Defect Scattering in Graphene

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(Received 23 March 2009; published 12 June 2009)

Irradiation of graphene on SiO_2 by 500 eV Ne and He ions creates defects that cause intervalley scattering as is evident from a significant Raman D band intensity. The defect scattering gives a conductivity proportional to charge carrier density, with mobility decreasing as the inverse of the ion dose. The mobility decrease is 4 times larger than for a similar concentration of singly charged impurities. The minimum conductivity decreases proportional to the mobility to values lower than $4e^2/\pi h$, the minimum theoretical value for graphene free of intervalley scattering. Defected graphene shows a diverging resistivity at low temperature, indicating insulating behavior. The results are best explained by ion-induced formation of lattice defects that result in midgap states.

DOI: 10.1103/PhysRevLett.102.236805 PACS numbers: 73.63.−b, 72.10.Fk, 81.05.Uw

The strong carbon-carbon sp^2 bonds which provide graphene with high intrinsic strength [1] and make possible the isolation of single atomic layers [2] also result in a very low density of lattice defects in graphene prepared by mechanical exfoliation [3,4]. However, lattice defects in graphene are of great theoretical interest [5,6] as a potential source of intervalley scattering, which in principle transforms graphene from a metal to an insulator [7,8]. Lattice defects are also likely to be present in various concentrations in graphene synthesized by reduction of graphene oxide [9,10], chemical vapor deposition [11,12], or segregation of carbon on the surface of SiC [13]; hence, it is important to understand their impact on electronic transport.

Here we show that ion-irradiation-induced defects in graphene cause a significant intensity in the Raman D band associated with intervalley electron scattering [14–16] and give rise to a constant mobility, similar to the effect of charged impurities, but with a magnitude 4 times lower than for a similar concentration of singly charged impurities. This result is in contrast to the carrier-density-independent conductivity for weak point disorder [17,18] but consistent with the theory of strong scattering by midgap states [5,6]. Unlike charged impurities [19], lattice defects (1) do not change the residual charge density in electron-hole puddles, (2) greatly depress the minimum conductivity, even below $4e^2/\pi h$ (the theoretical minimum value of the conductivity at the Dirac point in the absence of intervalley scattering [7]), and (3) induce insulating temperature dependence of the conductivity.

Transport with constant mobility is predicted for both charged-impurity scattering and scattering by midgap states. Charged-impurity disorder in graphene results in a conductivity

$$\sigma_c = ne\mu_c = \frac{2e^2}{h}\frac{n}{n_c}\frac{1}{G(2r_s)}, \tag{1}$$

where e is the electronic charge, h the Planck's constant, n_c the charged-impurity density, r_s the Wigner-Seitz radius, and $G(2r_s)$ an analytical function of the dimensionless interaction strength in graphene. For graphene on SiO_2, Eq. (1) gives $\mu_c \approx 5 \times 10^{15}\ \mathrm{V^{-1}\,s^{-1}}/n_c$ [19,20]. The random charged-impurity potential also gives rise to electron-hole puddles with a characteristic intrinsic carrier density n^*, which is a function only of n_c, d (the impurity-graphene distance,) and r_s, resulting in a minimum conductivity $\sigma_{\min} = n^* e\mu_c$. However, strong disorder, modeled as a deep potential well of radius R, is predicted to produce midgap states in graphene [6], and a conductivity which is also roughly linear in n [5]:

$$\sigma_d = ne\mu_d = \frac{2e^2}{\pi h}\frac{n}{n_d}\ln^2(k_F R), \tag{2}$$

where n_d is the defect density and k_F is the Fermi wave vector. A third type of scattering in graphene, weak point disorder, is predicted to give rise to a carrier-density-independent resistivity ρ_s [17], which has been observed experimentally [18].

To investigate the dependence of graphene's conductivity on defect density, cleaned graphene on SiO_2 was irradiated with 500 eV He^+ and Ne^+ in ultrahigh vacuum (UHV) at low temperature (10 K for He^+ irradiation and 40–80 K for Ne^+ irradiation), and the conductivity measured *in situ* in UHV to prevent subsequent reaction with molecules from the gas phase [21]. Ion irradiation of graphite at these energies produces one atomic-scale defect, most likely a carbon vacancy possibly with a trapped noble-gas atom, per incident ion [22,23].

