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Field Effect in a Graphene Oxide Transistor for Proton and Electron–Hole Conductivities

V. A. Smirnov[a]*, A. D. Mokrushin[b], V. P. Vasil'ev[a], N. N. Denisov[a], and K. N. Denisova[c]

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*
[b] *Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*
[c] *Moscow State University, Moscow, 119991 Russia*
**e-mail: vas@icp.ac.ru*
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Abstract—Proton (wet atmosphere) and electron (reduced graphene oxide) conductivities can be observed in graphene oxide films. The field effect in a graphene oxide transistor for different conductivity types has been discovered and investigated.

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The field effect (FE) in transistors with a small thickness of the two-dimensional carbon channel (up to a graphene monolayer deposited on the oxidized surface of a single-crystal silicon wafer) was implemented and analyzed in detail by K.S. Novoselov, A.K. Geim, S.V. Morozov, et al. [1]. Magnetic phenomena in such transistors were also investigated in this fundamental study. This work induced a great interest in graphene-type objects; the investigation results were given in reviews [2–4]. FE transistors based on graphene and oxidized silicon were studied in [5–7]. The mobility of charge carriers was investigated in a wide temperature range in [5]. The shift of the Dirac point upon treatment of the grapheme surface by a 30-keV electron beam was observed in [6]. In [7], the modified graphene (heterostructures) was used in FE transistors, which made it possible to change the current by four to five orders of magnitude by varying the gate voltage. It was proposed in [8] to use graphene oxide (GO) as an insulating layer. The use of GO as an insulating layer in an FE transistor was also considered in [9]: the conducting graphene layer was formed on the GO layer by hydrogen plasma, and GO served as an insulating layer at the gate. The GO insulating layer was also implemented in a transistor deposited on a flexible plastic substrate, with graphene used as the active layer and electrodes [10].

In dry atmosphere (relative humidity RH < 7%), GO is an insulator with conductivity $\sigma < 10^{-7}$ S/cm, whereas in wet atmosphere it becomes a conductor with proton conductivity [11, 12]. At partial reduction (for example, chemical (in hydrazine vapor), thermal (heating at $T > 130$°C), or by UV irradiation, GO becomes a conductor with electron–hole conductivity. There are no data in the literature on the influence of these GO properties on the characteristics of electronic devices. The purpose of this Letter was to analyze within the model of field effect transistor the influence of the transverse electric field on the proton and electron–hole conductivities of a GO film deposited on a SiO_2/Si wafer. The OG preparation method and experimental techniques were described in [11]. The GO film was about 1 μm thick, gold electrodes spaced by 2 mm were used, and the thickness of the SiO_2 oxide layer was 0.1 μm. The current characteristics were analyzed with a P-20X potentiostat. The entire series of experiments was carried out for the same sample.

Figure 1 shows the current characteristics for the proton conductivity of the transistor: the sample contains only unreduced GO, and electron conductivity is absent. In dry atmosphere, there is no current ($i < 1$ nA) at source–drain voltage $V_{sd} = 1$ V even at voltage V_g on the gate varying from –12 to 12 V. When placing the transistor in wet atmosphere with RH 75% (time t_1), current due to the proton conductivity appears in the sample (Fig. 1b). The current reaches saturation after about a minute, and then positive stepwise voltage is fed to the gate. The transistor current decreases and even changes sign at $V_g = 6$ V. The decrease in the current can be caused by the electron–proton recombination. The subsequent supply of negative voltage ($t > 200$ s) significantly increases the current. It can be seen in Fig. 1 that each switching of the gate voltage induces current peaks with gradual falloff to some stationary value. This phenomenon is due to the polarization properties of water molecules and charged fragments in the plane of the GO nanosheets.

