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## Effect of Coulomb scattering from trapped charges on the mobility in an organic field-effect transistor

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We investigate the effect of Coulomb scattering from trapped charges on the mobility in the two-dimensional channel of an organic field-effect transistor. The number of trapped charges can be tuned by applying a prolonged gate bias. Surprisingly, after increasing the number of trapped charges to a level where strong Coulomb scattering is expected, the mobility has decreased only slightly. Simulations show that this can be explained by assuming that the trapped charges are located in the gate dielectric at a significant distance from the channel instead of in or very close to the channel. The effect of Coulomb scattering is then strongly reduced.

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Many studies of organic field-effect transistors (OFETs) have shown that not all charges induced in the channel of the transistor by the gate field remain mobile. Under prolonged application of a gate bias an increasing number of the induced charges get trapped and become immobile.<sup>1–12</sup> These trapped charges lead to a shift of the threshold gate voltage at which the transistor switches on. Moreover, the Coulomb scattering by these trapped charges is expected to have a major effect on the mobility of the mobile charges in the transistor channel. The effect should be reflected in the electrical characteristics of the OFET. The precise location of the trapped charges plays a crucial role. If the trapped charges are located in the transistor channel a large influence on the mobility is expected, whereas if the trapped charges are located at a distance from the channel the Coulomb scattering should be much reduced. So far this has not been investigated experimentally or theoretically.

An interesting analogy can be drawn with the Coulomb scattering of mobile electrons by ionized donors in inorganic semiconductors. With homogeneous doping of the semiconductor the electron mobility significantly decreases with increasing donor concentration, because the electrons and donors are located in the same region of space.<sup>13</sup> However, in III-V semiconductor heterostructures a situation can be created where the electrons are located in a quasi-two-dimensional region that is spatially separated from the ionized donors. This spatial separation of electrons and donors is called “modulation doping.” It leads to a much reduced Coulomb scattering and an improved mobility of the two-dimensional electron gas.<sup>13</sup> We will argue in the present paper that in OFETs an effect occurs that is based on exactly the same physics.

A problem that hinders the analysis of the effect of trapped charges on the electrical characteristics of OFETs is the complex morphology of the organic semiconductors that are commonly used. These semiconductors often consist of well-ordered regions separated by less ordered regions. Charge trapping in the less ordered regions may be enhanced with respect to the well-ordered regions.<sup>9,14</sup> Another problem is the large thickness (typically of the order of 100 nm) of the commonly used organic layers, as compared to the thickness of the accumulation layer of the transistor (typically of the order of 1 nm). This leads to a large volume of the organic layer that does not take part in charge transport, but that could contain many traps.<sup>15</sup>

In order to avoid these problems we investigated in this paper the effects of trapped charges on the electrical characteristics of a field-effect transistor consisting of a quinquethiophene-based self-assembled organic monolayer (SAMFET); see Fig. 1. The self-assembled monolayer (SAM) in this system is very homogeneous and has a high degree of order. Furthermore, contrary to conventional OFETs, the entire volume of the organic layer participates in charge transport, so that there are no inactive regions where charge trapping can take place. Another important advantage of this system is that the charge transport is truly two-dimensional. This facilitates the modeling of the charge transport in this system enormously. In particular, it allows the evaluation of the effects of the static Coulomb field of trapped charges on the transport of the mobile charges.

The SAMFET was prepared on a heavily doped silicon wafer, acting as the gate, which was covered with a 200 nm layer of thermally grown SiO<sub>2</sub>. The Ti/Au source and drain contacts were defined by conventional photolithography and wet etchant chemistry. Further experimental details are explained elsewhere.<sup>16,17</sup> The length and width of the SAMFET channel are  $L = 10\ \mu\text{m}$  and  $W = 2500\ \mu\text{m}$ , respectively. The electrical characterizations were carried out at a temperature  $T = 30^\circ\text{C}$  in vacuum of  $10^{-6}$  mbar. Figure 2(a) shows the time evolution during 15 days of the transfer curve of the SAMFET while a voltage of  $V_G = -30\ \text{V}$  was applied to the gate. The transfer curves were measured by brief interruptions with a gate sweep, while applying a source-drain voltage of  $V_{SD} = -2\ \text{V}$ . Figure 2(b) shows the time evolution during an ensuing period of 15 days in which the gate was grounded.

