Electrical and Optical Properties of Nanocomposites MEH-PPV:CNT Thin Film

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Abstract **This paper investigates the electrical and optical properties of nanocomposites MEH-PPV:CNT thin film with different composition ratio of CNT. CNT was prepared using palm oil as precursor and ferrocene as catalyst in the furnace of the ATOMIZER equipment. The thin film was deposited on the glass substrate by using spin coating technique. The influence of composition ratio of CNT on the electrical properties and optical properties of conjugated polymer MEH-PPV was characterized by current-voltage measurement in dark and under illumination and UV-VIS-NIR spectrophotometer. The current-voltage measurements are show relationship between conductivity and resistivity of thin film. The conductivity of polymer MEH-PPV is increasing as increasing composition ratio of CNT. While the UV-VIS-NIR spectrophotometer measurement show the optical band gap decreases when composition ratio of CNT increases.**

Keywords: **carbon nanotubes, polymer MEH-PPV, thin films, electrical properties, optical properties**

I. Introduction

In recent year, there is increasing of investigating of the nanocomposites polymer based photovoltaic cell such as conjugated polymer of poly [2-methoxy 5 (2ethylhexyloxy-1, 4-phenylene vinylene] (MEH-PPV). The basic idea of nanocomposites is multiphase solid material where one phase has one/two dimension of less than 100nm and different in volume ratio. MEH-PPV has been considered as one of the most potential conducting polymers for various optoelectronic applications such as organic light emitting diodes (OLED), sensors and organic solar cells because of its good environmental stability, easy conductivity Control and cheap production in large quantities[1,2,4]. A practical advantage of these nanocomposites is the ease preparation of products with complex shapes and patterns by using processing technology reducing the manufacturing cost [1,4]. The MEH-PPV acts as an electron donor (p-type semiconducting polymer) with a relatively low conductivity due to the low hole and electron mobility, when compared to inorganic semiconductor materials [1].

Combination CNT with electron donor polymer is an innovative concept to harvest new application and improve properties of conjugated polymer. Normally, CNT have been found to be P-type with high predicted mobility. CNT have high enough electron conductivity, high thermal conductivity, robustness and are flexible by nature [6, 7]. Combination of CNT with electron donors signifies an innovative concept to harvest solar energy and convert it into electricity [3]. CNT is important to photovoltaic device with thin and transparent layers comprising bulk metallic CNT have been proposed for providing lateral electrical conductivity for collecting current from the front surface of thin-film solar cells [3, 6]. Semiconducting CNT is forming ideal heterojunctions and work function of CNT is in the range of 4.5–5.1eV [3]. In recent year, work has been focused on developing chemical vapor deposition technique using catalyst particle and precursor material to growth CNT. Mostly CNT are synthesis by methane, benzene, acetylene and etc. All the carbon sources are related to fossil fuels which are non-reproducible. In this research, the CNT are growth based on palm oil precursor which is natural, reproducible and not related to the fossil fuel.

In this paper, the thin film has been deposited on glass substrate using spin coating technique with different composition ratio of CNT. We are focusing on understanding the effect of properties of MEH-PPV due to the conductive material CNT. In this case, CNT can be providing opportunity to modify the structure and optimize solubility and dispersion due to the best electron filed-emitter possibility [7]. There is polymer of pure carbon and can be reacted and manipulated using the tremendously rich chemistry of carbon [6]. Due to advantages of CNT in nanocomposites MEH-PPV:CNT as discuss above, the electrical and optical properties of conjugated polymer MEH-PPV should be investigate. The polymer MEH-PPV will be directly changed due to varying composition ratio of CNT. The experimental result of optical, electrical and structural properties of thin film growth will be discussed.

II. Objectives

The main objectives of this project are:

1) To prepare nanocomposites MEH-PPV:CNT thin film.
2) To study electrical and optical properties of nanocomposites MEH-PPV:CNT thin film with different composition ratio of CNT.

