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Charge transport processes in organic light-emitting devices

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Abstract

The luminous efficiency of organic light-emitting diodes depends on the recombination probability of electrons injected at the cathode and holes at the anode. We have developed a numerical model to calculate the recombination profile in single- and multilayer structures, taking into account the built-in electric field, the charge injection process at each electrode, hopping transport with field-dependent mobilities, charge diffusion, trapping and Langevin recombination. By comparison of the simulation results, as well as approximate analytic solutions, with experimental data on MEH-PPV-based devices, we find that injection is thermionic with Schottky barriers for some electrode metals that are low enough to be considered Ohmic. Except at voltages close to threshold, diffusion and trapping effects are negligible. Both electrons and holes are mobile, with a field dependence that is independently confirmed both by single-carrier space-charge-limited current measurements and transient time-of-flight techniques.

Keywords: Organic electroluminescence; Charge mobility; Charge injection; Charge recombination; Models

1. Introduction

As device design, fabrication and characterization of organic light-emitting diodes (OLEDs) [1,2] are transferred out of the laboratory and into the manufacture of flat-panel displays, it will become increasingly necessary to develop accurate and reliable models of performance. Such models will permit design optimization, integration with existing tools for the design of silicon driver circuitry, the diagnosis of problems in process control, and the understanding of degradation mechanisms in the never ending quest for longer operating lifetimes. In this paper, we summarize efforts, in our own laboratory and elsewhere, to develop and validate a model describing the physics of OLED device operation, including charge injection, transport and recombination. Much of this work is already published, or will shortly appear in print. Hence, this paper includes a relatively extensive list of references.

The ultimate goal of any model of OLEDs is to describe the current–voltage–luminance behavior, which includes all the information necessary to obtain quantum and power efficiencies. We approach the problem in three steps: first, understand the basic principles involved with each physical process in device operation; second, test these principles and determine the relevant parameters, as unambiguously as possible in independent experiments; third, use analytical and numerical methods to provide results that can be compared directly with experimental data on carefully fabricated devices.

When we began this program over 3 years ago, it was not yet at all clear how to describe the basic physical processes involved in OLED operation. For example, it was considered likely that charge injection, of electrons from the cathode and holes from the anode, was best described in terms of Fowler–Nordheim tunneling [3]. Since then, we [4] and others [5] have shown that thermionic injection is the correct description (at least for modest barrier heights and most voltages of interest) and that the barrier height can be sufficiently small that the current is space-charge-limited rather than injection-limited. Similarly, some of the early work [6] suggested trap-limited currents. There is now a growing consensus [7–10] that nearly trap-free transport of holes provides a good description of many high-efficiency devices. In this paper, we summarize the evidence that the same is true for electrons. The temperature, field, and thickness dependence of the

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current in monopolar devices show clearly that the mobility of both holes and electrons occur via an activated hopping process, similar to that in materials used in organic photoconductors [11]. Bipolar hopping transport, in turn, suggests the Langevin mechanism of electron–hole recombination, which was assumed in our earliest modeling work [12], and later demonstrated experimentally [13]. The model was derived for, and applied to, single layer, polymeric devices, but we shall argue that it can be extended to the case of multilayers and small molecule OLEDs.

2. Built-in potential

Since the anode and cathode have different work functions, there is a built-in potential across the organic layers of an OLED structure [14]. There is therefore a corresponding built-in electric field, but it is not necessarily uniform, nor given simply by $\Delta\phi/eL$, where $\Delta\phi$ is the difference in work function and L is the thickness. Ionizable dopants may lead to the creation of a depletion layer close to one of the electrodes, as for example, in thermally converted PPV [15]. Even in a fully depleted device, interfacial dipole layers may give rise to an additional voltage, effectively changing the intrinsic work function of the electrode. Charged surface states may also act to pin the Fermi energy at the electrode interface, effectively a self-adjusting dipole layer.

