Modeling Hole Transport Mechanism in an Organic Photoconductor

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Abstract

Hole transport mechanism of the HP-Indigo organic photoconductor (OPC), is measured using the time-of-flight (TOF) technique. Transport is analyzed and found to be Gaussian throughout the whole temperature range, indicating the absence of deep traps in this material. Hole mobilities and diffusion coefficients are obtained as separate parameters for the various external fields and temperatures measured, and functional dependencies on these parameters are determined. Diffusion coefficients are found to grow with the electric field at much greater rates than mobilities, so that Einstein relation is violated. A relation between diffusivity and mobility is proposed for this MDP which displays dispersive Gaussian transport. The transient photocurrents are calculated by a one-dimensional Brownian motion model with reflecting and absorbing boundaries which fit the experimental results.

The dependencies of mobilities and diffusion coefficients on temperature and electric field are further used to numerically calculate xerographic discharge curves (V-light decay) which show good fitting to those measured on HP-Indigo's machines. This work can be further extended to several directions in order to describe processes affecting printing. Examples are: lateral conductivity, dot gain (2D), dark decay, and residual effects (V-light degradation) which can be studied by simulating cyclic repeating process of charging and discharging the OPC.

Introduction

Organic semiconductors are a topic of intensive research due to their application in various electronic devices. In electrophotography the rate of charging and discharging of an organic photoconductor (OPC) influences directly the minimal printing time required and effects seen upon printing [1]. Quantifying charge carrier transport is important in order to determine machine performance and print quality. Therefore, detailed investigation of the microscopic parameters that influence charge carrier motion as well as the development of techniques that permit its determination are of great importance. The most common experimental technique used to measure charge transport in OPCs is Time of Flight (TOF) [2]. The OPC is placed between two blocking electrodes and is initially charged so a capacitor is formed with an applied uniform electric field. A short monochromatic pulse of light is flashed upon the sample through one electrode which is semi-transparent. The induced photons create electron-hole pairs in the OPC which are swiftly pulled apart by the external field. Holes travel along the bulk of the sample over a distance of several micrometers until they discharge the exit electrode. Their transport through the OPC produces a displacement current which can be measured in an external electrical circuit. By the signal shape and magnitude we can determine hole transport parameters and study transport mechanism [3]. A TOF experiment is similar to the imaging step of the xerographic process, except that in the former the number of charge carriers is much smaller than the charge on the electrodes so that they scarcely perturb the external field [4].

Ideally (as in crystalline semiconductors [2]), a well-defined sheet of charges moves at a constant velocity across the sample thus creating a plateau in the current. The current falls off to 0 at the *transit time* t_τ, when the charge carriers arrive at the exit electrode. In an actual experiment, however, due to the system's finite temperature, diffusion is superimposed upon the drift. The charge packet progressively spreads out about its mean position during motion, and due to this *normal* or *Gaussian diffusion*, the transient current $I(t)$ shows a rounded fall-off near t_τ. For many amorphous organic and inorganic semiconductors a quite different behavior is observed [5] as the current decreases continuously up to very long times. In a double logarithmic plot two slopes are observed demarcated at an effective transit time. Such a current implies that drifting carriers slow down continuously and the spread of their arrival times is much greater than expected from conventional diffusion theory, i.e. *diffusion* is *anomalous* or *dispersive*.

HP-Indigo's OPC consists of two-layers: a thin Charge Generating Layer (CGL) of organic pigment combined with a thicker charge transport layer (CTL) which has good ability for hole transfer. The CTL is fabricated from a molecularly doped polymer (MDP); a solid solution of Charge Transferring Molecules (CTM) of hydrazone based organic molecules dispersed in an inert polymeric binder of polycarbonate. Absorbed laser light creates electron-hole pairs in the CGL. Holes generated close to the CTL boundary initiate transport process by an electron transfer from a neutral molecule in the CTL to a photoexcited hole in the CGL and this is followed by a field-driven chain of electron transfer events from neutral molecules to their radical cation derivatives, i.e. conduction occurs by a *hopping mechanism*. Charge transport in MDPs has been the subject of numerous investigations [1-4]. The mobility depends on the electric field, temperature, dopant concentration and the dopant molecule. In many MDPs dispersive transport is not correct and in some there is a transition between the two behaviors by changing the temperature [8]. Many models have been developed to describe the charge carrier transport mechanism including the Poole-Frenkel (PF) model, Polaronic models, Gaussian Disorder Model (GDM) and the correlated Gaussian disorder model [1-4]. However, the dependence of transport on external parameters is not fully understandable in terms of any available model.

