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Dependence of charge carrier mobility in hybrid nanostructures at the interface of graphene and molecular ions on their charge density

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Hybrid nanostructures with large interface between nanostructural elements play an important role in the modern electronics. Among these nanostructures are hybrid nanostructures formed at the interface of graphene with ensembles of molecular ions in the solution gated Graphene Field Effect Transistors (GFETs) that are promising for chemical and biological sensor fabrication. Therefore investigation of interfacial effects in electrical transport in these systems is interesting. This work is a theoretical study of dependence of the charge carrier mobility (μ) in these nanostructures on density of the interfacial molecular ions (N_{ii}). We show that dependence $\mu \propto 1/(N_{\text{ii}})^{1/2}$ obtained in free charge carrier model with short range scattering in case of the weak interaction between the charge carriers and the interfacial ions is in agreement with experimental transistor characteristics obtained at the high gate voltages.

Keywords: graphene, hybrid nanostructures, transistors, mobility, interface.

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1. Introduction

Interest in studies of the interface effect on electrical transport in hybrid nanostructures formed at the graphene interface with assemblies of molecular ions in GFETs with gate insulators in the form of ionic solutions is primarily associated with the importance of such nanostructures in creating chemical and biological sensors [1–12]. Currently, despite this interest, there is a number of unsolved problems in the description of electric transport in these nanostructures. In particular, currently the research groups have not come to an unambiguous conclusion about the mobility of charge carriers (μ) in graphene relationship on the density of Coulomb scattering centers. For example, in papers [13] and [14] for the mobility of charge carriers various parametric relationships on the concentration of charge carriers in graphene were obtained ($\mu \propto 1/(n)^{0.3}$ [13] and $\mu \propto 1/n$ [14]), respectively. Therefore, in addition to these applications, it is important to use such systems as a model object for establishing the regularities of two-dimensional transport of charge carriers in nanostructures in the presence of Coulomb scattering centers. For this purpose, a potential advantage of the considered GFETs is the possibility of density smooth variation over a wide range of interface ions (N_{ii}) (scattering centers) using a gate control voltage (V_g). Such a possibility is absent in samples of traditional materials, for each of which the density of impurity ions is fixed. Therefore, in this work, we use the transistor characteristics of GFETs with gate insulators in the form of aqueous solutions (see Fig. 1, *a* and *b*) to study the charge carrier mobility vs. the density of scattering centers. We also compare the results obtained on the basis of experimental data available in the literature and describing the transport of charge carriers in graphene field-effect transistors with gate insulators based on aqueous solutions with the conclusions of simple theoretical models.

2. Model of two-dimensional transport of charge carriers in GFETs in the presence of interface ion scattering centers

In the general case two-dimensional electric transport in the approximation of free charge carriers is determined by different types of their scattering. For graphene, the cases of scattering of charge carriers on phonons [15] and on impurity ions [16] are well studied. For high-quality graphene samples at room temperature, the contribution of these types of scattering to conductivity limitation can often be neglected. Other scattering mechanisms of charge carriers that are of particular interest in GFETs include their scattering on other charge carriers [17] and on dipole fluctuations of quasiperiodic ionic structures interfaced to graphene in liquid ionic gate insulators [18]. The correct choice of one or another model of scattering centers for a particular case is determined by the ratio of the parameters of the selected problem. In this paper we investigate the case of charge carriers scattering in GFETs with gate insulators in the form of deionized water, for which the concentration of molecular ions is much lower than in ionic liquids used in [18]. Therefore, the effects of the formation of quasiperiodic dense ionic structures on the graphene surface [18] are not considered by us. At the same time, it is necessary to consider the interface ions effect on the mobility of charge carriers in graphene. This is indirectly evidenced by the effect on the graphene conductivity of state memory effects associated with the formation of quasi-stationary ionic complexes [9] on its surface. Therefore, the proposed model assumes that scattering of free charge carriers in graphene can occur not only on free charge carriers (their two-dimensional (2D) density: n), but also on interface molecular ions. This consideration gives rise to two limiting cases, which we will call the strong-bonding case and the weak-bonding case.

