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CARRIER MOBILITY IN ORGANIC SEMICONDUCTOR THIN FILMS

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Abstract. Carrier mobility is an important parameter in determining device performance in electronics and the values of the electron and hole mobilities for organic semiconductor thin films are known to be rather low. This work studied some reported data on electron and hole mobilities in the literature and analyzed them using a barrier height modulation model and the better known "disorder" model. Our results indicated that the physics behind the two models could be correlated and both pointed to some limiting values pertaining to the localization of the carriers. By comparing the results with an evaluation of the potential profiles across a given cross section of the monomer backbone (for OC_1C_{10}PPV) with different subgroups, we were able to deduce that the "localized" states were not directly associated with the energy bands. This provides an opportunity to increase the carrier mobility to its upper limit by applying a transverse bias.

1. INTRODUCTION

A number of papers [1-3] have appeared recently reporting the evaluation of carrier transport parameters in organic semiconductor thin films with the objective of improving the understanding of the luminescent and current conduction properties. Of the different transport parameters evaluated, carrier mobility stands out to be particularly intriguing in view of its "unusual" dependence on electric field and temperature. The most common reason put forward to explain such dependence is the inherent disorder found in the thin films [4], and in many instances, the fact that carrier transport frequently involves trap/localized states. Methods such as time of flight measurement [5] and impedance spectroscopy [6] have been used to minimize effects such as dispersion, and most results pointed to a conduction mechanism linked to space charge limited current at low bias. At moderate field strength, trap-related carrier transport had been proposed [7] and this was correlated to the exponential square-root (electric) field dependence.

Models have also been put forward to compute parameters such as: the density of states function in the presence of traps [8]. Such computations however were cumbersome and it was difficult to extract accurately unknown physical parameters appearing in the model equations. This work examined mobility data recently reported in [9, 10] and analyzed them based on two known physical models: one related to barrier height modulation [11] and the other to "disorder" [4]. Interesting enough, the mathematical expressions resulting from applying these two models appeared quite similar in form. To a good extent, one could even correlate the physics. Based on these models, an analysis was made on the projection of the limiting values of the carrier mobilities for these materials at very low field, and suggestions were made as to how to increase the carrier mobilities in the disordered structure.

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Table 1. Values of μ_0 and α from [9].

Rate of Deposition, nm/s	μ_0, $cm^2/V{\cdot}s$	α, $(cm/V)^{1/2}$
0.2	$3.04{\cdot}10^{-7}$	$9.22{\cdot}10^{-3}$
0.4	$1.80{\cdot}10^{-8}$	$10.2{\cdot}10^{-3}$
0.7	$2.97{\cdot}10^{-9}$	$11.0{\cdot}10^{-3}$

2. PREVIOUS WORK

Data were taken from work by Chen *et al* [9] which provided values of the electron mobility for tris(8-hydroxyquinolinolato) aluminum (Alq_3) thin films and their devices had a configuration of ITO/NPB/Alq_3/Mg:Ag. For comparison, we also took data from Martens *et al* [10] for OC_1C_{10}PPV thin films deduced from J-V characteristics. In [9], the only process variation was the deposition rate of Alq_3, which varied between 0.2 to 0.7 nm/s. Electron mobility data for these thin films were determined using time of flight method and J-V curves. The mobility data reported in both cases were found to be field dependent and have the following form:

$$\mu=\mu_0 \exp(\alpha E^{1/2}), \qquad (1)$$

where μ_0 is the zero field mobility, α is an unknown parameter, and E is the electric field.

Values of μ_0 and α extracted from measurements [9] at the different film deposition rates for Alq_3 are listed in Table 1.

Hole mobility for OC_1C_{10}PPV thin films were obtained from J-V characteristics [10]. Different subgroups were attached to the polymer backbone. Fully and partially conjugated structures were also constructed. The mobility data for the different conjugated and partially conjugated structures as shown in Fig.1 are summarized in Table 2.

