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Temperature Effect on Structural and Optical Characteristics of Solution-processed Polytriarylamine (PTAA) Thin Films for Optoelectronic Applications

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Polytriarylamine (PTAA) is a promising yet trending organic semiconductor material in which has unique characteristics that are low-cost fabrication, flexible and stable in room condition. The unique characteristic of PTAA thin films have attracted researchers to explore more on its ability as future green technology solutions. In this works, the effect of annealing temperature towards PTAA thin films are focused. PTAA thin films is fabricated by solution processed technique and sintered onto the glass substrate by spin coating method. The spin coating speed are 1000 RPM to 5000 RPM. The PTAA thin films are further annealed for an hour with temperatures of 80 ^{o}C, 120 ^{o}C and 150 ^{o}C. It is shown that grain size of thin films are increasing as the temperature increased based on XRD analysis. As for 1000 to 5000 RPM, the highest grain size obtain are 26.46 nm, 31.34 nm, 37.19 nm, 39.96 nm and 42.72 nm, respectively. Optical characteristic also reveals that band gap energy value is perpendicular to the increasing in temperature obtain from the UV-Vis spectrum. The results strongly show that annealing temperature had significantly affected both structural and optical properties of PTAA thin films.

Keywords: Polytriarylamine; spin coating; grain size; band gap; annealing

I. INTRODUCTION

Organic semiconductor thin films had remarkably progressing and widely used in semiconductor industry especially in opto-electronic application. More semiconductor devices such as TFTs are develop using organic semiconductor materials as their active layer to cater to desired applications. Recently, an organic semiconductor polymer called polytriarylamine (PTAA) has attract many researchers to use it as an active layer not only in solar panel but also as thin film for semiconductor device (Miandal *et al.*, 2017). The versatility of PTAA properties such as great stability in ambient condition and large hole mobility from 10^{-3} up to 10^{-2} cm^{-2} V^{-1} s^{-1} convince the researcher of its good performance (Xu, 2015). Besides that, family of triarylamine are also highly soluble in common organic solvent such as chloroform and toluene (Kisselev & Thelakkat, 2004; Horie *et al.*, 2008). Huge gap between HUMO and LUMO of PTAA ranging from 1.8 eV – 5.1 eV shows that PTAA emit good optical properties thus secure its functionality in opto-electronics industries (Rani *et al.*, 2019).

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Moreover, PTAA appear to have a better band gap and work function than those measured PEDOT:PSS thus it possessed higher conductivity which are beneficial for future photovoltaic applications (Ghosh *et al.*, 2020). Therefore, in this article are mainly focusing on the structural morphology and the optical properties of PTAA thin films with respect to the effect of different annealing temperature and the spin speed (rms) during fabrication process. It is anticipated that, the annealing temperature would give significant effect towards the active layers of the thin films fabricated.

II. METHODOLOGY

Fabrication process is start with pre-cleaning process of substrate. In this research, soda lime glass is used as a substrate with dimensions of 2.5 cm x 2.0 cm. Soda lime glass is chosen as it can sustain the annealing temperature up to 700 ^{o}C (Malou *et al.*, 2013). The substrate will undergo cleaning process before it can be used to fabricate organic semiconductors. The substrate is soaked overnight with Decon 90 solution to remove any impurities on the surface of the glass. The process is then continued with cleaning the glass using an ultrasonic bath. The ultrasonic bath is set to a pulse mode and cleaned for minimum of 15 minutes for every solution. The solution used was distilled water, Methanol and Acetone. The process is repeated for distill water to wash away the remaining of acetone solution on the substrate. The last procedure was to dry the substrate by using Nitrogen gas. Lastly, every substrate will be placed separately in a petri dish. The PTAA solution is prepared by mixing PTAA (Ossila) powder with Chloroform solution and forming 0.2% solution per weight. This mixture of solution is kept in an amber bottle to avoid the effect of light towards the solutions. The solution is stirred for 12 hours before it can be used for fabrication process.

Once the cleaning process is done, the fabrication process of PTAA take place. PTAA is layered onto the substrate by spin coating method for 60 seconds. The spin speed (rms) and annealing temperature is set to be independent variables. As for spin speed, 1000 rpm to 5000 rpm is chosen as PTAA thin film work best in this layer of thickness (Rani *et al.*, 2019). As the rpm increase the thickness of thin film is decreased. As for annealing temperature, it is varied from room temperature, 80 ^{o}C, 120 ^{o}C and 150 ^{o}C. The thin films will be annealed for 1 hour for every sample in ambient condition.

