

Effect of iodine doping on the characteristics of polythiophene thin films prepared by aerosol assisted plasma jet polymerization at atmospheric pressure

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Abstract

Iodine-doped polythiophene thin films are prepared by aerosol assisted plasma jet polymerization at atmospheric pressure and room temperature. The doping of iodine was carried out in situ by employing iodine crystals in thiophene monomer by weight mixing ratios of 1%, 3%, 5% and 7%. The chemical composition analyses of pure and iodine-doped and heat-treated polythiophene thin films are carried out by FTIR spectroscopy studies. The optical band gaps of the films are evaluated from absorption spectrum studies. Direct transition energy gaps are determined from Tauc plots. The structural changes of polythiophene upon doping and the reduction of optical band gap are explained on the basis of the results obtained from FTIR spectroscopy, UV-VIS absorption studies, X-ray diffraction and atomic force microscope (AFM) analysis. The energy band gap will be different according to the concentration of polythiophene iodine. It can be concluded that iodine-doped polythiophene thin films can be prepared by aerosol assisted plasma jet polymerization and control the optical energy band gap regularly by controlling the thiophene-iodine weight mixing ratios.

Key words

Polythiophene iodine doping, thin films, optical properties, band gap, XRD.

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تأثير التطعيم باليود على خواص اغشية البولي – ثايوفين المحضرة والمبلعمة ببلازما النفط عند الضغط

الجوي والمعززة بالرذاذ

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الخلاصة

اغشية متعددة الثايوفين المطعمة باليود حضرت باستعمال البلمرة ببلازما النفط والعاملة بالضغط الجوي والمعززة بالرذاذ وعند درجة حرارة الغرفة. وانجز التطعيم باليود موضعياً وذلك بخلط بلورات اليود مع احادي الثايوفين وبنسب خلط وزنية هي 1% و3% و5% و7%. انجز التحليل الكيماوي التركيبي للاغشية متعددة الثايوفين النقية والمطعمة باليود والمعاملة حرارياً باستعمال مطياف تحليلات فورير للاشعة تحت الحمراء. حددت فجوة الطاقة البصرية للاغشية من دراسة طيف الامتصاص باستعمال رسم Tauc على اساس ان الانتقال من النوع المباشر. ان التغيير في تركيب متعدد الثايوفين المطعم تم الحصول عليه من دراسة طيف تحليلات فورير للاشعة تحت الحمراء وطيف الامتصاص في المنطقة فوق البنفسجية والمرئية. ومن تحليل نتائج حيود الاشعة السينية ومجهر القوة الذرية اثبت البحث ان فجوات الطاقة تتغير متوافقة مع تركيز اليود. ويمكن ان نستنتج امكانية تحضير اغشية متعددة الثايوفين المطعم باليود باستعمال البلمرة ببلازما النفط المعززة بالترديد والعاملة بالضغط الجوي والتحكم المنتظم بفجوة الطاقة البصرية من خلال التحكم في نسبة الخلط الوزني لمزيج احادي الثايوفين واليود.

Introduction

The employment of plasma polymerization for synthesis of novel thin film materials has become attractive and has been an active area of research in the past recent-years [1]. Originally this technique was employed to coat passive layers, but the current trend is to extend this technology to other applications as well, in which device performances are influenced by surface compositions. Controllability and reproducibility of the surface composition of plasma polymerized thin films is of most important to achieve superlative performance. It is known that several reaction parameters like power input, monomer flow rate, monomer vapor pressures, substrate temperature and positioning of substrates relative to the plasma torch end influence the structure and composition of plasma polymerized thin films [2,3]. The investigations of the optical properties of polymer thin films have gained attention due to their potential applications in optical sensors, LEDs and as antireflective coatings [4, 5]. The effect of doping on the band gap of polythiophene is already dealt with [6, 7] but a systematic study on the stability and the structure of the in situ iodine doped thiophene films by aerosol assisted plasma jet polymerization at atmospheric pressure has not been reported. Here, a report the preparation and optical properties of plasma polymerized thiophene thin films. Where the In situ iodine doping is carried out by aerosol assisted plasma jet polymerization at atmospheric pressure and room temperature. To investigate the effects of doping on the optical band gap, UV-VIS studies are carried out to determine the optical band gap and other optical parameters of plasma polymerized thiophene thin films. FTIR studies are carried out to elucidate the effect of doping on the chemical structure of the plasma polymerized thiophene thin films [8].

