Solid State Electronics 145 (2018) 49–53

Contents lists available at ScienceDirect

Solid State Electronics

journal homepage: www.elsevier.com/locate/sse

# Effect of traps on the charge transport in semiconducting polymer PCDTBT

Mohd Taukeer Khan[a,*], Vikash Agrawal[b], Abdullah Almohammedi[a], Vinay Gupta[b]

[a] Department of Physics, Faculty of Science, Islamic University of Madinah, Madinah, Saudi Arabia
[b] Physics of Energy Harvesting Division, CSIR-National Physical Laboratory, New Delhi 110012, India

ARTICLE INFO

The review of this paper was arranged by Prof. S. Cristoloveanu

*Keywords:*
Traps
Organic semiconductors
PCDTBT
Trap density
Hole mobility
Space charge limited current

ABSTRACT

Organic semiconductors (OSCs) are nowadays called upon as promising candidates for next generation electronics devices. Due to disorder structure of these materials, a high density of traps are present in their energy band gap which affect the performance of these devices. In the present manuscript, we have investigated the role of traps on charge transport in PCDTBT thin film by measuring the temperature dependent *J(V)* characteristics in hole only device configuration. The obtained results were analyzed by space charge limited (SCL) conduction model. It has been found that the room temperature *J(V)* characteristics follow Mott-Gurney square law for trap-free SCL conduction. But below 278 K, the current increases according to trap-filling SCL law with traps distributed exponentially in the band gap of semiconductor. Furthermore, after reaching a crossover voltage of $V_C \sim 12$ V, all the traps filled by injected carriers and the trap-filling SCL current switch to trap-free SCL current. The hole mobility of trap-free SCL current is about one order higher as compared trap-filling SCL current and remains constant with temperature.

## 1. Introduction

Organic semiconductors (OSCs) are now considered to be one of the most auspicious materials in photovoltaics technology because of their ability to provide environmentally safe, flexible, lightweight and cost-effective solar cells. The most studied and best understood system in organic photovoltaics (OPV) devices is poly(3-hexylthiophene) (P3HT) in combination with [6,6]-phenyl-$C_{61}$-butyric acid methyl ester ($PC_{60}BM$), which shows a power conversion efficiencies in the range of 3.5–6.5 % [1–4]. The efficiency of the P3HT/PCBM based device is limited due to (a) large bandgap of P3HT (1.9 eV) which limit the harvesting of solar radiation (350–650 nm) [5], (b) small energy difference between the lowest unoccupied molecular orbital (LUMO) of PCBM and the highest occupied molecular orbital (HOMO) of P3HT which results in a lower open circuit voltage ($V_{oc} \sim 0.60$ V) [6,7], and (c) poor carrier mobility ($10^{-5}$ to $10^{-6}$ $cm^2 V^{-1} s^{-1}$) [8].

Recently, due to better understanding of device physics and development of new materials for active layer, the device performance has dramatically improved and reached 10 –11% for single-junction device [9–11], more than 12% in tandem configuration [12] and 5.5% in organic/inorganic hybrid cells [13]. Among them, poly[N-9″-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) is the most promising low bandgap materials which gives some of the highest reported efficiencies for organic solar cells. PCDTBT surpasses the performance of P3HT and is now considered as one of the new benchmarks for the development of highly efficient bulk hetrojunctions solar cells [14,15]. Zhicai et al. [16] achieved a PCE of ~8.37% on a device configuration ITO/PEDOT:PSS/PCDTBT/$PC_{71}$BM/PFN/Al. Moreover, PCDTBT has been demonstrated to be a stable semiconducting polymer approximately with 7 years of lifetime [17,18]. PCDTBT has a relatively deeper HOMO of 5.45 eV compared to 5.1 eV of the P3HT, as a result, a high open circuit voltage ($V_{OC}$) of 0.9 V was achieved in PCDTBT:fullerene based OPV devices [16]. In addition, the HOMO level of the PCDTBT is below the air oxidation threshold of 5.27 eV, which ensures better air-stability [18].

