Electrical and Optical Properties of Nanocomposite MEH-PPV:ZnO Prepared at Different Composition Ratio

Mohd Hidayatullah Ibrahim Bin Abdul Rahim
Bachelor of Electrical Engineering (Hons)
Faculty of Electrical Engineering
Universiti Teknologi MARA
40450 Shah Alam
mohdhidayat86@gmail.com

***Abstract*—Research on organic based light emitting diode (OLED) has become current interest due to high potential as flat panel displays. OLED is form by a layer of organic compounds sandwiched between two electrodes. In this study, the compound that has been selected for OLED application is nanocomposite MEH-PPV:ZnO. The preparation of MEH-PPV and nanocomposite solution was done using toluene as the solvent. Nanocomposite MEH-PPV:ZnO thin films were deposited using spin-coating method. The objective of this paper is to find the optimum parameter of nanocomposite MEH-PPV:ZnO thin films for OLED application by preparing the thin films using different composition ratio. The electrical and optical properties have been observe for nanocomposite MEH-PPV:ZnO thin films. The electrical characterization was investigated for the conductance behavior of the thin films. By adding more compound of ZnO to the thin films, the conductivity was improved due to the increasing of carrier concentration. For optical measurement, there are two characterizations were applied which electrical and optical characteristics. The electrical properties were analyzed using 2-probe Current-Voltage (I-V) measurement system (Advantest R6243). For optical, Ultraviolet-Visible (UV-Vis) spectrophotometer and Photoluminescence (PL) spectroscopy were used. From the electrical results, it shows the composition ratios of MEH-PPV:ZnO nanocomposite give the inversely proportional relation to the resistivity which related to the carrier concentration. The optical measurement found that the quenching of luminescence with the presence of ZnO. This is due to the attributed of reduction in the emissive materials.**

***Index Terms* — nanocomposite, MEH-PPV, ZnO and composition ratio.**

I. Introduction

ZnO is attracting considerable attention for its possible application to light-emitting sources due to its advantages over GaN [1]. Recently, ZnO has attracted much attention for its application in various fields such as UV light-emitting devices, varistors, transparent high power electronics, optical waveguides and solar cells. In particular, ZnO has been considered as promising materials for short-wavelength optoelectronic devices because it has a direct bandgap of 3.3 eV and a low threshold voltage [1]-[4]. ZnO also has a number of advantages over GaN, the wide-bandgap semiconductor currently utilized in the short-wavelength optoelectronics industry. Some of these advantages include a large exciton binding energy (~60 meV), a higher radiation hardness, simplified processing due to amenability to conventional chemical wet etching and the availability of large area substrates at relatively low material costs [2].

Luminescent polymer poly (2-methoxy-5-(2-ethylhexyloxy)-1,4- phenylenevinylene) MEH-PPV has been chosen in the paper since it has been an attractive material in OLED fabrication because of its solubility in common organic solvents, in conjunction with a low operating voltage for light emission and relatively high conversion efficiency[3], [15]. MEH-PPV also been choose because of low driving potential, high luminescence efficiency and it has good ability to dissolve and dispersed in organic solvent [1]-[3].

Nanocomposite is one of composites class. The type of nanocomposite can be divided due to the dimensional properties of the dispersed particles in nanometer range. A nanocomposite is as a multiphase solid material where one of the phases has one, two or three dimensions of in nanometer range. Nanocomposite has several advantages due to substantial improvements which are mechanical properties e.g. strength, modulus and dimensional stability[3], decreased permeability to gases, water and hydrocarbons[3], thermal stability and heat distortion temperature[4], flame retardancy and reduced smoke emissions[7], [8], chemical resistance, surface appearance, electrical conductivity, optical clarity in comparison to conventionally filled polymers[4], [14].

