Effect of adsorbed macromolecule on the carriers mobility in single layer graphene: Dangling bonds model

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Within the framework of the previously proposed model (S.Yu. Davydov. Phys. Solid State 64, 2018 (2022)), in which the interaction of a macromolecule (MM) with single-layer graphene (SLG) is carried out by stitching of dangling MM bonds with carbon atoms, the effect of these stitching on the mobility of carriers in graphene was studied. It is shown that short-range scattering of MM-SLG stitching prevails over Coulomb scattering. It has also been found that the effect of induced by stitching graphene deformation on mobility can be neglected compared to short-range scattering. The cases of free and epitaxial graphene are considered. The use of the MM-SLG-substrate structure as the basis of a biosensor is discussed.

1. Introduction

The unique ability of graphene to detect the adsorption of a single molecule [1] predetermined its use in various sensors, including biosensors [2–10]. In [11], a dangling bonds model (DBM) was proposed to describe the adsorption of an organic macromolecule (MM) on single-layer graphene (SLG). In this model, a simple theoretical scheme was used to estimate the interaction energy of the i-th dangling bond of a MM molecular fragment with the carbon atom adjacent to the SLG (or adsorption energy E_i^{ads}), which allows obtaining analytical results. Molecules of O_2, NO, NH, CH_2, NH_2, CH_3 were considered as fragments of MM, and bonds of C, N and O atoms were considered as dangling bonds. The adsorption energy of the entire MM, or adhesion energy E_{adh}, was determined as the sum of $E_i^{ads} N_i$, terms, where N_i being concentration of dangling bonds. In [11], the charge transition between MM and SLG was determined and E_{adh} values were estimated for a number of MM molecular fragments. In this study, we will consider the effect of MM on the mobility of charge carriers in graphene.

The uniquely high mobility of carriers in graphene from the very beginning of the graphene story was with a good reason considered the main feature of SLG and aroused great interest [12,13], which has not yet faded [14,15]. In this study we will consider scattering at the so-called stitching of dangling bonds of MMs with the SLG atoms closest to them (MM-SLG stitching) as the first effect affecting the mobility of carriers in graphene. These bonds can be considered as particles adsorbed on graphene (adparticles) and the results of numerous studies devoted to the scattering of carriers by charged impurities and neutral defects in graphene [12–22] can be used.

In recent years, interest in the effect of induced (by some external factor) deformation fields on the physical properties of 2D materials and devices based on them has grown noticeably. This area of research is called straintronics [23,24]. Graphene is of particular interest among all 2D materials because of its Young's modulus of ~ 1 TPa, its capability of withstanding reversible elastic deformation upon stretching up to 25% [23], and its promising potential for development of flexible electronics [24]. Deformation affects the phonon and electronic subsystems, so that its effect changes almost all the characteristics of graphene, which allows suggesting the deformation engineering. In this study, the deformation caused by MM-SLG stitching will be considered as the second mechanism of carrier scattering.

2. Carrier scattering at MM-SLG stitching

Then, we will consider the situation when the SLG conductivity σ is described by the quasiclassical Boltzmann theory in the relaxation time approximation and, in accordance with the Drude theory, with $\sigma = en\mu$, where e is elementary charge. This description is valid at a high concentration of free carriers in graphene. We will assume that the condition of $n \gg n_{imp}, n_{def}$ is valid, where n_{imp} and n_{def} are the concentrations of charged impurities and neutral defects, respectively. According to various theoretical models, it is now generally accepted that $\mu \propto n_{imp}^{-1}, n_{def}^{-1}$ [13,22]. In the scattering theory, two limiting cases are considered: Coulomb and short-range scattering centers [12,13], which have corresponding carrier mobilities of the following form:

$$\mu_C = \frac{e}{\hbar} \frac{(\hbar v_F)^2}{n_{sc} u_C^2}, \quad \mu_{SR} = \frac{e}{4\hbar} \frac{(\hbar v_F)^2}{n n_{sc} u_{SR}^2}. \quad (1)$$

