Localization of charge carriers in monolayer graphene gradually disordered by ion irradiation

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Gradual localization of charge carriers was studied in a series of micro-size samples of monolayer graphene fabricated on the common large scale film and irradiated by different doses of C+ ions with energy 35 keV. Measurements of the temperature dependence of conductivity and magnetoresistance in fields up to 4 T showed that at low disorder, the samples are in the regime of weak localization and antilocalization. Further increase of disorder leads to strong localization regime, when conductivity is described by the variable-range-hopping (VRH) mechanism. A crossover from the Mott regime to the Efros-Shklovskii regime of VRH is observed with decreasing temperature. Theoretical analysis of conductivity in both regimes showed a remarkably good agreement with experimental data.

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INTRODUCTION

Investigation of the influence of disorder on the properties of graphene is attracting a tremendous interest due to possibility to modify this novel and promising material using weak or strong localization of charge carriers. Previously, there were observed separately either weak localization (WL) or different kinds of Variable-Range-Hopping (VRH) conductivity of strongly localized carriers in graphene samples disordered by different methods like doping, oxidation, ion irradiation (see, for example,1,2). However, we are not aware of observations of all regimes of localization with gradual increase of disordering in graphene. In this paper we report the results of systematic study of the localization process in monolayer graphene (MG) samples subjected by different doses of ion irradiation.

Six groups of mini-samples (200 × 200 μm) were fabricated by means of electron-beam lithography (EBL) on the common large-scale (5 × 5 mm) film. Initial sample before EBL was marked as sample 0. The samples from the first group, marked as 1, were not irradiated, while 5 others groups were subjected to different doses (from 5 × 1013 up to 1 × 1015 cm−2) of irradiation by C+ ions with energy 35 keV.

In our previous work,3 a concentration of structural defects ND was determined for each group of samples using measurements of the Raman scattering. These values are shown in the inset in Fig. 1 (It turns out that sample 1 is also slightly disordered due to EBL process). Measurements of the current-voltage characteristics (I – V ) for all samples, performed at room temperature, showed that for samples 5 and 6, I – V is strongly non-linear even at very small current. That is why in this paper, the temperature dependences of resistance R(T) are shown only for samples 0 - 4.

The resistance was measured by two-probe method in helium cryostat down to 1.8 K in zero magnetic field and in magnetic fields up to 4 Tesla. Fig. 1 shows the general picture R(T) for all samples.

The sample 0 shows typical metallic behavior, when R slightly decreases with decrease of T. For sample 1 R slightly increases with decreasing T, which is characteristic for ”dirty” metals. For other samples R changes with T exponentially, which is characteristic for strongly localized carriers.

![Graph](image-url)

FIG. 1: Resistivity of disordered monolayer graphene samples as a function of temperature. Inset shows the density of structural defects in samples.

WEAK LOCALIZATION

Fig. 2 shows the experimental dependences of magnetoconductance (MC) of sample 1 in wide temperature
interval, from 300 K down to 1.8 K. Plot of the temperature dependence of conductivity on the scale $\sigma$ vs. $\ln T$ (Fig. 3) shows the logarithmic temperature behavior of $\sigma$ at low $T$, characteristic for regime of WL [9], with tendency to saturation at very low temperatures.

WL regime of conductivity in monolayer graphene has important features due to the facts that charge carriers are chiral Dirac fermions, which are reside in two inequivalent valleys at the $K$ and $K'$ points of the Brillouin zone. Due to chirality, Dirac fermion acquires a phase of $\pi$ upon intravalley scattering, which leads to destructive interference with its time-reversed counterpart and weak antilocalization (WAL). Interv valley scattering leads to restoration of WL because fermions in $K$ and $K'$ valleys have opposite chiralitites.

Quantum corrections to the conductivity of graphene have been intensely studied theoretically [10,13]. It was predicted that at relatively high temperatures WAL corrections will dominate, while with decreasing $T$ the WL corrections will dominate. There were several experimental papers reporting logarithmic dependence of conductivity on temperature and magnetic field at low temperatures [10,11,12]. However, in our sample 1, the logarithmic dependence is observed in wide temperature interval, starting from 300 K, which gives an opportunity to check in a very detailed way the theoretical predictions.

For the MC the theory [13] predicts

$$\Delta \sigma(B,T) = \frac{e^2}{\pi\hbar} \left[ F\left(\frac{B}{B_{\varphi}}\right) - F\left(\frac{B}{B_{\varphi} + 2B_i}\right)\right] - 2F\left(\frac{B}{B_{\varphi} + B_s}\right)$$

$$F(z) = \ln(z) + \psi\left(\frac{1}{2} + \frac{1}{z}\right), \quad B_{\varphi,i,s} = \frac{hc}{4Dc} \tau_{\varphi,i,s}^{-1},$$

where $\psi$ is the digamma function, $\tau_{\varphi}$ is the coherence time, $\tau_{i}^{-1}$ is the intervalley scattering rate, $\tau_{s}^{-1}$ is the combined scattering rate of intravalley and intervalley scattering and of trigonal warping.