Experimental work

Iodine-doped polythiophene thin films have been prepared by aerosol assisted plasma polymerization. Thin films were prepared by dielectric barrier discharge plasma jet a homemade [9]. The thin films were deposited on glass substrates. Pure thiophene monomer was used as the organic precursor. Fig.1 schematic diagram for the non-equilibrium atmospheric pressure plasma Iodine-doped polythiophene thin films preparation. Argon gas with flow rate of 1 l/min passes through the nobilizer which contains a mixture of iodine and thiophene with weight mixing ratios of 1%, 3%, 5% and 7%. the mixture convert to aerosol where the Ar gas passes through the mobilizer, this aerosol was guided by the Ar gas to the plasma torch. 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 at suatabal distance from the plasma torch end as shown in Fig. 1. The films deposition was carried out for 5min under constant carrier gas flow rate and the substrate at room temprtar. The substrate moved on the x and y diraction mechanically for the purpose of obtaining a homogeneous films thickness a long the substrat area. To test the stability of the iodine doped films, these films are heat-treated at 373 K for 24 h in an oven and then the absorption spectrum is recorded. The Film thickness was measured using the optical interferometer method A double -beam UV-VIS-NIR 210A Spectrophotometer was used to measure the absorption of the Iodine-doped polythiophene and heat-treated polythiophene thin films which deposited at different iodine concentration in the range of 200-1200 nm. The background correction was taken for each scan. The absorption data with films thickness can be used to calculate absorption coefficients of the films at different Wave length, which

have been used to determine the energy band gap E_g .

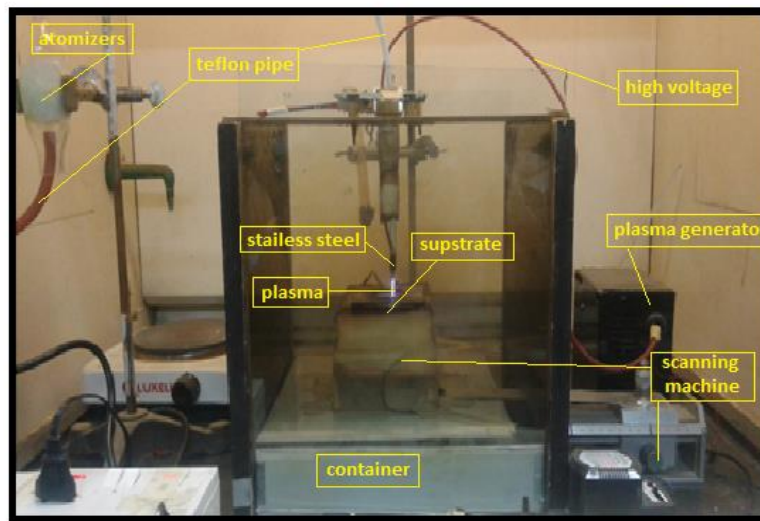


Fig. 1: The non-equilibrium atmospheric pressure plasma Iodine-doped polythiophene thin films preparation experimental set-up.

For FTIR spectroscopy poly thiophene is scraped from the glass substrates and is mixed with KBr before pelletizing. These pellets are then loaded into the sample holder of the FT-IR Shimadzu Co. FT-IR 8000 series Fourier transform, infrared spectrophotometer from wavelength range $400\text{--}4000\text{ cm}^{-1}$ under identical conditions. The morphological surface analysis is carried out employing an atomic force microscope (AA3000 Scanning Probe Microscope SPM, tip NSC35/AIBS) from Angstrom Advanced Inc. In order to study the structural properties, the structure is analyzed with a SHIMADZU 6000 X-ray diffractometer system which records the intensity as a function of Bragg's angle. The source of radiation is Cu- α with wavelength $\lambda = 1.5406\text{ \AA}$, current 30mA and voltage 40 kV. The scanning angle 2θ is

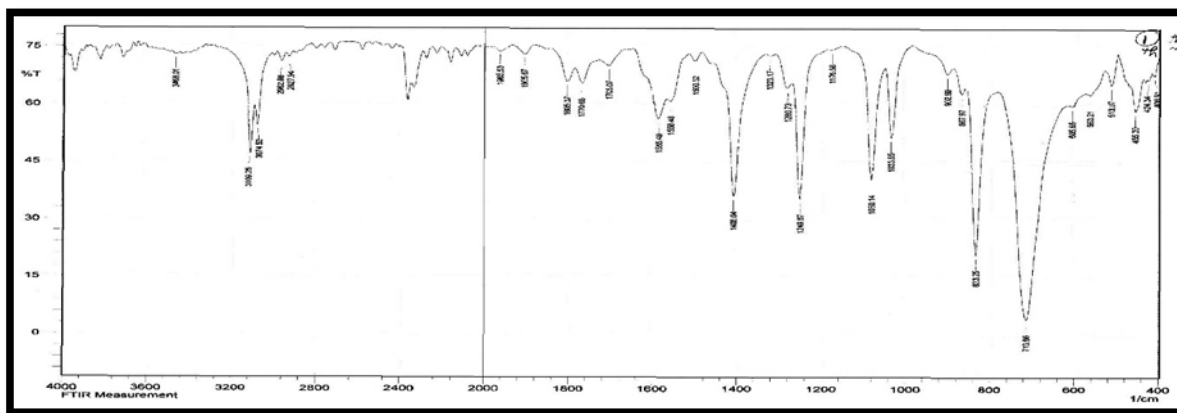
varied in the range of $10\text{--}80$ degree with speed of 5 deg/min .

