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Simulation of Injection Currents into Disordered Molecular Conductors

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Abstract

During the past decades, the development of microelectronic devices based on polymeric active layers experienced considerable progress. The improved understanding of the physics of π-conjugated materials led to the realization of novel devices like photovoltaic cells, thin-film transistors, and light-emitting diodes. The role of Technology-CAD software for molecular films is essentially the same as that for inorganic semiconductors. The obstacles and peculiarities encountered by the underlying numerical simulations however are quite different. We present results obtained with our Kinetic Monte Carlo simulator modeling an organic sandwich structure in situ. The active layer is an intrinsic amorphous Zinc Phthalocyanine film embedded between two gold contacts.
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Keywords: Zinc Phthalocyanine, Kinetic Monte Carlo, Technology-CAD, Organic Semiconductors

1. Introduction

Almost 25 years ago Heinz Bässler established the gold standard for simulating the propagation of currents through disordered, π-conjugated bulks [1]. The molecular topography of a technologically relevant device is characterized by disorder and so is its density of states. In the Bässler-model, all states are assumed to be localized. It is moreover taken as granted that the energies ε_i of the electronic spectra are sampled from a Gaussian with width σ

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mirroring the degree of disorder. Transitions between overlapping localized states separated by some distance a, $\Psi=e^{-r/a}$ are facilitated by

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Nomenclature

ZnPc	Zinc Phthalocyanine
FePs	Iron Phthalocyanine
DOS	Density of states
IPES	Inverse photoemission spectroscopy
UPS	Ultraviolet photoelectron spectroscopy
HOMO	Highest occupied molecular π-orbital
LUMO	Lowest unoccupied molecular π^*-orbital
MA	Miller-Abrahams
KMC	Kinetic Monte Carlo
WKB	Wentzel-Kramers-Brillouin
k_B	Boltzmann constant (J/K)
h	Planck's constant (Js)
f_D	Linear Debye frequency (1/s)
E_D	Debye energy (eV)
Θ_D	Debye Temperature (K)
a	Lattice constant (m)
T	Temperature (K)
r	Spatial distance between two sites (m)
ε_i	Energy of site I (eV)
γ	Wave function overlap (1/m)

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the combined action of tunneling $e^{-2\gamma a}$ and Boltzmannian, single phonon-absorption from the surrounding heat bath, $e^{-\Delta E/kT}$. ΔE denotes the energetic difference of the states participating in a charge transfer. Together with a cumulative factor ν_0 subsuming the acoustical properties and the applied electric field F the transition rate between the oxidized departure- and the reduced target orbital is finally thus casted into the well-known Miller-Abrahams rate for the endothermic and the exothermic case [1]:

$$\nu_{ij} = \nu_0 \times e^{-2\gamma a} \times \Big\{ \begin{array}{c} e^{-\left[\varepsilon_i - \varepsilon_j - eF(x_i - x_j)/k_B T\right]} \\ 1 \end{array}$$

The Bässler-formalism and its numerous variations were successfully applied to numerous problems and phenomena governing organic devices' electrical characteristics. Five years after Bässler's celebrated paper the seminal work of Wolf, Arkhipov and Bässer [2] even extended the Gaussian disorder formalism to the simulation of current injection. With regard to the opaque physics of organo-metallic interfaces this was an indeed bold undertaking. According to the textbook of Köhler and Bässler [3] Gartstein and Conwell [4] were originally the first researchers having the idea to integrate metal electrodes self-consistently as hopping sites at the electrode's Fermi level. Irrespective of this drastic simplification, Wolf et al. [2] obtained simulation results with good congruence when compared to empirical findings. Wolf et al. considered the attraction of injected carriers with their mirror charges. The mutual interaction between carriers and with space charges as well, however, was neglected. On the other hand, the competition between metal and polymer states as jump targets for excited metal electrons was included very well. The hopping lattices used by Wolf and co-workers were anything else than simple. In fact, depending on the dissociation of carriers from their image charge, the lattice was once viewed as „real lattice" and once as „simulation lattice" consisting of a stack of injection planes adjacent to the contact.

2. Simulations

Several researchers since the works of Wolf et al. also simulated charge injection, either by using a fixed rate [5], the Miller-Abrahams rate [6], the Marcus Rate [7] or no rate at all by assuming an Ohmic contact providing a certain amount of carriers in the first layer [8].

