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Macroscopic modeling of spin injection and spin transport in organic semiconductors

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ABSTRACT

We describe device models for spin injection, transport, and magneto-resistance in structures consisting of an organic semiconductor layer sandwiched between two ferromagnetic contacts. Carrier transport in the organic semiconductor is modeled with spin-dependent transport equations in drift-diffusion approximation. The effectiveness of spin-selective tunnel contacts on spin-polarized injection and magneto-resistance is examined on the basis of a simple analytical model. In agreement with earlier results, we find that spin injection from ferromagnetic metallic contacts into organic semiconductors can be greatly enhanced if (spin-selective) tunneling is the limiting process for carrier injection. We then explore the effects of the injected space charge and of spin relaxation in the semiconductor by comparing the results of a numerical calculation with the analytical model. For relatively thick organic semiconductor layers the injected space charge has strong effects on charge injection and, hence, on spin injection at high bias. Lastly, we consider a simple model for the bias dependence of the tunnel contacts and find that this effect may limit spin injection to relatively low currents.

1. Introduction

Organic semiconductors – primarily certain π-conjugated polymers and crystals of relatively small hydrocarbon molecules – have in recent years become viable materials for optoelectronic and photovoltaic devices, in particular for certain low-cost and large-area applications [1,2]. Displays based on organic light emitting diodes (OLEDs) are already seeing commercial use. On the other hand, spin-based electronic devices, a set of ideas that has been called spintronics, have shown considerable potential for a great extension of device functionality [3,4]. Commercial success of metal-based spintronic devices has been achieved with recording heads and magnetic memories that use the giant magneto-resistance (GMR) and tunneling magneto-resistance (TMR) effects of so-called spin valves [5]. Intense research efforts are now devoted to extend these phenomena into the realm of semiconductors, and there has been some success in spin injection and detection using inorganic semiconductors [6,7]. However, organic semiconductors appear to have certain unique advantages for spin transport because the weak spin–orbit coupling and hyperfine interaction is expected to lead to very long spin-coherence times [8]. The potential for integrating organic semiconductors with extremely spin-polarized (half-metallic) materials provides additional potential for organic semiconductor spintronics, and the prospect of spin-polarized carrier injection in OLEDs could ultimately increase the efficiency of these devices (recent experiments have indicated that spin-polarized injection may enhance the electroluminescence of OLEDs [9], and we reported model results that show how spin-polarized injection affects the formation and distribution of (emissive) singlet excitons) [10]. However, strongly spin-polarized injection from a ferromagnetic (FM) metal contact into any semiconductor is a challenging task [11]. In order to achieve significant spin injection, either very strongly polarized magnetic contacts, i.e. essentially half-metallic materials, or tunnel barriers with spin-selective transmission probability between the contact and the semiconductor are needed [12–16].

Although injection of spin-polarized charge carriers may be accomplished through half-metallic contacts or spin-selective tunnel contacts, the detection of the resulting current polarization is a separate and non-trivial task. Direct gap III–V semiconductors offer a unique opportunity for the detection of spin-polarized electrons through the measurement of the polarization of light generated by the radiative recombination of these electrons [7]. Unfortunately, the selection rules that enable this detection mechanism are not applicable to organic semiconductors. Efforts to detect spin-polarization in these latter materials therefore have focused on the measurement of the magneto-resistance of organic spin valves. Indeed, magneto-resistance effects in organic spin valve structures have been reported in the literature [17–21]. These devices typically

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consist of an organic semiconductor layer sandwiched between two FM contacts. In some cases the FM contacts were made from materials that are thought to be essentially half-metallic, i.e. nearly all electrons at the Fermi level are of the same spin. If the organic semiconductor layer thicknesses are much larger than tunnel lengths, carrier transport in the semiconductor is expected to be diffusive, and the observed magneto-resistance is not attributed to tunneling from one metal contact to the other (TMR). However, not all experimental studies reported magneto-resistance for comparable organic semiconductor spin valves [22]. In the latter study, the lack of measurable magneto-resistance was attributed to a lack of appreciable spin-polarization of the current. The present situation clearly calls for further exploration, in particular of the relationships between spin-polarized carrier injection, transport, and extraction that can give rise to magneto-resistance.

