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Electric Field Control of Charge Transport in Doped Polymers[†]

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Abstract

Recent observation of a large "field effect" for conducting polymers is in conflict with a fact that the electric field cannot penetrate in a conductor further than the molecular scale Debye radius. We review the experimental results for gate voltage control of conductivity in a FET structure. We propose that the field effect is related to inhomogeneous structure and remnant ions. The free space within the polymer network enables ions to move in and out. The electronic screening at the dielectric/conducting polymer boundary transforms the electric potential into the shift of chemical potential for ions inside leading to ionically charging/discharging of the polymer film. The ionic charge is compensated by the variation of the electron concentration. In the linear response to the gate voltage, the charging capacity is $c = \varepsilon\varepsilon_0(r_i^2 + r_e^2)$, where $r_{i,e}$ is the Debye radius for ionic and electronic subsystems. For low concentration of ions ($r_i >> r_e$) the charging response increases exponentially with applied voltage and approaches saturation $c_0 = e^2N(E_F)$ that is a few hundred F/cm^3. Surprisingly, the experimental "off state" is reached with only a few percent of compensation. Therefore we propose that the main effect of the ionic invasion is suppression of the charge conduction between metallic grains of the inhomogeneous polymers.

Keywords: Transport measurements, Metal/electrolyte interfaces, Conducting polymers, Polymer field effect transistors

1. Introduction

Since the discovery of the possibility of their doping, conjugated polymers have been shown to have a number of novel phenomena that do not have analogies in conventional conductors [1]. At light doping the extra charges do not represent conventional electrons or holes as in conventional semiconductors, but they are the strongly bound states of charge and backbone distortion whose energy levels are inside the electronic gap [2]. For isolated degenerate polymer chains the bound states are classified as neutral with spin or charged without spin solitons. Coulomb and interchain interactions couple the solitons and convert them into more conventional polarons and bipolarons.

In the last decade remarkable progress was made in study of heavily doped conjugated polymers. Experiments indicate that in spite of the large σ_{RT} and finite residual conductivity at $T \rightarrow 0$, transport properties of these highly conducting polymers are far from being those of typical metals. Using Drude model analysis it was shown [1,3] that the low frequency electromagnetic response of metallic samples is provided by an extremely small fraction ($\sim 10^{-3}$) of total number of electrons but with very high mobility or very long relaxation time ($\sim 10^{-12}$ s). These data enabled the proposal that a new mechanism of charge transport dominates highly conducting doped polymers [4].

It is well established that the conjugated polymers are strongly inhomogeneous materials [1]. One can distinguish the "crystalline" regions within which polymer chains are dense packed and well-ordered. These metallic grains remain spatially separated by disordered regions and direct electric connection between them strongly is suppressed. The intergrain charge transfer is possible via resonance tunneling. Within the model of resonance hopping the low concentration of charge carriers in dc-transport corresponds to small density of resonance states and the long relaxation time is related to the narrow width of those resonance levels.

Recently a new interesting phenomenon, an electric field effect, was reported for the doped highly conducting polymers [5-7]. Fig. 1 shows I-V characteristics of such a transistor [8] in which conducting polymer PEDOT:PSS [poly(ethylene dioxythiophene): poly(styrenesulfonic acid)] with $\sigma_{RT} \sim 30$ S/cm is used as active electronic element and PVP [poly(vinylphenol)] is used as a dielectric separating the gate and source-drain channel. As it is shown on Fig. 1 the I_D current decreases with gate voltage V_G similarly to that normally observed for conventional semiconductors. The ratio I_{ON}/I_{OFF} reaches up to 10^4 in some devices [5-9].

We suggest that the observed field effect in conducting polymers based "transistor" is closely related to the mesoscopic inhomogeneity of conducting polymers. We emphasize that the field effect cannot be observed if the conducting polymer is a conventional conductor.

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2. Screening of electric field

2.1. Screening length

The screening length for a degenerate electron gas is given by the equation $r_e^{-2} = (e^2/(\varepsilon\varepsilon_0))N(E_F)$, where $N(E_F)$ is the total density of states at the Fermi level, ε_0 is the vacuum permittivity, and ε is the relative dielectric constant. In heavily doped conducting polymers the typical charge carrier concentration is estimated to be $n_e \sim b^{-3} \sim 10^{21}$ cm^{-3} at typical repeat constant b < ~ 1 nm. Taking the Fermi energy as $E_F \sim 1$ eV, the density of state at the Fermi level is $N(E_F) \sim n_e/E_F \sim 10^{21}$ cm^{-3} (eV)$^{-1}$. For polymers with characteristic dielectric constant $\varepsilon \sim 100$, the Debye radius is $r_e \sim 2$ nm, which is negligible as compared with typical polymer film thickness ~ 100 nm.

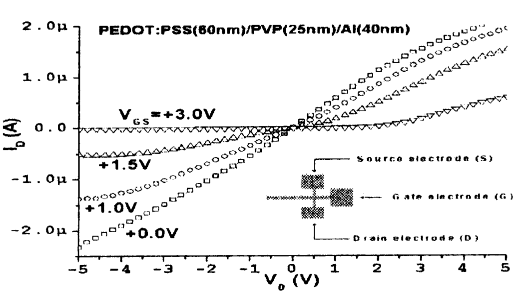

Figure 1. The drain-source current as the function of drain voltage of a thin PEDOT:PSS/PVP film. The insert shows the polymer-based transistor configuration (after Park et al. [8]).

