Diffusion theory of spin injection into organic polymers

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Abstract
Instead of spin electrons or holes, the carriers in polymers are supposed to be spin polarons or spinless bipolarons. Based on the spin diffusion theory and Ohm's law, we studied spin-polarized injection into organic polymers. It was obtained that only spin polarons are responsible for the current spin polarization in a ferromagnetic (FM)/organic system. Effects of the conductivity matching and the interfacial resistances on the current spin polarization were discussed.

1. Introduction

Magnetoelectronics or spintronics is a field of growing interest since the discovery of giant magnetoresistance (GMR) [1–3]. Electron spin injection and spin dependent transport are essential aspects of spintronics and have been extensively studied in a number of different contexts including from FM metals to superconductors [4], from FM metals to normal metals [5], from FM metals to nonmagnetic semiconductors [6] and from magnetic semiconductors to nonmagnetic semiconductors [7]. Spin injection and transport in some other systems have also been suggested and studied. For example, Gomez *et al* suggested a nanocontact MRAM (magnetoresistive random access memory) [8]. Tsukagoshi and co-workers demonstrated that the $I–V$ curve of a carbon nanotube sandwiched between two Co contacts presents hysteresis when a magnetic field is applied, which makes carbon nanotubes very attractive for spintronics applications [9]. Coey *et al* showed evidence for a strong induced magnetic polarization at room temperature in a graphite system with embedded FM nanoclusters [10]. In particular, Dediu's group has observed spin injection into thin films of the conjugated organic material sexithienyl (T_6) at room temperature [11]. The half-metallic manganite $Re_{1-x}Sr_xMnO_3$ (in which electron spins at the Fermi surface are completely

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polarized) was used as the electron provider. A strong magnetoresistance (up to 30%) was measured on a nanostructured planar hybrid junction $La_{0.7}Sr_{0.3}MnO_3/T_6/La_{0.7}Sr_{0.3}MnO_3$. The spin diffusion length in T_6 is about 200 nm at room temperature. Following this experimental result, Xie *et al* suggested a first theoretical model for the $Re_{1-x}Sr_xMnO_3$/polymer structure and studied the lattice displacements, charge density and spin density distribution of the system [12]. More recently, important developments in experiments were made by Xiong *et al* [13], who have built an organic spin valve with the small π-conjugated molecule 8-hydroxy-quinoline aluminium (Alq_3). The Alq_3 is sandwiched between a layer of cobalt and an alloy of lanthanum, strontium and manganese ($La_{0.7}Sr_{0.3}MnO_3$). The measured magnetoresistance can be as high as 40% at low temperature. Ruden and Smith have suggested a theoretical model to describe electrical spin injection from an FM contact into a conjugated organic semiconductor [14]. The carriers in the organic semiconductors were supposed to have spin $1/2$, and then the thermionic emission, surface recombination, tunnelling through the Schottky barrier and drift–diffusion were discussed.

Most of the proposed applications and mechanisms may simply translate the well known concepts of conventional inorganic semiconductors into organic systems. However, there are instinct differences in the organic semiconductors and the inorganic ones. An inorganic semiconductor has a 'rigid' lattice and energy band structures. The carriers are extended electrons or holes with spin $1/2$. Organic semiconductors have the character of low dimension. The lattice and the energy band structure are 'soft'. Any changes of the external conditions can induce the reorganizing of the structure. Doping or photo-exciting can induce some self-trapping states, such as polarons and bipolarons, which may be the carriers in the organic polymers (e.g. polyacetylene) as indicated in [12, 15–17]. As a polaron has spin $1/2$ while a bipolaron no spin, only the spin polarons are responsible for the spin-polarized transport in organic polymers. Due to the effect of temperature, pressure and external electric field, bipolarons and polarons in organic polymers are not stable but can transform into each other. Two spin polarons can annihilate into one spinless bipolaron, while a bipolaron can be decoupled into two spin polarons. In this paper we do not study the formation of polarons and bipolarons but just suppose that they coexist in the organic layer with a density proportion γ. We assume that the injected polarized electrons will be converted into polarons and bipolarons, which coexist with a given proportion $\gamma = n_p/(n_p+n_{bp})$ in the organic polymer layer. Based on the diffusion theory and Ohm's law, we studied the current spin polarization in the FM/organic structure. The model is set up and the formulae derived in the next section. Section 3 presents the results and section 4 gives a summary.

