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The distribution of field-induced charges in C_{60} fullerite

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The profile of injected charges in a C_{60}-based field-effect transistor (FET) is considered. A simple scheme for calculations of the charge distribution between the 2D layers of C_{60} molecules is founded on a small magnitude of the interball electron hopping. Analytical solutions of the equations for the charge distributions are obtained in the limits of thick and thin crystals. The charge density is shown to drop exponentially with the crystal depth. The calculations predict the relative part of induced charges involved in the surface layer to be 3/4 and 2/3 in the cases of electron and hole injection, respectively.

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Introduction

The phenomenon of charge injection controlled by electric field is observed in the field-effect transistor (FET) structure with both pristine and doped fullerene C_{60} [1–4]. Because fullerene C_{60} with its unique properties is considered as a prospective material for FET devices, the important problems determining the FET characteristics are connected with the shape of the distribution of gate-induced charges in the C_{60} crystal.

A rough estimation of the charge distribution is obtained from the observed dependence of the conductivity on the gate voltage at different film thicknesses [5]. The authors have concluded that all of the induced charges are located on the one or two top monolayers.

The problem of the charge profile in the field-doped C_{60} crystal is considered theoretically in connection with the possibility of superconductivity in organic FETs. Though reports on its observation have now been retracted [6], the calculation of the charge distributions in the FET is important by its own rights. The study [7] of this problem within the tight-binding model taking into account electron repulsion via mean field shows that induced charges of a significant amount are distributed nearly completely in the top fullerite monolayer. Moreover, the calculations by the modified Thomas–Fermi approach show that the field-induced charge is concentrated in a layer near the interface even smaller than the C_{60} diameter [8]. However, in view of the C_{60} electronic characteristics these results should be taken with care. Specifically, in the fullerite crystal the Hubbard repulsion U on a C_{60} molecule is estimated to be 1 eV or more [9], whereas the maximal magnitude of the interball hopping t is below 50 meV. Thus, with a ratio U/t of more than 20, the C_{60} crystals have to be classified as systems with strong electron correlation which has not taken into account properly within both the above approaches.

The present study considers the charge-profile problem in fullerite from other positions which are in better correspondence with the correlation characteristics of this material. We apply the approach used earlier by us for the calculations of charge transfer in the fulleride crystals A_3C_{60}. It is just the smallness of the hopping in comparison with electrostatic energies that enables us to develop the simple scheme in the present case also. Correspondingly, the scheme explicitly takes into account only electrostatic interactions between the C_{60} molecules, neglecting the intermolecular hopping. More accurately, some minor hopping is formally present, allowing an equilibrium electron distribution to be reached.

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In principle, our scheme is based on the known Hohenberg–Kohn theorems [10] stating that (i) the electron density is in one-to-one correspondence with the electric field, and (ii) with the outer potential fixed, the electron distribution is determined by the minimum condition of energy considered as a functional of this distribution with the electron number fixed. In the preliminary brief report [11] the equations for the charge distribution are solved numerically. Considering that approach in more detail here, we present analytical solutions of the equations defining the charge distribution in the C_{60}-based FET structure in the limits of thin and thick crystals.

Model and method

As in Ref. 7, we consider the fcc fullerite lattice with a (001) plane parallel to the gate. We are interested in the distribution of injected charges between the parallel (001) layers of C_{60} molecules that form square lattices with the side length b = 10 Å.

Let ρ_n be the total number of extra electrons per molecule in layer n, so their charge is $-e\rho_n$ (the case of injected holes is represented by negative ρ_n). We consider a system with a total number of layers N+1, with the surface layer labeled by zero.

The basic assumption of our model that was proposed in Ref. 11 is neglecting the overlap between C_{60} molecules. Accordingly, the total energy of the crystal is the sum of the energies of the separate layers of molecules that interact electrostatically. The energy E_n per molecule in a layer n with the potential U_n is

$$E_n = E_0(\rho_n) - eU_n\rho_n, \tag{1}$$

where $E_0(\rho_n)$ is the energy of a free molecule with ρ_n extra electrons.

This expression is accurate for integer ρ_n, so that $E_0(\rho_n)$ can be treated as the energies of C_{60} ions with corresponding charges. For noninteger ρ_n, it is naturally assumed that $E_0(\rho_n)$ can be interpolated by the quadratic fit,

$$E_n(\rho_n) = E_0(0) + E_1\rho_n + \frac{1}{2}E_2\rho_n^2. \tag{2}$$

Then the minimum condition of total energy with respect to ρ_n leads to equation

$$E_1 + E_2\rho_n - eU_n = \theta, \tag{3}$$

where θ is a Lagrange multiplier taking into account the additional restriction of fixing total electron number,

$$\sum_n \rho_n = \rho_{\text{tot}}. \tag{4}$$

On the other hand, the layer potentials are, in turn, related to the charges by the Poisson equations. Because of negligible hopping, as it is adopted in our model, the C_{60} molecules interact only electrostatically and can be represented by point charges due to their near spherical form. According to Ref. 7, the potential U_n of layer n is determined by the equation

$$-eU_n = \xi\sum_{m=0}^{N}\min(m,n)\rho_m - \eta\rho_n, \tag{5}$$

where the coefficients ξ and η are expressed in terms of the C_{60} dielectric constant ε and the distance b between neighboring molecules:

$$\xi = \frac{4\pi e^2}{\varepsilon b\sqrt{2}}, \quad \eta = \frac{3{,}9e^2}{\varepsilon b}. \tag{6}$$

