

Study on Doping Temperature of Iodine in MEH-PPV: I-MWCNTs Organic Solar Cell

Muhammad Ehsaani Bin Zainal Abidin

Faculty of Electrical Engineering

University Teknologi MARA

40450 Shah Alam, Selangor

muhammadehsaani@gmail.com

Abstract — The performance of nanocomposited poly [2-methoxy-5-(2'-ethylhexyloxy)-(p-phenylene vinylene)] (MEH-PPV) and iodine doped multiwall carbon nanotube (MWCNT) for organic solar cell application were investigated. 120mg of MWCNTs was first doped with 1gram of iodine using thermal chemical vapour deposition method (CVD) with temperature varied at 90, 100, 110, 120, 130 and 140°C. Then, 80mg of MEH-PPV was stirred for 48 hours with tetrahydrofuran (THF). Next, the CNT was added to the solution to form nanocomposited MEH-PPV: I-MWCNT solution. The solution was then deposited on ITO using spin-coating method. The current density – voltage (J-V) were measured in dark and under illumination using solar simulator. Optical properties such as absorbance and transmittance were measured using UV-Vis Spectrophotometer. For physical properties, the characterization was done using Field Emission Scanning Electron Microscopy (FESEM) and Atomic Force Microscope (AFM). From the I-V curve characteristic, thin film with doping temperature of 100°C gives the best result considering some response it gives towards light. In optical properties, the thin film also gives out the 0.45 unit of absorption spectra which is the highest value among others.

Key words — MEH-PPV: I-MWCNT, organic solar cell

I. INTRODUCTION

Organic solar cell is a type of solar cell based on conjugated polymer and has led to great attention with the aim or replacing conventional inorganic solar cells. It can be processed at lower cost, low weight and ease of synthesis with greater versatility than today's solar cell. However, organic solar cells also suffer from limitation in performance such as low absorption coefficient, limited absorption spectra and poor stability under illumination which contribute to the limitation of the device performance for practical applications [1]. The main limiting factor of polymer photovoltaic or organic solar cell (OSC) is the low amount of absorbed photos due to the narrow absorption spectra of the organic film [2]. OSC have a number of potential advantages such as lower production cost and flexibility (which makes the addition of other material to enhance its performance possible). The band gap of the organic material used in OSC can be tuned by altering the chemical structure of the organic material [3]. The important aspects of an organic solar cell are short circuit current, open circuit voltage, fill-factor and reliability [4].

MEH-PPV has been considered as one of the potential and useful conducting polymers for various optoelectronic applications, such as sensors and organic solar cells, and organic light emitting diodes (OLED) because of its environmental stability, easy conductivity control and cheap production in large quantities [5]. It is also one of the most interesting PPVs due to the enhanced solubility of this polymer which implies ease in some fabrication processes. For electrical properties, the MEH-PPV acts as an electron donor (p-type semiconducting polymer) with a relatively low conductivity due to its low hole and electron mobility when compared to inorganic semiconductor materials. MEH-PPV has a band gap of 2.27 eV and is known to have one of the highest occupied molecular orbital (HOMO) levels at 5.3eV and one of the lowest unoccupied molecular orbital (LUMO) levels at 3.2eV [6]. Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. It got names from its size, since the diameter of a nanotube is on the order of a few nanometers. CNT are nowadays very interesting materials due to their large range of applications. CNT are nanostructures whose electronic properties can be controlled. One possible way to modify the electronic and vibronic properties is a charge transfer during their intercalation and functionalization [7]. For this reason, doping of CNT has been widely explored to understand the modifications carried out by guest molecules [7]. However, there are a few problems regarding CNT doping. Recent studies [8] state that CNT has a saturated value that if too much CNT was added, it may wipeout. Yao Zhao [9] also found that CNTs which physically bonded with iodine are weak and can be removed by washing and sonicating and also heating in vacuum. Iodine was chosen to be doped with MWNTs because recent study [10] shows that it can be effectively doped and exchange electron with iodine. With the help of iodine doping, the CNT can be well dispersed in organic solvent which usually good solvent for most polymers. As a result, CNT can uniformly distribute in polymer matrices [11]. This work was done because iodine is the best candidate to alter and enhance the electrical and physical properties of CNT. Hence, the main goal is to study the effect of different iodine doping temperature to the thin film characteristic.