III. Scope of work

The research has been completed after several parts of this project have been done. A literature review and research from journal and website on polymer MEH-PPV and CNT has been carried out in the initial stage of this research. In addition the material or process that used in this preparation of nanocomposites MEH-PPV:CNT thin films was studied in details.

The second stage is the process to prepare the nanocomposites MEH-PPV:CNT thin film with different composition ratio of CNT has been used spin coating technique. Finally, the thin films were characterized using Current-Voltage (I-V) Measurement and UV-VIS-NIR Spectrophotommeter.

IV. Methodology

In this research, we used polymer MEH-PPV as electron donor and CNT as a conductive material. The process of preparation of nanocomposites MEH-PPV:CNT was shown following the flow chart in figure 1.

A*)* SUBSTRATE CLEANING PROCESS

Cleaning the substrate is important part preparation before preparation of thin film deposition. In this research, glass was used as a substrate. A glass substrate was cut into square of 2cm by 2cm is used. The glass substrates were cleaned in an ultrasonic bath with acetone for 15minutes, followed by methanol and de-ionized water, before being dried in nitrogen gas flow.

B) PREPARATION OF SOLUTION MEH-PPV

The MEH-PPV powder was dissolved in tetrahydrofuran (THF) solvent at a concentration of 1 mg/ml. In this research, its needs five solutions needed 5 samples. The solution MEH-PPV was prepared by stirring for 48h and then the solution were blend with CNT due to the composition ratio; 0wt%, 10wt%, 15wt%, 20wt% and 25wt%. Then the solution is stir for another 1h and ultrasonic effect in 1h. The chemical structure of polymer MEH-PPV was shown in figure 2(a).

C) THIN FILM DEPOSITION

In this research, spin coating technique was used as preferred method that setting at speed 3000rpm for 1 minute to prepare the thin film of the nanocomposites MEH-PPV:CNT. Spin coating technique can be control the thickness of thin film due to the rotational speed, acceleration, timing and etc. Higher of angular speed of spinning will be resulted the thinner film [8]. The nanocomposites MEH-PPV:CNT thin film was prepared by evaporating the solvent from a solution with subsequent drying of the film deposited on glass substrate. After deposition process by spin coating, the thin film was dried at 60C for 10 min on an oven to evaporate the solvent [1].

D) CHARACTERIZATION OF THIN FILM

The thin film must be depositing with gold that act as metal contact when characterization of thin film. The standard geometry of MEH-PPV:CNT structure was shown in Fig. 2(b). The optical properties were characterized using the UV-Visible near Infrared (UV-VIS-NIR) equipment over the spectral range from 200nm to 800nm of wavelength. Then, electrical properties were measured by using current-voltage (I-V) measurement was performed by computer measurement that using ADVANTEST equipment. The I-V measurements are taken while the sample is under illumination and in dark condition. The surface morphologies and electrical measurement were carried out for the structures prepared at different concentration of CNT.