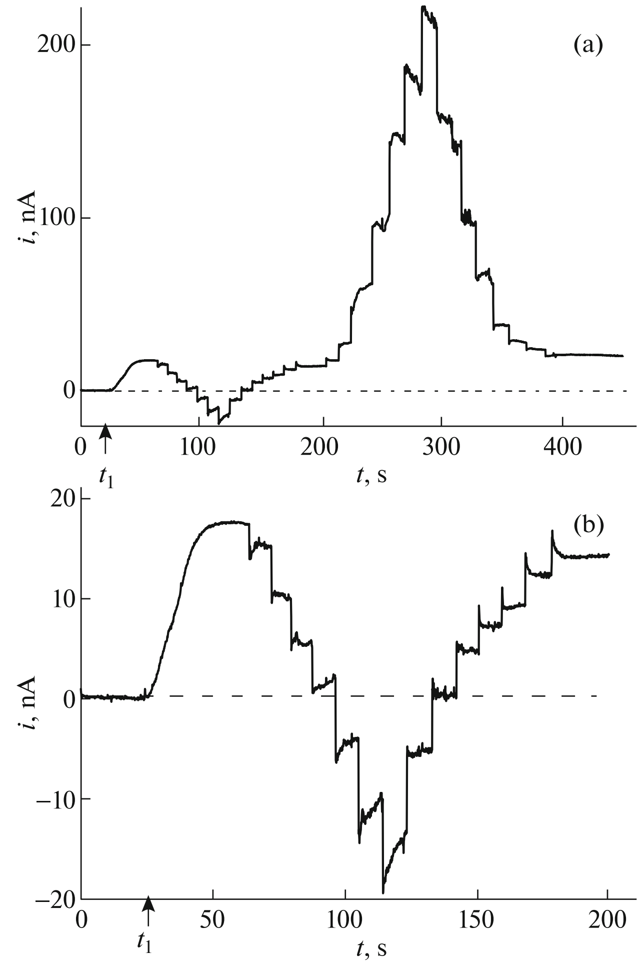

Fig. 1. Proton conductivity: (a) current characteristics for the transistor placed in wet atmosphere with RH 75% (t_1), gate voltage V_g is changed stepwise in the range 0–(+12 V)–0 –(–12 V)–0 with a step of 1.5 V, V_{sd} = 1 V; (b) initial stage of Fig. 1a on an enlarged scale.

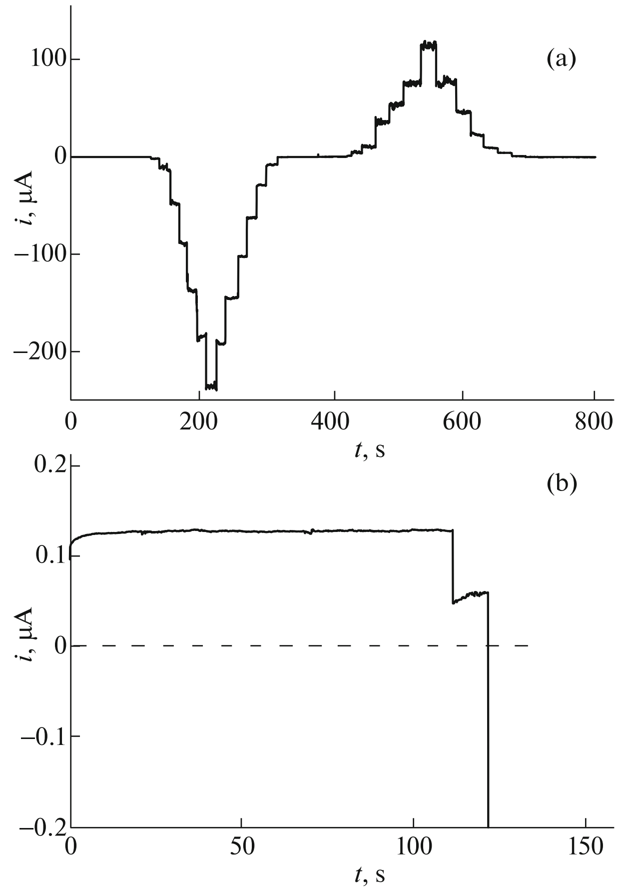

Fig. 2. Electron–hole conductivity: (a) current characteristics of the dry transistor (RH < 7%) after partial reduction of the GO film in hydrazine vapor (the measurement conditions are the same as in Fig. 1); (b) initial stage of Fig. 2a, $i_0 \approx$ 120 nA.

The subsequent partial GO reduction induces the electron–hole conductivity (Fig. 2), and the conductivity type (electron or hole) is determined by the bias sign. The initial current is $i_0 \approx$ 120 nA and depends on the degree of GO reduction. In this case, the field effect becomes radically different: the transistor current increases when the positive voltage is fed to the gate (Fig. 2a, left peak); this situation corresponds to the electron conductivity in the GO layer. These currents are three orders of magnitude higher than the proton-conductivity currents shown in Fig. 1. It can be seen that at the negative bias (Fig. 2a, right peak) the hole current is lower than the electron current by a factor of about 2, which can be explained by different drift mobilities of electrons and holes. Figure 3 shows linear anamorphoses of the dependences given in Figs. 1 and 2.