Problem Statement

The problem regarding carbon nanotube

1. CNT without doping has problems in terms of agglomeration
2. Difficulties in achieving good dispersion of CNT on a thin film

Objectives

There are three main objective of this experiment:

1. To characterize the electrical properties of nanocomposited MEH-PPV: I-MWCNT
2. To characterize the optical properties of nanocomposited MEH-PPV: I-MWCNT
3. To characterize the physical properties of nanocomposited MEH-PPV: I-MWCNT

II. METHODOLOGY

A. Nanocomposited MEH-PPV: CNT thin film preparation

i. Substrate preparation

Glass, silicon and indium tin oxide (ITO) will be used as a substrate. The glass was first cut into 2cm x 2cm. The substrate then cleaned by sonicated process by putting them in acetone, methanol and deionized water for 10 minutes respectively. For silicon substrate, it need to be rinse with hydrofluoric acid and deionized water with a ratio of 1:10. Then the substrates were dried by blowing it with nitrogen gas, N₂.

ii. CNT preparation

Multi Wall CNT (MWCNT) was first goes through annealing for 30 minutes at 450°C to remove the impurity. Then, 120mg of MWCNT was then doped with 1g of iodine using thermal chemical vapor deposition (CVD) method for 1hour. The temperature on the MWCNT side was fixed to 800°C while on the iodine side the temperature was set to 90°C. This step was repeated for the next five samples with temperature of 100, 110, 120, 130 and 140°C.

iii. MEH-PPV preparation

The MEH-PPV powder first weighed and dissolves with tetrahydrofuran (THF) solvent with a ratio of 4:1 which is 80mg to 20ml and stirred for 48 hours to make sure the polymer solution is well dispersed. The nanocomposited MEH-PPV: I-MWCNT was prepared by mixed the polymer solution with 60wt% CNT powder which has undergone annealing and doping process. The solutions were prepared in a heated ultrasonic bath at 50°C for 1 hour to improve the solubility between the two. The polymer solutions were then deposited on a substrate using spin coating technique for 1 minute at 2000 rpm. To characterize the optical properties, the substrate that will be use is glass. For physical properties the substrate used is silicon while the electrical properties the indium tin oxide (ITO) will be used as a substrate. After the

deposition process, the thin films go through thermal evaporation treatment at 50°C for 5 minutes. The deposition and heating process were repeated 10 times to obtain the 10 layer thickness.

B. Nanocomposited MEH-PPV: I-MWCNT thin film characterization

In the experiment, there are 3 main characterization which are electrical, optical and physical properties. For electrical characterization, current-voltage was measured in dark and under illumination using CEP-2000 Solar Simulator. Absorbance, transmittance and optical bandgap are measured using UV-vis (JASCO/V-670EX) Optical spectrophotometer for optical characterization. Meanwhile for physical properties, the thickness, roughness and thin film surface topography the characterization done using Veeco Dektak 750 Surface profiler, Field emission scanning electron microscopy (FESEM) and Atomic force microscopy (AFM).