Results and discussion

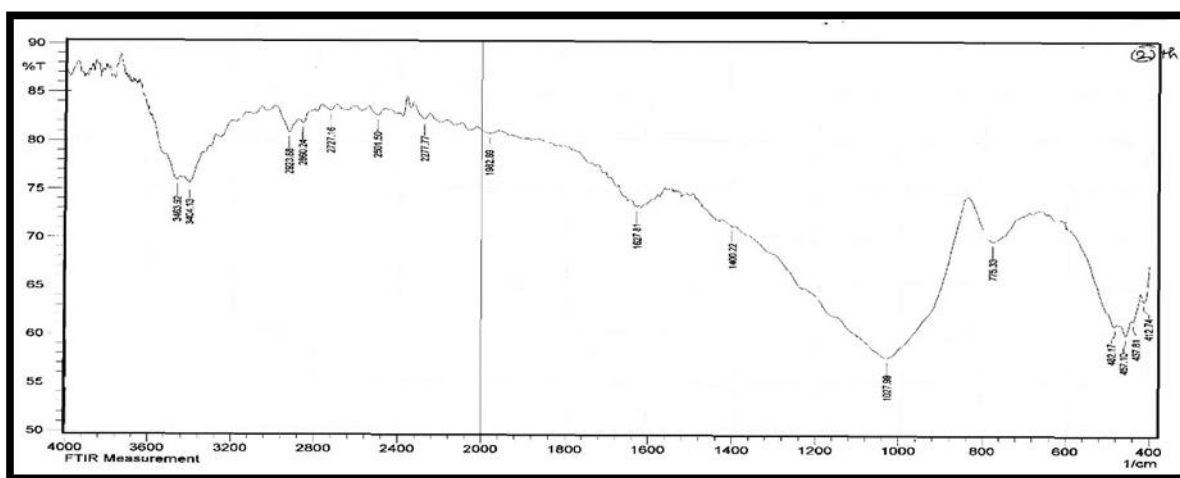
A. FTIR analysis:

The FTIR spectra of thiophene as a monomer and Iodine-doped polythiophene thin films polymerized by plasma shown in Figs.2(a, b, c, d and e). The polythiophene spectrum, Fig. 2-b shows peaks at 484 cm^{-1} indicating that the ring is retained in the polymer[9]. The peak at 3468 cm^{-1} is due to O-H stretch of water absorbed water. The peak at $3073\text{--}3108\text{ cm}^{-1}$ is due to C-H stretch on double bonded carbon, and 2927 cm^{-1} is due to C-H stretch on saturated carbon.

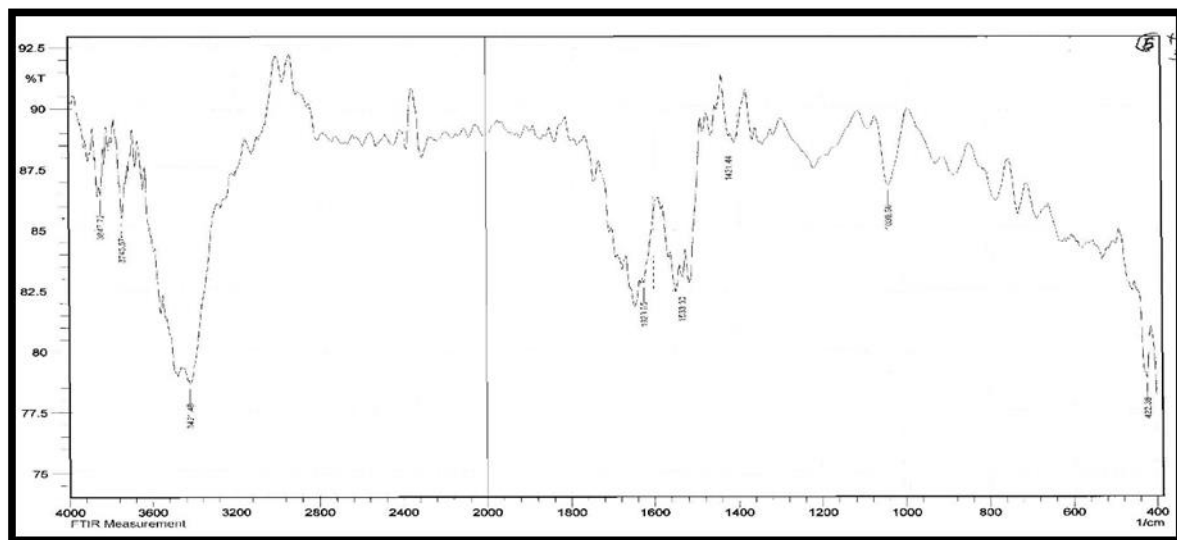
The FTIR spectrum for both monomer and plasma polymerized thiophene are comparable for their respective functional groups.



