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Optimization of graphene transistor sensors based on quantum capacitance and charge carrier mobility analysis

© A.V. Butko, V.Y. Butko¶, Y.A. Kumzerov

Ioffe Institute,
St. Petersburg, Russia

¶ E-mail: vladimirybutko@gmail.com

Received July 16, 2022
Revised August 8, 2022
Accepted August 8, 2022

Charge density of molecules (N_m) in hybrid nanostructures that is formed at the interface of graphene and liquid in solution gated graphene field effect transistors (SGFETs) determines the selective response of chemical and biological sensors based on these SGFETs. For optimization of this response it is important to determine how it depends on characteristics of SGFETs such as quantum capacitance (C_q) and charge mobility (μ) which are functionally linked to N_m. The proposed model shows that when the gate voltage (V_{gate}) is near the minimum point of graphene conductivity (Dirac point) the sensor response is low and increases with gate voltage until C_q is approximately equal to the capacitance of the formed double layer (C_{dl}) in SGFETs. A decrease in sensor response is predicted upon further increase of V_{gate} in cases where there is a stronger dependence of μ on N_m than $\mu \propto 1/N_m$. A comparison of the predicted results of the model and literature data obtained in SGFET sensors for lysine in an aqueous solution are in agreement with the assumption that the optimal condition of $C_q \approx C_{dl}$ is reached approximately in the V_{gate} region of (0.5−1.4) V from the Dirac Point.

Keywords: graphene, hybrid nanostructures, transistor sensor, charge mobility, interface.

DOI: 10.21883/PSS.2022.12.54405.441

1. Introduction

Field-Effect Transistors with Solution Gate insulators (SGFETs) are promising for creating chemical and biological sensors of a new generation [1–11]. Their sensory response is determined by hybrid nanostructures formed on the graphene interface in SGFETs due to quasi-stationary electrostatic coupling [8,9] between charge carriers in graphene and charges of various molecules located at its interface with a liquid gate insulator, see Fig. 1, *a* and *b*. Despite the large number of works devoted to the creation of effective SGFET sensors, the determination of optimal parameters for the sensory response requires additional research. Therefore, we propose a simple model for determining the optimal gate voltage parameters in graphene-based SGFETs to obtain a selective sensor response, depending on the type of detected molecules. Due to the general nature of the approach used, the main conclusions of this work can be applied to various SGFET sensors (for example, SGFETs based on carbon nanotubes and semiconductor thin films). The model is based only on a sufficiently small quantum capacity (C_q) of the studied nanostructures [12–14] and on the fact that the condition $C_{dl} \approx C_q$ can be performed at gate voltages achievable in practically realizable SGFETs.

2. Sensory Response Model in Graphene GFETs

The current density in graphene is given by the well-known formula $j = env$, in which e is the charge of an electron, n is the density of charge carriers, and v is the average velocity of charge carriers moving under the action of voltage between the drain and the source in SGFETs. The surface conductivity (σ) can be calculated using the formula $\sigma = en\mu$, in which μ is the mobility of charge carriers in graphene. The mobility of charge carriers can be obtained based on the expression $\mu = (e/2m)\tau$, in which m is the mass of charge carriers, and τ is the average time between scattering of charge carriers in graphene. This time, to the greatest extent, depends on the average scattering times on charged defects in graphene (τ_0) and on the charges of molecules located at the graphene interface (τ_m), $1/\tau \approx 1/\tau_0 + 1/\tau_m$.

From this expression it can be seen that for small values of V_{gate} (decreasing V_{gate} usually increases τ_m) μ is limited from above due to the presence of defects in graphene (see Fig. 2, *a*) (this conclusion remains valid even in the case of possible partial compensation of impurity charges in graphene by charges introduced by these molecules). At the same time, for large V_{gate}, the first term in this expression can be neglected and μ, first of all, depends on N_m (see Fig. 2, *b*). The scientific literature reports various dependencies of μ on N_m for different types of graphene SGFETs, including $\mu \propto 1/N_m^x$, where x — exponent equal to 0.3, 1/2 and 1 [10,11,14].

