Field Dependent Charge Carrier Transport for Organic Semiconductors at the Time of Flight Configuration

Ali Mahmoudloo[*] **and Sohrab Ahmadi-Kandjani**

Research Institute for Applied Physics and Astronomy (RIAPA), University of Tabriz, Tabriz, Iran

[*]**Corresponding Author Email:** mahmodlo@tabrizu.ac.ir

ABSTRACT—In this paper, we used the time-of-flight (TOF) of a charge packet, that injected by a voltage pulse to calculate the drift velocity and mobility of holes in organic semiconducting polymers. The technique consists in applying a voltage to the anode and calculating the time delay in the appearance of the injected carriers at the other contact. The method is a simple way to determine the charge transport properties of organic semiconductors. The effect of charge trapping mechanism on the carrier mobility in the organic layer is investigated and it was shown that at higher applied voltage, 100 V, hole mobility increases rapidly in comparison with lower applied voltage (50 V).

KEYWORDS: time of flight, charge carrier transport, localized state, transit time, charge trapping

I. INTRODUCTION

In recent years, there have been interests in the field of organic semiconductors because of their some especial features. Organic semiconductors are the base of the modern electronic and optoelectronic devices such as organic light emitting diodes, organic solar cells, organic transistors etc [1-3]. Organic semiconductors share some common features.

All are van-der-Waals bonded crystals, where the intermolecular interactions are much weaker than the intra-molecular bonds. With van-der-Waals distances of the order of 3.8 to 4 Å, individual molecules are well separated [4]. Due to the weak bonding, the structural and mechanical behaviors of these materials differ markedly from inorganic materials. For instance, hardness is usually lower than inorganic materials, and the thermal development coefficient tends to be larger [4, 5].

Organic semiconductors mainly come in two varieties: first is small molecule and second is polymer. Small molecules as the name suggests are relatively small molecular weight molecules with conjugated carbon atoms [4]. These substances can be prepared as molecular single crystals. Due to the close coupling of the π-systems of the molecules in these crystals, they display remarkable transport properties with mobilities of 1-10 $cm^2V^{-1}S^{-1}$ in a purified form [6]. Most molecules can be easily evaporated to form polycrystalline layers. Organic semiconducting polymers are long chain of conjugated carbon atoms which composed of smaller repeating units named monomers. The advantage of polymers is that, when modified with suitable side chains, they can self-organize upon room temperature solution deposition, yielding a fairly high mobility layer [4]. Therefore they can be used to print electronic circuits at a low manufacturing cost [7].

It is important to measure the fundamental limits of charge carrier mobilities in organic semiconductors in order to develop organic electronics [4,8]. Although devices such as organic field effects transistors (OFETs), organic thin film transistors (OTFTs) and organic light emitting diodes (OLEDs) are already used in commercial applications [8]. There is still no complete understanding of the final restriction of performance and stability in these devices at this time [3]. It is essential to

determine the electronic properties in organic semiconductors. It needs being able to grow ultra-pure, fully ordered molecular crystals for the measurement of intrinsic charge transport [4]. Organic crystals show mobilities as high as amorphous silicon. Dislocations and grain boundaries, which may limit charge transfer, are important in these crystals [9]. Thermal expansion has to be taken into score when devising crystal growth procedures, since the (often anisotropic) expansion tensor produces large stress/strain fields in the presence of temperature gradients. Most important features of the charge transport directly follow from the basic structural features of organic glasses [10]. These glasses are molecular materials with rather weak interactions between molecules and, at the same time, they have important disorder in positions and orientations of molecules. This means that all relevant states are localized and charge carrier transport occurs by the hopping mechanism. It is well known that for hopping transport, disorder in the material is the most important parameter [11, 12].

In this work, we discuss the theoretical aspects of this method and calculate the time of flight as a function of the drift mobility of carriers in an organic layer.

II. THEORY AND NUMERICAL CALCULATION

The key to charge transport and other optoelectronic properties in organic disordered semiconductors, such as conjugated and molecular polymers is in its energy spectrum, also called the density of states (DOS). Therefore, the way to determine the DOS is to contrast experimental data with the suitable theory using some trial DOS function, $g(\varepsilon)$ aiming at the best agreement between experimental and theoretical results. It has been identified in time-of-flight (TOF) studies that the DOS in such systems is close to a Gaussian one, $g(\varepsilon) \propto \exp\left\{-(\varepsilon/\sigma)^2\right\}$ [13]. In charge transport simulation, the ideal condition does not exist because, firstly there is always a finite rise time for the pulse to reach its maximum. Secondly, the mobility of an

organic semiconductor is dependent on a variety of conditions containing the local field and the charge concentration. Thirdly, traps in an organic semiconductor often overcome transport. Finally, non-ideal injection from contacts cans incompatible affect transport of charge carriers.