Here $\hbar$ is reduced Planck's constant, n is concentration of carriers in graphene, n_{sc} is concentration of scattering centers, $u_C = Z_C e^2 / \varepsilon_{st}$ ($Z_C e$ is charge of the Coulomb center, ε_{st} is static dielectric constant of graphene), u_{SR} is determined by the expression for the short-range potential $U_{SR}(\mathbf{r}) = u_{SR} \delta(\mathbf{r} - \mathbf{r}_0)$ ($\mathbf{r}_0$ is two-dimensional radius vector defining the position of a point defect) [12,13].

Going over to the adsorption of MM on SLG, to stitch the i-th dangling bond with a graphene atom, we introduce an effective scattering potential of the following form:

$$u_i = |Z_i| u_C + (1 - |Z_i|)(2u_{SR}) \qquad (2)$$

and replace n_{sc} with N_i. Then the contribution of i-th stitching μ_i and the total mobility is

$$\mu_i = \frac{e}{\hbar} \frac{(\hbar v_F)^2}{N_i u_i^2}, \quad \frac{1}{\mu_{sc}} = \sum_i \frac{N_i}{\mu_i}. \qquad (3)$$

Let us going over to numerical estimates by assuming $Z_C = 1$, because we believe that before the interaction with graphene, the dangling bonds contained one electron. Values of Z_i are given in the table of [11]. Static dielectric constant is $\varepsilon_{st} = 3$ [25,26]. Then $u_C \approx 5 \cdot 10^{-8}$ eV · cm. If we assume, as in [13], $u_{SR} = 10$ eV · nm² (or even lower by an order of magnitude), we have $2u_{SR} \gg u_C$ (here it is taken into account that $|Z_i| \sim (1 - |Z_i|)$ — see the table and [11]), so $u_i \approx 2(1 - |Z_i|)u_{SR}$. Thus, $\mu_i \propto N_i^{-1}(1 - |Z_i|)^{-2}$. Due to the fact that $v_F \approx 10^8$ cm/s, with $N_i = 4 \cdot 10^9$ cm⁻² [13] and $u_{SR} = 10$ eV · nm² we get $\mu_i \approx 2700/(1 - |Z_i|)^2$ cm²/V · s. Naturally, the same mobility will be obtained for $N_i = 4 \cdot 10^{11}$ cm⁻² and $u_{SR} = 1$ eV · nm². It should be noted that graphene samples with $\mu > 10^4$ cm²/V · s are currently available [22].

The total charge transferred from MM to SLG is $Z = -\sum_i Z_i$ [11]. If the concentration of carriers in SLG without the MM was equal to n_0, then now we have the concentration of $n = n_0 + \Delta n$, where $\Delta n = -Z|/S$, $S_{uc} = 3\sqrt{3}a^2/2$ being area of the lattice cell of graphene, $a = 1.42$ Å being distance between the nearest neighbors in graphene. The change in mobility is $\Delta \mu = \mu_{sc} - \mu_0$. If $(\mu_0 - \mu_{sc})/\mu_0 \ll 1$, then the change in conductivity due to the interaction of SLG with MM can be represented as $\Delta \sigma \approx e(n_0 \Delta \mu + \mu_0 \Delta n)$, where it is taken into account that $|\Delta n| \ll n_0$ [11].

