

Analytic model of carrier mobility in doped disordered organic semiconductors

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We suggest an analytic model of charge transport in weakly and heavily doped disordered organic materials. Doping of such materials increases the density of carriers but also creates deep Coulomb traps. The net effect is typically a decreasing mobility at low doping levels. At high doping levels the Coulomb traps overlap spatially, which leads to smoothening of the potential landscape and to strongly increasing mobility. The model is used to fit experimental data on the mobility in electrochemically (EC) doped polythiophenes. It also explains why increasing the carrier density by the field-effect results in a much higher mobility than an equivalent increase of the carrier density by EC doping.

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I. INTRODUCTION

The purpose of doping a semiconductor with acceptor-type or donor-type atoms or molecules is usually to produce an increase in the density of free carriers. High carrier density can be achieved by accumulation of carriers in a sufficiently strong gate field of a metal-insulator-semiconductor structure [field-effect (FE) doping] (Ref. 1) or by (electro)chemical (EC) doping.^{2,3} In conventional inorganic semiconductors, these doping modes are virtually equivalent and neither of them noticeably affects the carrier mobility. However, it turns out that the situation is strikingly different in disordered organic semiconductors. Recently, the authors of Ref. 4 directly compared the mobility in poly(3-hexylthiophene) (P3HT) polymer films as a function of carrier concentration controlled by either FE or EC doping. The mobility of EC doped carriers at the moderate doping levels of 1% was found to be two orders of magnitude smaller than the FE mobility at the same carrier concentration, as shown in Fig. 1. A sharp rise of the mobility with the doping level was found for the EC doping while, in sharp contrast, the FE mobility had much smaller dependence on the carrier concentration. Earlier experimental studies of conductivity in doped P3HT (Ref. 5) have shown that (i) at low-to-moderate doping levels, the carrier mobility decreases with increasing dopant concentration while (ii) the mobility steeply increases at doping levels of around and larger than 0.1–1% as depicted in Fig. 2(a). The aim of the present work is to explain the difference between these two ways of creating charge carriers. We suggest a model of hopping transport that accounts for the interaction between charge carriers and counterions in both weakly and heavily doped disordered organic semiconductors. This model is shown to be able to reproduce the experimentally observed nonmonotonous dependence of the mobility upon the dopant concentration⁵ and the difference between mobilities in FE and EC doped organic semiconductors.⁴

The model is based on the concept of strong Coulomb interaction between charge carriers and ionized dopants. This concept has been used in previous studies in order to explain

low doping efficiency in hydrogenated amorphous silicon⁶ and carrier hopping in weakly doped disordered organic semiconductors.⁷ However, the models formulated in Refs. 6 and 7 are not applicable to heavily doped materials in which the Coulomb traps cannot be considered as fully independent. In the present work, at variance with the model adopted in Ref. 7, the barrier height for charge carrier motion between Coulomb traps is calculated by taking into account the overlap between their potential wells, which essentially reduces the energetic disorder.

II. THE MODEL

The Coulomb interaction has to play an important role in disordered organic materials in which the dielectric constant is low and carriers are strongly localized within either individual molecules or conjugated molecular segments. As a matter of fact, doping of an organic semiconductor simultaneously produces extrinsic charge carriers and deep Cou-

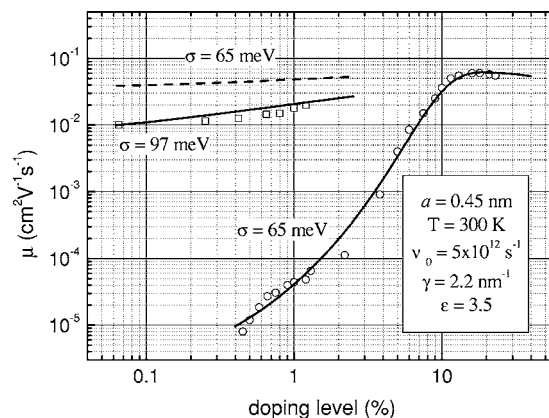


FIG. 1. Field-effect carrier mobility (squares) and carrier mobility in electrochemically doped P3HT (circles) plotted against the doping level (Ref. 4). The solid and dashed lines show the fit of the data (see the text for details).