2. Model

Schmidt *et al* have studied theoretically the spin injection and transport in an FM/semiconductor/FM sandwich structure. The carriers are divided into spin-up electrons and spin-down electrons; two channels of the electrocircuit were discussed through the diffusion equation and Ohm's law [18–20]. Spin injection was enhanced from an FM to a semiconductor in a structure with a spin-selective interfacial resistance. Rashba [21], Smith and Silver [22], Fert and Jaffrés [23], and Yu and Flatté [24, 25] have considered such an interfacial resistance.

For an FM/organic system structure, spin-polarized electrons in the FM layer are injected into the organic layer. Suppose the injected electrons are converted into polarons and bipolarons completely; we can imagine that there are three channels for carrier transport in the organic layer, spin-up polarons, spin-down polarons and spinless bipolarons. For the prime work, the bipolarons in the organic layer are supposed to exist stabilized. The bipolarons are supposed to be transformed by those injected spin-polarized electrons in the FM layer, which have the
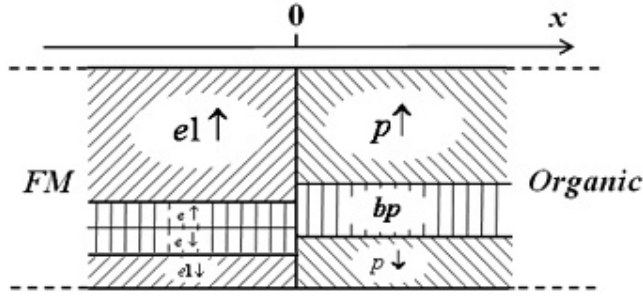
Figure 1. A sketch of the FM/organic system structure. The spin-polarized current was injected from the FM layer ($x < 0$) into the organic polymer layer ($x > 0$). There are three channels in the organic layer: spin-up polarons, spin-down polarons and spinless bipolarons.

same quantity but different spin. Neglecting the transition between polarons and bipolarons, we can give a sketch of the FM/organic system as shown in figure 1.

We can derive the current spin polarization from the diffusion equation in the FM/organic system. Near the interface $x = 0$, the electrochemical potentials $\mu_\uparrow$ and $\mu_\downarrow$ of each layer obey the diffusion equation,

$$\frac{\mu_\uparrow - \mu_\downarrow}{\lambda^2} = \frac{\partial^2(\mu_\uparrow - \mu_\downarrow)}{\partial x^2}. \tag{1}$$

For spin-polarized carriers in the FM layer and the spin polarons in the organic layer, we have solutions

$$\begin{aligned}
\mu_\uparrow - \mu_\downarrow &= A e^{x/\lambda_{\mathrm{FM}}} & x < 0 \\
\mu_\uparrow - \mu_\downarrow &= B e^{-x/x_0} & 0 < x < x_0
\end{aligned} \tag{2}$$

where λ_{FM} is the spin diffusion length in the FM layer. We assume that the spin diffusion length of polarons is larger than the thickness x_0 of the polymer layer. Coefficients A and B are determined by the continuity of the electrochemical potential at the interface.

The current across the system obeys Ohm's law,

$$j_s = -\sigma_s \frac{\partial(\mu_s/e)}{\partial x} \tag{3}$$

where $s = \uparrow, \downarrow$, σ_s is the conductivity. As the injected electrons will be converted into polarons and bipolarons in the organic layer, we have

$$\frac{\partial(\mu_\uparrow - \mu_\downarrow)}{\partial x} = -e\left(\frac{j_\uparrow}{\sigma_\uparrow} - \frac{j_\downarrow}{\sigma_\downarrow}\right) = \begin{cases} -e\left(\dfrac{j_{\mathrm{e}1\uparrow}}{\sigma_{\mathrm{e}1\uparrow}} - \dfrac{j_{\mathrm{e}1\downarrow}}{\sigma_{\mathrm{e}1\downarrow}}\right) & x < 0 \\[3mm] -e\left(\dfrac{j_{\mathrm{p}\uparrow}}{\sigma_{\mathrm{p}\uparrow}} - \dfrac{j_{\mathrm{p}\downarrow}}{\sigma_{\mathrm{p}\downarrow}}\right) & 0 < x < x_0 \end{cases} \tag{4}$$

