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CONDUCTIVITY OF GRAPHENE ON FERROELECTRIC PVDF-TrFE

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The theory of conductivity in graphene grown by the chemical vapor deposition on a poly[(vinylidenefluoride-co-trifluoroethylene] (PVDF-TrFE) ferroelectric film has been developed with regard for the charge carrier scattering at large-scale potential nonuniformities created by both the domain structure of the ferroelectric and a nonuniform distribution of chemical dopants over the graphene surface. As the correlation length of nonuniformities increases, the graphene resistivity has been shown to decrease, and, in the case of a sufficiently uniform distribution of chemical dopants and the sufficiently large domain sizes, to achieve values of 100 Ω and less. Such values make the "graphene on PVDF-TrFE" system competitive with standard conductive and transparent indium tin oxide coverings for photovoltaics. The theoretical results have been compared with experimental data.

K e y w o r d s: conductivity of graphene, PVDF-TrFE ferroelectric film, chemical vapor deposition.

Interest in studying the properties of graphene on ferroelectric substrates has considerably grown recently (see reviews [1–3] and references therein). The "graphene–ferroelectric substrate–gate" system has a number of unique parameters. First of all, these are the capability to obtain high (of about 10^{12} cm^{-2}) concentrations of charge carriers at low (of the order of one Volt) gate voltages and the hysteresis in the dependence of the resistivity of a graphene channel on the gate voltage. Even today, the application of ferroelectric substrates for graphene made it possible to create reliable enough elements for the nonvolatile memory of a new generation. Such elements, for which the difference between the states "0" and "1" is provided by considerably different states of the minimum and maximum resistivities in the channel of a graphene field-effect transistor, sustain up to 10^5 switching cycles and store the recorded information for more than 1000 s. In the long term, those systems can be characterized by record switching rates (tens of femtoseconds) [4–9]. A possibility of the creation, on the basis of such systems, of modulators for the medium and near IR frequency ranges [10] and bistable optical systems [11] is under discussion.

Recently, a successful attempt [12] was made to use graphene as a technological transparent electrode for probable applications to photovoltaics, organic light-emitting diodes, touch screens, displays, and so forth. The main task at the solution of this problem is to obtain the best combination of the transparency (97.3% for a monoatomic graphene layer in the optical and near IR ranges [13]) and the 2D resistivity. The latter, for those systems to be competitive with available indium tin oxide (ITO) coatings, has to be less than 100 Ω. However, the quantitative (and, in some cases, even qualitative) understanding of physical processes that govern the conductivity in such system is still absent, which makes it impossible to talk about directions of the effective improvement of their parameters.

In this work, a quantitative theory is developed for the conductivity in graphene doped with the poly[vinylidenefluoride-co-trifluoroethylene] (PVDF-TrFE) relaxor. The theory is based on the model of charge carrier scattering by large-scale static nonuniformities proposed in work [14]. The results of theoretical description are compared with experimental data [12].

The resistivity of graphene on a substrate is driven by several competitive mechanisms of charge carrier scattering: at acoustic vibrations in the plane xy, at vibrations that occur out of this plane, at various nonuniformities both generated by the substrate (e.g., the Coulomb potential of charged impurities) and already available in graphene (defects) (see review [15] and references therein). The real scenario of scattering critically depends on the graphene manufacture

technology, the interface and substrate states, and so forth.

In the absence of an external field, the PVDF-TrFE film spontaneously breaks up into domains with opposite polarizations, with the domain sizes ranging from nanometers to microns depending on the ferroelectric fabrication technology [16]. As a result, the regions with the electron or hole conductivity emerge in graphene under the correspondingly polarized PVDF-TrFE domains, as well as p–n junctions between those regions with the formation of barriers that intensively scatter charge carriers (Fig. 1). In what follows, we consider a situation where this scattering mechanism considerably dominates over others by intensity. This can be done if the mean free path of charge carriers in graphene on the ferroelectric, which is determined by scattering at various defects (this is the dominant mechanism of scattering in graphene at a high concentration of charge carriers [15]) and can be of the order of 100 nm at room temperature for high-quality substrates), exceeds the average size of domains [17].