Recently, the performance of these devices has been enhanced by the incorporation of inorganic semiconductors to form hybrid organic–inorganic [1]-[5]. Polymer is one of example for organic material. For inorganic material, semiconductor oxides have been applied in optoelectronics with great success due to the possibility to overcome polymer charge-transfer limitations by the high electron-injection properties observed from the oxide. There have been a lot of research due to semiconductor such as TiO_2 [2], [3], Nb_2O_5 [2], ZnO [1], [2], CeO_2 [2] and SiO_2 [3]. These oxides present exceptional stability against photocorrosion, absorb in the UV [12] and have a large band gap.

For preparation of MEH-PPV solutions, the toluene is choosing for the solvent to dissolve MEH-PPV polymers. The solution was being stirred at room temperature for 48 hours to obtain the solution of MEH-PPV.

Uniform thin films for nanocomposite MEH-PPV:ZnO have been produced by spin coating technique to form flat substrates. In short, an excess amount of a solution is placed on the substrate, which is then rotated at high speed in order to spread the fluid by centrifugal force. Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved [1], [6].

II. METHODOLOGY

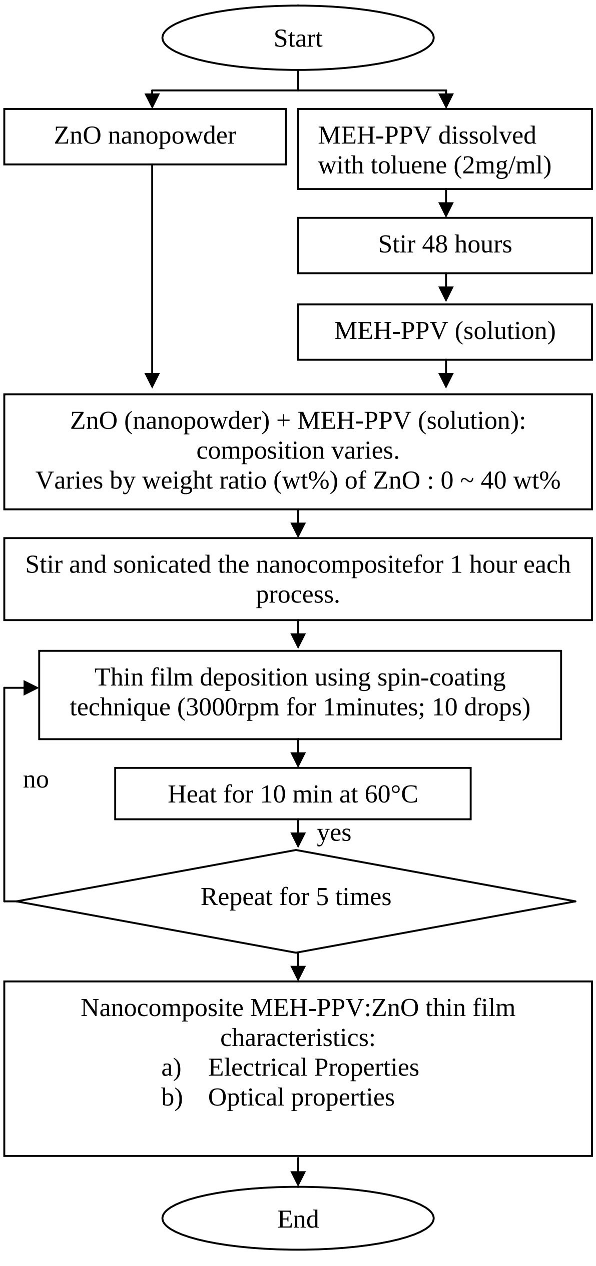

Fig. 1. Methodology flowchart

Fig. 1 shown the methodology flowchart for nanocomposite MEH-PPV:ZnO thin films. The preparation of MEH-PPV solution was done using toluene as the solvent. The polymer was dissolved to form solution with a concentration 2mg/ml. Five solutions of MEH-PPV were mixed with ZnO nanopowder with different composition ratios (0%, 10%, 20%, 30% and 40%). The mixtures of nanopowder ZnO with MEH-PPV solutions was stirred and heated to mix them together using the hot plate stirrer, followed by ultrasonication for 1hour to improve the dispersion of ZnO nanopowders. The substrates were cleaned by standard cleaning method to remove all contamination which could be affecting the thin film properties. The nanocomposite MEH-PPV:ZnO thin films were deposited by spin coating technique. After the spin coating, the film will be dried to evaporate the solvent and to remove organic residual. The coating/drying process will be repeated for 5 times