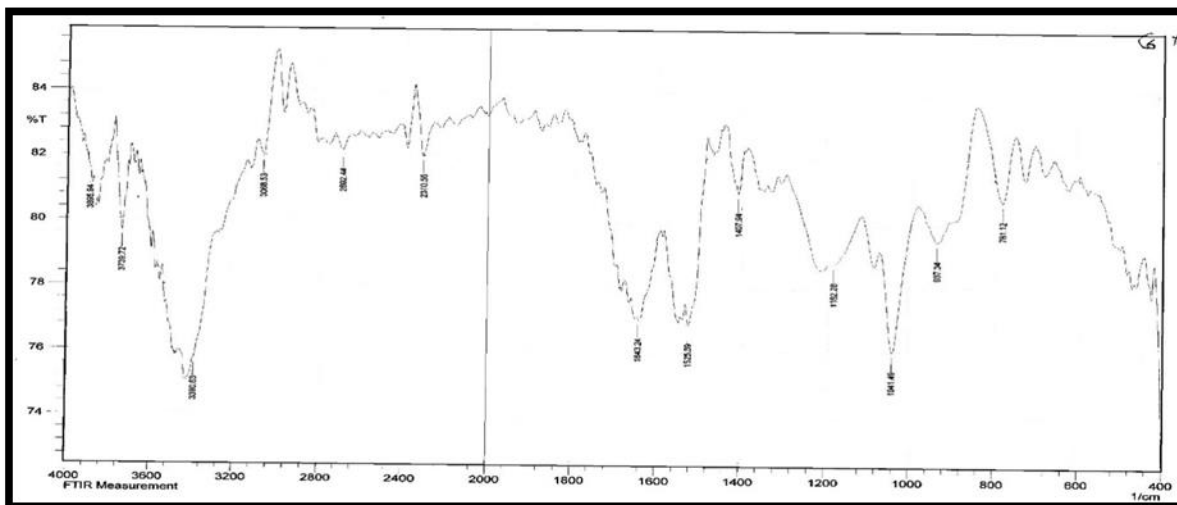
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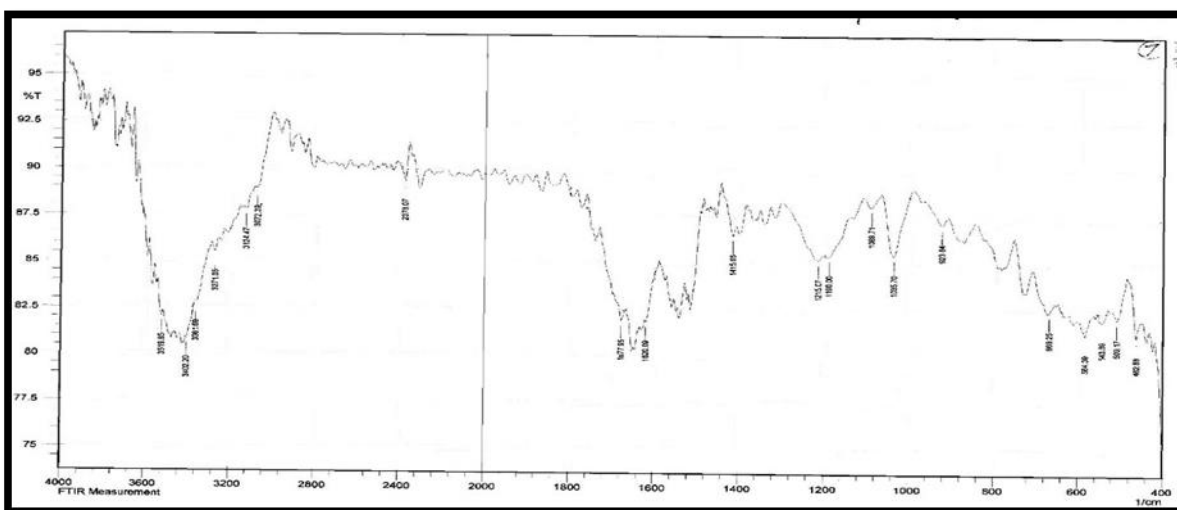
b



c



d



e

Fig.2: FTIR spectra *a* for thiophene monomer, *b* for polythiophene thin films without doping *c* for 3% iodine doping *d* for 5% iodine doping and *e* for 7% iodine doping.

The band assignments of the FTIR absorption bands for thiophene pure polythiophene, and iodine-doped polythiophene thin films are given in Table 1. It is clear from the table that there is a shift in C–H stretching bands in the iodine-doped polythiophene. The O–H stretch shifts towards high wave number. The shifts observed in C–H bands indicate that the iodine atoms might be getting attached polythiophene [10]. The key bands corresponding to the polythiophene rings in

the iodine-doped polythiophene are found to be shifted towards high wave number. This is an indication that iodine doping causes a change in the structure of the plasma polymerized thiophene samples.

