SOLID STATE ELECTRONICS

Spontaneous Transverse Field in Impurity Graphene

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Abstract—The periodic Anderson model and the average electron method are used to show that an electric field normal to an applied dc electric field can spontaneously appear in impurity-containing graphene. This effect can be related to a nonequilibrium electron subsystem in graphene. The characteristics of the spontaneous field are revealed as a function of the problem parameters.

INTRODUCTION

Growing interest in nonlinear phenomena in the last few years significantly stimulates the creation of materials that can exhibit nonlinear properties under easily achieved experimental conditions. Graphene, which has a structure consisting of one carbon atom layer and a planar hexagonal lattice, is one of these materials [1–4]. A high electron mobility in graphene and its unique electrophysical characteristics have attracted attention to it as one of the alternatives to the silicon base of modern microelectronics [1–4].

Experimental studies [5] demonstrated that electromagnetic waves propagating in carbon structures become strongly nonlinear even at relatively low fields, which can result in the propagation of individual electromagnetic waves (which are analogs of solitons or even are solitons) in carbon nanotubes and graphene. These properties of carbon nanostructures have provoked particular theoretical interest and attempts to use them in nonlinear optics devices [5]. According to the conclusions drawn in these works, nonlinearity is caused by a change in the classical electron distribution function and a nonparabolic electron dispersion law.

The study of phase transitions represents one of the paradigms of modern fundamental physics. In particular, the nonequilibrium phase transition induced by an applied field of a certain nature occupies one of the most important places in the variety of phase transitions.

It was theoretically shown in [6, 7] that a strong electric field causes nonequilibrium phase transitions in the electron gas of semiconductors with the body-centered cubic lattice. This effect manifests itself in spontaneous appearance of transverse electric field E_x, which plays the role of an order parameter. In this case, applied electric field E_y directed along the axis of symmetry of a crystal is a control parameter. As shown in those works, a necessary condition for the appear-

ance of a transverse field is the nonadditivity of an electron spectrum, $\varepsilon(\mathbf{p}) \neq \varepsilon(p_x) + \varepsilon(p_y) + \varepsilon(p_z)$, where $\mathbf{p}$ is the electron quasi-momentum. An electron spectrum in the body-centered cubic lattice becomes nonadditive,

$$\varepsilon(\mathbf{p}) \propto \cos(p_x a/2\hbar)\cos(p_y a/2\hbar)\cos(p_z a/2\hbar),$$

where a is the lattice parameter.

Note that the nonadditivity condition is met in pure graphene, whose band structure was predicted in the middle of the 20th century [8]. However, graphene with impurities is physically more interesting, since graphene can easily adsorb various atoms [9] and impurity-containing graphene has a high electron concentration in the conduction band (which is important for practical applications). Moreover, the spectrum should be limited; that is, the electron energy cannot exceed a certain value.

All these conditions are also met for graphene with impurities; therefore, we can study the possibility of phase transitions in impurity graphene, which should manifest itself in the appearance of transverse component E_x in the presence of field E_y (which plays the role of a control parameter).

The appearance of a spontaneous transverse field is also important in terms of modern tendencies of using graphene as a transistor base: this spontaneous transverse field will deflect electrons, which can substantially affect the $I–V$ characteristics of a graphene transistor. Therefore, the problem of studying the response of a two-dimensional electron system with allowance for the interaction of impurity electrons with graphene electrons is a challenging problem.

MODEL AND BASIC EQUATIONS

It is convenient to describe the electron subsystem of impurity-containing graphene in terms of the periodic Anderson model [11] using the Hückel approxi-

mation [12], which takes into account the dynamics of only π electrons. This model takes into account the kinetic energy of electrons and the energy of impurity electrons and neglects the energies of the electrons in inner atomic shells and the electrons involved in the formation of σ-type chemical bonds and the energy of atomic vibrations in a crystal lattice. The interaction of host and impurity electrons in the model is taken into account with a hybridization potential. This model was successfully applied to studying the atomic adsorption on the surfaces of metals and semiconductors [13].