In this paper we report a study of hole transport in HP-Indigo's OPC by the TOF experiment. We show by the method of

analysis proposed by [6] that the transient is non-dispersive and extract mobilities and diffusion coefficients. The functional dependencies of these parameters on temperature and electric field are studied and hole transport mechanism is proposed. The TOF signal is retrieved from the transport data both analytically and numerically. The transport parameters are further used to simulate the xerographic process (V-light decay). These results can be extended to obtain other processes occurring during printing such as residual effects upon subsequent charging and discharging of the OPC. Also 2D effects such as dot-gain can be simulated once transport parameters are known.

Experimental

A sample configuration of the OPC is shown in Figure 1. A thick layer (~70μm) of Mylar serves as a substrate and a film of an Al electrode (~0.5μm) is deposited on the Mylar. The CGL (~0.5μm) and CTL (L~18μm) are spread coated on the Al electrode. The doping concentration of the CTMs in the CTL is 30% by weight. A top conductive and semi transparent gold electrode (~0.1μm) is spattered on the CTL, and finally silver paint is padded for electrical conduction. The sample is connected to a resistor and is used as a capacitor in an RC circuit. The product RC~3μsec is much smaller than the transit time t_τ which is in the order of 1$msec$.

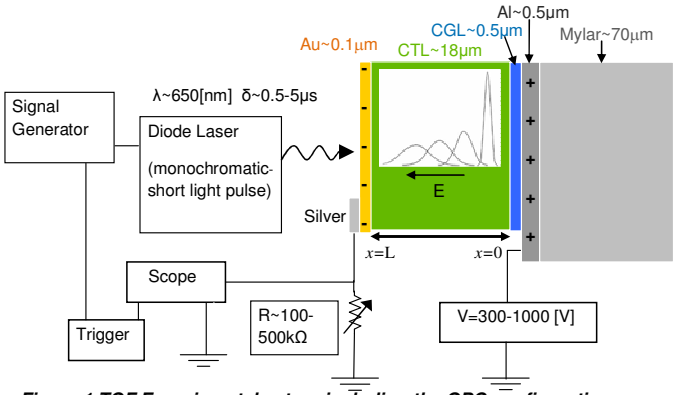

Figure 1 TOF Experimental set-up including the OPC configuration

High voltages of 300-1000V charge the sample, with electric fields of E~1.5·10^5–5·10^{5}V/cm. After charging, a diode laser pulse with wavelength of 650nm (passes through the transparent CTL and) photogenerates holes in the highly absorbing CGL. The penetration depth in the CGL is very small compared with the CTL thickness so we assume that a quasi 2D charge packet is formed. Electrons go immediately to the Al electrode while holes drift through the CTL to the gold electrode. For light modulation, a high frequency Agilent signal generator is used with pulse duration of 0.5-5μsec, much shorter than the transit time of ~1$msec$. The incident laser power is adjusted to ~7mW so that maximum charge generation is less than 0.03CV in order to prevent space charge effects. The applied pulse signal and experiment photocurrents are monitored by Tektronix e-scope, the latter by showing a voltage drop at a resistor in parallel with the oscilloscope. Measurements are done at temperatures of T=12.5^{0}C-66^{0}C, close to those in the printing machine. Higher temperatures are voided in order not to reach the glass transition temperature of the CTL. Photocurrents are reproducible among different samples.

Results and Discussion

Typical TOF smoothed transients on bilinear axis are shown in Figure 2 (main part). The results seen are for 30^{0}C data however at all temperatures transients show similar features and in what follows the same analysis is done and will be reported for all temperatures measured. The general features of a Gaussian TOF transient are seen; an initial spike, followed by a plateau region (though sometimes there is a small increase or decrease in the signal) after which appears a long decaying tail i.e. the transit time is clearly discernible.