Clearly, then, it is important to measure directly the built-in potential across devices of interest. Two experimental methods have been shown to be applicable to depleted devices. Electroabsorption (EA) relies on the change in optical absorption spectrum in the presence of an applied dc electric field. The built-in potential is determined by a nulling method, in which an external field, equal and opposite to the built-in field, is applied until the EA signal is zero [14,16]. In principle, this is a direct and generally applicable method, but it suffers from the poor signal-to-noise inherent in a nonlinear effect.

An alternative approach employs a photovoltaic nulling method [16,17] wherein the OLED is illuminated and an external voltage is applied until the photocurrent is equal to the dark current. It was shown [16] that this method gives results that are nearly the same as EA, except for a small, temperature-dependent correction, that arises as a result of carrier diffusion dominating the current close to the flat band condition.

Using a combination of EA and the photovoltaic compensation voltage, it is quite straightforward to determine the built-in field across the bulk of single-layer OLED structures. In all subsequent analyses, this field must be subtracted from the field applied to the sample in order to obtain the true internal field acting on the charges within the bulk.

3. Charge transport

The sequence of charge processes leading to exciton formation are injection, transport and recombination. We address transport first, because the it fundamentally affects the other two. As we shall show, in the MEH-PPV devices that we examine, electrons and holes have comparable mobilities. We were led to this conclusion by a sequence of four experimental results, providing increasingly stronger evidence.

First, we showed [18] that, in MEH-PPV diodes with calcium as cathode, decreasing the anode barrier led to higher quantum efficiency (see Fig. 1). The inevitable conclusion of this observation is that the recombination rate is hole-limited, and that a significant electron current must pass, without recombination, from the cathode to the anode. Electrons are therefore mobile in MEH-PPV.

The second experiment [4,19] compared the current in hole-only devices (e.g., Au/MEH-PPV/Au) with that in bipolar devices (e.g., Au/MEH-PPV/Ca, see Fig. 2, and PAni/MEH-PPV/Ca). It was found in devices of comparable thickness, that the bipolar current was an order of magnitude greater than in hole-only devices. Again, one must conclude that electrons possess a significant mobility in MEH-PPV.

Third, by careful choice of electrode materials (TiN and Ca), it is possible to prepare stable electron-only devices in which Ca forms an Ohmic contact [9]. The resulting space-charge-limited current behavior then permits the evaluation of the field and temperature-dependent electron mobility. It was found that the mobility is thermally activated and has the characteristic field dependence ($\ln\mu \sim \sqrt{E}$) associated with hopping transport [11]. Moreover, at fields in the range of interest for operating diodes, the mobilities of holes and electrons are quite comparable and in the range of a few times 10^{-6} cm^2/V s.

The fourth experimental checks for a possible ambiguity in the steady-state SCLC method, where an Ohmic

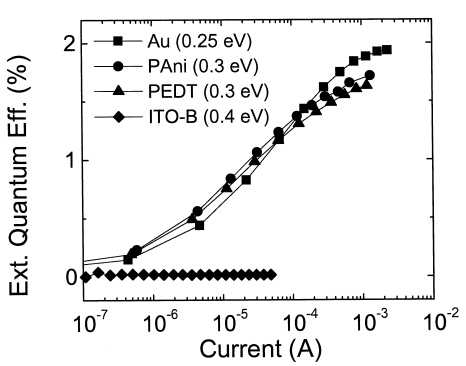

Fig. 1. External quantum efficiencies of a series of MEH-PPV diodes made with Ca cathodes and various anodes. The legend gives the nominal anode Schottky barrier heights as determined in the same devices by photovoltaic measurements [18].

contact is required. Since it is possible that injection-limited currents, through the Schottky barrier lowering effect, could give the same voltage dependence as the field-dependent mobility [10], we undertook a transient time-of-flight determination of the electron mobility. Using a transient SCLC technique that we have adapted explicitly for use with the thin ($\sim$ 100 nm) organic layers used in OLEDs [20], we have measured directly the transient times of both holes [20] and electrons [21] in MEH-PPV (See Fig. 3). Not only do the values confirm the determination by steady-state SCLC, they also reveal that the MEH-PPV samples are essentially trap-free.

