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Annealing heat treatment of Poly(triarylamine) (PTAA) thin films deposited using spin coating



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ARTICLE INFO	ABSTRACT
Article history: Received 29 October 2016 Received in revised form 8 December 2016 Accepted 10 December 2016 Available online 19 December 2016	Poly(triarylamine) is one of the semiconducting layers and has huge advantages, for example, can dissolve in solvent and stable in ambient condition. In this work, Poly(triarylamine) thin films deposited at different annealing temperature on the glass substrate in order to investigate the dependence of annealing temperature on the optical and structural of the films. The UV-Vis results show that there is a modification in the absorption spectrum of PTAA thin films as the annealed layers where there is an increase in the absorptive with the increase in annealing temperature and the estimated band gap within 3.05-3.14 eV. All PTAA films share the same pattern of XRD with a broad diffraction peak at 22.33-22.85° and result in the better crystallite at 100 °C. The value of the films thickness measured by the profilometer is consistent.
Keywords:	
Structural properties, Optical properties,	
Annealing temperature, Grain size	Copyright ${f C}$ 2016 PENERBIT AKADEMIA BARU - All rights reserved

1. Introduction

Organic semiconductors have gained much consideration during the most recent decades driven by the aspiration to acknowledge electronic devices such as organic light-emitting diodes, organic field-effect transistors and organic solar cells with novel properties [1]. Electronic devices taking into account solution-process able polymers are among the most encouraging utilizations of organic semiconductors [2]. Choosing a suitable organic semiconductor material is very important and poly(triarylamine) (PTAA) is one of the well-known organic materials with the hole mobility of 10^{-3} up to 10^{-2} cm2/ V⁻¹s⁻¹ [3-5]. PTAA has the huge advantages such as stable in ambient and can be dissolved in the solvent [6-8]. There are many deposition techniques is feasible and most of the research activities related to organic thin-film devices used spin coating method [2]. Spin coating method produces a high width of thickness ration, the high degree of the permeability reduction thin film [9], allows for uniform deposition onto flat substrates [10] and instrument requirement is small cost where the sample can be coated and tested in the short period [11]. The final condition of the PTAA

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thin films depends on the preparation condition such as spin speed, choice of solvent, annealing condition (time and temperature) and solvent concentration [12].

Generally, when semi-crystalline are heated to increase temperature under their melting point; their physical properties will change. These changes involve in alterations of their morphological structures. It is found that in the most cases, the polymeric sample is not in their thermodynamic equilibrium. Hence, the heat treatment was needed to reorganize the structures to a state of order with decreased free energy [13]. Olubunmi reported that the morphology, optical, structural properties of P3HT:PCBM are significantly affected by the annealing heat treatment. He also reported that the solar cell annealed at 200 °C have the lowest fill factor and the carrier mobility increase with the increasing of the temperature [10]. Ahn et al. reported the result of the effect of the post fabrication thermal annealing on physical and electrical modification to pentacene organic thin-film transistor (OTFT). The transistor annealed at 50 °C shows the improvement in mobitity, from 0.19-0.366 cm²/Vs and at the device annealed at 70 °C and above show the OTFT performance is decreased [14]. Chow et al. reported that the post-annealing treatment improve the field-effect mobility, threshold voltage and the on/off current ratio of the device and show the device annealed at 150 °C has optimal electrical properties [15]. Here we report the effect of annealing temperature to optical and structural of PTAA thin films. This is because there are only a few report regarding PTAA thin films especially on the physical characterization [5-7].

2. Materials and methods

PTAA thin film was deposited on glass substrate by spin coating. PTAA powdered dissolved in chloroform and stirred for one day at room temperature to form 0.1 wt % solution. Before the deposition step, the substrate cleaned using an ultrasonic bath by dipping the substrate in distilled water, ethanol and acetone for 3 minutes, three times in each solution. After that, the substrate was rinsed with distilled water and blow with Nitrogen gas. The PTAA solution was filtered through a 0.25 μ m mesh size filter paper. This was done to ensure a smooth layer when spin coated. 130 μ L of PTAA solution was dispensed and spread across the substrate by spinning at 500 rpm for 5 seconds and then spun at 2000 rpm for 30 seconds. PTAA thin films were then annealed at 50°C, 100°C, 150°C, 200°C, 250°C to study the dependence of annealing temperature on the physical properties of thin films. Different tools were used to examine the PTAA thin films. To measure the optical properties of the thin film, UV-Vis spectrometer Lambada EZ210 has been utilized for this purpose. Whereas to figure out the thickness and structural properties of thin films, Nanomap LS500 Profilometer and X-Ray Diffraction Philip Expert Pro were used respectively.