where $j_{\mathrm{e}1,s}$, $\sigma_{\mathrm{e}1,s}$ are the currents and conductivities of electrons that will be converted into polarons in the FM layer, and the conductivities can be expressed as

$$\sigma_{\mathrm{e}1\uparrow} = \left(\frac{1 + \beta_0}{2} - \frac{1 - \gamma}{2}\right)\sigma_{\mathrm{FM}} = \frac{\gamma + \beta_0}{2}\sigma_{\mathrm{FM}},$$

$$\sigma_{\mathrm{e}1\downarrow} = \left(\frac{1 - \beta_0}{2} - \frac{1 - \gamma}{2}\right)\sigma_{\mathrm{FM}} = \frac{\gamma - \beta_0}{2}\sigma_{\mathrm{FM}}.$$

σ_{FM} is the total conductivity of the FM layer; β_0 is the polarization of the FM bulk. $j_{\mathrm{p},s}$ is the current and $\sigma_{\mathrm{p}\uparrow} = \sigma_{\mathrm{p}\downarrow} = \gamma\sigma/2$ is the conductivity of polarons in the organic polymer, which can be considered to be approximately spin independent.

At the FM/polymer interface, we write the total current as

$$j = -\sum_s G_s(\Delta\mu_s/e) - G_{bp}(\Delta\mu_{bp}/(2e)) \tag{5}$$

which includes the contribution of both polarons and bipolarons. G_s and G_{bp} refer to the corresponding conductance respectively.

Define the current spin polarization as $\alpha = (j_{p\uparrow} - j_{p\downarrow})/(j_{p\uparrow} + j_{p\downarrow} + j_{bp})$. The continuity of the current at the interface gives

$$B - A = -\left(\frac{ej_\uparrow}{G_\uparrow} - \frac{ej_\downarrow}{G_\downarrow}\right) = -e \cdot j \cdot \frac{1}{2}\left(\frac{\gamma + \alpha_0}{G_\uparrow} - \frac{\gamma - \alpha_0}{G_\downarrow}\right) \tag{6}$$

where α_0 is the current spin polarization at the interface in the FM/organic system.

In another way, at the interface, from equations (2) and (4), we can find that

$$-\frac{2ej}{\sigma_{FM}} \cdot \frac{(\alpha_0 - \beta_0) \cdot \gamma}{(\gamma^2 - \beta_0^2)} = A/\lambda_{FM}$$
$$-\frac{2ej}{\sigma} \cdot \frac{1}{\gamma} \cdot \alpha_0 = -B/x_0. \tag{7}$$

Combining equations (6) and (7), the current spin polarization at the interface is obtained,

$$\alpha_0 = \beta_0 \cdot \frac{\lambda_{FM}}{\sigma_{FM}} \cdot \frac{\sigma}{x_0} \cdot \frac{1 + \frac{1}{4\beta_0} \cdot \frac{\sigma_{FM}}{\lambda_{FM}} \cdot \left(\frac{1}{G_\downarrow} - \frac{1}{G_\uparrow}\right) \cdot (\gamma^2 - \beta_0^2)}{\left(\frac{\lambda_{FM}}{\sigma_{FM}} \cdot \frac{\sigma}{x_0} + 1\right) - \left(\frac{1}{\gamma} \cdot \beta_0\right)^2 + \frac{1}{4\gamma} \cdot \frac{\sigma}{x_0} \cdot \left(\frac{1}{G_\downarrow} + \frac{1}{G_\uparrow}\right) \cdot (\gamma^2 - \beta_0^2)}. \tag{8}$$

If the interface resistances are neglected, i.e., $\frac{1}{G_\downarrow} = \frac{1}{G_\uparrow} = 0$, then the current spin polarization is simplified as

$$\alpha_0 = \beta_0 \cdot \frac{\lambda_{FM}}{\sigma_{FM}} \cdot \frac{\sigma}{x_0} \cdot \frac{1}{\left(\frac{\lambda_{FM}}{\sigma_{FM}} \cdot \frac{\sigma}{x_0} + 1\right) - \left(\frac{1}{\gamma} \cdot \beta_0\right)^2}. \tag{9}$$