The consequences of ''essentially trap-free'' transport are worth commenting on. Extensive work throughout the 60s and 70s [11,22] showed that trap-free behavior results when the concentration of deep traps is small compared to the free carrier concentration. Thus in the steady state, all the traps are filled, but there are no sufficient charges stored in them to make a significant contribution to the space-charge field, nor do they substantially affect the mobility, because, being full, they cannot trap additional free carriers.

The role of diffusive transport also requires comment. The method of analysis applied to our steady-state and transient SCLC data implies that diffusion is negligible in field range of interest. This conclusion is confirmed by numerical simulation studies [10,23] that show minimal changes in current–voltage behavior for an order of magnitude change in diffusion constant.

Both trapping and diffusion may be seen at very low fields where the current deviates significantly from ''ideal'' behavior (e.g., the deviations from linearity in Fig. 2). This is to be expected since the free carrier density is lower and may become comparable to the trap concentration. Similarly, at low fields, the drift contribution to carrier motion is small and the diffusive component becomes more significant.

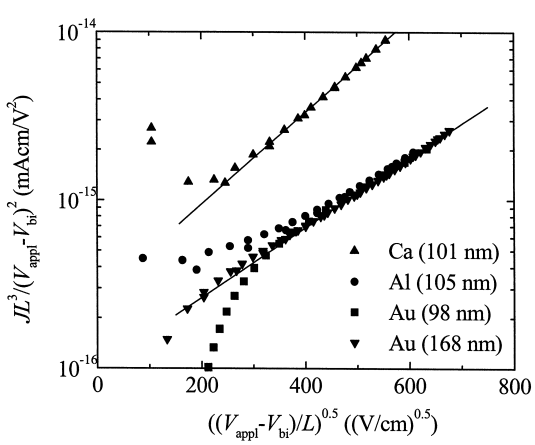

Fig. 2. Current–voltage behavior for MEH-PPV diodes with Au anodes and various cathodes. Two thicknesses of Au/Au devices are shown. The data are plotted in the form applicable to space-charge limited currents with a field-dependent mobility, $\mu \sim \exp\sqrt{E}$.

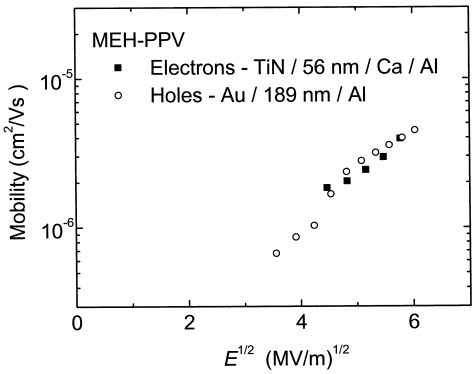

Fig. 3. Mobility of holes and electrons in MEH-PPV, determined by time-of-flight in transient space-charge limited current measurements. Sample thickness and electrode composition are given in the legend.

4. Recombination

In view of the hopping nature of charge transport in OLEDs, it is to be expected that the Langevin [24,25] mechanism of recombination is applicable. In this process, which occurs for low carrier mean-free-paths, an electron and hole that approach each other within a distance such that their mutual binding Coulomb energy is greater than the thermal energy, kT, will inevitably recombine. In the earliest work on organic electroluminescence in crystalline anthracene, Helfrich and Schneider [26,27] showed that the recombination rate was close to the Langevin prediction. It is therefore to be expected that in the amorphous materials used in OLEDs, the shorter mean-free-path leads even more clearly to the Langevin mechanism. This was the assumption of our earliest theoretical analysis of OLEDs [12], and was demonstrated experimentally by Blom et al. [13] in a dialkoxy-PPV derivative. Further support for the Langevin hypothesis is given by the agreement of numerical simulations with experimental data [10].

5. Charge injection

The problem of charge injection from a metal into a low-mobility amorphous (organic) material remains an area of active theoretical research [28,29] for which few experimental tests are available. We have recently developed [30] a semi-classical approach that relates the charged injection rate to experimentally determinable parameters of the organic material. We have used the results to generate numerical simulations of OLED current–voltage-efficiency relations, which are in good agreement with experimental data [10].