The density of charge carriers in graphene is given by the formula $n = n_0 + n_m$, in which n_0 is the initial density of charge carriers in graphene associated with impurities and other graphene defects, and n_m is the density charge carriers in graphene caused by the accumulation of charges of molecules at the interface of graphene with a liquid

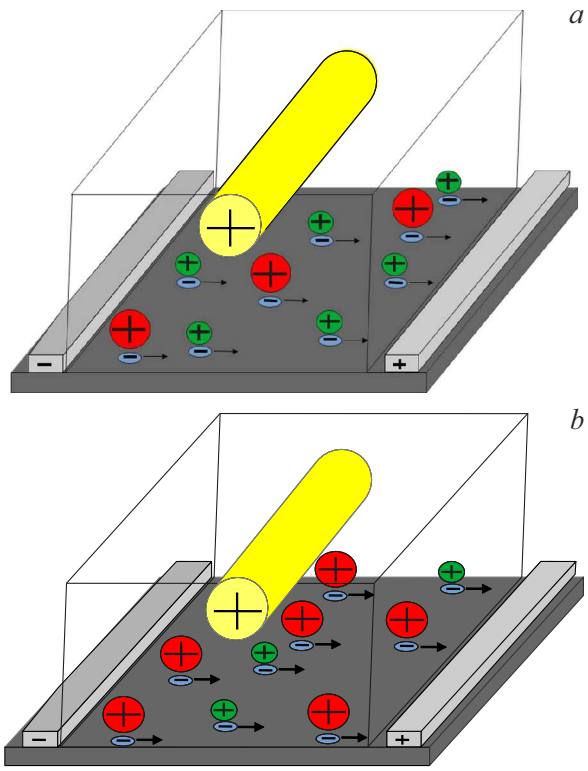

Figure 1. *a* — schematic representation of SGFET for a liquid gate insulator of type (1) containing a small concentration of detectable molecular ions (large red circles) and other ions (small green circles), for example, hydronium ions *b* — schematic representation of SGFET for a liquid gate insulator of type (2) containing a greater concentration of detectable molecular ions (large red circles) and other ions (small green circles) than in Fig. 1, *a*, for example, hydronium ions.

gate insulator in SGFETs (see Fig. 2, *a* and 2, *b*). n_{m} can be represented as the sum of two terms n_{m0} and $n_{\mathrm{m\,gate}}$. The density of charge carriers n_{m0} does not depend on the applied gate voltage, and, as evidenced by the data on the conductivity of graphene in SGFETs [1], primarily depends on the pH of the liquid gate insulator. Thus, n_{m0} corresponds to a sensory response that is not selective to the type of detected molecules. $n_{\mathrm{m\,gate}}$ is the density of charge carriers depending on the accumulation of charges of molecules at the graphene interface in SGFETs under the action of voltage on the gate. The density of $n_{\mathrm{m\,gate}}$ can be calculated using the formula $n_{\mathrm{m\,gate}} = CV_{\mathrm{gate}}/e$, where C — capacity at the interface of graphene and liquid gate insulator in SGFETs. To define C, we, similarly to other groups [11,14,15], consider the equivalent interface scheme in graphene-based SGFET as consisting of two series-connected capacitances (see Fig. 2, *c*). The capacity of such a scheme is $C = C_{\mathrm{q}}C_{\mathrm{dl}}/(C_{\mathrm{q}} + C_{\mathrm{dl}})$, where C_{q} and C_{dl} is the quantum capacity of graphene and the capacity of the double layer on the graphene interface, respectively [11,14,15]. In the case of low temperatures $kT \ll eV_{\mathrm{ch}}$, where k is the Boltzmann constant, and V_{ch} is the graphene potential, $C_{\mathrm{q}} \approx 2e^2n^{1/2}/\left(\hbar v_{\mathrm{F}}(\pi)^{1/2}\right)$ [13,14], where $\hbar$ —Planck constant, v_{F} — the Fermi velocity of Dirac electrons. As can be seen from this formula, C_{q} increases with increasing density of charge carriers in graphene. A double electric layer is formed at the graphene interface due to the accumulation of a mixture of polarized and ionized molecules. The capacity of this layer, in general, depends on the type and size of these molecules (see, for example, [14]). Therefore, the change in the capacitance of this layer at different concentrations of detectable molecules in the liquid gate insulator (see Fig. 1, *a* and 1, *b*) can be considered as the basis of the sensory response, selectively depending on the type and size of the molecules. Unlike quantum capacitance, it is usually assumed that C_{dl} does not depend on V_{gate} and n [11,14,15]. Thus, to optimize the sensory response, by controlling V_{gate},