Fitting Eq. (1) to experimental data for magnetoconductance of sample 1 at different temperatures is illustrated on Fig. 2. In the process of fitting we were able to extract all three parameters $B_{\varphi,i,s}$ entering the equation. These parameters shown in inset in Fig. 3. It turns out, that they are temperature–dependent which was not predicted by theory. Using these parameters we can calculate conductance at zero magnetic field according to Eq. (10) of Ref. [13], which can be rewritten in the form

$$\sigma(B = 0, T) = -\frac{e^2}{\pi\hbar} \left[ \ln \left(1 + 2\frac{B_i}{B_{\varphi}}\right) + 2\ln \left(1 + \frac{B_s}{B_{\varphi}}\right) \right] + 2\ln \left(\frac{B_{\varphi}}{1 + B_{\varphi}}\right) + A,$$

where $A$ is a constant, dependent upon the unit of magnetic field (chosen as 1 T). We compare Eq. (2) with the experimentally measured conductivity $\sigma(B = 0, T)$. The

![FIG. 2: Magnetoconductance of sample 1 as function of magnetic field; solid lines – experiment, dashed lines – formula (1) with fitted parameters.](https://example.com/fig2.png)

![FIG. 3: Conductivity of sample 1 as function of temperature. Circles present experimental data, squares present Eq. (2) with parameters determined from fitting the magnetoconductance ($A$ was chosen to be 11.7 $\cdot e^2/\pi\hbar$). The inset: The values of $B_{\varphi}$ (solid line) and $B_i$ (short-dashed line) and $B_s$ (long-dashed line, right axis).](https://example.com/fig3.png)
The inset to Fig. 3 shows that, apart from the lowest temperatures, $B_\varphi \sim 1/\tau_\varphi \sim T$. Mechanisms that can give the dependence $\tau_\varphi \sim 1/T$ are: electron–electron scattering in dirty limit [13], electron–phonon scattering, [14, 15], and electron–flexural phonon interaction [16]. The saturation of $\tau_\varphi$ at low temperatures is well known in classical 2d systems and may be connected with existence of dephasing centers (for example, magnetic impurities) [17, 18].

Obtained value of $B_\varphi$ allow us to determine the values of dephasing length $L_\varphi = \sqrt{D/\tau_\varphi} = \sqrt{\hbar/4B_\varphi \epsilon}$. When the temperature decreases from 300 K to 3 K, the dephasing length $L_\varphi$ increases from 7 nm to 70 nm and then saturates. The maximal value of $L_\varphi$ allows us to estimate the density of dephasing centers as $2 \times 10^{10}$ cm$^{-2}$.

**STRONG LOCALIZATION**

Let's discuss now samples 2–4 with pronounced insulating behaviour. Plotting the data on the Arrhenius scale $\ln R$ vs. $1/T$ showed that energy of activation continuously decreases with decreasing $T$ which is characteristic for the variable-range-hopping (VRH) conductivity [19]. There are two kinds of VRH depending on the structure of the density-of-states (DOS) $g(\epsilon)$ in the vicinity of the Fermi level (FL) $\mu$: when $g(\epsilon) = g(\mu) =$ const, $R(T)$ is described by the Mott ($T^{-1/3}$) law in the case of two-dimensional (2d) conductivity:

$$R(T) = R_0 \exp(T_M/T)^{1/3}, \quad T_M = C_M[g(\mu)a^2]^{-1}. \quad (3)$$

Here $C_M = 13.8$ is the numerical coefficient [19], $a$ is the radius of localization.

The Coulomb interaction between localized carriers leads to appearance of the soft Coulomb gap in the vicinity of FL which in the case of 2d has a linear form

$$g(\epsilon) \sim |\epsilon - \mu|(\epsilon^2/\kappa)^{-2}, \quad (4)$$

where $\kappa$ is the dielectric constant of the material. This leads to the Efros-Shklovskii (ES) VRH or $T^{-1/2}$ law:

$$R(T) = R_0 \exp(T_{ES}/T)^{1/2}, \quad T_{ES} = C_ES(\epsilon^2/\kappa a), \quad (5)$$

where the numerical coefficient $C_ES = 2.8$ [19].

Coulomb interaction can alter the DOS only near the FL. Far from FL, the DOS is restored to its initial value, which is approximately equal to $g(\mu)$, see inset in Fig. 3. Denoting the half-width of the Coulomb gap as $\Delta$ one can conclude, therefore, that $T \ll \Delta$, ES law has to be observed, while in the opposite case ($T \gg \Delta$), the Mott law should dominate.