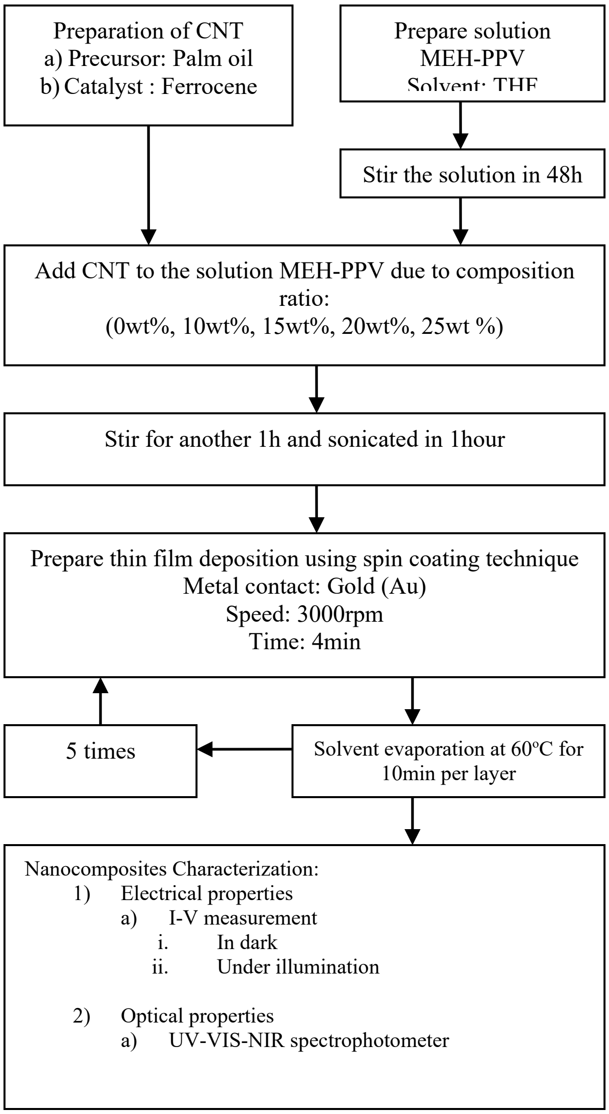
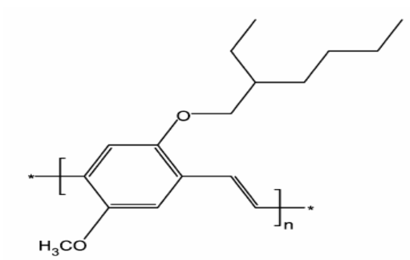
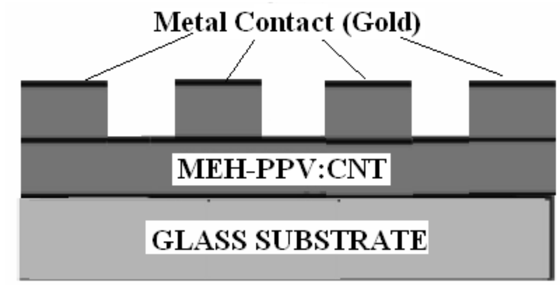


Fig. 1. Flow chart of the experimental procedure for the project



(a)



(b)

Fig. 2. (a) Chemical structure of the polymer MEH-PPV [9] (b) Nanocomposites MEH-PPV:CNT thin film structure.

V. Result & Discussion

There is an effect on electrical and optical properties of polymer MEH-PPV by adding the conductive material CNT to the polymer MEH-PPV. The effect can be seen in optical and electrical characteristic of nanocomposites MEH-PPV:CNT thin film.

A. Current-Voltage Measurement

In the semiconductor technology, the efficiency of a photovoltaic cell is measured by the external quantum efficiency (EQE), which is defined as electron collected per incident photon [15]. The electrical characteristic have been performed on the nanocomposites MEH-PPV:CNT thin film. The Current-Voltage (I-V) graphs of the thin film in different composition ratio of CNT under white light illumination and in dark at room temperature are display in figure 3 and figure 4. From the I-V measurement, the conductivity and resistivity of the thin film can be determined.

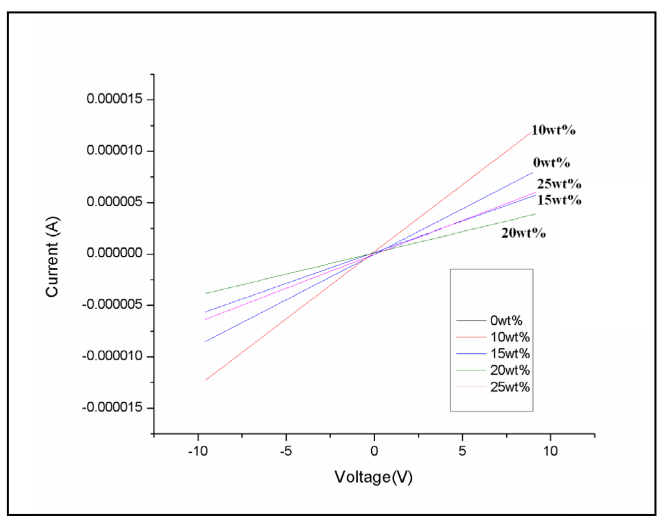


Fig. 3. Current-voltage characteristics of nanocomposites MEH-PPV:CNT thin films in dark condition

