Electrode Injection into Conjugated Polymers

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When conjugated sites of an electroactive polymer are placed a few angstroms from a metal electrode, carriers flow from the metal to these sites and remain trapped in the negative part of the generalized image force potential. We determine the consequences of this event and calculate explicitly the charge transfer rate from the electrode to the polymer molecules as a function of temperature and electric field. [S0031-9007(98)06843-4]

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Recently, there has been increased interest in organic devices, such as light emitting diodes or transistors. The optimization of the performance of these devices requires a good theoretical description of metal-polymer contacts. Earlier models often considered the polymer as a homogeneous semiconductor. Various macroscopic theories of metal-semiconductor interface rectification [1] were invoked such as charge injection from Schottky barriers [2], Fowler-Nordheim field emission [3], or the thermoionic emission-diffusion theory of Cromwell and Sze [4].

Other models explicitly took into account the polaronic nature of the carrier in the polymer. The organic device current voltage characteristic arises from tunneling of the charge carrier into polaron levels [5], or is determined by a bipolaron lattice that is created near the interface [6,7].

An important consideration in a quantitative description of the contact is the image force exerted on the charge carrier near the interface. In the Monte Carlo simulation by Garnstein and Conwell [8], this effect is included and results in the great majority of carriers returning to the electrode at low fields. In this paper, we draw attention to the negative part of the image force potential and the possibility of Coulomb trapping of carriers at the interface. We shall show that this trapping within the first two polymer monolayers results in an increase of the effective Schottky barrier.

Another new result of the present paper is the calculation of the charge transfer rate from the metal electrode to a single conjugated molecule. The calculation was carried out in the spirit of the quantum mechanical extension of the Marcus charge transfer theory by Kestner, Logan, and Jortner [9]. Moreover, Emin's theory of small polaron hopping [10], based on Holstein's molecular model of the polymer chain, provides a microscopic definition of the charge transfer parameters. Consequently, we are able to compare quantitatively the injection rate at a given electrode with typical values of the space charge limited current in the polymer [11].

For an ideal Schottky contact, the potential barrier is given by the difference between the metal Fermi energy E_{F} and the semiconductor electron affinity χ_0. Because the polaron is the lowest singly charged state in the polymer, the Schottky barrier results in the difference between the metal Fermi energy and the polaron level χ_P. Then, in the presence of an image force and external electric field F, the potential energy $\chi_P(x) - E_{\mathrm{F}}$ for charge emission from the metal into the polymer, as a function of the distance x from the metal surface, is written as

$$\chi_P(x) = \chi_P - qFx - \frac{q^2}{16\pi\varepsilon\varepsilon_0 x}, \tag{1}$$

where q is the charge carrier, $\varepsilon \cong 3$ is the relative dielectric constant of the conjugated polymer, and ε_0 is the permittivity of the vacuum. The respective positions of the relevant levels are presented in Fig. 1. Close to the electrode $[x < q(16\pi\varepsilon_0\varepsilon F)^{1/2}]$, the image force potential is strongly negative over a distance of a few angstroms. This condition leads to the existence of bound states which can be filled when the chemical potential E_{F} in the metal is high enough. However, these charges will not be trapped in the form of singly charged polarons but in pairs, in the form of bipolarons. Indeed, the image force increases the bipolaron stability as emphasized recently by Brazovskii *et al.* [12]. The presence of such layers of bipolarons, in turn, modifies the potential energy for charge emission which becomes $\chi_P' - E_{\mathrm{F}}$ instead of $\chi_P - E_{\mathrm{F}}$, where

$$\chi_P'(x) = \chi_P(x) + qS(x). \tag{2}$$

Here, $S(x)$ is a series of Coulombic terms originating from the different trapped charges that we can write as

$$S(x) = \frac{1}{4\pi\varepsilon\varepsilon_0} \times \sum_i \left[\frac{q_i}{\sqrt{\mathbf{r}_i^2 + (x - x_i)^2}} - \frac{q_i}{\sqrt{\mathbf{r}_i^2 + (x + x_i)^2}} \right], \tag{3}$$

where q_i are the different trapped charges placed at the distance x_i of the interface and occupying the site $\mathbf{r}_i$ in the plane parallel to this interface. We note that the image force potential for each trapped charge is included.