3. Results and discussion

For a usual sandwich device $La_{0.7}Sr_{0.3}MO_3/T_6/La_{0.7}Sr_{0.3}MO_3$, the total resistance is in the gigaohm region [11]. As the ferromagnetic phase metallic conductivity for $La_{0.7}Sr_{0.3}MO_3$ is about $10^2 \ \Omega^{-1} \ cm^{-1}$, so the conductivity of the organic layer (T_6) is much smaller than that of the $La_{0.7}Sr_{0.3}MO_3$ layer. In our calculation, the conductivity of the organic layer is supposed to be 100 times smaller than that of the FM metal. In order to compare with the present theoretical calculation on traditional inorganic semiconductors [22], we set $\sigma_{FM} = 1 \ \Omega^{-1} \ cm^{-1}$, $\sigma = 0.01 \ \Omega^{-1} \ cm^{-1}$, the thickness of the organic layer $x_0 = 10$ nm and the spin diffusion length in the FM layer $\lambda_{FM} = 100$ nm in the present calculations. Based on those parameters, we calculated the dependence of the interfacial current spin polarization α_0 on the polaron proportion γ of all the carriers in the organic layer. The results are shown in figure 2. It was found that the current spin polarization of the system decreases rapidly with the increasing of γ at first and then it tends to a constant. The maximum polarization appears at the position of $\gamma = \beta_0$. At this point, the spin-minority electrons in the FM layer will be completely converted into bipolarons when they are injected into the organic layer. $\gamma = 1$ means that there are no bipolarons created in the polymer layer and all the carriers are spin polarons. As stated above, both polarons and bipolarons act as electric chargers in real organic materials. Their proportion γ depends upon the concrete material as well as the external circumstance such as temperature and external electric field. Polarons and bipolarons can transfer into each other under certain conditions. For example, a bipolaron can be decomposed into two spin polarons
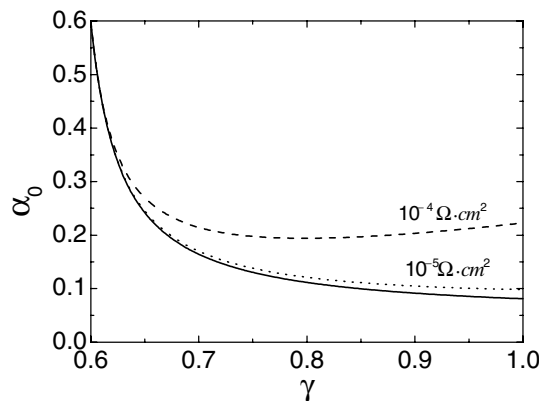
Figure 2. Dependence of interfacial current spin polarization α_0 on the polaron proportion γ. Solid curve for zero interfacial resistance and dashed curve for $1/G_\downarrow = 10/G_\uparrow = 10^{-4}$ Ω cm^2; dotted curve for $1/G_\downarrow = 10/G_\uparrow = 10^{-5}$ Ω cm^2. Other parameters are $\beta_0 = 0.6$, $\sigma_{FM} = 1$ Ω^{-1} cm^{-1}, $\sigma = 0.01$ Ω^{-1} cm^{-1}, $\lambda_{FM} = 100$ nm and $x_0 = 10$ nm.
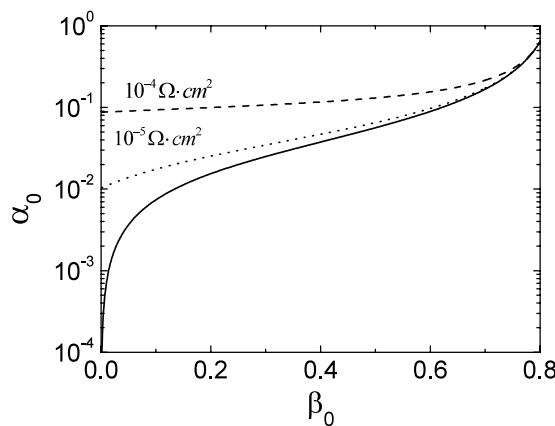

Figure 3. Dependence of current spin polarization α_0 on the bulk spin polarization of the FM layer. The polaron proportion is set to 0.8. Other parameters are the same as in figure 2.

through photo-excitation. Maybe the present prediction could be experimentally confirmed by photo-irradiating the device. This may initiate a variety of exciting new applications in organic spintronics.