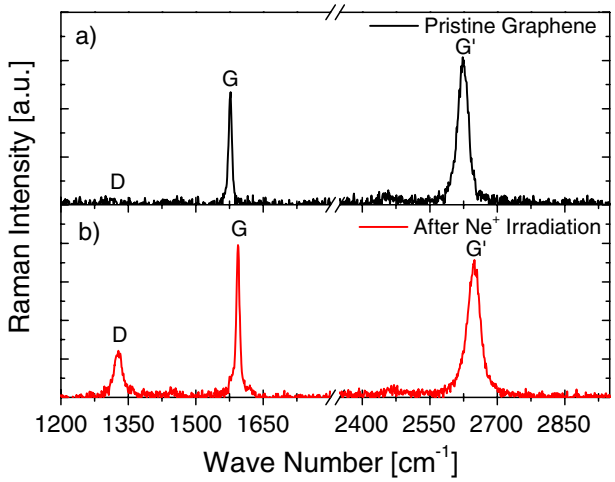

FIG. 1 (color online). Raman spectra (wavelength 633 nm) for (a) pristine graphene and (b) graphene irradiated by 500 eV Ne^+ ions at a dose of 10^{12} cm^{-2}.

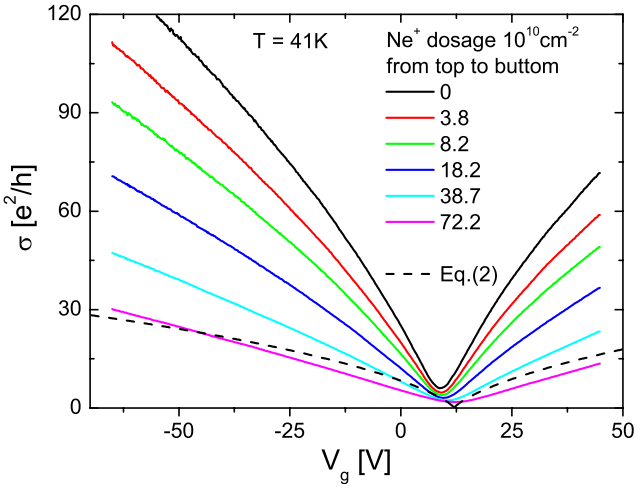

FIG. 2 (color online). Conductivity vs gate voltage curves for pristine graphene and following Ne^+ ion irradiation doses with cumulative exposures indicated. Irradiation and measurements were performed at $T = 41$ K in a ultrahigh vacuum. The dashed curve shows the predictions from Eq. (2) with the experimentally extracted defect radius $R = 2.3$ Å at defect density $n_d = 7.22 \times 10^{11}$ cm^2.

Figure 1 shows the Raman spectra, taken under ambient conditions, for a representative graphene sample before irradiation, and after irradiation by Ne^+ at a dose of 10^{12} cm^{-2} ($\sim$1 Ne^+ per 4×10^3 carbon atoms). The pristine sample shows a Lorentzian G' band characteristic of single layer graphene, and no detectable D band. Upon irradiation, the appearance of the D band indicates significant intervalley scattering [14,16]. A very rough estimate of the defect spacing can be made using the empirical formula $L_a = [2.4 \times 10^{-10}\ \mathrm{nm}^{-3}]\lambda^4(\frac{I_D}{I_G})^{-1}$, which relates the grain size L_a in disordered graphite to the ratio of the integrated D and G band intensities I_D and I_G, and λ the excitation wavelength (633 nm) [24]. Applying this formula to our irradiated graphene gives $L_a \sim 60$ nm, larger than the expected defect spacing of 10 nm, but comparable to the transport mean free path of $\sim$50 nm (see below).