In disordered organic systems, charge transport arises via incoherent hopping of carriers (electrons or holes) between strongly localized states. We assume that the energies of localized states are distributed via a DOS of the form [11] and [14]:

$$g(\varepsilon) = \frac{N}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right) \tag{1}$$

where N is the total concentration of localized states and σ is the energy measure of the order of 0.1 eV [12]. The hopping transition rate for a charge carrier from an occupied localized state i to an empty localized state j over a distance r_{ij} is explained by the Miller-Abrahams statement [12]:

$$v_{ij} = v_0 \exp\left(-\frac{2r_{ij}}{a}\right) \exp\left\{-\frac{\varepsilon_j - \varepsilon_i + |\varepsilon_j - \varepsilon_i|}{KT}\right\} \tag{2}$$

where a is the localization length, which is assumed equal for sites i and j the pre-exponential factor $v_0 \approx 10^{12} s^{-1}$ depends on the interaction mechanism that reason transitions [13].

In a disordered material the lattice phonons are strongly coupled to the charge carrier. Therefore the charge carrier motion at each lattice site is randomized by scattering. The strong phonon-electron coupling results in the formation of a localized polaron. This type of motion, namely a series of disassociate jumps is called hopping transport. The hopping mobility can be written as [13]:

$$\mu = \frac{ea^2}{KT} P \tag{3}$$

where P is the hopping probability per unit time.

In trap controlled hopping, a carrier is activated from its trapped state with an activation energy that is higher than the activation energy for small polaron hopping. This energy is used by the carrier to get de-trapped and hop from one state to another, until it encounters another trap state. As the name indicates the transit time for time-of-flight mobilities is controlled by the concentration of traps and therefore follows an exponential dependence on the concentration of traps as given in the Eq. (4) [15]:

$$t_T = \exp\left(\frac{2\rho}{\rho_0}\right) \qquad (4)$$

where ρ is the concentration and ρ_0 is the spatial distribution of charge density outside a molecule, also known as its localization radius. In the multiple traps and release model (MTR) a majority of the carriers injected into the semiconductor are trapped into states localized in the forbidden band. Carriers undergo thermal de-trapping and get excited into mobile states where they take part into conduction, until they come among a defect site and get localized into a trapped state by releasing a phonon. The conductivity is therefore given by the concentration of free carriers n_f times a microscopic mobility μ_0 which varies slowly with temperature [10].

$$\sigma = e n_f \mu_0 \qquad (5)$$

where e represents the electronic charge. θ is a parameter indicating the fraction of free carriers introduced as:

$$\theta = \frac{n_f}{n_{tot}}; \qquad n_{tot} = n_f + n_t \qquad (6)$$

where n_{tot} is the total (free plus trapped) density of charges, Eq. (5) can be rewritten as

$$\sigma = e n_{tot} \theta \mu_0 \qquad (7)$$

Eq. (7) shows that a thermally-activated conductivity can be interpreted by a thermally activated charge density.
The achievement of the MTR model lies in its ability to explain temperature and voltage dependence of mobility. But it often yields unnaturally high values of traps density states.

This is because the multiple trap and release model is valid only for a trap distribution consisting of a shallow different energy level close to the main transport band.