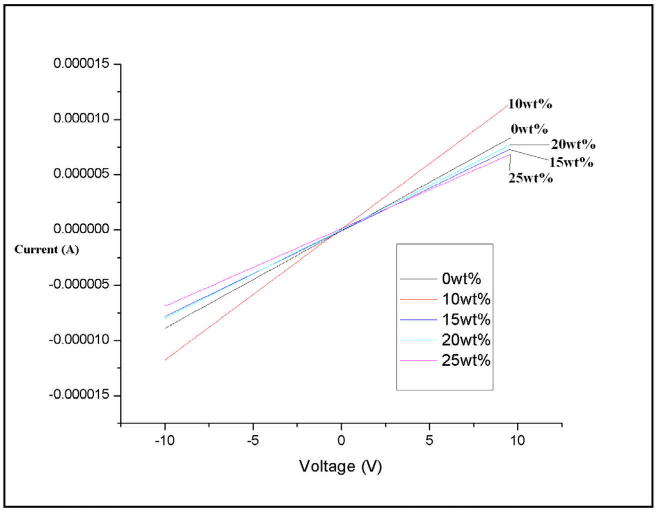


Fig. 4. Current-voltage characteristics of nanocomposites MEH-PPV:CNT thin films under illumination

The I-V measurement result indicated the electrical behavior of thin film. I-V curves will give the details information about resistivity and conductivity of the thin film. From Ohm's law, the relationship between the resistivity and conductivity is inversely proportional to each other. From the I-V curves, the resistivity,ρ and conductivity of nanocomposites MEH-PPV:CNT thin film were calculated using the equation (1.0):

$$\rho = \frac{Rwt}{L} \quad (1.0)$$

Where *ρ* is resistivity, t is the thickness of thin film, w is the width of metal contact and L is distance between metal contacts. The literature studies shows, the electrical conductivity of the nanocomposites would be expected increases continuously from that of the pure MEH-PPV to 25wt% composition of CNT (high concentration of CNT), as increasing composition ratio of CNT [3]. This is because the CNT have unique conductive material that can be proposed for providing electrical conductivity for collecting current by carrier generation movement through polymer. CNT can help to improve exciting dissociation into free electron and hole at the nanocomposites MEH-PPV:CNT thin film interface and provide efficient carrier transportation due to high carrier mobility[14]. The thickness of thin film can be measured directly using surface profiles and found to be decreasing from 34.6nm to 6.5nm as increasing composition ratio of CNT. This is because CNT is highly conductive and high thermal stability, the structure of polymer MEH-PPV was changed directly. The relationship between conductivity and resistivity is written in equation (2.0) and equation (3.0):

$$\sigma = \frac{L}{Rwt} \quad (2.0)$$

$$\sigma = \frac{1}{\rho} \quad (3.0)$$

Where σ is conductivity level and ρ is resistivity of thin film. From figure 5 and figure 6, the resistivities of the thin films are decreases with increases composition ratio of CNT while the conductivity are also continuously increase due to increase composition ratio of CNT. As the fraction of CNT increases further, the average distance between the nanotubes becomes sufficiently small allowing electron tunneling in through the polymer [7]. From result showed that the conductivity levels are increasing from 10wt% to maximum 25wt% composition of CNT. As refer to the figure 5, these implies that nanocomposites MEH-PPV:CNT thin film is more conductive under illumination rather than in dark condition because there is high photocurrent due to more charge carriers overcome the activation energy barrier and participate in the electrical conductivity. The photocurrent enhancement results mainly change of the conformation of the polymer chain in these dilute composites, since larger composition of nanotubes are needed to form continuous path for electron.