In work [12], single-layered graphene obtained by the chemical vapor deposition (CVD) method was studied. This method allows devices with a large area to be obtained, which are required for the practical applications mentioned above; first of all, to photovoltaics. Owing to its technology (a necessity of etching a copper wafer preliminarily covered with a graphene film, which results in the chemical doping), this method is known to produce only graphene with the hole type of conductivity (in the absence of "field doping", the Fermi level is always located under the Dirac point (see, e.g., works [2, 17] and references therein)).

The concentrations of electrons and holes in the regions that correspond to domains with different polarizations (P_+ corresponds to dipole's "plus" orientation toward graphene, and P_- away from graphene) equal

$$\begin{aligned} n &= \beta P_+/e - p_d, \\ p &= \beta P_-/e + p_d. \end{aligned} \tag{1}$$

Here, β is the constant of coupling interaction between the dipoles in the ferroelectric and the charge carriers in graphene (for numerical estimations, it is put to equal 1 [12]), and p_d is the concentration of holes that emerge owing to the "chemical doping" of CVD-formed graphene (it equals the concentration of chemical dopants "fixed" on the graphene surface). Since the spontaneous polarization of PVDF-TrFE ($P_+ = P_- \sim 10^{-5}$ C/cm^{-2} [16]) induces a high doping level in graphene ($\sim 5 \times 10^{13}$ cm^{-2}), the term p_d, which is usually by an order of magnitude smaller, can be neglected in a first approximation. Note that, at this stage, the distribution of holes created by "chemical doping" is considered to be uniform over graphene.

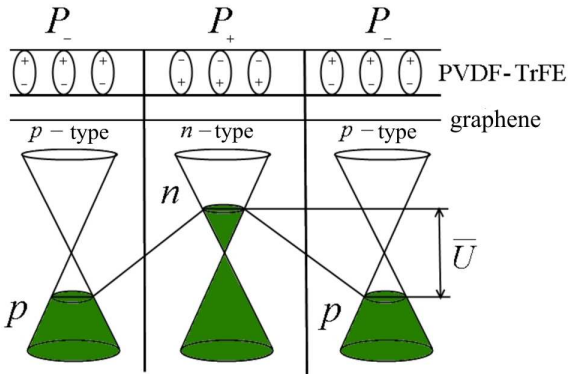

Fig. 1. Graphene on a PVDF-TrFE film with domains. Domains have different polarization directions and are responsible for the presence of p–n junctions in graphene. $\bar{U}$ is the averaged energy of potential nonuniformities

In the framework of the Boltzmann transport theory and in the approximation of high charge carrier concentrations (when the edge of the distribution function can be considered as sharp), the conductivity in graphene equals [15]

$$\sigma = \frac{e^2 v_{\mathrm{F}}^2}{2} D(E_{\mathrm{F}}) \tau(E_{\mathrm{F}}). \tag{2}$$

Here, $v_{\mathrm{F}} \approx 10^8$ cm/s, E_{F} is the chemical potential level (the Fermi energy) in graphene, $D(E_{\mathrm{F}})$ the electron density of states in graphene at the chemical potential level, and $\tau(E_{\mathrm{F}})$ the time of momentum relaxation for charge carriers with the Fermi energy. With regard for the expression

$$E_{\mathrm{F}} = \hbar v_{\mathrm{F}} (\pi n)^{1/2}, \tag{3}$$

which relates the Fermi energy in the field-doped graphene to the 2D concentration of charge carriers n and which follows from a linear character of the graphene band spectrum near the Dirac point [15], the expression for the density of states looks like

$$D(E_{\mathrm{F}}) = \frac{2\sqrt{n}}{\sqrt{\pi}\hbar v_{\mathrm{F}}}. \tag{4}$$