For graphene, any interacting atom is an adsorbed atom (adatom), which can be considered as an impurity. A large number of works dealing with graphene indicate that hydrogen adsorption is of particular interest. One of the causes of deep interest consists in the semimetal–insulator transition that occurs in graphene at a certain hydrogen atom concentration [14]. Therefore, it is reasonable to consider adsorbed atomic hydrogen as an impurity.

The Hamiltonian of the periodic Anderson model can be written in a form convenient for analyzing the electron spectrum in graphene [11],

$$
H = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^+ c_{k\sigma} + \sum_a \varepsilon_a \sum_\sigma a_\sigma^+ a_\sigma + U n_{a\sigma} n_{a-\sigma}
$$

$$
+ \sum_{ak\sigma} V_{ka} c_{k\sigma}^+ a_\sigma + \sum_{ak\sigma} V_{ka}^* a_\sigma^+ c_{k\sigma}, \tag{1}
$$

where $c_{k\sigma}(c_{k\sigma}^+)$ are the Fermi production and annihilation operators for electron with wave-vector $\mathbf{k}$ and spin σ in the crystal respectively; $a_\sigma(a_\sigma^+)$ are the Fermi production and annihilation operators for electron with spin σ at an impurity atom, respectively; $n_{a\sigma} = a_\sigma^+ a_\sigma$ is the operator of the number of impurity electrons; ε_a is the energy of an electron at an impurity atom; ε_k is the electron spectrum (band structure) of the ideal crystal; V_{ka} is the matrix element of the hybridization of impurity and carbon atom states; and U is the Coulomb energy of the interaction of electrons at an impurity atom.

The dispersion law ε_k that describes the properties of ideal graphene is well-known [8],

$$
\varepsilon_k = \pm\gamma \sqrt{1 \pm 4\cos(ap_x)\cos\left(\frac{ap_y}{\sqrt{3}}\right) + 4\cos^2\left(\frac{ap_y}{\sqrt{3}}\right)}, \tag{2}
$$

where $\gamma \approx 2.7$ eV, $a = 3b/2\hbar$, $b = 0.142$ nm is the distance between neighboring carbon atoms in graphene, $k = (p_x, p_y)$ is the quantum-momentum of electrons in the Brillouin zone, and the signs before the root belong to the conduction and valence bands. Degeneration at certain singular points in the Brillouin zone of graphene at the Fermi level (0 eV) indicates conducting properties of graphene [4, 8].

We now calculate the parameters of effective Hamiltonian (1) using atomic hydrogen adsorbed on the graphene surface as an example. For this type of impurity, we have $U = 0$, since atomic hydrogen only contains one electron in the valence shell.

The hybridization potential in Anderson Hamiltonian (1) represents the energy of an electron passing from an impurity to the crystal. It is generally accepted that the matrix element is $V_{ka} = V$; i.e., it is independent of wave-vector $\mathbf{k}$ [13]. Therefore, we propose to estimate it using a quantum-chemical approach, namely, as a resonance matrix element in semiempirical MNDO-based methods [12]. In this case, potential V is determined by the overlap integral of the wave functions of the s orbital (hydrogen atom) and the p_z orbital (carbon atom),

$$
V = \frac{1}{2}(\beta_H + \beta_C)S_{HC}, \quad S_{HC} = \int \Psi_{1s}(\mathbf{r})\Psi_{2p_z}(\mathbf{r})d\mathbf{r},
$$

$$
\Psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{3/2} e^{-\rho}, \quad \rho = \frac{zr}{a_0}, \quad z(H) = 1,
$$

$$
\Psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{z}{a_0}\right)^{3/2} \rho e^{-\rho/2}\cos\theta, \quad \rho = \frac{zr}{a_0}, \tag{3}
$$

$$
z(C) = 6,
$$

where S_{HC} is the overlap integral of the wave functions, $\beta_H = -6.99$ eV and $\beta_C = -7.93$ eV are the resonance parameters of the quantum-chemical semiempirical MNDO method [12], a_0 is the Bohr radius, and z is the atomic nucleus charge. The hybridization potential was estimated to be $V = -1.43$ eV.

