

Optical and electrical properties of polythiophene thin films: Effect of post deposition heating

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This article reports the effect of post deposition heating on the optical and mechanical properties of polythiophene thin film prepared by vacuum evaporation technique. The post deposition heating strongly affects on the structural, surface morphological, optical and electrical properties. As deposited thin film showed uniform surface morphology with very small grain size, whereas the heat treated thin film was highly dense with larger grains. It was observed that, the absorbance of the polythiophene thin films increases due to post deposition heating, while the band gap found to be decrease and refractive index increases. However the activation energy of the polythiophene thin films was decreased due to post deposition heating.

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1. Introduction

A tremendous advancement has taken place in the development of organic conducting polymers in recent years due to their interesting physical, electrical and chemical properties [1]. Among the conjugated polymers, polythiophene (PTh) and its derivatives have been studied for various applications in optoelectronics like light emitting diodes (LED) [2], field effect transistors (FET) [3], super capacitors [4], photovoltaic and photoconductive devices and optical modulator devices etc. [5]. Polythiophenes have also been exploited in sensor applications [1]. Polythiophene exhibit superior properties such as low density ease of fabrication [6] as compared to conventional conductors. In addition the conductivity of these materials can be controlled from conducting to insulating range by using different routes of polymerization. This polymer is restricted its use in commercial application due to its poor solubility. Also the presence of inert sulphur atom in thiophene increases the oxidation potential which makes the preparation of polythiophene more difficult [1]. There are several routes for the synthesis of polythiophene like electrochemical and chemical; the chemical oxidative polymerization is a suitable route for the polymerization of polythiophene because it gives high yield [7]. The synthesis conditions and the nature of the dopant anion play a vital role in the polymerization process; they strongly affect the various properties of the material [8].

This paper reports the effect of post deposition heating on the structural morphological, optical and electrical properties of the polythiophene thin films deposited by vacuum evaporation technique on glass, as per authors knowledge the electrical properties of vacuum evaporated polythiophene are sparse, also there is no report on the

refractive index of vacuum deposited polythiophene thin films.

2. Experimental details

Polythiophene powder was synthesized by oxidation polymerization method using iron chloride [7]. The monomer solution was obtained by dissolving 0.25M of thiophene (AR, Merck) in 100ml of chloroform. The oxidant solution was prepared by dissolving 0.5M of FeCl₃ (Sd-Fine) in 100 ml chloroform, in which monomer solution of thiophene was added drop wise, under nitrogen atmosphere and constant stirring. After complete addition of the monomer the reaction mixture was kept at room temperature under constant stirring for 24 hours. The dark brown precipitate of polythiophene was formed which was mixed with a known quantity of methanol. The precipitate was further washed by methanol, chloroform and HCl to remove residual oxidant and unreacted monomer and collected in a filter paper. During this process the dark brown colour of precipitate changes to brown, then the precipitate was deprotonized by 0.5M ammonia, the precipitate further washed by 0.5M of HCl, acetone and chloroform. The PTh powder was dried under vacuum at 600 C for 24 hours. which was used as source material for the vacuum evaporation. The polythiophene thin films were deposited by using resistive heating vacuum deposition technique at 10⁻⁴ Torr. Initially the as obtained polythiophene thin films were studied and then these thin films were heat treated at 473 K for 60 minutes, and all the properties were studied.

FTIR spectra of polythiophene thin films were recorded by using a Perkin-Elmer's Spectrum Spectrometer in the range of 400–4000 cm⁻¹. For FTIR, these films were scratched from glass substrate and mixed

with KBr. The optical absorption in the wavelength range 300–850 nm of the thin films of polythiophene was measured by UV–VIS spectrophotometer (U-2800, Hitachi, Japan) and surface morphology was investigated using Scanning Electron Microscopy (SEM). The thickness (~150 nm) of the films was measured by Tolansky interferometric method; refractive indices of the thin films were measured by Abele's method [9] as well as analytical method [10]. The electrical conductivity was measured using Keithley 2010 multimeter.