3. The effect of graphene deformation induced by MM-SLG stitching on the carrier mobility

We will assume that the stitching i corresponds to the central force $F_i(r - r_i) = F_{iz} \delta(r - r_i)$, where $\mathbf{r} = (x, y)$, acting on the graphene carbon atom with the coordinate $\mathbf{r}_i = (x_i, y_i)$. For simplicity, considering the SLG to be an elastically isotropic sheet, we obtain the following

expressions for the displacements $u_{ir} = \sqrt{u_{ix}^2 + u_{iy}^2}$ in the graphene plane:

$$u_{ir} = -AF_i/(r - r_i), \quad A = \frac{(1 + \nu)(1 - 2\nu)}{2\pi(Y_{2D}/h)}, \qquad (4)$$

where ν and Y_{2D} are Poisson's ratio and Young's modulus [27], $h = 3.35$ Å,[1] the z subscript of the force F_{iz} is omitted. With $Y_{2D} = 340$ N/m, $\nu = 0.165$ [28] and $Y_{2D} = 342$ N/m, $\nu = 0.19$ [29] we get $A \sim 0.1$ (TPa)⁻¹. The deformation corresponding to displacement (4) is $u_{irr} = \partial u_{ir}/\partial r = -AF_i/(r - r_i)^2$. If the average distance between dangling bonds is taken to be $2R$, then the average deformation is $\bar{u}_{irr} \approx -AF_i/Ra$. According to estimates of [11], the average length of dangling bonds (extended along the z axis) for atoms of C, N, and O is equal to $d_i \sim 2.5$ Å. For the σ-bond of the dangling p-orbital of MM with the p_z-orbital of SLG we have $V_i = V_{pp\sigma} = 2.22(h^2/m_0 d_i^2)$ [30–32], which yields $V_i \sim 3$ eV for the average $d \sim 2.5$ Å² Then $F = F_i = \partial V_i/\partial d = -2V_i/d \sim -2.4$ eV/Å, which yields

$$\bar{u}_{rr} = \sum_i \bar{u}_{irr} \approx 2AVM/dRa, \qquad (5)$$

where $M = \sum_i m_I$ is total number of i-bonds per lattice cell of graphene. Then we get $\bar{u}_{rr} \sim 3 \cdot 10^{-3} M/R$, where R is measured in nm. Due to [11] we have $M < 0.01 - 0.1$ [11], then $R \sim \sqrt{S_{uc}}/2M \sim (2 - 20)$ nm. Thus, $(\bar{u}_{rr})_{max} \sim 10^{-4}$.

Using the low-energy approximation [12], we represent the density of states of free graphene (per one graphene atom) in the following form:

$$\rho_{SLG}(\omega) = (2|\omega|/\xi^2)\Theta(\xi - |\omega|), \qquad (6)$$

where ω is energy measured from the Dirac point $\varepsilon_D = 0$, $\xi = t\sqrt{2\pi\sqrt{3}} \sim 3t$ is cutoff energy [33], $t \sim 3$ eV is electron hopping energy between the nearest graphene atoms, $\Theta(\dots)$ is Heaviside function. Then, at zero temperature the energy of the electronic subsystem of graphene is $E(\varepsilon_F) = 2(\xi^3 + \varepsilon_F^3)/3\xi^2$, where ε_F is Fermi level, and concentrations of free electrons (at $\varepsilon_F > 0$) and holes (at $\varepsilon_F < 0$) are equal to $2(\varepsilon_F/\xi^2)/S_{uc}$. Due to the fact that the number of electrons in the lattice cell of graphene does not change during deformation, it is easy to derive the relation of $\delta\varepsilon_F = -2\varepsilon_F \bar{u}_{rr}$. Then we have $\delta E(\varepsilon_F) = -2\varepsilon_F^3/\xi^2)\bar{u}_{rr}$, so the deformation potential is $w_{dp} = -2\varepsilon_F^3/\xi^2$. To estimate

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[1] The h factor is introduced for dimensional reasons, because in the 3D case the Young's modulus is measured in N/m², whereas in the 2D case it is measured in N/ m. It should be noted that $h = 3.35$ Å corresponds to the interlayer distance in graphite and is sometimes referred to as the graphene thickness. The introduction of this factor allows using the results of the standard theory of elasticity, for example, [27].

