MEH-PPV/Alq_3-based bulk heterojunction photodetector*

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In this paper, we present the effect of varied illumination levels on the electrical properties of the organic blend bulk heterojuction (BHJ) photodiode. To prepare the BHJ blend, poly(2-methoxy-5(2′-ethylhexyloxy) phenylenevinylene (MEH-PPV) and aluminum-tris-(8-hydroxyquinoline) (Alq_3) are used as donor and acceptor materials, respectively. In order to fabricate the photodiode, a 40-nm thick film of poly(3, 4-ethylendioxythiophene):poly(styrensulfonate) (PEDOT:PSS) is primarily deposited on a cleaned ITO coated glass substrate by spin coating technique. The organic photosensitive blend is later spun coated on the PEDOT:PSS layer, followed by the lithium fluoride (LiF) and aluminium (Al) thin films deposition by thermal evaporation. The optical properties of the MEH-PPV:Alq_3 blend thin films are investigated using photoluminescence (PL) and UV-Vis spectroscopy. The photodiode shows good photo-current response as a function of variable illumination levels. The responsivity value ~ 8 mA/W at 3 V is found and the ratio of photo-current to dark current ($I_{\rm Ph}/I_{\rm Dark}$) is found to be 1.24.

Keywords: MEH-PPV, Alq_3, bulk heterojunction, photodiode

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1. Introduction

Detection of radiations is very important for air quality monitoring, accurate measurement of radiation for the treatment of UV irradiated skin, spectroscopy, fiber-optic communications, time-gated distance measurements, etc.[1,2] The wideband gap semiconductors ($E_{\rm g} > 3$ eV), SiC and III–V compounds, e.g., (Al, In, Ga) nitride are considered as suitable materials for UV light detection.[2] For visible light and near infrared detection, silicon is envisaged to be most promising material by virtue of its suitable band gap ($E_{\rm g} \sim 1.12$ eV) and silicon nanowires (SiNWs) have shown very interesting results.[3] These SiNWs are generally grown from photolithographicaly located gold nanoparticles using plasma-enhanced chemical vapour deposition (PECVD).[4] Luo *et al.*[5] reported on a visible light photodetector based on selenium nanowires, whereby NWs were grown in a high temperature tube furnace. II–VI semiconductor compounds, e.g., CdTe, ZnTe, CdSe, ZnSe, and CdS (sulfides, selenides, and tellurides) are also widely employed for visible light detection.[6] However, problems associated with these inorganic nanostructures-based photodetectors are complicated and time-consuming fabrication methods viz, vapor–liquid–solid growth,[7] metalorganic chemical vapor deposition (MOCVD),[8,9] molecular beam epitaxy (MBE), radio frequency magnetron sputtering, pulsed laser deposition (PLD), plasma enhanced chemical vapor deposition (PECVD),[10,11] etc. Furthermore, these fabrication techniques require high temperatures and complex vacuum deposition, which consequently results in a high production cost.

Contrariwise, organic optoelectronic devices have the advantages, not only in terms of the low temperature and environmental friendly manufacturing techniques but in mechanical flexibility, and the ease in large area fabrication as well.[12–15] Due to these interesting properties of organic semiconductors, these materials have been intensively investigated in the past decades, and they have emerged as an enticing alternative for the development of low cost electronics. If we trace back to the history of organic photoconductors and sensors, the first devices were of single layer, but in the early 1980s, double-layer devices appeared to separate the charge-generation. Recently, extensive research efforts have been devoted to the bulk heterojunction (BHJ) concept in particular. A detailed review of the organic photoresponsive materials and devices is given in Ref. [16]. Many other reports show that the organic compounds are also very suitable for developing the multifunctional sensors with only a little variation in synthesis, and it is possible to obtain sensors with different sensitivities and responses.[13,17–20]

In the organic BHJ technique one enables to incorporate the efficient charge transport of organic materials into the device and also increases the device performance, by controling the concentration of blend materials.[15] It has been reported

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by Sayhan *et al.*[21] that the use of polymer material together with an organic dye content enhances the harvesting of photons from light. There are a number of processing parameters that may remarkably affect the formed BHJ structure, including selected material, selected solvent used, blend composition, etc. Thus, parameter optimizations need to be addressed properly so that highly performed devices can be developed.