3. Results and discussion

3.1 FTIR spectroscopy

The comparison of FTIR spectra of those as deposited and heat treated polythiophene thin films are presented in figure 1. The peaks corresponds to 2922 cm^{-1} in as deposited and 2929 cm^{-1} in heat treated thin films represents C-H symmetric aromatic stretching, while the peaks at 2850 cm^{-1} and 2855 cm^{-1} in as deposited and heat treated thin films respectively belongs to C-H asymmetric stretching, the peaks observed at 1622 cm^{-1} and 1402 cm^{-1} in as deposited thin films corresponds to C=C symmetric and C=C asymmetric stretching [11], these bands were found to be shifted at 1633 cm^{-1} and 1426 cm^{-1} in the heat treated thin films. This shifting may be due to cross linking of back bone polymer due to heating [12]. The region belonging to 1500 cm^{-1} to 600 cm^{-1} corresponds to fingerprint region of polythiophene. The sharp absorption peak at 1024 cm^{-1} in as deposited thin film represents the out of plane deformation in C-H which is slightly shifted and appears with comparatively low intensity at 1034 cm^{-1} , the peak at 829 cm^{-1} in the as deposited thin film and 814 cm^{-1} in heat treated thin film represents C-S stretching the characteristics peak of thiophene. The peak at 662 cm^{-1} in as deposited thin film representing C-S-C ring deformation [13] is shifted at 683 cm^{-1} in the heat treated thin films.

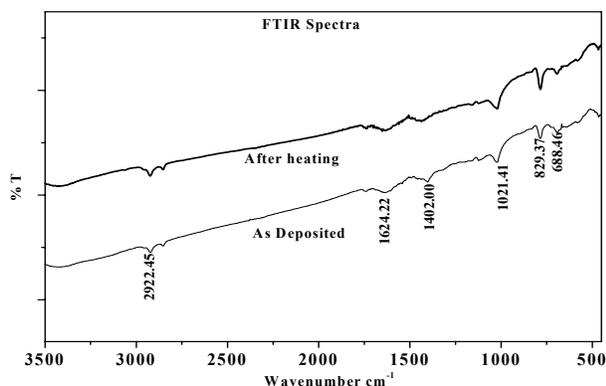


Fig.1. FTIR spectra of polythiophene thin film.

Fig. 2 shows the surface morphology of both as deposited as well as heat treated polythiophene thin films,

as deposited thin films shows uniform, smooth surface morphology with very small grains (grain size 36 nm) whereas the heat treated thin films shows rough, nonuniform surface morphology having larger grains (grain size 84 nm) with increased grain to grain contact.

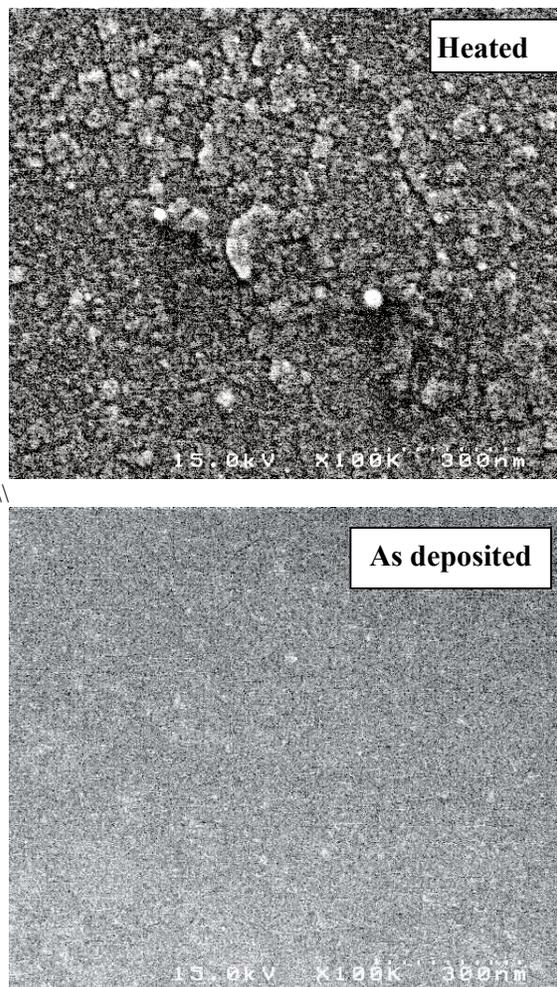


Fig.2. SEM images of polythiophene as deposited thin film and heat treated thin film.