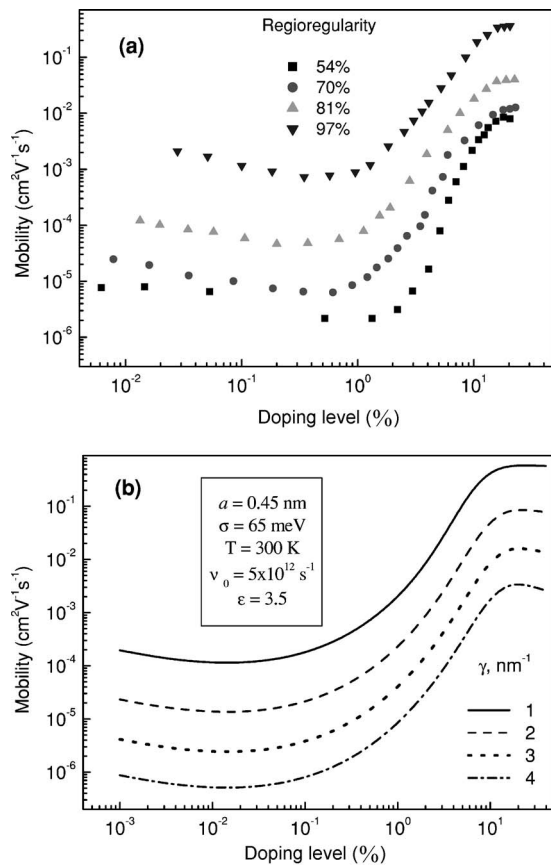


FIG. 2. Dopant-concentration dependence of the mobility (a) measured in electrochemically doped P3HT with different degrees of regioregularity (Ref. 5) and (b) calculated with the DOS distribution given by Eq. (4) parametric in the reciprocal localization radius γ .

lomb traps for those carriers.⁷ Taken separately, these two phenomena have opposite effects on the charge carrier mobility. An increase in the carrier density is expected to result in an increased mobility and conductivity.^{8,9} Concerning the effect of the creation of deep states in the density-of-states (DOS) distribution, it has recently been shown both experimentally¹⁰ and theoretically⁷ that the Coulomb traps associated with ionized dopants strongly enhance energetic disorder manifested by expansion of the lower tail of the intrinsically Gaussian DOS $g_i(E)$. In this tail, the density of states decreases with energy even weaker than an exponential function featuring a power-law dependence $g(E) \sim E^{-4}$ at moderate doping levels. It was found⁷ that, at low-to-moderate doping levels, carrier localization in the Coulomb traps prevails and the mobility decreases if the Coulomb-induced disorder is stronger than the intrinsic energetic disorder. Otherwise, excess carriers released from the Coulomb traps of dopants fill vacant deep intrinsic states and the mobility increases upon doping.

There are two possible ways to chemically dope organic semiconductors. Electrochemical doping^{4,5} can be accomplished if the ionization potential of the electrolyte electrode matches the energy of the highest occupied molecular orbital (HOMO) of the organic semiconductor provided that the electrolyte also supplies appropriate counterions. The alter-

native method is doping by a neutral moiety whose electron affinity is large enough to allow for charge transfer from the semiconductor to the dopant.¹¹ In view of the redox potential of real donor-acceptor systems complete charge transfer and creation of free carriers in the dark should in practice be never possible. However, in a disordered organic material, charge transfer from a host molecule to a nearby dopant produces a strongly Coulombically bound short electron-hole pair rather than free charge carriers. The size of such a pair is equal to the intermolecular distance a that typically ranges from 0.4 to 1.0 nm and its Coulomb binding energy is then 0.5–1.2 eV if the permittivity retains its typical macroscopic value of 3 and 0.7–1.8 eV if the permittivity goes down to 2 at such short distances. This energy gain can be sufficient in order to compensate for the dissociation enthalpy upon charge transfer of, for instance, an electron from the HOMO of a host molecule to the lowest unoccupied molecular orbital (LUMO) of an acceptor even if LUMO of the dopant is ~ 1 eV above HOMO of the host.