2. Model description

In this paper, we present a model of spin injection, diffusive transport, extraction, and magneto-resistance for organic spin valves. The spin valves envisioned consist of an organic semiconductor layer (thickness d) sandwiched between two FM contacts. The organic semiconductor is not doped, i.e. all charge carriers involved in transport are injected carriers (this is quite different from the cases usually encountered with conventional, inorganic semiconductors). For convenience, the model is formulated for negative charge carriers (electrons). In many cases, the current in the organic semiconductor may in fact be due to positive charge carriers (holes), but this does not affect the results and conclusions reached. The model allows for spin-selective tunnel contacts between the ferromagnets and the organic semiconductor. Fig. 1 shows a schematic energy band diagram for the injecting contact under bias. The tunnel barrier has thickness δ, and $\mu_\uparrow$ and $\mu_\downarrow$ are the quasi-Fermi levels for spin-up (SU) and spin-down (SD) electrons.

In the spin valve geometry envisioned, the left electrode is the injecting contact and right electrode is the extracting contact. The polarization of the left electrode is always in the up-direction. For parallel alignment of contact magnetizations, the polarization of the right electrode is in the up-direction, whereas for anti-parallel alignment, the polarization of the right electrode is in the down direction. In the case of parallel polarization, the quasi-Fermi levels of spin-up and spin-down carriers have to cross inside the organic semiconductor. For anti-parallel contact magnetization the quasi-Fermi levels do not cross (a schematic band diagram of the entire structure may for example be found in Ref. [15]).

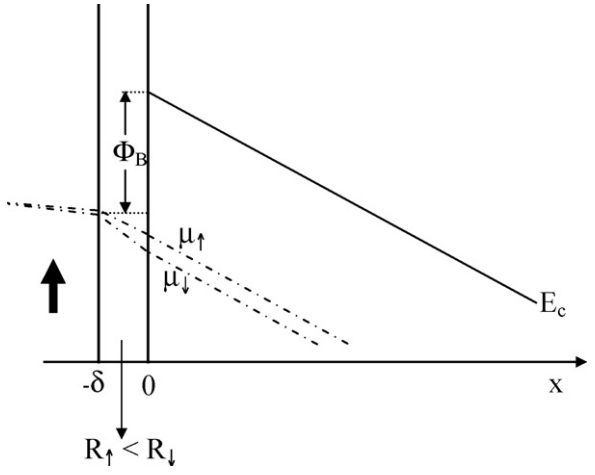

Fig. 1. Schematic band diagram of injecting contact under electron injecting bias conditions. E_c is the conduction band energy. An analogous structure is envisioned as the carrier extracting contacts with a tunnel barrier at $d \le x \le d+\delta$.

In our model, the FM metal contacts are described by four parameters: the conductivity, σ, a conductivity polarization coefficient, α, the spin diffusion length, Λ, and the Schottky barrier height, Φ_B. The conductivities of SU and SD electrons are related to σ by $\sigma_\uparrow = \alpha\sigma$ and $\sigma_\downarrow = (1-\alpha)\sigma$, with $0 < \alpha < 1$. Subscripts L and R refer to the left and right contacts.