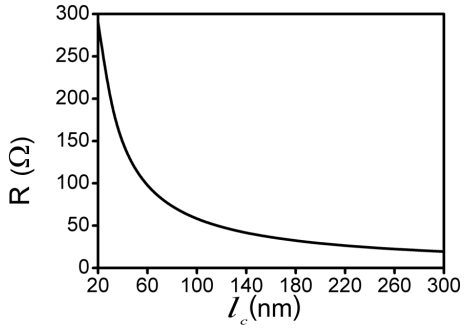

Fig. 2. Resistivity of the graphene layer R as a function of the domain size l_c for $n = 5 \times 10^{13}$ cm^{-2}

At the same time, the expression for $\tau(E_{\rm F})$ can be obtained in the framework of model assumptions concerning the dominating mechanism of scattering. When the scattering at the potential of random p–n junctions dominates, we face the problem of the scattering at large-scale and randomly located nonuniformities of the potential. Let us describe this nonuniform and coordinate-dependent potential $U(r)$ in the framework of a mathematical formalism developed in work [18]. Namely, let us introduce the Gauss correlation function

$$\langle U_{\mathbf{r}} U_{\mathbf{r}'} \rangle = \bar{U}^2 \exp\left[-\frac{(\mathbf{r}-\mathbf{r}')}{l_c}\right]^2. \tag{5}$$

Here, $\bar{U}$ is the averaged energy of potential nonuniformities (in our problem, this quantity depends on the polarization field), and l_c is the correlation length determined by the nonuniformity scale (the size of domains with the identical polarization) in the ferroelectric.

The application of the formalism aimed at finding the times of charge carrier scattering in graphene, which was proposed in work [14], gives the scattering time, the substitution of which into Eq. (2) results, in view of Eq. (4), in the following formula for the resistivity:

$$\frac{1}{\sigma} \equiv R = \frac{\hbar}{e^2}\left(\frac{\pi \bar{U} l_c}{2\hbar v_{\rm F}}\right)^2 \Psi\left(\frac{E_{\rm F} l_c}{v_{\rm F}\hbar}\right), \tag{6}$$

where

$$\Psi(z) = \frac{e^{-\frac{z^2}{2}}}{z^2} I_1\left(\frac{z^2}{2}\right), \tag{7}$$

and $I_1(z)$ is the Bessel function of the first order. Note that the resistivity in 2D systems has a dimensionality of Ω, in contrast to 3D systems, where this dimensionality is $\Omega \cdot$ cm (see, e.g., work [19]).

Let us assume that the parameter $\bar{U}$, as qualitatively follows from expressions (1), is determined, by the order of magnitude, by the energy $E_{\rm F}$ (Fig. 1),

$$\bar{U} = 2E_{\rm F} = 2\hbar v_{\rm F} (\pi n)^{1/2}. \tag{8}$$

In this case, Eq. (6) can be rewritten in the form

$$R = \frac{h}{e^2}\left(\frac{e^{-\frac{z^2}{2}}}{2} I_1\left(\frac{z^2}{2}\right)\right), \qquad z = \sqrt{\pi n} l_c. \tag{9}$$

Hence, the resistivity of the graphene layer on the ferroelectric is determined as the product of the von Klitzing quantum resistivity

$$R_K = \frac{h}{e^2} = 25.812807572\ \text{k}\Omega \tag{10}$$

and a function depending on the ratio between the interelectron distance in the graphene layer, $1/\sqrt{n}$, and the domain size l_c. The dependence of quantity (6) on l_c calculated for $n = 5 \times 10^{13}$ cm^{-2} (this value is determined by the spontaneous polarization of PVDF-TrFE) is depicted in Fig. 2.

One can see that the resistivity expectedly decreases as the parameter l_c grows. For domain sizes larger than 60 nm, a resistivity lower than 100 Ω can be obtained, which makes the coating "graphene on the relaxor" an effective alternative to standard ITO films in photovoltaic devices. It is clear that one may hardly expect that the resistivity falls down to values of a few tens of Ohms as is predicted by the curve in Fig. 2, because, in reality, there also exists a strong nonuniformity in the distribution of chemical dopants, which is connected with the imperfection of the CVD technology at fabricating large graphene films [17, 20], which we neglected till now.