Excluding U_n from (3) and (5), one obtains a system of linear inhomogeneous equations that determine, together with the condition (4), the charge densities ρ_n,

$$\lambda\rho_n + \sum_{m=0}^{n} m\rho_m + n\sum_{m=n+1}^{N}\rho_m = C, \quad n = 0,1,\ldots,N, \tag{7}$$

where the parameter λ is defined by the equality

$$\lambda = (E_2 - \eta)/\xi \tag{8}$$

and $C = (\theta - E_1)/\xi$ is a new constant. As can be seen from Eq. (7) at $n = 0$, this constant is in close relationship to the charge density in the surface layer, $C = \lambda\rho_0$.

The parameter λ can be treated as a localization parameter. Indeed, the solutions of the system (7) in the limiting cases

$$\rho_n = \rho_{\text{tot}}\delta_{n0} \quad \text{at} \quad \lambda = 0, \tag{9}$$

$$\rho_n = \rho_0 = \rho_{\text{tot}}/(N+1) \quad \text{at} \quad \lambda \to \infty \tag{10}$$

show that at $\lambda = 0$ all of the injected charge is concentrated in the surface layer, but in the opposite case of great λ the charge turns to be uniformly distributed between the layers.

For a finite $\lambda > 0$ and a thick crystal ($N \to \infty$), the set (7) is found to have a solution in the form of a descending geometric progression:

$$\rho_n = ax^n. \tag{11}$$

For the proof, consider the dependence on x of the left-hand side of Eq. (7) with ρ_n in the form (11) divided by a normalization constant a,

$$R_{nN}(x) = \lambda x^n + S_{1n}(x) + n[S_{0N}(x) - S_{0n}(x)], \tag{12}$$

where $S_{0n}(x)$ and $S_{1n}(x)$ are the sums

$$S_{0n}(x) = \sum_{m=0}^{n} x^m, \quad S_{1n}(x) = \sum_{m=0}^{n} m x^m. \quad (13)$$

Expressing the sums in explicit forms

$$S_{0n} = \frac{1 - x^{n+1}}{1 - x},$$

$$S_{1n}(x) = x\frac{dS_{0n}(x)}{dx} = \frac{x - x^{n+1}(1 + n - nx)}{(1 - x)^2} \quad (14)$$

we arrive at the following functional form of R_{nN}:

$$R_{nN}(x) = \lambda x^n + \frac{x(1 - x^n)}{(1 - x)^2} - \frac{nx^{N+1}}{1 - x}. \quad (15)$$

For $N \to \infty$, the last term in (15) diminishes at $x < 1$. So, all the functions $R_{nN}(x)$ have the same, independent of n, value at x satisfying by the equation

$$\lambda = x/(1 - x)^2. \quad (16)$$

From its two roots, both positive, just the least one

$$x = 1 + t - \sqrt{t^2 + 2t}, \quad t = 1/2\lambda \quad (17)$$

obeys the inequality $x < 1$, thus providing the validity of the solution (7) for $N \to \infty$.

Results and discussion

The solution obtained shows that the shape of charge distribution among the layers is independent of total charge ρ_{tot} that determines only the normalization constant a in (12), $a = \rho_{tot}(1 - x)$. Finally, one obtains from (11)

$$\rho_n = \rho_{tot}(1 - x)x^n. \quad (18)$$

Due to a relation that follows from (18),

$$x = 1 - \rho_0/\rho_{tot}, \quad (19)$$

the value of x can be treated as the relative part of the injected charge in the deep layers of the crystal.

It is of interest to compare the results in the limit $N \to \infty$ with those for the cases of a few layers. Solving (7) for $N = 1$ and $N = 2$, one can evaluate x defined by (19),

$$x = \lambda/2(\lambda + 1) \quad \text{at} \quad N = 1, \quad (20)$$

$$x = \lambda(2\lambda + 1)/(3\lambda^2 + 4\lambda + 1) \quad \text{at} \quad N = 2. \quad (21)$$

The dependencies of x on λ tabulated by the expressions (20) and (21) are depicted in Fig. 1. The plots show that the charge density, which at $\lambda = 0$ is completely localized in the surface molecules, sharply expands into deeper layers as λ rises. However, further increase of x becomes slower, so that even at moderate λ the surface charge remains dominant.