Several important conclusions can be drawn from Fig. 2. (1) During the first period, the transfer curve shifts toward the applied gate voltage. This shift is generally understood as a result of trapping of mobile charges.<sup>1,8,9,11,14</sup> When an increasing number of the charges induced by the gate field is trapped, the transistor switches on at a larger magnitude of the gate voltage. (2) With an increasing number of trapped charges there is a subtle change in the shape of the transfer curve. In particular, the slope of the linear part of the transfer curve shows a slight decrease. Such behavior is also observed in more conventional thin-film OFETs<sup>5,7,18</sup> and should have the same origin. (3) During the second period, in which the

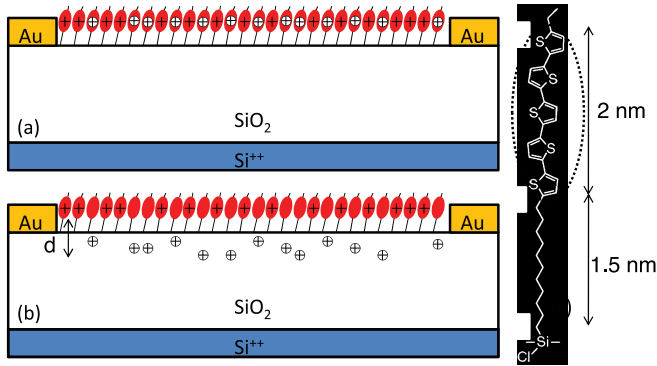


FIG. 1. (Color online) (a) and (b) Schematic of the SAMFET. In (a) the trapped charges (circles) are lying in the monolayer. In (b) they are distributed in the gate dielectric to a depth *d*. (c) Chemical structure of the self-assembling molecule.

gate was grounded, the transfer curve shifts back. This points at a decreasing number of trapped charges. (4) Although after the second period (which is equally long as the first period) the transfer curve has not completely returned to the initial transfer curve, the shape of the transfer curve at the end of the experiment is exactly the same as that at the start. This shows that the change in shape of the transfer curve is a reversible effect that should be attributed to the presence of the trapped charges and not to an irreversible degradation mechanism.

Our explanation for the change in the shape of the transfer curve with increasing amount of trapped charges is the effect of Coulomb interactions between the trapped and mobile charges on the charge transport in the SAMFET. In the remainder of this paper we will make a quantitative analysis of this effect. We will show that the size of the effect provides important information about the location of the trapped charges.

We model the monolayer as a square lattice of sites with lattice constant *a*. The relatively low mobility and the thermally activated behavior of the SAMFET<sup>16</sup> indicate that charge transport occurs by phonon-assisted hopping of charges between molecules. For the case of coupling to

acoustical phonons this process is appropriately described by the Miller-Abrahams hopping rate,<sup>19,20</sup>  $W_{ij} = v_0 \exp[-2\alpha R_{ij} - \beta(E_j - E_i)]$  for  $E_j \geq E_i$  and  $W_{ij} = v_0 \exp[-2\alpha R_{ij}]$  for  $E_j < E_i$ . Here,  $\beta = 1/k_B T$ , where  $k_B$  is Boltzmann's constant;  $v_0$  is a phonon frequency,  $R_{ij} \equiv |R_i - R_j|$  is the distance between sites *i* and *j*, and  $E_i$  and  $E_j$  are the on-site energies of these sites. The value taken for the inverse localization length of the wave function  $\alpha$  only influences the prefactor of the hopping rate, as long as it is large enough to suppress further than nearest-neighbor hopping. For the value  $\alpha = 10/a$  that we have taken<sup>21</sup> this is the case.