3.2 Optical properties

The optical properties of as deposited and heat treated polythiophene thin films are shown in figure 3 the absorption peak at 331 nm in as deposited thin films and at 322 nm in heat treated thin films is due to $\pi - \pi^*$ transitions in thiophene ring [1]. The weak absorption peak observed at 632 nm in as deposited thin films and at 630 nm in heat treated thin films may be due excitation of short chain oligomers [12]. It has seen (fig. 3) that the heat treated thin films shows lower transmission in the lower wavelength region where as in higher wavelength region it is nearly same to the as deposited thin films. Due to larger grain size of the heat treated film suffers from scattering

losses this may a cause of reduction of transmittance in the heat treated thin film.

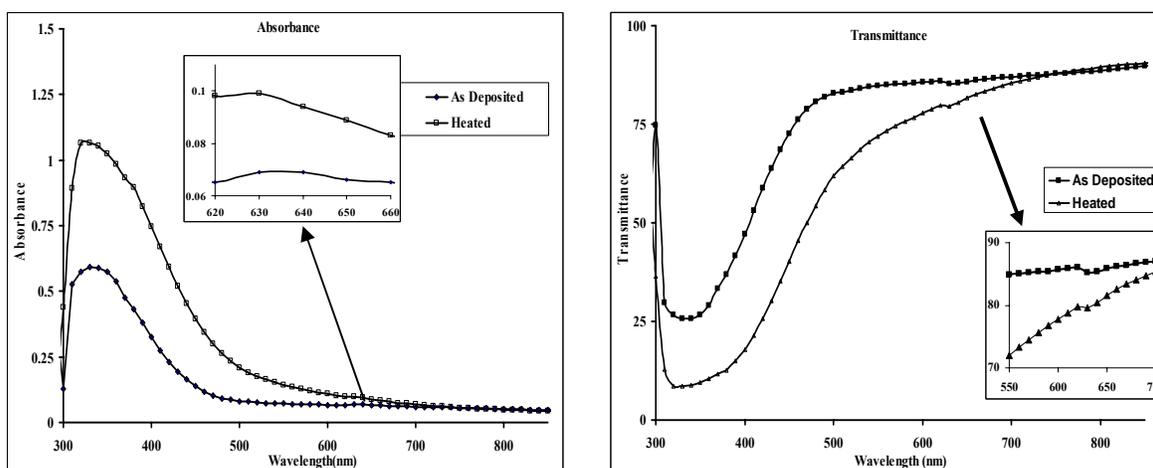


Fig.3. Optical absorbance and transmittance of as deposited and heat treated polythiophene thin films.

3.3 Refractive Index

The refractive indices (n) of as deposited and heat treated thin films of polythiophene were measured by Abele's method [9] and also calculated by using analytical method using following formula [10]

$$n = \left[\frac{n_s^2 T_f + n_s (1 + \sqrt{R_f})^2}{T_f + n_s (1 - \sqrt{R_f})^2} \right]^{1/2} \quad (1)$$

Where, n_s - Refractive index of the substrate, T_f - transmittance, R_f - Reflectance.

The refractive index values of the as deposited and heat treated polythiophene thin films are tabulated in

Table 1: Refractive index and band gap of as deposited and heat treated polythiophene thin films

Nature of the Film	Refractive Index		Band Gap
	Analytical method	Abele's method	
As Deposited	1.64	1.71	3.05
Heat treated	1.77	1.83	2.75

3.4 Optical band gap

Fig. 4 gives the graph of $(\alpha h\nu)^2$ as a function of $h\nu$. From the absorption data, the band gap energy was calculated using formula

$$\alpha = [\alpha_0 (h\nu - E_g)^n] / (h\nu) \quad (2)$$

Where 'Eg' is the separation between bottom of the conduction band and top of the valence band, $\alpha =$

table 1. The refractive index of heat treated thin films was found to increase as compared to as deposited thin films this increase in the refractive index may be due structural changes observed from surface morphology. However the free volume density, polarizability and the wavelength difference of experimental wavelength and absorption peak wavelength of the material all these factors will be affect the refractive index of the material [14]. Aromatic polymers have denser structure and high polarizability than aliphatic polymers the heating make the structure of the polythiophene denser because of which the refractive index increases with decrease in the transmittance [15]. The refractive index of thin film measured by Abele's and analytical methods showed similar values.

absorption of thin film and $\alpha_0 =$ Absorption Coefficient, ' $h\nu$ ' is the photon energy and ' n ' is a constant. The value of n depends on the probability of transition; it takes values as 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transition respectively.

