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Abstract: We study electron transport properties of graphene in the presence of correlated charged impurities via adsorption and thermal annealing of potassium atoms. For the same density of charged scattering centers, the sample mobility sensitively depends on temperature which sets the correlation length between the scatterers. The data are well understood by a recent theory that allows us to quantitatively extract the temperature dependence of the correlation length. Impurity correlations also offer a self-consistent explanation to the puzzling sub-linear carrier density dependence of conductivity commonly observed in monolayer graphene samples on substrates.

Understanding disorder in graphene [1] is essential for electronic applications; in contrast to conventional materials, the extraordinarily low electron-phonon scattering [2,3] in graphene implies that disorder [4-8] dominates its resistivity even at room temperature. Charged impurities [6,9-11] have been identified as an important disorder type in graphene on SiO_2 substrates [12,13], giving a nearly linear carrier-density-dependent conductivity $\sigma(n)$, and producing electron and hole puddles [14-16] which determine the magnitude of graphene's minimum conductivity σ_{min} [11]. Correlations of charged impurities are known to be essential in achieving the highest mobilities in remotely-doped semiconductor heterostructures [17-19], and are present to some degree in any impurity system at finite temperature. Here we show that even modest correlations in the position of charged impurities, realized by annealing potassium on graphene, can increase the mobility by more than a factor of four. The results are well understood theoretically [20] considering an impurity correlation length which is temperature dependent but independent of impurity density. Impurity correlations also naturally explain the sub-linear $\sigma(n)$ commonly observed in substrate-bound graphene devices [3,12,13,21].

Our experiment probes the influence of thermal annealing on the electronic transport properties of a graphene device with adsorbed potassium (K) atoms; potassium donates an electron to graphene leaving a positive ion as a charged scattering center. We previously studied [22] charged impurity scattering in potassium/graphene at low temperature (20 K) where the K adatoms are presumed to be frozen randomly on graphene. Here we measure the transport properties of graphene as the temperature is raised. We expect potassium ions on graphene to experience mutual Coulomb repulsion

which drives them away from each other producing correlations in their positions. Indeed, early low-energy electron diffraction (LEED) studies of K adsorbed on graphite revealed a distinct diffraction peak, which is linked to the nearest-neighbor spacing of the dispersed K layer [23]. A recent scanning tunneling microscope (STM) study reached similar conclusions [24].

The graphene on SiO_2/Si sample was prepared by mechanical exfoliation of natural graphite (Nacional de Grafite Ltda.). Electrical contacts are defined with standard electron beam lithography and thermal evaporation of chromium/gold (5/90 nm). A photomicrograph of the device is shown in Fig. 1 (left inset). The sample is then annealed in H_2/Ar gas at 350°C for an hour before mounted on a cold finger inside an ultra-high vacuum (UHV) chamber with a base pressure of 6×10^{-10} Torr. We bake the sample at 200°C under vacuum for a few days to further improve surface cleanliness. Figure 1 (right inset) shows the conductivity σ of the pristine device after baking as a function of electron density $n = c_g(V_g - V_{g,min})/e$ where V_g is the gate voltage, $V_{g,min}$ is the gate voltage of minimum conductivity, $c_g = 11$ nF/cm^2 is the gate capacitance, and e is the elementary charge. The field effect mobility $\mu_{FE} = \dfrac{1}{e}\dfrac{d\sigma}{dn}$ and Drude mobility

$\mu_{Drude} = \dfrac{1}{e}\dfrac{\sigma}{n}$ of the sample are about 20,000 cm^2/Vs at a typical charge density of 10^{12} cm^{-2}, which are among the highest for graphene deposited on SiO_2/Si substrates [12]. Assuming Matthiessen's rule for long range and short range scatterers the transport curve can be quantitatively described (red curve) by

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$$\sigma_{pristine}(n) = \left(\frac{1}{ne\mu_L} + \rho_S \right)^{-1} \qquad (1)$$

(details of the fitting procedure are given in [25]). Equation (1) has been interpreted as reflecting scattering by uncorrelated charged impurities with μ_L = 26,530 (21,700) cm^2/Vs and weak point disorder with ρ_s = 53 (55) Ω for holes (electrons) [3,4,12,13,21], though no physical origin for the latter has been identified.

Potassium was deposited by electrically heating up a getter source (SAES Getters) with the sample kept at low temperature T = 20 K. Figure 1 (main panel) summarizes the effects of increasing potassium density on $\sigma(V_g)$ at T = 20 K. $V_{g,min}$ shifts to increasingly negative gate voltages with increased potassium density, reflecting electron doping by potassium. The sample mobility decreases by more than an order of magnitude. These observations agree well with our previous studies [22].

We then measure $\sigma(n)$ at various temperatures from 20 K to 180 K with a fixed $V_{g,min}$ caused by potassium doping. This comprises one set of data with the same density of charged impurities while the impurity location and configuration are changed gradually by the rising temperature.

The K atoms are weakly bound to the graphene surface and desorb at high temperatures. Making use of this property, after completing one set of measurement we bake the sample at 200°C to remove K adsorbates. The sample becomes charge neutral again with mobility returning to the 20,000 cm^2/Vs range. We then cool down to low temperature, and the experiment was repeated with a different K density. We observed no degradation

of sample quality upon repeated experiments; after each baking prior to K doping the sample mobility varied by ±10% and the σ_{min} occured at gate voltages -1V $\leq V_{g,min} \leq$ 1V [25].