to yield thickness of the thin films. To obtain the good quality of thin film, annealing process was applied. Annealing process will help to optimize and stabilize the characteristics of the nanocomposite MEH-PPV:ZnO thin films [1]. The electrical properties were analyzed using 2-probe Current-Voltage (I-V) measurement system (Advantest R6243). For optical measurement, there are two characterized using Ultraviolet-Visible spectrophotometer (UV-Vis) and Photoluminescence (PL) spectroscopy.

III. RESULTS AND DISCUSSION

A. Electrical Properties

Current-Voltage measurement was performed to the thin films structure using gold (Au) as the metal contact. The I-V measurements were done using 2-probe Current-Voltage (I-V) measurement system (Advantest R6243). The I-V curve obtained shows that different composition of ZnO will gave the effect in electrical properties for the thin films. Fig. 2 illustrated the I-V measurement of pure MEH-PPV and nanocomposite MEH-PPV:ZnO thin films at 0.0000662 m metal contact distance. The relation of composition ratio of ZnO is the higher composition ratio causing the of I-V increase. It could also be seen that current value at respective voltage increased with the increasing of composition ratio nanocomposite MEH-PPV:ZnO, it shows the increment of electron concentration at higher composition ratio of ZnO. The increased in the current value indicates that the resistivity value is decreased.

For resistivity calculation, the value of resistivity (ρ) effected by presence of ZnO due to resistance (R) with constant width of metal contact (w), thickness of thin film (t) and distance between metal contact (l) are expected to be constant. The relationship can described as in (1):

$$\rho = \left(\frac{V}{I}\right)\left(\frac{w \times t}{l}\right)[\Omega.cm] \qquad (1)$$

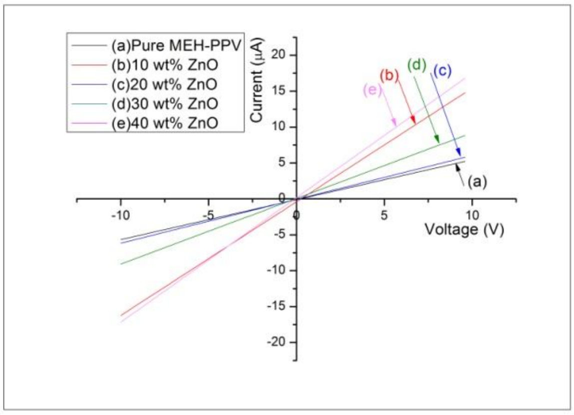

Fig. 2. I-V curve of (a) pure MEH-PPV (black) and MEH-PPV:ZnO nanocomposite at different composition ratio ((b) 10wt%-red, (c) 20wt%-blue, (d) 30wt%-green and (e) 40wt%-light violet) for metal contact distance 0.0000662m.

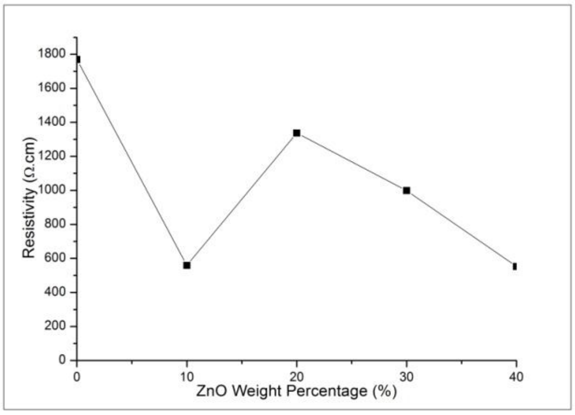

Fig. 3. Resistivity of of pure MEH-PPV and MEH-PPV:ZnO nanocomposite at different composition ratio (10wt%, 20wt%, 30wt% and 40wt%).