Specifically, we considered [30] a model of thermionic injection, with a Schottky barrier at the metal organic

interface. In order to determine the charge injection rate, we calculate first the inverse process, namely the ''surface recombination current'' in which a charge in the organic layer ''recombines'' with its image charge in the metallic electrode. In analogy with electron–hole recombination in the bulk, this process was described by the Langevin mechanism. At equilibrium, the injection current is equated to this surface-recombination current, leading to a result in terms of a Richardson–Dushman equation in which the effective Richardson constant is found to be proportional to the charge carrier mobility. The electric field dependence of the injection current is found by invoking the Schottky barrier lowering effect, in the presence of the image potential of the charge near the electrode. At low electric field, the result exactly reproduces the behavior expected from the analysis of Emtage and O'Dwyer (EO) [31] and at higher field, it provides a good approximation to the more exact theory. Most importantly, the intermediate field behavior, for which EO provide no solution and which is applicable to real OLEDs, is given by the same simple equation.

6. Device modeling

In general, there is no analytic solution for the bipolar current behavior relevant to OLEDs. Only when both electron and hole mobilities are field-independent, when diffusion and trapping can be completely ignored, and when both anode and cathode provide Ohmic contacts can a complete solution be obtained [12,32]. For most realistic cases, one must resort to numerical methods, which have been applied to OLEDs by a number of groups [5,10,16,33]. The algorithm used is typically a simple forward integration in time of the relevant differential equations.

Based on the above discussion of physical processes active in OLEDs, we have included the following features in our numerical simulations [10]: thermionic injection at the electrodes, with an electric field dependence described by the Schottky barrier lowering effect; surface recombination of charge–image pairs; field-dependent mobilities of both holes and electrons; Langevin recombination. We also include diffusion, using a diffusion coefficient given by the Einstein equation. As discussed above, this has only a minor effect on the results, but it is important to improve the stability of the numerical method and permit larger time-steps and therefore more rapid convergence to steady-state values. These concepts are sufficient to obtain the complete current–voltage relations for the device. The quantum efficiency is, to a first approximation, related to the electron–hole recombination current: that is, the difference between the electron currents at the cathode and anode, or, equivalently, between the hole currents at the anode and the cathode. This is also easily obtained from the simulation data.

A more accurate calculation of quantum efficiency requires knowledge of the recombination profile, that is, the rate of exciton creation as a function of position across the device. This, too, can be obtained from the numerical simulations. One must then compute the probability of the exciton decay radiatively. Because of microcavity effects and quenching of the exciton near the metallic electrodes, the radiative decay rate is a function of wavelength and emission angle, as well as position [34]. These aspects are the subject of ongoing investigation.

Numerical modeling frequently obscures the physics underlying device operation. We have found [35] that two variables, namely, the electron and hole charge densities, provide useful criteria to establish the regime of operation. The comparison of carrier density and trap concentration determines whether one is in the trap-free or trap-controlled regime. Comparing total injected charge to the capacitive charge stored on the electrode dictates whether space-charge limitation is more or less important than injection-limited currents. Lastly, the charge density can be used in conjunction with the Langevin capture cross-section to yield a mean-free-path for recombination that delineates regimes of low and high efficiency. It should be remembered in making these comparisons that there is a continuum of behavior between all of the limits: trap-free or trap-controlled; space-charge or injection-limited; short or long recombination mean-free-path.

Indeed, as one examines the results of the simulations of single-layer devices, it becomes clear that the overriding factor in achieving high quantum efficiency is the enhancement of both electron and hole densities, as in devices with two Ohmic contacts where the charge densities tend to diverge at the respective electrodes. The charge density consideration also helps to put on a more quantitative basis, the empirical observation (and intuitive interpretation) that multilayer devices enhance efficiency by confinement of the carriers at organic–organic interfaces [1,36].

Additional tests of the inputs to the model and to the numerical methods will come from more detailed examination of multilayered devices, the dynamic response and comparison with transient electroluminescence [37,38] and capacitance–voltage [39,40] experiments.

