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Characterization and improvement of the contact between indium tin oxide and triphenyl diamine-doped polycarbonate

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Abstract

We have measured the electrical characteristics at the contact between indium tin oxide (ITO) and the molecularly doped polymer *N*-*N*′-diphenyl-*N*-*N*′-bis(3-methylphenyl)-1-1-biphenyl-4,4′-diamine-doped polycarbonate (PC:TPD). We find that the contact is current-limiting, supplying the sample with a current that is considerably smaller than the space charge limited current. When an ultra-thin layer of Pt or Pd is introduced between ITO and PC:TPD an increase in the injected current is observed as the contact becomes ohmic.

Keywords: Indium tin oxide; Current-limiting; PC:TPD

1. Introduction

Organic light emitting diodes (OLEDs) have emerged over the last 10 years as viable candidates for applications in display technologies. A combination of advantages, such as high efficiency, availability of various colors, Lambertian emission, capability for large areas and/or flexible structures etc. has motivated research in industry and academia both here and overseas [1]. Early prototypes and commercial products, such as a car stereo display manufactured by the Japanese company Pioneer in 1997, demonstrate the potential of organic light emitting diodes for commercialization.

An OLED consists of one or more organic semiconductor layers sandwiched between two metallic electrodes. Its operation is based on the recombination of opposite carriers injected into the organic layer(s) from the two electrodes. Numerical simulations show that the process of charge injection plays a fundamental role in determining the device efficiency [2]. The maximum efficiency is achieved when both contacts are ohmic, i.e. they do not pose any limitation in the current flow through the sample. Unfortunately, it is difficult to establish whether a contact is ohmic or not on the basis of device characteristics alone, since the latter are a complex function of both injection and bulk transport [1].

Recently, Abkowitz et al. [3] described a straightforward technique to characterize contact performance. The technique is based on an independent mobility measurement and leads to a separation of bulk transport from injection. In this paper, we use this technique to study the contact between indium tin oxide (ITO) (the most commonly used anode in OLEDs) and the model organic semiconductor *N*-*N*′-diphenyl-*N*-*N*′-bis(3-methylphenyl)-1-1-biphenyl-4,4′-diamine-doped polycarbonate (PC:TPD). We find that the contact is current-limiting. By introducing ultra-thin layers of high work function metals the contact is made ohmic.

2. Experimental

In all experiments described here, the polymer contained 60% w/w TPD. ITO coated glass substrates were bought from thin film devices and cleaned by UV/ozone treatment at slightly elevated temperatures. Immediately after cleaning, the PC:TPD films were deposited on the ITO substrates by either screen coating or spin coating from a THF solution. A semitransparent Al layer was vacuum-deposited on all samples as the back contact, defining six devices with an active area of 3 mm^2 each. Ultra-thin layers of Pt and Pd with a thickness of 5 Å were deposited under high vacuum and cleaned before the deposition of the organic with UV/ozone cleaning. Their optical transmission was over 90% throughout the visible spectrum.

The hole mobility in PC:TPD was measured with a time-of-flight (TOF) experiment [4]. The Al electrode was brought under positive bias (reverse bias) and a 10 ns pulse from a nitrogen laser was used to excite the sample from the Al side. Al was found to serve as a non-injecting ("blocking") contact, injecting a negligible dark current. The current injected from ITO was subsequently measured

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on the same sample, by switching the polarity of the applied bias (forward bias).

3. Results and discussion

PC:TPD is a prototypical organic semiconductor whose transport properties have been studied extensively in the past [4]. It is a unipolar transport material where trap-free hole transport takes place via hopping among the TPD molecules [4]. A typical TOF trace is shown in Fig. 1, where the current exhibits a clear plateau, followed by the usual decay which is characteristic of anomalous diffusion [5]. The mobility is extracted from the transit time, which corresponds to the moment the current reaches half of its plateau value [4]. The inset of Fig. 1 shows the characteristic dependence of mobility μ on electric field E

$$\mu = \mu_0 \exp\left[\left(\frac{E}{E_0}\right)^{1/2}\right] \quad (1)$$

where μ_0 is the zero field mobility and E_0 a characteristic electric field. This dependence is understood to arise from the interaction of carriers with randomly oriented and randomly located dipoles in the organic medium [6]. The data of Fig. 1 is in agreement with literature values [7].