In this study, poly(2-methoxy-5(2′-ethylhexyloxy) phenylenevinylene (MEH-PPV) and aluminum-tris-(8-hydroxyquinoline) (Alq_3) are used as donor and acceptor materials, respectively. Liu *et al.*[22] showed that the main absorption peaks of the pure MEH-PPV and Alq_3 are located in the vicinities of 500 nm and 395 nm, respectively. The complementary absorption of Alq_3 lies in a range of 350 nm–450 nm where MEH-PPV absorbs the light weakly, thereby broadening the absorption spectrum of the active layer. Comparing the PL spectrum of Alq_3 with the absorption spectrum of MEH-PPV, they found an effective spectral overlap, which indicates a probability of Forster energy transfer from Alq_3 to MEH-PPV. To further confirm this phenomenon, they have also studied the PL spectra of MEH-PPV:Alq_3 with various blend ratios $(1:x,\ x=0,0.3,0.6,1)$.

The purpose of the present study is to explore the potential of the MEH-PPV and Alq_3 for their potential applications in visible light detection. The detector is fabricated, which consists of sandwich-type geometry and its photo-response characteristics are investigated under different conditions of illumination.

2. Experiment

Poly(3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS) and aluminum-tris-(8-hydroxyquinoline) (Alq_3) were purchased from Sigma-Aldrich. MEH-PPV polymer was synthesized in laboratory by established Gilch's polymerization reaction.[23] For the device fabrication, a transparent ITO anode and Al cathode were used. The ITO coated glass was cleaned sequentially by ultra-sonication in propanol, acetone, and deionized water for 10 min, respectively. Then the substrates were dried by N_2 blow. PEDOT:PSS as a hole transport layer was spin-coated onto the anodes and then annealed at 100 °C for 30 min. 1 wt% solutions of MEH-PPV and Alq_3 were prepared in chloroform and mixed with different volume ratios. Then the blend was spun-coated onto the top of PEDOT:PSS and baked at 100 °C for 30 min followed by the deposition of 0.8-nm thick LiF film as electron transport layer. Finally, the top Al electrode was deposited by thermal evaporation. During the thermal evaporation the pressure in the vacuum chamber was 1.33×10^{-4} Pa. The film deposition rate was 0.1 nm/s. Figure 1 shows a schematic diagram and band structure of the ITO/PEDOT:PSS/MEH-PPV:Alq_3/LiF/Al device.

The absorption spectra of the thin films were obtained by using Jasco 570 UV-VIS/NIRUV-VIS-NIR spectrophotometer and the photoluminescence (PL) spectra were obtained by RENISHAW Raman microscope instrument. WS400B-6NPP, spin coater was used for the solution-based film deposition. The thickness values of the films were measured by DEKTAK 8000 KLA Tensor P-6 profilometer. The Keithley 236 SMU was used for measuring both current and voltage simultaneously. All the measurements were performed under an ambient atmosphere at room temperature.