B- UV-VIS absorption studies

The photon absorption in many amorphous materials is found to obey the Tauc relation [10]:

$$\alpha h\nu = B(h\nu - E_{opt})^n$$

where (α) is the absorption coefficient, $h\nu$ is the photon energy, B constant and the index n is connected with the distribution of the

density of states. The index $n = 1/2$ corresponds to the direct allowed transition energy gap and $n = 2$

Table 1: FTIR absorption bands for thiophene, pure polythiophene and iodine-doped polythiophene.

Vibration	Wavenumber (cm ⁻¹) mon-Thiophene	Wavenumber (cm ⁻¹) polythiophene	Iodine- doped polythiophene (cm ⁻¹)3%	Iodine- doped polythiophene (cm ⁻¹)5%	Iodine- doped polythiophene (cm ⁻¹)7%
O-H stretch absorbed water	3468	3463	3407	3415	-----
C-H stretch on triple bonded carbon	-----	-----	-----	-----	2369
C-H stretch on double bonded carbon	3073 3108	-----	3062	3062	3056 3191
C-H stretch on saturated carbon	2927	2923	-----	2810	2812
C≡C stretch	-----	2277	-----	2310	-----
C=C stretch	1408 1558 1590	1400 1627 1682	1519	1510	1419 1510
C-H in plane bends	950-1250	1027	1031	1043-1245	1026-1222
C-S stretch	833	775	781	754	754
C-H out of plane bend	710	-----	692	692	692
Ring deformation	Saturation	484	460	-----	420

represents the indirect allowed transition energy gap [11].

Fig.3 shows $(ah\nu)^2$ vs. photon energy graph of plasma polymerized thiophene in its pure and, iodine doped. It is seen from this figure and Table 2 that the iodine doping decreases the optical band gaps from 2.5 eV for pure polythiophene to 2.05 eV for polythiophene doped with 7% iodine the reduction in the optical band gap is probably due to the modification of the polymer structure.

Doping induces a structural ordering of the

polymers due to the insert of the charged species. There are signatures supporting these changes in the FTIR and UV- VIS spectra. To test the stability of the iodine doped films, the films were heat-treated at 373 K for 24 h in an oven and then the absorption spectrum is recorded. It is found that these samples produce little change in the band gap, suggesting that the reduction in the band gap upon iodine doping is permanent and stable as shown in Fig. 4 and Table 2.

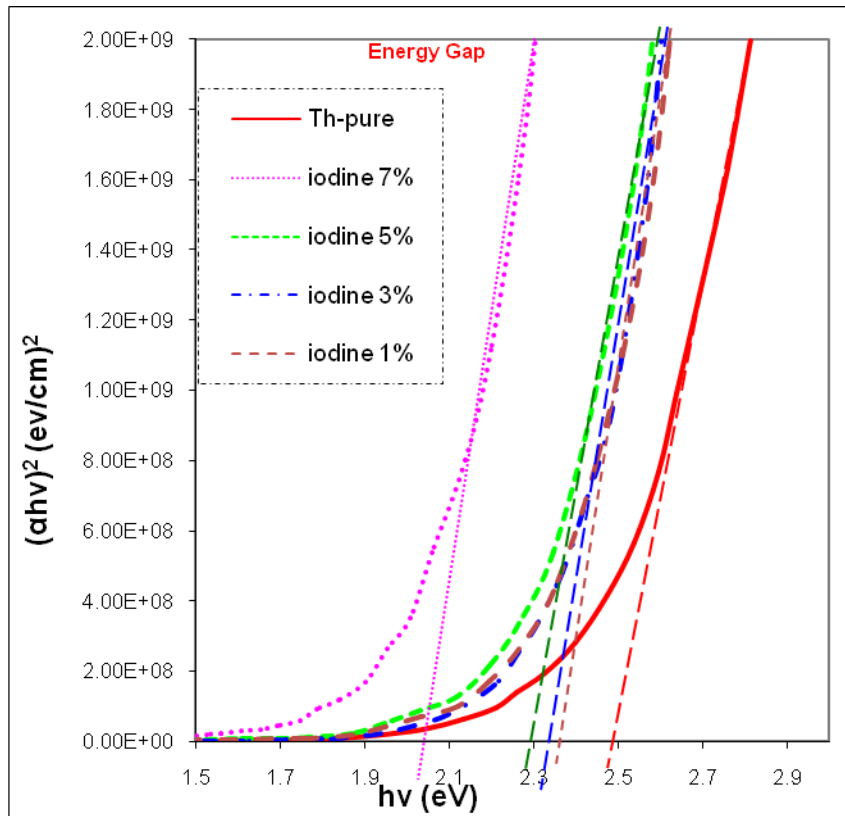


Fig. 3: $(ahv)^2$ vs. photon energy graph of plasma polymerized thiotpene thin films in its pure and iodine doped form.