Inside the bulk FM contact, the different conductivities of SU and SD electrons give rise to a net spin current (current due to SU electrons minus current due to SD electrons), that is equal to $(2\alpha - 1)J$, where J is the charge current, i.e. SU current plus SD current. Under steady-state conditions the charge current is constant throughout the entire structure. The spin current tends to decrease towards the interface to the non-magnetic semiconductor. The spin current, J_s and the charge current at the interfaces $x = -\delta$ and $x = d + \delta$ are related to the difference in the quasi-Fermi levels at the left (L) and right (R) electrodes by [15],

$$J_s(-\delta) = (2\alpha_L - 1)J + 2\alpha_L(1-\alpha_L)\frac{\sigma_L}{\Lambda_L}\frac{2kT}{e}\left(\frac{\Delta\mu(-\delta)}{2kT}\right), \tag{1a}$$

$$J_s(d+\delta) = (2\alpha_R - 1)J - 2\alpha_R(1-\alpha_R)\frac{\sigma_R}{\Lambda_R}\frac{2kT}{e}\left(\frac{\Delta\mu(d+\delta)}{2kT}\right). \tag{1b}$$

Here $\Delta\mu = \mu_\uparrow - \mu_\downarrow$ and e is the fundamental charge.

Assuming no spin scattering at the contact interface, i.e. $J_s(-\delta) = J_s(0)$ and $J_s(d+\delta) = J_s(d)$, and describing the spin-selective tunneling process through the contact barriers by resistances $R_\uparrow$ and $R_\downarrow$, yields the differences of the quasi-Fermi levels at $x = 0^-$ and $x = d^+$.

$$\Delta\mu(0^-) = \Delta\mu(-\delta) + \frac{1}{2}e(R_{\uparrow L} - R_{\downarrow L})J + \frac{1}{2}e(R_{\uparrow L} + R_{\downarrow L})J_S(0) \tag{2a}$$

$$\Delta\mu(d^+) = \Delta\mu(d+\delta) - \frac{1}{2}e(R_{\uparrow R} - R_{\downarrow R})J - \frac{1}{2}e(R_{\uparrow R} + R_{\downarrow R})J_S(d) \tag{2b}$$

(Here we allow for a possible additional discontinuity in the quasi-Fermi levels at the semiconductor interfaces as it occurs for example if carrier injection is limited by thermionic emission in the absence of the tunnel barrier). It is convenient to combine the effects of the FM metal and the tunnel contacts and to express the polarization effect in the semiconductor in terms of $\Delta\mu(0^-)$ and $\Delta\mu(d^+)$:

$$\Delta\mu(0^-) = \frac{1}{2}e(R'_{\uparrow L} - R'_{\downarrow L})J + \frac{1}{2}e(R'_{\uparrow L} + R'_{\downarrow L})J_S(0) \tag{3a}$$

$$\Delta\mu(d^+) = -\frac{1}{2}e(R'_{\uparrow R} - R'_{\downarrow R})J - \frac{1}{2}e(R'_{\uparrow R} + R'_{\downarrow R})J_S(d) \tag{3b}$$

where the effective resistances are defined by:

$$R'_{\uparrow L,R} - R'_{\downarrow L,R} = R_{\uparrow L,R} - R_{\downarrow L,R} - \frac{(2\alpha_{L,R} - 1)\Lambda_{L,R}}{\alpha_{L,R}(1-\alpha_{L,R})\sigma_{L,R}} \tag{4a}$$

$$R'_{\uparrow L,R} + R'_{\downarrow L,R} = R_{\uparrow L,R} + R_{\downarrow L,R} + \frac{\Lambda_{L,R}}{\alpha_{L,R}(1-\alpha_{L,R})\sigma_{L,R}} \tag{4b}$$

Because the last terms in Eqs. (4a) and (4b) are proportional to Λ/σ, they tend to be very small for conventional ferromagnetic metals on the scale of resistances relevant to semiconductor devices.

The organic semiconductor is characterized by the electron mobility, μ_n, a spin relaxation time constant, τ_s, and an effective density of states for the conduction band, n_0, which is approximately equal to the molecular (or monomer) density. Steady-state carrier transport in the organic semiconductor is governed by the spin-dependent continuity equations,

$$0 = \mu_n\frac{d}{dx}\left(n_\uparrow E + \frac{kT}{e}\frac{dn_\uparrow}{dx}\right) - \frac{n_\uparrow - n_\downarrow}{\tau_s}, \tag{5a}$$