The composition ratios of MEH-PPV:ZnO nanocomposite give the inversely proportional relation to the resistivity. From the I-V measurements result, the resistivity was affected by the composition ratio of MEH-PPV:ZnO nanocomposite. The resistivity plot of nanocomposite MEH-PPV:ZnO thin films is shown in Fig. 3. Higher value of composition ZnO added to the MEH-PPV causes the resistivity of the thin films to decrease. The average of resistivity of every point was taken from the I-V measurement data. The lowest resistivity was found at 40wt% thin film which is 552.4923712Ω. The lower value of resistivity thin films is a promised for exploring efficient optoelectronic devices [9]. The lower resistivity may attribute from the increasing Zn species with higher solution concentration in the thin films [16]. Higher composition ratio used increased the particles composition in the thin films surface and increase the surface contact between particles and improve packing density in the thin films. This resulting reduction of oxygen adsorption in grain boundaries thus reducing carrier trapping phenomenon in the thin films to decrease thin films resistivity with higher solution concentration [16]. By releasing the trapped electrons back to the film cause to increasing its conductivity. Moreover, improvement in surface contact between particles as a result of particle concentration increment at the surface produce better electron mobility in the thin films to reduce resistivity with improvement of conductivity.

The more conductive thin films will give better optoelectronics devices. Since the conductivity (σ) is inversely proportional to the resistivity (ρ) as refer to (2) :

$$\sigma = \frac{1}{\rho}[s.cm^{-1}] \qquad (2)$$

Therefore the value of conductivity was increased by the increasing of composition ratio of MEH-PPV:ZnO. The high conductivity observed can be explained by the large surface area of the due film, due to the small size of ZnO particles. Conductivity related to the Zn species increase for increments in composition ratio of ZnO. Due to Zn species also caused of increment of carrier concentration give the thin films more conductive [9], [16]. The increased in conductivity is due to the carrier concentration can be described by (3):

$$\sigma = \frac{Qnv}{E}\ [s.cm^{-1}] \qquad (3)$$

It also has probability the increased in conductivity also due to the charge on each particle(Q), velocity drift(v), and also for electrical field (E).

B. Optical Properties

The optical properties were studied using UV-Vis-NIR spectrometer and photoluminescence (PL) spectrofluorophotometer. The PL spectra of pure MEH-PPV and MEH-PPV:ZnO nanocomposites in the wavelength range from 500 to 800nm are presented in Fig. 4. In this range, MEH-PPV is primarily responsible for the luminescence emission with little contribution from ZnO. Then spectra show all films have UV emission which originated from recombination of photogenerated charge carriers from the conduction band into valence band. The dominant peak of pure MEH-PPV at 583 nm is an emission characteristic of the PPV backbone that arises from the relaxation of excited π-electrons to the ground state. Furthermore, incorporation of ZnO nanoparticles into MEH-PPV results in luminescence quenching of the polymer. The wavelength shift depends on the ZnO content with a maximum shift of 10.9nm observed for 20 wt% and 10.2nm at 30 wt% in Fig. 5. From the main peak of pure MEH-PPV which at 583nm indicates the yellow region wavelength. Incorporation with ZnO indicates that all composition ratio still in the yellow emission with different colour concentration.

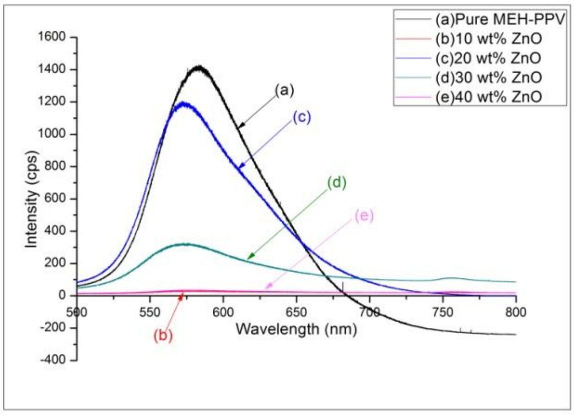

Fig. 4. PL spectra of (a) pure MEH-PPV (black) and MEH-PPV:ZnO nanocomposite at different composition ratio ((b) 10wt%-red, (c) 20wt%-blue, (d) 30wt%-green and (e) 40wt%-light violet).