3. Results and discussions

3.1. Optical properties

Figure 1(a) shows the optical absorbance spectra of PTAA thin films deposited at different annealing temperature. The optical absorbance spectra have been investigated in range of 300-700 nm. There is a consistency of the absorbance peak with respect to annealing temperature and absorbance peak occurs at 354 nm. Annealing temperature at 100° C shows the highest peak while at 150° C shows the lowest peak. The figure shows that there is a modification in the absorption spectrum of PTAA thin films as the annealed layer where there is an increase in the absorptive with the increase in annealing temperature. In the same figure, there was very low optical absorption. This situation may be clarified from the energy band gap. At the point when there is an interaction between the photon and electron, the electron across the band gap E_g from the files valence-band



level to the unfilled conduction-band states [16]. Fig. 1(b) demonstrate the PTAA thin films band gap of PTAA thin films deposited at 100°C which is obtained from Tauc Equation, for direct optical band gap as in Eq. 1 [17].

$$(\alpha h v)^{1/2} = (h v - E_g) \tag{1}$$

Where α is the absorption coefficient, and hv is the quantum energy (eV). The value of the absorption coefficient, α can be calculated by using absorbance (Abs) and thickness (t), utilizing Equation 2.

$$\alpha = \frac{2.303 \, x \, Abs}{t} \tag{2}$$

The estimated value of optical band gap for PTAA thin films is within 3.05-3.14 around the value corroborated by the literature review [5,8]. The estimation of the band gap, E_g for allowed transitions got from extrapolation of the straight line part of $(\alpha hv)^{1/2} = 0$.



Fig. 1. (a) Optical absorbance spectra of PTAA thin films deposited at different annealing temperature (b) plots of $(\alpha h \nu)^{1/2}$ vs photon energy for PTAA thin films deposited at 100 °C

3.2. Structural properties

Figure 2 show the X-ray diffraction (XRD) pattern for PTAA thin films deposited at 150 °C. All films are in amorphous phase which has a broad peak and a significant bump distributed in a wide range (2 thetas). All PTAA films show a peak within 22.33° to 23.85° agreed well with the finding by Zhang [7] and has satisfied interlayer stacked chain-to-chain distance. The entire PTAA thin films share the same pattern of XRD and the value of FWHM are within 9.12-9.62 as shown in Table 1. The estimated crystallite size can be calculated using Scherrer's formula in Eq. 3 [18].

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{3}$$

Where k is a shape factor with the value of k = 0.94 for cubic crystallites. λ , β , and Θ are 1.54056 Å, observed FWHM and Bragg diffraction angle, respectively. The value of crystalline size for PTAA thin as deposited and annealed at 50°C, 100°C, 150°C, 200°C is 0.84, 0.86, 0.89, 0.88 and 0.87nm, respectively indicating better crystallite grain size quality at 100°C. The estimated grain size of PTAA



thin films increased as the annealing temperature increased to 100°C but reduces upon further increase in annealing temperature. This might be due the high annealing temperature could damage the structure of PTAA thin films.



Wavelength (nm)

Fig. 2. X-Ray diffraction pattern for PTAA thin films deposited at 150°C

Table 1

The full-width half- maximum (FWHM) and grain size of PTAA thin films as deposited and annealed at 50 °C, 100 °C, 150 °C, 200 °C

Annealing temperature (°C)	FWHM	Grain size (nm)
Room temperature	9.45	0.84084
50	9.28	0.85589
100	8.92	0.89022
150	9.06	0.87700
200	9.10	0.87313

3.3. Surface morphology

Table 2

Thickness of PTAA thin films deposited at different annealing temperature

Annealing temperature (°C)	Thickness (nm)	Root mean square (RMS) (nm)
Room temperature	59.36	1.6932
50	59.57	1.7510
100	60.59	1.9428
150	60.14	2.3244
200	60.93	2.3829

The thickness and root mean square (RMS) of the PTAA thin films after undergoing at different annealing temperature is presented in table 2. There are no significant in thickness of the thin film as deposited and annealed at 50 °C, 100 °C, 150 °C and 200 °C means that the annealing temperature does not influence the thickness and surface morphology from result shown in Fig. 3 that obtained from profilometer. It can be observed from the figure that the morphology shows smooth and uniform surface as the increasing the annealing temperature. The root mean square (RMS) roughness of the samples as deposited and after undergo heat treatment at 50 °C, 100 °C, 150 °C and 200 °C for



10 minutes, equals 1.70 nm, 1.75 nm, 1.94 nm, 2.32 and 2.38 nm, respectively. The value of RMS increase as the increasing of the annealing temperature same like reported by Aziz *et al.* [19].



Fig. 3. Surface roughness for PTAA thin films deposited at different annealing temperature

4. Summary

In summary, we have successfully deposited the PTAA thin films by spin coating method at the different annealing temperature. This parameter does not influence the X-ray diffraction pattern and the films thickness. There is a modification in the absorption spectrum of PTAA thin films with estimated band gap values of 3.05-3.14 eV. The estimated grain size of PTAA thin films increased and start decreased at thin film deposited at 100°C, maybe the high annealing temperature could damage the structure of PTAA thin films.

