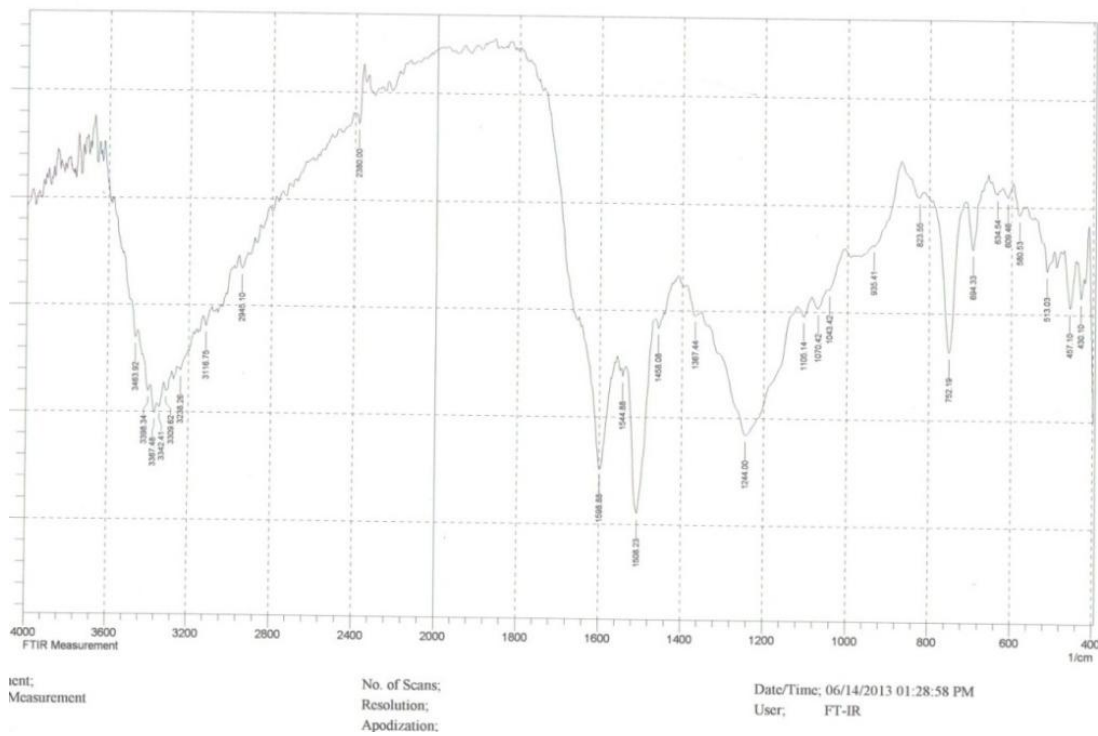
Figure 2b: FTIR spectra for polyaniline thin films prepared by non-thermal low temperature plasma jet.
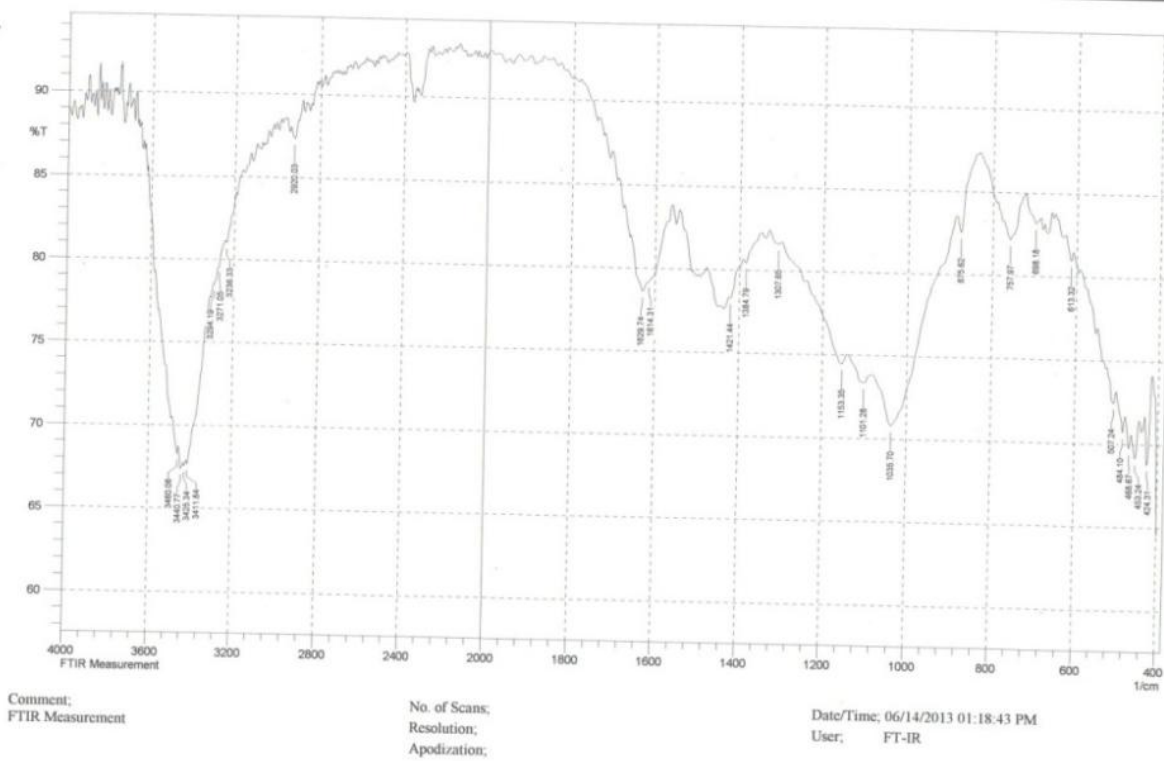
Figure 2c. FTIR spectra for polyaniline thin films