In the first of them, (the case of strong bond), due to the strong Coulomb attraction free charge carriers of the opposite sign are so close to any of the interface ions (see Fig. 1, *a* and Fig. 2, *a*) that almost complete screening of the electric field of the interface ions occurs, and the contribution to the scattering of free charge carriers from the dipoles created in this case can be neglected. Due to the field effect $n \approx n_0 + N_{\text{ii}}$, where n_0 — is the equilibrium density of charge carriers in graphene in the absence of gate voltage. Therefore, for the case under consideration, the contributions to the scattering of free charge carriers from the electric fields of interface ions and from the electric fields of free charge carriers injected into graphene due to the field effect mutually compensate each other, leading to almost complete independence of the mobility of charge carriers from the density of interface ions and the gate voltage.

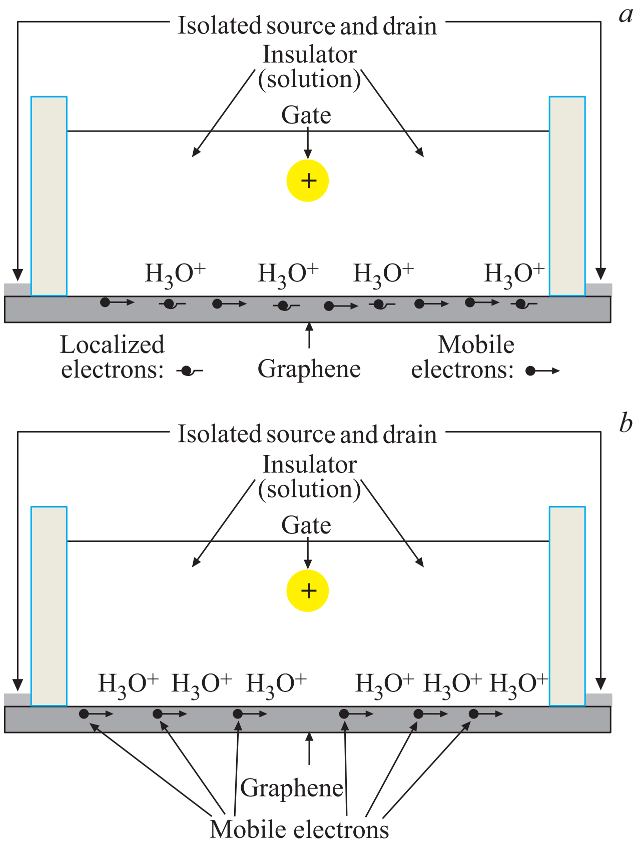

Figure 1. *a* — schematic representation of GFET with a water gate insulator for the case of strong bond between positive interface ions and electrons. *b* — schematic representation of GFET with water gate insulator for the case of weak bond between positive interface ions and electrons.

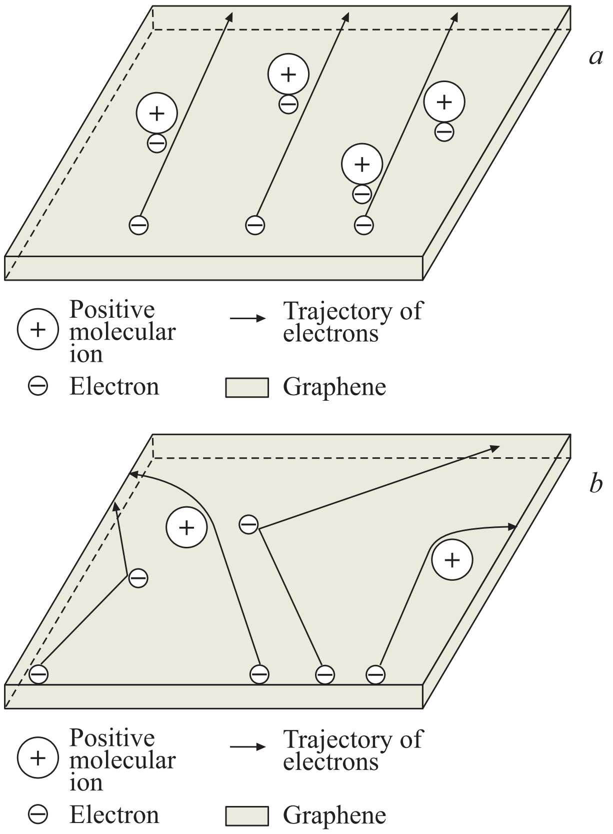

Figure 2. *a* — schematic representation of electrons transport in GFET with a liquid gate insulator for the case of strong bond between positive interface ions and electrons. *b* — schematic representation of electrons transport in GFET with liquid gate insulator for the case of weak bond between positive interface ions and electrons.