The observed values of band gap are tabulated in table 1. The variation in band gap values was observed due to heat treatment. The change in the band gap of the heat treated thin film and as deposited thin film may be due to

changes observed from surface morphology, the as deposited polythiophene thin films shows larger band gap, the heating causes decrease in the band gap of the thin films of polythiophene [16].

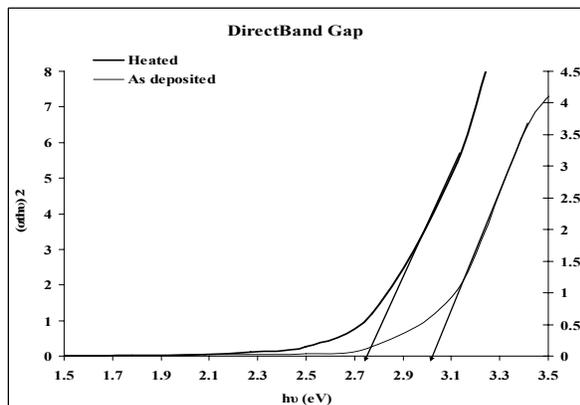


Fig.4. Optical band gap of thin film of polythiophene with heating effect.

3.5 Electrical Conductivity

The electrical behaviour of the thin films of polythiophene was studied by two probe resistivity measurement technique. The study of the temperature dependence of the electrical conductivity of both as deposited and heat treated polythiophene thin films provides interesting information about the electric behaviour of these thin films. Figure 5 (a) shows the temperature dependence electrical conductivity of as deposited and heat treated polythiophene thin films. Polythiophene thin films exhibit electrical conductivity in the range of $10^{-7} \Omega^{-1} \text{cm}^{-1}$. It can be seen from the graph that electrical conductivity decreases with increase in temperature in the low temperature range and again increases at 400 K this may be because of elimination of different impurities like residual solvent molecules, or absorbed gases [17]. The heat treated thin film also shows decrease in the electrical conductivity within lower temperature range but this decrease is large as compared to the as deposited polythiophene thin films. Post deposition heating the film modifies the structural characteristics (grain size and shape, different structural defects) [18], which may a cause of increase in the electrical conductivity. However in the higher temperature range the electrical conductivity increases exponentially from a certain temperature which is known as transition temperature of the material (T_c). The intrinsic conduction domain begins at certain temperature, T_c (transition Temperature), characteristic for each sample, and the values of T_c shifts to lower temperature From 370 K to 353 K due to post deposition heat treatment [17]. We observed that within the higher temperature range ($T_c > 370 \text{ K}$) the electrical conductivity σ obeys exponential law [17]

$$\sigma = \sigma_0 \exp(-\Delta E/2kT) \quad (3)$$

Where σ_0 is a parameter depending upon semiconducting nature, ΔE is thermal activation energy of electrical conduction and k is Boltzmann's constant.

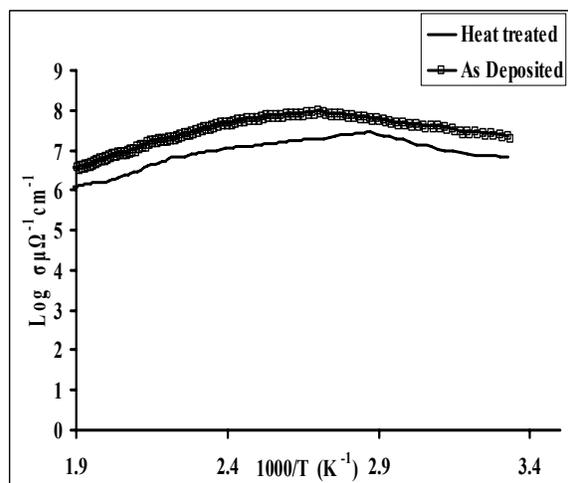
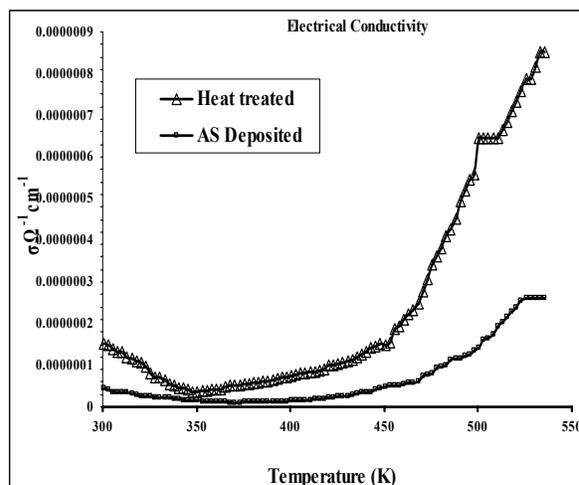