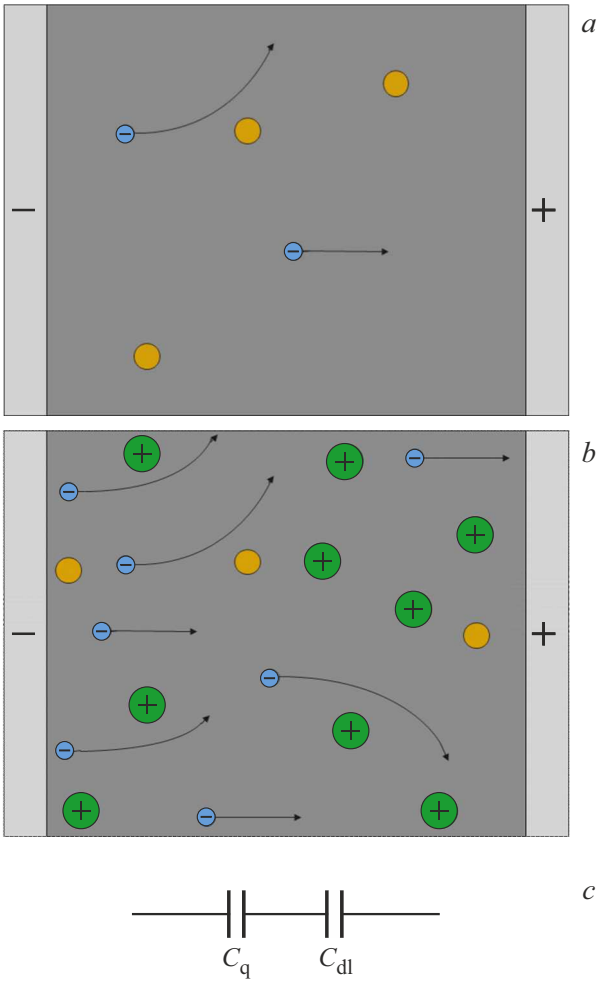

Figure 2. *a* — schematic representation of electron transport (blue circles) in graphene when they are scattered only on impurities (orange circles). *b* — schematic representation of electron transport (blue circles) in a graphene SGFET when they are scattered on impurities (orange circles) and on charges of molecules (large green circles) located at the interface of graphene with a liquid gate insulator. *c* — capacitive equivalent charge density accumulation scheme on graphene surface when gate voltage is applied in SGFETs.

it is possible to change n, and, consequently, the ratio between the values of C_q and C_{dl}. As the studied response, we will consider the difference in the conductivity of graphene at different concentrations of detected molecules ($N_{dm} = N_{dm1}$ and $N_{dm} = N_{dm2}$) in a liquid gate insulator: $\Delta\sigma = \sigma(N_{dm1}) - \sigma(N_{dm2})$. To optimize the efficiency of such a gate voltage response , this expression can be written as

$$\Delta\sigma = \text{const1}\big((n_0 + n_{m0} + C(N_{dm1})V_{gate}/e)^{1-x} - (n_0 + n_{m0} + C(N_{dm2})V_{gate}/e)^{1-x}\big),$$

where const1 — independent of V_{gate} and N_{dm} constant, $C(N_{dm1})$ and $C(N_{dm2})$ — interface capacities, generally depending on N_{dm}.

Consider $\Delta\sigma$ in two extreme cases.

1. V_{gate} is close to the voltage corresponding to the Dirac point [1] (the voltage at which the minimum conductivity of graphene is observed, and the type of charge carriers in graphene changes from electronic to hole or vice versa). For this case, as noted above, μ is limited from above by the presence of defects in graphene. At the same time, it can be seen from the formula for quantum capacitance that ($C_q \sim n^{1/2}$). Considering that at the Dirac point n_m is minimal, we can conclude that when V_{gate} approaches this point, the density of charge carriers is small and $C_q \ll C_{dl}$. In this case, the conductivity of graphene in SGFETs is primarily determined by C_q, independent of N_{dm}, and we get that $\Delta\sigma$ will be close to zero.

2. V_{gate} is large enough to ensure that the ratio $C_{dl} \ll C_q$ is fulfilled. In this case, the interface capacitance C and the measured conductivity mainly depend on C_{dl}. Therefore, in this case, selective detection of molecules contained in a liquid gate insulator is possible. It is important to note that the detection efficiency of molecules decreases due to a decrease in the mobility of charge carriers in graphene during the formation of interface molecular Coulomb scattering centers [10,11,16]. Having considered the previously mentioned dependencies μ from N_m, we get.

$$\Delta\sigma = \text{const2}(V_{gate})^{1-x}\big(C_{dl}^{1-x}(N_{dm1}) - C_{dl}^{1-x}(N_{dm2})\big),$$

where const2 — independent of V_{gate} and of N_{dm} constant. From this expression it can be seen that the sign and magnitude of the change in the conductivity of graphene for each type of detected molecules is determined, first of all, by the dependence of C_{dl} on their concentration. It is also seen that due to different mobility dependencies (exponent x) the sensory response with an increase in V_{gate} can demonstrate a different degree of growth. For the case of a stronger dependence μ on N_m than $\mu \propto 1/N_m$ after the condition $C_q \approx C_{dl}$ there may be a drop in the selective sensory response with a further increase in V_{gate}. Thus, for this case, the model predicts its optimum. In addition, in practically important cases, the value of V_{gate} is usually limited. For example, in aqueous solutions with a large value of V_{gate}, it is possible to conduct an electrolysis reaction that leads to a change in the ionic composition of the gate insulators under study. Therefore, the considered limiting case can provide a selective sensory response, but in some important cases it is not effective or not implemented in practice.

