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Transient Trap-Limited Field Dependence Charge Carrier Transport in Organic Semiconductors for Time of Flight Configuration

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Abstract Organic semiconducting polymers are for use in low cost electronics and photovoltaic application has technological and scientific interest in organic materials. In this paper we use the time of flight of a charge packet injected by a voltage pulse to calculate the drift velocity and mobility of holes. This technique is based on the application of a voltage applied at the anode and calculating the delay time in the appearance of the injected carriers at the other contact. This method is a simple way to determine the charge transport properties of the organic semiconductors .The effect of charge trapping mechanism on the carrier mobility in the organic layers are investigated and we discussed the theory of a electronic method to obtain the drift mobility of holes in an organic layer. Finally time of flight calculations were done on organic layers and it was observed that the mobility reduces at low electric field.

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1. INTRODUCTION

Organic semiconductors share common features. All are van-der-Waals bonded crystals, where the intermolecular interactions are much weaker than the intramolecular bonds. With van-der-Waals distances of the order of 3.8 to 4Å, individual molecules are well separated. 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 in inorganic materials, and the thermal expansion coefficients tend to be larger. [1]

Organic semiconductors mainly come in two varieties: Small molecules and polymers. Small molecules as the name suggests are relatively small molecular weight molecules with conjugated carbon atoms. These substances can be prepared as molecular single crystals. Due to the close coupling of the π-systems of the molecules in these crystals, in a purified form remarkable transport properties with mobilities of 1-10 cm^2/vs. Most molecules can be easily evaporated to form polycrystalline layers. Organic semiconducting polymers are long chain of conjugated carbon atoms when composed of smaller repeating units called monomers. The advantage of polymers is that, when modified with suitable side chains, they can self organize when deposited from solution at room temperature yielding a fairly high mobility layer, hence they can be used to print circuits at a low manufacturing cost. [2]

It is important to measure the fundamental limits of the charge carrier mobilities in organic semiconductors in order to develope the organic electronics. Although devices such as OFETs*, OTFTs† and OLEDs‡ are already used in commercial applications. There is still no complete understanding of the final limitations of performance and stability in these devices at this time. It is necessary to determine the electronic properties in organic semiconductors for being able to grow ultra-pure, fully ordered molecular crystals for measurements of intrinsic charge transport. The organic crystals show mobilities as high as amorphous silicon. Dislocations and grain boundaries, which may limit charge transfer, are important in these crystals [3]. Thermal expansion has to be taken into account when devising crystal growth procedures, since the (often anisotropic) expansion tensor

* organic field effect transistors
† organic thin film transistors
‡ organic light emitting diodes

produces large stress/strain fields in the presence of temperature gradients. Charge carrier transport in organic semiconductors is a research for over three decades. Most important features of the charge transport directly follow from the basic structural features of organic glasses .These glasses are molecular materials with rather weak interactions between molecules and, at the same time, they have significant 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 the hopping transport the disorder in the material is the most important. [4]

The charge transport properties of homogenous amorphous organic semiconductors are studied. Such phenomenon has been reported previously for a variety of amorphous charge transport materials, but not clearly observed in conjugated semiconducting polymers. [5, 6]

2. Theory and numerical calculation

The key of charge transport and other optoelectronic properties in organic disordered semiconductors ,such as conjugated and molecularly polymers is its energy spectrum, also called DOS[§].Therefore, the only way to determine the DOS is to compare experimental data with the appropriate theory using some trial DOS function, $g(\varepsilon)$, aiming at the best agreement between experimental and theoretical results, it has been recognized in time-of-flight studies that the DOS in such systems is close to a Gaussian one, $g(\varepsilon) \propto exp[-(\varepsilon/\sigma)^2]$. [7, 8]

In charge transport simulation the ideal condition do not exist because, firstly there is always a finite amount of rise time for the pulse to go to its maximum, secondly the mobility of an organic semiconductor is dependent on a variety of condition including the local field and the charge concentration etc .Thirdly traps in an organic semiconductor dominate transport, and finally non-ideal injection from contacts can adversely affect transport of charge carriers.

