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Estimating the Density of Trap States in the Middle of the Bandgap using Ambipolar Organic Field-Effect Transistors

Roger Häusermann[1†], Sophie Chauvin[1*] Antonio Facchetti[2], Zhihua Chen[2] and Bertram Batlogg[1]

[1] Laboratory for Solid State Physics, ETH Zurich, Zurich 8093, Switzerland
E-mail: hroger@phys.ethz.ch
[2] Polyera Corporation, 8025 Lamon Avenue, Skokie, Illinois 60077, USA

Trap states, present in any semiconductor, have a large influence on charge transport as well as various other physical processes relevant for device performance. Therefore, quantifying the density of trap states (trap DOS) in an organic semiconductor is a crucial step towards understanding and improving organic field effect transistors (OFET), organic photovoltaic cells (OPV) and organic light-emitting diodes (OLED). In recent years there has been a huge progress in characterizing the trap DOS for n- as well as p-type OFETs. Most trap DOS extraction methods, however, are limited to an energy range close to the respective transport level, leaving a large part of the bandgap unexplored. Here we present an estimation of the density of trap states in the whole bandgap using ambipolar organic field effect transistors. The ambipolar OFETs employ the semiconductor PDIF-CN_2 with hybrid V_2O_5/gold contacts to inject electrons and holes.

1. Introduction

Charge transport in organic field-effect transistors is affected by trap states close to the respective transport level (0-0.5 eV), where charge carriers are repeatedly trapped/detrapped while drifting from the source to the drain electrode. Already in the very first study of OFETs the importance of these trap states was recognized and their spectral distribution has been measured. [1] In the following years various methods have been used to investigate trap states in organic semiconductor devices in a wide range of processing conditions and layer configurations. [2][3][4] In rubrene it has recently been shown that the density of deep trap states relevant for the subthreshold region is lower than in the best Si/SiO_2 field-effect transistors. [5] Such a low density of trap states is quite surprising considering the flip-crystal fabrication in ambient air.

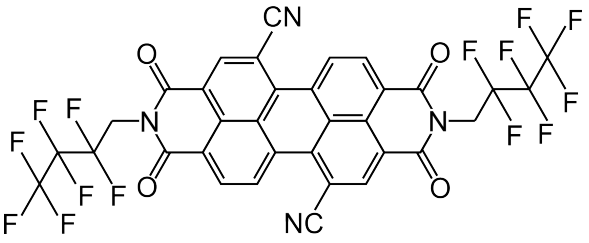

Figure 1: Molecular structure of PDIF-CN_2

All of these studies focused on the density of trap states relatively close to the respective transport level therefore leaving a huge energy range of these wide bandgap organic semiconductors unexplored. These very deep lying trap states are especially important for charge recombination and therefore a loss of efficiency in OLEDs and OPVs. [6] Here we present an analysis of ambipolar OFETs to estimate the density of trap states in the whole bandgap of the semiconductor.

2. Experimental Setup

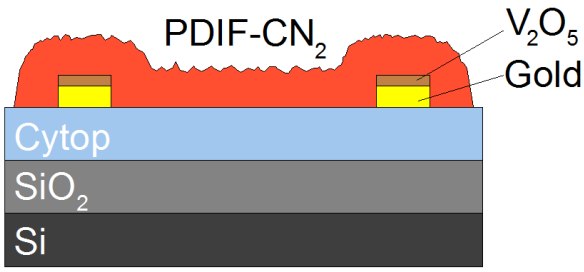

Figure 2: Layer structure of the organic field-effect transistors

We build ambipolar evaporated organic thin-film transistors using N,N'-1H,1H-perfluorobutyl dicyanoperylene carboxydiimide, PDIF-CN_2 (Polyera Corp.), as semiconductor. PDIF-CN_2 is very well known as a high mobility n-type semiconducting material which can be processed using a wide range of methods. [4] The lowest unoccupied molecular orbital (LUMO) is at an energy of -4.5 eV and the material therefore is perfectly suited for electron injection

† Present address: Department of Advanced Materials Science, The University of Tokyo, Chiba 277-8561, Japan

* Present address: Centre de Physique Théorique, École Polytechnique, 91128 Palaiseau cedex, France

through gold contacts. The highest occupied molecular orbital (HOMO), however, sits very deep -6.6 eV and therefore the injection of holes is not possible using standard electrodes. Here, we modify the gold contacts with a thin layer of evaporated Vanadium pentoxide (V_2O_5), a transition metal oxide with a workfunction between 6-7 eV [7] and therefore allowing holes to be injected into the HOMO level of PDIF-CN_2. All evaporation steps are done in a high-vacuum environment (< 10^{-7} mbar). The samples are transferred to an attached probe station without breaking the vacuum. The devices are exposed to oxygen in a controlled fashion to improve the injection of charge carriers.

