Two-Layer Multiple Trapping Model for Charge Transport in Molecularly Doped Polymers

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Abstract

Organic materials are being investigated for their electronic properties. Such materials are especially attractive for lightweight, flexible, and low-cost solar cells and light emitting devices, as well as transistors and electrophotographic photoreceptors. Yet, even after 40 years of work and a large database, the physics and chemistry that determines the electronic properties of organic materials are not well understood. This paper briefly summarizes data obtained from a new experimental variant of the time of flight (TOF) technique called TOF1a, which are compared to the predictions of a two-layer multiple trapping model (MTM) with an exponential distribution of traps. In TOF1a the charge generation depth is varied continuously, from surface generation to bulk generation, by varying the energy of the electron-beam excitation source. This produces systematic changes in the shape of the current transient that can be compared to the predictions of the two-layer MTM. We find that we can semi-quantitatively fit current transient data over the whole time range of the experiment, but only by using theoretical parameters that lie in a narrow range, the extent of which we quantify here.

Results and Discussion

It is the purpose of this paper to summarize data obtained from a new experimental variant of the time of flight (TOF) technique called TOF1a, which are compared to the predictions of a multiple trapping model (MTM) with an exponential distribution of traps. In the TOF1a experimental variant, the charge generation depth is varied continuously, from surface generation to bulk generation, by varying the energy of the electron-beam excitation source, as recently reported by Dunlap et al [1]. This produces systematic changes in the shape of the current transient that can be compared to the predictions of the two-layer MTM. In the model one additional assumption is added to the homogeneous MTM, namely: that there exists a surface region, on the order of one micron thick, in which the trap distribution is identical to the bulk, but has a higher trap concentration. We find that the characteristic experimental features of an initial spike, flat plateau, and anomalously broad tail, as well as the sometimes observed cusp or decreasing current near the transit time, can all be described by such a two-layer model, i.e. they can arise as a result of carriers delayed by a trap rich surface layer. We find that we can semi-quantitatively fit current transient data over the whole time range of the experiment, but only by using theoretical parameters that lie in a narrow range.

Shown in Fig. 1 is a current transient obtained in time-of-flight experiments with 30% DEH:PC (p-diethylaminobenz-aldehyde diphenylhydrazone in bisphenol-A polycarbonate) plotted on linear-current linear-time (t) axes. The initial spike and long tail are universally observed in time-of-flight transport experiments in molecularly doped polymers (MDP). The tail can be characterized two ways:

(1) The time ($\tau_{1/2}$) for the current to drop to one half the value of the plateau at the transit time (τ) can be determined and a parameter w can be calculated which characterizes the half width, where $w = (\tau_{1/2} - \tau)/\tau_{1/2}$. For almost all published MDPs it is found that w equals 0.5 ± 0.15. Physically this means that at the time that the fastest carriers are exiting the sample (defined as the transit time, τ) there are carriers spread throughout the whole sample. w can be measured as a function of the electric field. w is found to be independent of E (see Fig. 2), a characteristic with the name of universality in the literature of dispersive transport.

(2) The second way to characterize the tail is to plot data such as Fig. 1 on log-current log-time axes, as shown in Fig. 3. Now the initial spike appears as an algebraic decay followed by a plateau. The tail is an algebraic decay that follows an approximately t^{-2} power law. Such curves can be superimposed as a function of electric field as shown in Fig. 4. Universality (independence of electric field) is approximately observed over more than two decades in current and time. In their present form, existing models including Gaussian transport, field diffusion, Coulomb repulsion, intrinsic shallow trap controlled mobility, the Gaussian Disorder Model, Correlated Disorder Models, polaron theory, and Scher-Montroll theory, are unable to account for all the experimentally observed features of charge transport in disordered systems [2].

Recently a two-layer model of charge transport [1] has been proposed. In this model it is assumed that there is a surface layer on the order of one micron thick. Both the surface layer and the bulk have an exponential distribution of trapping states, which is at the heart of the Scher-Montroll theory of dispersive transport [3], and the surface layer has a higher concentration of traps. Once the thickness (L) of the sample is determined (by capacitance measurements), this theory has only three parameters to fit the data, the thickness of the surface layer (d), the dispersion parameter (α) which is assumed to be equal in the surface and bulk thereby giving universality, and the ratio of traps in the surface layer to traps in the bulk (c_1/c_2). This theory is able to predict the spike, plateau and tail semi-quantitatively as can be seen in Fig. 6 (the predicted slope of the initial spike is a little too small). The parameter ranges which can fit this data are:

(1) $10 < c_1/c_2 < 30$ - When this ratio is less than 10 a cusp develops. When this ratio is greater than 30 a double knee appears in the log-log plot which is not observed experimentally. The reason for the double knee is that charge held up in the surface region comes out much later, and there are two distinct arrival times visible on the logarithmic scale. This manifests itself as a broad tail on a linear scale.