In disorederd organic systems, charge transport occurs 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:[9]

§ density of states

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

where N is the total concentration of localized states and σ is the energy scale of the order of 0.1 eV [10].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 described by the Miller-Abrahams expression:[11]

$$\nu_{ij} = \nu_0 \exp\left(-\frac{2r_{ij}}{a}\right)\exp\left(-\frac{\varepsilon_j - \varepsilon_i + |\varepsilon_j - \varepsilon_i|}{KT}\right) \quad (2)$$

Where a is the localization length, which is assumed equal for sites i and j,and the pre-exponential factor $\nu_0 \approx 10^{12} s^{-1}$ depends on the interaction mechanism that causes transitions.[12]

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 uncorrelated jumps is called hopping transport. The hopping mobility can be written as. [13, 14]

$$\mu = \frac{ea^2}{KT} P \quad (3)$$

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 detrapped and hop from one state to another until it encounters another trap state. As the name suggests the transit time for time-of-flight mobilities is controlled by the concentration of traps and therefore it follows an exponential dependence to the concentration of traps as given in Equation (11).

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

Where ρ denotes the concentration and ρ_0 is the spatial distribution of charge density outside a molecule, also known as its localization radius.
In the MTR model [**] a majority of the carriers injected into the semiconductor are trapped into states localized in the forbidden band. Carriers undergo thermal detrapping and get excited into mobile states where they participate in conduction, until they come across a defect site and get localized into 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 is varies slowly with temperature. [15, 16]

$$\sigma = e.n_f.\mu_0 \quad (5)$$

where e representes the electronic charge. θ is a parameter representing the fraction of free carriers,and introduced as:

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

where n_{tot} is the total(free plus trapped) density of charges, equation (6) can be rewritten as

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

Equation (7) shows that a thermally-activated conductivity can be interpreted by a thermally activated charge density.
The success of the MTR model lies in its ability to explain temperature and voltage dependence of mobility. However it often yields unnaturally high values of traps density states. This is because the multiple trap and release model is valied

[**] multiple trap and release model

only for a trap distribuation consisting of a shallow distinct energy level close to the main transport band.

We used TOF technique as a model to calculate the drift mobility in organic layers .It involves the injection of carriers at the anode electorde followed by their subsequent extraction at the collector electrode .The delay between the two events is used to extract the velocity of the carriers. When 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 at ground. The carriers are injected from the contact at higher potential, so that the exiting carrier current produces a voltage that can be used to identify the time of their transit. Also in this model the higher potential is applied to the first electrode and the second electrode is connected to ground. Therefore the variation of TOF mobility with pulse voltage can be due to the dependence of mobility on the anode-cathode bias. This model is deals with the time dependent carrier distribution $\rho(x,t)$ flowing through the two electrodes with the distance $x = L$ from each other and we consider a organic semiconductor film with a a slice on infinitesimal thickness dx as shown in figure .The current is flowing between the circuit due to hole transport across the sample alone.

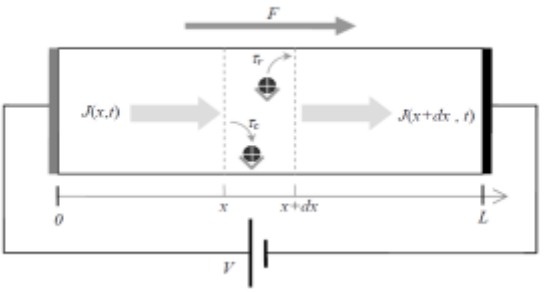

Fig.1. current is flowing between the circuit due to hole transport across the sample

The number of holes in the slice may increase either due to the net flow of holes into the slice, or a net thermal release of the trapped charge carriers within the slice. The effect of recombination is ignored in the sample. Equation (9) shows the rate of change in the number of free holes in the slice is: [17, 18]

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

where $p(x,t)$ 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

$$J(x,t) = -\mu e p\frac{\partial V}{\partial x} - eD\frac{\partial p}{\partial x} \quad (9)$$

$$\frac{\partial J}{\partial x} + \frac{\partial \rho}{\partial t} = 0 \quad (10)$$

The conduction current density for holes is expressed as

$$J(x,t) = -\mu e p\frac{\partial V}{\partial x} - eD\frac{\partial p}{\partial x} \quad (11)$$

In above equation drift of the charge carriers under the influence of applied bias has more contribution than the charge carrier diffusion $J_{Drift} \gg J_{Diff}$

$$J = -\mu e p\frac{\partial V}{\partial x} \quad (12)$$

By eliminating J from equations (10, 11)

$$\frac{\partial}{\partial x}(\mu.p\frac{\partial V}{\partial x}) = \frac{\partial p}{\partial t} \quad (13)$$

Where μ by the Pool-Frenkel behavior the mobility of an organic semiconductor, under high fields given as

$$\mu = \mu_0 \exp(\frac{\beta\sqrt{F} - \Delta}{kT}) \quad (14)$$

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 [19] .The expression of field dependence of mobility given in above equation . The value of β is about $10^{-5} - 10^{-4} eV/(V/cm)^{1/2}$

By putting the field dependence of mobility equation (13) in equation (12), we get the field dependent transport equation:

$$\frac{\partial}{\partial x}(\mu_0(\frac{\beta(\frac{\partial V}{\partial x})^{\frac{1}{2}}}{KT})V\frac{\partial V}{\partial x}) = \frac{\partial V}{\partial t} \quad (15)$$

In this calculation the room temperature transient time is supposed with β varying between $10^{-5} - 10^{-3} eV/(V/cm)^{1/2}$ the result of shown in figure (2).