Structural properties of the PTAA thin film is characterised using an X-ray diffractor machine. This technique enables the determination of Full width half maxima (FWHM) value of the thin films thus relates to the crystallinity properties of PTAA thin films. The thickness of thin film are also obtained by using scanning electron microscope (SEM). The cross-sectional area of thin film is tilt to 90° in order to determine the thickness of PTAA films. As for the optical properties, the transmittance and absorbance value are obtained from the UV-Vis spectrometer Lambda EZ210. The transmittance and absorbance value enable the measurement of bad gap of the PTAA thin films. Both of these techniques are done to see the effect of different deposition speed and temperature affects towards the diversity of PTAA thin films in terms of structural and optical properties.

III. RESULTS AND DISCUSSIONS

A. Structural Properties

The XRD diffraction image of PTAA thin films is clearly shown in the Figure 1. Structural characteristic of the thin film are obtained by using X-ray diffraction analysis. During the characterisation process, the X-ray was scattered and diffracted depending on the crystallite structure of thin films in wide range of 2θ. Difference topography of crystalline structure leads to certain peaks in the XRD results. As for PTAA thin films, broad peak are usually seen at the angle between 21^{o} to 25^{o} as per mentioned in literature (Zhang & Srinivasan, 2008; Miandal *et. al.*, 2017; Rani *et al.*, 2019). The FWHM value obtain for PTAA thin films are ranging from 0.198 rad to 0.886 rad. XRD patterns reveals that the orientation of PTAA is in amorphous state as there is no clear peak can be observed from the patterns results.

By using the FWHM value, the crystallite size or grain size of PTAA is determined using Scherrer's Equation (1) and the data is tabulated in Table 1.1 (Ingham & Toney, 2013; Popelka, Zavahir & Habib, 2020).

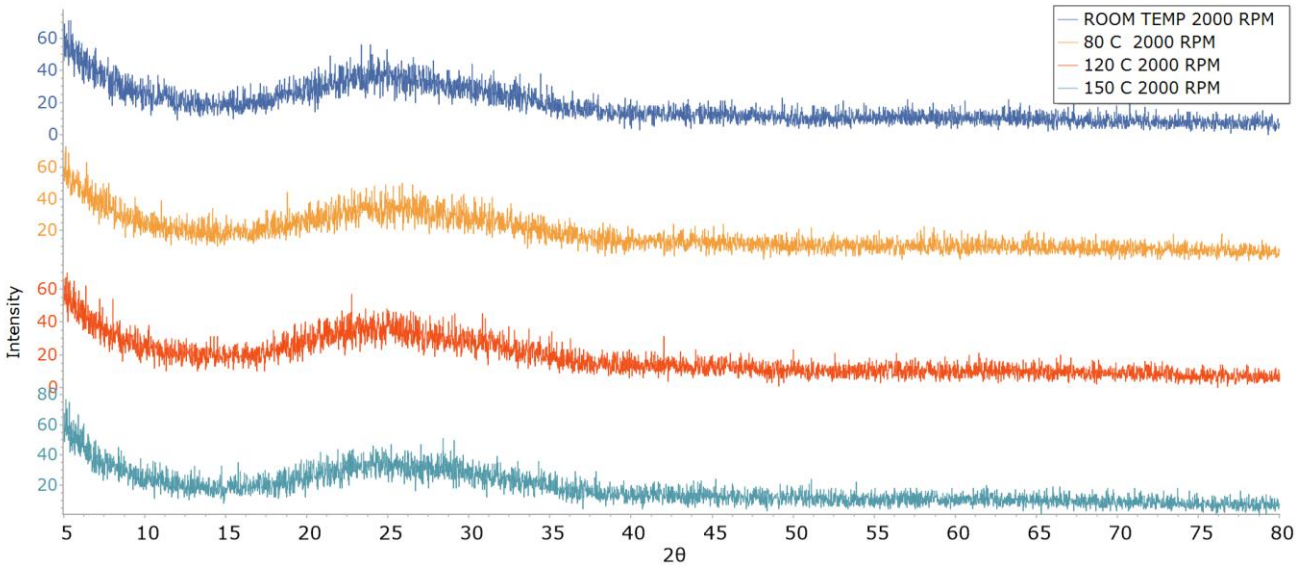


Figure 1. Amorphous XRD pattern at different annealing time of 2000 rpm spin speed

$$Grain\ Size, G = \frac{0.9\,\lambda}{\beta \cos\theta} \quad (1)$$

whereby λ is the wavelength of the X-ray used by the diffractor (0.15406 nm), β represent the FWHM in radians and θ is the diffraction peak or Bragg's angle in radian.