[2] As in [11], we have chosen the V_i-bond of p_z-orbitals characterized by a factor of 2.22 for the estimates of the matrix element. For the bonds of p_z-orbitals with sp, sp^2, and sp^3 the factors are 2.57, 2.63, and 2.63, respectively [31], which does not result in any significant change in the estimates made.

the relaxation time due to the deformation of graphene τ_{deform}, we use the relation (the Fermi's golden rule):

$$\tau_{\text{deform}}^{-1} = (2\pi/\hbar)|w_{dp}\bar{u}_{rr}|^2\rho_{SLG}(\varepsilon_F), \qquad (7)$$

which yields $\tau_{\text{deform}}^{-1} \sim 7 \cdot 10^9 \, \text{s}^{-1}$. On the other hand, the relaxation time at short-range centers τ_{SR}, determined by the formula

$$\frac{1}{\tau_{SR}} = \frac{N_{SR}u_{SR}^2}{4(\hbar v_F)^2}\,(\varepsilon_F/\hbar) \qquad (8)$$

(see [13]), with $N_i = 4 \cdot 10^9 \, \text{cm}^{-2}$ yields $\tau_{SR}^{-1} \sim 3 \cdot 10^{15} \, \text{s}^{-1}$. Thus, the carrier scattering caused by the deformation of the graphene sheet by its stitching with MMs can be neglected in comparison with the scattering on the stitching itself.

4. Macromolecule on epitaxial graphene

The diffusive conductivity of free graphene can be represented in the following form

$$\sigma(\varepsilon_F) = e^2\rho_{SLG}(\varepsilon_F)v_F^2\tau(\varepsilon_F)/2A_{uc}, \qquad (9)$$

resulting from the Einstein relation of $\sigma(\varepsilon_F) = e^2\rho_{SLG}(\varepsilon_F)D(\varepsilon_F)$, where the diffusion constant is $D(\varepsilon_F) = v_F^2\tau(\varepsilon_F)/2A_{uc}$ [13]. Based on the Fermi's golden rule, expression (9) for epitaxial graphene (epigraphene) can be rewritten as

$$\tilde{\sigma}(\varepsilon_F) = e^2\hbar\tilde{v}_F^2/4\pi A_{uc}V_{\text{sub}}^2, \qquad (10)$$

where $V_{\text{sub}}^2 = \langle|V_{a\mathbf{k}}|^2\rangle_{BZ}$ is square of the matrix element of the interaction of the graphene atom with the electronic spectrum of the substrate (hereinafter the tilde refers to epigraphene) averaged over $|\mathbf{k}\rangle$ states of the substrate. As shown in [34,35], the effect of the semiconductor substrate on the Fermi velocity in SLG is determined by the following relationship:

$$\tilde{v}_F/v_F = \eta(\varepsilon_F), \ \ \eta(\varepsilon_F) = \left(1 - \left(\frac{d\Lambda_{\text{sub}}(\omega)}{d\omega}\right)_{\varepsilon_F}\right)^{-1}, \quad (11)$$

where

$$\Lambda_{\text{sub}}(\omega) = V_{\text{sub}}^2 P\int\limits_{-\infty}^{\infty} \rho_{\text{sub}}(\omega')(\omega - \omega')^{-1}d\omega'$$

is function of the shift of electronic states of graphene due to the interaction with the substrate, P is symbol of the main value of the integral, $\rho_{\text{sub}}(\omega)$ is density of states of the substrate. Assuming $\rho_{\text{sub}}(\Omega) = \rho_s\Theta(|\Omega| - E_g/2)$, where

$\Omega = \omega - \omega_0$, ω_0 is center of band gap with a width of E_g, $\rho_s = \text{const}$, we get

$$\Lambda_{\text{sub}}(\omega) = \rho_s V_{\text{sub}}^2 \ln|\Omega - E_g/2|/(\Omega + E_g/2)|$$