Obviously, there are always numerous technical differences between different special purpose Monte Carlo simulators and thus we may safely assume that we are far from knowing in how many details our software deviates from those of others. Concerning our Kinetic Monte Carlo algorithm, all observables were plugged as 64-bit long doubles into a monolithic ANSI-C source code "as is". Neither did we use reduced quantities nor did we scale anything or submit the currents to any post-processing. To capture finite-size effects no periodic boundaries were applied. Each node of the hopping lattice hosted both the p-conductive π- as well as the n-conductive π^*-state. In other words, we left it up to the dynamics to which extend n-conduction participates in the transport due to space charge accumulations or statistically scattered electronic spectra. The question of whether an organic material is n- or p-conductive cannot be answered by intrinsic material properties but depends solely on the constellation of the involved materials. For the sake of simplicity transitions between the two bands were not considered. Technically it would be no problem to include interband transitions and their characteristic time scales into the Kinetic Monte Carlo simulator.

Our motivation to inject naively into real space is based on the fact that i) spatial effects especially at the hetero-junction can then be modeled straightforwardly and, ii) even more important, our carrier gases are interacting. Modeling interacting electrons becomes intractable in an abstract lattice as used in Wolf's single particle simulations.
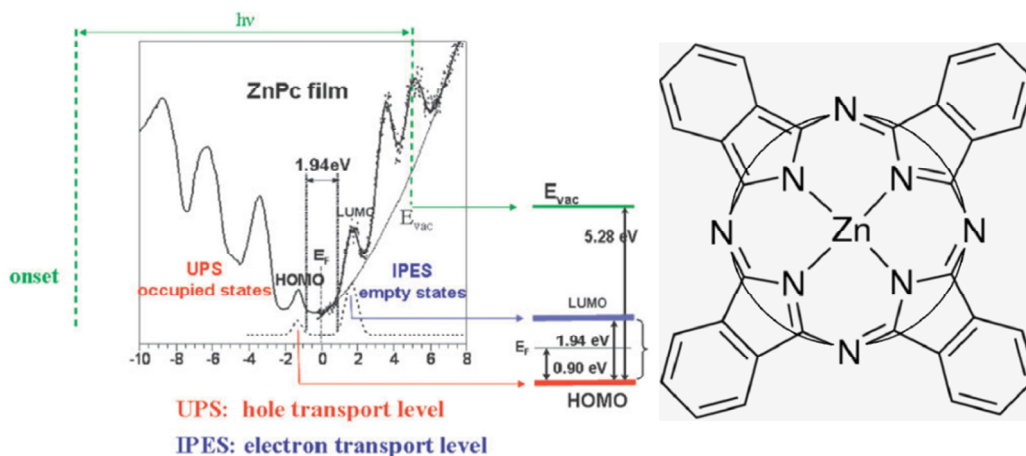

Fig. 1. (a) UPS- and IPES-measurements for an intrinsic 100 Å thin ZnPc film on an Au-substrate [9]. With permission from Elsevier, Flores et al. [14] reprinted the figure published by [9] and enriched it with the here shown colored remarks to illustrate how the HOMO- and the LUMO-level are extracted from these spectroscopic data. The bands are the means for the Gaussian densities of states; (b) The electronic spectrum of the ZnPc-monomer can excellently be predicted by the perimeter (particle-on-a-ring) model. Hence, the electrons may be assumed to propagate freely on the ring, a strong hint that the WKB-method is applicable to the molecular electron exchange.

Unsurprisingly, the Miller-Abrahams based simulations replicated thermionic IV-characteristics, contradicting the experimental data recorded by [9]. More surprisingly, thereby it made no big difference whether remote Coulomb interactions between the carriers were fully taken into account or simply reduced to a hard-ball interaction for particles on the same level. Third, the produced curves showed a significantly weaker temperature-dependence than predicted by the Richardson-Schottky formula - a consequence of emitting not into vacuum but into a system of discrete localized electron states. Finally, the simulated currents depended on the film thicknesses and, hence were bulk-limited, contradicting clearly the injection-limited regime observed by [9].

In his master thesis Yevgeni Preezant formulates the heart of the problem quite nicely, when he states literally [10]: „*It is clear that Miller-Abraham's expression [...] gives the right ratio between the real hopping rates. However, all the structural information embedded in "T" (tunneling probability) is lost and the rates themselves are not accurate. Moreover, effects imposed by external field, applied to the system, on T are lost as well*".

Countless papers have been dedicated to the refinement of the spatial portion of the hopping rate. As one example amongst many others let us cite Jakobsson et al.[11], who modeled the "true off-diagonal disorder".

