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Thin Solid Films 503 (2006) 196 – 200

thin solid films

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Polarons and bipolarons in polythiophene contacted with half-metallic ferromagnetic manganite

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Received 14 March 2005; received in revised form 25 November 2005; accepted 25 November 2005
Available online 13 February 2006

Abstract

Organic spintronics has been a field of growing interest due to the recent experimental work on half-metallic ferromagnetic colossal magnetoresistance (CMR) manganite/sexithienyl/CMR or CMR/Alq$_3$/Co. The characteristic of carriers in sexithieny1-like organic polymers contacted with a CMR manganite is studied in the framework of a tight binding model. It is found that the formation of spin polarons can be energetically favorable than that of spinless bipolarons. Spin polarons can act as the main transport carriers in organic semiconductors. Effects of the interfacial coupling, spin splitting of the magnetic contact and lattice disorder with Coulomb interactions on the stability of polarons are discussed.

PACS: 85.75.-d; 71.70.Ej; 42.70.Jk
Keywords: Spintronics; Spin splitting; Organic semiconductors

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1. Introduction

Polarons and bipolarons are supposed to be charge carriers generated upon doping or photo-excitation in organic semiconductors especially in high conjugated conducting polymers. A polaron has spin 1/2 and electronic charge $\pm e$ whereas a bipolaron is spinless with charge $\pm 2e$. Theoretical calculations [1] as well as experimental studies of doped oligomers [2] have established that the two-peak feature actually corresponds to a polaron rather than a bipolaron. On the other hand, the existence of bipolarons has also been suggested by the observation of a single photo-induced absorption peak in an improved sample of polythiophene [3].

With the rapid development of spintronics in organic field, the characteristic of carriers in organic semiconductors becomes important as only polarons carry spins and can realize spin polarized transport. Experimentally, Dediu et al. reported the magneto resistance (MR) in a sandwich structure of La$_{0.7}$Sr$_{0.3}$MnO$_3$/sexithienyl/Re$_{0.7}$Sr$_{0.3}$MnO$_3$ [4], which means a spin injection from La$_{0.7}$Sr$_{0.3}$MnO$_3$ into sexithienyl. Recently, Xiong et al. designed a spin valve of La$_{0.67}$Sr$_{0.33}$MnO$_3$/Alq$_3$/Co and observed low-temperature giant magnetoresistance effects as large as 40%, which indicates that π-conjugated organic semiconductors may offer a promising alternative approach to semiconductor spintronics by virtue of their relatively strong electron–phonon coupling and large spin coherence [5]. Both of them show that the organic layers at least have spin carriers even if not all of the carriers had spins. Some studies also have shown that polarons are the primary carriers in long oligothiopehene chains [6].

Present theoretical investigations based on the physical models, such as the Brazovskii–Kirova (BK) model [7] and the well-known Su, Schrieffer, and Heeger (SSH) model [8], indicate that a double charged bipolaron is energetically favorable to two single charged polarons. The inclusion of electron–electron interaction may block the forming of bipolarons, but some studies cannot give a satisfying solution due to the difficulty in treating the electron–electron interactions [9].

In the present work, we investigate the characteristic of electronic carriers in sexithieny1-like organic polymer (polythiophene) contacted with a half-metallic ferromagnetic colossal

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doi:10.1016/j.tsf.2005.11.113

magnetoresistance (CMR) manganite in the frame work of an extended SSH model. The electron–electron interactions are considered in the Hartree–Fock approximation [10]. The model is described and the formulae are derived in the next section. Section 3 presents the results and Section 4 gives a summary.

2. Model

Sexithienyl is a small molecular oligomer. It can be polymerized to form polymer polythiophene (T_n), which has a nondegenerate ground state. This kind of polymer or oligomer has a one-dimensional chain structure and can be described in the framework of a tight binding model [11],

$$\begin{aligned} H_{\mathrm{P}} = & -\sum_{n,\sigma} e_{\mathrm{P}} a^{+}_{n,\sigma} a_{n,\sigma} \\ & -\sum_{n,\sigma} t_{n,n+1,\sigma}\left(a^{+}_{n+1,\sigma} a_{n,\sigma} + a^{+}_{n,\sigma} a_{n+1,\sigma}\right) \\ & -\sum_{n,\sigma} t_2\left(a^{+}_{4n-3,\sigma} a_{4n,\sigma} + a^{+}_{4n,\sigma} a_{4n-3,\sigma}\right) \\ & -\sum_{n,\sigma} t_3\left(a^{+}_{4n-3,\sigma} a_{4n-3,\sigma} + a^{+}_{4n,\sigma} a_{4n,\sigma}\right) \\ & +\frac{1}{2}\sum_{n} K_{\mathrm{P}}(u_{n+1}-u_n)^2 \end{aligned} \quad (1)$$

