Optik 124 (2013) 2701–2708

Contents lists available at SciVerse ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Investigation of optical and chemical properties of poly(3-methylthiophene) and polypyrrole for solar cell fabrication

Maryam Namvar[a,*], Seyed Mohammad Bagher Ghorashi[d], Abbas Behjat[a,b], Hamid Reza Zare[c]

[a] *Atomic & Molecular Group, Faculty of Physics, Yazd University, Yazd, Iran*
[b] *Photonics Research Group, Engineering Research Center, Yazd University, Yazd, Iran*
[c] *Chemistry Department, Yazd University, Yazd, Iran*
[d] *Atomic & Molecular Group, Faculty of Physics, Kashan University, Kashan, Iran*

ARTICLE INFO

Article history:
Received 29 February 2012
Accepted 3 August 2012

Keywords:
Organic solar cell
HOMO–LUMO energy level
Absorption spectra
Poly(3-methylthiophene)
Polypyrrole

ABSTRACT

In this study, we have investigated the optical and chemical properties of thin film layers based on poly(3-methylthiophene) and polypyrrole through experiment and simulation point of view. Optical band gap of poly(3-methylthiophene-co-pyrrole) (poly(3-MeT-co-py)) and poly(3-methylthiophene) (PMeT) were investigated through UV–vis spectroscopy. Electrochemical data were used to estimate the onset oxidation and reduction potential, energy band diagram and chemical band gap of PMeT and poly(3-MeT-co-py). The experiments were carried out in a three-electrode cell with ITO as the working electrode. Influence of different electrodes on PMeT thin film's energy levels was studied in electrochemical polymerization. Different thin films by poly(3-methylthiophene) and polypyrrole were utilized in order to fabricate organic solar cells and their photovoltaic properties were offered. Moreover, an optical modeling based on thin film matrix formalism has been carried out which investigated absorption processes in single layer solar cell by PMeT. From the simulation, photons absorbed profiles and energy dissipation in term of wavelength and distance in depth of cell were derived in active layer.

1. Introduction

Plastic electronics which is based on organic semiconductors is a very promising technology to enter the low-cost materials into the electronic market [1]. In this category, Photovoltaic cells based on organic materials have been a hot issue, since they are expected to offer inexpensive and flexible light-electric energy conversion tools [2–7]. The magnitude of the band gap and the positions of the HOMO and LUMO energy levels are the most important characteristics for determining the optical and electrical properties in photovoltaic device [8,9]. It is highly desirable to develop conjugated polymers with broader absorptions through narrowing their optical band gap [10]. The most straightforward way to reduce the band gap is simply by either raising the HOMO or lowering the LUMO level of polymer or by compressing the two levels closer together simultaneously [11–13]. Unfortunately, the optical properties associated with light harvesting are not the only one under consideration. Each couple of donor–acceptor materials should be in the specific energy band diagram in order to satisfy the boundary condition for generating photo-current [14–18]. Therefore, choosing the appropriate materials for active layer, which is heart of the organic solar cells, is another issue that should be noticed in device designing [19–21]. Although individual donor or acceptor material can show the good Photovoltaic properties as the single layer solar cell but they may not to be an efficient organic solar cell together since they are not well matched in terms of energy band diagram. Energy gap of polymers can be obtained from absorption spectra. Also, electrochemical data obtained by cyclic voltammetry can give valuable information and allow the estimation of the relative position of HOMO/LUMO levels of materials. The knowledge of these values is required for compiling suitable donor–acceptor pairs [22]. Moreover all these investigations in experimental research and fabrication works, further works in optical modeling and computer simulation has been figured out to analyze the light process circumstance in different layers of devices which can lead us to obtain a deeper approach of light absorption. The modeling of light absorption has a great importance in describing the electro-optical properties. In this study, we determined the band gap of poly(3-MeT-co-py) and PMeT by absorption spectra and we estimated HOMO and LUMO energy for PMeT and poly(3-MeT-co-py). We fabricated solar cells with PMeT and polypyrrole thin film as the active layer and characterized their photovoltaic characteristics. Also, we investigated the optical properties of poly(3-methylthiophene) by the simulation based on optics thin film which describes absorption in device as the main operation in solar cell for generation excitons and final photocurrent (Fig. 1).

---

* Corresponding author. Tel.: +98 5842254843.
E-mail address: maryam_namvar@stu.yazduni.ac.ir (M. Namvar).

0030-4026/$ – see front matter © 2013 Elsevier GmbH. All rights reserved.
http://dx.doi.org/10.1016/j.ijleo.2012.08.096

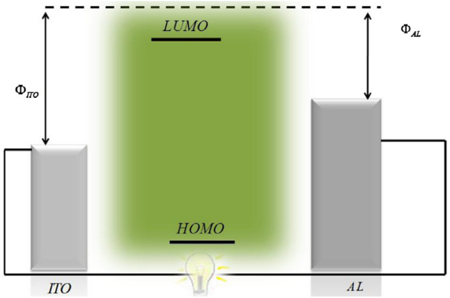

Fig. 1. Configuration of heterojunction single layer organic solar cell.

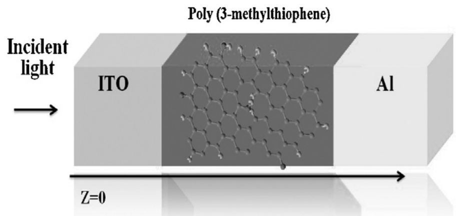

Fig. 2. Wave transmission and reflection process and energy dissipation in term of *z*, distance in depth of active layer, derive from optical light distribution.