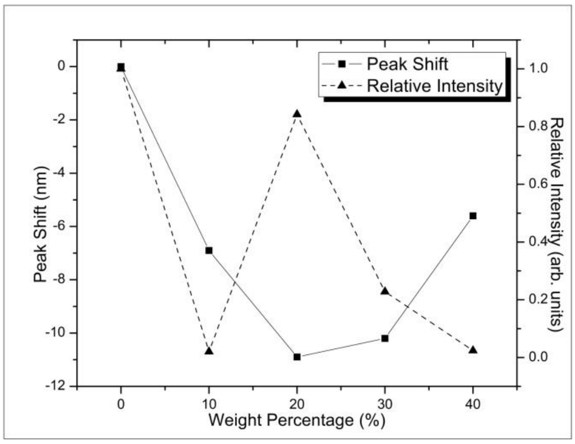

Fig. 5. Variations of the wavelength shift and the relative intensity of the PL spectrum as a function of ZnO composition ration in the films.

At 40 wt% ZnO, 97.6% of the original MEH-PPV emission intensity is lost. Considering the amount of ZnO incorporated into the nanocomposite films, the luminescence quenching may be attributed to a reduction in the volume of the emissive material, and the thin films properties now had to more ZnO behavioural. It also to either energy or exciton transfer from the polymer to ZnO [1]. In addition, the observed fact that an increase in ZnO nanoparticles concentration influences the recombination channel by quenching PL intensity can also be related to the charge transfer between ZnO nanoparticles and MEH-PPV [4]. Fig. 6 indicates the relation of PL, absorption and also transmittance for the thin films. The intensity of PL is depending on the absorption and transmittance properties of thin films. PL intensity was at the lowest value when the value of different between absorption and transmittance approximately to maximum. This is happen when there is either less absorption (higher transmittance) or less transmittance (higher absorption) occurs. The increment of PL intensity peak is also due to absorption and transmittance properties. PL intensity increases when there are photon energy been released.

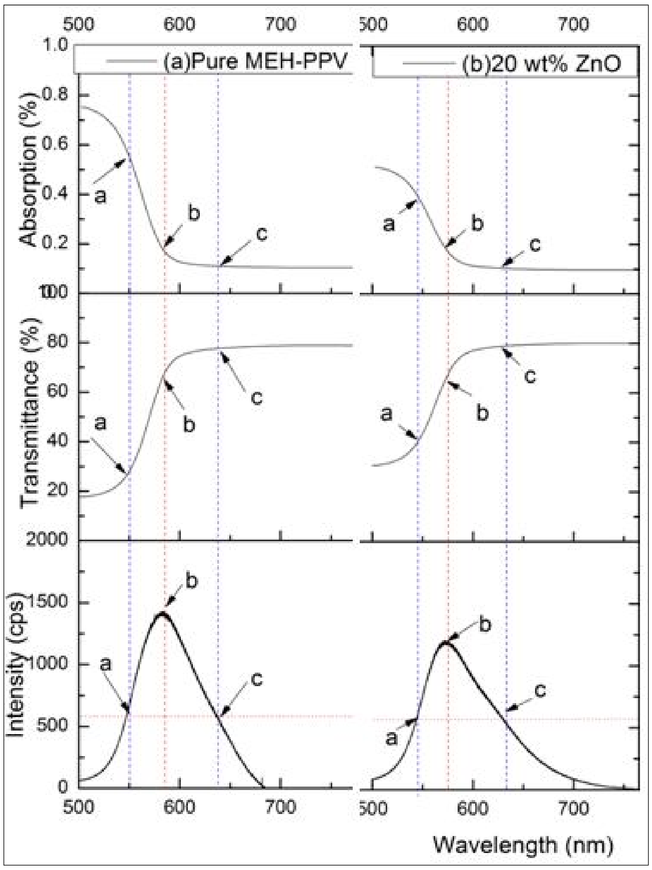

Fig. 6. Relation of nanocomposite MEH-PPV:ZnO thin films between PL, absorption and transmittance spectral due to amplitude.