We close this section with a comment on an alternative approach to OLED modeling, namely the trapped-charge limited behavior suggested by the Princeton group [6,41] and developed by Yang and Shen [33]. This analytical framework is motivated by the observation that the current–voltage relation in bilayer Alq_3 diodes follows a temperature-dependent power law, as predicted for SCLC controlled by an exponential distribution of single-trap levels [22,42]. However, we find three areas where such a description may have some shortcomings. First, none of the data are corrected for the built-in potential that exists between the asymmetric electrodes. As we have shown [4], the current–voltage characteristics change dramatically when the built-in potential is accounted for. Second, the field within (and voltage drop across) the hole-transport

layer [43] is ignored in the analysis, in spite of the facts that a significant hole injection barrier may exist at the anode interface and that holes in TPD [44] and electrons in Alq_3 [45] have mobilities that differ by only one order of magnitude. Lastly, there appears to be some confusion as to whether the traps are pre-existing at a density close to that of the Alq_3 molecules themselves, or are a result of polaronic self-trapping. In the latter case, the trapped-charge limit should not apply, and the carriers exhibit the field-dependent mobility of polaronic transport. It will be interesting to see whether our numerical modeling, developed for single polymer layers, provides a different interpretation of the data on multilayer small-molecule OLEDs.

7. Conclusions

By a combination of experiment, analytical theory and numerical simulation, we have developed a model for OLED device operation that includes the processes of thermionic injection, bipolar field-dependent transport, and Langevin electron–hole recombination. At voltages of interest for device operation, diffusive contributions to charge transport are minimal. In the most efficient devices, the anode and cathode injection barriers are both sufficiently low that they may be considered Ohmic contacts. Furthermore, charge trapping can be neglected, and the transport is well described in terms of trap-free space-charge-limited currents. In particular, we provide evidence from four independent experiments that electrons in MEH-PPV have comparable mobility to holes.