Figure 2 shows the $\sigma(V_g)$ curves measured for the pristine sample and following sequential Ne^+ irradiation doses at $T = 41$ K in UHV, which is one of the four experimental runs shown in this Letter. Also shown are predictions from Eq. (2) with the experimentally extracted defect radius R at $n_d = 7.22 \times 10^{11}$ cm^{-2} (see below). Mobility μ and the minimum conductivity $\sigma_{\min}$ partially recover after heating to 485 K between each run, possibly due to annealing or passivation of the defects. To determine μ, and the resistivity ρ_s due to weak point disorder, the $\sigma(V_g)$ curves are fitted to the form $\sigma(V_g)^{-1} = [c_g(V_g - V_{g,\min})\mu]^{-1} + \rho_s$ [18]. We fit the hole side of the $\sigma(V_g)$ curve ($V_g < V_{g,\min}$) because the data span a wider V_g range. Figure 3(a) shows $1/\mu$ vs ion dosage for four experimental runs on two different graphene samples as well as behavior for charged impurities [19,20]. For the irradiated samples, $1/\mu$ increases linearly with ion dosage as expected for uncorrelated scattering. Fitting yields a proportionality of 7.9×10^{-16} V s for the Ne^+ irradiation runs and 9.3×10^{-16} V s for the He^+ irradiation runs and an offset that yields the initial mobility in the graphene prior to each irradiation run [21]. Assuming midgap scattering [Eq. (2)], at carrier density $n = 2 \times 10^{12}$ cm^{-2}, the proportionality constant yields the defect radius $R = 2.3$ Å for Ne^+ irradiation and 2.9 Å for He^+ irradiation. If the proportionality is attributed to charged impurity scattering [Eq. (1)], it would require addition of charge $Z \sim 4e$ per incident ion. Figure 3(b) shows the density-independent resistivity ρ_s for the same four experimental runs; ρ_s is very small (on order $10^{-3}h/e^2$) and does not change significantly with ion irradiation dose.

Figure 4(a) shows the change in the voltage of the minimum conductivity $\Delta V_{g,\min}$ as a function of the inverse mobility $1/\mu$ (proportional to ion dose) for the four ion irradiation runs. For comparison, the magnitude of $\Delta V_{g,\min}$ for potassium (K) dosing (addition of charged impurities) is also shown (data from Ref. [19]), which is 5 times larger than a similar concentration of ion irradiation. Note that $\Delta V_{g,\min}$ is positive for ion irradiation, and negative for K dosing. Figure 4(b) shows $\sigma_{\min}$ vs μ for the same four ion irradiation runs and the K dosing run [19]. In sharp contrast to the charged impurities introduced by K dosing, where $\sigma_{\min} = n^* e \mu_c$ varies slowly and nonmonotonically because n^* increases with increasing dose (decreasing μ), ion irradiation has a large effect on $\sigma_{\min}$, reducing $\sigma_{\min}$ roughly proportional to μ.

We now discuss the changes in $\sigma(n)$ upon ion irradiation. The density-independent resistivity [Fig. 3(b)] $\rho_s \sim 3 \times 10^{-3}h/e^2$ and is roughly independent of ion dose; at a carrier density of 10^{12} cm^{-2}, this corresponds to a mean free path >2 μm. The dominant signature, linear

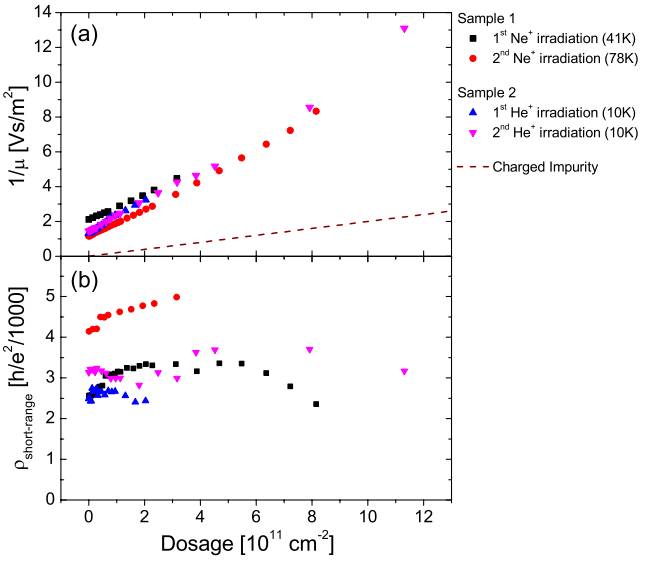

FIG. 3 (color online). (a) Inverse of mobility $(1/\mu)$ vs ion dosage for two Ne^+ irradiation runs on sample 1 and two He^+ irradiation runs on sample 2. The dashed line represents behavior for the same concentration of charged impurities (potassium on graphene from Ref. [19]). (b) Density-independent resistivity ρ_s vs ion dosage.