Organic semiconductors are prone to have defect due to their imprecise chain length and structural disorder. Photocurrent generation in OPV devices greatly depends on the efficiency with which charge carriers move within the OSCs. The presence of defects may trap the charge carriers in trap states, as a results these carriers no longer participate in opto-electrical process or may interrupt the conjugation system and decrease the carrier mobility, therefore, increase of recombination probability of electrons and holes. Consequently, the open circuit voltage ($V_{OC}$), short circuit current ($J_{SC}$) and the fill factor (FF) are reduced, leading to significant decrease in the PCE [19–21]. Various electrical [22–24] and optical (photoluminescence and electroluminescence) [25–27] techniques have been employed to investigate the defects present in OSCs. By using optical techniques, we can get the evidence for the defect present in OSCs but quantitative investigation cannot obtained. Quantitative investigation of defects is essential for

* Corresponding author.
*E-mail address:* khanmtk@iu.edu.sa (M.T. Khan).

https://doi.org/10.1016/j.sse.2018.04.005
Received 4 December 2017; Received in revised form 13 March 2018; Accepted 15 April 2018
Available online 21 April 2018
0038-1101/ 

the evaluation of the performance of OSC based devices. The best suitable method for the quantitative analysis of defect is electrical methods. In the present work, we have used electrical method for the quantitative evaluation the traps in PCDTBT thin film by measuring the temperature dependent *J-V* characteristics. The characteristics trap depth were quantified for each temperature, then used to obtain the carrier mobility, carrier density, trap density, trap energy, and quasi Fermi levels.

## 2. Nature of traps in organic semiconductors

In OSCs, two kind of carrier traps are reported namely, shallow and deep traps. The probability for a trap to capture a hole follows the Fermi-Dirac statics [28]

$$f(E) = \frac{1}{1 + g^{-1} e^{\frac{E_F - E}{k_B T}}} \tag{1}$$

Where $E$ is energy, $E_F$ quasi-Fermi level for hole, $k_B$ Boltzmann constant and $T$ is the absolute temperature.

If the quasi-Fermi energy $E_F$ located above the trap energy level ($E = E_t$) it is called shallow trap, on the other hand if $E_F$ lies below the trap level, it is called deep trap for hole as shown in Fig. 1(a). The converse is true for electron with respect to LUMO level [29].

The traps are distributed spatially and energetically in a semiconducting layer. There are two important distribution functions that are used to characterize the dispersion of traps in the forbidden energy gap. One is exponential distribution function proposed by Rose [30] and modified by Mark and Helfrich [31] and other is a Gaussian distribution proposed by Silinsh [32]. The distribution function for the traps that are exponential distributed within the energy bandgap, is given by [28]:

$$H(E) = \frac{H_t}{E_t} \exp\left(\frac{E_{HOMO} - E}{E_t}\right) \tag{2}$$

Where $H_t$ is the total density of traps and $E_t$ is a characteristic trap energy, which signify the decay of exponential distribution of traps. It is defined as the energy at which the density of traps reduces to 1/e as compared to density of traps at the edge of valance band. $E_t$ is often expressed in terms of the characteristics temperature of trap distribution $T_C$ as $E_t = k_B T_C$. $H_t$ and $E_t$ are very important parameters and determine the quality of material.

The Gaussian distribution of traps is given by Eqn. [30]:

$$H(E) = \frac{H_t}{\sqrt{2\pi\sigma^2}} \exp\left[\frac{(E_{HOMO} - E)^2}{2\sigma^2}\right] \tag{3}$$

Where $E_m$ is the energy level with maximum trap distribution and $\sigma$ is the dispersion of trap energies around $E_m$.

In OSCs the charge carriers are injected from Ohmic contacts. Due to the low carrier mobility, the injected carriers accumulates a space charge near the injecting electrodes. As a result, space charge limited currents have been proposed the dominant conduction mechanism in these materials [30–33]. Experimentally, it is difficult to distinguish between the Gaussian and exponential distribution, because quantitatively both distributions give the same results for SCL current [34]. In the present work we have used exponential distribution of traps due to simplicity of the method.