Figure 2 shows that, as the annealing temperature increase the grain size of PTAA also increase. As for room temperature, the grain size of thin films for 1000 to 5000 rpm is 10.33 nm, 12.62 nm, 21.95 nm, 28.30 nm, and 29.85 nm. The grain size show significant increase when it is annealed at 150 °C whereby the value for the grain size is 26.46 nm, 31.34 nm, 37.19 nm, 39.96 nm, and 42.72 nm for 1000 to 5000 rpm. This is due to recrystallisation process of PTAA polymer chain during the annealing process (Ahn *et. al.*, 2009; Guo *et al.*, 2006). The polymer chain of PTAA start to rearrange itself as it is receiving energy from the annealing process. This recrystallisation process leads to a stronger binding network between PTAA and chloroform molecule thus forming a more saturated cluster of PTAA thin films (Hostnik *et al.*, 2020). This thermal annealing had increase the adhesion between PTAA thin film with the substrate surfaces thus PTAA thin films is treated and the defects are repaired due to the annealing process (Ahn *et al.*, 2009).

As for thickness of thin films, it is obtained that the thickness of PTAA from 1000 rpm to 5000 rpm are approximately 85.78μm, 80.60 μm, 76.72 μm, 71.68 μm, and 68.50μm.

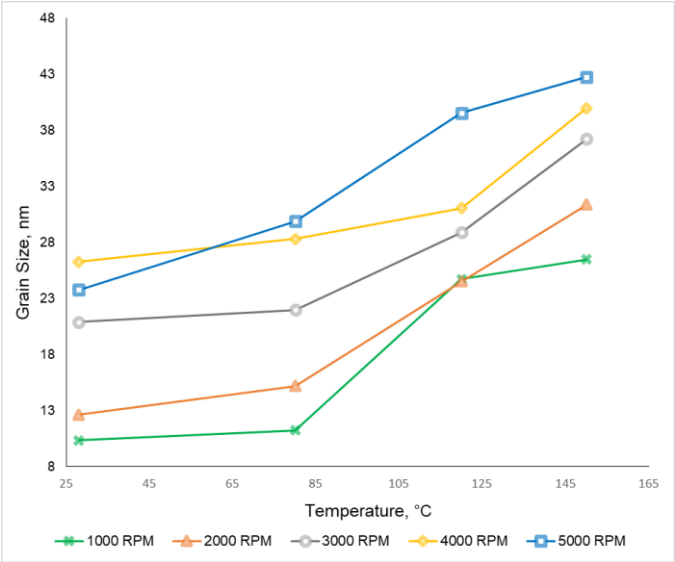


Figure 2. Grain size against annealing temperature

B. Optical Analysis

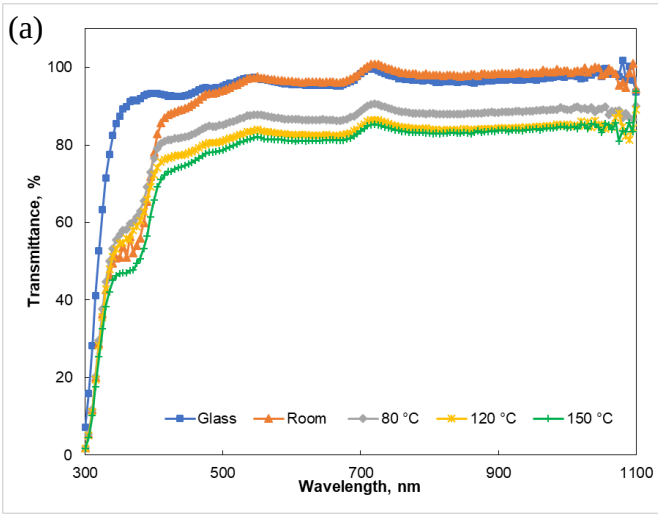
The optical transmittance (T) curves obtained at room temperature and annealed PTAA thin films are shown in Figure 3(a) as a function of wavelength. The spectra is measure in the range of 300 nm to 1100 nm in which are within the visible light and infrared spectrum. The PTAA thin films exhibit 70% - 80% of transmittance whereby the glass substrate shows the highest transmittance as nothing was layer on to the substrate. As for the analysis, Tauc Equation is used to obtain the band gap of each thin films (Makuła, Pacia & Macyk, 2018). The band gap of the thin films is the

key results for the future optoelectronics device as the thin films should be able to emits or absorb light efficiently.

