Engineering carrier transport across organic heterojunctions by interface doping

S. W. Tsang, Z. H. Lu, and Y. Tao

Citation: Applied Physics Letters 90, 132115 (2007); doi: 10.1063/1.2718273
View online: http://dx.doi.org/10.1063/1.2718273
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/90/13?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Charge transfer at n-doped organic-organic heterojunctions
J. Appl. Phys. 105, 123711 (2009); 10.1063/1.3153962

Charge transport across pressure-laminated thin films of molecularly doped polymers

Charge transfer and doping at organic/organic interfaces

High-efficiency organic electrophosphorescent devices with tris(2-phenylpyridine)iridium doped into electron-transporting materials

Bipolar transport organic light emitting diodes with enhanced reliability by LiF doping
Engineering carrier transport across organic heterojunctions by interface doping

S. W. Tsang and Z. H. Lu
Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario M5S 3E4, Canada

Y. Tao
Institute for Microstructural Sciences, National Research Council of Canada, Ottawa Ontario K1A 0R6, Canada

(Received 1 October 2006; accepted 23 February 2007; published online 28 March 2007)

Two common hole transporting materials, 4,4’,4”-tris(N-3-methylphenyl-N-phenyl-amino) triphenylamine (MTDATA) and N,N’-diphenyl-N,N’-bis(1-naphthyl) (1,1’-biphenyl)-4,4’ diamine (NPB), and a p-type dopant tetrafluorotetracyanoquinodimethane (F4-TCNQ) were used to build various hole-only heterojunction devices. Both experimental results and theoretical modeling show that the current flow in such devices is limited by the heterojunction potential barrier or band offset at the MTDATA/NPB interface. It was found that the device current flow can be modulated to increase or decrease dramatically by introducing a 2 nm p-doped NPB:F4-TCNQ or MTDATA:F4-TCNQ interlayer, respectively. The observed phenomena were discussed using quasi-Fermi energy level realignment at the doped/undoped organic-organic interface.

Organic light-emitting diode (OLED) is becoming an important technology for flat-panel displays and has tremendous potential for future lighting applications. The current high level of research activities in the OLED area was triggered by the first report of practical devices using organic-organic heterojunctions, which has become the basic device platform in the commercial production of OLEDs. Heterojunctions provide a practical engineering method to modulate carrier (electron or hole) concentration in OLED devices, thus leading to much improved stability and efficiency. For multilayered structures with no intrinsic free carriers inside the device, charge carriers (electrons/holes) must be injected from two opposite electrodes (cathode/anode). These injected carriers have to pass through different organic layers before they form excitons in the emission layer. In the past decade, there have been numerous studies on metal/organic (MO) interfaces. It has been successfully demonstrated that carrier injection can be improved by modifications at the MO interface. In some cases, true Ohmic contacts at the MO interface have been demonstrated. As a result, the operating voltage in OLEDs has been reduced steadily over the last decade. One of the current challenges in OLED device physics is to understand and control carrier transport across organic-organic interfaces (OOIs). It is well known that an energy offset, the potential energy difference between transporting channels, exists at any heterojunction. In conventional inorganic semiconductor devices, such as the laser diode, heterojunctions play a critical role in device performance. In organic electronic materials, such energy offsets have been shown to be an important factor limiting the injection of current at the OOI. It is therefore important to understand and to control the carrier transport across the OOI. The current approaches to this problem have mostly been by chemical means, i.e., synthesizing and matching various classes of organic derivatives. Due to many restrictions such as optical path, molecular stability, carrier mobility, etc., the choice of practical materials and even the thickness for each layer are quite often limited. In this letter, we report an alternative physical method which involves inserting a thin p-doped interlayer at the MOI to effectively modulate the carrier transport across the heterojunction. Furthermore, theoretical modeling was used to explain the current-voltage characteristics using the physical parameters of those materials that were independently extracted by time-of-flight (TOF) measurements, using a method reported in Ref. 5.