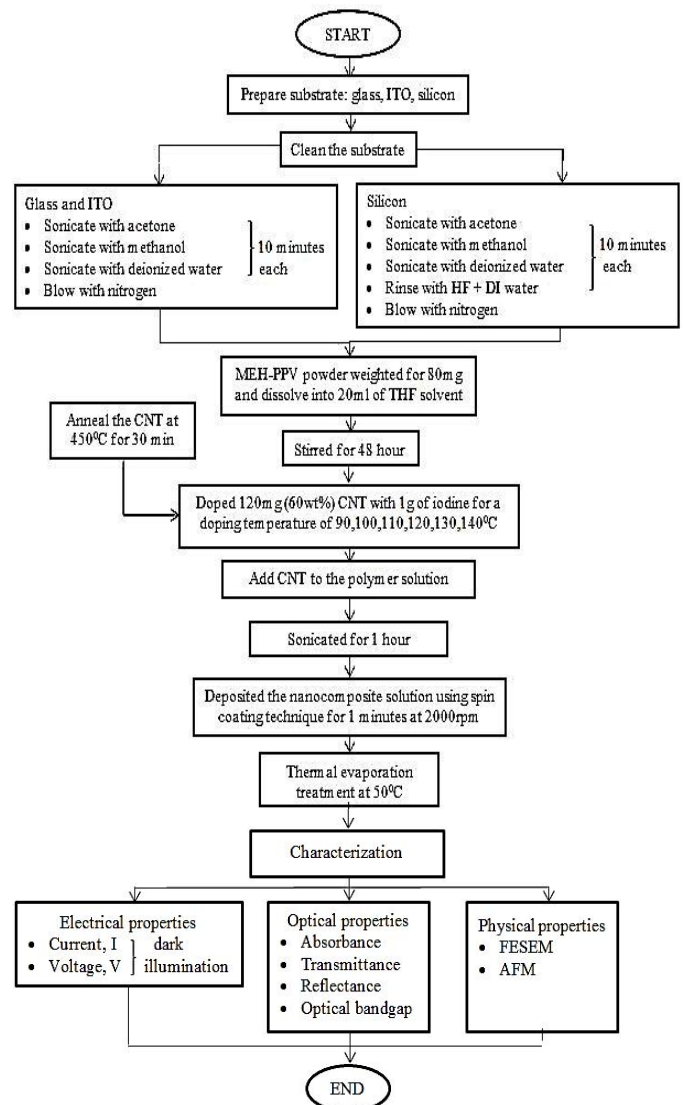


Figure 1: Flow chart of methodology

III. RESULTS AND DISCUSSION

I. Electrical properties

To measure the electrical properties, the nanocomposited MEH-PPV: I-MWCNT thin film is clipped with Gold (Au) which sputters coated on ITO as a metal contact. The measurement was done both in dark (Figure 2(a)) and under illumination (Figure 2(b)). Comparing the two graphs, there is no much different between them as they give very similar result while in dark and under illumination. For doping temperature of 90°C, 100°C and 120°C, the current density shows some response towards light but the J-V curve decrease instead of increase. Only the thin film with 100°C shows some increment in the value probably because it has the highest absorbance value (Figure 4(a)). When the light hit the sample, very little photon absorbed thus the carrier has least amount of energy to excite. We found that when the doping temperature is low, there are some response in J-V curve between dark and illumination. However, higher doping temperature shows no response (negligibly small) between dark and illumination.

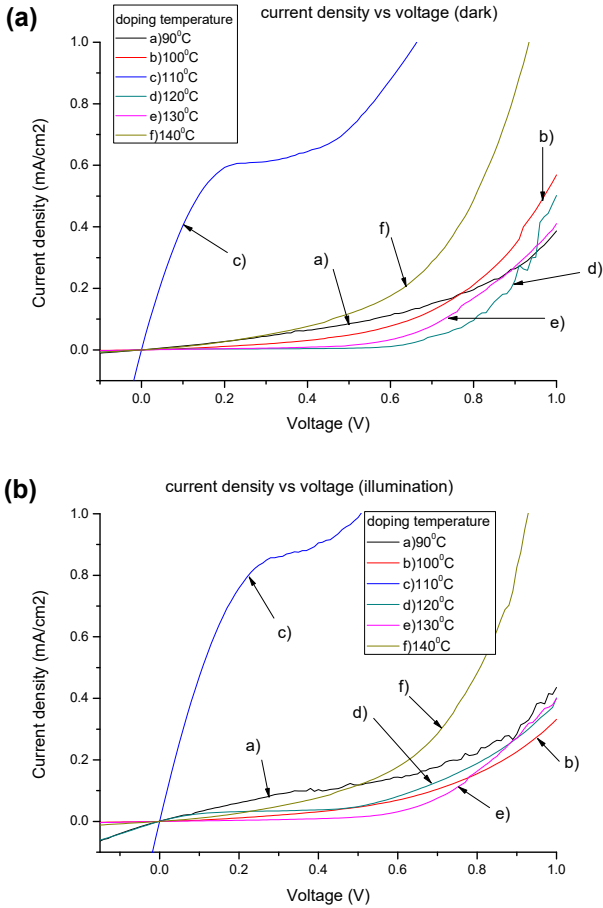


Figure 2: Current density vs voltage curve measurement a) in dark b) under illumination of various doping temperature