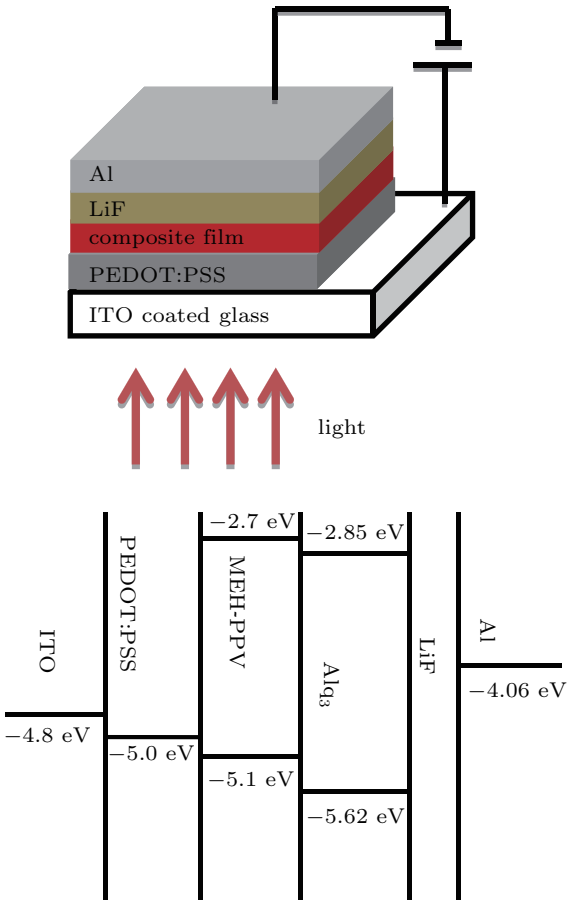


Fig. 1. (color online) (a) Schematic device structure of the photodiode. (b) Energy-level diagram showing the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of each component material.

3. Results and discussion

Thickness values of the MEH-PPV:Alq_3 blend films are monitored at different spin speeds of spin coater. As expected, the film becomes thinner with the increase of spin speed. The film thickness decreases linearly from 170 nm to 100 nm with the spin speed increasing from 3000 rpm to at 8000 rpm. For the photodetectors fabrication, 100-nm thick films are prepared at a spin speed of 8000 rpm.

The absorption spectra of the MEH-PPV, Alq_3, and MEH-PPV:Alq_3 composite thin films are shown in Fig. 2. It is observed that the composite thin film shows a broad absorption peak at $\sim$ 500 nm and a shoulder peak at 395 nm. The results

are in agreement with the UV-VIS spectra of MEHPPV[24] and Alq_3.[25] The broad peak at 500 nm can thus be attributed to MEH-PPV and the narrow peak at 395 nm may be ascribed to Alq_3. The spectral response of the MEH-PPV film is limited to the 375 nm–580 nm region, while the Alq_3 film exhibits a strong absorption from 350 nm to 450 nm. It is obviously indicated in Fig. 2 that the addition of Alq_3 into the MEH-PPV enhances the absorption spectrum in a range from 350 nm to 450 nm. As a result the MEH-PPV:Alq_3 composite-based film exhibits good absorption with a wider bandwidth as compared with the MEH-PPV alone. However, the main purpose of the Alq_3 doping is not to increase the absorption bandwidth but it is added as an acceptor material to make the bulk heterojunction photodiode. The energy-level diagram (Fig. 1) shows a good combination of materials so that the generated charges can flow to the appropriate direction. The highest occupied molecular orbital (HOMO) energy level of Alq_3 (-5.62 eV) is lower than those of MEH:PPV (-5.01 eV) and PEDOT:PSS (-5.0 eV), indicating that holes can be easily transported from Alq_3 to both MEH:PPV and PEDOT:PSS.

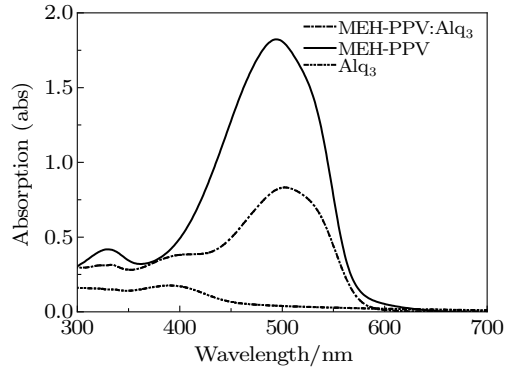


Fig. 2. Absorption spectra of the MEH-PPV, Alq_3, and MEH-PPV:Alq_3 blend films on glass substrates.

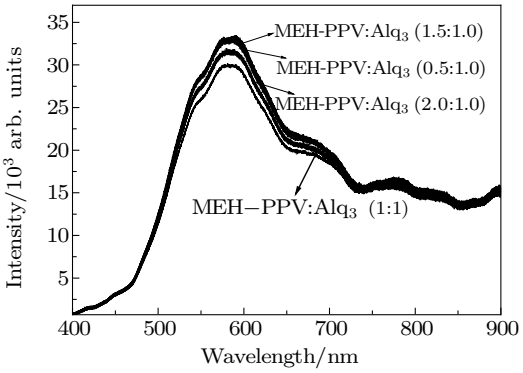


Fig. 3. PL spectra of MEH-PPV:Alq_3 blend films on glass substrates at different concentrations of MEH-PPV.