Let us try to describe the influence of this nonuniformity in the framework of the simplest model. Let the chemical dopants be uniformly distributed with the concentration p_d within some chaotically arranged regions, whereas the rest of the graphene surface is absolutely free of them. It is clear that the local concentration p_d can turn out much higher than the concentration averaged over the whole graphene surface, being of the same order as doping concentrations obtained due to the polarization of domains. In this

case, we consider the sizes of ferroelectric domains to be large, and the resistance of domain boundaries to be low in comparison with the resistance resulting from the doping nonuniformity.

It is clear that this situation can also be described by expression (5). However, the correlation length l_c is now determined by the characteristic distribution of dopant "spots", in which dopants regulate the local hole concentration p_d. In the absence of an external field generated by ferroelectric dipoles, the potential $\bar{U}$ in this simple model looks like

$$\bar{U} = \hbar v_{\mathrm{F}} (\pi p_d)^{1/2}. \tag{11}$$

Qualitatively, the dependence of the resistivity of the graphene sheet on the correlation length l_c has the same behavior as is shown in Fig. 2, but with different specific values owing to other parameter values resulting from badly controllable details of the CVD technological process [20].

Now, let us consider the external field generated by dipoles in the ferroelectric. In our approximation of "large" domains, when the whole working region is contained within the limits of a single domain, this field is uniform. In the case of P_+-polarization, the electron concentration equals

$$n = \beta P_+ / e - p_d \tag{12}$$

within the limits of chemical dopant accumulation "islands" and

$$n = \beta P_+ / e \tag{13}$$

beyond them. If the local concentration of chemical dopants p_d is high and exceeds $\beta P_+ / e$, this means that there are local regions in graphene with the electron and hole conductivities, and p–n junctions between them (Fig. 3, *a*).

In the case of P_--polarization, the hole concentration equals

$$p = \beta P_- / e + p_d \tag{14}$$

in the regions of chemical dopant accumulation and

$$p = \beta P_- / e \tag{15}$$

beyond them. It is of importance that, in this case, the entire substance has the hole conductivity (Fig. 3, *b*), and the height of the potential barrier between the regions with higher and lower doping levels is smaller owing to the root dependence of

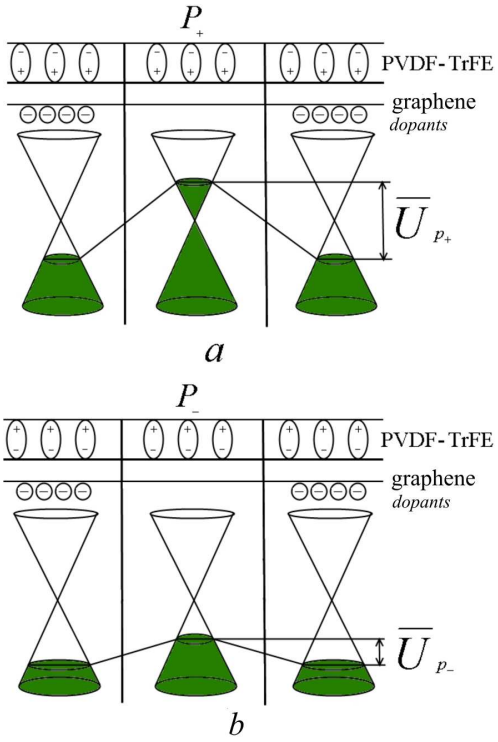

Fig. 3. Graphene on a single-domain ferroelectric under the condition of nonuniform chemical dopant distribution: (*a*) P_+-polarization of the domain: p–n junctions are available; (*b*) P_--polarization of the domain: p–n junctions are absent. The figure illustrates that $\bar{U}_{P_+} > \bar{U}_{P_-}$

the Fermi energy in graphene on the concentration (Eq. (3)). The absence of p–n junctions also means the absence of the electron-hole scattering, whose role can be substantial at high concentrations [14]. Then, if the scattering at nonuniformities induced by chemical doping dominates, the electrical resistance has to substantially increase at large external fields giving rise to the maximum polarization of the ferroelectric in the case of P_+-polarization and, on the contrary, has to substantially decrease in the case of P_--polarization.