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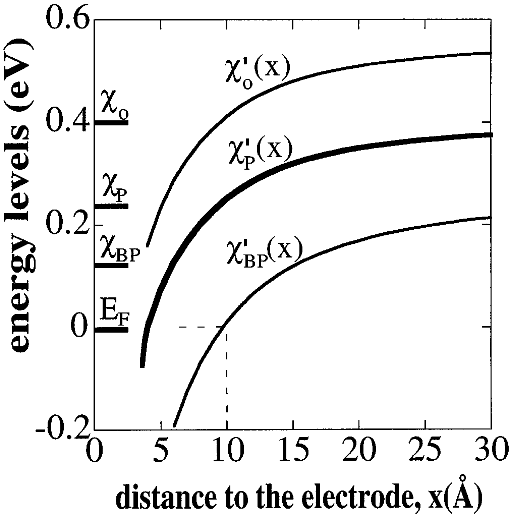

FIG. 1. The relevant electronic levels which determine charge injection are presented (in the case of electrons) as a function of the distance x from the metal electrode. The electron affinity χ_0, polaron χ_P, and bipolaron χ_{BP} levels defined in the bulk of the polymer in the absence of the electrode are replaced by functions $\chi'_0(x)$, $\chi'_P(x)$, and $\chi'_{\mathrm{BP}}(x)$ which contain the generalized image force dependence. The electronic levels are for zero external field and include the lattice deformation (polaron and bipolaron formation energy). The electrical double layer resulting from trapped bipolarons centered at the distance $x_1 = 10$ Å is, in this case, responsible for a Schottky barrier $\chi'_P(\infty) - E_{\mathrm{F}} \sim 0.4$ eV which is approximately 2 times larger than the value $\chi_P - E_{\mathrm{F}} \sim 0.2$ eV in the absence of generalized image force.

Far from the interface, these trapped charges can be viewed as a dipole layer formed at the metal-polymer interface in which one side of the dipole layer is the charged bipolarons in the polymers and the other side is the screening charge distribution in the metal.

Of course, as emphasized by several authors [6,7], when the density of surface bipolarons is of the order of $D \approx 10^{18}$ m^{-2} (density of chains at the metal electrode), the bipolarons organize into a lattice. The conditions for the stability of the bipolaron lattice in the presence of Coulomb forces have been studied in detail by Davids, Saxena, and Smith [7] in the continuous (1D) ordered limit. They find that the condition $E_{\mathrm{F}} > \chi_{\mathrm{BP}}$ pins the Fermi level at the bipolaron energy χ_{BP} (per charge) and defines a good contact, while in the case of the bad contact ($E_{\mathrm{F}} < \chi_{\mathrm{BP}}$) no double layer can be formed. This calculation from Ref. [7] needs to be extended in two respects. First, the use of the 1D Poisson equation excludes the individual image force as a possible solution, which, as we shall demonstrate, is the main contribution to charge emission potential. Second, the use of the continuous 1D limit for the bipolaron lattice is only valid at high concentrations of carriers that are not reached in real situations. More precisely, the present calculation yields a typical concentration of occupied sites of 5% in the first polymer layer from the interface, a value not typical of the 1D continuous model. This situation allows us to neglect the interactions between bipolarons but requires us to treat the discreteness of the bipolaron lattice explicitly.

In fact, close to the electrode, the important consequence of this discreteness is that, even when $E_{\mathrm{F}} < \chi_{\mathrm{BP}}$ (the bipolaron formation energy), a lattice of trapped charges can be formed in the first polymer layer, provided that the less restrictive condition $\chi_{\mathrm{BP}}(x_1) < E_{\mathrm{F}} < \chi_{\mathrm{BP}}$ is satisfied, where

$$\chi_{\mathrm{BP}}(x) = \chi_{\mathrm{BP}} - qFx - \frac{2q^2}{16\pi\varepsilon_0\varepsilon x}. \tag{4}$$

Here x_1 is the average distance from the interface of the first layer of bipolaron centers. Consequently, because of these trapped charges, the Schottky barrier becomes $\chi_P(x) - \chi_{\mathrm{BP}}(x_1)$ instead of $\chi_P(x) - \chi_{\mathrm{BP}}$ in the absence of these Coulomb effects.