Figure 3 shows the PL spectra of the MEH-PPV:Alq_3 blend measured at room temperature. The PL spectra of the blend thin films are obtained by an excitation wavelength of 325 nm in a range from 400 nm to 1000 nm. It is evident from Fig. 3 that when MEH-PPV:Alq_3 are mixed with volume ratio 1:1, the intense PL of the blend shows quenching. Therefore MEH-PPV:Alq_3 (1:1) blend is selected for further investigation.

The electrical characteristics of ITO/PEDOT:PSS/MEH-PPV:Alq_3 (1:1)/LiF/Al photodiode are measured under different illumination intensities. Figure 4 shows that the photocurrent of the MEH:Alq_3 composite is enhanced as illumination increases. In other words, the more photons irradiate on the organic composite, the more charge carriers are generated. The same trends are observed when photocurrents are measured under different applied bias voltages. As the bias voltage increases, the sensitivity of the sensor also increases. The photo-response of the detector can be explained as the fact that the MEH-PPV:Alq_3 organic blend absorbs light and the electrons are transferred to Alq_3 and holes move towards the MEH-PPV. The photo-response in ITO/PEDOT:PSS/MEH-PPV:Alq_3(1:1)/LiF/Alphotodetector is based on the formation of excitons and subsequent dissociation due to bulk heterojunction and charge collection at the electrodes. The photovoltaic parameters of the device are poor for solar cell applications, but they are fair enough for photodiode applications. As a matter of fact, the solar cells are designed to minimize energy loss, whereas photodiodes are designed to achieve a rapid time response and spectral response.[26]

Figure 4 clearly explains that the currents at different bias voltages increase as illumination intensity increases. Figure 5, however depicts the increase in photocurrent with the increase in light intensity at 3-V input bias voltage. Here in our study, we use 3 V as the bias voltage for our fabricated photodetector but as the biasing increases, the sensitivity of the sensor also increases. The light intensity-dependent change in photocurrent can be expressed by the following equation:[27]

$$I_{\text{light}} = AF^{\alpha}, \tag{1}$$

where I_{light} is the current under illumination, F is the light intensity, A is a constant and α is an exponent. The value of α can be determined by the slope of I_{light} versus F (light intensity) graph. Typically, α is dependent on the type of relaxation mechanism. If the response is linear ($\alpha = 1$), then it is assumed that all recombination centres are empty, indicating monomolecular recombination. If the α value is 0.5, then it signifies that the density of carriers trapped below the Fermi level is less than the density of carriers trapped above the Fermi level indicating bimolecular recombination. However if the value of α falls between 0.5 and 1, then it is referred to as a sub-linear behaviour and it indicates that the trap state density exhibits an exponential dependence on energy.[28,29] In our composite film the response is almost linear but not exactly, which may be due to the random distribution of the traps.

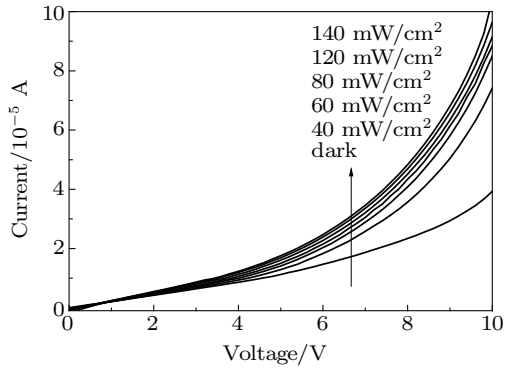


Fig. 4. Current–voltage characteristics of the ITO/PEDOT:PSS/MEH-PPV:Alq_3(1:1)/LiF/Al photodetector.