3. Results and Discussion

The field-effect transistors clearly show ambipolar behavior (Fig. 3). Even though the bandgap is large (2.1 eV) the hybrid V_2O_5/gold contacts therefore allow injection of charge carriers into LUMO level as well as the very deep lying HOMO level. This is a first demonstration of ambipolar transport in this usually n-type semiconductor.

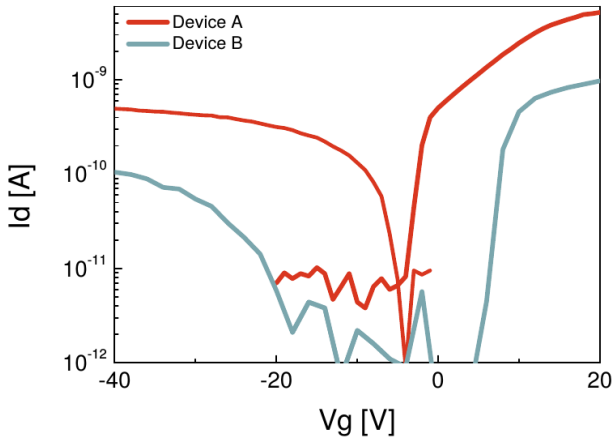

Figure 3: Transfer curves show ambipolar transport in PDIF-CN_2

A short exposure of the OFETs to oxygen improves the charge injection slightly, whereas longer exposure suppresses p-type transport completely. This is due to the reaction of V_2O_5 with oxygen and the high sensitivity of the workfunction on the chemical composition of the V_2O_5. [7] Contact resistance becomes visible at a larger current, but the subthreshold as well as saturation regime the devices are unaffected by the contact resistance.

Several OFETs are built, measured and analyzed. Each device shows a unique transfer behavior in terms of subthreshold swing and the difference between the respective turn-on voltage for p- and n-type transport. These variations originate from a difference in the density of trap states close to the respective transport level, as well as in the middle of the bandgap. We use an analytical framework and a simulation model to analyze the density of trap states close to the respective transport levels, [5][8] whereas the cumulative number of trap states in the middle of the bandgap is estimated from the difference of the turn-on voltage between n- and p-type transport.

We find the density of trap states close to the transport level as well as in the middle of the bandgap to vary by about one order of magnitude. The number of trap states in the middle of the band gap is consistent with the extrapolation from the spectral distribution close to the bandgap. Therefore, this study gives a first hint, that there is no accumulation of defect states in the middle of the bandgap for PDIF-CN_2.

4. Conclusion

We have built ambipolar transistors with a normally n-type semiconductor using hybrid V_2O_5/gold source-drain contacts. These hybrid contacts allow charge to be injected in the LUMO level as well as the deep lying (-6.6 eV) HOMO level. The estimation of the density of trap states reveals that there is no pool of defect states in the middle of the bandgap.

These findings are especially important for devices using ambipolar properties of organic semiconductors. In OLEDs as well as OPVs for example, a low density of trap states in the middle of the bandgap reduces charge recombination resulting in a higher device efficiency. [6]

References

[1] Ebisawa, F., Kurokawa, T. & Nara, S. *Electrical properties of polyacetylene/polysiloxane interface*. J. Appl. Phys. **54**, 3255 (1983).

[2] Kalb, W. L. & Batlogg, B. *Calculating the trap density of states in organic field-effect transistors from experiment: A comparison of different methods*. Phys. Rev. B **81**, 35327 (2010).

[3] Kalb, W. L., Haas, S., Krellner, C., Mathis, T. & Batlogg, B. *Trap density of states in small-molecule organic semiconductors: A quantitative comparison of thin-film transistors with single crystals*. Phys. Rev. B 81, 155315 (2010).

[4] Willa, K. et al. From organic single crystals to solution processed thin-films : Charge transport and trapping with varying degree of order. J. Appl. Phys. 113, 133707 (2013).

[5] Blülle, B., Häusermann, R. & Batlogg, B. *Approaching the Trap-Free Limit in Organic Single-Crystal Field-Effect Transistors*. Phys. Rev. Appl. **1**, 034006 (2014).

[6] Street, R. A., Krakaris, A. & Cowan, S. R. *Recombination Through Different Types of Localized States in Organic Solar Cells*. Adv. Funct. Mater. **22**, 4608–4619 (2012).

[7] Meyer, J., Zilberberg, K., Riedl, T. & Kahn, *A. Electronic structure of Vanadium pentoxide: An efficient hole injector for organic electronic materials*. J. Appl. Phys. **110**, 033710 (2011).

[8] Oberhoff, D., Pernstich, K. P., Gundlach, D. J. & Batlogg, B. *Arbitrary density of states in an organic thin-film field-effect transistor model and application to pentacene devices*. IEEE Trans. Electron Devices **54**, 17–25 (2007).