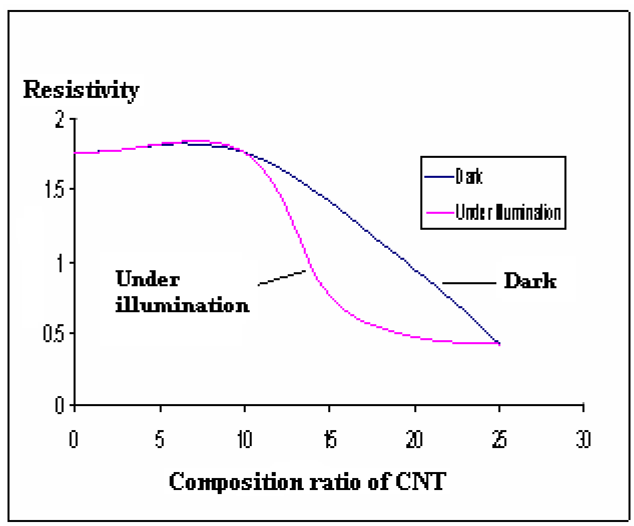


Fig. 5. Conductivity of nanocomposite MEH-PPV:CNT thin film at different composition ratio of CNT under illumination and in dark.

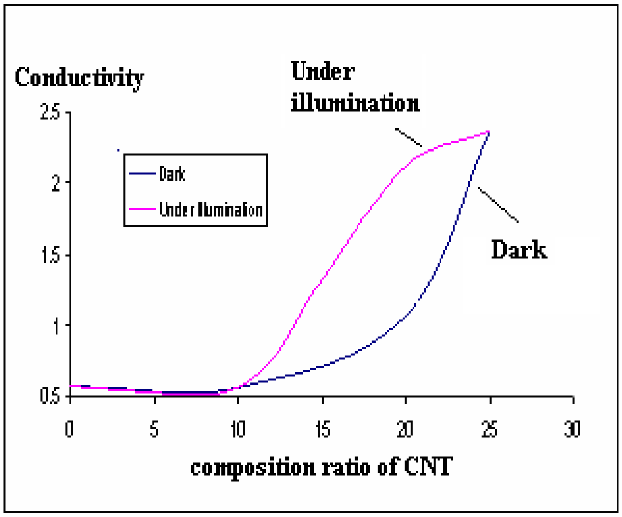


Fig. 6. Resistivity of nanocomposites MEH-PPV:CNT thin film at different composition ratio of CNT under illumination and in dark.

The measured conductivity under illumination of the pure MEH-PPV is 0.571689 S/m. In samples containing CNT concentration between 15wt% the conductivity dramatically increase around 21.321931 S/m. A moderate increase of the composite conductivity to 2.118276 S/m is observed in 20wt%. The composite conductivity displays a moderate increase in 25wt% that reaching 2.366763 S/m. the conductivity in dark of pure MEH-PPV is same as under illumination 0.571689 S/m and then starting to increase between 15wt% and 25wt% until reaching 2.366768 S/m. this is because there excitation were generated on conjugated polymer under illumination and were dissociated at the interface on polymer/CNT due to charge transfer, where transported by CNT and holes were transported through polymer. It is related to the properties of CNT as highly conductive and high stability to transport the carriers [13].

B. UV-Visible Characteristic

The absorption spectra of MEH-PPV and a mixture of nanocomposites MEH-PPV:CNT are presented in figure 7 for different concentration of CNT. These spectra are just the sum of the absorption spectra of the components of the thin films, where the absorption is investigated in wavelength spectral range between 200nm to 800nm. The typical absorption peak of thin film excited at 500 nm is reported in the correspondent inset of figure 7. The absorbance peak is shifted to longer wavelength with respect to the main absorbance band as reference sample. From the figure 7, the absorbance decrease of the band associated with MEH-PPV is due to the reduction in the optical volume of MEH-PPV at high CNT concentration (15wt% to 25wt %). The highest absorbance was recorded for the sample 10wt% CNT at average absorbance 0.2898 in wavelength 500nm. As display in figure 7, it can seen where at pure MEH-PPV and 10wt% of nanocomposites MEH-PPV:CNT is the best absorbance of wavelength. This is because thin film used high quality of polymer and uniformity of the thin film. The absorption of thin film are expected increases as increases composition of CNT. CNT are absorb light in the infra red (IR) region of the solar spectrum while semiconducting polymer absorb light in the ultra-violet (UV) and visible region [14].