As shown in Table 1, the efficiency obtained in each parameter is very small and approaching zero value and most of it are in the dark. The efficiency can be calculated using the following equation (1):

$$\eta\% = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \quad (1)$$

Where V_{oc} is the open circuit voltage, J_{sc} is the current density, FF is the fill factor and P_{in} is the input power and should be set equal to 1. Generally, J_{sc} is directly related to the light harvesting capabilities of organic material and V_{oc} is determined by the energy level difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the acceptor material [12]. The reduction in surface roughness and smoother morphology will consequently reduce the J_{sc} and FF value of the cells [13] as shown in Table 1. Hence, the lower the J_{sc} and FF, the lower the power conversion efficiency.

temperature °C	dark				illuminate			
	Jsc (mA/cm2)	Voc (V)	FF	efficiency	Jsc (mA/cm2)	Voc (V)	FF	efficiency
90	-0.00006	-0.00053	0.000014	4.452E-13	-0.00006	-0.00058	0.000012	4.176E-13
100	0	-0.00018	0.000039	0	0	-0.00009	0.00008	0
110	-0.00001	0	0.000014	0	-0.00011	-0.00002	0.000012	2.64E-14
120	0	0	0.015822	0	0	-0.00002	0.000292	0
130	0	-0.00019	0.000038	0	0	-0.00029	0.000025	0
140	-0.00004	-0.0005	0.000014	2.8E-13	-0.00004	-0.00057	0.000013	2.964E-13

Table 1: Current density, open circuit voltage, fill factor and efficiency of the sample at different doping temperature

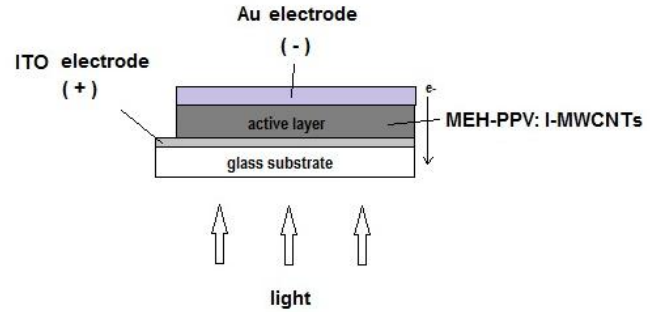


Figure 3: MEH-PPV: I-MWCNTs device structure

Figure 3 above shows the device structure consist of glass layer, ITO layer, active layer (MEH-PPV: I-MWCNT) and gold (Au) layer. Gold contacts are commonly used in high reliability connector application [14] and for solar cell contacts [15]. Recent research says that coating ITO with a layer of gold dramatically enhance injection properties and the contact with hole transport layer (HTL) becomes ohmic [16]. When light are given to the cell, the photon with energy equal or higher to the bandgap will be absorbed and creates electron hole pair. The electron current will flow out of the device from ITO electrode (+) and goes back into Au (-).

II. Optical properties

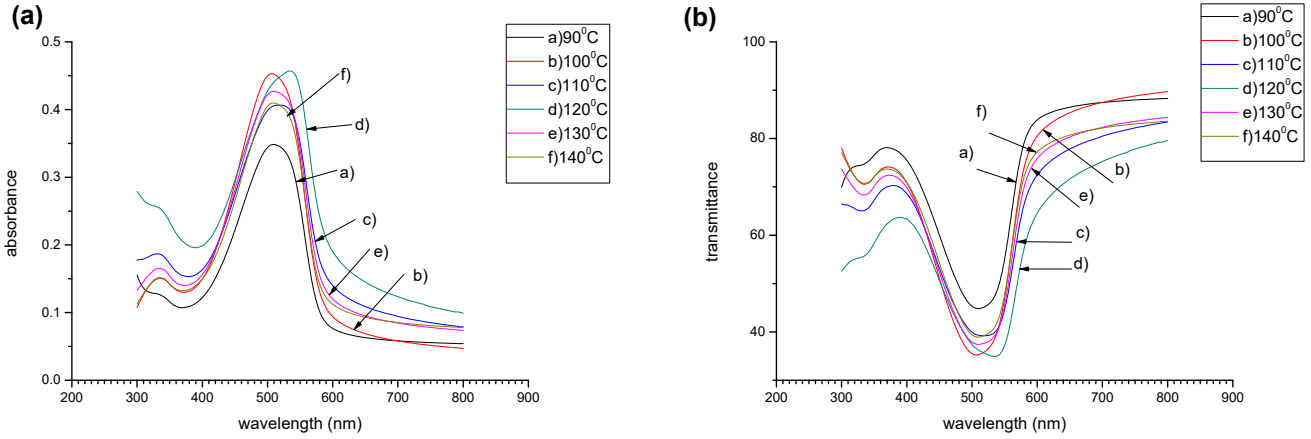


Figure 4: a) absorbance spectra b) transmittance spectra of the nanocomposited MEH-PPV: I-MWCNT thin film