The symbols for the above parameters have the following meaning: μ_∞ is the hole mobility when

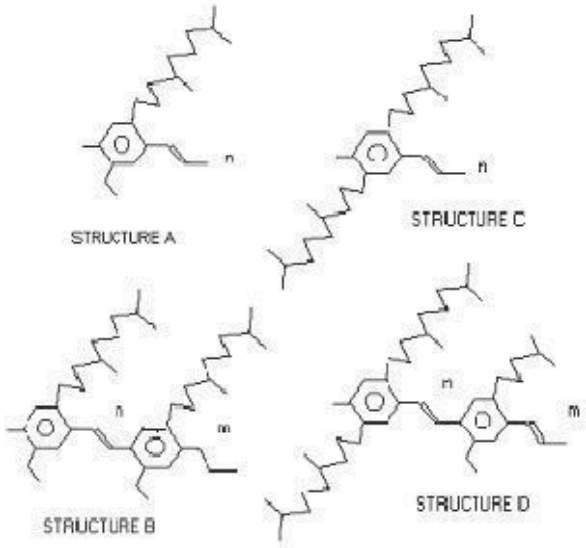

Fig.1. Different conjugated and partially conjugated OC_1C_{10}PPV [10].

$T \to \infty$ and $E \to 0$; σ is the width of the Gaussian DOS (density of states); C is a constant; a is the site spacing; and L is a localization length.

3. THEORY AND ANALYSES

To model carrier transport in organic semiconductor thin films, we assume that the current density J at reasonable field strength can be expressed in terms of an effective carrier density $n_{effective}$ and a velocity parameter v (this is usually the parameter measured by the time of flight method) which controls the movement of the carriers. Thus,

$$J = n_{effective} q v, \qquad (2)$$

where q is the electron charge.

Since by definition $v = \mu E$, where E is the electric field, Eq.(2) when combined with Eq.(1) becomes:

$$J = n_{effective}\, q\mu_0 \exp(\alpha E^{1/2})\, E. \qquad (3)$$

Table 2. Transport parameters obtained from conjugated and partially conjugated OC_1C_{10}PPV with different subgroups [10].

	μ_∞, $cm^2/V{\cdot}s$	σ, meV	C, $(cm/V)^{1/2}$	a, nm	L, nm
Structure A	5.1×10^{-5}	112	4×10^{-4}	1.2	0.3
Structure B	4.0×10^{-6}	121	4.3×10^{-4}	1.7	0.3
Structure C	1.6×10^{-3}	93	3.8×10^{-4}	1.1	0.5
Structure D	1.5×10^{-3}	99	4.0×10^{-4}	1.2	0.5

Eq.(3) allows one to determine $n_{effective}$ if J, μ and E are known. Generally speaking, $n_{effective}$ may not be the same as the "free" carrier density. To evaluate μ_0, we assume that the carriers move between trap states in the organic semiconductor and the amount of time they spend in the traps gives rise to a "reduced" mobility. For trap states with a barrier height equal to Φ_B, the current density has the form:

$$J = n_{effective}\, q\mu' \exp(-\Phi_B/E_\infty)\, E, \qquad (4)$$

where μ' and E_∞ are unknown constants.

Physically, Φ_B defines the average energy required for a carrier to escape from a trap, and E_∞ is a measure of the effectiveness of the carrier escape process (in energy unit). A large E_∞ will enhance the carrier escape process. In the presence of space charge near the trap, it is possible to include a barrier height modulation term due to the image effect [11] which would reduce Φ_B (in Eq.(4)) to $\Phi_B - \Delta\Phi$, where $\Delta\Phi = q(qE/4\pi\varepsilon_s)^{1/2}$. Taking into account this barrier height lowering effect gives:

$$J = n_{effective} q\mu' \exp\left(-\frac{\Phi_B}{E_\infty}\right) \exp\left[q\left(\frac{qE}{4\pi\varepsilon_s}\right)^{1/2} / E_\infty\right] E$$
$$= n_{effective} q\mu_0 \exp\left(\alpha E^{1/2}\right) E \qquad (5)$$

where $\alpha = q(q/4\pi\varepsilon_s)^{1/2}/E_\infty$ and $\mu_0 = \mu' \exp(-\Phi_B/E_\infty)$.