The decrement of PL intensity occur when the absorption become less which means less electron been excited to higher energy band. This is due to recombination process which absorption and transmittance behaviour is needs to release the photon energy. An electron needs enough energy to be excited from a low energy level to a high energy level. When an electron at higher energy level transits down in energy to a low energy level, it emits a photon. The energy that need by electrons to be excited is due to the band gap energy.

The optical transmittance spectra of pure MEH-PPV and nanocomposite MEH-PPV:ZnO thin films in the UV-Visible-NIR wavelength range (200-800 nm) are presented in Fig. 7. From the result, the contribution from ZnO affects the optical properties of the thin films. There are peak in range (350-400nm) which due to ZnO particles. The PL spectrum of ZnO nanoparticles exhibits a strong PL maximum ($\lambda \sim 360$ nm), which corresponds well to the band gap energy of ZnO[4]. From the result, the highest transmittance was obtained in samples 10 wt% ZnO, while the lowest transmittance was obtained in samples pure MEH-PPV. The second highest transmittance at 40 wt% ZnO was taken as the highest transmittance due to photo-oxidized at samples 10 wt% ZnO. The increase in the ZnO nanoparticles concentration in the composite film leads to increment in transmittance properties at 360 nm. For the wavelength range 500-800 nm, MEH-PPV is primarily responsible for the optical properties [1]-[3]. At this range, all films exhibits high transmission of above 75 %. The result for wavelength range 500-800 nm shows all films exhibits low absorption due to high transmission.

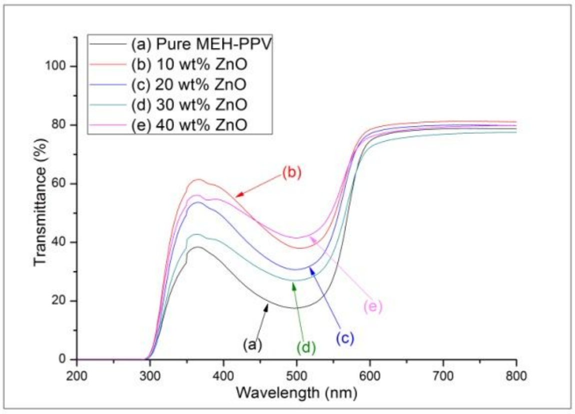

Fig. 7. Optical transmittance spectra of (a) pure MEH-PPV (black) and MEH-PPV:ZnO nanocomposite at different composition ratio ((b) 10wt%-red, (c) 20wt%-blue, (d) 30wt%-green and (e) 40wt%-light violet).

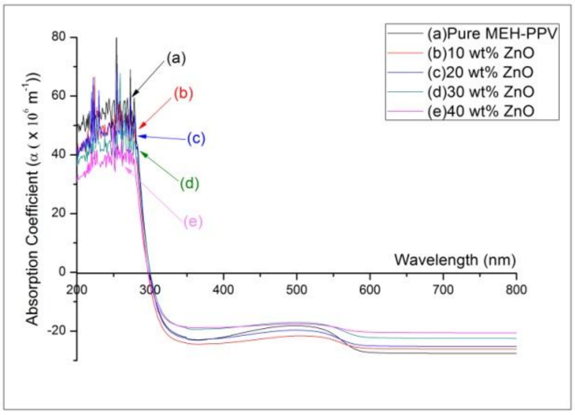

Fig. 8. Absorption coefficient of (a) pure MEH-PPV (black) and MEH-PPV:ZnO nanocomposite at different composition ratio ((b) 10wt%-red, (c) 20wt%-blue, (d) 30wt%-green and (e) 40wt%-light violet).