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References

[1] C.W. Tang, S.A. Van Slyke, Appl. Phys. Lett. 51 (1987) 913.
[2] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackey, R.H. Friend, P.L. Burns, A.B. Holmes, Nature 347 (1990) 539.
[3] I.D. Parker, J. Appl. Phys. 75 (1994) 1656.
[4] G.G. Malliaras, J.R. Salem, P.J. Brock, J.C. Scott, Phys. Rev. B 58 (1998) R13411.
[5] B.K. Crone, I.H. Campbell, P.S. Davids, D.L. Smith, Appl. Phys. Lett. 73 (1998) 3162.
[6] P.E. Burrows, Z. Shen, V. Bulovic, D.M. McCarty, S.R. Forrest, J.A. Cronin, M.E. Thompson, J. Appl. Phys. 79 (1996) 7991.
[7] P.W.M. Blom, M.J.M. de Jong, Philips J. Res. 51 (1998) 479.
[8] P.S. Davids, I.H. Campbell, D.L. Smith, J. Appl. Phys. 82 (1997) 6319.
[9] L. Bozano, S.A. Carter, J.C. Scott, G.G. Malliaras, P.J. Brock, Appl. Phys. Lett. 74 (1999) 1132.
[10] G.G. Malliaras, J.C. Scott, J. Appl. Phys. (in press).
[11] P.M. Borsenberger, D.S. Weiss, Organic Photoreceptors for Electrophotography, Marcel Dekker, New York, 1993.
[12] J.C. Scott, S. Karg, S.A. Carter, J. Appl. Phys. 82 (1997) 1454.
[13] P.W.M. Blom, M.J.M. de Jong, S. Breedijk, Appl. Phys. Lett. 71 (1997) 930.
[14] I.H. Campbell, T.W. Hagler, D.L. Smith, J.P. Ferraris, Phys. Rev. Lett. 76 (1996) 1900.
[15] S. Karg, M. Meier, W. Riess, J. Appl. Phys. 82 (1997) 1951.
[16] G.G. Malliaras, J.C. Scott, J. Appl. Phys. 84 (1998) 1583.
[17] X. Wei, M. Raikh, Z.V. Vardeny, Y. Yang, D. Moses, Phys. Rev. B 49 (1994) 17480.
[18] J.C. Scott, G.G. Malliaras, W.D. Chen, J.-C. Breach, J.R. Salem, P.J. Brock, S.B. Sachs, C.E.D. Chidsey, Appl. Phys. Lett. 74 (1999) 1510.
[19] L. Bozano, S.E. Tuttle, S.A. Carter, P.J. Brock, Appl. Phys. Lett. 73 (1998) 3911.
[20] J.C. Scott, S. Ramos, G.G. Malliaras, J. Imaging Sci. Technol. 43 (1999) 234–237.
[21] S. Ramos, P.J. Brock, J.C. Scott (unpublished).
[22] M.A. Lampert, P. Mark, Current Injection in Solids, Academic Press, New York, 1970.
[23] G.G. Malliaras, J.C. Scott, J. Appl. Phys. 83 (1998) 5399.
[24] P. Langevin, Ann. Chem. Phys. 28 (1903) 289.
[25] M. Pope, C.E. Swenberg, Electronic Processes in Organic Crystals, Oxford Univ. Press, New York, 1982.
[26] W. Helfrich, W.G. Schneider, Phys. Rev. Lett. 14 (1965) 229.
[27] W. Helfrich, W.G. Schneider, J. Chem. Phys. 44 (1966) 2902.
[28] V.I. Arkhipov, E.V. Emelianova, Y.H. Tak, H. Bässler, J. Appl. Phys. 84 (1998) 848.
[29] M.N. Bussac, D. Michoud, L. Zuppiroli, Phys. Rev. Lett. 81 (1998) 1678.
[30] J.C. Scott, G.G. Malliaras, Chem. Phys. Lett. 299 (1999) 115.
[31] P.R. Emtage, J.J. O'Dwyer, Phys. Rev. Lett. 16 (1966) 356.
[32] R.H. Parmenter, W. Ruppel, J. Appl. Phys. 30 (1959) 1548.
[33] J. Yang, J. Shen, J. Appl. Phys. 84 (1998) 2105.
[34] K.A. Neyts, J. Opt. Soc. Am. A 15 (1998) 962.
[35] J.C. Scott, G.G. Malliaras, J.R. Salem, P.J. Brock, L. Bozano, S.A. Carter, Proc. SPIE-Int. Soc. Opt. Eng. 3476 (1998) 111.
[36] N.C. Greenham, S.C. Moratti, D.D.C. Bradley, R.H. Friend, A.B. Holmes, Nature 365 (1993) 628.
[37] D. Braun, D. Moses, C. Zhang, A.J. Heeger, Appl. Phys. Lett. 61 (1992) 3092.
[38] C. Hosokawa, H. Tokailin, H. Higashi, T. Kusumoto, Appl. Phys. Lett. 60 (1992) 1220.
[39] I.H. Campbell, D.L. Smith, J.P. Ferraris, Appl. Phys. Lett. 66 (1995) 3030.
[40] M. Meier, S. Karg, W. Riess, J. Appl. Phys. 82 (1997) 1961.
[41] S.R. Forrest, Z. Shen, P.E. Burrows, V. Bulovic, M.E. Thompson, in: R.H. Mauch (Ed.), Inorganic and Organic Electroluminescence, Wissenschaft und Technik Verlag, Berlin, 1996, pp. 83–88.
[42] A. Rose, Concepts in Photoconductivity and Allied Problems, Wiley Interscience, New York, 1963.
[43] C. Giebeler, H. Antoniadis, D.D.C. Bradley, Y. Shirota, J. Appl. Phys. 85 (1999) 608.
[44] M.A. Abkowitz, D.M. Pai, Philos. Mag. B 53 (1986) 193.
[45] R.G. Kepler, P.M. Beeson, S.J. Jacobs, R.A. Anderson, M.B. Sinclair, V.S. Valencia, P.A. Cahill, Appl. Phys. Lett. 66 (1995) 3618.