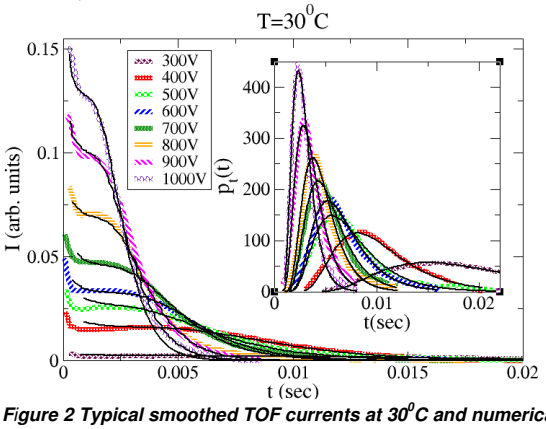

Figure 2 Typical smoothed TOF currents at 30^{0}C and numerical fitting of a 17.2μm sample measured at electric fields ranging from 1.74·10^{5}V/cm to 5.81·10^{5}V/cm. Inset: Fitting the normalized currents derivatives to the Inverse Gaussian formula of Eq. (4) as a first passage waiting time distribution from which mobilities and diffusion coefficients are extracted.

In most previous studies, transit times were measured from the intersection of the tangents prior to and after the sharp pulse signal decrease [4]. Mobilities thus derived represent those of the first carriers reaching the electrode and not of the mean carrier arriving. In order to find a measure for the average carrier mobility, the signal is analyzed by a method [6] which also allows finding the diffusion coefficient. We fit the signal to a function describing the current which would flow if the sample were semi-infinite $I_0(t)$ multiplied by a reduction factor that accounts for arrival of carriers at the collecting electrode, i.e.

$$I(t) = I_o(t) \cdot \left[1 - \int_0^t p_t(t')dt'\right] \qquad (1)$$

where the factor in brackets is the proportion of charge carriers still contributing to the current such that $p_t(t)$ is the *first passage time distribution*, i.e. the probability that a carrier will arrive at the electrode between times t-t+dt. In most cases $I_0(t)$ decreases initially as a result of trapping or relaxation in a density-of-states (DOS) energy distribution, though it can also rise in some cases because of delayed generation effects (as seen in some of our data). Thus, trial functions for $I_0(t)$ are chosen to allow for both dispersive and non-dispersive transport [5]

$$I_o(t) = A \cdot t^{-(1-\alpha)} \qquad 0 \le \alpha \le 1 \qquad (2)$$

The parameter A provides an overall scale for the signal and is a function of laser-pulse intensity, charge generation efficiency and electrical circuit parameters. α is the dispersion parameter which

is less than 1 for dispersive transport, close to 1 for a non-dispersive signal, but can also exceed 1 (for delayed generation).

All transients are analyzed as follows: The signal is fit for short times (right after the very short initial spike) to the form of Eq. (2) and parameters A and α are extracted. Then, the entire transient is divided by $I_0(t)$ so that arrival time distribution is found by using the derivative form of Eq. (1)

$$p_t(t) = -\frac{d}{dt}\left[\frac{I(t)}{I_o(t)}\right] \tag{3}$$

Fitting to a power-law form of Eq. (2) gives values of α close to 1 as is also expected by observation of the current signals. This implies the applicability of the Gaussian model. However, the strongest evidence for its correctness is obtained by fitting the first passage time distributions (inset of Figure 2) to the function

$$p_t(t) = \frac{L}{2\sqrt{\pi D t^3}}\exp\left[-\frac{(L-\bar{v}t)^2}{4Dt}\right] \tag{4}$$

which is the *inverse Gaussian distribution*, i.e. the first passage waiting time if carrier positions are Gaussian, $x(t) \sim N(\bar{v}t, Dt)$ [7].