The energy difference in  $E_j - E_i$  contains a contribution  $-eFR_{ijx}$  due to an electric field *F* in the *x* direction of the lattice (*e* is the unit charge) and a contribution due to the Coulomb interactions with all other—mobile and immobile—charges. Since charge transport occurs in a two-dimensional surface on top of a dielectric the Coulomb interaction has to be adapted to this geometry. The Coulomb interaction energy between two unit charges, of which one is at the interface between vacuum and a dielectric with relative dielectric constant  $\epsilon_r$  (3.9 for SiO<sub>2</sub>) while the other is at an arbitrary position at a distance *R*, is  $V_{ij} = 2e^2/[4\pi\epsilon_0(\epsilon_r + 1)R]$ , with  $\epsilon_0$  the vacuum permittivity.<sup>22</sup> Finally, the on-site energies  $E_i$  contain a random contribution that we will draw from a Gaussian density of states (DOS) with a standard deviation  $\sigma$ . We note that the combination of Miller-Abrahams hopping and Gaussian disorder has been very successfully used in describing charge transport of organic semiconductors.<sup>21,23</sup>

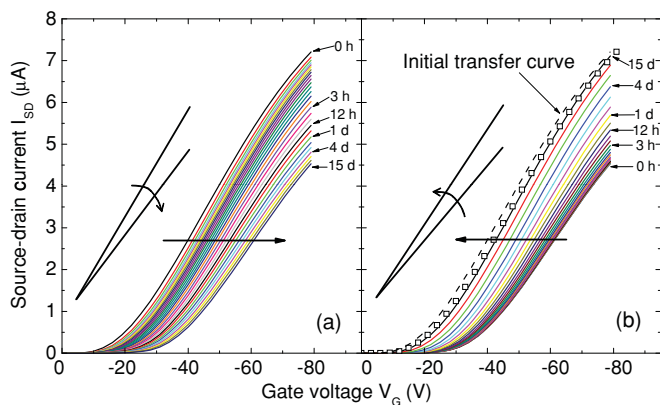


FIG. 2. (Color online) (a) Transfer curves of the SAMFET during application of a gate bias voltage of  $V_G = -30$  V for 15 days. (b) Transfer curves during the ensuing period of 15 days in which the gate was grounded. Dashed line: initial transfer curve. Squares: initial transfer curve shifted by  $-2$  V. The tilted lines indicate the slope of the linear part of the initial and final transfer curve.

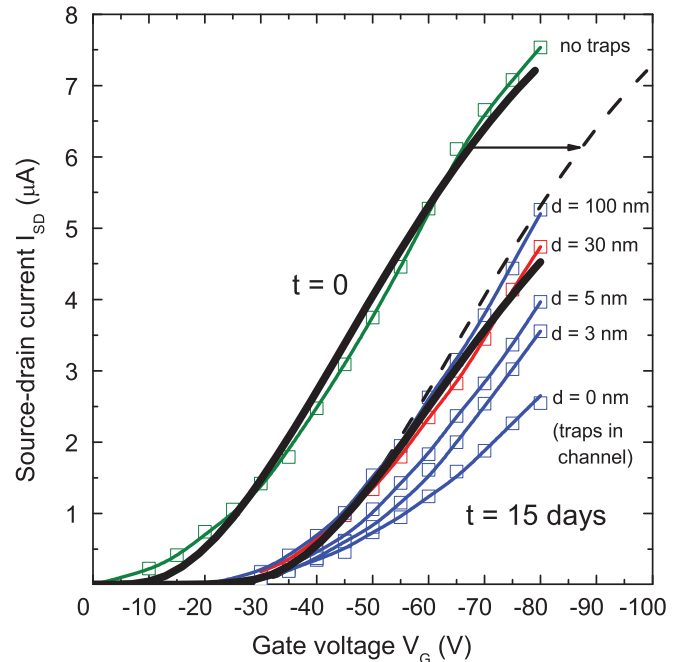


FIG. 3. (Color online) Thick solid lines: measured transfer curves from Fig. 2(a) at the start of the experiment and after 15 days of applying a gate voltage of  $V_G = -30$  V. Dashed line: initial transfer curve shifted by  $-20$  V. Thin lines and symbols: simulated transfer curves without trapped charges and for a uniform trapped charge distribution with a surface density of  $2 \times 10^{12} \text{ cm}^{-2}$  in a layer of thickness *d*.