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References

- [1] Pingel, Patrick. "Morphology, charge transport properties, and molecular doping of thiophene-based organic semiconducting thin films." (2014).
- [2] Abdellah, Alaa, Bernhard Fabel, Paolo Lugli, and Giuseppe Scarpa. "Spray deposition of organic semiconducting thin-films: Towards the fabrication of arbitrary shaped organic electronic devices." Organic Electronics 11, no. 6 (2010): 1031-1038.
- [3] Xu, Yong, Takeo Minari, Kazuhito Tsukagoshi, Romain Gwoziecki, Romain Coppard, Francis Balestra, and Gerard Ghibaudo. "Power transfer-length method for full biasing contact resistance evaluation of organic field-effect transistors." *Organic electronics* 12, no. 12 (2011): 2019-2024.



- [4] Celle, Caroline, Clément Suspène, Jean-Pierre Simonato, Stéphane Lenfant, Marc Ternisien, and Dominique Vuillaume. "Self-assembled monolayers for electrode fabrication and efficient threshold voltage control of organic transistors with amorphous semiconductor layer." *Organic Electronics* 10, no. 1 (2009): 119-126.
- [5] Intaniwet, Akarin, Christopher A. Mills, Paul J. Sellin, Maxim Shkunov, and Joseph L. Keddie. "Achieving a stable time response in polymeric radiation sensors under charge injection by X-rays." *ACS applied materials & interfaces* 2, no. 6 (2010): 1692-1699.
- [6] Sendner, Michael, Jens Trollmann, and Annemarie Pucci. "Dielectric function and degradation process of poly (triarylamine)(PTAA)." *Organic Electronics* 15, no. 11 (2014): 2959-2963.
- [7] Zhang, Zhiming, Liqun Wang, Junying Deng, and Meixiang Wan. "Self-assembled nanostructures of polyaniline doped with poly (3-thiopheneacetic acid)." *Reactive and Functional Polymers* 68, no. 6 (2008): 1081-1087.
- [8] Madec, Marie-Beatrice, John J. Morrison, Michael Rabjohns, Michael L. Turner, and Stephen G. Yeates. "Effect of poly (triarylamine) molar mass distribution on organic field effect transistor behaviour." *Organic Electronics* 11, no. 4 (2010): 686-691.
- [9] Lue, Shingjiang Jessie, Yu-Li Pai, Chao-Ming Shih, Ming-Chung Wu, and Sun-Mou Lai. "Novel bilayer well-aligned Nafion/graphene oxide composite membranes prepared using spin coating method for direct liquid fuel cells." *Journal of Membrane Science* 493 (2015): 212-223.
- [10] Olubunmi, Olalekan Deborah. "annealing heat treatment of organic material for controlled bulk heterojunction solar cells." phd diss., african university of science and technology, 2013.
- [11] Hu, Longyu, Aubrie Pfirman, and George Chumanov. "Stabilization of 2D assemblies of silver nanoparticles by spincoating polymers." *Applied Surface Science* 357 (2015): 1587-1592.
- [12] Parry, Adam Valentine Sheridan. "Small molecule organic field effect transistors: vacuum evaporation and solution processable monolayer devices." PhD diss., University of Manchester, 2013.
- [13] Fischer, E. W. "Effect of annealing and temperature on the morphological structure of polymers." *Pure and applied chemistry* 31, no. 1-2 (1972): 113-132.
- [14] Ahn, Taek, Hoon Jung, Hye Jung Suk, and Mi Hye Yi. "Effect of postfabrication thermal annealing on the electrical performance of pentacene organic thin-film transistors." *Synthetic Metals* 159, no. 13 (2009): 1277-1280.
- [15] Chou, D. W., C. J. Huang, C. M. Su, Cheng-Fu Yang, W. R. Chen, and T. H. Meen. "Effect of rapid thermal annealing on pentacene-based thin-film transistors." *Solid-State Electronics* 61, no. 1 (2011): 76-80.
- [16] Lin, Su-Shia, Jow-Lay Huang, and Ding-Fwu Lii. "The effects of rf power and substrate temperature on the properties of ZnO films." *Surface and Coatings Technology* 176, no. 2 (2004): 173-181.
- [17] Chandrasakaran, Devi Shantini, Irwana Nainggolan, Mohd Nazree Derman, and Tulus Ikhsan Nasution. "Spinach Ferredoxin (Fdx) as an Organic Material to Improve Optical Band Gap of Chitosan (Cs) Biofilm." In Applied Mechanics and Materials, vol. 754, pp. 939-943. Trans Tech Publications, 2015.
- [18] Fewster, Paul F. "X-ray analysis of thin films and multilayers." *Reports on Progress in Physics* 59, no. 11 (1996): 1339-1407.
- [19] Aziz, Fakhra, K. Sulaiman, M. R. Muhammad, M. Hassan Sayyad, and Kh Karimov. "Influence of thermal annealing on the structural properties of vanadyl phthalocyanine thin films: A comparative study." *Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering* 5, no. 8 (2001): 693-695.