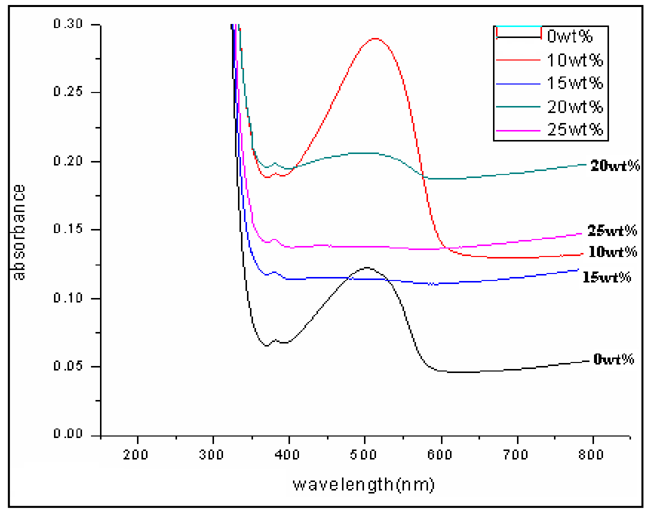


Fig. 7. Absorbance of nanocomposites MEH-PPV:CNT thin film

The optical band gap energy, E_g were applied from Lambert Law. The Lambert's law state that the amount of light absorbed by a sample is depended on its concentration, path length and a constant. The optical band gap, Eg of thin films can be determined using the spectra of measured absorption coefficient, α of the thin films. The α near the absorption edge was derived from the measured transmittance (T). From the transmittance spectra in figure 8, the absorption coefficient of thin film could be calculated using Lambert law as shown in equation (4.0).

$$A = (1/t)(\ln 1/T) \qquad (4.0)$$

Where α is absorption coefficient, t is thickness of thin film and T is transmittance of thin film. The optical band gap energy, Eg is derived assuming a direct transition of electron between the edged of the valence band and the conduction band, for which the variation in the absorption coefficient with the photon energy. The relationship of direct band gap energy with the absorption coefficient and photon energy is given in equation (5.0):

$$Ah\nu = A\,(h\nu - Eg)^{1/2} \qquad (5.0)$$

Where A is the constant and hν is the photon energy. Values for all catalyst samples were determined by plotting $(\alpha h\nu)^2$

versus the photon energy at the wavelength, λ. The resulting diagram was called Tauc's Plot. The respective band gaps were obtained by extrapolation of the Tauc plot dataset to $(\alpha h\nu)^2 = 0$. Figure 9 are showing the tauc plot.