This conclusion makes it possible to discriminate between the two cases that are considered in this work, because, if the chemical doping is uniform, the maximum polarization of the ferroelectric will mean the disappearance of p–n junctions in the case of P_+-polarization and the resulting graphene with the uniform electron conductivity, as well as the uniform hole conductivity in the case of P_--polarization. Therefo-

re, the resistivity of graphene will decrease in both cases if an external field larger than the critical one is applied. However, it will be lower for the P_--polarization, because the hole concentration will be higher than the electron one in this case, in accordance with formulas (1).

In work [12], the energy-independent "doping" of graphene by the field of dipoles located in a PVDF-TrFE film of micron thickness was experimentally carried out for the first time. This made it possible to obtain high charge carrier concentrations of about 3×10^{13} cm^{-2}, which resulted in a 2D resistivity of about 120 Ω at room temperature. The "ferroelectric–graphene" system demonstrated a high transparency (more than 95%), an excellent mechanical flexibility, and chemical inertness. The technology of its fabrication turned out simple, which allowed the cited authors [12] to say about the breakthrough in the creation of graphene transparent electrodes and optoelectronic devices of a new generation.

However, it should be noted that the indicated resistivity values were obtained only when the ferroelectric was completely polarized by the applied external field with the corresponding direction. At the fields lower than the critical ones, the obtained resistivity values were about hundreds of Ohms.

It is also important that, when a strong external electric field of about 70 mV/m was applied to PVDF-TrFE, a pronounced effect of the resistivity growth at the P_+-polarization and the resistivity reduction (by an order of magnitude: from 1200 to 120 Ω) at the P_--polarization was observed [12]. This phenomenon completely confirms the scenario predicted above in the case where the scattering at the nonuniformities in the spatial distribution of chemical dopants resulting from the imperfections of the CVD technology at fabricating large graphene sheets dominates. Hence, the numerical estimations made above demonstrate that the improvement of the technology, the creation of a more uniform distribution of impurities, and, at the same time, the application of films with large enough (100 nm and more) dipoles can result in the creation of transparent systems "graphene on ferroelectric" with a specific resistance of 100 Ω and less.

In this work, the theory of conductivity in graphene grown up by the CVD method on a PVDF-TrFE ferroelectric film was developed with regard for the charge carrier scattering at large-scale potential nonuniformities arising owing to both the domain structure of the ferroelectric and the nonuniformities in the distribution of chemical dopants over the graphene surface. It is shown that the increase of the nonuniformity correlation length gives rise to the decrease of the resistivity. In the case where the distribution of chemical impurities is sufficiently uniform, and the domains in the ferroelectric are large enough, the resistivity can reach a value of 100 Ω and less. Such values make the system "graphene on ferroelectric" competitive against standard conducting transparent ITO coatings for photovoltaics.

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ПРОВІДНІСТЬ ГРАФЕНУ
НА СЕГНЕТОЕЛЕКТРИКУ PVDF-TrFE

Р е з ю м е

Побудовано теорію провідності графену, вирощеного методом осаджування з парової фази (CVD), на плівці сегнетоелектрика полівініледен флюорид трифлуороетилен (PVDF-TrFE) з урахуванням розсіяння носіїв на великомасштабних неоднорідностях потенціалу, зумовлених як наявністю доменної структури сегнетоелектрика, так і неоднорідностями розподілу хімічних допантів на поверхні графену. Показано, що зі збільшенням кореляційної довжини, яка описує неоднорідності, питомий опір зменшується, і для випадку достатньо однорідного розподілу хімічних домішок і достатньо великих розмірів доменів може становити 100 Ом і менше. Такі значення роблять систему "графен на PVDF-TrFE" конкурентною щодо стандартних провідних прозорих ITO (індій–оксид олова) покриттів для фотовольтаїки. Проведено порівняння результатів теоретичного опису з експериментальними даними.