prepared by non-thermal low temperature plasma jet.
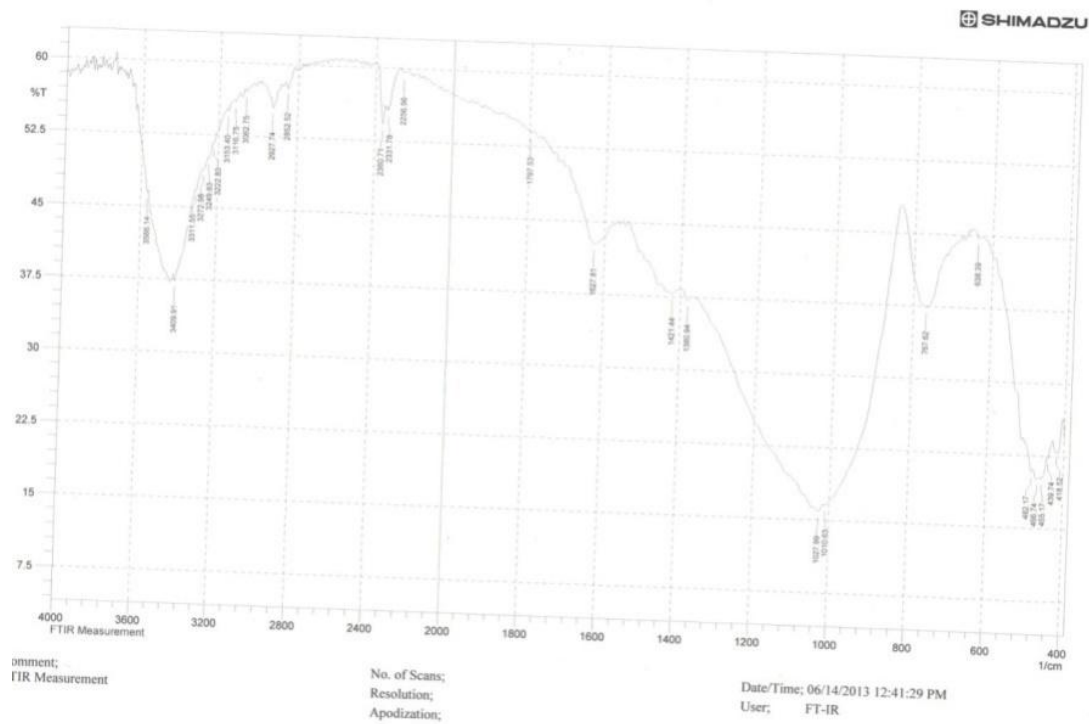
Figure 2d. FTIR spectra for polyaniline thin films prepared by non-thermal low temperature plasma jet.
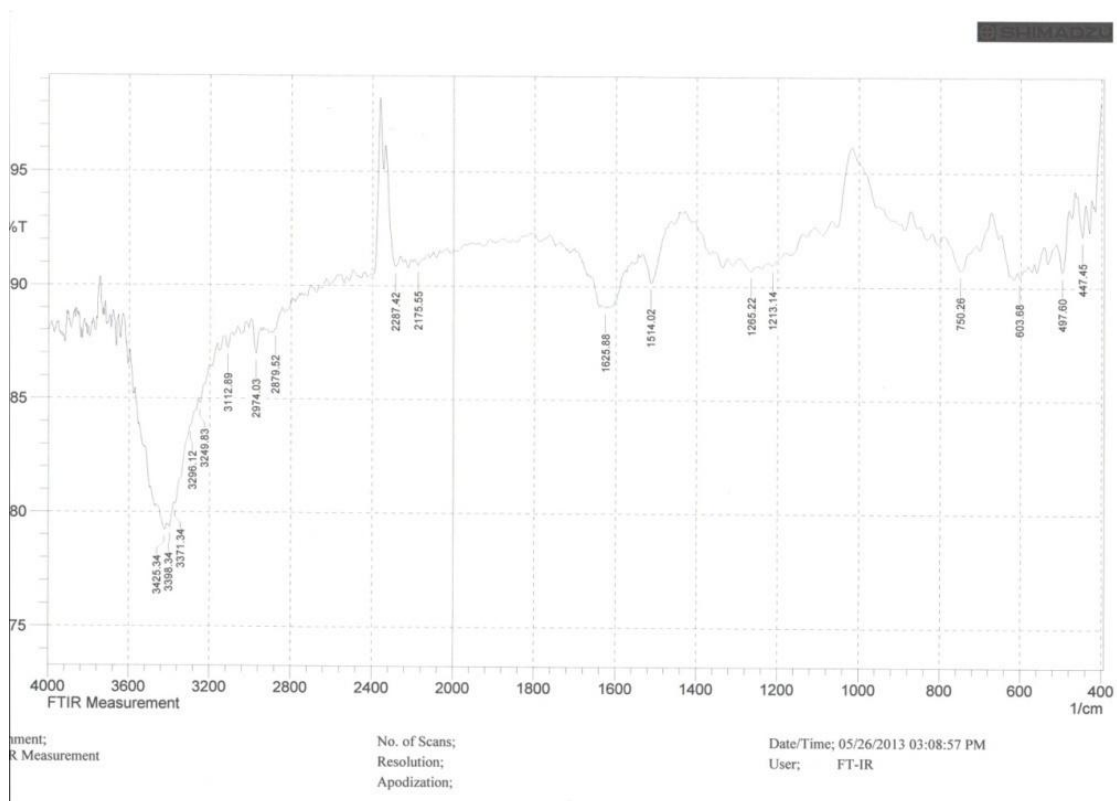