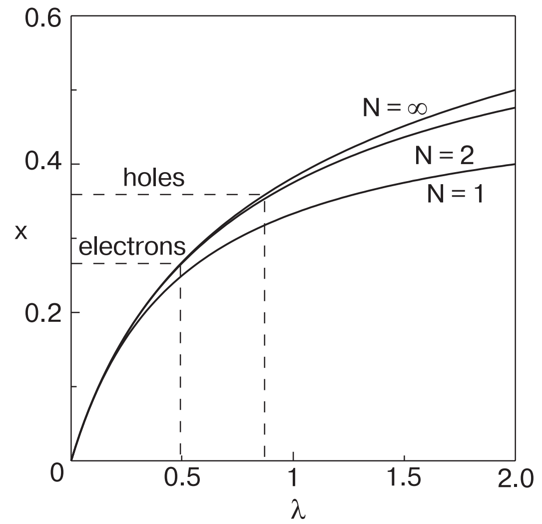

Fig. 1. Relative occupation x of subsurface layers as a function of the localization parameter λ in Eq. (8) and in the C_{60}-based FET structure with N+1 layers.

So far the quantities ρ_n are treated as electron densities. However, the above consideration is equally applicable to the case of injected holes, the densities of which are characterized by negative ρ_n. As can be easily seen, replacing ρ_n by $-\rho$ does not change the relative density distributions derived. Thus, the obtained dependencies $x(\lambda)$ presented by Eqs. (20), (21) and the plots in Fig. 1 are valid both for electrons and holes.

To obtain numerical estimates in real C_{60} crystals one should evaluate only E_2 in the approximation (2). Considering the latter as a fit to the ground-state energies of C_{60} molecule and its ions, one obtains

$$E_2 = E(0) + E(2) - 2E(1) = A(C_{60}) - A(C_{60}^-) =$$
$$= 2.7 \text{ eV (for electrons)},$$

$$E_2 = E(0) + E(-2) - 2E(-1) = -I(C_{60}) + A(C_{60}^+) =$$
$$= 3.8 \text{ eV (for holes)},$$

where A are electron affinities and I are ionization potentials with known experimental values (in eV) [12,13]:

$$A(C_{60}) = 2.7, \quad A(C_{60}^-) \approx 0,$$

$$I(C_{60}) = 7.6, \quad I(C_{60}^+) = 19.0 - 7.6 = 11.4.$$

Using these data we obtain the estimates presented in Table for injected charges of both signs.

Table. Curvature E_2 of energy-harge fit, localization parameter λ and relative occupation x of subsurface layers in the C_{60}-based FET structure

Carriers	E_2, eV	λ	x
Electrons	2.7	0.492	0.266
Holes	3.8	0.871	0.359

It can be seen that injected charges, both electrons and holes, are located predominantly in the surface layer. However, their localization is far from complete: no less than a quarter of the charges come from the top layer, mainly to the next one. Note that the relative surface occupation in the case of electrons markedly exceeds that of holes: one third of the holes turn to be beneath the surface.

The charge profile is formed as the result of competition between the effect of the gate field and charge interactions inside the C_{60} crystal. The latter prevents charge concentration, firstly, because of charge repulsion and, secondly, because too many molecules could appear to be in higher-ionic states that are unfavorable by energy, especially, in the case of great E_2. Electrostatic charge repulsion is treated identically in our approach and in Ref. 7, but the factor of higher ionicity is taken into account in different manners. In [7] the on-site repulsion of extra charges is represented by the parameter U_0 in the electrostatic potential. Our approach directly uses the ion energies determining E_2 and thus avoids the separate estimations of U_0.

Finally, it should be noticed that the possibility of our simple analytic consideration of the charge-profile problem is essentially based on the quadratic approximation (2) of the charge-energy dependence for ions. An analysis of the results of quantum mechanical calculations both semiempirical and *ab initio* [14–16] shows that the approximation (2) is rather accurate for several electrons or holes. The higher-order terms can violate the independence of the charge-profile shape on the concentration of injected charges. However, a pronounced effect of these terms should be expected for much greater charges corresponding to the gate voltage beyond the physically admitted values.

Conclusion

To conclude, we summarize the main differences of our results from those obtained in Ref. 7. (i) The charge profile in [7] depends substantially on the charge concentration, whereas our relative distribution is independent of it. (ii) According to [7] the total charge is confined almost completely to the surface layer, contrary to our calculations showing a relative surface-layer population of less than three quarters.

The approximation used here takes into account properly the electronic characteristics of the C_{60} crystal, which is treated as a strongly correlated system. Thus, our model, though simple, is believed to describe, at least semiqualitatively, the main features of the charge distribution in the C_{60}-based FET system. The polarization and interball hopping effect neglected in our study, apparently should be taken into account to get quantitative results. The question on the role of non-negligible occupation of subsurface layers in the electronic properties of fullerite in FET structures needs a separate consideration.

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