We used TOF technique as a model to calculate the drift mobility in organic layers. This technique involves the injection of carriers at the anode electrode followed by their future production at the collector electrode [9]. The delay between the two events is used to extract the velocity of the carriers. When an electric field is applied, carriers inside the organic semiconductor move in response to an electric field. The electric field is created by applying a voltage bias between two contacts, one kept grounded. The carriers are injected from the contact at higher potential, so that the exiting carrier current produces a voltage that can be used to recognize the time of their transit [10]. Also in this model the higher potential is applied to the first electrode and the second electrode is grounded. Therefore the variation of TOF mobility with pulse voltage can be due to the dependence of mobility on the anode-cathode bias. This model deals with the time dependent carrier distribution $\rho(x,t)$ current through the two electrodes with the distance $x=L$ from each other and we consider an organic semiconductor film with a slice on infinitesimal thickness dx as shown in Fig. 1. The current is flowing through the circuit due to hole transport across the sample alone.
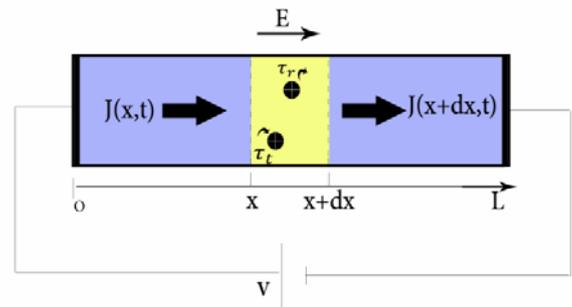

Fig. 1 Current flow and trapping and release processes in a semiconductor with a single trapping level. The number of holes within an organic semiconductor slices of thickness dx increases due to the flow of holes into the slice and due to the release of trapped holes within the slice.

The number of holes in the slice may increment either due to the pure flow of holes into the slice, or a net thermal release of the trapped charge carriers within the slice. The effect of recombination is deleted in the sample. The rate of change in the number of free holes in the slice is [16, 17]:

$$\frac{\partial p(x,t)}{\partial t} = -\frac{1}{e}\frac{\partial j(x,t)}{\partial x} - \frac{\partial p_t(x,t)}{\partial t} \quad (8)$$

Where $\partial p(x,t)$ is the concentration of the free holes in the sample, $J(x,t)$ is the net current density in the slice and $p_t(x,t)$ is the trapped hole concentration.

The continuity equation is given by

$$\frac{\partial J}{\partial x} + \frac{\partial \rho}{\partial t} = 0, \quad \text{where } \rho = ep(x,t) \quad (9)$$

The conduction current density for holes is explicited as

$$J(x,t) = -\mu ep\frac{\partial V}{\partial x} - eD\frac{\partial p}{\partial t} \quad (10)$$

In above equation, drift of the charge carriers under the dominance of applied bias has more share than the charge carrier diffusion $J_{drift} >> J_{Diff}$,

$$J = -\mu ep\frac{\partial V}{\partial x} \quad (11)$$

By omitting J from Eq. (9) and Eq. (10) we have,

$$\frac{\partial}{\partial x}\left(\mu p\frac{\partial V}{\partial x}\right) = \frac{\partial p}{\partial t} \quad (12)$$

where μ is controlled by the Poole-Frenkel behavior, the mobility of an organic semiconductor. Under high fields it is given as

$$\mu = \mu_0 \exp\left(\frac{\beta\sqrt{F} - \Delta}{kT}\right) \quad (13)$$

where k is Boltzmann's constant, T is the temperature, F is electric field, Δ is zero field hopping barrier of the carriers, μ_0 is intrinsic mobility without a hopping barrier, and β is the field–dependent coefficient. In the explanation of the field dependence of

mobility given in the above equation, the value of β is about $10^{-5} - 10^{-4}\ eV/(V/cm)^{1/2}$ [11,17].

By inserting the field dependence of mobility Eq. (13) into Eq. (12), we get the field dependent transport equation [17]:

$$\frac{\partial}{\partial x}\left\{\mu_0\left[\frac{\beta}{kT}\left(\frac{\partial V}{\partial x}\right)^{1/2}\right]V\frac{\partial V}{\partial x}\right\} = \frac{\partial V}{\partial t} \quad (14)$$

In this formulation the room temperature transient time is considered, the result of which is shown in Fig. **2**.

We have used a simple model including in a single trap level determined by a carrier lifetime τ. The current equation is:

$$\frac{1}{e}\frac{\partial J_P}{\partial x} + \frac{\partial P}{\partial t} = \frac{p - p_0}{\tau} \quad (15)$$

III. RESULTS AND DISCUSSION

In this work we used P3HT as the organic layer with recombination constant 1.95×10^{-12} and dielectric constant $3.37\times10^{-11}\ F/cm$ and effective density of states $1.4\times10^{18}\ cm^{-1}$.

Eq. (12) and (13) provide an approximate solution to the problem of pulse voltage calculation of electronic TOF mobility. It is helpful to understand the dynamics of the carrier transport in organic semiconductors.