We initially examine the case where only the first available conjugated sites of the polymer, which determine a first layer at $x = x_1$, satisfies the trapping condition $\chi_{\mathrm{BP}}(x_1) < E_{\mathrm{F}}$. Then a layer of trapped bipolarons is formed which subjects the individual carrier (polaron) to the potential $\chi'_P(x)$ as defined in Eqs. (2) and (3). Assuming a local thermal equilibrium of the first layer with the metal reservoir, the probability of occupation $\langle q\rangle/q$ of a typical conjugated site in the first layer is

$$\frac{\langle q(x_1)\rangle}{q} = \frac{2\exp[-2(\chi'_{\mathrm{BP}}(x_1) - E_{\mathrm{F}})/k_{\mathrm{B}}T]}{1 + \exp[-2(\chi'_{\mathrm{BP}}(x_1) - E_{\mathrm{F}})/k_{\mathrm{B}}T]}, \tag{5}$$

where $\chi'_{\mathrm{BP}}(x) = \chi_{\mathrm{BP}}(x) + qS(x)$. $S(x)$ is evaluated on a regular lattice of conjugated sites using the occupation factor given by Eq. (5). The two geometrical parameters needed in this calculation are the distance x_1 and the density D of chains at the metal electrode. The latter parameter was determined experimentally for MEH-PPV in Ref. [13]. In the case of a self-assembled monolayer of molecules grafted at the LED interface, a similar order of magnitude ($D \sim 10^{18}$ m^{-2}) was also found [14]. More explicitly,

$$S(x) = \frac{\langle q\rangle}{q}\bar{S}(x), \tag{6}$$

where $\langle q\rangle$ is given by Eq. (5) and

$$\begin{aligned}\bar{S}(x) &= \frac{q}{4\pi\varepsilon_0\varepsilon} \\ &\quad\times \sum_i \left[\frac{1}{\sqrt{\mathbf{r}_i^2 + (x - x_1)^2}} - \frac{1}{\sqrt{\mathbf{r}_i^2 + (x + x_1)^2}}\right] \\ &= \bar{S}(x, x_1, D)\end{aligned}$$

depends only on the geometry of the polymer at the interface. This function $\bar{S}(x, x_1, D)$ is plotted in Fig. 2.

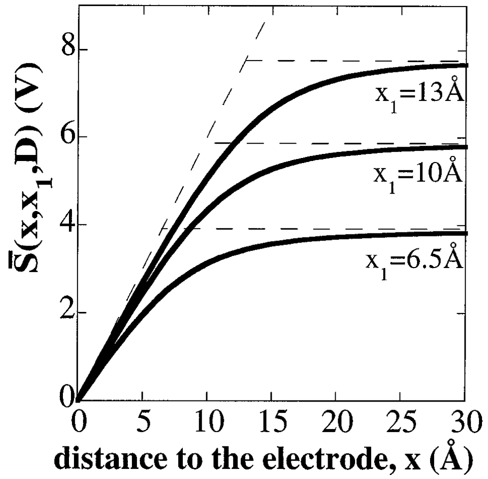

FIG. 2. The generalized image force function $\bar{S}(x, x_1, D)$ represents the potential at the distance x of a layer of charges placed at distance x_1 from the electrode, with a surface density $D = 10^{18}$ m^{-2}. Far from the electrode, this distribution behaves like a simple electrical double layer. The dotted curve represents the capacitor limit of this function.