Figure 2e. FTIR spectra for polyaniline thin films prepared by non-thermal low temperature plasma jet.
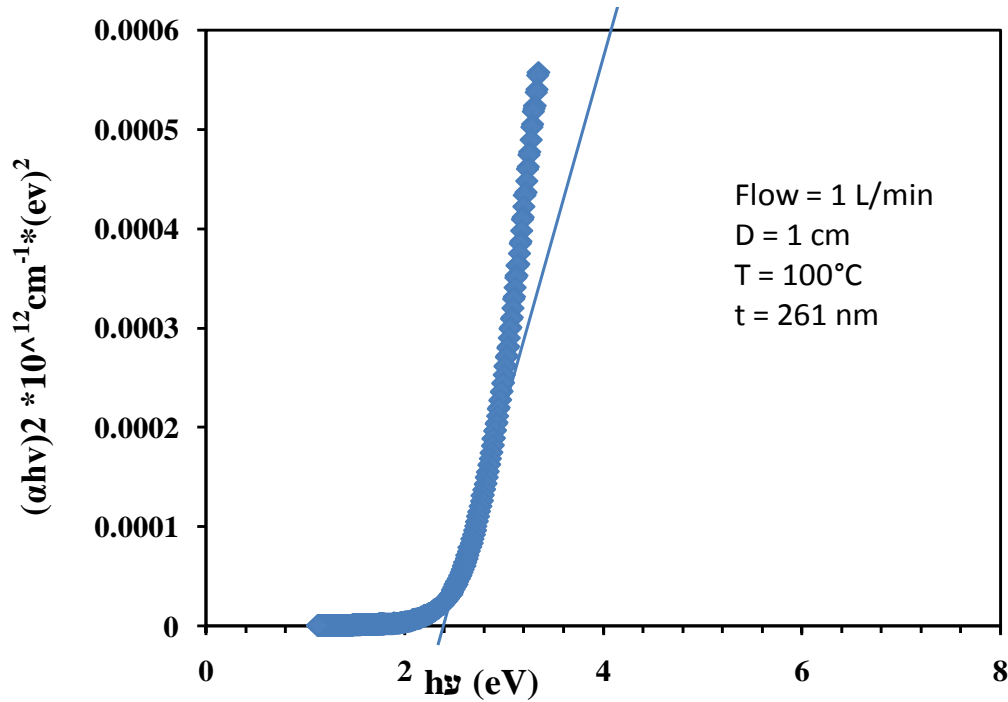
Figure 3a. Optical energy gap.
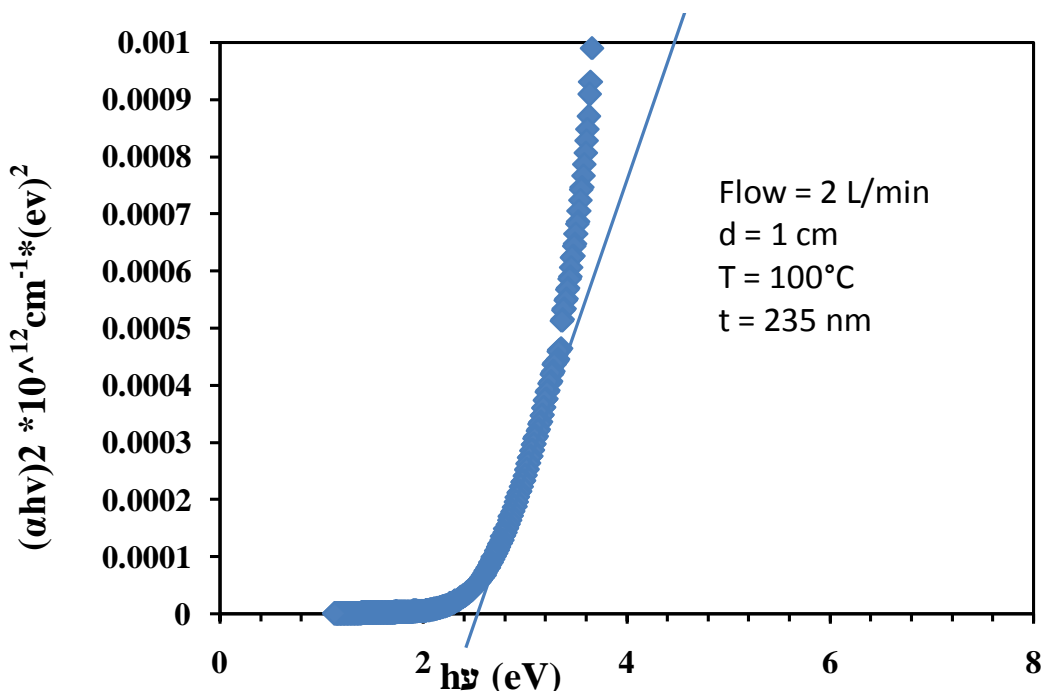
Figure 3b. Optical energy gap.