It should be noted that the field effect for the proton and electron–hole conductivities is qualitatively and quantitatively different. First, there is an inversion of the dependence of the current on the gate-voltage sign: negative voltage significantly increases the proton-conductivity current, whereas the positive bias increases the electron conductivity. Second, the current at the electron conductivity is much higher than that at the proton conductivity for the same gate voltage; this effect can be explained by different mobilities of charges (electrons, holes, and protons) in different cases.

It can be seen in Fig. 3a that, at positive biases, the proton-conductivity currents barely change and are not interesting. The left branch of this plot (negative bias) allowed one to estimate the conduction-proton concentration at different biases. In our case, the proton drift mobility is assumed to be equal to the value obtained in [13] for ice at a temperature of –5°C: μ_p = 6.4 × 10^{-3} $cm^2/(V\,s)$. In this case, the proton concentration at zero bias is n_p = 0.4 × 10^{17} cm^{-3}, whereas at

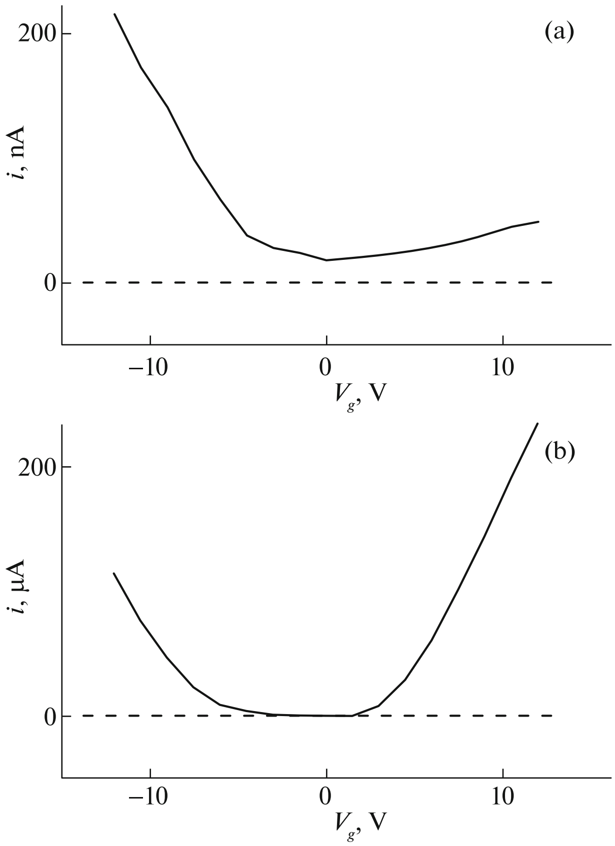

Fig. 3. Dependence of current on gate voltage V_g for the (a) proton and (b) electron–hole conductivities of the transistor plotted based on the data in Figs. 1 and 2.

$V_g = -12$ V it is $n_p = 4.4 \times 10^{17}$ cm^{-3}; i.e., the proton concentration at this bias increases by an order of magnitude.

An analysis of Fig. 3b for the electron–hole conductivity makes it possible to obtain the values of drift mobility of electrons and holes at different V_g values proceeding from the general relation $\sigma = ne\mu$ and taking into account that $V_{sd} = 1$ V. For example, at bias voltage $V_g = 10$ V, the electron mobility is $\mu_e = 1.2 \times 10^2$ cm^2/(V s) and the hole mobility is $\mu_h = 0.6 \times 10^2$ cm^2/(V s) (which is lower by a factor of about 2). Note that in [14] the ratio of these parameters for the graphene layer has an inverse character and the mobilities ($\mu \approx 10^4$ cm^2/(V s)) exceed our values significantly. This fact is quite natural because graphene films have much more perfect structure in comparison with thicker (by a factor of several tens and even several hundred) GO films where graphene sheets (reduced GO sheets) have random arrangement and are reduced only partially.

It was shown that at a certain degree of reduction the GO field-effect transistor can exhibit either proton or electron–hole conductivity. The transistor currents in the latter case exceed the proton-conductivity currents by about three orders of magnitude. These phenomena can be used for controlling the transistor properties (for example, in sensor and probe circuits). At the same time, the environmental humidity may significantly affect the operation stability of a field-effect transistor with GO used as an insulating layer.

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