For simplicity, double layer hole-only devices were used for this study. The devices have a general structure: substrate/ indium tin oxide (ITO)/organic layer I/organic layer II/Ag. Prepatterned ITO on glass substrates was used. In order to ensure that the carrier mobilities extracted by TOF were applicable to the simulated current-voltage characteristics of the double layer devices, the organic films used here were relatively thicker than those used in OLEDs. The ITO/glass substrate was cleaned by acetone, then methanol, in an ultrasonic bath, and followed by uv-ozone treatment. Two hole transporting materials 4,4’,4”-tris(N-3-methylphenyl-N-phenyl-amino) triphenylamine (MTDATA, from Syntec GmbH) and N,N’-diphenyl-N,N’-bis(1-naphthyl)(1,1’-biphenyl)-4,4’ diamine (NPB, from H. W. Sands) were used to construct various types of organic heterojunctions. The highest occupied molecular orbital (HOMO) of MTDATA and NPB are 5.1 and 5.4 eV, respectively. Therefore there may exist a hole injection barrier of about 0.3 eV at the MTDATA/NPB interface. All organic films were deposited on top of the ITO substrate in a vacuum chamber with a base pressure of 10−6 Torr. It was then followed by depositing silver (Ag) as the top contacting electrode. Due to a large energy difference between the work function of Ag (4.3 eV) and the lowest unoccupied molecular orbital (<2.5 eV) of the organic materials, the Ag electrode is restricted from injecting electrons into these devices.

In some devices, a p-doped interlayer was inserted at the OOI. The p-doped interlayer was achieved by coevaporation of host (MTDATA or NPB) and p-type dopant, tetrafluorotetracyanoquinodimethane (F_{4}-TCNQ, 99.9% purity, from Lumtec Co. Ltd.). The doping ratio (in mol %) was controlled by independently monitoring the evaporation rates of the host and the dopant. The device structures used for this study are summarized in Table I.

For TOF measurements, a thick film (3–4 μm) of MTDATA or NPB was thermally evaporated onto an ITO coated glass substrate. A semitransparent aluminum (Al) electrode was used as a positively biased electrode. The organic film was photoexcited by a frequency-tripled neodymium doped yttrium aluminum garnet pulsed laser (λ=355 nm, pulsed width=6 ns). A dc power supply (Stanford PS310) was used to provide a bias to extract photogenerated holes. The photocurrent was monitored by a digital oscilloscope (Agilent 54622A) through a sensing resistor in series contact with the sample. Current density-voltage (J-V) measurements were carried out using a Keithley 236 meter. The active area for all samples was 0.16 cm². The thicknesses of the organic films were measured by a profilometer. For all measurements, J-V and TOF, the samples were mounted inside a cryostat in vacuum with a base pressure of 10⁻⁶ Torr at 300 K.

To demonstrate the effect of energy barrier on carrier transport across an organic heterojunction, Fig. 1 shows J-V characteristics (open squares) measured from an ITO/MTDATA (236 nm)/Ag single layer hole-only device or device E. The solid line is a theoretical J-V curve calculated based on the trap-free space-charge-limited current (SCLC) model with field-dependent mobility,

\[
J_{\text{SCLC}} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \exp(0.89 \beta |E|^{1/2}) \frac{V^2}{L^3},
\]

where \( \varepsilon_r \) is the relative permittivity obtained by measuring the device capacitance, \( \varepsilon_0 \) is the absolute permittivity, \( E \) is the applied electric field, \( V \) is the applied voltage bias, and \( L \) is the organic film thickness. The zero-field hole mobility \( \mu_0 = 1.28 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) and field-dependent coefficient \( \beta = 1.88 \times 10^{-3} \text{ (V/cm)}^{1/2} \) were obtained independently by TOF technique. The excellent agreement between the measured and calculated current densities indicates that the conduction is dominated by carrier transport in the bulk of the organic film. The contact resistance between ITO and MTDATA is negligible in this case.

The measured J-V characteristics of an ITO/MTDATA (236 nm)/NPB (82 nm)/Ag filled square) double layer device, device A, are also shown in Fig. 1. By using the TOF technique, \( \mu_0 \) and \( \beta \) of NPB were found to be 5.27 × 10⁻⁶ cm² V⁻¹ s⁻¹ and 1.80 × 10⁻⁳ (V/cm)⁻¹/₂, respectively. Although the hole mobility of NPB is more than one order of magnitude higher than that of MTDATA, the measured J of the double layer device was found to be much lower than that of the single layer device. This suggests that a large hole transport barrier exists at the MTDATA/NPB interface. In order to illustrate the effect of the transport barrier at this interface, the maximum attainable current in the double layer device was simulated (shown in cross symbols in Fig. 1) using a time-domain simulation method, by assuming that no barrier exists at the OOI. Briefly in the simulation, holes were injected at the anode with no resistance, and drifted along the applied electric field moving through MTDATA, then through NPB. In this case, the current is only limited by the space charges inside the organic layers. By comparing the simulation results with the measured J, especially at the low field region, it is clear that the current in the double layer device is significantly limited by the presence of a potential barrier at the OOI.