B and D, as shown in Table 1. The optical energy gap decrease with the increasing of annealing as shown in samples B and C. The reduction in the optical band gap is probably due to the modification of the polymer structure (Wise et al., 1998), when the distance increase the energy gap is decrease as in samples B and E. The optical energy gap decreases with increasing thickness as shown in all samples and as given in Table 1.
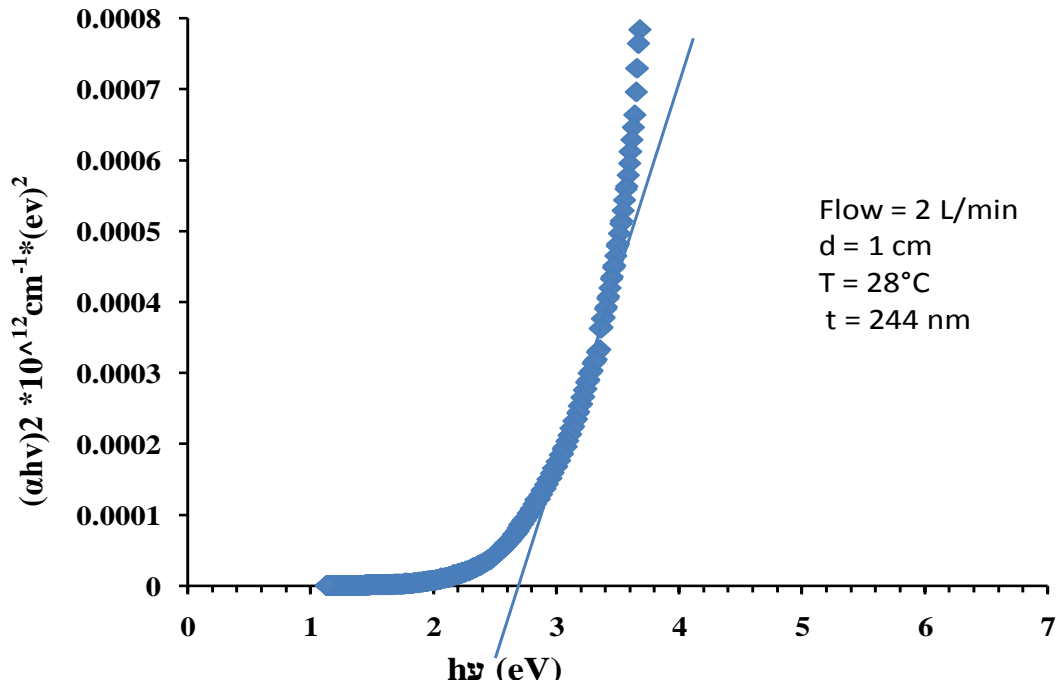
Figure 3c. Optical energy gap.
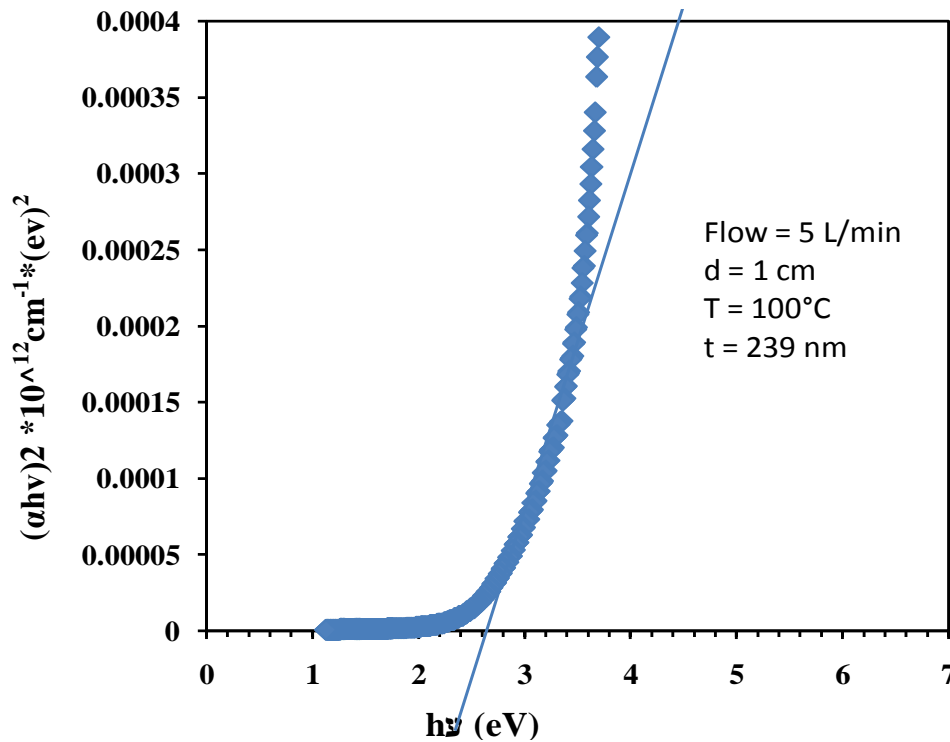
Figure 3d. Optical energy gap.