(the Haldane–Anderson model [36]). Then, with $|\varepsilon_F - \omega_0| < E_g/2$ we get

$$\eta(\varepsilon_F) = \left(1 + \frac{V_{\text{sub}}^2(E_g/2)}{(E_g/2)^2 - (\varepsilon_F - \omega_0)^2}\right)^{-1}, \qquad (12)$$

so that $\tilde{v}_F/v_F < 1$. Taking this effect into account, instead of formulae (1) we get

$$\tilde{\mu}_C = \mu_C\eta^2(\varepsilon_F), \ \ \tilde{\mu}_{SR} = \mu_{SR}\eta^2(\varepsilon_F), \qquad (13)$$

i.e. $\tilde{\mu}_C/\tilde{\mu}_{SR} = \mu_C/\mu_{SR}$.

Now the change in the charges of dangling bonds Z_i included in expression (2) should be taken into account. First, let us take into account that if there is a substrate, expression (6) should be replaced with $\tilde{\rho}_{SLG}(\tilde{\omega}) = (2|\tilde{\omega}|/\xi^2)\Theta(\xi - |\tilde{\omega}|)$, where $\tilde{\omega} - \Lambda_{\text{sub}}(\omega)$. Using the results of [11], the shift function $\Lambda_I(\omega)$ of the energies of dangling MM bonds takes the following form:

$$\tilde{\Lambda}_i(\tilde{\omega}) = (V_i^2\tilde{\omega}/\xi^2)\ln|\tilde{\omega}^2/(\xi^2 - \tilde{\omega}^2)|.$$

In the modes of weak interaction of SLG with the substrate (i.e., at $V^2/t^2 \ll 1$) and dangling bonds with graphene (see [11]), the difference between $\tilde{\omega}$ and ω in the expression for $\tilde{\Lambda}_i(\tilde{\omega})$ can be neglected[3]. So we can still use the Z_i values calculated in [11]. It follows therefrom that the presence of a substrate does not change the conclusion made in Section 2 about the predominance of short-range scattering over Coulomb scattering.

In [7,8,37] the MM−SLG−SiC-substrate system was considered as the basis of the biosensor. The MM was a biomolecule known as antibody (Ab) or a bioreceptor in biosensorics. The biomolecule under test (antigen (Ag) or biomarker) is brought into contact with Ab and the change in current flowing in the SLG is recorded. In [37], the charge transition ΔQ between Ab and epitaxial graphene and the change ΔQ in the presence of Ag were assessed. The change in conductivity as a result of contact of Ab with Ag is equal to $\Delta\tilde{\sigma} = \hat{\sigma} - \tilde{\sigma}$, where $\tilde{\sigma}$ means the conductivity of epigraphene without Ag, and $\hat{\sigma}$ is the conductivity of the epigraphene in the presence of Ag.

5. Conclusion

So, within the previously proposed model of dangling bonds [11] for the case of Drude−Lorentz diffusive conductivity, we have succeeded to establish the following:

1) short-range scattering on MM-SLG stitching prevails over Coulomb scattering;

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[3] It is worth reminding that we are considering a situation where the carrier concentration in graphene is high, so that ε_F and $\tilde{\varepsilon}_F$ are distant from the Dirac point. It is also taken into account that the logarithm is a weakly varying function.

2) the effect of stitching-caused deformation on mobility can be neglected in comparison with the short-range scattering;

3) conclusions 1) and 2) are valid for both free graphene and epitaxial graphene.

In this study, gapless graphene was considered. In the presence of a gap, it is convenient to use the so-called formula of Tagaki et al. to estimate the mobility [37] (see also [38–40]). In this case, the effective mass can be estimated using formula (12) of [41].

Unfortunately, at present the results obtained here cannot be compared with experimental data, because the studies of [7,8] mainly considered technological issues of creating a resistive biosensor based on single-layer graphene and systematic current measurements have not yet been carried out.

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Conflict of interest

The authors declare that they have no conflict of interest.

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