The intermediate case of the quantities V_{gate}, in which $C_q \approx C_{dl}$ is of practical interest, since a selective sensory response is also possible for it, as for the second limiting case and, in addition, there are no disadvantages associated with an additional decrease in the mobility of charge carriers in graphene and with too high a voltage level at the gate.

3. Comparison of model results with experiment

The sensory response observed in a number of papers devoted to the study of graphene SGFETs [1,3] is a shift in transistor characteristics by V_{gate}, determined by the pH of the gate fluid. This shift, described in the model by the term n_{m0}, is not selective for various detected molecules. Therefore, the selective sensory response considered in this paper is primarily characteristic of liquid gate insulators having different ionic composition at almost equal pH [7,17]. A comparison of the results of these studies indicates that for different types of detected molecular ions, the $\Delta\sigma$ response may be of different sign. Fig. 3 demonstrates the typical dependence of the sensory response to graphene conductivity on V_{gate} when lysine molecules are added to an aqueous solution, without a significant change in pH according to [7]. It can be seen from Fig. 3 that the sensory response is small with a small deviation of the voltage from the value corresponding to the Dirac point. It is also seen

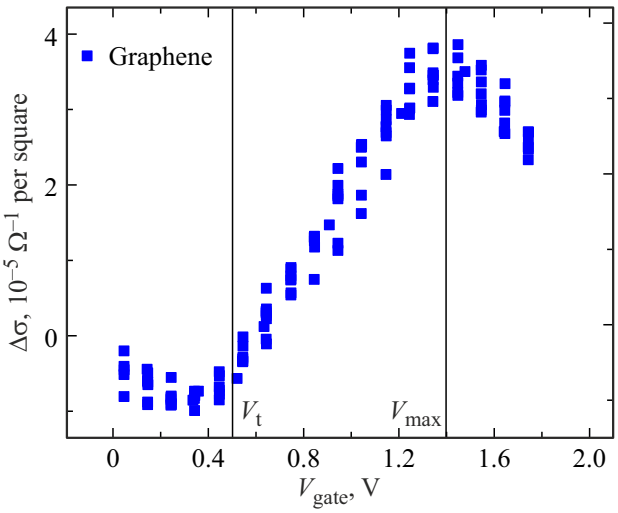

Figure 3. Experimental dependence of the sensory response when lysine molecules are added to water on the gate voltage for graphene SGFETs. This dependence is obtained using the data presented for water and lysine solution in water (concentration n_2) in Fig. 3, *a* of the study [7]. During the construction, the gate voltage was shifted by 0.65 V to correspond to the reference point of Dirac.

that there is a significant increase in the selective sensory response, starting from the threshold values of the gate voltage ($V_t \approx 0.5$ V) and until it reaches its maximum values at ($V_{max} \approx 1.4$ V). These observations correspond to the conclusions of the proposed model. The subsequent decline in the sensory response with a further increase in V_{gate} may be due to the effects considered in the second limiting case of the model. In addition, this decline may be related to the peculiarities of the dependence of $C_{dl}(N_{dm})$due to a decrease in interface capacity with an increase in V_{gate}, including due to changes in the molecular composition and mutual arrangement of various molecules, the gate solution bordering the graphene surface.

4. Conclusion

A simple model is formulated to describe the selective sensory response in graphene SGFETs. Its findings are important for optimizing such a response. And specifically, optimization should take into account the predicted small response value at the gate voltage corresponding to the vicinity of the Dirac point, as well as its significant increase, starting from the threshold values of the gate voltage, near which the ratio $C_q \approx C_{dl}$. A drop in response is also predicted with a further increase in V_{gate} for the case of a stronger dependence μ on N_m than $\mu \propto 1/N_m$. Comparison of the model conclusions with the literature data for graphene SGFETs based on aqueous lysine solutions is consistent with the assumption that the optimal ratio for an effective response $C_q \approx C_{dl}$ is achieved at a voltage measured from the Dirac point V_{gate} in the range (0.5−1.4) V.

Acknowledgments

The authors are grateful for the help of V.Y. Davydov, A.A. Lebedev, S.P. Lebedev, I.A. Eliseev, A.A. Sysoeva and A.V. Fokin.

Funding

The study was supported by a grant from the Russian Science Foundation (project No. 21-72-20038).

Conflict of interest

The authors declare that they have no conflict of interest.

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