X-ray diffraction

Figure 4 shows X-ray diffraction thin film of PANI

prepared by plasma polymerized and at room temperature. Diffraction pattern of PANI has abroad amorphous scattering peak at about 2θ = 25.392° which
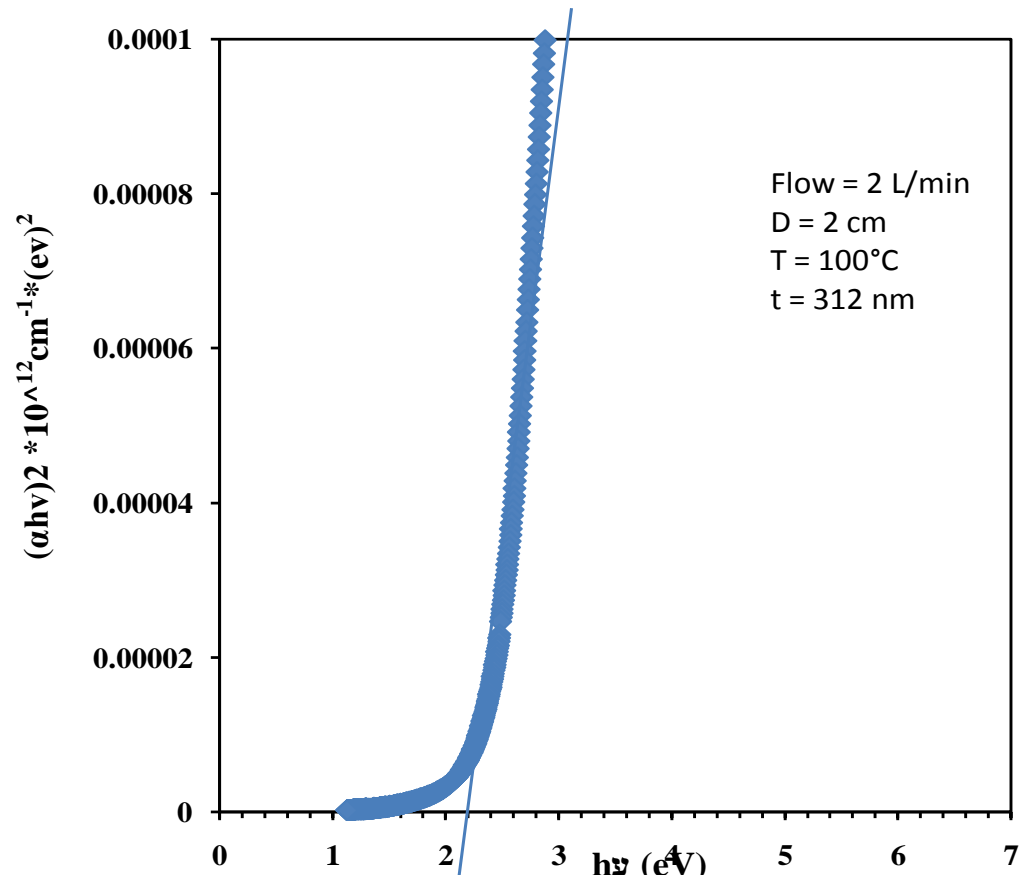
Figure 3e. Optical energy gap.
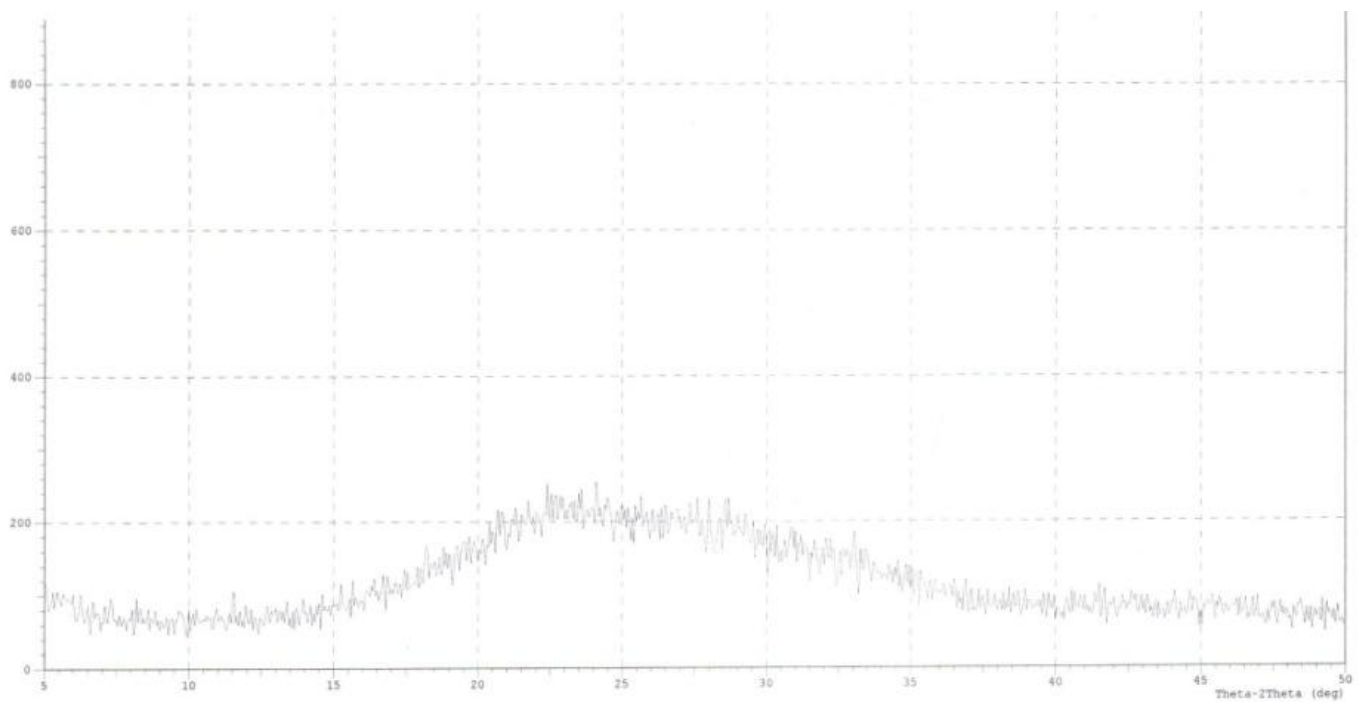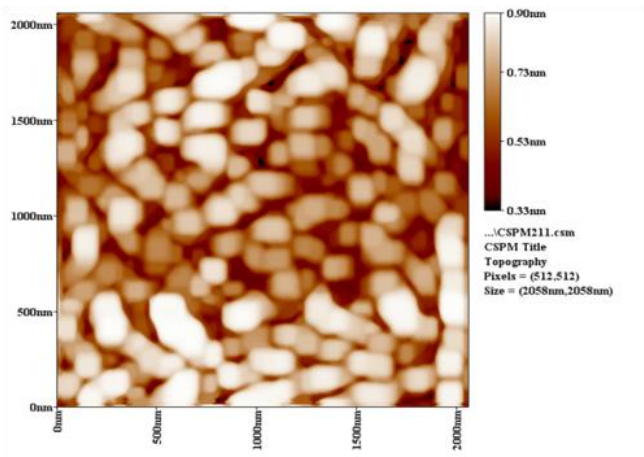