Figure 2 shows the J-V characteristics of double layer devices with the inclusion of various types of p-doped interlayers. In device B, a thin layer of NPB:F_{4}-TCNQ (2 nm) was placed between MTDATA and NPB. It was found that the measured J (filled circles) significantly increases upon the insertion of the NPB:F_{4}-TCNQ interlayer. However, when the interlayer is replaced by MTDATA:F_{4}-TCNQ (2 nm) as in device C, the measured J (filled upward triangles) is dramatically reduced. In device D, the measured J (filled downward triangles) was found to be further suppressed by increasing the doping ratio to 15%.

It is well known that doping can effectively increase the charge-carrier concentration in organic semiconductors. Furthermore, it has also been suggested that doping can in-
duce energy level realignment at the MO and OO interfaces.\textsuperscript{13,14} Devices B, C, and D all contain a heavily p-doped interlayer at the junction. Despite the fact that the hole concentration in the p-doped interlayer is presumably higher than that in the undoped matrix,\textsuperscript{11,12} the measured current densities of p-type devices C and D are much lower than that of undoped device A. Therefore, it is reasonable to assume that the effective injection barriers in devices C and D are increased. Now let us discuss some possible causes for this increase in the interface injection barrier. Although the detailed mechanism of interface energetics is not yet clearly understood, some recent experimental results suggest that there are energy level realignments in doped organic materials.\textsuperscript{13,14} To help explain the current experimental findings, the schematic energy diagrams of the double layer devices are depicted in Fig. 3. In device A, the hole injection barrier was assumed to be equal to the HOMO energy level difference (0.3 eV) between MTDATA and NPB, and the device hole current was mainly determined by the efficiency of hole injection across the MTDATA/NPB heterojunction. In the following discussion, effective p-type doping of NPB and MTDATA has been assumed. The p-type doping induced changes in the Fermi level and carrier concentration have been reported.\textsuperscript{11,12,15} In device B, the p-type doping reduces the energy separation between the Fermi level and the HOMO of NPB inside the interlayer. As a result, the HOMO offset at the NPB/NPB:F$_8$-TCNQ interlayer is effectively reduced and consequently the transport barrier at the MTDATA/NPB is also reduced. In this case, the interlayer functions as an intermediate energy level that facilitates hole injection into NPB. In device C or D, similarly, the energy separation between the Fermi level and the HOMO of the MTDATA:F$_8$-TCNQ interlayer is reduced by p doping. In this case, however, this uplifting of the HOMO energy level leads to an increase in the hole injection barrier at the NPB/MTDATA:F$_8$-TCNQ interface. The injected holes from the MTDATA will be initially trapped inside the interlayer, and subsequently these carriers will have to overcome a larger energy barrier in order to be injected from the interlayer into NPB. As a result, the current density in devices C and D are much reduced when compared with undoped device A.

In conclusion, we have shown, by both experiment and theoretical simulations, that charge transport in a double layer device is limited by a potential barrier at the organic-organic heterojunction. We have demonstrated that this transport barrier at the organic heterojunction can be effectively modulated by introducing a thin (2 nm) p-doped interlayer at the heterojunction. It has been found that charge transport across the MTDATA/NPB heterojunction can be easily modulated by inclusion of a doped interlayer at the junction, a NPB:F$_8$-TCNQ interlayer to increase the hole current and a MTDATA:F$_8$-TCNQ interlayer to decrease the hole current. A change in the quasi-Fermi level upon doping together with energy level alignment at the heterojunctions was proposed to explain the observed phenomena. The junction doping technique provides a promising alternative engineering technique to modulate electron or hole current in organic electronic devices using commonly available organic semiconductor molecules.

The authors wish to acknowledge funding support for this project by Emerging Materials Knowledge (EMK) Network of the Ontario Centres of Excellence (OCE).

\begin{thebibliography}{99}
\bibitem{5} P. M. Bosenberger and D. S. Weiss, Organic Photoreceptors for Imaging Systems (Dekker, New York, 1993), Chap. 9, p. 273.
\bibitem{7} A. Wan, J. Hwang, F. Amy, and A. Kahn, Org. Electron. 6, 47 (2005).
\end{thebibliography}