We attempted to make the simulations more realistic. We are not aware if the Wentzel-Kramers-Brillouin (WKB) method has already been used for hopping simulations before. We think that this idea is quite obvious because this computationally cheap approximation plays such an overwhelming role in solid-state microelectronics. We assumed the potential barriers between metal- and bulk-sites as triangular and rectangular barriers with the thickness of the lattice constant (the simplest conjecture, as we think) were placed between bulk sites. All local three-dimensional field strengths and all one-dimensional barrier shapes were updated rigorously, the rectangular barriers of course become trapezoidal under the influence of fields. To understand how we justify the application of the WKB-method to molecular orbitals, we refer to Fig. 1 b).

The second modification we applied concerns the energy mismatches appropriate for the MA-rate. The latter assumes that all energy differences are equilibrated by the absorption of a single phonon. In other words, it is assumed that there are no intermediate excited states during an upward hop. Inspired by an early work of Sergei Baranovskii on chalcogenides [12], we used an expression from Mott's classical textbook [13] to correct the transition rate for multi-phonon processes. The Debye energy $E_D = \Theta_D \times k_B$ indicates the transition from the single phonon to the multi-phonon regime [13]. We are aware that incorporating the resulting correction $\exp(-|\varepsilon_i - \varepsilon_j|/\hbar\, f_D)$ for a van der Waals-bound and hence, a soft organic lattice is questionable and at best a zero-order approximation, however, we are not aware of any better assumption.
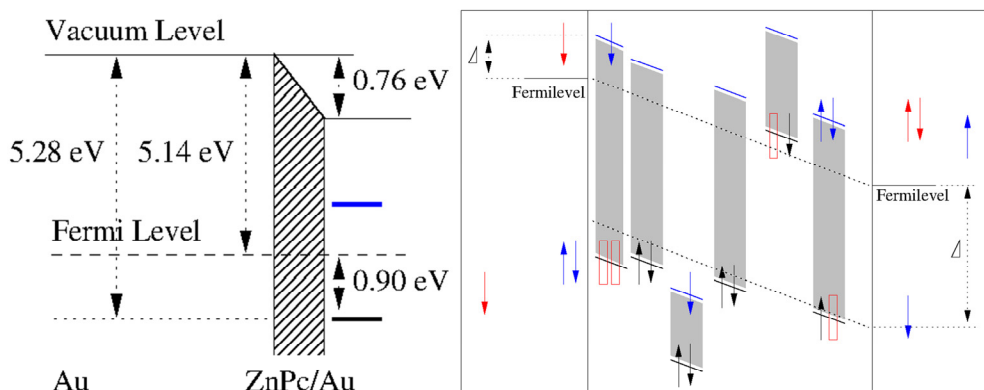

Fig. 2. (a) Due to the opaque interface physics, the spectral offsets at metal-organic heterojunctions cannot simply be calculated as differences but have to be measured in-situ [9]; (b) Two-level Hubbard cells form the nodes of the hopping lattice. Each level is capable to host two spin-paired bonding or antibonding electrons. In case of saturation the levels become insulating. A saturated HOMO-level is electrically neutral, HOMO-vacancies are immobile and positively charged. A hard-ball on-site Coulomb interaction (0.9eV) is used to cut off the Coulomb force between carriers residing on the same level. Due to the low dielectric constant ($\varepsilon_r \approx 3.2$) mirror charges have to be incorporated.

3. A Glimpse of Results

We focus the presentation of results on problems occurring when fine-tuning the parameter set. The simulation domain is a cube of 20nm edge length, charge extraction and injection by the electrodes was included self-consistently. One and the same rate is used for the whole device. Each electron feels its own mirror charge and also that of the others. The image charges in both the cathode and anode are consistently considered. The mean distance between the disordered monomers depends on the morphologic phase. In the ordered herringbone-stacked phase the distances are around 0.6nm, for the amorphous film we thus view a = 0.8nm as realistic. An electric field $F = 2 \times 10^7$ V/m has been applied at room temperature T=300 K. The energetic disorder σ is 3 eV. As a first guess, 5eV high

