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Assessing the width of Gaussian density of states in organic semiconductors

Francesco Maddalena [a], Carlo de Falco [b,c,*], Mario Caironi [a], Dario Natali [d,a,1]

[a] Center for Nano Science and Technology @PoliMi, Istituto Italiano di Tecnologia, via Pascoli 70/3, 20133 Milano, Italy
[b] MOX Modeling and Scientific Computing, Dipartimento di Matematica "F. Brioschi", Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy
[c] CEN Centro Europeo di Nanomedicina, Piazza L. da Vinci 32, 20133 Milano, Italy
[d] Dipartimento di Elettronica, Informazione e Bioingegneria, Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy

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ABSTRACT

The Density of States (DOS) is an ingredient of critical importance for the accurate physical understanding of the optoelectronic properties of organic semiconductors. The disordered nature of this class of materials, though, renders the task of determining the DOS far from trivial. Its extraction from experimental measurements is often performed by driving the semiconductor out of thermal equilibrium and therefore requires making assumptions on the charge transport properties of the material under examination. This entanglement of DOS and charge transport models is unfavorable since transport mechanisms in organic semiconductors are themselves still subject of debate. To avoid this, we propose an alternative approach which is based on populating and probing the DOS by means of capacitive coupling in Metal Insulator Semiconductors (MIS) structures while keeping the semiconductor in thermal equilibrium. Assuming a Gaussian shape, we extract the DOS width by numerical fitting of experimental Capacitance–Voltage curves, exploiting the fact that the DOS width affects the spatial distribution of accumulated charge carriers which in turn concurs to define the MIS capacitance. The proposed approach is successfully tested on two benchmark semiconducting polymers, one of n-type and one of p-type and it is validated by verifying the robustness of the extraction procedure with respect to varying the insulator electrical permittivity. Finally, as an example of the usefulness and effectiveness of our approach, we study the static characteristics of thin film transistors based on the aforementioned polymers in the framework of the Extended Gaussian Disorder transport model. Thanks to the extracted DOS widths, the functional dependence of current on the gate voltage is nicely predicted and physical insight on transistor operation is achieved.

1. Introduction

Organic electronics has been rapidly advancing in the last thirty years, with impressive performance improvements for organic transistors [1,2], light emitting diodes [3,4] and solar cells [5,6]. In spite of the progress so far, the fundamental properties of these materials are still not fully understood and the Density of States (DOS), the accurate description of which is mandatory to rationalize semiconductor optoelectronic properties, makes no exception [7–17]. The determination of the DOS is a far-from-trivial problem in van der Waals, disordered molecular solids such as organic semiconductors, where every molecule has its own unique environment created by its

* Corresponding author at: CEN Centro Europeo di Nanomedicina, Piazza L. da Vinci 32, 20133 Milano, Italy.
E-mail addresses: francesco.maddalena@iit.it (F. Maddalena), carlo.defalco@polimi.it (C. de Falco), mario.caironi@iit.it (M. Caironi), dario.natali@polimi.it (D. Natali).
[1] Principal corresponding author.

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neighbors [18,19]. Atomistic Simulations based on realistic morphologies are in principle possible, but the overwhelming computational cost of this approach strongly limits the system sizes it allows to access [20,21].

From the experimental point of view, various techniques have been proposed to assess the DOS. Approaches based on electrical measurements rely upon driving the semiconductor out of thermal equilibrium and measuring carrier mobility under a variety of experimental conditions (space charge limited current [22], Thin Film Transistor (TFT) transfer characteristic curves [23–26], photoconductivity [10], impedance spectroscopy [27]). Since carrier transport actually depends on the DOS, there is a strong concern whether the extracted DOS is really the physical one or rather an *effective* one. Such effective DOS, together with the chosen transport model, can often reproduce the experimental mobility of a specific device, but its use in determining other optoelectronic properties of the organic semiconductor would be questionable [16,15].

Other methods not involving carrier transport have been proposed such as photoemission spectroscopy (PES) [28–30], thermally stimulated luminescence (TSL) [31], electron spin resonance (ESR) [32,33], Kelvin probe method (KP) [34–36], scanning Kelvin probe force microscopy (SKPM) of TFT channel, electrochemical methods (ECM) [37,38]. Until now none of them has gained enough consensus to be regarded as the reference benchmark [39]: PES suffers from charging in case of thick samples [36], TSL requires non trivial theoretical models for interpretation [40,41]; ESR requires a very specialized experimental setup; KP involves the non-trivial preparation of a set of samples of increasing thickness; SKPM is mostly suited for very thin active layer [14,41]; in ECM doping is likely to introduce additional structural and electrostatic disorder, making it very difficult to assess the neat material properties [42].