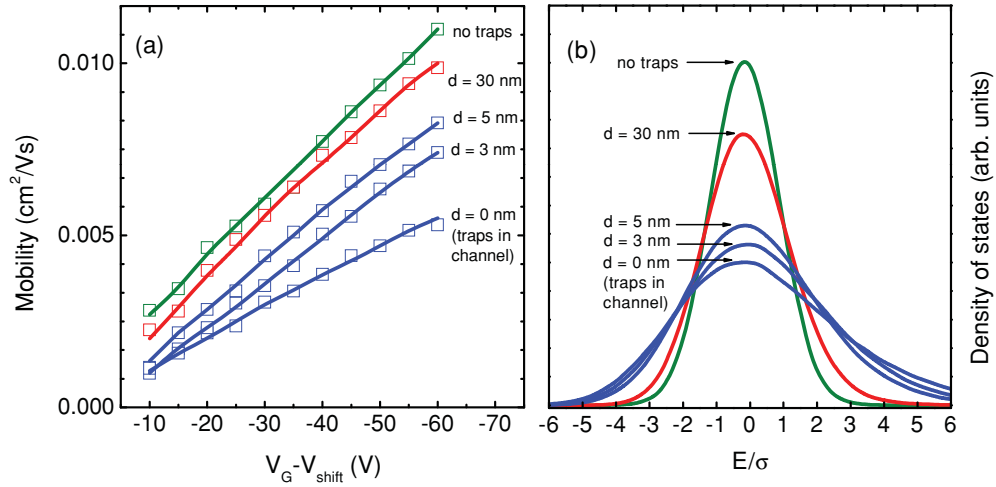


FIG. 4. (Color online) (a) Lines and symbols: simulated mobilities as a function of  $V_G - V_{\text{shift}}$ , corresponding to the results in Fig. 3. (b) Corresponding effective densities of states.

We performed Monte Carlo simulations for the charge transport in two-dimensional square lattices of  $100 \times 100$  sites. An applied electric field of  $F = 0.1\sigma/ea$  was taken in the simulations, which is well within the linear regime of the charge transport. Starting from an equilibrium configuration for  $F = 0$  a stationary situation was obtained after about 10 million Monte Carlo steps and then the current was determined. An average over the currents for 10 disorder configurations was taken, leading to an uncertainty in the average current of less than 5%. For a gate voltage  $V_G$  the surface density of charges is given by  $C|V_G|/(eWL)$ , where  $C = 4.35$  pF is the transistor capacitance. This corresponds to an increase of the filling of the lattice of about 1% for every  $-10$  V in  $V_G$ . At the beginning of the experiment ( $t = 0$ ) all charges are assumed to be mobile. We obtain a very good fit to the experimental transfer curve at  $t = 0$  with a standard deviation of the Gaussian DOS of  $\sigma = 0.13$  eV and a lattice constant of  $a = 1$  nm; see Fig. 3. The value for  $\sigma$  is quite typical for organic semiconductors. The fact that  $a$  is larger than the shortest known packing distance of 0.47 nm between the molecules<sup>16</sup> could account for a certain amount of correlation between the random energies of neighboring molecules. A free numerical prefactor in the simulated current was used in the fitting of the initial transfer curve and kept constant for all following calculations.

We note that the experimental transfer curve at  $t = 0$  appears to have a nonzero threshold voltage. However, since the transfer curve can be reproduced by our simulations without assuming trapped charges at  $t = 0$ , we conclude that the apparent nonzero threshold voltage is not related to any initial trapped charges being present in the SAMFET. Also, for the channel length considered here (10  $\mu\text{m}$ ) contact effects are negligible.<sup>16</sup> Instead, the apparent initial threshold voltage offset is related to the filling of energetically low-lying states in the tail of the DOS. The difference between the simulated and experimental transfer curve at low gate voltage could be due to deviations from a Gaussian in the tail of the DOS.