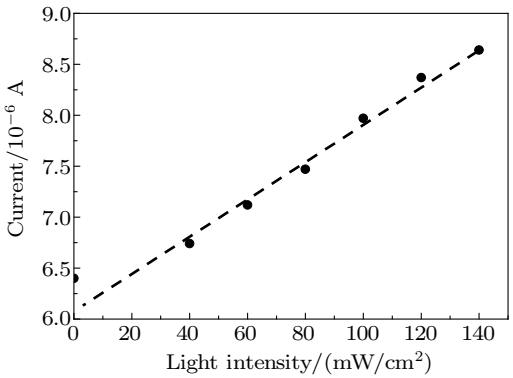


Fig. 5. Light Intensity versus current for ITO/PEDOT:PSS/MEH-PPV:Alq_3(1:1)/LiF/Al.

The photo-responsive characteristics of ITO/PEDOT:PSS/MEH-PPV:Alq_3(1:1)/LiF/Al show photo-switch performance as presented in Fig. 6. With the light irradiation on and off, the current across the devices shows two distinct states, a "low" current state with amplitude of $\sim$ 467 nA in the dark and a "high" current state of $\sim$ 565 nA at an incident light intensity of 100 mW/cm^2 under a bias voltage of 1 V. The switching between these two states is very fast and reversible upon exposure to a series of pulsed incident light. When the photodetector is exposed to light, the current promptly increases and then gradually reaches a relatively stable value. Response time and recovery time are both $\sim$ 2 s but the stability time is $\sim$ 5 s. The reason for the photo-switch effect should be attributed to the photo-induced carrier in the ITO/PEDOT:PSS/MEH-PPV:Alq_3(1:1)/LiF/Al, which gives a net increase in the concentration of the charges, therefore enhancing the electrical conductivity. The photo-sensitivity of the device can be determined by the following relation:[30]

$$S = \frac{I_{\text{light}} d}{PAV}, \tag{2}$$

where I_{light} is the current under illumination, P is the power of incident light, d is the film thickness, A is the area of the device, and V is the applied potential. The photo-sensitivity value for the detector is found to be 0.19 S·m/W. The responsivity is found to be 8mA/W while the ratio of photocurrent to dark current ($I_{\text{Ph}}/I_{\text{Dark}}$) is $\sim$ 1.24 under 100 mW/cm^2 illuminations at 3 V. Stability of the sensor under ambient conditions is also studied, and no significant change in the photoresponse performance is observed over a period of 1 week.

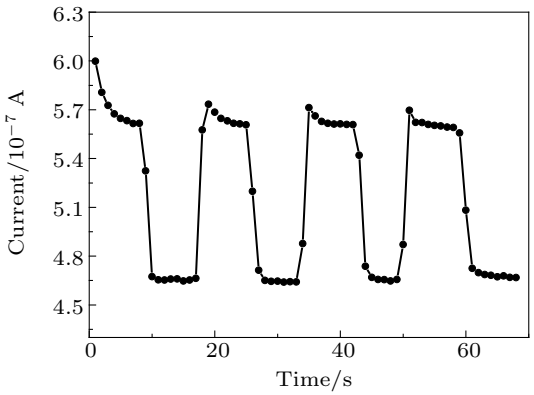


Fig. 6. Time response of the ITO/PEDOT:PSS/MEH-PPV:Alq_3 (1:1)/ LiF/Al under pulsed optical illumination with an intensity of 100 mW/cm^2 at a bais voltage of 1 V.

4. Conclusion

It is found that the donor–accepter organic MEH-PPV:Alq_3 blend has the potential to be utilized as a visible wavelength photo-detector. The organic blend-based photodetector exhibits a rapid, reversible, and sensitive response to visible light. The responsivity is found to be 8 mA/W while the ratio of photocurrent to dark current ($I_{\text{Ph}}/I_{\text{Dark}}$) is found to be $\sim$ 1.24 under 100 mW/cm^2 illumination at 3-V bias voltage. Stability of the sensor under ambient conditions is studied, and no significant change in the photoresponse performance is observed over a period of 1 week. Overall we can say that MEH-PPV:Alq_3 blend has the potential to be applied to photoconductive devices.