We have used a simple model consist a single trap level characterized by a carrier lifetime τ. [20]

The current equation is:

$$\frac{1}{e}\frac{\partial J_P}{\partial x} + \frac{\partial P}{\partial t} = \frac{p - p_0}{\tau} \quad (16)$$

Applying this model, the simulation results is shown in Figure (3). As it can be seen, since the time delay is increased by the presence single trap level, mobility is reduced.

3. Results and Disscussion

Equation (12, 13) provides an approximate solution to problem of pulse voltage measurement of electronic TOF mobility .It is helpful in understanding the dynamics of the carrier transport in organic semiconductors.

The time delay is inversely proportional to the mobility of the organic layer .Calculation were done at room temperature. Transient time is:

$$t = \frac{L^2}{\mu V_0} \quad (17)$$

β is varying between $10^{-5} - 10^{-4} eV / (V / cm)^{1/2}$.

Figure (2) shown the current density vs time in a trapless system. The sample length is 1 micrometer and applied voltage is 100 volte. The electric field isn't also high enough to cause appreciable difference .Hence the delay time is given by the zero field mobility of the semiconductor .Defect and impurities, which lead to carrier localization play a major role in transport of charge carriers in organic materials.

The density of state trial into the forbidden gap forming a band tail .The effect of localized states is to slow down the carriers, therefore the response of the pulse voltage can also be exected to be slowed down by the presence of traps.

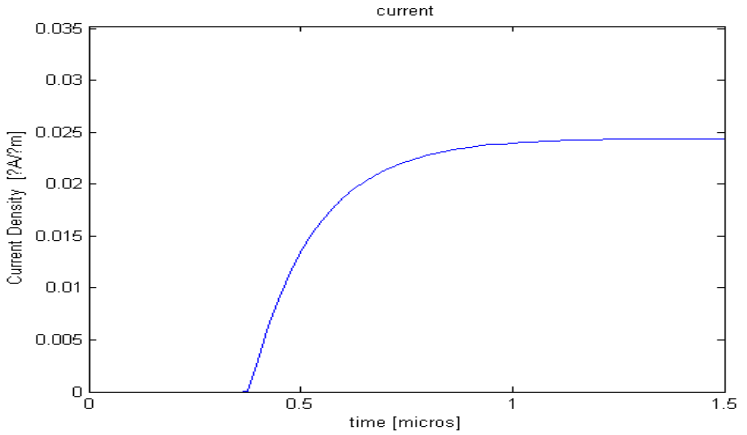

Fig.2.current density of transport of carriers along the organic layer (L=1 μm)

Figure (3) represents transient response in the present of traps which carriers is delay time for reach to second electrode .This is because the holes are transported across the layer before of the trapped .The steady state current decreases as the lifetime is reduced because of the reduction in the number of carriers that conduction by trapping. The result for multiple with finite number of trap levels would be similar with the lowest lifetime trap level dominating the transport.

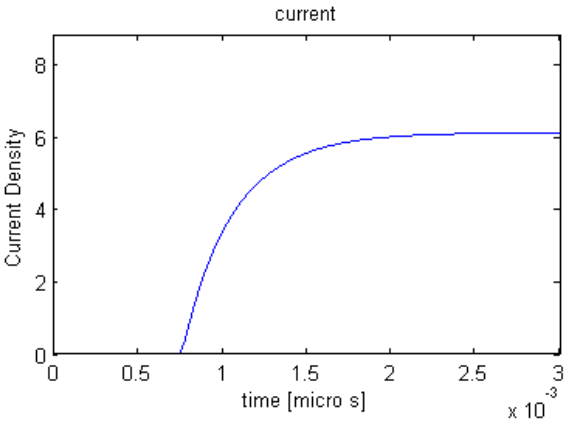

Fig.3.current density in simulation of transport of carriers along the organic layer With single trap level (L=1 μm)

The pulse voltage response is shown in figure(4) along with the pulse voltage applied to the electrodes.The graph of transient TOF mobility transient mobility show an increasing tend to voltage of the pulse