$$(ahv)^{\frac{1}{2}} = (hv - E_g) \quad (2.1)$$

$$\alpha = \frac{2.303\ x\ Abs}{t} \quad (2.2)$$

where α is the absorption coefficient, hv is the quantum energy, Abs is absorbance and t is the thickness of fabricated PTAA thin films. The value E_g is determined by extrapolating the straight line onto the graph obtain by plotting for the equation $(\alpha hv)^{1/2} = 0$. The obtained value of band gap for 1000 rpm is ranging from 4.10 eV to 4.30 eV, 2000 rpm is ranging from 4.18 eV to 4.34 eV, 3000 rpm is ranging from 4.09 eV to 4.31 eV, 4000 rpm is ranging from 4.11 eV to 4.33 eV while for 5000 rpm is ranging from 4.13 eV to 4.35 eV. The band gap obtain from different spin speed does not show significant increment value but it is increasing in small amount due to the annealing temperature that rearrange the molecule thus providing mobility to the electrons (Tsutsumi *et al.*, 2015). The trends also shows that the higher the annealing temperature the higher the value of the band gap. This is due to the properties of organic materials whereby it is naturally low in thermal conductivity and thus helping the electron to transient to a higher level and increase in value (Yadav *et al.*, 2012).



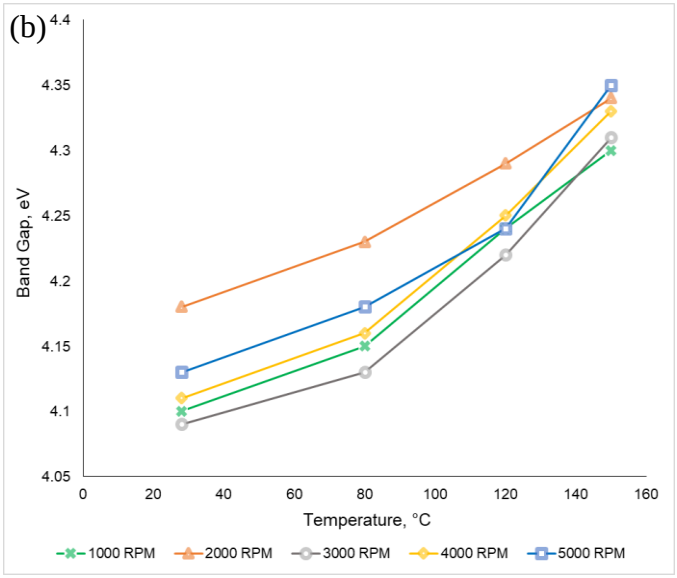


Figure 3. Spectra of; (a) PTAA thin films at 1000 RPM and (b) Band gap of PTAA thin films at different annealing time

Table 1. Grain Size of PTAA thin films at the spin speed of 1000 RPM to 5000 RPM with different annealing temperature of 80 ˚C, 100 ˚C, 120 ˚C and 150 ˚C

Spin Speed/ RPM	Temperature / ºC	Diffraction Peak/ rad	Interlayer Spacing (FWHM)/ rad	Grain Size, nm	Band Gap/ eV
1000	Room Temperature	23.23	0.753	10.33	4.10
	80	23.09	0.693	11.23	4.15
	120	23.16	0.315	24.70	4.24
	150	23.28	0.294	26.46	4.30
2000	Room Temperature	23.63	0.616	12.62	4.18
	80	23.47	0.512	15.19	4.23
	120	23.33	0.273	24.49	4.29
	150	23.80	0.248	31.34	4.34
3000	Room Temperature	23.62	0.405	20.89	4.09
	80	23.38	0.385	21.95	4.13
	120	23.38	0.294	28.86	4.22
	150	23.82	0.227	37.19	4.31
4000	Room Temperature	23.87	0.284	26.24	4.11
	80	23.45	0.272	28.3	4.16
	120	23.43	0.253	31.04	4.25
	150	23.5	0.212	39.96	4.33
5000	Room Temperature	23.93	0.323	23.75	4.13
	80	23.93	0.276	29.85	4.18
	120	23.86	0.214	39.5	4.24
	150	23.44	0.198	42.72	4.35

IV. CONCLUSIONS

In this research work, PTAA thin films are successfully fabricated by using spin coating technique. Structural and optical properties of PTAA thin films are analysed. It is shows that, the increase in temperature had affected the growth and optical characteristics of the thin films. As the annealing temperature increase, the grain size of thin films and the band gap are also increasing. It is reveal that, PTAA thin films are in amorphous state as shown by the XRD analysis. Annealing temperature significantly helps the polymer chain to execute the recrystallisation process of the thin films thus decreasing the defects and repair the arrangement of atom in the PTAA films. Optical properties had shown that the transmittance value are decreasing as the temperature increase and exhibit higher bad gap value.

V. ACKNOWLEDGEMENT

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