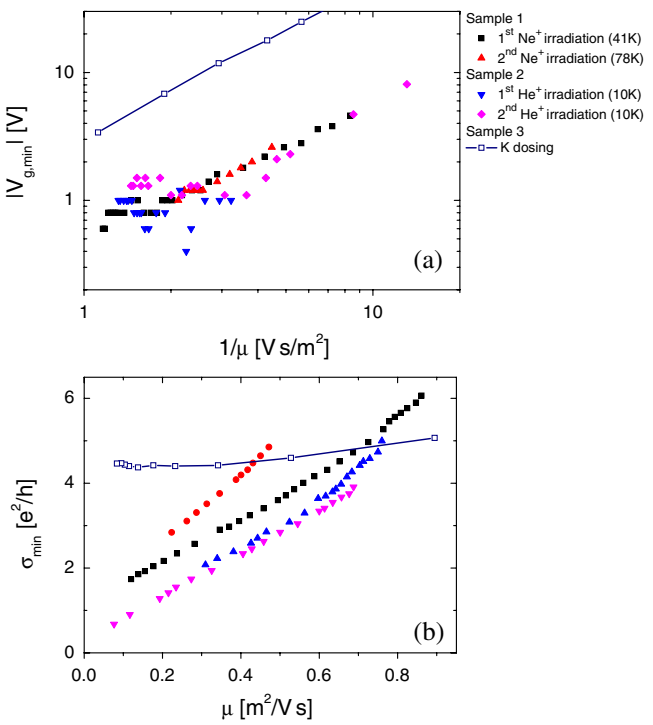

FIG. 4 (color online). (a) Magnitude of the shift in the gate voltage of minimum conductivity $(|\Delta V_{g,\min}|)$ vs inverse mobility $(1/\mu)$. The shift is with respect to the initial value of $V_{g,\min}$, 8.8 V and 6.4 V for the Ne^+ and He^+ irradiated samples, respectively. (b) Minimum conductivity $(\sigma_{\min})$ vs μ for two Ne^+ irradiation runs on sample 1 and two He^+ irradiation runs on sample 2. Data for potassium dosing (Ref. [19]) are shown for comparison. $V_{g,\min}$ is positive for ion irradiation, negative for K dosing.

$\sigma(n) = ne\mu_d$ with μ_d independent of n, indicates that ion irradiation either creates midgap states or charged impurities. However, several observations argue that the observed changes in $\sigma(n)$ are dominated by midgap states: (1) The intervalley scattering observed in Raman spectroscopy (Fig. 1) with scattering length on order 60 nm is inconsistent with ρ_s, but consistent with the associated mobility $\mu = 1300\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$, at an ambient doping level of $\sim 10^{13}\ \mathrm{cm^{-2}}$, from which we calculate a mean free path $l \sim 50$ nm. This correspondence suggests that the transport mean free path significantly probes intervalley scattering from lattice defects. (2) The sign $\Delta V_{g,\min}$ for ion irradiation is positive, opposite to the expectation for deposition of positive ions near the graphene and also opposite to what was observed for ion-irradiated metal-oxide-semiconductor field-effect transistors [25]. (3) The reduction in mobility, if due to charged impurities, would require $\sim$4 added charges per incident ion, while $\Delta V_{g,\min}$ indicates only $\sim 1/5$ of a net charge per incident ion; this would require a delicate balance between creation of positive and negative impurities, and such balance would need to hold for incident Ne^+ and He^+, which have very different momenta. (4) Within the Boltzmann transport picture, $\sigma_{\min} = n^* e\mu$ [20] where the total mobility $\mu = (\mu_d{}^{-1} + \mu_c{}^{-1})^{-1}$. The roughly proportional relationship between $\sigma_{\min}$ and μ for ion-irradiated samples indicates that n^*, which is a function of n_c, is nearly independent of ion dose [26].

We therefore conclude that the data of Fig. 3(a) are dominated by uncharged lattice defects in graphene. The impurity radius $R \sim 2.3$ Å–2.9 Å obtained from the linear fits of Fig. 3 is a reasonable value for single-carbon vacancies generated by ion knockoff [23]. Using this value of R in Eq. (2) yields a $\sigma(V_g)$ similar in magnitude to the experimental curve, but with a stronger sublinearity (Fig. 2). We do not understand this discrepancy, but it may be related to carrier density inhomogeneity persisting to carrier densities much larger than n^* [27], or to the addition of a small amount of deep charged impurities [25] which would contribute a supralinear $\sigma(V_g)$. As discussed in the EPAPS material [21], the possible trapped noble-gas atoms are not likely to contribute significantly to the resistivity in our irradiated graphene samples.