To estimate impurity electron energy ε_a, researchers use the method [13, 14] based on the fact that an adatom electron undergoes repulsion from a substrate electron. As a result, the following formula is obtained [14]:

$$
\tilde{\varepsilon}_a = A + I + \frac{e^2}{4l},
$$

where I is the hydrogen atom ionization potential (-13.6 eV); e is the unit charge; $l = 1.2$ Å is the distance from the center of adatom to the plane of its image in the substrate, which is on the order of the adatom atomic radius (adsorbed bond length), estimated by quantum-chemical semiempirical methods; and A is the work function of graphene (5.11 eV) [14]. The calculations by this formula give $\varepsilon_a = -5.72$ eV.

To find the spectrum of unit excitations described by effective Hamiltonian (1), we use the mathematical apparatus of Green's functions [15]. For example, equations for the Fourier transforms of single-particle Green's functions (hereafter, simply Green's functions) have the form

$$
\omega\langle\langle a_\lambda | a_\lambda^+ \rangle\rangle = \frac{i}{2\pi} + \varepsilon_a\langle\langle a_\lambda | a_\lambda^+ \rangle\rangle + \sum_k V_{ka}^*\langle\langle c_{k\lambda} | a_\lambda^+ \rangle\rangle,
$$

$$\omega\langle\langle a_\sigma|c_{k\sigma}^+\rangle\rangle_\omega^r = \varepsilon_a\langle\langle a_\sigma|c_{k\sigma}^+\rangle\rangle_\omega^r + V_{ka}^*\langle\langle c_{k\sigma}|c_{k\sigma}^+\rangle\rangle_\omega^r,$$

$$\omega\langle\langle a_\sigma|c_{l\nu}^+\rangle\rangle_\omega^r = \varepsilon_a\langle\langle a_\sigma|c_{l\nu}^+\rangle\rangle_\omega^r + \sum_q V_{qa}^*\langle\langle c_{q\nu}|c_{l\nu}^+\rangle\rangle_\omega^r,$$

$$\omega\langle\langle a_\sigma|c_{k\sigma}^+\rangle\rangle_\omega^r = \varepsilon_a\langle\langle a_\sigma|c_{k\sigma}^+\rangle\rangle_\omega^r + V_{ka}^*\langle\langle c_{k\sigma}|c_{k\sigma}^+\rangle\rangle_\omega^r,$$

(4)

where ω is the energy variable and the double angle brackets designate the corresponding Green's functions.

Set of equations (4) is solved analytically owing to the model approximations, which neglect Coulomb correlations. As a result, an expression for the Green's function of the crystal lattice (where the effect of the spin variable is neglected) with allowance for an adsorbed atomic defect has the form

$$\langle\langle c_{k\sigma}|c_{k\sigma}^+\rangle\rangle = \frac{i}{2\pi}\frac{1}{(\omega-\varepsilon_k)-\sum_a\frac{|V_{ka}|^2}{\omega-\varepsilon_a}}. \quad (5)$$

Analytical expression for Green's function (5) of the graphene lattice can be used to determine the electron spectrum of the crystal with an adsorbed hydrogen atom. Since the adsorbed atoms have the same type, the sum in the denominator of Eq. (5) can easily be computed. The eigenvalues of the electron energies in the lattice with adsorbed atoms give the poles of Green's functions [15],

$$E(k) = \frac{1}{2}\left[\varepsilon_a+\varepsilon_k\pm\sqrt{(\varepsilon_a-\varepsilon_k)^2+4\frac{N_H}{N}|V|^2}\right], \quad (6)$$

where N is the number of unit cells in the crystal and N_H is the number of hydrogen atoms adsorbed on graphene.

Actually, the ratio N_H/N determines the concentration of impurity atoms. The Anderson model is applicable for the case of a low defect concentration; that is, when the condition $N_H/N \ll 1$ is met. As follows from the general properties of the Anderson model [11], a gap appears near the defect level in the quasiparticle spectrum. As calculated above, impurity level ε_a lies deep in the valence band; therefore, low impurity concentrations cannot substantially change the band structure near the Fermi level and the properties of graphene on the whole. However, impurities and, hence, a gap in the valence band lead to the appearance of electrons in the conduction band [19].