Fig.5. Electrical conductivity of polythiophene thin film against temperature.

Fig.5 (b) shows the graph $\text{Log } \sigma (10^3/T)$ the values of ΔE were calculated from this graph, it was found that the activation energy of the as deposited thin film is 0.35 eV which decreases due to post deposition heating to 0.34eV. This decrease in the activation energy also can be seen from larger grain to grain contact from SEM.

4. Conclusion

Polythiophene synthesized by an oxidative polymerization process has been successfully deposited as thin film on glass substrate using vacuum evaporation. A

shift in fundamental vibration mode of the thiophene ring, increase in the grain size, decrease in the transmittance and band gap while increase in the refractive index and decrease in the activation energy results due to post deposition heating of the polythiophene thin film.

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References

- [1] X. Ma., G. Li., H. Xu., Wang M., Chen H., *Thin solid Films*, **515**, 2700 (2006).
- [2] N. S. Sariciftci, D. Braun, C. Zhang, I.V. Srdanov, A.J. Heeger, G. Stucky, F. Wudl, *App Phy. Lett.* **62**, 585 (1993).
- [3] D. H. Kim, Y. D. Park, Y. Jang, H. Yang, Y. H. Kim, K. Cho, *Adv Fun. Mater.*, **15**, 77 (2005).
- [4] A. Laforgue, P. Simon, C. Sarrazin, J.F. Fauvarque *J Pow sour.*, **80**, 142 (1999).
- [5] F. Bloisi, A. Cassinese, R. Papa, L. Vicari, V. Califano., *Thin Solid Films.*, **516**, 1594 (2008).
- [6] X.S.Wang, Y.H. Deng, Y.Q. Li, *J. Mat. Sci.* **37**, 4865 (2002).
- [7] A.K. Narula, R.J.Singh, *App.Bioc. & Biot.*, **96**, 109 (2001).
- [8] O. Yu Posudievskii, N.V. Konoshchuk, A. L. Kukla, A. S. Pavlyuchenko, G. V. Linyuchev, V. D. Pokhodenko, *Thero. and Exp. Chem.* **42**, 339 (2006).
- [9] F. Abeles, *J. Phys. Radium*, **19**, 327 (1958).
- [10] S. H. Tamboli, R. B. Patil, S. V.Kamat, Vijaya Puri, R. K. Puri, *J. Ally. and Comp.* 855-859 (2009).
- [11] M. R. Karim, K. T. Lim, C. J. Lee, M. S. Lee., *Synth. Met.*, **157**, 1008 (2007).
- [12] J. B. Yadav, R. K. Puri, Vijaya Puri, *App. Sur. Sci.*, **254**, 1382 (2007).
- [13] A. Gok, M. Omastova, A. G. Yavuz, *J. Syn. Met.*, **157**, 23 (2007).
- [14] B. H. Ma, A. K.Y. Jen, L.R. Dalton, *Adv. Mater.*, **14**, 1339 (2002).
- [15] J. B. Yadv, R. B. Patil, R. K. Puri, Vijaya Puri, *App.Sur.Sci.*, **255**, 2825 (2008).
- [16] J. C. Osuwa, C. I. Oriaku, I. A. kalu, *Chal. Lett.*, **06**, 433 (2009).
- [17] G. I. Rusu, A. Airinei, M. Rusu, P. Prepelita, L. Marin, V. Cozan, I. I. Rusu, *Acta. Mat.* **55**, 433 (2007).
- [18] G. I. Rusu, V. Sunel, D. Sirbu, A. Amariei, I. Caplanus, G. G. Rusu, *Mat.Res. Innovat.* **06**, 247 (2002).

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