Figure 4. X-ray diffraction of PANI.
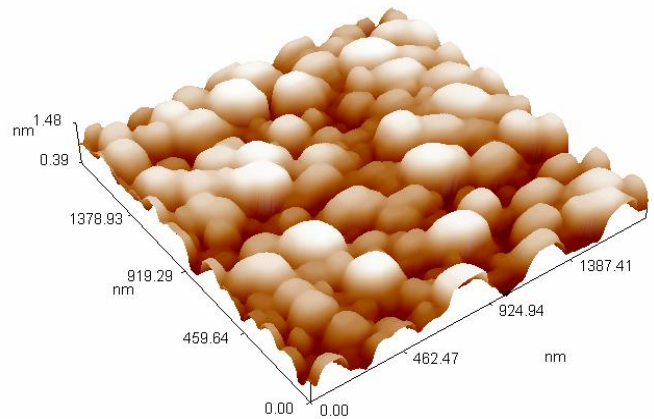
Figure 5a. Atomic force microscopy of PANI.
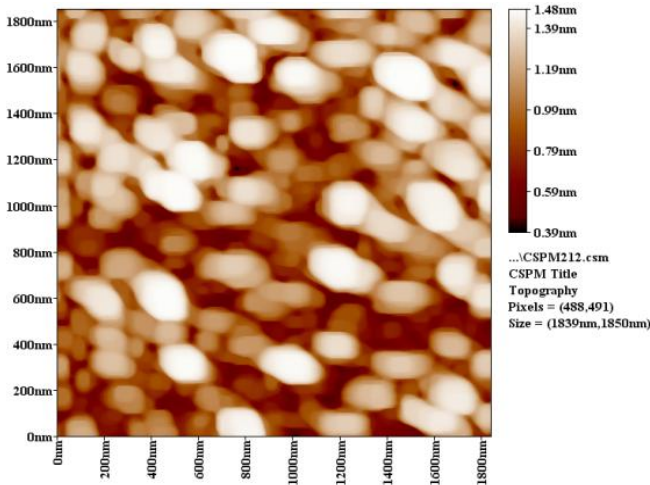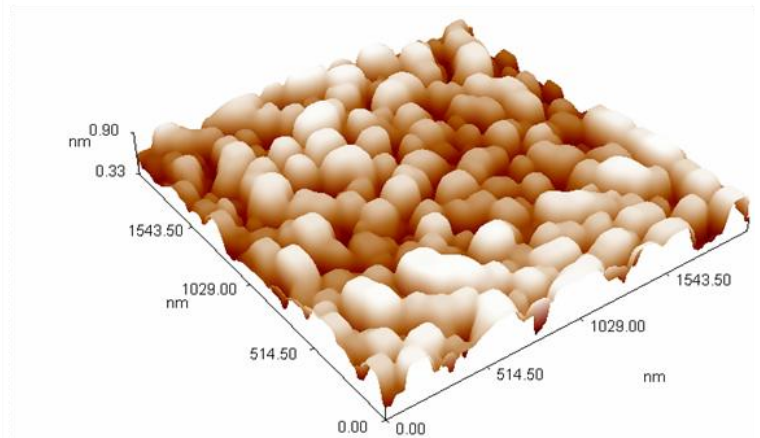
Figure 5b. Atomic Force Microscopy of PANI.

is a characteristic peak of PANI (Tarachiwin et al., 2002).

Atomic force microscopy

The surface morphology of the thin films of PANI as observed from the atomic force microscopy (AFM) micrograph confirms that the grains are uniformly distributed within the scanning area (2000 nm × 2000 nm). An initial visual investigation of the deposited film substrate has shown that they are compact and have good adherence to the substrate. Figure 5a, b, c, d and e, shows 2D and 3D that nanostructure PANI thin films have been deposited on glass substrates by using DBD plasma jet at films deposited with temperature (28,100°C), so when the temperature increases the grain size decrease. The surface roughness value for film

deposited is increased with temperature decrease as shown in Table 4. When flow rate increase the grain size decrease, same with the distance. By observing these results, it can be seen that the thin films surface prepared is very soft and smooth.