Iodine was chosen to be doped with CNT to form nanocomposited MEH-PPV: I-MWCNT solution. The doping was done by varying the temperature in the CVD process. Because of MEH-PPV and iodine was a p-type material, the mixture of both will result in highly p-type material to be used as an active layer. With the help of iodine doping, the CNT can be well dispersed in organic solvent which usually good solvent for most polymers. Figure 4 shows the absorbance and transmittance spectra of nanocomposited MEH-PPV: I-MWCNT thin film at various doping temperature. From the Figure 4(a), it can be seen that the absorbance value starts low for 90°C doping temperature sample but starts to increase starting at 100°C sample become greater than 0.4 absorbance values and peak at around 500nm wavelength. As shown in Figure 4(a), the absorbance of 120°C sample showing bathochromic shift or red shift which is the shift to the longer wavelength. The red shift in the absorption peak may due to increase in the interfacial charge carrier concentration (charge density at the interface) which improves the extension of the band tails in the forbidden bandgap of the organic compounds [17]. Therefore the optical absorption occurs at higher wavelength. The decrease in doping temperature also contributed to the occurrence of peak shifting of the wavelength [18].

To estimate the value of optical bandgap, tangent line should be drawn in the Tauc's model touching most of the plot until intercepting the x-axis. The interception value is the optical bandgap value and measured in eV. The result in Figure 5 shows the optical bandgap of 2.14, 2.126, 2.124, 2.11, 2.15 and 2.15eV for MEH-PPV: I-MWCNT with iodine temperature of 90,100,110,120,130 and 140°C respectively. Although the result shows very little difference, it can be said that the optical bandgap of the thin film can be tuned by varying the iodine doping temperature. Comparing the results with the optical bandgap of pure MEH-PPV which is 2.27eV, this work manages to reduce the optical bandgap value around

0.12 to 0.15eV. The low optical bandgap is important for photovoltaic cell as it will become easier for the electron to excite from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO).

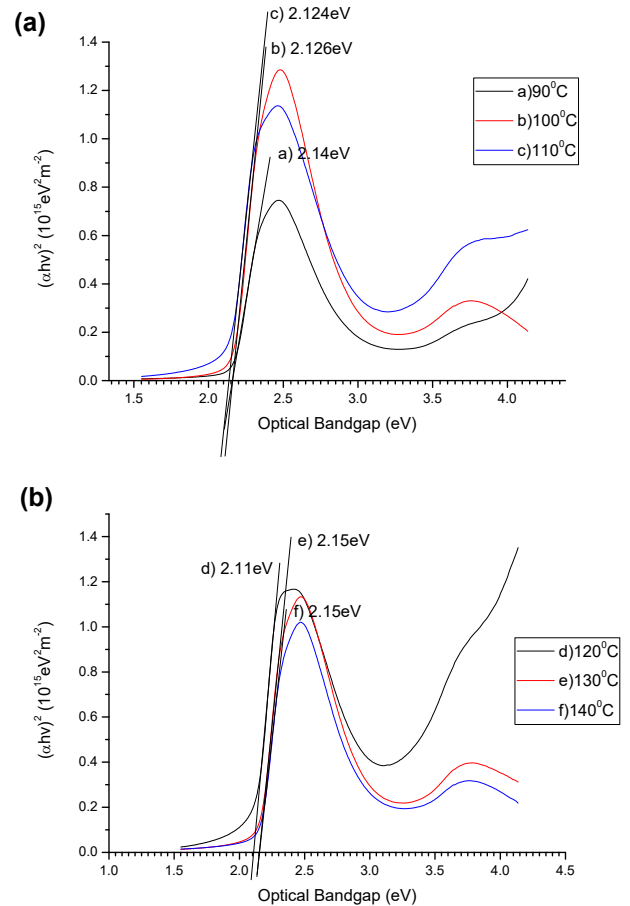


Figure 5: Optical bandgap estimation a) 2.124, 2.126, 2.14eV for 90, 100 and 110°C b) 2.11, 2.15, 2.15eV for 120,130 and 140°C.