It is worth noting that the intrinsic disorder further facilitates creation of doping-induced pairs of carriers.¹² Despite the large energy deficit disordered organic semiconductors can be doped efficiently by both donors and acceptors due to the fact that the mobility in pristine materials is also due to hopping of carriers localized in the deep tail of the intrinsic DOS distribution. The maximum of the equilibrium carrier distribution within a Gaussian DOS of the width σ is located at the energy of $E_m = \sigma^2/kT$ where T is the temperature.¹³ In a rather strongly disordered material with $\sigma = 0.15$ eV the energy E_m is as large as 0.9 eV at room temperature and 1.4 eV at $T = 200$ K. This estimate shows that disordered organic materials can be efficiently doped by virtually deep traps because free equilibrated carriers also occupy deep-tail states of the intrinsic DOS distribution.

Despite the apparent differences between chemical-doping mechanisms they have essentially the same effect on the electronic structure of the doped material; they both produce excess charge carriers localized within Coulomb traps of ionized dopants. At variance with intrinsic localized states, Coulomb traps are rather large. Their radius r_c can be estimated as a distance at which the energy of Coulomb interaction is equal to kT that yields $r_c = e^2/4\pi\epsilon_0\epsilon kT \approx 19$ nm in a material with $\epsilon = 3$ at room temperature. This estimate shows that the Coulomb traps must start overlapping at the critical dopant concentration of $N_d \approx r_c^{-3} = (4\pi\epsilon_0\epsilon kT/e^2)^3$, i.e., $N_d \approx 1.5 \times 10^{17}$ cm⁻³. The overlap of neighboring Coulomb traps effectively lowers the energy barrier between them and, thereby, diminishes the effective energy disorder. Since the carrier concentration further increases with increasing dopant concentration the Fermi level has to shift upwards and the mobility should steeply increase at high doping levels. This effect has indeed been observed in electrochemically doped P3HT films.^{4,5}

Since the Coulomb interaction is strong between an ionized dopant and a charge carrier occupying the nearest host molecule (i) the latter should almost always be the bottom of the Coulomb trap irrespective of the contribution from the intrinsic energy disorder and (ii) at any given time most charge carriers will be bound to dopant ions and form randomly oriented dipoles. Although the electric field of these

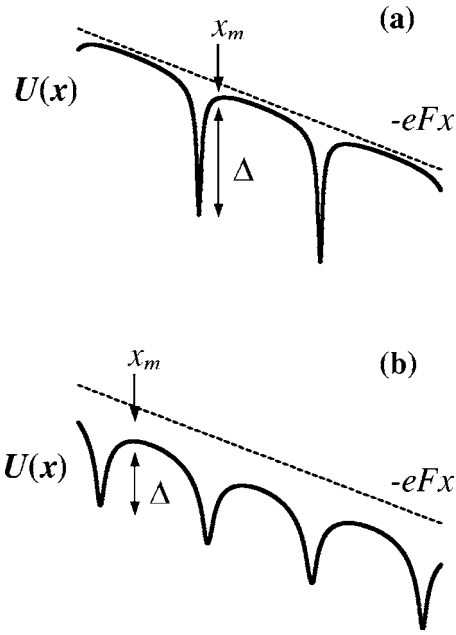


FIG. 3. The effect of Coulomb traps on the potential landscape at (a) low and (b) high doping levels.

dipoles will also contribute to the doping-induced disorder their effect on charge transport is small as compared to that of Coulomb traps. Under such conditions, motion of every carrier will be predominantly controlled by an external electric field and by the Coulomb field of the nearest dopant ion [Fig. 3(a)] unless another nearby Coulomb trap is currently vacant and the overlap between these potential wells is sufficiently strong [Fig. 3(b)]. Note that a vacant Coulomb trap can have more than one neighbor. However, it will most probably attract the carrier from its neighbor along the direction opposite to the external field F . In fact, this process can be visualized as a motion of a vacant “Coulomb hole” similar to hole transport in the HOMO band of an organic semiconductor.