(2) 0.3 < d < 1.2 µm - At d = 0.3 µm the curve decays. At d = 1.2 µm a double knee appears in the log-log plot.
(3) 0.75 < α < 0.85 - At 0.85 a cusp develops. At 0.75 the curve decays too much. Therefore α has to be quite close to the value of 0.80.

If the electron-beam energy is increased so that charge carriers are created in some of the bulk as well as the surface, there are systematic changes in the transient current as can be seen in Fig. 5, where the label on the curves is the depth at which the electron beam generates the charges. These curves can be predicted with two-layer theory with just one set of the three parameters as can be seen in Fig. 6. Their range is: $3 < c_1/c_2 < 15$, 1.0 < d < 1.7 µm, 0.75 < α < 0.85. The agreement is quite compelling.

This theory has some shortcomings: the range of parameters over which data can be fit is narrow, the electric field dependence of the mobility has not been accounted for, and the surface layer has not been independently detected. On the other hand, all of the observed transient's shapes are predicted and the agreement between theory and experiment, even when the charge generation depth is varied, is compelling. Some basic elements in the theory almost certainly correspond to TOF experiments and the results do suggest that charge transport in MDPs is dispersive, with the dispersion parameter α of about 0.8.

References

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Author Biography

Lawrence B. Schein received his Ph.D. in experimental solid state physics from the University of Illinois in 1970. He worked at the Xerox Corporation from 1970 to 1983 and at the IBM Corporation from 1983 to 1994. He is now an independent consultant. He has helped implement development systems in IBM laser printers, has proposed theories of most of the known electrophotographic development systems, and has contributed to our understanding of toner charging, toner adhesion, and charge transport mechanisms in photoreceptors. He is the author of Electrophotography and Development Physics, a Fellow of the Society of Imaging Science and Technology and the American Physical Society, recipient of the Carlson Memorial Award in 1993 and the Johann Gutenberg Prize in 2009, a Senior Member of the IEEE, and a member of the Electrostatics Society of America and the American Chemical Society.
(Lawrence B. Schein passed away on June 7, 2011. The co-authors wish to express their sadness at his untimely loss. Larry was highly regarded as a scientist and as a person. His drive to find the answers to questions fundamental to science and technology will be greatly missed.)

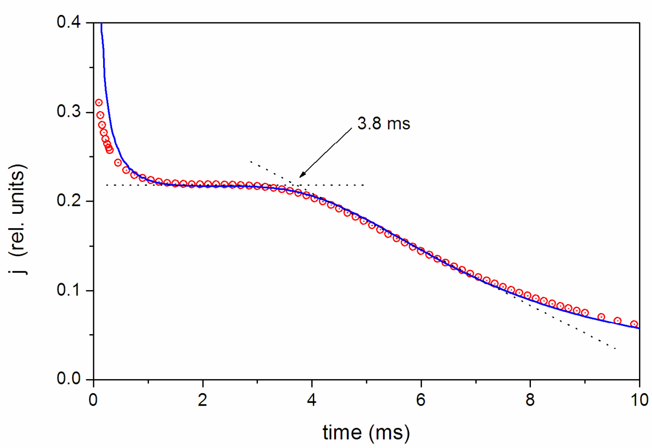

Figure 1. A current transient (blue solid line) with a theoretical curve added (red circles) - see text (Ref. 1, Fig. 1a). The sample thickness was 14 microns and the electric field was 43 V/µm.

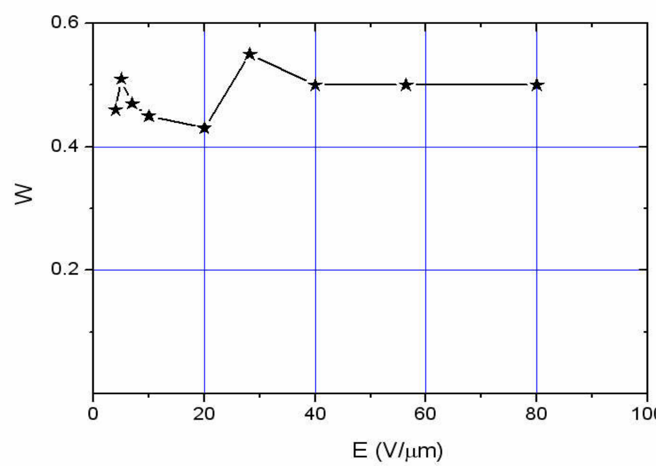

Figure 2. ***w*** (see text) vs. electric field (Ref. 2, Fig. 3).