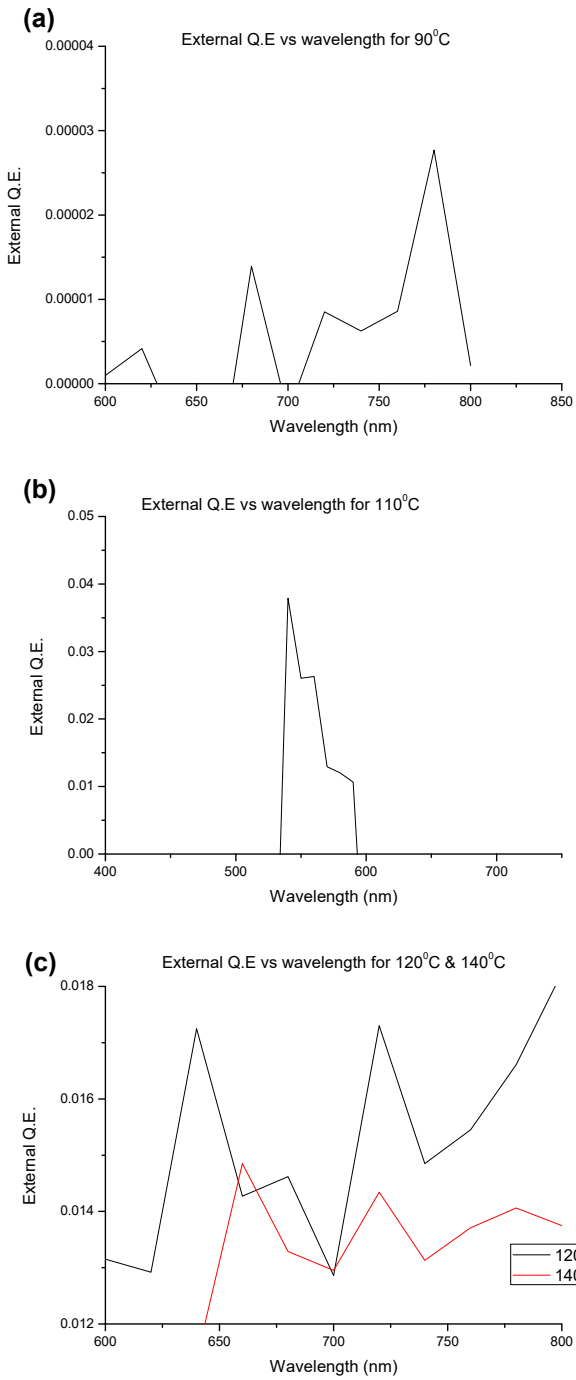


Figure 6: Constant photon plot at varied iodine doping temperature a) 90°C b) 110°C c) 120 & 140°C d) 100 & 130°C

External quantum efficiencies (EQE) is defined as the ratio of the number of charges extracted out of the device to the number of incident photons [17]. Figure 6 shows constant photon plot obtained at different doping temperature for a specified wavelength range. The EQE exhibit decrease-increase-decrease-increase trend while the highest value obtained from 110°C doping temperature. The photocurrent collected at different wavelengths relative to the number of photons incident on the surface at that wavelength determines the EQE or collection efficiency at each wavelength [19].

III. Physical properties

Iodine doping temperature	thickness (nm)
90°C	72.08
100°C	71.69
110°C	67.7
120°C	72.36
130°C	71.68
140°C	72.51

Table 2: Average thickness of the thin film at different doping temperature

Table 2 shows the nanocomposited MEH-PPV: I-MWCNTs thin film average thickness at different doping temperature. The thickness trend between 71nm to 73nm value but thickness for 110°C sample shows inconsistencies. This probably due to incompetency in experimental technique which contributed to the slightly lower thickness reading. The trend conclude that the doping temperature does not affect the thin film thickness.