The electrostatic energy barrier $U(x)$ that separates overlapping Coulomb traps is described by

$$U(x) = -eFx - \frac{e^2}{4\pi\epsilon_0\epsilon|x|} - \frac{e^2}{4\pi\epsilon_0\epsilon|x-b|}, \quad (1)$$

where b is the distance between Coulomb traps and the x -axis is directed along the external field. In order to find the barrier height one has to find the maximum $U_m = U(x_m)$ of the potential energy distribution given by Eq. (1) which leads to the following equation for the coordinate of the maximum:

$$\frac{1}{z_m^2} - \frac{1}{(1-z_m)^2} = f, \quad (2)$$

where $z_m = x_m/b$ and $f = (4\pi\epsilon_0\epsilon b^2/e)F$ are the dimensionless coordinate of the maximum and the dimensionless external field, respectively. Although this equation still has an analytic solution it is too long to be presented here. Substituting this solution into Eq. (1) yields the barrier height for carrier jumps between neighboring Coulomb traps.

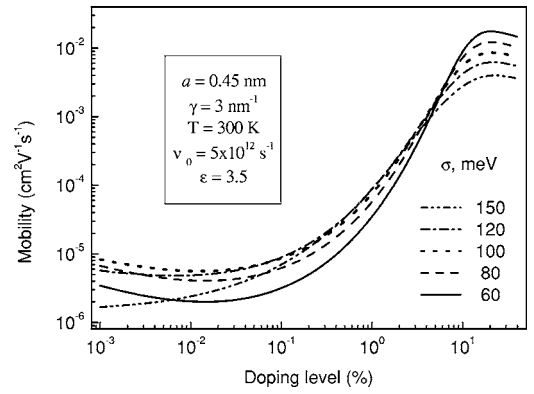


FIG. 4. Dopant-concentration dependence of the mobility plotted for different intrinsic DOS widths. A weak dependence of μ upon σ implies a dominant role of the doping-induced Coulomb energetic disorder in doped materials.

A single Coulomb trap of the radius of 10–20 nm should include several hundreds of intrinsic hopping sites and carrier release from such a trap is in fact a multistep Onsager-like process facilitated by the external electric field. Exact analytic consideration of this not-stationary process is hardly possible and one needs to formulate a simplified model. As it has been suggested in Ref. 7 (i) every Coulomb trap can be replaced by a single deep localized state nearest to the ionized dopant and (ii) the energy of this site is a sum of the intrinsic disorder energy and the barrier Δ whose height is counted from the top of the electrostatic potential barrier as

$$\Delta = \frac{e^2}{4\pi\epsilon_0\epsilon a} + U_m. \quad (3)$$

Under these assumptions the effective DOS distribution in a doped material takes the form

$$g(E) = \frac{N_i - N_d}{N_i} g_i(E) + \frac{N_d}{N_i} g_i\left(E + \frac{e^2}{4\pi\epsilon_0\epsilon a} + U_m\right), \quad (4)$$

where N_i is the total (energy-integrated) density of intrinsic hopping sites and N_d the density of dopants. The latter also determines the average distance between dopants that can be estimated as $b \approx N_d^{-1/3}$.

Further on, the carrier mobility μ can be calculated within the framework of the variable-range hopping model based on the concept of effective transport energy.⁸ The dopant-concentration dependences of the mobility, calculated with the DOS determined by Eqs. (2) and (4), are shown in Fig. 4 for different values of the intrinsic Gaussian DOS variations σ . The calculated mobility increases at high dopant concentrations due to (i) strong overlap of the Coulomb traps that smoothens the random potential landscape and (ii) increasing density of charge carriers that fill increasingly large number of remaining deep traps. Remarkably, at high doping levels the mobility only weakly depends upon the intrinsic DOS width, which can explain the experimentally observed universal relation between mobility, conductivity, and the dopant concentration in amorphous organic semiconductors.^{14,15} At lower dopant concentrations, the mobility decreases upon doping in more ordered materials because the Coulomb traps

are deeper than practically all intrinsic states in these materials and, therefore, the effect of doping-induced traps prevails. However, the mobility steadily increases with increasing dopant concentration in materials with large intrinsic energy disorder because carriers released from the Coulomb traps can fill even deeper intrinsic states, which leads to an upward shift of the Fermi level and concomitant increase of the carrier jump rate.