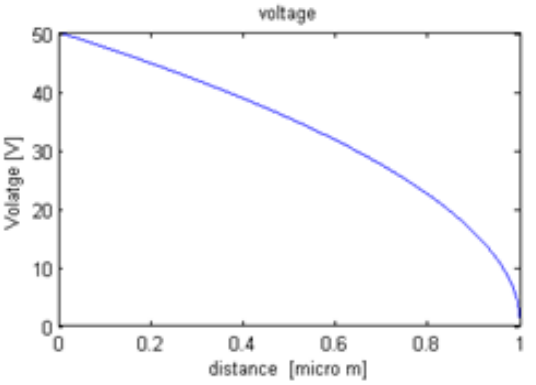

Fig.4.voltage behavior simulation of transport of carriers along the organic layer (L=1 μm

We also have simulated the transport it will be seen that the approximation is justified dut to the linear profile of the voltage distribution after it reaches the collector electrode, see figuree (5).

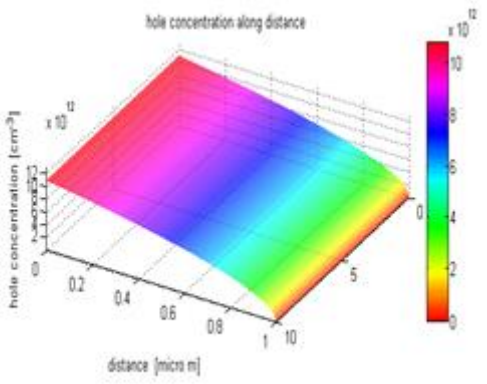

Fig.5.hole concentration along the organic layer (L=1 μm)

An increase in mobility of carriers with increasing voltage of between electrods has been observed and explained in terms of multiple trap and release (MTR) with a distribution of traps located in the cathode boundaries. It can be seen from figure (6) that the drift mobility increases with the voltage of the pulse applied.

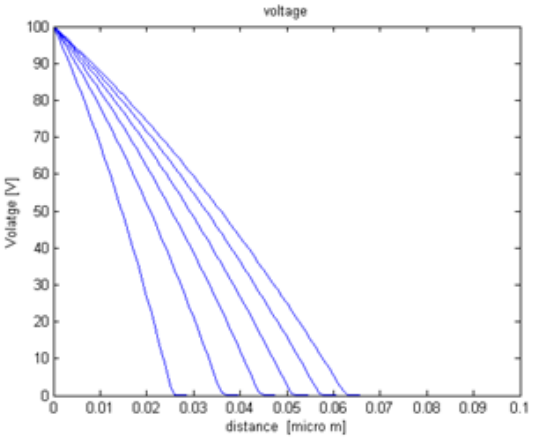

Fig.6.the voltage disturbution along the layer in interval of 10 nanoseconds

An increase in mobility of carriers with increasing voltage of between electrods has been observed and explained in terms of multiple trap and release (MTR) with a distribution of traps located in the cathode boundaries. It can be seen from figure (7) that the drift mobility increases with the voltage of the pulse applied.Thus the increased in mobility with pulse voltage observed can be effect of anode – cathode voltage.The result were explained within the framework of the disorder transport formalism.

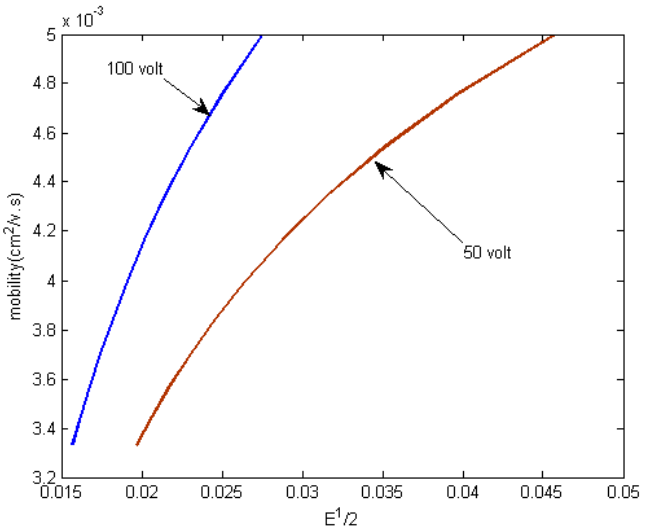

Fig.7. Transient TOF mobility as a function of the electric field

4. Conclusion

In this paper we discussed the theory of a electronic method to obtain 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 and this technique is a easy way to determine the mobility .Finally TOF calculations were done on organic layers and it was observed that the mobility reduces at low electric field.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this manuscript

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