The time delay is inversely proportional to the mobility in the organic layer. Calculations were done at room temperature. Transit time is:

$$t = \frac{L^2}{\mu V_0} \quad (16)$$

Fig. 2 shows the current density versus time in a trap-less system. The sample length is 1 μm and applied voltage is 100 V. Subscribe a linear rise from zero to maximum of the pulse voltage we have calculated the transient response. Defects and impurities, which lead to carrier localization, play a main role in the transport of charge carriers in organic materials.
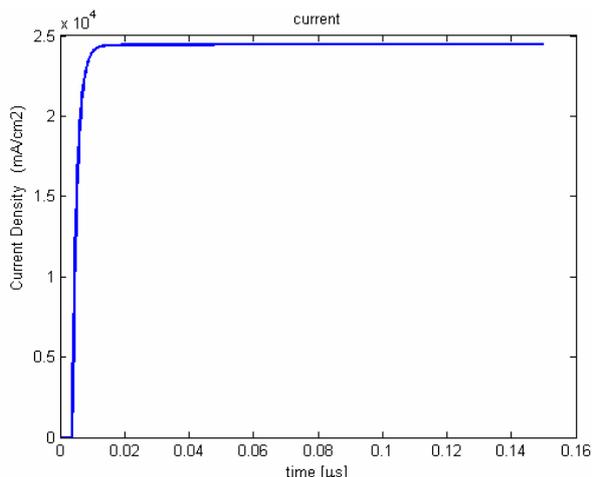
Fig. 2 current density in simulation of transport of carriers along the organic layer (*L*=1 *μm*)

The qualities density of states forms a band tail into the band gap. The effect of localized states is to slow down the carriers; therefore the response of the pulse voltage can also be attended to be slowed down by the presence of traps [11].
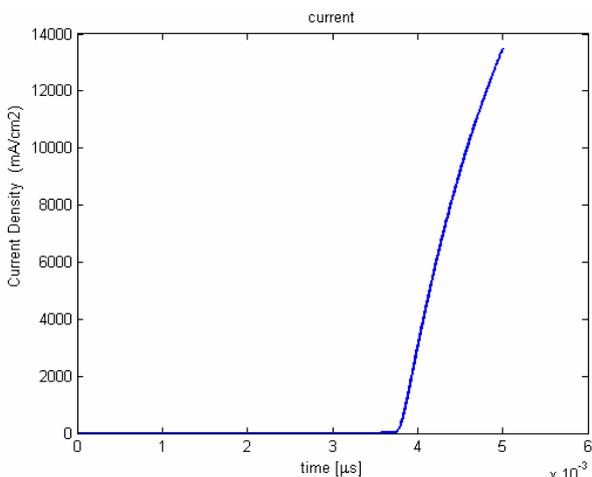

Fig. 3 current density in simulation of carrier transport along the organic layer with single trap level (*L*=1μm)

Fig. 3 shows the effect of a finite rise time on the primary delay, which represents the transient reply in the presence of a single trap, while the lifetime of the carriers is about 5-10 nanosecond. It can be seen that lifetimes should be larger than or equal to the delay time. Since the holes are transported among the layer before they can get trapped. The steady state current decreases as the lifetime is decreased because of the decline in the number

of carriers those chips in to conduction by trapping.

The pulse voltage response is shown in Fig. 4 (a) ahead the organic layer with TOF configuration. It shows by increasing the layers width that the pulse voltage decays and shows a linear profile before it reaches the cathode electrode. Fig. 4 (b) shows the voltage distribution along the layer at intervals of 10 nanoseconds. Fig. 5 shows hole concentration along the organic layer.
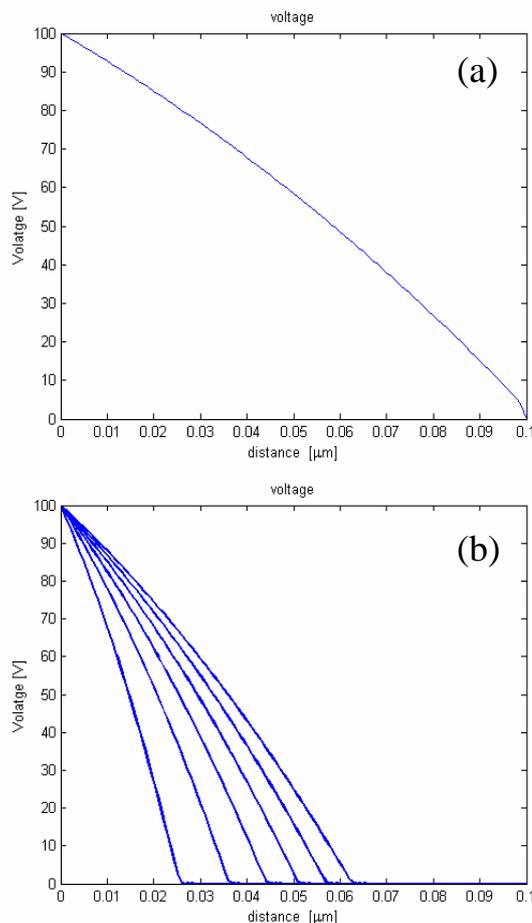