Equations (5) and (6) determine $\chi_{\mathrm{BP}}(x_1)$ self-consistently. Crudely speaking, we find that the situation $\chi_{\mathrm{BP}}(x_1) < E_{\mathrm{F}}$ implies $\chi'_{\mathrm{BP}}(x_1) \cong E_{\mathrm{F}}$ as in Fig. 1. In this case, the fraction of polymer chains at the interface occupied by bipolarons is $\langle q(x_1)\rangle/2q = [E_{\mathrm{F}} - \chi_{\mathrm{BP}}(x_1)]/2\bar{S}(x_1, x_1, D)$. However, when $\chi_{\mathrm{BP}}(x_1) > E_{\mathrm{F}}$, we then find $\chi'_{\mathrm{BP}}(x_1) \cong \chi_{\mathrm{BP}}(x_1)$ and there is no significant trapping of bipolarons at the interface.

We have also examined the case where the first two layers of bipolaron sites located at distances x_1 and $x_2 \sim 2x_1$ satisfy the trapping condition $\chi_{\mathrm{BP}}(x_2) < E_{\mathrm{F}}$. We find that the fast decrease with x of the Coulomb image force and the consequent shift in the potential barrier induced by the first layer leave the second layer nearly unoccupied. For instance, in the case $x_2 \sim 2x_1$, one finds that

$$\langle q(x_2)\rangle/\langle q(x_1)\rangle \cong \exp\{[- q^2/(8\pi\varepsilon_0\varepsilon x_1) - qS(x_2) + qS(x_1)]/k_{\mathrm{B}}T\}.$$

Davids, Saxena, and Smith also found a very narrow distribution of charges (less than one layer) in the continuous model [7].

It is also interesting to check our assumption that the polaron population is negligible compared to that of the bipolarons in the first layer. The ratio of the number of polarons n_P to the number of bipolarons n_{BP} is $n_P/n_{\mathrm{BP}} \sim \exp[-(\chi_P - \chi_{\mathrm{BP}} + q^2/16\pi\varepsilon_0\varepsilon x_1)/k_{\mathrm{B}}T]$. Indeed, the image force enhances the bipolaron population drastically [12].

The next step is to calculate the charge transferred from the metal electrode to the polymer. The principle of this calculation of the charge transfer is as follows. The polymer chain, in contact with the electrode, is deformed by thermal vibrations. Because of the electron-phonon coupling, the electronic levels in the polymer change according to these deformations. For a given value of the deformation coordinate $u(x)$, certain electronic levels in the metal will be in coincidence with the appropriate charge transfer level in the polymer chain. Upon coincidence, tunneling can occur efficiently from the metal electrode to the polymer through the potential barrier that we have just determined above.

To be more precise, we shall work within the framework of Emin's semiclassical theory of small polaron hopping [10] derived from the initial work of Holstein. The difference here is that coincidence and hopping do not occur between two polymer deformable sites but between a metallic level of energy E and a polaronic site at distance x of the interface with energy $\chi'(x) - Au(x)$ where A is the coupling constant to the lattice deformation $u(x)$ and

$$\chi'(x) = \chi_0 - qFx - \frac{q^2}{16\pi\varepsilon_0\varepsilon x} + qS(x) \qquad (7)$$

(χ_0 is just the free particle level in the polymer, i.e., the lowest unoccupied or highest occupied molecular orbital (LUMO or HOMO) level depending on the sign of the carrier q).

The coupling J between the metal surface wave function and the polymer wave function reflects the transmission through the tunnel barrier of Eq. (7). In the WKB. approximation, the transmission factor J for a jump at the distance x is given by

$$J^2(E_\perp, x) \sim J_\perp^2 \exp\left[-2\sqrt{\frac{2m}{\hbar^2}} \int_{x_0}^{x} \sqrt{\chi'(x) - E_\perp}\, dx\right], \qquad \text{if } E_\perp < \chi'_{\max}(x)$$

($\chi_{\max}$ is the height of the barrier), and $J^2(E_\perp, x) \sim J_\perp^2$ above the barrier. Here $E_\perp$ is the electron energy in the direction x of tunneling, m is the effective mass of the carrier, and x_0 is the smallest zero of the integrand $[\chi'(x_0) = E_\perp]$. The bare coupling $J_\perp$ reflects the overlap between the evanescent wave function in the metal and the appropriate extended state of the polymer, in the absence of barrier and image force. A reasonable value for $J_\perp$, depending on the geometry of the interface, would be $0.02 < J_\perp < 0.05$ eV.