If the interfacial resistances are spin dependent, we will find that the polarization of the injected current can be changed. The results are shown in figure 2, where the solid curve expresses the result of no interfacial resistance. It was found that the current spin polarization in the organic polymer was enhanced remarkably when the interfacial resistance $1/G_\downarrow (= 10/G_\uparrow)$ existed. For example, at $\gamma = 0.8$, the current polarization will increase from 0.10 to 0.22 when the interfacial resistance changes from $1/G_\downarrow = 0$ to 10^{-4} Ω cm^2.

Figure 3 shows the dependence of α_0 on β_0 with different interfacial resistances. It can be seen that the polarization intensity increases with the bulk polarization of the FM layer. Again, we found that an interfacial resistance will be helpful to the spin injection in the system.

Current spin polarization is dependent upon the thickness of the spacer, as shown in figure 4. The solid curve expresses the result of no interfacial resistance and the dashed
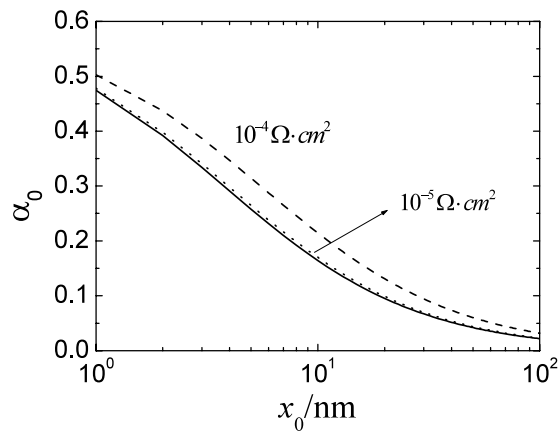
Figure 4. Dependence of current spin polarization α_0 on the thickness of the organic layer. The polaron proportion is set to 0.7 and the bulk spin polarization of the FM layer is 0.6. Other parameters are the same as in figure 2.
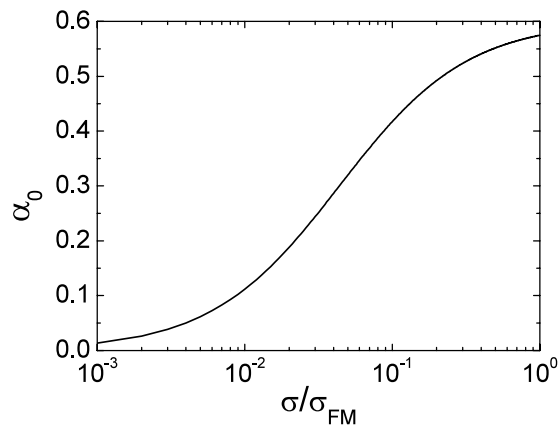

Figure 5. Dependence of current spin polarization α_0 on the conductivity ratio σ/σ_{FM} for the two materials without interfacial resistances ($1/G_\downarrow = 1/G_\uparrow = 0$). The polaron proportion is set to 0.8 and the bulk spin polarization of the FM layer is 0.6. Other parameters are the same as in figure 2.

curves that of different interfacial resistances. It is obvious that the current spin polarization α_0 decreases with increasing polymer thickness x_0. There is almost no polarization if the polymer layer is thicker than 100 nm.

Conductivity matching of the organic layer to the FM layer is another factor in the current spin polarization. The dependence of α_0 on σ/σ_{FM} is shown in figure 5. It was found that current spin polarization α_0 increases when the conductivities of the two layers are close to each other. Therefore, it is possible to get a larger spin injection by adjusting the matching of the conductivities of the two layers.

4. Conclusion

It is well known that the main carriers in organic polymers may be spin polarons or spinless bipolarons, which is a definite difference of organic polymers from traditional semiconductors

or metals. For the recent experimental observation of spin injection and transport in an FM/organic/FM system, we theoretically studied the current spin polarization in the structure of the FM/organic system. The current spin polarization was obtained from the spin diffusion theory. Polarons and bipolarons as the main carriers were stressed. It was concluded that only the spin polarons have a contribution to the current spin polarization. However, the existence of spinless bipolarons will affect the intensity of the current spin polarization. With increasing thickness of the organic spacer, the polarization decays. It was predicted that a suitable interfacial resistance or conductivity matching of the layers would be beneficial for the spin injection.

Acknowledgments

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