The absorption coefficient, α of pure MEH-PPV and MEH-PPV:ZnO nanocomposite thin films as a function of the wavelength at different weight percentage of ZnO is shown in Fig. 8. The result shows all films exhibit very low absorption in the visible and near infra red (NIR) range (300-800 nm) but exhibit high absorption in the ultraviolet (UV) range. The properties indicate transparency characteristic of ZnO thin films in the visible and NIR region [16]. High absorbance characteristic in the UV range are due to its wide band gap properties. When photon energy which is equal or higher than optical band gap energy is supply, the electron will have adequate energy to jump from valence band to conduction band. The wide band gap semiconductors usually considered for applications to ultraviolet (UV) opto-electronic devices since it lowered the leakage current in the device.

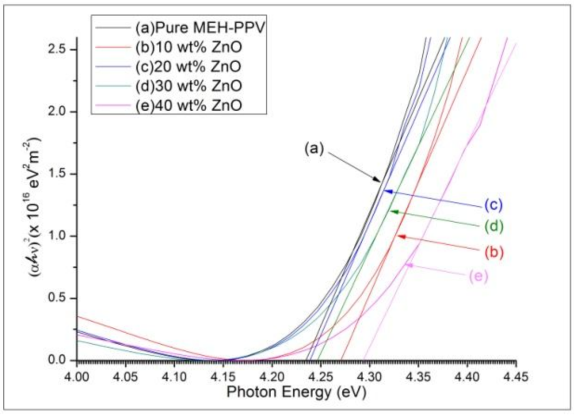

Fig. 9. Optical band gap energy estimation using Tauc's plot of (a) pure MEH-PPV (black) and MEH-PPV:ZnO nanocomposite at different composition ratio ((b) 10wt%-red, (c) 20wt%-blue, (d) 30wt%-green and (e) 40wt%-light violet).

The direct band gap of pure MEH-PPV and nanocomposite MEH-PPV:ZnO thin films is estimated by plotting $(\alpha h\upsilon)^2$ versus photon energy and extrapolating the linear portion near the onset of absorption edge to the photon energy axis as shown in Fig. 9. It shows that the extrapolation of the graph gave the band gap energy value of 4.2400 eV, 4.2735 eV, 4.2405 eV, 4.2470 eV and 4.2935 eV for pure MEH-PPV, 10 wt%, 20 wt%, 30 wt% and 40 wt% ZnO composition ratio respectively. The nanocomposite MEH-PPV thin films have optical band gap energy which is in the range of UV band. The situation explained the strong absorbance properties of pure MEH-PPV and nanocomposite MEH-PPV:ZnO thin films in the UV region where the photon energy is used for electron excitation from valence band to conduction band. It could be conclude that the thin films with higher ZnO composition ratio performed wider optical band gap energy compare to pure MEH-PPV. The enhancement of optical band gap energy in MEH-PPV thin films with ZnO contribution might due to the increasing of carrier concentration increase the band gap energy. As ZnO concentration is increased, the carrier concentration increased resulting in the optical band gap widening with doping concentration [16]. The Burstein-Moss effect explained the broadening of band gap energy with the increasing of carrier concentration as given by a relation shown in the (5) [16]:

$$\Delta E^{BM} = \left(\frac{h^2}{8m^*}\right)\left(\frac{3N}{\pi}\right)^{2/3} \quad (5)$$

Where ΔE^{BM} is the energy band gap broadening, h is the Planck constant, m^* is the effective mass of the electron and N is the carrier concentration. As ZnO concentration is increased, the carrier concentration increased resulting in the optical band gap widening with ZnO concentration. This are supported the I-V measurement result, which conductivity is change due to increasing carrier concentration. The wide band gap materials typically have high break down voltages, and high electron mobility.

IV. Conclusion

We have investigated the electrical properties of nanocomposite based on MEH-PPV with embedded ZnO nanoparticles. For the current-voltage (I-V) measurement showed that as current increased, the voltage also increased and it indicates that the thin films has good ionic contact. There also seen, the conductivity of the thin films was improved as more contributed from ZnO nanoparticles due to increased carrier concentration. From the optical properties also proved that the thin films optical band gap increased due to ZnO nanoparticles contribution and been supported by Burstein-Moss effect.

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