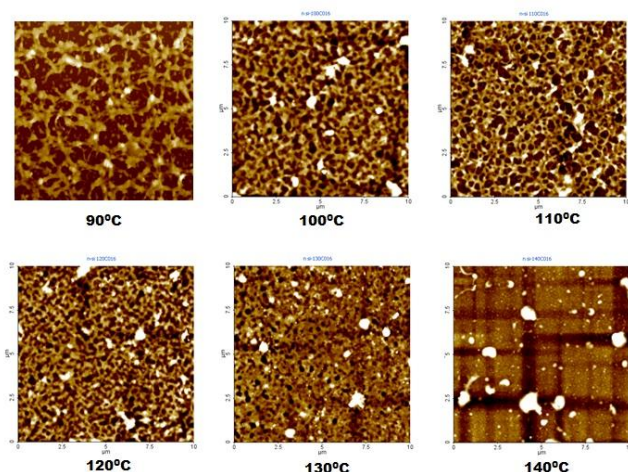


Figure 8: AFM image of MEH-PPV: I-MWCNTs at six different doping temperature

Figure 8 above shows the AFM image view of 10nm at their respective temperature. The uniformity of surface on the sample of 100°C, 110°C and 120°C clearly visible. As the temperature rises, the thin film uniformity getting better but starting at 130°C it becoming less uniform. The doping process will allow control of the electronic properties of carbon materials through reaction by intercalation with electron donor or acceptors. The intercalation of dopant can occur in between the graphitic shells and cause the expansion of the interlayer distance [18]. In conclusion, the increasing of iodine doping temperature will reduce the thin film uniformity.

IV. CONCLUSION

The nanocomposited MEH-PPV: I-MWCNTs organic solar cell has been fabricated and studied. The effects of iodine doping temperature to the thin film were also examined. The characterization of electrical properties shows very little and almost no response to light of the J-V curve. Thin film with 100°C doping temperature gives the best response under illumination. In optical characterization, red shift occur on the 120°C sample may due to increase in the interfacial charge carrier concentration (charge density at the interface) which improves the extension of the band tails in the forbidden bandgap of the organic compounds. While the optical bandgap shows almost similar value on each temperature, it is significantly lower compared to pure MEH-PPV which is good for electron excitation. In the future, the experiment should be focusing on increasing the power conversion efficiency including fill factor, short circuit current density and open circuit voltage.

V. ACKNOWLEDGEMENT

Author would like to thank all the member of Nano Electronic NET and Nano-Sci Tech center especially to Puan Puteri Sarah Mohamad Saad and Encik Uzer Mohd Noor for all the support and advice upon completing this technical paper.