III. RESULTS AND DISCUSSION

The model of Coulomb-trap-controlled mobility explains the nonmonotonic dependence of the mobility upon dopant concentration EC doped P3HT films.⁵ The curves shown in Fig. 2(b) were calculated by the use of the effective transport energy concept⁸ with the DOS distribution determined by Eqs. (2) and (4) and with the material parameters indicated in the figure. The theoretical curves nicely reproduce both the decrease of the mobility at low doping levels, the steep increase of the mobility at higher dopant concentrations, as well as saturation or even decrease of the mobility at doping levels around and above 20%. It is worth noting that different degrees of regioregularity in P3HT were simulated by different values of the reciprocal localization radius γ , which would, probably, not be sufficient for a detailed quantitative description of the doping in regioregular materials. In order to pretend for a quantitative fit of the data one has to account for the possibility of mesoscopically inhomogeneous distribution of dopants between the ordered and amorphous phases of the material as well as for the additional doping-induced positional disorder in the ordered phase.

The model of Coulomb traps is also able to explain the difference between the effects on the mobility of the charge concentration induced by the field effect, on the one hand, and of EC doping, on the other hand. The solid lines in Fig. 1 are the calculated dependences of the mobility on the charge-carrier concentration with (EC doping) and without (FE) account of Coulomb interaction with counterions. The presence of Coulomb traps does strongly enhance the disorder, especially at low doping levels, which leads to a much steeper increase of the mobility at high doping levels due to progressive filling of the deep-tail localized states. The FE mobility, calculated for the same width of the intrinsic DOS distribution, turns out to be much higher and depends much less on the carrier density—see the dashed line in Fig. 1. The experimental FE mobility was fitted with a larger width of the intrinsic Gaussian DOS distribution, which reflects the fact that DOS distribution at a polymer/oxide interface can

be broadened due to the presence of interfacial dipoles,¹⁶ electrostatic interaction with charges on the gate,¹⁷ and smaller degree of regioregularity. In principle, the Coulomb interaction between charge carriers in the channel of an organic field effect transistor also contributes to the energetic disorder. However, this is a repulsive interaction that only prohibits carriers from getting close to each other but creates neither traps nor barriers that could considerably reduce the mobility.

It is worth noting that Coulomb interaction of mobile polarons with ionized dopants can facilitate formation of “trapped bipolarons,” i.e., polaron pairs localized within the Coulomb potential wells of dopants. Since Coulomb repulsion is effectively reduced in the presence of the immobile countercharge such anchored “trions” can be formed even if the reorganization energy is not large enough for coupling of charge carriers in free bipolarons.

IV. CONCLUSIONS

The effect of doping on conductivity and carrier mobility in a disordered organic semiconductor strongly depends upon the degree of intrinsic disorder in the pristine material. Low-to-moderate doping of a weakly disordered semiconductor leads to decreasing carrier mobility and a sublinear increase of conductivity due to strong carrier localization in Coulomb traps of dopants. In order to shift the Fermi level to the effective transport level and thereby increase the carrier mobility one needs doping levels in excess of typically 1%. At such high concentrations of dopants, their Coulomb potential wells overlap, which results in decreasing activation energies of Coulomb traps and concomitant smoothening of the random potential landscape. The latter process also occurs in strongly intrinsically disordered materials which leads to a similarly strong increase of the mobility at high doping levels. However, in such materials the mobility weakly increases upon doping at low dopant concentrations as well as due to filling of deep intrinsic states with carriers released from the Coulomb traps. In contrast, the field-effect mobility increases with increasing charge-carrier concentration over the complete range of carrier concentrations, because it is not accompanied by the creation of additional Coulomb traps by counterions.

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