Using exactly the same parameters, simulations were performed for the case that a fixed amount of charges induced by the gate field is trapped. After 15 days of application of the

gate voltage of  $V_G = -30$  V, the shift of the transfer curve of about  $V_{\text{shift}} = -20$  V corresponds to a trapped charge density of about  $2 \times 10^{12} \text{ cm}^{-2}$ . For the case that these trapped charges are randomly distributed in the transistor channel, i.e., in the monolayer, the predicted transfer curve lies significantly below the measured curve; see Fig. 3. We also display in Fig. 3 the results for the case that the trapped charges are randomly distributed in a layer with thickness  $d$  of 3, 5, 30, and 100 nm. Since the length of the spacer in the self-assembling molecule is about 1.5 nm [see Fig. 1(c)] for  $d = 3$  nm about half of the trapped charges would be located in the gate dielectric. For both  $d = 3$  and  $d = 5$  nm the predicted transfer curves lie above the transfer curve for trapped charges located in the channel but still significantly below the experimental transfer curve. We obtain a good fit to the experimental data for  $d = 30$  nm. For  $d = 100$  nm, the trapped charges interact only very weakly with the mobile charges in the transistor channel. As a result, the shape of the transfer curve is almost indistinguishable from the initial transfer curve and now lies above the measured curve.

In Fig. 4(a) we plot the simulated mobilities as a function of  $V_G - V_{\text{shift}}$  for the different values of  $d$ . The increase of the mobility with gate voltage is a well-known effect of state filling.<sup>21,24</sup> We clearly see the influence of  $d$  on the mobility. The further away the trapped charges are from the monolayer, the weaker is the effect of the Coulomb scattering. In Fig. 4(b) we show the effective DOS for the different values of  $d$ . This effective DOS is obtained by adding to the random energy of each site in the lattice the Coulomb interaction energy with all the trapped charges. The effective DOS is significantly narrower for the case that the trapped charges have penetrated deep into the gate dielectric as compared to when they are in the monolayer. This then leads to a much higher mobility. The effect is completely analogous to the modulation doping in III-V semiconductor heterostructures, where the spatial separation of donors from the mobile carriers reduces the effect of Coulomb scattering. The interesting additional aspects of the present work are that the effect is tunable and reversible; see Fig. 2.

Our conclusion that trapped charges in the SAMFET are located in the dielectric is compatible with an experiment

in which the semiconducting organic layer of an OFET was removed from the SiO<sub>2</sub> dielectric after a gate bias was applied for an extended period of time.<sup>11</sup> Using scanning Kelvin probe microscopy it was shown that after removal of the organic layer the dielectric was carrying charge with a magnitude in agreement with the measured shift of the transfer curve. That experiment was not able to distinguish trapping on the surface of the dielectric from trapping in the dielectric. Our present analysis shows that in fact trapping takes place in the bulk of the dielectric. This is in line with a trapping mechanism recently proposed by us, which is based on a reversible transformation of holes into protons in an electrolytic reaction involving water and the reversible migration of these protons into the gate dielectric.<sup>25</sup> The rectangular shape of the distribution of trapped charges assumed in the present work is in good agreement with predicted shapes.<sup>18</sup> Apparently, under the vacuum conditions used by us water is not fully removed, in agreement with previous observations.<sup>26</sup>

In summary, we have investigated both experimentally and theoretically the effect of Coulomb scattering by trapped charges on the mobility in a two-dimensional channel of a self-assembled organic monolayer field-effect transistor. The detrimental reduction of the mobility is greatly reduced by penetration of the trapped charges into the gate dielectric, in analogy to the effect of modulation doping in heterostructures of III-V semiconductors. Finally, we stress that our results are applicable to organic field-effect transistors in general, because at typical gate biases the thickness of the accumulation layer in a conventional thin film organic field-effect transistor is very comparable to the height of the semiconducting core of the molecule in the self-assembled organic monolayer.

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