Mobilities Analysis

The hole mobility μ is related to the average velocity by [2] $\mu = \bar{v}/E = \bar{v}\cdot L/V$ Typical to MDPs the mobility shows a Poole-Frenkel (PF) behavior (see Figure 3 where $\ln\mu$ is linear with $E^{1/2}$), with field and temperature dependence that can be described by [8]

$$\mu(E,T) = \mu_0(T)\cdot e^{\beta(T)\sqrt{E}} = \mu_0 e^{-\left(\frac{2\sigma}{3kT}\right)^2} e^{C\left[\left(\frac{\sigma}{kT}\right)^2-\Sigma^2\right]} \tag{5}$$

where $\mu_0(T)$ is the zero field mobility, $\beta(T)$ is the PF factor. The right hand side of Eq. (6) is a result of the Gaussian Disorder Model (GDM) [8]. In the GDM charge carriers are viewed as hopping in a Gaussian distribution of localized states whose widths are determined by the disorder. There are two types of disorder: energetic (diagonal) with standard deviation σ that reflects the width of the DOS and positional (off-diagonal) with standard deviation Σ. Imposing an external field tilts the DOS and thus lowers the activation energy and increases hole mobility as in Eq. (5). μ_0 is the high temperature limit of the zero field mobility and C is an empirical constant. From fitting $\beta(T)$ and $\mu_0(T)$ (inset of Figure 3) we calculate the GDM parameters σ=0.107eV, Σ=2.584, C=1.7·10^{-4}(cm/V)$^{1/2}$ and μ_0=4.36·10^{-4}(cm^2/V·sec) which are similar to published results [3,4].

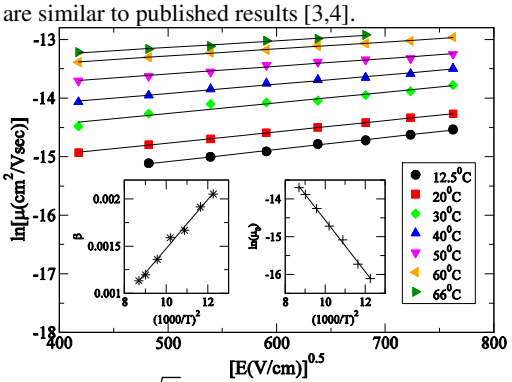

Figure 3 lnμ vs. $\sqrt{E}$ for various temperatures and fitting to the PF formula. Insets: Plot of the slopes (β) and intercepts (lnμ$_0$) of the main part of the figure as functions of T^{-2} to obtain the GDM parameters.

Diffusion Coefficients Analysis

The proposed signal analysis allows us to extract the diffusion coefficients separately. Similar to mobilities the logarithms of the diffusion coefficients increase with the electric field at a rate proportional to $\sqrt{E}$ and with a slope decreasing with temperature (Figure 4) [3]. Therefore, the following formula was proposed [9]:

$$D(E,T) = D_0(T)\cdot e^{\left[\gamma(T)\sqrt{E}\right]} = D_0 e^{\left[-\left(\frac{T_1}{T}\right)\right]^2} \cdot e^{C_d\left[\left(\frac{T_1}{T}\right)^2-\Delta\right]\sqrt{E}} \tag{6}$$

where D_0 is the zero-field high temperature mobility and T_1, C_d and Δ are parameters. Fitting gives D_0=3.192·10^{-3}cm^2/sec, T_1=846.2K, C_d=6.90·10^{-4}(cm/V)$^{1/2}$ and Δ=0.14.

According to Einstein's relation $D=\mu kT/eE$, however, as seen in the inset of Figure 4, this is not the case and diffusion coefficients grow at much greater rates than mobilities. Thus although TOF currents display Gaussian statistics, they vary from conventional normal transport, because the spread of velocities is anomalously large. This was previously observed for other amorphous OPCs [10] as anomalous broadening of the tails and also in MC simulations [11,12]. In deriving Einstein's law one assumes the medium is isotropic and electric fields are low so that response is linear. Though in ordinary crystalline semiconductors this holds, in random amorphous systems it is not true. Random molecules retain their identity, interacting only weakly through van-der-Waals forces and transport is controlled by a distribution of transition rates reflecting the randomness of the medium. Under the action of a field, a packet of charge carriers spreads faster with time because carriers have more possibilities to reside in favorable and unfavorable sites. If the time to reach equilibrium exceeds the mean transit time, diffusion becomes anomalous, its signature being the dispersive current signal. The behavior seen here which stands between the two extremes is termed *Dispersive Gaussian Transport* (DGT) [11] and was also shown by simulations for finite energy dispersion parameters.