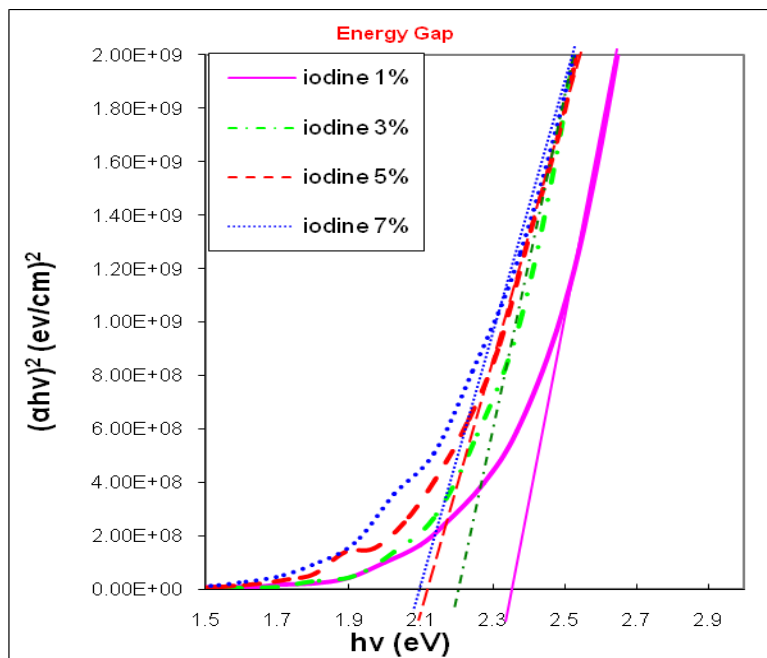


Fig.4: $(ahv)^2$ vs. Photon energy graph of heat-treated plasma polymerized iodine-doped thiotpene thin films.

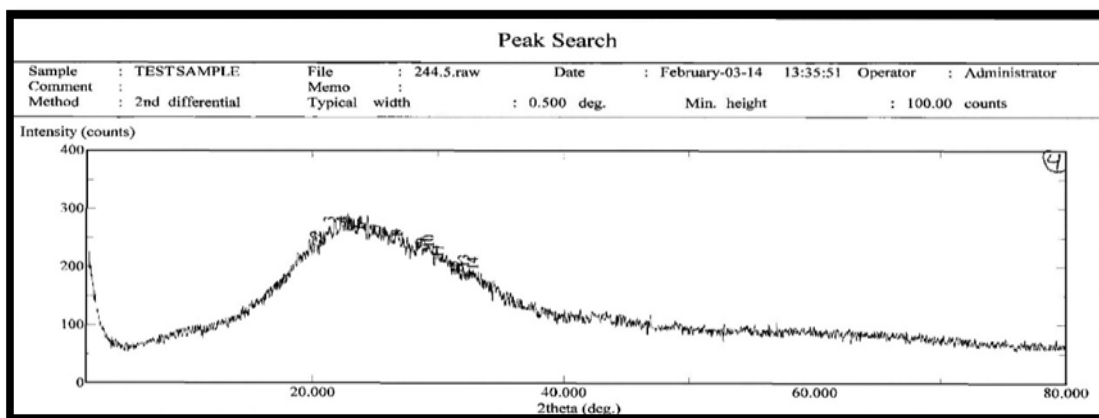
Table 2: Energy band gap of polythiophene iodine doped thin films as deposited and after heat-treated.

Sample name	Pure Polythiophene	1% Iodine doped polythiophene	3% Iodine doped polythiophene	5% Iodine doped polythiophene	7% Iodine doped polythiophene
Direct allowed transition energy gap (eV)	2.5	2.48	2.34	2.3	2.05
Direct allowed transition energy gap heated at 373 K for 24 h	2.47	2.37	2.2	2.12	2.1

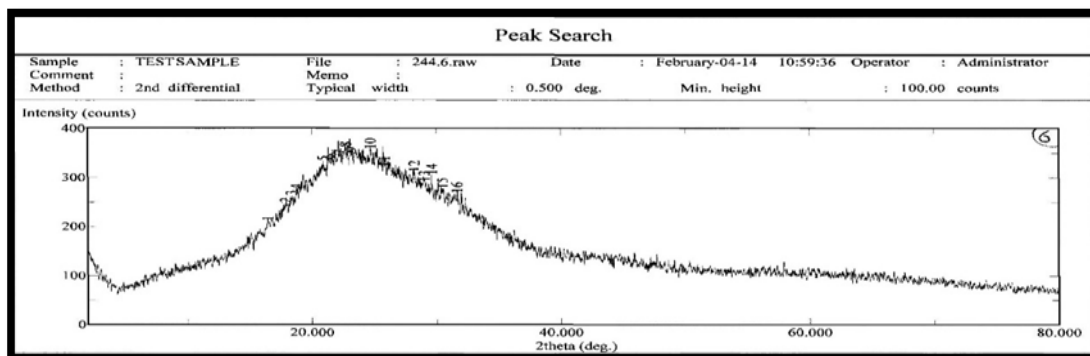
C-X-ray diffraction analysis

X-ray diffraction pattern was employed to characterize the structure of the samples. Fig.5-a shows the pattern of the as-deposited

pure polythiophene, while Fig.5-b represents the 7% iodine doped sample. It is clearly indicated that samples are of weak crystalline.