PHASE TRANSITION IN GRAPHENE WITH ADSORBED HYDROGEN ATOMS

We now consider the response of a system of impurity graphene layers to external electric field E_y applied along the y axis (Fig. 1). To this end, we apply the procedure [16] tested to study the phase transitions in graphene with substitutional defects and use the average electron method [17], according to which an electron motion equation can be written as
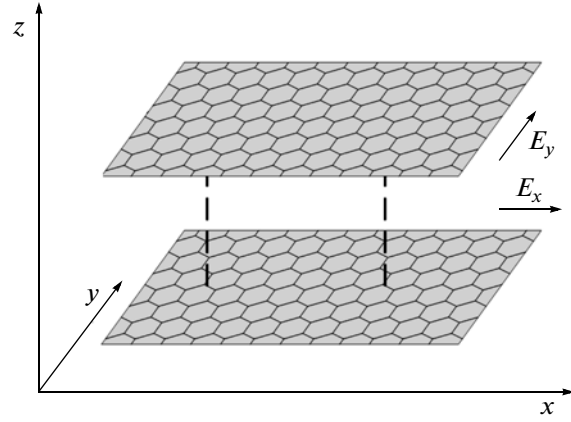
Fig. 1. Geometry of the problem.

$$\frac{d\mathbf{p}}{dt} = q\mathbf{E}, \quad (7)$$

where q is the electron charge.

Equation (7) can easily be solved by analytical integration with the given initial conditions

$$p_x = p_{0x} + qE_x t$$

$$p_y = p_{0y} + qE_y t,$$

where p_{0x} and p_{0y} are the initial values of momentum $\mathbf{p} = \hbar\mathbf{k}$.

Electron velocities v_x and v_y in the corresponding zones can be determined using the standard rule

$$v(p_x) = \frac{\partial E(p_x, p_y)}{\partial p_x}, \quad v(p_y) = \frac{\partial E(p_x, p_y)}{\partial p_y}.$$

According to the average electron method, we use the definition of the current density [18] written in units of relaxation time,

$$\mathbf{J} = \int_0^\infty q v(p(t))\exp(-t)dt, \quad (8)$$

where $\mathbf{p}(t)$ is the solution to Eq. (7) and the relaxation time is taken to be unity.

It is convenient to represent dispersion law (6) of graphene with impurities in the form of the Fourier series

$$E(p_x, p_y) = \sum_{m,n} A_{mn}\cos(mp_x)\cos(np_y),$$

$$A_{mn} = \frac{1}{(2\pi)^2}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\varepsilon(p_x, p_y)\cos(mp_x)\cos(np_y)dp_x dp_y.$$

In this case, the final expression for the x component of the current density after rather simple computations has the form
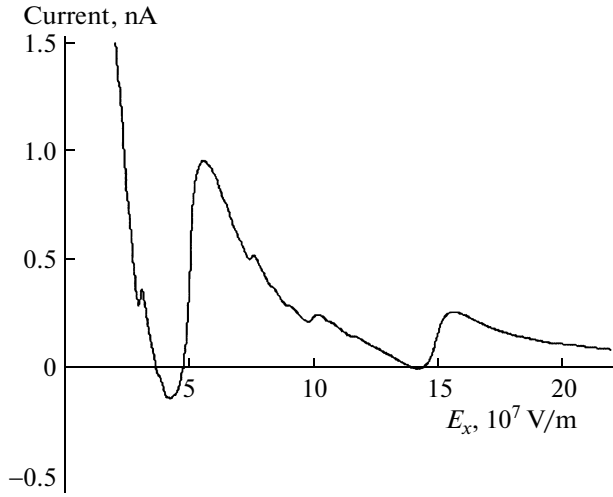
Current, nA

Fig. 2. Current vs. field E_x at fixed field E_y ($E_y = 6 \times 10^7$ V/m).

$$j_x = \sum_{m,n} A_{mn}\left[\cos\left(2\pi\frac{m}{3}\right) + (-1)^i\cos\left(\pi\frac{k}{3}\right)\right]$$

$$\times \frac{m^2 E_x(n^2 E_y^2 - 1 - m^2 E_x^2)}{(1 + (nE_y + mE_x)^2)(1 + (nE_y - mE_x)^2)}. \quad (9)$$