Last we discuss the possibility of a metal-insulator transition in graphene with defects. Disorder-free graphene is expected to have a minimum conductivity of $4e^2/\pi h$ [7]. The introduction of intravalley scattering only (e.g., charged impurities) is expected to induce weak antilocalization, increasing the conductivity [7,8] with decreasing temperature. However, intervalley scattering (which gives rise to the Raman D band) is expected to induce weak localization, and insulating behavior, i.e., $\sigma \to 0$ as $T \to 0$, in graphene [7,8]. From Fig. 4(a), we can see that $\sigma_{\min}$ in ion-irradiated samples can be reduced well below $4e^2/\pi h$, the minimum metallic value. Figure 5 shows the conduc-

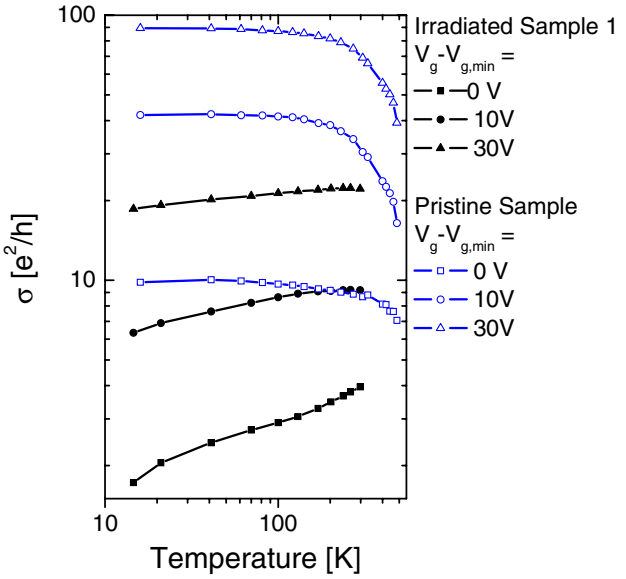

FIG. 5 (color online). Temperature dependence of the conductivity $\sigma(T)$ of pristine (open symbols) and irradiated (solid symbols) graphene at three different gate voltages. $\sigma(T)$ taken on cooling is shown for sample 1 after run 1 (irradiation by Ne^+, dose 7×10^{11} cm^{-2}) and annealing to $T = 300$ K. $\sigma(T)$ for the pristine sample is from Ref. [28].

tivity of the Ne^+ irradiated graphene sample as a function of temperature for three different gate voltages. The T-dependent conductivity of pristine graphene from Ref. [28] is also shown for comparison. The pristine graphene has metallic behavior, e.g., $d\sigma/dT < 0$. However, even a small amount of irradiation (that changes the room-temperature mobility $<4\times$) drastically affects the low-temperature behavior. In stark contrast to graphene without irradiation, where $\sigma_{\min}$ is largely temperature independent from $T = 4$–100 K [29], our irradiated sample is insulating with diverging resistivity as $T \to 0$. More work is needed to understand the exact nature of the insulating state in ion-irradiated graphene, but the data are consistent with the expectation that intervalley scattering produces localization [7].

In conclusion, we have measured charge transport in graphene with defects induced by ion irradiation in ultrahigh vacuum. Defects cause significant intervalley scattering, as seen in a prominent Raman D band. Defects give rise to a constant mobility, with a magnitude $\sim 4\times$ lower than for similar concentration of potassium ions on graphene, and consistent with scattering by midgap states. In contrast to charge impurity disorder, lattice defects reduce the minimum conductivity dramatically, and produce an insulating temperature dependence of the conductivity.

This work has been supported by NSF Grant No. DMR 08-04976 (J. H. C., M. S. F., and E. D. W.), NSF-UMD-MRSEC Grant No. DMR 05-20471 (J. H. C. and W. G. C.), and U.S. ONR Grant No. N000140610882 (C. J.). The MRSEC SEFs were used in this work. Infrastructure support has also been provided by the UMD NanoCenter and CNAM.

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