DC conductivity

In conducting polymers, the total conductivity is a function of the interchain conductivity. According to Wudl et al. (1987), the DC conductivity ($\sigma_{d.c}$) for film polyaniline has been studied as a function of temperature $10^3/T(K^{-1})$. Figure 6a, b, c and d shows the variation of Lnσ with reciprocal of temperature for all thin film polyaniline samples which were prepared different reaction temperature respectively. And it is clear from these
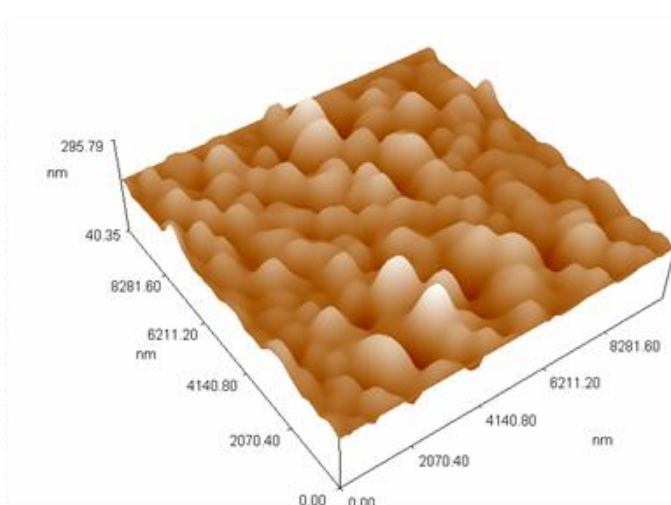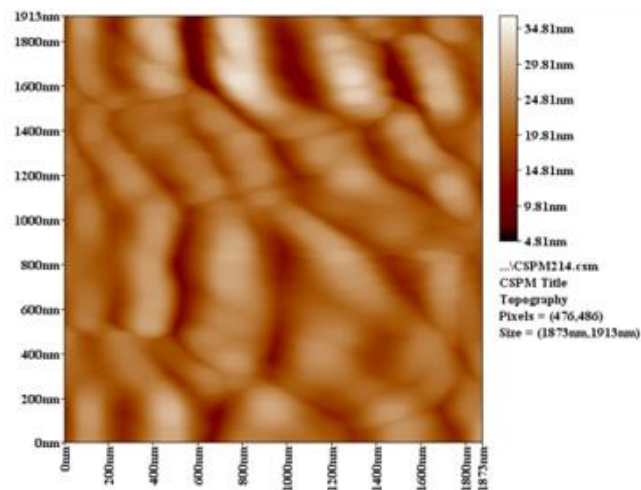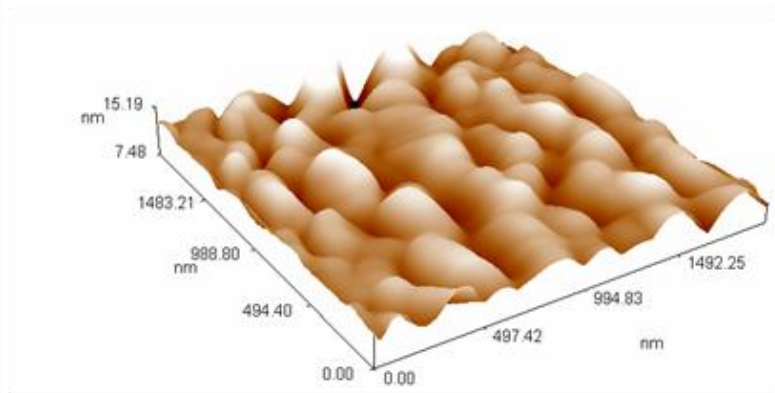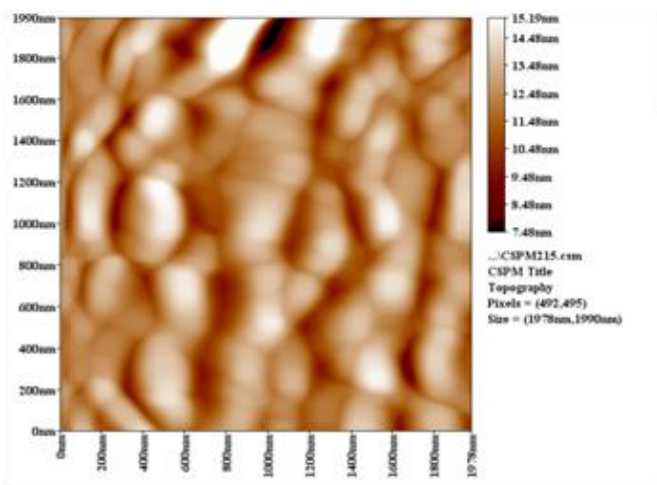
Figure 5c. Atomic force microscopy of PANI.