REFERENCE

- [1] F. S. S. Zahid, M. S. P. Sarah, and M. Rusop, "Effect of thickness on the electrical and optical properties of MEH-PPV:TiO₂ nanocomposite for organic solar cell application," in *Industrial Electronics and Applications (ISIEA)*, 2011 IEEE Symposium on, 2011, pp. 449-453.
- [2] O. Yangping, W. Yang, Y. Lixin, L. Chunjun, and L. Yuan, "Organic solar cells with improved spectral coverage based on copper phthalocyanine : MEH-PPV : C60 bulk heterojunctions," in *Nano-Optoelectronics Workshop, 2007. i-NOW '07. International*, 2007, pp. 146-147.
- [3] R. Vairavan, M. Mohamad Shahimin, and N. Juhari, "Fabrication and characterisation of MEH-PPV/CdTe/CdS solar cell," in *Humanities, Science and Engineering (CHUSER)*, 2011 IEEE Colloquium on, 2011, pp. 454-458.
- [4] M. A. Alam, B. Ray, and M. R. Khan, "Untangling the essence of bulk heterostructure organic solar cells: Why complex need not be complicated," in *Semiconductor Device Research Symposium (ISDRS)*, 2011 International, 2011, pp. 1-2.
- [5] M. S. P. Sarah, R. Yaacob, F. S. Zahid, U. M. Noor, and M. Rusop, "Photoconductivity of nanocomposited MEH-PPV: CNTs thin film for organic solar cells application," *Electronic Devices, Systems and Applications (ICEDSA)*, 2011 International Conference on, pp. 267-271, 25-27 April 2011
- [6] S. S. Shariffudin, M. H. Mamat, M. Rusop, N. S. Jumali, Z. Shaameri, and A. S. Hamzah, "Electrical & optical properties of nanocomposite MEH-PPV/ZnO thin film," in *Electronic Devices, Systems and Applications (ICEDSA)*, 2010 Intl Conf on, 2010, pp. 380-383.
- [7] S. Costa, E. Borowiak-Palen, "Raman Study on Doped Multiwall Carbon Nanotubes" in *Proceedings of the Symposium A of the European Materials Research, Warsaw, September 2008*, vol. 116 pp.1
- [8] X. Sha, Z. Xiaoxin, H. Kotadia, L. Hua, S. H. Mannan, C. Bailey, and Y. C. Chan, "Remedies to control electromigration: Effects of CNT doped Sn-Ag-Cu interconnects," in *Electronic Components and Technology Conference (ECTC)*, 2012 IEEE 62nd, 2012, pp. 1899-1904.
- [9] Zhao Y., Wei, J., Vajtai, R., Ajayan, P.M. & Barrera, E.V. "Iodine doped carbon nanotube cables exceeding specific electrical conductivity of metals" .Sci. Rep.1, 83; DOI:10.1038/srep00083 (2011).
- [10] W. Zhou, S. Xie, L. Sun, D. Tang, Y. Li, Z. Liu, L. Ci, X. Zou, G. Wang, P. Tan, X. Dong, B. Xu, and B. Zhao, "Raman scattering and thermogravimetric analysis of iodine-doped multiwall carbon nanotubes," *Applied Physics Letters*, vol. 80, pp. 2553-2555, 2002.
- [11] Xu-Ming, Z. Zhi-Ling, L. Yi-Tao, F. Qing-Ping, Z. Wei, and Y. Xiong-Ying, "Polymer assisted dispersion and alignment of carbon nanotubes," in *Nanotechnology, 2009. IEEE-NANO 2009. 9th IEEE Conference on*, 2009, pp. 123-125.
- [12] J. Kim, J.-S. Kim, S.-W. Kwak, J.-S. Yu, Y. Jang, J. Jo, T.-M. Lee, and I. Kim, "Effects of the Al cathode evaporation rate on the performance of organic solar cells," *Applied Physics Letters*, vol. 101, pp. 213304-3, 2012.

- [13] J. Kim and S. Yim, "Influence of surface morphology evolution of SubPc layers on the performance of SubPc/C60 organic photovoltaic cells," *Applied Physics Letters*, vol. 99, pp. 193303-3, 2011.
- [14] N. Gabel, H. Hardee, and P. Lees, "Comparison of coefficient of friction and contact resistance during sliding wear on clad gold-nickel surfaces," in *Electrical Contacts, 2001. Proceedings of the Forty-Seventh IEEE Holm Conference on*, 2001, pp. 271-281.
- [15] V. G. Weizer and N. S. Fatemi, "Contact formation in gallium arsenide solar cells," in *Photovoltaic Specialists Conference, 1988., Conference Record of the Twentieth IEEE*, 1988, pp. 629-634 vol.1.
- [16] K. Lin, R. S. Kumar, C. Peng, S. Lu, C. Soo-Jin, and A. P. Burden, "Au-ITO anode for efficient polymer light-emitting device operation," *Photonics Technology Letters, IEEE*, vol. 17, pp. 543-545, 2005.
- [17] Y. A. M. Ismail, T. Soga, and T. Jimbo, "Features in optical absorption and photocurrent spectra of organic solar cells due to organic/organic interface," *Journal of Applied Physics*, vol. 109, pp. 103109-7, 2011.
- [18] N. F. A. Zainal, T. I. T. Kudin, A. Azira, A. Z. Ahmed, S. Abdullah, and M. Rusop, "Preparation and Characterization of Iodine-doped Multi-wall Carbon Nanotubes," *AIP Conference Proceedings*, vol. 1017, pp. 159-163, 2008.
- [19] T. Yohannes, F. Zhang, M. Svensson, J. C. Hummelen, M. R. Andersson, and O. Ingana's, "Polyfluorene copolymer based bulk heterojunction solar cells" in *Thin Solid Films* 449 (2004) 152–157