For a given applied electric field E_y, transverse field E_x is determined using boundary conditions. The circuit along the x axis is assumed to be open; that is, we have

$$j_x = 0. \quad (10)$$

This condition corresponds to a certain solution to the transverse field, $E_x = E_x(E_y)$. Equation (10) has two solutions

$$\begin{cases} E_x = 0, \\ \sum_{m,n} A_{mn}\left[\cos\left(2\pi\frac{m}{3}\right) + (-1)^i\cos\left(\pi\frac{k}{3}\right)\right] \\ \times \dfrac{m^2(n^2 E_y^2 - 1 - m^2 E_x^2)}{(1 + (nE_y + mE_x)^2)(1 + (nE_y - mE_x)^2)} = 0. \end{cases} \quad (11)$$

At certain parameters entering into the second equation of set (11), a transverse field spontaneously appears in one of the two mutually perpendicular directions. In this case, we deal with a nonequilibrium first-order phase transition. The appearance of a transverse field component is likely to be a simple example of self-organization in impurity graphene.

RESULTS OF NUMERICAL ANALYSIS

The second equation of set (11) was solved numerically to obtain the dependence of the transverse component on the applied electric field, $E_x = E_x(E_y)$.
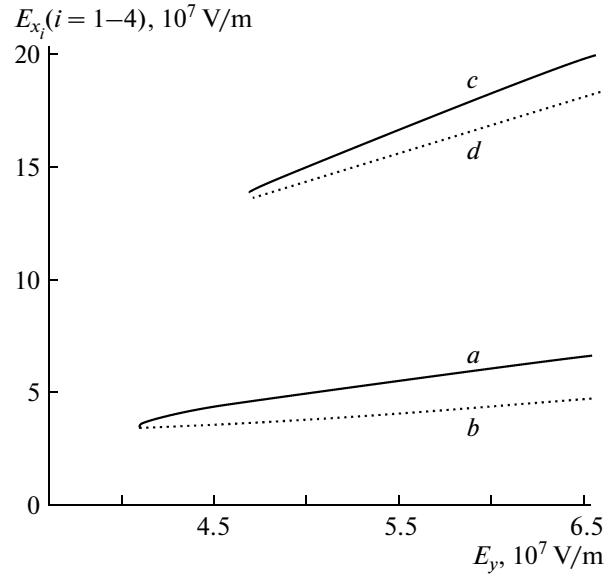
$E_{x_i}(i = 1–4)$, 10^7 V/m

Fig. 3. Field E_x vs. field E_y at $\varepsilon_a = -5.22$ eV and $V = -1.43$ eV: (a, c) stable solution and (b, d) unstable solution.

Figure 2 shows the typical dependence of current density j_x on E_x that is described by set (11). This dependence demonstrates that, apart from a conventional segment with a negative differential conductivity (which is characteristic of substances with a periodic dispersion law), the $I–V$ characteristic has a segment with an absolute negative conductivity, which can be related to the nonequilibrium of the electron system in graphene with impurities that is mainly caused by a strongly nonparabolic dispersion law. Note also that such a state can result in the division of a carbon nanotube into domains, which is beyond the scope of this work.

Figures 3 and 4 show the dependence of transverse field component E_x on E_y determined as a nonzero solution to set (11). It is seen from the curves that there are two nonzero solutions. Note that the similar dependence on parameter ε_a is weak and, what is more important, there are two nonzero solutions. As will be shown below, one of these solutions (with a smaller modulus) is thermodynamically unstable.

Note that a dc field appears from nonzero values, which means that the appearing effect in terms of the theory of phase transitions should be interpreted as a first-order phase transition. The appearance of a dc field can be related to the segment in the $I–V$ characteristic with an absolute negative conductivity. Since the electron system is nonequilibrium, electrons are redistributed in the momentum space so that the appearing field tends to compensate for the action of a transverse field.