According to Eq.(5), Φ_B can be deduced from a plot of $|\ln(\mu_0)|$ versus $1/|E_\infty|$, where $|E_\infty| = q(q/4\pi\varepsilon_s)^{1/2}/\alpha$. For this calculation, we assume $\varepsilon_s = 2.5\varepsilon_0$ and a plot of $|\ln(\mu_0)|$ versus $1/|E_\infty|$ for electrons based on the data in Table 1 is shown in Fig.2 (Legend: Alq3).

An approximately linear relationship is observed giving a barrier height Φ_B of 0.615 eV. This value does not match any of the interface barrier heights appearing in the band structure of this device [12] suggesting that it is not linked to direct transition involving normal band states. The low field mobility μ_0 is inherently temperature dependent and is often expressed as the product of a temperature independent parameter μ_∞ and a temperature dependent term $\exp(-\Delta/kT)$ [13]. Δ is a form of activation energy and kT is the thermal energy. μ_∞ will therefore be the limiting value of μ_0 at high temperature assuming Φ_B/E_∞ is temperature independent.

Other authors [4] have proposed models for the carrier mobility based on the existence of "localized" states. In [10] for instance, the authors used the following expression for the low field carrier mobility ($T \to \infty$):

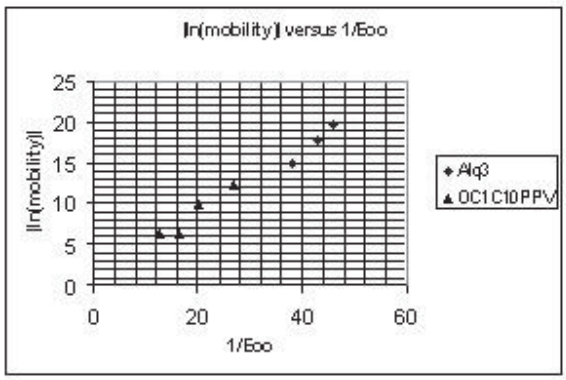

Fig.2. A plot of $|\ln(\mu_0)|$ or $|\ln(\mu_\infty)|$ versus $1/|E_\infty|$.

$$\mu_\infty = qa^2\nu_{ph}\frac{\exp\left(-\frac{2a}{L}\right)}{\sigma}, \qquad (6)$$

where a is the site spacing; ν_{ph} is the attempt frequency for hopping; L is a localization length; and y is the width of the Gaussian density of states (DOS).

Note that $\mu_0 = \mu_\infty$ when $T \to \infty$ and within this limit one may compare Eqs.(5) and (6). This results in the following equalities:

$$\frac{\Phi_B}{E_\infty} = \frac{2a}{L},$$
$$\frac{qa^2\nu_{ph}}{\sigma} = \mu'. \qquad (7)$$

Physically, the first equality may be viewed as two different ways to express the "obstacles" (either in terms of energy or distance) presented to the stressed carriers *vis-à-vis* their tendency to "escape" the obstacles. To first order, these ratios are considered temperature independent. The second equality aims at defining the mechanism for the "escape" process, which favors larger site spacing and less "disorder" (which increases with σ). In the limit when the site spacing is sufficiently large, a approaches the value of the mean free path λ. If we were to replace λ by $\tau\nu_{th}$ (where τ is the mean free time, and v_{th} is the thermal velocity) and σ by $m^*v_{th}^2$ (where m^* is a mass parameter), $qa^2\nu_{ph}/\sigma$ becomes: $q\tau/m^*\cdot\tau\nu_{ph}$, which implies a reduction to the "normal" mobility through the factor $\tau\nu_{ph}$. The product $\tau\nu_{ph}$ (expected to be small in the presence of traps) imposes an upper limit to the value of μ_∞.