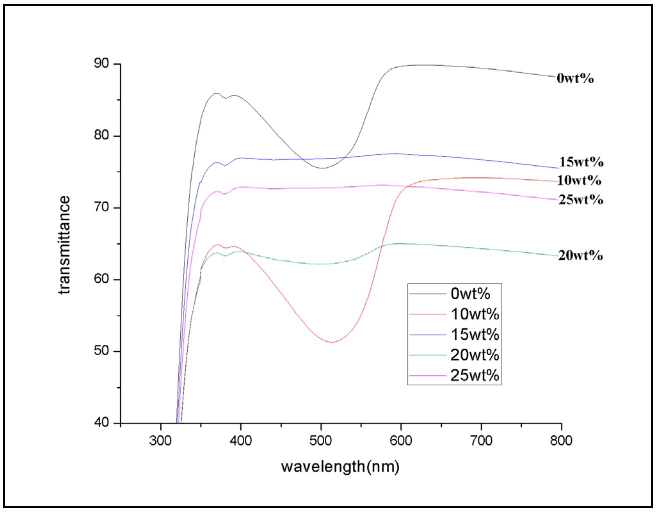


Fig. 8. Transmittance spectra of nanocomposites MEH-PPV:CNT thin film

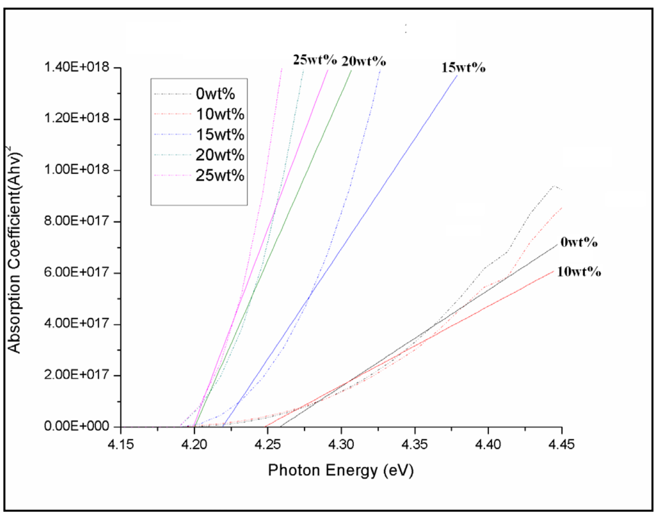


Fig. 9. The $(\alpha h\nu)^2$ vs hν graph for nanocomposites MEH-PPV:CNT thin film.

TABLE 1 Optical band gap energy of nanocomposites MEH-PPV:CNT thin films

Composition Ratio of CNT	Optical Band Gap Energy(eV)
0wt%	4.2625
10wt%	4.2480
15wt%	4.2248
20wt%	4.2000
25wt%	4.1980

Figure 9 and Table1 has shown the optical band gap of the thin films with different composition ratio of CNT. In order to get optimizing optical properties, the optical band gap energy should be decreases at higher composition of CNT with result high conductivity. It is because CNT can be provide free electron and hole movement through the polymer. The result optical band gaps supported that the thin film is higher conductivity as higher composition of CNT. This is because the carrier easy to conduct at higher level of conduction band with smaller optical band gap.

VI. Conclusion

In this paper, the conductive material, CNT are growth based on palm oil precursor which is natural, reproducible and not related to the fossil fuel. These natural resources are synthesis by using atomizer and thermal CVD to growth the CNT. The deposition process of thin film on glass substrate is presented and the properties of thin film are studied in detail. The electrical of thin film are varied significantly with different composition ratio of CNT. At higher composition ratio (25wt%) gave high conductivity level and low resistivity of thin film. The result of conductivity level increases from $0.571659 Sm^{-1}$ to $2.366768 Sm^{-1}$ in dark condition, while the conductivity under illumination is change from $0.57168 Sm^{-1}$ to $2.366768 Sm^{-1}$. However, the absorption spectrum for thin film due to different composition ratio CNT was taken using UV-VIS-NIR spectrophotometer. The optical band gap, E_g values for samples were determined by plotting $(\alpha h\nu)^2$ versus photon energy at equivalent wavelength. The result of optical band gap energy values are in the range of 4.198eV to 4.263eV. These results are found to be very important to understand and investigated the properties of the nanocomposites MEH-PPV:CNT thin films.

VII. Future Development

Future research should focus on the optimization of the properties of nanocomposites MEH-PPV:CNT thin films in term of electrical conductivity, resistivity, optical properties and its performance for electronics and semiconductor application by using spin coating process and thermal CVD. The thin film can be perform with different annealing temperature and number of layer thin film. The quality of polymer and purifying of CNT must be optimizing in order to get a quality thin film applied to the organic photovoltaic cell.

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