In the second limit case of weak bond (see Fig. 1, *b* and Fig. 2, *b*) the Fermi energy or thermal energy of free charge carriers is large enough to prevent their localization (stationary approach to the interface ions). In this case, there is no complete compensation of the electric fields created by interface ions and free charge carriers, and the contributions to scattering from these fields shall be considered independently when determining the mobility of charge carriers. Both of these contributions decrease the mean free path of charge carriers (τ).

Thus, by studying the experimental relationships of the charge carriers mobility on the density of interface ions and the gate voltage, it is possible to determine which of these limit cases is the best fit to experiment.

Graphene conductivity (σ) can be estimated using the following formula: $\sigma \approx e^2 \cdot n \cdot \tau/(2m)$, where e — is the electron charge, n — is the density of free charge carriers in graphene, m — is the weight of free charge carrier, which we will further assume to be equal to the electron weight. Assuming that the cause of scattering of free charge carriers are partially screened Coulomb short-range forces (short-range as compared to the mean free path), the mean free path of charge carriers in graphene (λ) is given by the following formula: $\lambda \approx \tau v_{\mathrm{F}}$, where v_{F} — is Fermi velocity of charge carriers in graphene. The free path τ for the weak bond case is given by the formula: $1/\tau = 1/\tau_{\mathrm{fc}} + 1/\tau_{\mathrm{ii}}$, where τ_{ii} — is the mean free path of charge carriers before scattering by interface ions and τ_{fc} — is the mean free path of charge carriers before they are scattered by other free charge carriers. In this case, the mobility of charge carriers is given by the formula $\mu \approx e \cdot \lambda/(2m \cdot v_{\mathrm{F}})$. Assuming v_{F} constant value, the main relationship of the charge carrier mobility on N_{ii} is determined by the mean free path relationship on it. For the two-dimensional case, the mean free path of charge carriers between scattering on interface ions $\lambda_{\mathrm{ii}} = \tau_{\mathrm{ii}} v_{\mathrm{F}} \propto 1/(N_{\mathrm{ii}})^{1/2}$. At high gate voltages, due to the field effect, the relationship $n \approx N_{\mathrm{ii}}$ is satisfied. For this case, the mean free path of charge carriers between scattering on other free charge carriers is given by the expression $\lambda_{\mathrm{fc}} = \tau_{\mathrm{fc}} v_{\mathrm{F}} \propto 1/(N_{\mathrm{ii}})^{1/2}$. Thus, assuming weak bond, using the expression $1/\lambda = 1/\lambda_{\mathrm{fc}} + 1/\lambda_{\mathrm{ii}}$ we receive $\lambda \propto 1/(N_{\mathrm{ii}})^{1/2}$ and, accordingly, the relationship of the charge carrier mobility on the interface charge density is determined by the formula: $\mu \propto 1/(N_{\mathrm{ii}})^{1/2}$.

3. Comparison of experimental and theoretical results

The obtained mobility of charge carriers in graphene as function of density of interface ions in GFETs require experimental verification. To this end, we used the experimental data on the graphene conductivity in GFETs with a gate insulator in the form of deionized water, published in [7]. The schematic images of the GFET used in this paper are shown in Fig. 1,*a* and Fig. 1,*b*. Fig. 3,*a* shows the conductance as function of gate voltage for two different measurements. When plotting this function, we performed voltage shift +0.5 V. Besides, the graphene conductivity value at the Dirac point was substracted to align this point with the origin. We assume that at high gate voltages, the capacitance of the double layer (C_{dl}), independent of the density of the interface ions, is much less than the quantum capacitance (C_{q}), which, as it is known [19], increases with charge carrier density increasing ($C_{\mathrm{dl}} \propto (n)^{1/2}$). Under this condition the voltage applied to the gate is directly proportional to the interface density of molecular ions on the graphene surface ($V_g \propto N_{\mathrm{ii}}$). (The aspect ratio depends on C_{dl}). Considering $n \approx N_{\mathrm{ii}}$ valid at high gate voltages, we obtain that $V_g \propto n$. To compare the predictions of our model ($\mu \propto 1/n^{1/2}$) we substitute this expression into the formula for conductivity $\sigma \approx en\mu$, get, $\sigma \propto n^{1.2}$, and hence the conductivity $\sigma \propto V_g^{1/2}$. Fig. 3,*b* shows the result of dividing the graphene conductivity by the square root of the gate voltage. As can be seen from this Figure, as a result of such a division we obtain an approximately constant level. So, the proposed model satisfactorily describes the mobility of charge carriers as function of interface density of molecular ions for the case of weak bond. For another graphene sample with worse morphology, studied in the same paper [7], a similar approach gives the relationship $\mu \propto 1/n^{0.3}$, which corresponds to the results of [13]. Probably, a larger number of defects in this sample makes N_{ii} independent contribution to the scattering of free charge carriers, thereby weakening the observed dependence on N_{ii}.