The expression for current – voltage characteristics *J(V)* for exponential distribution of traps is given by [28]:

$$J = q^{1-l} \mu N_{HOMO} \left(\frac{2l+1}{l+1}\right)^{l+1} \left(\frac{l}{l+1} \frac{\varepsilon_r \varepsilon_0}{H_t}\right)^{l} \frac{V^{l+1}}{d^{2l+1}} \tag{4}$$

Where, $q$ is the electronic charge, $\mu$ is the carrier mobility, $N_{HOMO}$ is the effective density of traps at the edge of HOMO level, $d$ is the thickness of the film, $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$is the dielectric constant of materials and $l = E_t/k_B T = T_C/T$.

## 3. Results and discussions

To characterize the traps in PCDTBT, we have measured temperature dependent *J(V)* characteristics on hole only device configuration *viz.* indium tin oxide (ITO)/poly(3,4-ethylendioxythiophene)-poly (styrene sulfonate) (PEDOT:PSS)/PCDTBT/Au as shown in Fig. 1(b). For the fabrication of hole only devices, ITO coated glass substrates have been carefully cleaned and treated with oxygen plasma. A PEDOT:PSS (1.3% in water, Sigma Aldrich-USA) layers were spin-casted onto the ITO substrate and cured at 120 °C for 30 min in vacuum. PEDOT:PSS work as a hole injecting electrode in the device. Active materials PCDTBT (Sigma Aldrich product no 753998, $M_w$ 100,000–140,000) were spin casted under inert atmosphere, followed by annealing at 120 °C for 10 min. Finally, gold (99.9%) contacts (200 nm) was applied via thermal evaporation through a shadow mask at $2 \times 10^{-6}$ Torr.

Fig. 2(a) shows log – log plot of temperature dependent current vs. voltage (*J-V*) characteristics of PCDTBT thin film in hole only device configuration. For the temperature 304 K and 278 K the slope of *J-V* characteristics is 2 which corresponds to trap free-space SCL given by Mott-Gurney square law:

$$J = \frac{9}{8} \varepsilon \mu \frac{V^2}{d^3} \tag{5}$$

This equation does not implying that the traps are absent, but state that at these temperatures (304 K and 278 K), thermal energy is sufficient to de-traps all charge carriers. The energy required to de-trap the charge carrier is called activation energy $E_a$. We have calculated activation energy from the slope of log(J) and (1000/T) plot at 8 V shown in Fig. 2(b). The calculated value of activation energy is 24 meV which is corresponds to 278 K. At 278 K all the trapped charges get sufficient

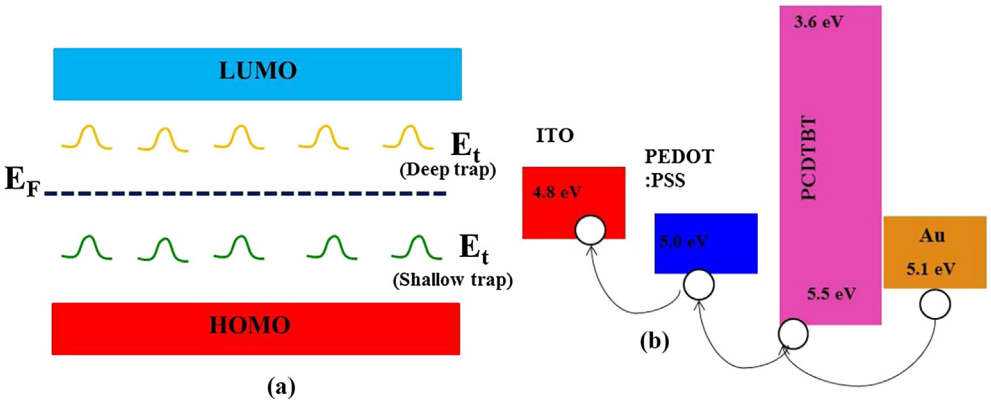


**Fig. 1.** (a) Schematic representation of shallow and deep traps for hole. (b) Schematic.