References

[1] Konstantatos G and Sargent E H 2010 *Nat. Nanotechnol.* **5** 391
[2] Basak D, Amin G, Mallik B, Paul G and Sen S 2003 *J. Crystal Growth* **256** 73
[3] Servati P, Colli A, Hofmann S, Fu Y, Beecher P, Durrani Z, Ferrari A, Flewitt A, Robertson J and Milne W 2007 *Physica E: Low-dimensional Systems and Nanostructures* **38** 64
[4] Hofmann S, Ducati C, Neill R, Piscanec S, Ferrari A, Geng J, Dunin-Borkowski R and Robertson J 2003 *J. Appl. Phys.* **94** 6005
[5] Luo L B, Yang X B, Liang F X, Jie J S, Li Q, Zhu Z F, Wu C Y, Yu Y Q and Wang L 2012 *CrystEngComm* **14** 1942
[6] Soci C, Zhang A, Bao X Y, Kim H, Lo Y and Wang D 2010 *J. Nanosci. Nanotechnol.* **10** 1430
[7] Amin M, Manzoor U, Islam M, Bhatti A S and Shah N A 2012 *Sensors* **12** 13842
[8] Walker D, Zhang X, Kung P, Saxler A, Javadpour S, Xu J and Razeghi M 1996 *Appl. Phys. Lett.* **68** 2100
[9] Li J, Fan Z, Dahal R, Nakarmi M, Lin J and Jiang H 2006 *Appl. Phys. Lett.* **89** 213510
[10] Ahn D 2012 *Photodetector Capable of Detecting the Visible Light Spectrum* 2012, US Patent 20 120 235 028
[11] Volintiru I 2008 *Eindhoven: Technische Universities Eindhoven*
[12] Sayyad M H, Ahmad Z, Karimov K S, Yaseen M and Ali M 2009 *J. Phys. D: Appl. Phys.* **42** 105112

[13] Ahmad Z, Sayyad M H, Yaseen M, Aw K C, M-Tahir M and Ali M 2011 *Sensors and Actuators B* **155** 81
[14] Sayyad M, Shah M, Karimov K, Ahmad Z, Saleem M and Maroof Tahir M 2008 *J. Optoelectron. Adv. Mater.* **10** 2805
[15] Abdullah S M, Ahmad Z, Aziz F and Sulaiman K 2012 *Organic Electronics* **13** 2532
[16] Dong H, Zhu H, Meng Q, Gong X and Hu W 2012 *Chem. Soc. Rev.* **41** 1754
[17] Aziz F, Sayyad M, Karimov K S, Saleem M, Ahmad Z and Khan S M 2010 *J. Semicond.* **31** 114002
[18] Ahmad Z, Abdullah S M and Sulaiman K 2012 *Sensors and Actuators A: Physical* **179** 146
[19] Sayyad M H, Shah M, Karimov K S, Ahmad Z, Saleem M and Tahir M M 2008 *J. Optoelectron. Adv. Mater.* **10** 2805
[20] Saleem M, Sayyad M H, Karimov K S, Ahmad Z, Shah M, Yaseen M, Khokhar I and Ali M 2008 *J. Optoelectron. Adv. Mater.* **10** 1468
[21] Sayhan I, Bauersfeld M L, Woellenstein J and Becker T 2008 *Microsystem Technologies* **14** 659
[22] Liu X D, Xu Z, Zhang F J, Zhao S L, Zhang T H, Gong W, Song J L, Kong C, Yan G and Xu X R 2010 *Chin. Phys. B* **19** 118601
[23] Gilch H and Wheelwright W 1966 *Journal of Polymer Science Part A-1: Polymer Chemistry* **4** 1337
[24] Reddy V S, Das K, Ray S and Dhar A 2012 *Proceeding of ASID's* **6** 8
[25] Wang X Y and Weck M 2005 *Macromolecules* **38** 7219
[26] Pierret R F 1996 *Semiconductor Device Fundamentals* (MA: Addison-Wesley Reading)
[27] Yakuphanoglu F 2008 *Sensors and Actuators A: Physical* **141** 383
[28] Pejova B, Tanuševski A and Grozdanov I 2005 *J. Solid State Chem.* **178** 1786
[29] Qasrawi A and Gasanly N 2002 *Physica Status Solidi (a)* **194** 81
[30] Park S H, Ogino K and Sato H 2000 *Synthetic Metals* **113** 135