We propose an approach based on Capacitance–Voltage (CV) measurements on Metal–Insulator–Semiconductor (MIS) structures: thanks to suitably low-frequency applied signals, MIS capacitors work in the quasi static regime thus keeping the semiconductor in thermal equilibrium. In addition, the relatively simple experimental setup is in favor of a wide applicability of the method. We assume a Gaussian shape for the DOS: the justification for this choice-indeed very commonly adopted [43–45] – lies in the fact that coupling between a charge carrier and a random distribution of static or induced dipoles leads to a Gaussian function [46]. We focus our efforts to extract the DOS width and we accomplish this by numerical fitting of experimental measurements, exploiting the fact that the DOS width has a sizable impact on the spatial distribution of accumulated carriers, which in turn affects the shape of the CV curve. Apart from few exceptions [47,48], the correlation between the dependence of the MIS capacitance on the gate bias and the DOS width has been overlooked, and CV measurements on organic MIS structures have been analyzed in the framework of Mott-Schottky depletion region [49–51] or have been used to extract the contact resistance at the metal/semiconductor interface [52,53].

We report on the application of our method to two model and widely studied materials: the n-type polymer poly[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-dithiophene) (P(NDI2OD-T2)) and the p-type polymer poly(2,5-bis(3-tetradecylthiophen-2-yl) thieno[3,2–50]thiophene) (PBTTT) (see Fig. 1). For both materials we are able to obtain very good fittings of experimental CV curves and to robustly extract DOS widths. In addition, we show that the extracted DOS widths, combined with the Extended Gaussian Disorder Model for transport, allow for a detailed modeling of the linear regime of (P(NDI2OD-T2)) and PBTTT based transistors.

2. Methods

2.1. Numerical model

The structure of a MIS capacitor is sketched in Fig. 1a. It consists of a stack comprised of: a metal (back) contact which is kept grounded, a semiconducting layer, an insulating layer and a top (gate) metal contact where the external voltage bias is applied. The geometrical setting for the numerical model is reported in Fig. 2. We denote by z the spatial coordinate normal to the semiconductor/insulator interface and we place the origin of the z axis in correspondence of such interface. We denote by t_{sc} (t_{ins}) the thickness of the semiconductor (insulator) layer. We assume the extension of the device in the x and y directions (the coordinates in the plane parallel to the interface) to be much larger than both t_{ins} and t_{sc} and we consider both materials to be homogeneous and isotropic. We further assume that: (i) the semiconductor is intrinsic, as it is very often the case in organic semiconductors; (ii) the semiconductor is unipolar and to fix ideas is of n-type; (iii) thermal carrier generation can be disregarded, as energy gaps are usually relatively large; (iv) insulator leakage currents are negligible.

In DC, the MIS capacitor is in quasi equilibrium irrespective of the gate bias, as no DC current can flow across the structure; therefore we can introduce a well-defined Fermi level E_F independent of z. With no loss of generality, we can set $E_F = 0$. We denote by $E_{LUMO}(z)$ the energy of the Lowest Unoccupied Molecular Orbital and by $E_{HOMO}(z)$ the energy of the Highest Occupied Molecular Orbital at a given point z in our computational domain. We define the energy barrier for electron injection at the metal/semiconductor interface as

$$\Phi_B := E_{LUMO}(-t_{sc}) - E_F(-t_{sc}) = E_{LUMO}(-t_{sc}).$$

The total amount of charge per unit volume at a given point z in the device can be expressed as the sum over all admissible energies of the DOS, $g_\sigma(E)$, times the occupation probability for that state, $f(E)$, *i.e.*

$$n = \int_{-\infty}^{\infty} g(E - E_{LUMO}) f(E - E_F)\, dE. \quad (1)$$

In the following we will always assume that Fermi statistics applies. As to the DOS we adopt a single symmetric Gaussian centered at E_{LUMO} and parametrized by its standard deviation

$$g_\sigma(\cdot) = \frac{N_0}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(\cdot)^2}{2\sigma^2}\right), \quad (2)$$

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