Fig. 4 (a) Voltage behavior simulation of transport of carriers along the organic layer (*L*=1 μm). (b) Voltage distribution along the layer in intervals of 10 ns.

In Fig. 6 an increase in mobility of carriers with increasing voltage between electrodes is been observed and explained in terms of multiple trap and release (MTR) with a distribution of traps located in the cathode electrode. The TOF mobilities are plotted

against the square root of average electric field in the layer. As it is observed in Fig. 6, for higher electric field existing in the layer (blue line), the mobilities tend to increase with applied voltage. So it can be derived that mobility increases proportionally to the square root of the electric field. This emphasizes the Poole-Frenkel effect.
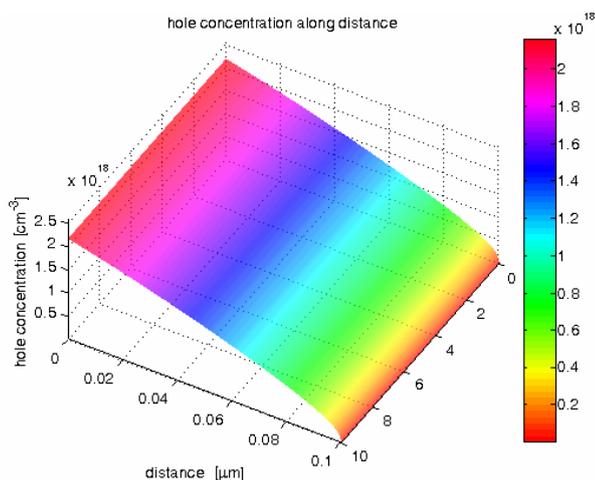

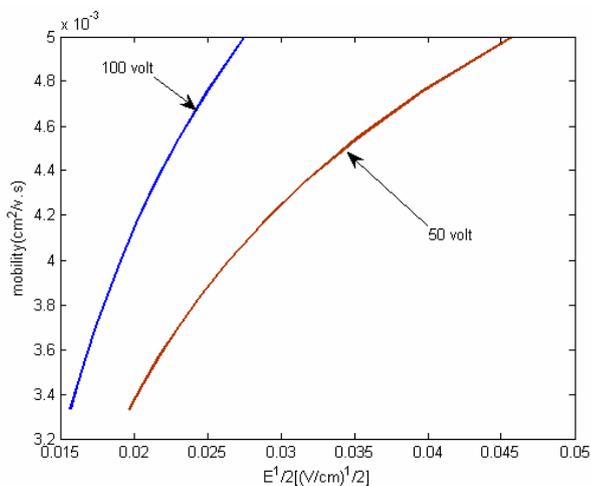Fig. 5 Hole concentration along the organic layer (L=1 μm)

Fig. 6 Transient TOF mobility as a function of the electric field

IV. CONCLUSION

In this paper we discussed theoretically the method to take the drift mobility of holes in an organic layer. This method is based on the application of a step voltage at the first contact and calculating the delay time in the injected carriers at the second electrode. This technique is an easy way to determine the mobility. TOF calculations were carried in organic layers and

it was seen that at higher applied voltage, 100 V, hole mobility increases rapidly in comparison with lower applied voltage (50 V).

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Ali Mahmoudloo is a PhD student of photonics in Tabriz University. Since 2010 until now he is working on Study of charge carrier in organic semiconductor systems and their applications.

Sohrab Ahmadi-Kandjani is associate professor of photonics in Department of photonics, University of Tabriz. He is a member of Iranian Society of Physics and Optics and Photonics Society of Iran. Nonlinear optics, Organic Solar cells, Organic Light Emitting Diode and Organic Electronics are some of his research areas.

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