Knowing the mobility allows us to calculate the space charge limited current (SCLC), i.e. the maximum current that can flow through the sample under dc conditions. This is given by the Mott-Gurney law [8], which has been modified by Murgatroyd [9] to account for a field dependent mobility as in Eq. (1). The space charge limited current density, J_{SCLC}, is approximately equal to

$$J_{SCLC} \approx \left(\frac{9}{8}\varepsilon\varepsilon_0\mu_0 V^2 \exp\frac{[0.89(V/(E_0L))^{1/2}]}{L^3}\right) \quad (2)$$

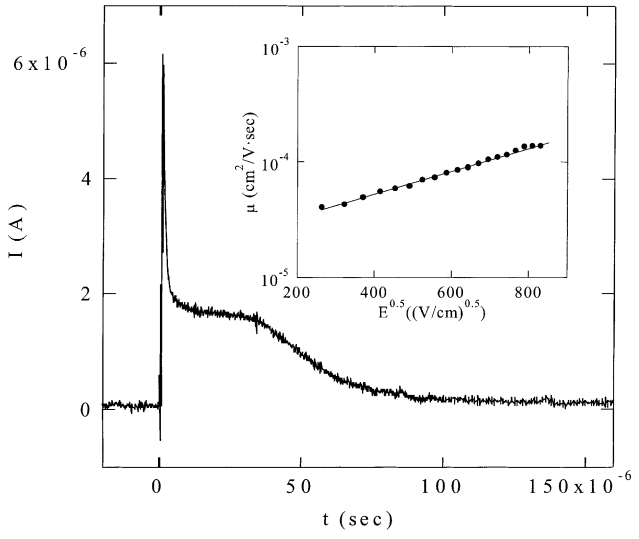

Fig. 1. Typical time-of-flight trace from a PD:TPD sample. Inset: field dependence of mobility.

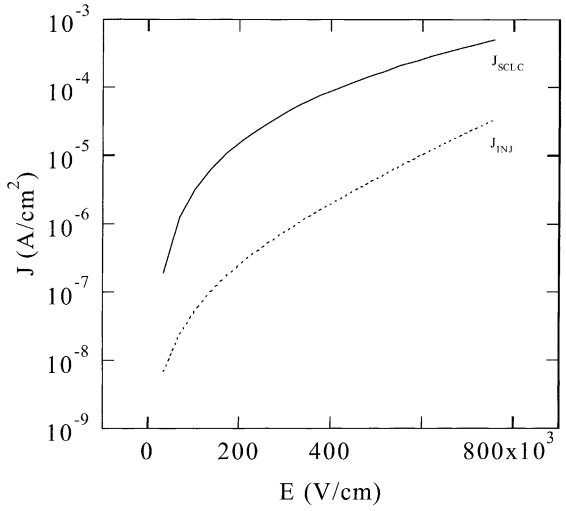

Fig. 2. Electric field dependence of the space charge limited (solid line) and injected (solid circles) current densities for a 14 μm thick PC:TPD sample.

where V is the applied bias, L the thickness of the organic layer and $\varepsilon\varepsilon_0$ is the dielectric constant. The calculated space charge limited current density is shown in Fig. 2 as a solid line.

Shown also in Fig. 2 is the actual current density, J_{INJ}, measured on the same sample under forward bias. This current is due to hole injection from ITO and it is two orders of magnitude lower than the space charge limited current. This means that the ITO/PC:TPD contact is causing a bottleneck in the current flow through the sample, i.e. the current is injection-limited. A figure of merit for the contact is the injection efficiency η

$$\eta = \frac{J_{INJ}}{J_{SCL}} \quad (3)$$

By definition, $\eta = 1$ for an ohmic contact and $\eta < 1$ for a current-limiting contact. The injection efficiency for the ITO/PC:TPD contact is shown in Fig. 3 to vary between 10^{-2} and 10^{-1}. The dependence of η on electric field was found to be in reasonable agreement with the predictions of a model by Scott and Malliaras [10] and consistent with the presence of an energy barrier of 0.5–0.6 eV at the ITO/PC:TPD interface [11].