2.3. Screening time

Although the screening length is determined solely by the thermodynamic density of states, it implicitly is assumed that charge carriers are mobile. For conducting polymers near the metal-insulator transition, some portion of the carriers is expected to be strongly localized and their mobility is very low, especially, at low temperature. However, the mobility determines only how fast the screening occurs. Indeed, if we assume the charge redistribution in the process of screening is established by diffusion of charge carriers the screening time is estimated as $t_e \sim r_e^2/D$, where D is the diffusion coefficient. Taking into account that $\sigma_e = e^2N(E_F)D$ we conclude that the characteristic screening time is limited by the conductivity $t_e \sim \varepsilon\varepsilon_0/\sigma_e$. The present relationship holds irrespectively of band or hopping mechanism of charge transport is realized.

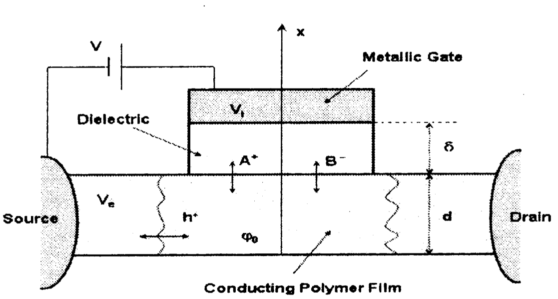

Figure 2. The distribution of charge and electric field in polymer transistor. $A^+ = H^+, Na^+, K^+, \ldots, B^- = Cl^-, SO_4, OH^-, O_2^-, \ldots$, and h^+ is for the holes, primary charge carriers in polymers.

For the polymers with $\sigma_{RT} \sim 10$ S/cm and $\varepsilon \sim 100$, the screening time should be very short $t_e \sim 10^{-9}$ s. Thus, the consideration of conducting polymers as conventional conductors fails to explain the observable field effect.

3. Ionic charging

We propose that the field effect in conducting polymers is due to the ionic component of their charge conductivity. The inhomogeneous structure leaves enough free space for mobile ions. The ions inside the polymers produce the additional screening of the external field, but the crucial feature of ions is the ability of ions to migrate between the conducting polymer film and external dielectric layer interface (see Fig. 2). As a result the concentration of ions inside of the polymer is controlled by the gate potential. Due to electroneutrality the internal ionic density determines the concentration of primary charge carriers in the polymer and therefore it is anticipated that the polymer conductivity is governed by the gate potential.

3.1. Coupled electron-ion system

To describe this phenomenon we introduce the ionic density n_i (cations or anions) and the polymer primary carrier density n_e (holes or electrons). The corresponding charge density is $\rho_\alpha = z_\alpha n_\alpha$ with z_α being a charge and $\alpha = i, e$. The equilibrium charge density and chemical potential take values ρ^0_α and ζ^0_α. In the presence of the weak electric potential φ in the linear approximation the electrochemical potential and the charge density become

$$\rho_\alpha = \rho^0_\alpha + \rho^*_\alpha; \qquad \zeta_\alpha = -z_\alpha\varphi + \zeta^*_\alpha + \zeta^0_\alpha, \qquad (1)$$

where ζ^*_α and ρ^*_α are the change induced by the potential φ

$$\zeta^*_\alpha = \rho^*_\alpha/(z_\alpha\eta_\alpha); \qquad \eta_\alpha = (d/d\zeta^0_\alpha)n^0_\alpha. \qquad (2)$$

Here η_α is the thermodynamic density of states. The electrical potential φ depends on the total charge density ρ^* and it is found from the Poisson equation

$$\varepsilon\varepsilon_0\Delta\varphi = \rho^*; \qquad \rho^* = \Sigma_\alpha\,\rho^*_\alpha, \qquad (3)$$

The partial density ρ^*_α obeys

$$\Delta\rho^*_\alpha = \rho^*/r_\alpha^2; \qquad \varepsilon\varepsilon_0/r_\alpha^2 = z_\alpha^2\eta_\alpha; \qquad (4)$$

and the total density ρ^* is satisfied with the equation

$$\Delta\rho^* = \rho^*/r_D^2; \qquad 1/r_D^2 = \Sigma_\alpha 1/r_\alpha^2, \qquad (5)$$

where r_α is the partial and r_D is the total Debye radius.

The general solution of equations (3-4) can be expressed in the term of the total $\rho^*(x)$ as

$$\varphi(x) = (\varepsilon\varepsilon_0)^{-1}r_D^2[\rho^*(x)-\rho^*(0)] - Fx + \varphi_0; \quad J = \sigma F, \quad (6)$$

where $\sigma = \Sigma_\alpha\sigma_\alpha$ is the total conductivity and F represents the integration constant or the internal field. Similarly, the distribution of charge and current for components are

$$\rho^*_\alpha = (r_D/r_\alpha)^2\rho^* + s_\alpha x + q_\alpha; \qquad J_\alpha = \sigma_\alpha F - D_\alpha s_\alpha, \quad (7)$$

provided that the integration constants s_α and q_α satisfy the conditions $\Sigma_\alpha s_\alpha = 0$ and $\Sigma_\alpha q_\alpha = 0$.

For the one dimension sandwich structure shown on Figure 2, the general solution of (5) is