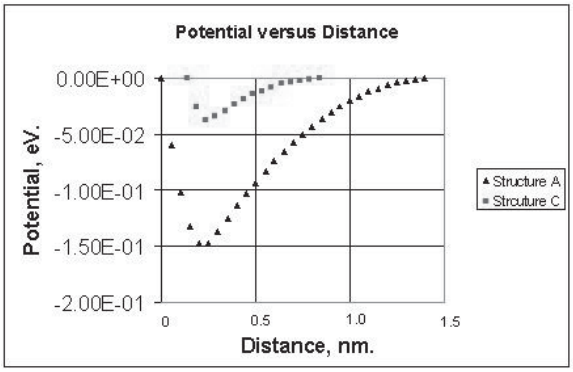

Fig.3. Potential profiles for Structure A (asymmetric) and Structure C (symmetric).

Since $1/|E_8|$ is associated with α, one can use α (in [10]: it is denoted as γ) to compute $1/|E_\infty|$. A plot of $|\ln(\mu_\infty)|$ versus $1/|E_8|$ for OC_1C_{10}PPV thin films is shown in Fig.2 (Legend: OC1C10PPV). As observed, the curves generated from data for Alq_3 and OC_1C_{10}PPV thin films have similar slopes indicating possibly identical carrier "escape" processes. The *y*-intercepts are also close by. When $|E_\infty|$ is large, for the conjugated and partially conjugated OC_1C_{10}PPV thin films $|\ln(\mu_\infty)| \approx 0$, or $\mu_\infty \sim 1$ cm^2/V·s. The low field mobility μ_0 (= $\mu_\infty \exp(-\Delta/kT)$) is expected to be lower. For the Alq_3 thin films, the limit for $|\ln(\mu_0)|$ is larger, suggesting potentially higher carrier mobilities (note that both $\ln(\mu_\infty)$ and $\ln(\mu_0)$ are negative for the data appearing in the two tables).

An attempt has been made to examine if "localized" states in organic semiconductors are associated with the energy bands. This was done by comparing the potential change in barrier height Φ_B encountered by carriers in Structures A and C shown in Fig.1 (whose parameters are listed in Table 2) with the change in the potential minimum caused by the different subgroups attached to the monomer. Assuming that the OC_1C_{10}PPV backbone is slightly negatively charged and the subgroups are slightly positively charged, one could estimate the band bending in a cross-section. Using appropriate values of the physical dimensions for the back bone and the subgroups, we arrived at a ratio of the negative space charge density to the positive space charge density given by: qN_a/qN_d = 4.184. Fig. 3 shows the band bending for Structures A and C when $qN_a = 4 \cdot 10^{-7}$ C·m^{-3} (this corresponds to a very small amount of space charge) [14]. The observed energy difference between the two potential minima is approximately 0.1 eV.

Using Eq.(5) and assuming no major variations in the parameters for $\mu' = qa^2\nu_{ph}/\sigma$ and a value of α = 0.00081 (for Structure A [10]), the computed change in the potential minima for the two structures was 0.102 eV. This is very close to the value of 0.1 V shown in Fig. 3. Assuming that the space charge mentioned earlier exists, the implication here would be that the "localized" states may not be associated with the energy bands and any shift in the energy bands (say, through a transverse bias) could potentially be used to increase the carrier mobility through a reduction of the barrier height for the "localized" states. This technique if applicable would be very effective in minimizing the effect of traps in disorder materials.

4. CONCLUSIONS

We have examined carrier mobilities reported in the literature and analyzed them [9,10] in terms of a barrier height modulation model and the "disorder" model. Clearly, there are similarities in the two models with respect to the effect of localization and disorder in the organic thin films. An examination of the low field mobility brings forth the notion that even with small disorder (small σ or large E_∞), a limiting mobility exists and the value is expected to be higher in Alq_3 when compared with OC_1C_{10}PPV. This mobility limit may be linked to the product of $\tau\nu_{ph}$, (the ratio between the carrier mean free time and their escape delay). A separate investigation into whether localization states in organic thin films are associated with the energy bands suggested little evidence that they are. This was demonstrated by the fact that a computed shift in the band structure due to a change in the charge state of the subgroup correlates closely with the computed change in the barrier height (for traps) based on the different values of μ_∞. Such an observation suggests the possibility of improving the value of the carrier mobility in a disorder semiconductor by imposing a transverse bias.

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