where e_{P} denotes the on-site electron energy of carbon atom which depends on the chemical potential of the corresponding material, $a^{+}_{n,\sigma}$ ($a_{n,\sigma}$) denotes the electron creation (annihilation) operator at site n with spin σ ($\sigma=\uparrow, \downarrow$). The electron transfer integral is $t_{n,n+1}=t_{\mathrm{P}}-\alpha_{\mathrm{P}}(u_{n+1}-u_n)-t_1\cos(n\pi/2)$ with t_{P} as the transfer integral in a uniform (undimerized) lattice, u_n is the displacement of carbon atom n, α_{P} is the electron–phonon coupling constant and t_1 to guarantee the nondegenerate characteristic of the ground state. The third and forth terms describe the influence of sulfur atoms on π electrons. It depends in general upon the coupling strength between sulfur atom and its two neighboring carbon atoms. There are two sources of contributions. The electron hopping between lattice points $4n-3$ and $4n$ via sulfur atom is given by the third term, and the forth term is the effective confinement of π electrons due to the sulfur atom. Taking the carbon atom binding energy to be e_{P}, the renormalized couplings are approximately represented by parameters t_2 and t_3. In the actual calculation, we assume $t_2=t_3$. The motion of the sulfur atoms is entirely ignored because of its much bigger mass than that of carbon atoms. The last term means the elastic energy.

CMR manganites can form half-metallic ferromagnets and are therefore very interesting materials as spin polarized electron injecting contacts. CMR materials have a chemical composition such as $\mathrm{Re}_{1-x}\mathrm{Ak}_x\mathrm{MnO}_3$, where Re represents a rare earth atom, e.g. La and Nd, and Ak represents an alkaline earth metal such as Ca, Sr and Ba. Mn has a valence of $(3+x)$ which depends on the doping concentration x. Depending on doping, the material can be either a metal or an insulator and either ferromagnetic or antiferromagnetic [12]. In particular, $\mathrm{Re}_{1-x}\mathrm{Ak}_x\mathrm{MnO}_3$ can be a half-metallic ferromagnet when $0.2<x<0.5$, for example, with Re=La and Ak=Ca. In this state all the electrons at the Fermi surface have the same spin orientation [13].

For the ferromagnetic contact, here we suppose for simplicity that a one-dimensional model is established along the z-direction of CMR manganite $\mathrm{Re}_{1-x}\mathrm{Ak}_x\mathrm{MnO}_3$ lattice, which contains the basic properties of a half-metallic CMR manganite. The following one-dimensional model captures its essential features [13],

$$H_{\mathrm{CMR}} = H_{\mathrm{ke}} + H_{\mathrm{Hund}} + H_{\mathrm{el-lat}} + H_{\mathrm{elastic}} \quad (2)$$

$$H_{\mathrm{ke}} = -\sum_{n,\sigma} t_F\left(a^{+}_{n,\sigma} a_{n+1,\sigma} + a^{+}_{n+1,\sigma} a_{n,\sigma}\right) \quad (3)$$

$$H_{\mathrm{Hund}} = -\sum_{n} J_n\left(a^{+}_{n,\uparrow} a_{n,\uparrow} - a^{+}_{n,\downarrow} a_{n,\downarrow}\right) \quad (4)$$

$$H_{\mathrm{el-lat}} = \sum_{n,\sigma} \lambda_F\left(\phi_{n+1}-\phi_n\right) a^{+}_{n,\sigma} a_{n,\sigma} \quad (5)$$

$$H_{\mathrm{elastic}} = \sum_{n} \frac{1}{2} K_F\left[(\delta_n-\phi_n)^2 + (\phi_{n+1}-\delta_n)^2\right] \quad (6)$$

where ϕ and δ_n are the displacements of the nth oxygen and manganese atom respectively. H_{ke} describes electron hopping between two nearest manganese atoms. H_{Hund} describes the spin splitting of manganese atom that results from interaction with the core spins. We have $J_n=J_M$ for the ferromagnetic state (core spins aligned) and $J_n=(-1)^n J_M$ for the antiferromagnetic state. $H_{\mathrm{el\text{-}lat}}$ gives the on-site energy of the manganese atoms, which depends on the displacement of the nearest neighboring oxygen atoms, and λ_F denotes the electron–lattice coupling strength. The last term H_{elastic} represents the elastic energy and includes nearest neighbor interactions.

The electron–electron interactions within the two segments can be both treated in the Hartree–Fock mean-field approximation [10,14],

$$\begin{aligned} H_{\mathrm{ee}} = & \frac{1}{2} U \sum_{n,\sigma} a^{+}_{n,\sigma} a_{n,\sigma} a^{+}_{n,-\sigma} a_{n,-\sigma} + V \\ & \times \sum_{n,\sigma,\sigma'} a^{+}_{n,\sigma} a_{n,\sigma} a^{+}_{n+1,\sigma'} a_{n+1,\sigma'} \end{aligned} \quad (7)$$

where U and V express the on-site and nearest-neighbor repulsion separately.

We assume a T_n chain parallel to a CMR manganite lattice at the z-direction. They interact through electronic transition integral $t_\perp$ between the neighbored atoms of T_n and CMR manganite,

$$H_{T_n-\mathrm{CMR}} = -\sum_{m,n,\sigma} t_\perp\left(a^{+}_{m,\sigma} a_{n,\sigma} + a^{+}_{n,\sigma} a_{m,\sigma}\right) \quad (8)$$

Where m is the site index of T_n and n is the corresponding neighboring one of the CMR manganite lattice at the z-direction.