Figure 5d. Atomic force microscopy of PANI.
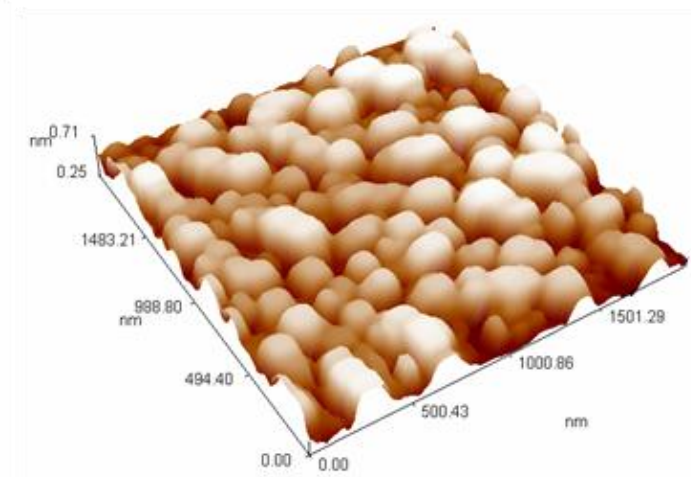
Figure 5e. Atomic force microscopy of PANI.
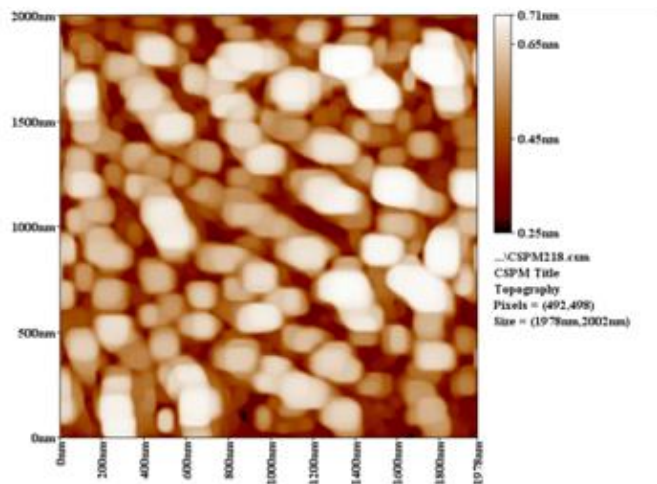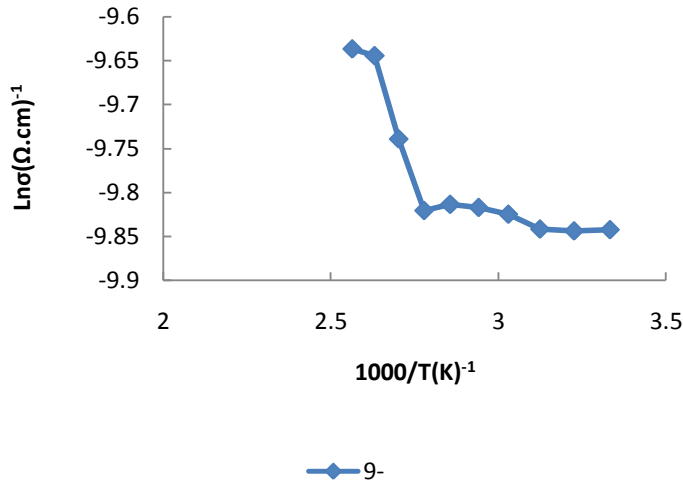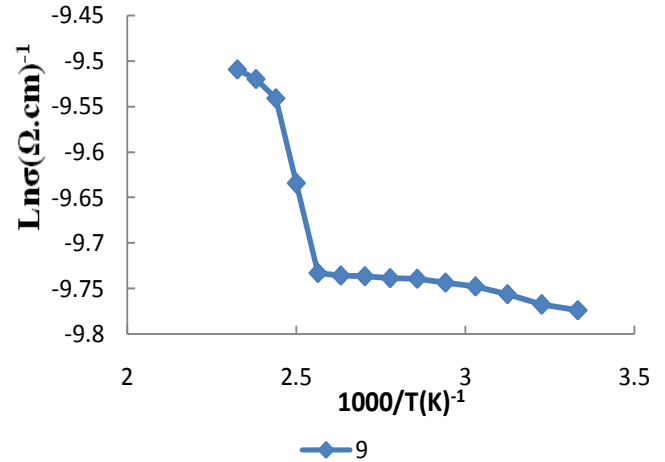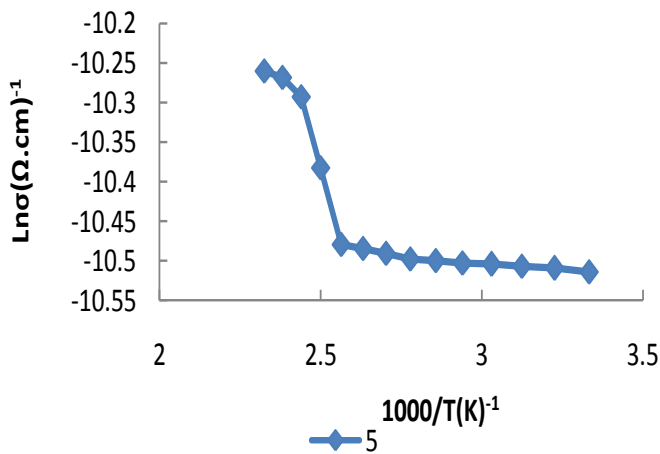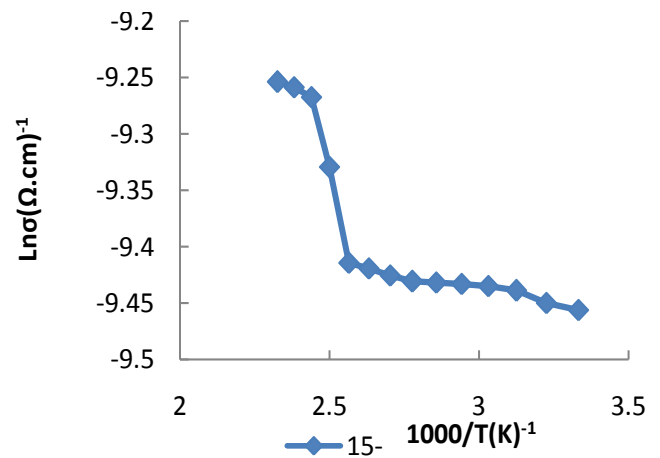
Table 4. Atomic force microscopy.

Sample	Gas flow (L/min)	Distance (cm)	Thicknesses (nm)	Annealing temperature (⁰C)	Energy gap (eV)
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Figure 6a. Conductivity of PANI.

Figure 6b. Conductivity of PANI.

Figure 6c. Conductivity of PANI.

Figure 6d. Conductivity of PANI.

figures that the conductivity increases with increasing of the temperature and there are two transport mechanisms, giving rise to two activation energies Ea_1 and Ea_2. At higher temperature range (393 to 433 K), the conduction mechanism is due to carrier excited into the extended states beyond the mobility edge and at lower temperature range (303 to 383 K); the conduction mechanism is due to carrier excited into localized states at the edge of the band (Wudl et al., 1987), as shown in Table 5.

CONCLUSIONS

The nanostructured PANI thin films have been prepared under inductively dielectric barrier discharges plasma jet. The ultra thin films of PANI were prepared by varying

Table 5. The conduction mechanism.

Sample	AFM of plane grain size (nm)	Roughness average (nm)
1	117.55	0.115
2	131	0.23
3	170.17	17.9
4	165.28	0.997
5	101	4.58

the conditions under the LF plasma operated in a pulsed manner. The LF frequency was directed and controlled the PANI cross-linking growth rate on the substrate. The prepared ultra thin film showed emeraldine base state of PANI and showed. The optical energy band gap values of the as-grown samples demonstrated that these materials would have potential applications at semiconductor devices. The AFM observed is much smoother and more uniform soft films.

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