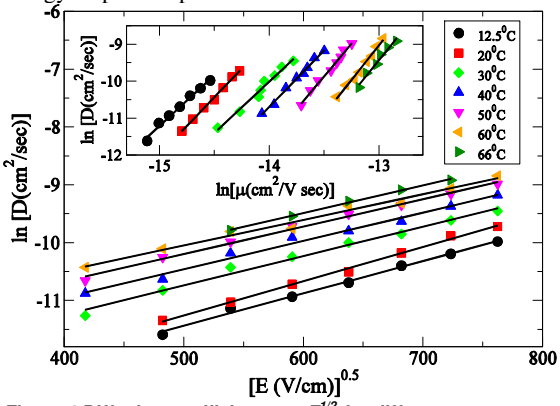

Figure 4 Diffusion coefficients vs. E$^{1/2}$ for different temperatures. Inset: ln D vs. ln μ showing that diffusion increases at much greater rates than mobility.

TOF and V-Light Decay Calculation

The photocurrents transients can be calculated both numerically and analytically [7]. Numerically we solve the advection-diffusion equation (10) for carrier distribution $\rho(x,t)$ with a reflecting and an absorbing boundary:

$$\frac{\partial \rho(x,t)}{\partial t} = D(E,T)\cdot\frac{\partial^2 \rho(x,t)}{\partial x^2} - \bar{v}(E,T)\cdot\frac{\partial \rho(x,t)}{\partial x} \quad (7)$$

A reflecting boundary models the fact that holes cannot diffuse across the CGL and an absorbing boundary represents holes arrival and recombination at the counter electrode. Initial positions are distributed normally at around 0.5μm from x=0 to mimic diffusion from the CGL to the CTL and the finite penetration length of the laser. Inserting $\bar{v}(E,T)$ and $D(E,T)$ from Eqs. (5) and (6) to Eq. (10) and calculating the current as

$$I(t) = \int_0^L J(x,t)dx = \int_0^L \left[\bar{v}(E,T)\cdot\rho(x,t) - D(E,T)\cdot\frac{\partial \rho(x,t)}{\partial x}\right]dx \quad (8)$$

yields a current which fits the experimental transients (Figure 2).

Charge transport parameters are further used to study V-light decay, i.e. the OPC voltage decay as a function of time from the exposure on HP Indigo's printing machines. Experimentally several electrometers are placed around an OPC drum and the residual voltages are measured. As mentioned, in contrast to TOF experiments, upon printing the voltage on the OPC is not constant. Advection-diffusion model is now calculated provided that the values of mobilities and diffusion coefficients are continuously changing during the course of discharging the OPC as the electric field changes. The simulation shows very good prediction of V-light decay at high voltages where space charge effects can be neglected. However, at low voltages the simulation does not tilt to a constant V-light as the experimental curve, since this model does not take into account space charge effects that screen the electric field and reduce the drift current. The Poisson equation which models interactions between holes should be coupled to the advection-diffusion equation in this limit.

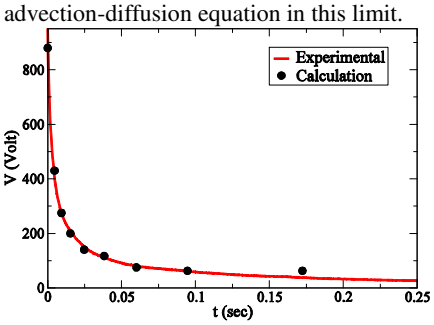

Figure 5 A plot of the OPC voltage vs. time as measured on Indigo's machines and calculating for mobilities and diffusivities which change with the electric field at T=30C.

Conclusions

In conclusion, hole transport in MDP is studied using the TOF technique. Transport is found to be Gaussian, although diffusion coefficients increase with field at much greater rates than mobilities. The advection-diffusion equation is further used to simulate V-light decay employing the relations between mobilities and diffusivities and the electric fields.

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Author Biography

Nurith Schupper received her B.Sc. in chemistry and physics (1996) from the Hebrew University. She finished her M.Sc. (1999) and PhD (2005) research at Bar-Ilan University in pulse propagation, light scattering from amorphous materials and also in statistical and polymer physics. She completed her postdoctoral studies (2008) at the Weizmann institute focusing on glass transition phenomena. She is currently a physicist in the materials department at the Research and Development Division of HP-Indigo, Rehovot, studying photoconduction in OPCs and the mechanical properties of printing blankets.

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