2. Experimental and theory

2.1. Material and instrument

3-methylthiophene (monomer) and acetonitrile and tetramethylammonium tetrafluoroborate and sodium perchlorate were purchased from Merck. A three-electrode cell was used for electrodeposition of polymer film on ITO and Ag/AgCl [Ag in 0.1 M KCl] was applied as a reference electrode. Indium tin oxide (ITO) coated glass was used as the working electrode. The sheet resistance of the ITO was 50 Ω/□. Au (purity of 99%) and Al coated glass was applied as the counter electrode. Al (purity of 99%) was used for solar cell fabrication. Keithley 2400 Source Meter was used for solar cell *I–V* measurement. Cyclic voltammetry (CV) and electrochemical investigation were accomplished with Sama 500 electro analyzer system. Absorption spectra were obtained using an Avantes spectrophotometer model avaspec-2048. Al coated on glass and Au coated on solar cell top layer have done by VAS coating, 78535 model.

2.2. Methods

The Au over layer (100 nm) was deposited by thermal evaporation on glass plates that had evaporated Cr under layer (10 nm) at 1.4×10^{-6} Torr and deposition rate of 8 Å s^{-1} for Cr and 30 Å s^{-1} for Au. Although the thickness of the Cr over layer can be considered larger than necessary for our purposes, thinner layer (e.g., 20–100 Å) sometimes led to diminished adhesion of Au on the glass plates. The Al (78 nm) was prepared by thermal evaporation at 1.4×10^{-6} Torr and deposition rate of 8 Å s^{-1}. In order to obtain absorption spectra of polymer thin film, ITO substrate were cleaned thoroughly in acetone, de-ionized water in sequence by an ultrasonic cleaner. After cleaning, the substrates were dried in an oven. For formation of PMeT thin film, the electrolyte was a 0.03 mol l^{-1} solution of tetramethylammonium tetrafluoroborate (TMTFB) in acetonitrile containing 0.1 mol l^{-1} 3-methylthiophenein. For poly(3-MeT-co-py) thin film, the electrolyte was a 0.03 mol l^{-1} solution of tetramethylammonium tetrafluoroborate (TMTFB) in acetonitrile containing 0.1 mol l^{-1} 3-methylthiophenein and 0.049 mol l^{-1} pyrrole. Both thin films were synthesized electrochemically on ITO substrate as the working electrode by applying potentiostatic method in three-electrode cell. In the polymerization reactions of a PMeT film, counterions from the electrolyte diffuse into the material and allow forming the p doping of the material. The value 2 V, applied while monomers (3-MeT) were synthesized on ITO to form the film. The synthesis of low band gap polymer was successfully carried out via oxidative polymerization. Constant potential 0.8 V was applied during polymerization of copolymer. Copolymer thin film was smooth in comparison with homopolymer. Polymer films for the photovoltaic devices investigated in this work were prepared in the same way but we used 0.04 mol l^{-1} sodium perchlorate ($NaClO_4$) for copolymer electrolyte. After polymer deposition onto ITO, the second electrode (Al) was deposited by thermal evaporation. Electrochemical behaviors of the PMeT were investigated by cyclic voltammetry (CV). Cyclic voltammetry was performed using electrochemical instrument with a three-electrode cell with ITO as the working electrode, Ag/AgCl as the reference electrode and Au as the counter electrode in same electrolyte at a scan rate of 100 mV/s.

2.3. Simulation

In this section, we present a simulation of optical absorption due to energy dissipation based on matrix formalism. The optical modeling and simulation theory with details can be defined by the Fresnel formulas described in [23,24] but in brief, we have described calculations by the knowledge of optical thin film. In this modeling, a plane wave incident from the ITO side propagates through the layers of device toward the metal side and optical electric field at the position *z* can be achieved by the system transfer matrix which obtains by using the interface matrixes and the layer matrixes so that the distribution of optical electric field through multilayer device can be calculated from the components of transfer matrix. As an input to the optical modeling, the optical constants (*k*, *n*) of materials were taken from the literatures [25,26]. Electric field inside layer *j* in term of *z*, depth in cell, describes as follow (Fig. 2):

$$E_j(z) = \frac{M''_{j,11} e^{i\varepsilon_j(z-d_j)} + M''_{j,21} e^{i\varepsilon_j(d_j-z)}}{M'_{j,11} M''_{j,11} e^{-i\varepsilon_j d_j} + M'_{j,12} M''_{j,21} e^{i\varepsilon_j d_j}} E_0^+ \tag{1}$$

where ε_j is $\varepsilon_j = (2\pi/\lambda)(n_j + ik_j)$ and M'_j, M''_j, denote as a function of the lower and upper transfers and interfaces matrix (*I*, *L*) of layer *j* by these formulas:

$$M'_j = \left(\prod_{\nu=1}^{j-1} I_{\nu-1,\nu} L_\nu \right) \cdot I_{j-1,j} \tag{2}$$

$$M''_j = \left(\prod_{\nu=j+1}^{s} I_{\nu-1,\nu} L_\nu \right) \cdot I_{s,s+1} \tag{3}$$

The time average of the energy dissipation in layer *j* of cell, as a well representation of light absorption, is given by:

$$Q_j(z) = \frac{1}{2} c\varepsilon_0 \alpha_j n_j |E_j(z)|^2 \tag{4}$$

where n_j is the real index of refraction, α is the absorption coefficient:

$$\tilde{n} = n_j + ik_j \tag{5}$$

$$\alpha_j = \frac{4\pi k_j}{\lambda} \tag{6}$$