barriers were introduced between the bulk sites. No statistical distribution was assumed for these bulk-internal barriers. We did for this case not succeed in retrieving the Debye temperature for ZnPc in any morphologic phase. Thus the value for FePc had to be used as a surrogate. For α-FePc, $\Theta_D = 143$ K and for the β-phase the Debye temperature is 199 K [15]. The Debye temperature for Gold can be found in any standard textbook, 165 K.
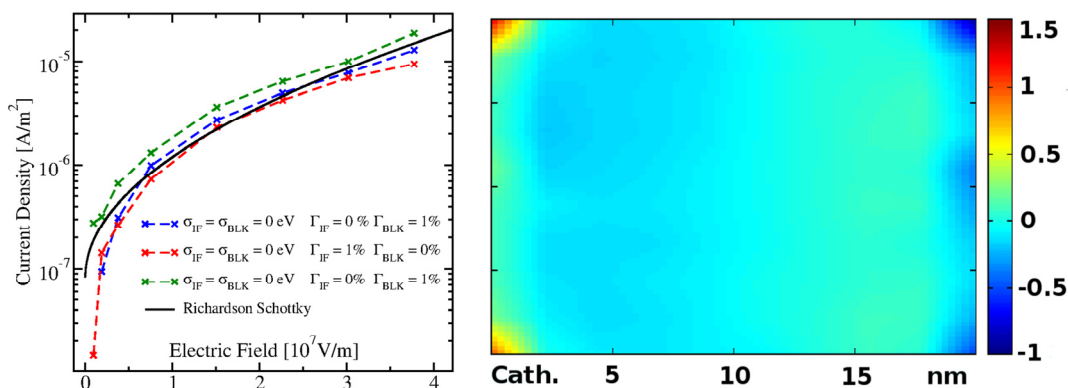

Fig. 3. (a) MA-injection into the Hubbard-cells gives thermionic behavior in sharp contrast to the experiment. Γ denotes the width of the Gaussian distribution used for sampling the wave function overlap ("spatial disorder"); (b) Local current densities in A/m². The charge backflow into the electrodes is much too high and prevents a stabile charge flow. The red areas at the cathode are frequently called "hot spots", regions of enhanced injection into favorable tail states.

As the color-mapped currents and potentials indicate, the contacts are extremely dominant. Contact-dominated devices are typical for organic electronics. However, in our virtual device the mirror charges exert an attraction reaching far beyond the Coulombic injection barrier maximum at ~2.2nm. Consequently the HOMO-electrons are
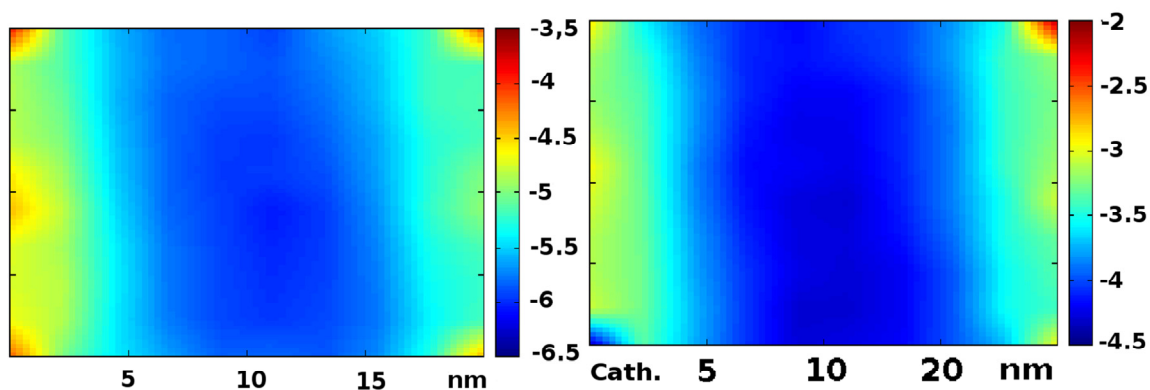

Fig. 4. (a) Site potentials of the p-conductive HOMO-sites, tilted by the applied field. The units are eV. The applied bias is shielded by the inert positive counter-charges which have been uncovered by the depletion of the HOMO-level; (b) Density of n-conductive LUMO-states in eV as "dressed" by space-charge and image-force effects, the applied field has been disregarded for this chart. The dressed sites are even more correlated. Potential fluctuations, as an essential ingredient for the localization of states are hardly noticeable.

evacuated and uncover the hitherto shielded positive background charges of the σ-bound molecular skeleton. The effect of the emerging potential is twofold. Firstly it implies strongly correlated levels and, secondly, it shields the

applied field. To conclude we report an observation concerning long range jumps. The influence of remote tunneling events is currently lively discussed in organic microelectronics. We observed that about 50% of all electron hops in the bulk and at the interface take place over a distance of about two lattice constants. These long range transfers contribute to the excessive π-electron mobility and thus stand in causal interrelationship with the depletion of the HOMO-band. Antibonding π^*-electrons are hardly injected into the LUMO band, n-conduction does not occur.

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