The above expression for $J^2(E_\perp, x)$ corresponds to weak coupling, where the hop is obviously nonadiabatic. In this case, the hopping rate is controlled by the coincidence time that we have determined following Ref. [10]. The hopping frequency from the energy level E of the metal to a polymer site located at a distance x from the interface is obtained as

$$\nu_{M,P}(E_\perp, E, x) = J_\perp^2(E_\perp, x)\sqrt{\frac{\pi}{(\chi_0 - \chi_P)k_{\mathrm{B}}T}} \times \exp\left[-\frac{(\chi'(x) - E)^2}{4(\chi_0 - \chi_P)k_{\mathrm{B}}T}\right]. \qquad (8)$$

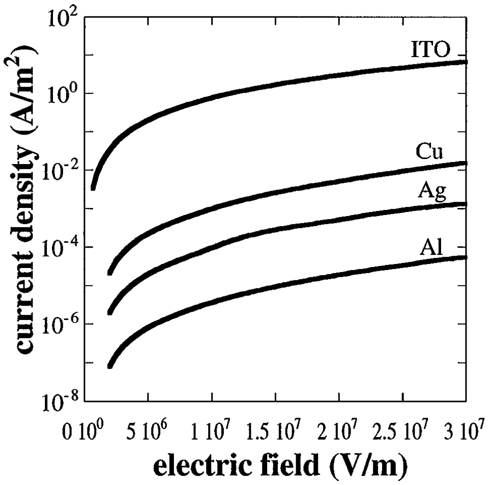

FIG. 3. The hole current density j_+ that is extracted from the metal through the image force barrier and transferred to the vibrating polymer is plotted as a function of the field F at the interface for different values of the difference between the ionization potential of the polymer and the Fermi level of the metal ($\Delta = 0.7\,\text{eV}$ for Cu, $\Delta = 0.95$ for Ag, and $\Delta = 1.05$ for Au). The polymer chain density is $D = 10^{18}\,\text{m}^{-2}$; the temperature is $T = 300$ K. The upper curve named ITO (indium tin oxide) concerns the case where the current is not contact limited but space charge limited. Here we have used our calculation from Ref. [11].

The current density $j_+(F)$ extracted from the metal can thus be obtained by integration over all possible energies in the metal and all possible distances from the top of the barrier χ' at abscissa $x = x_\text{m}$, to infinity:

$$j_+(F) = D\sigma q \int_{x_m}^{\infty} dx\, \frac{2\pi(2m)^{3/2}}{h^3} \times \int \frac{dE}{1 + \exp[(E - E_\text{F})/k_\text{B}T]} \times \int^{E} \frac{dE_\perp}{\sqrt{E_\perp}}\, v_{M,P}(E_\perp, E, x)\,, \tag{9}$$

where σ is the cross section of the polymer chain and D is the chain density at the interface.

In Fig. 3, the hole current j_+ is plotted as a function of the electric field F at the interface for different values of the difference between the ionization potential of the polymer and the Fermi level in the metal. These theoretical results compare favorably with recent experimental data [15].

The other important, unexpected, conclusion of this work is that the presence of conjugated sites too close to the metal electrode does not favor charge injection: the formation of a layer of bipolarons, trapped in the generalized image force potential, increases the Schottky barrier by values $\chi'_{BP}(x_1) - \chi_{BP}$ of several tenths of eV. This explains why the control of the interface by a self-assembled monolayer of well-known molecular dipoles is so useful [14,16,17], provided that these grafted molecules cannot trap charges from the electrode, too close to it. This could also explain why a thin layer of lithium fluoride or of another insulating material exempt of traps can be of some use in improving charge injection [18].

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