Appearing spontaneous transverse electric field E_x can be thermodynamically unstable in contrast to the always stable solution for the circuit open in the x direction, $E_x = 0$. For a stability investigation, we use
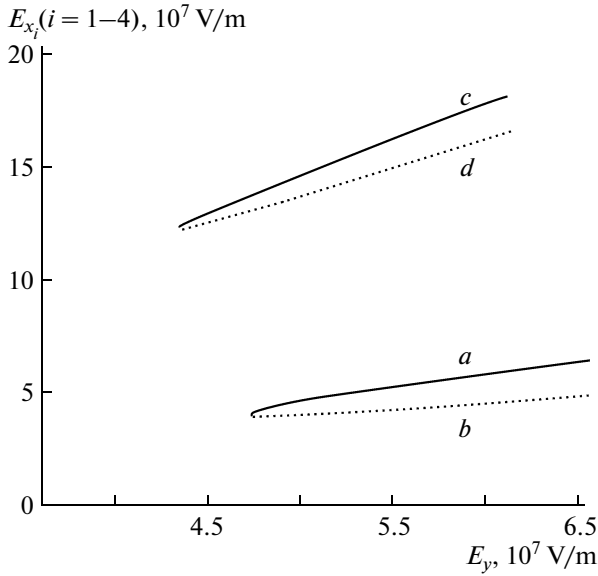
Fig. 4. Field E_x vs. field E_y at $\varepsilon_a = -2.61$ eV and $V = -1.43$ eV: (a, c) stable solution and (b, d) unstable solution.
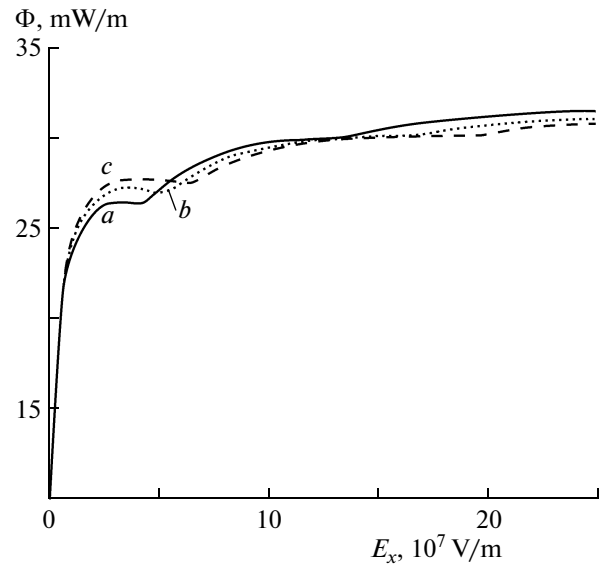

Fig. 5. Function Φ vs. E_x at $E_y =$ (a) 6.0×10^7, (b) 6.2×10^7, and (c) 6.4×10^7 V/m.

the method described in [6] and introduce the function

$$\Phi(E_x) = \int_0^{E_x} j_x(E_x') dE_x' + \text{const}, \quad E_y = \text{fixed}. \quad (12)$$

This function is usually called a synergetic potential and plays the role of an analog of a thermodynamic potential for nonequilibrium problems. According to [6], the solution stability conditions are

$$\frac{d\Phi}{dE_x} = 0, \quad \frac{d^2\Phi}{dE_x^2} > 0. \quad (13)$$

Actually, these conditions mean that function (12) in a certain nonequilibrium situation reaches its minimum in a steady state; therefore, function Φ can be an analog of a thermodynamic potential for nonequilibrium systems. For example, the dependence of "potential" Φ on field E_x for a number of values of E_y is shown in Fig. 5.

As follows from the calculation results, function Φ has two minimum points and two maximum points. Note that the maximum points correspond to the nonzero solution to Eq. (11) with a smaller modulus and the minimum points, to the nonzero solution with a larger modulus. In turn, this finding means that the solution with a larger modulus is stable. Note that the dashed branches in Figs. 3 and 4 correspond to the maximum of function Φ (unstable solution) and the solid branches correspond to its minimum (stable solution).

This transition, in which an electric field appears spontaneously, should be attributed to a ferroelectric type; the role of an order parameter is played by trans-

verse field E_x; and field E_y is an analog of temperature (control parameter).

CONCLUSIONS

(1) We revealed the appearance of an electric field normal to an applied electric field in graphene with adsorbed hydrogen atoms, which can be described in terms of the Anderson model.

(2) The spontaneously appearing electric field depends most strongly on the matrix element of the transition of an electron from an adsorbed atom to graphene, namely, on the hybridization potential.

(3) An analysis of the synergetic potential demonstrates that the appearing state with a spontaneous transverse electric field is stable.

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