Improving the efficiency of metal/organic contacts is a subject that has recently received a great deal of attention from the OLED community. This is driven by the need to replace the low work function metals like Ca that are used in OLEDs as electron injectors. Recent experiments indicate that good electron injection can be achieved from Al electrodes when an ultra-thin layer of a low work function metal such as Li or Cs is inserted between the organic and Al [12–14]. This effect has been observed with a variety of low work function metals, in both small molecule and polymer-based devices and it is attributed to doping of the organic semiconductor by direct transfer of electrons

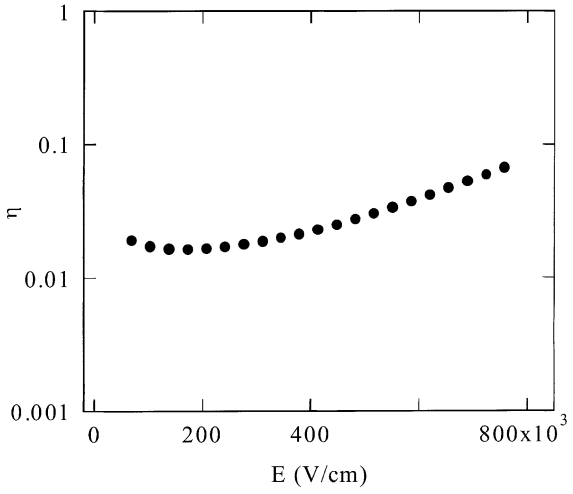

Fig. 3. Electric field dependence of the injection efficiency of the ITO/PC:TPD contact.

from the low work function metal to the organic semiconductor.

Following the same argument, the presence of an ultra-thin layer of a high work function metal at the ITO/PC:TPD interface might lead to an increase of the (hole) injection efficiency. Since the current in ITO/PC:TPD is injection-limited, any improvement of the injection efficiency at the contact will be directly manifested as an increase in the current. This is shown in Fig. 4, where the characteristics of four devices are shown. The devices with the thin metal layers clearly exhibit over an order of magnitude larger current that the one with the bare ITO electrode. The magnitude of this enhancement in the current and the fact that it is independent of the metal used is a strong indication for the formation of an ohmic contact.

The origin of this enhancement is unclear at the moment. Tadayyon et al. [15] have recently shown that ultra-thin Pt films increase the work function of ITO. Since, the Fermi

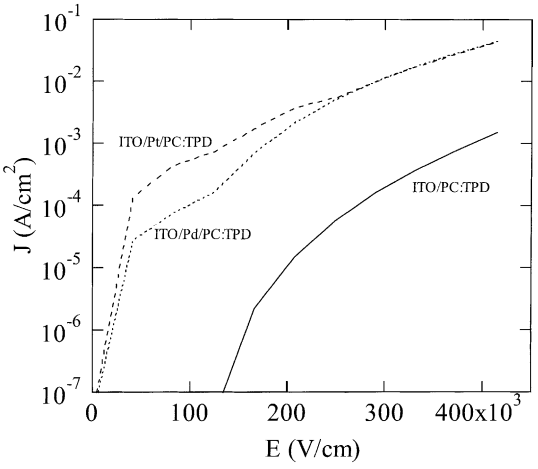

Fig. 4. Electric field dependence of the injected current densities for 120 nm thick PC:TPD samples with various contacts.

levels of Pt and Pd are lower than or close to the highest occupied molecular orbital of TPD, direct transfer of electrons from the organic semiconductor to the electrode might take place. This would create a reservoir of holes near the contact and would make the contact ohmic. We are currently examining the energetics of the modified interfaces to check this hypothesis.

4. Conclusions

In conclusion, we measured the hole injection efficiency from ITO into the organic semiconductor PC:TPD. We find that the contact is current-limiting and causes a bottleneck in the current flow though the sample. Its injection properties can be improved with the introduction of ultra-thin layers of high work function metals at the interface between ITO and PC:TPD.

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