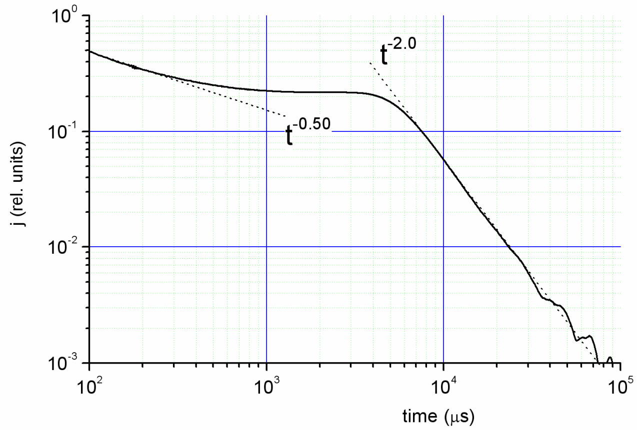

Figure 3. The data of Figure 1 plotted log current vs. log time. (Ref. 1, Fig. 1b replotted).

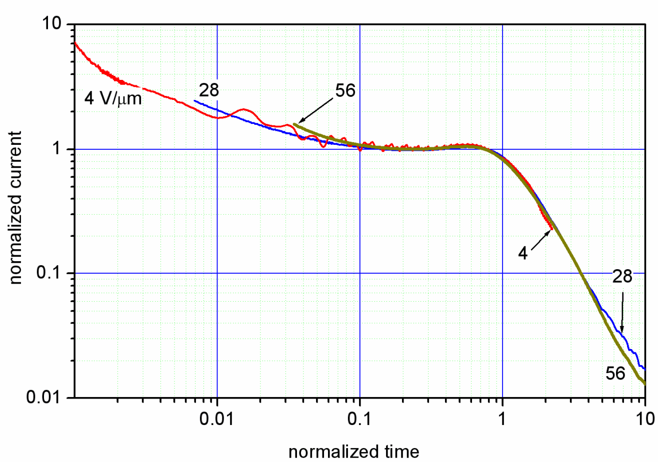

Figure 4. Log-log plot of a 17.5 µm thick sample for electric fields of 4, 28, and 56 V/micron, showing universality over an electric field range spanning more than one decade. Note the universality also applies to the cusp (Ref. 1, Fig. 3).

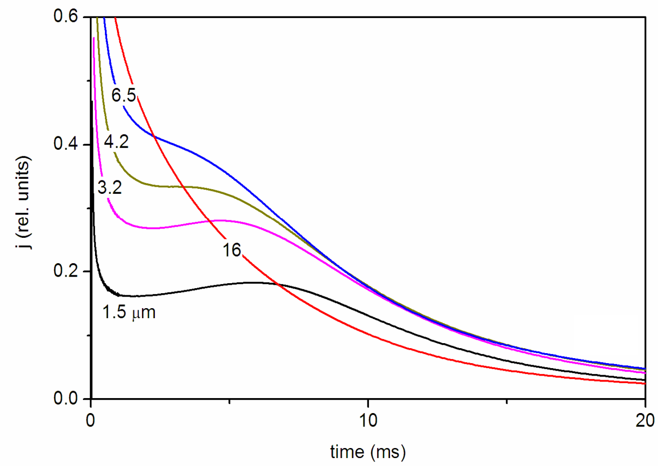

Figure 5. Current transients from a 16 µm thick film with variable electron beam energy, from 7 to 46 keV corresponding to charge generation depths of 1.5 µm to 16 µm (approximately uniform generation) as indicated by the graph labels. The 16 µm curve's vertical amplitude was divided by 3 so that it can be seen on the graph (Ref. 1, Fig. 2a).

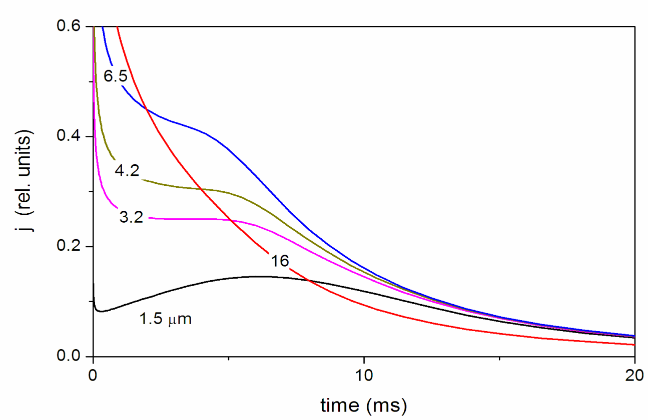

Figure 6. Fits of the experimental data of Fig. 5 using the two-layer model with L = 16 µm. Curves are labeled by their charge generation depths. The best fit occurs with a surface layer d = 1.4 µm, a trap concentration ratio c1/c2 = 7 and dispersion parameter α = 0.80. Each curve is vertically scaled by the corresponding electron energy, except for the 46 keV curve (labeled by the 16 µm sample thickness) which is also reduced by a factor of 3 to place it on the graph (Ref. 1, Fig. 4a).