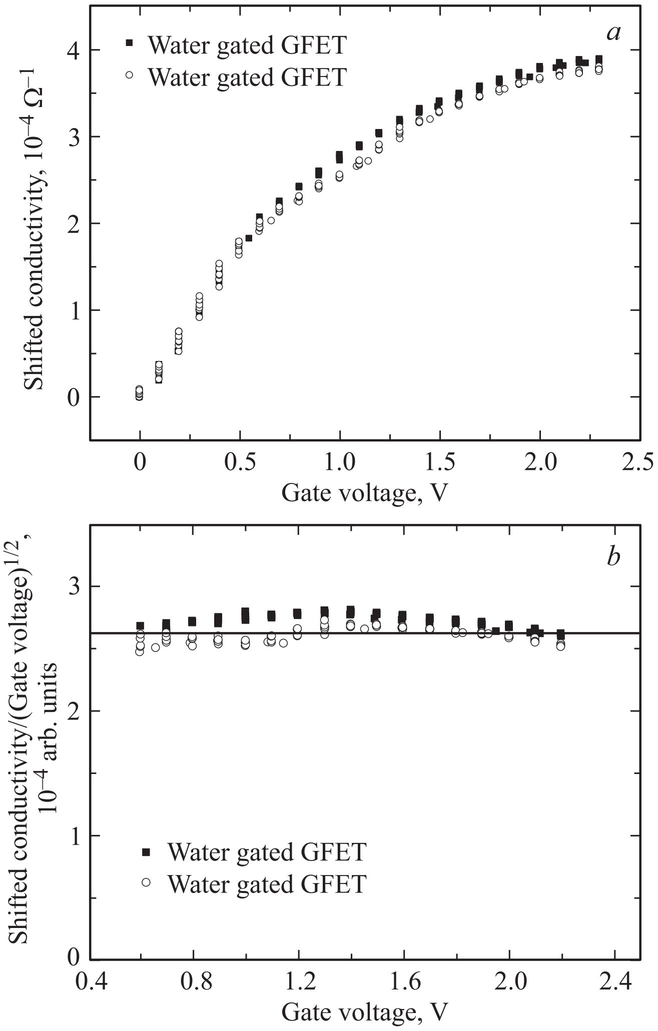

Figure 3. *a* — the results of measurements of the dependence of the GFET conductivity on the gate voltage, performed in [7], after the gate voltage was shifted by 0.5 V and its value was subtracted from the measured conductivity at the minimum of the curve (at the Dirac point). *b* — data obtained by dividing the conductivity values shown in Fig. 3,*a*, by $V_g^{1/2}$. The horizontal line is an auxiliary plotting for visual confirmation of the weak dependence of the obtained value in the presented voltage range.

4. Conclusion

For samples of high-quality graphene for the case of weak bond, the proposed model satisfactorily describes the relationship of the mobility of free charge carriers on the density of interface ions ($\mu \propto 1/(N_{\text{ii}})^{1/2}$). For graphene samples with a large number of defects, a weaker relationship is observed than predicted by the proposed model. In addition to the larger contribution of defects to the scattering of charge carriers, this circumstance may also be due to the not quite accurate fulfillment of the estimated assumptions made when obtaining such a relationship.

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Conflict of interest

The authors declare that they have no conflict of interest.

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