(a)



(b)

Fig. 5: XRD a) for pure polythiophene thin films and b) for iodine doped polythiophene thin films.

D- Surface morphology

The surface morphology of pure polythiophene and 7% iodine doped thin films were examined by AFM. The surface roughness of plasma polymerized pure polythiophene thin films was around 0.118 nm and for the iodine doped thin films 0.0939 nm. The low surface roughness of plasma polymerized polythiophene confirms that the technique of plasma polymerization can be employed to produce extremely smooth films with very small surface roughness when compared to films prepared

by other techniques. It is clear that the grains are uniformly distributed within the scanned area. Figs.6-a and b represent the 3-D and 2-D images of the pure polythiophene thin films surface and Fig.6-c shows the granularity distribution chart. The average diameter of clusters is 87 nm. Figs.7-a and b represent the 3-D and 2-D images of the 7% iodine doped polythiophene thin films surface and Fig.7-c shows the granularity distribution chart. The average diameter of clusters was 79 nm.

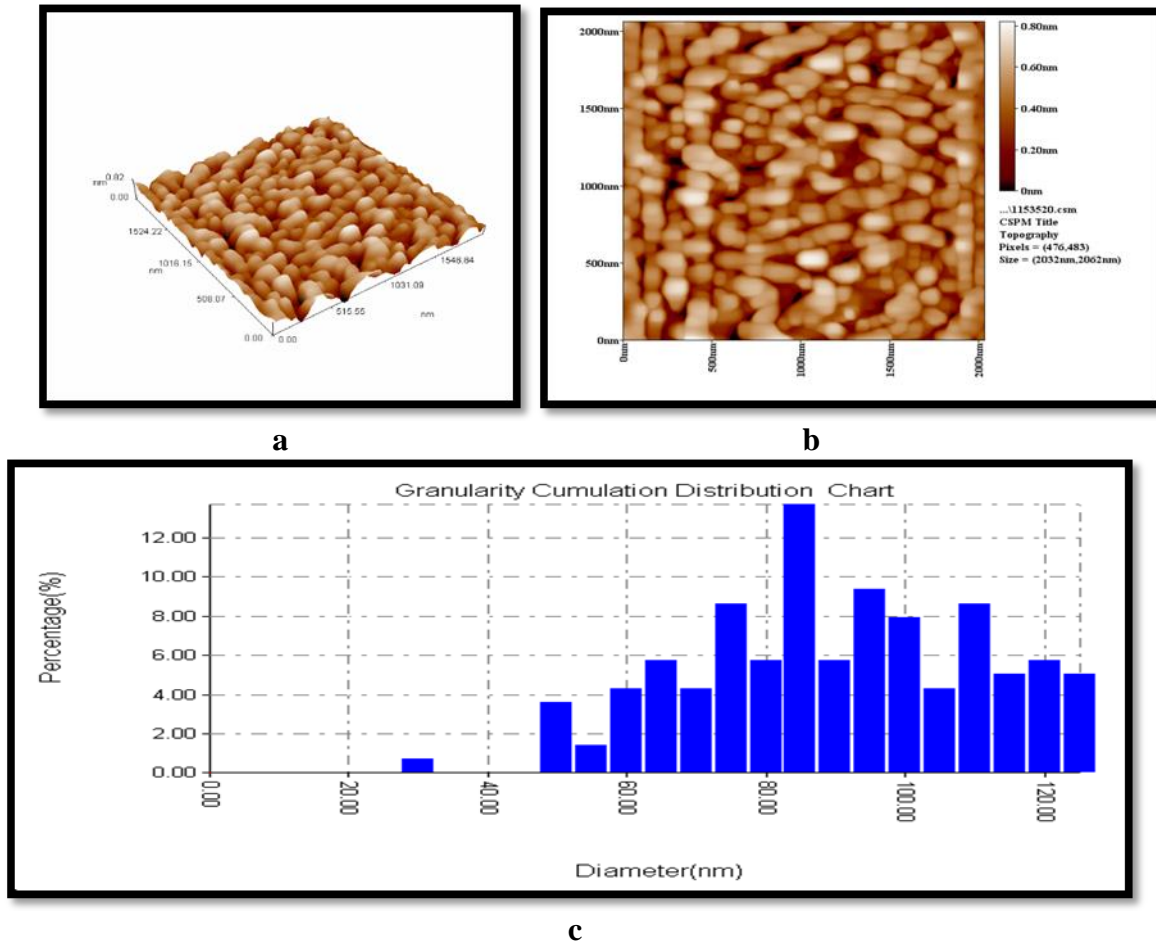


Fig. 6: AFM photographs of plasma polymerized pure thiophene thin films surface. a 3D view b 2 D view and c the granularity distribution chart.