There is a number of reports about observation of either Mott or ES laws in different disordered graphene-based materials [21, 22]. We show that in samples 3 and 4, both VRH laws are observable at different temperatures. (For sample 2, the VRH regime will be observed at lower temperatures). In Figs. 3 and 5 $\log R$ is plotted versus $T^{-1/3}$ and $T^{-1/2}$. At high temperatures, dependences $R(T)$ are straightened on the scale $T^{-1/3}$, while at low temperatures they are straightened on the scale $T^{-1/2}$. The latter shows the approach to the ES law which should be observed at the lowest temperatures. These plots allow us to determine both parameters $T_M$ and $T_{ES}$ (Table 1) and calculate the temperature $T_c$ of deviation from $T^{-1/3}$ law to $T^{-1/2}$ law. In VRH, only localized states in an optimal band of width $\epsilon(T)$ near the Fermi level are involved in the hopping process. The band becomes continuously narrower with decreasing $T$. Hopping resistance is determined by the critical parameter $\xi_c$:

$$R = R_0 \exp\xi_c, \quad \xi_c = (2r/a) + (\epsilon/T). \quad (6)$$

Here energy and temperature are measured in the same units, $r$ is the mean distance of hopping. In the Mott regime, $g(\epsilon) = g(\mu) =$ const and, therefore, the total number of states in the optimal band is $N(T) = g(\mu)\epsilon$ and the mean distance between states in two dimensions is $r \approx [g(\mu)\epsilon]^{-1/2}$. Substituting in (6), one can find $\epsilon(T)$ from the minimal value of $\xi_c$ determined from $d\xi_c/d\epsilon = 0$:

$$\epsilon(T) = T^{2/3}[g(\mu)a^2]^{-1/3}. \quad (7)$$

This gives the relationship between $T$ and the width of the optimal band: $T = [g(\mu)a^2]^{1/2}c\epsilon^{3/2}$. At the crossover temperature $T_c$, $\epsilon = \Delta$, so

$$T_c = [g(\mu)a^2]^{1/2}\Delta^{3/2}. \quad (8)$$

Being inside the Coulomb gap, the crossover temperature can be determined from $g(\epsilon = \Delta) = g(\mu)$ which gives $\Delta = g(\mu)(c^2/\kappa)^2$. Substituting into Eq. (8) and using expressions for $T_M$ and $T_{ES}$, Eqs. (3) and (5), we get

$$T_c = (C_M^2/C_ES^3)(T_{ES}/T_M^2) \approx 8.6(T_{ES}/T_M^2) \quad (9)$$

The calculated values of $T_c$ for samples 3 and 4 are given in the Table 1 and shown as arrows in Fig. 4. One can see a surprisingly good agreement with experiment. We can also estimate other important parameters: width of the Coulomb gap $\Delta$ and the radius of localization $a$. The value of $\kappa = 2.45$ for the monolayer graphene was chosen as $\kappa = (\kappa_1 + \kappa_2)/2$, where $\kappa_1 = 3.9$ (for SiO$_2$) and $\kappa_2 = 1$ (for air). One can see that indeed, the ES law is observed when $T < \Delta$.

| S # | $T_M$(K) | $T_{ES}$(K) | $T_c$(K) | $\Delta$(K) | $a$(nm) |
|-----|---------|-------------|--------|------------|--------|
| 3   | 308 ± 54 | 50 ± 7      | 11.4 ± 0.8 | 12 ± 1     | 385 ± 54 |
| 4   | 5962 ± 305 | 490 ± 12    | 29 ± 5  | 60 ± 6     | 39 ± 1  |

**TABLE I: Hopping conductivity parameters for samples 3.4.**
Comparison of samples 3 and 4 shows that increase of the density of defects $N_D$ leads to stronger localization which manifests in a significant decrease of $a$ and increase of the energy band needed for hopping. This looks like increase of the amplitude of the random potential relief in classical semiconductors induced by randomly distributed positively charged donors and negatively charged acceptors in the case of compensation. Hence we assume that structural defects in graphene are of amphoteric nature, i.e. they can be either acceptors or donors and compensate each other. Thus, increase of $N_D$ leads to the random potential relief amplitude increase.

In conclusion, a gradual transformation of conductivity measured in a wide interval of temperatures (300 - 1.8 K) and magnetic fields (up to 4 T) was observed in a series of monolayer graphene samples subjected by different dose of ion irradiation. Increasing the density of structural defects $N_D$ induced by irradiation has led to change the mechanism of electron transport from metallic conductivity to the regime of WL and finally to the VRH of strongly localized carriers. It is shown that WL regime in slightly disordered sample starts from high (room) temperatures.

Comparison of experimental magnetoconductance curves with theory allowed us to find the parameters which determine the logarithmic temperature dependence of conductivity in WL regime. In VRH, a crossover from the Mott law to the Efros-Shklovskii law was observed in the same samples with decreasing temperature. The calculated crossover temperatures are in good agreement with experimental values. It is suggested that strengthening of localization with increase of $N_D$ can be explained by amphoteric nature of graphene structural defects induced by ion irradiation.

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