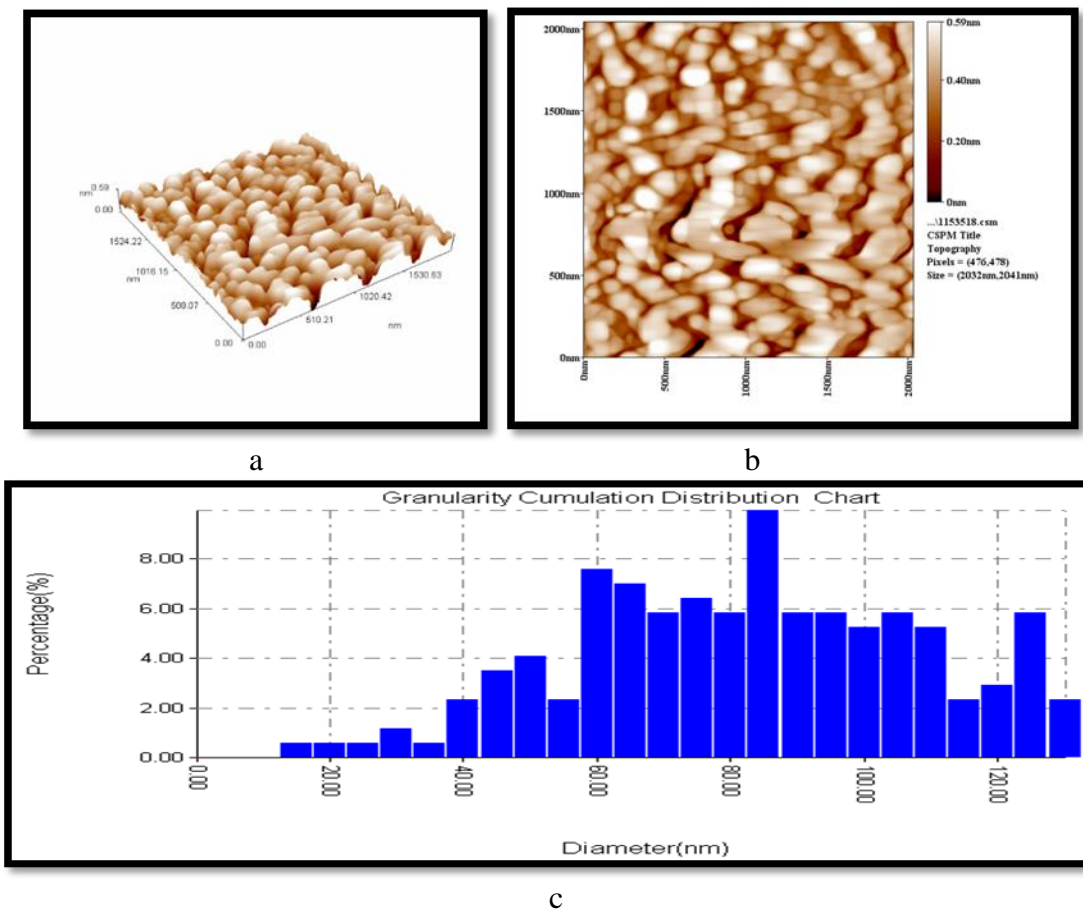


Fig.7: AFM photographs of plasma polymerized 7% iodine doped polythiophene thin films surface. a 3D view b 2D view and c the granularity distribution chart.

Conclusions

The technique of plasma polymerization can be employed to produce extremely smooth films with very small surface roughness when compared to films prepared by other techniques. The grains are uniformly distributed within the scanning area. The insitu iodine doping Polythiophene thin films prepared by aerosol assisted plasma jet polymerization at atmospheric pressure decreases the optical band gaps and modifies the polymer structure. Heat-treated does not change the band gap. Hence, insitu method of doping is reliable and the change in the band gap is permanent.

References

[1] H. Biederman and D. Slavynska, Surf. Coat. Technol.125 (2000) 371.

[2]F. F. Shi, Surf. Coat.Technol. 82 (1996)1.
 [3] R. D. Agostino, "Plasma Deposition, Treatment and Etching of Polymers", Orlando, FL: Academic, 1990.
 [4] K. J. Nagagawa, Appl. Polymer. Sci. 41(1990) 2049.
 [5] Y. Koike, E. Nihei, N. Tanio and Y. Ohtsuka, Appl. Opt, 29 (1990) 2686.
 [6] H. K. Chaudhar and D. S. Kelkar, Polymer International and Company, 1997.
 [7] J. Tauc. "Optical Properties of Solids", ed A Ables, Amsterdam: North-Holland, 1970
 [8] E. A. Davis and N. F. Mott, Phil. Mag. 22 (1970) 903.
 [9]Hammad R. Humud, Thikra Kh. Obayes and Qusay A. Abbas, International Journal

of Current Engineering and Technology, 4, 4
(2014) 2580-2584.

[10] J. I. Pankovem, "Optical Process"
Englewood Cliffs, NJ Prentice-Hall, 1971

[11] A. B. M. Shah Jalal, S. Ahmed, A.H.
Bhuiyan and M. Ibrahim, Thin Solid Films
288 (1996) 108.