Figure 2(a-c) shows $\sigma(V_g)$ at different temperatures for potassium doping levels that result in $V_{g,min}$ shifts $\Delta V_{g,min} \approx$ 78, 41, and 10 V respectively. At all potassium doping levels, the conductivity increases with temperature, more rapidly for $T >$ 100K. The minimum conductivity point $V_{g,min}$ remains fixed for $T <$ 180 K, indicating that doping by potassium persists. (For T > 180 K, we observe $V_{g,min}$ shifts toward 0 V, indicating potassium migration off the sample or desorption.) In addition to mobility improvements, $\sigma(V_g)$ also becomes significantly sub-linear at elevated temperatures, in contrast to the linear $\sigma(V_g)$ expected [6,9-11,26] and observed [22,27] for isolated or clustered charged impurity scattering, and observed here at $T =$ 20 K. The mobility improvement and non-linearity are most pronounced for the largest potassium doping (largest $\Delta V_{g,min}$); the field effect mobility increases over fourfold for the largest $\Delta V_{g,min}$.

In the Boltzmann formalism for charge transport, the square of screened Coulomb scattering potential $\left|\tilde{V}(q)\right|^2$ enters the relaxation time approximation when the charged impurities are uncorrelated. In the presence of correlation, estimation of relaxation time needs to take into account the structure factor $S(q)$ of the scattering centers and $\left|\tilde{V}(q)\right|^2$ is replaced with $\left|\tilde{V}(q)\right|^2 S(q)$ [28]. The structure factor is linked to the spatial distribution of potassium ions via a Fourier transformation. Here we model the spatial correlation with a

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simple pair distribution function $g(r)$ recently proposed by Li *et al.* in Ref.[20]: $g(r)$ is 0

for $r < r_c$ and 1 for $r > r_c$ where r_c is the correlation length, the single additional fit

parameter. The corresponding structure factor is

$$S(q) = 1 - 2\pi n_K \frac{r_c}{q} J_1(qr_c) \tag{2}$$

where J_1 is the Bessel function of the first kind, and n_K is the potassium density. The

resistivity $\rho_K(n, n_K, r_c)$ due to scattering by correlated potassium ions may then be

calculated by numerical integration [25].

Taking further into account the fact that there is some initial disorder in pristine graphene

(right inset of Fig.1) and that there exists temperature-dependent acoustic phonon

scattering [2,29], we fit our transport curves with the following expression:

$$\sigma(n, n_K, T) = \left(\sigma_{pristine}(n)^{-1} + \rho_{ph}(T) + \rho_K(n, n_K, r_c(T))\right)^{-1}. \tag{3}$$

$\sigma_{pristine}(n)$ is determined by fitting to equation (1) (see Fig. 1 right inset) and $\rho_{ph} = [0.1$

$\Omega/\text{K}] \times T$. The only free fitting parameters in equation (3) are n_K and r_c.

For each set of data we treat n_K as a global parameter while r_c varies with temperature.

We note that r_c cannot be smaller than 4.9Å since the densest K overlayer on graphene is

the close packed 2×2 (C_8K) structure [23]. In our fits we fix r_c = 4.9Å at base

temperature. With these considerations we find that our data are well described by

equation (3) as shown by the dashed lines in Fig. 2(a-c) (four additional data sets as well

as fits are shown in [25]). The fits not only describe the mobility increase but also capture the increase in the curvature in σ(n).

Figure 3 summarizes the fit parameters. The correlation length is found to increase monotonically with temperature, and is insensitive to potassium density which varies over an order of magnitude. The lack of variation of r_c with density indicates that the short-ranged pairwise potential between potassium ions dominates the interaction, and the hard-sphere repulsion model is appropriate. The correlation lengths found in Fig.3 are smaller than the K-K distances $\pi n_K r_c^2 < 1$ even at the highest temperatures, consistent with this regime where the pair distribution model [20] is applicable. Using the convention that the close packed 2×2 K overlayer corresponds to the coverage θ=1, the regime that is studied here is 0.001< θ <0.01. At similar K coverage, LEED studies reveal that the K overlayer on graphite gives rise to a distinct diffraction peak that moves to higher wavevectors with adding of potassium and becomes better defined at higher temperatures [30]. These observations are in accord with our experimental results, further substantiating our interpretation that correlation between potassium ions improves with temperature and strongly influences the transport properties of graphene devices. A recent study reported [24] strongly correlated potassium ($\pi n_K r_c^2 \approx 1$) deposited on graphite at 11 K at a density about twice the highest density studied here, probably reflecting a much more disordered landscape for potassium on highly-corrugated [31] graphene on SiO_2.

Figure 3 inset shows n_K as a function of $\Delta V_{g,min}$. At low potassium densities $n_K < n_{imp} \sim 4 \times 10^{11}$ cm^{-2}, there is no theoretical prediction, but the simple prediction from geometric capacitance $n_K = \dfrac{C_g \Delta V_{g,min}}{e}$ (red line) describes our data well. At high potassium densities (greater than the initial impurity density $n_{imp} \sim 4 \times 10^{11}$ cm^{-2}; see below), the experimentally extracted n_K vs. $\Delta V_{g,min}$ can be described by the self-consistent theory for graphene in the presence of random charged impurity disorder [11,22] with the fitting parameter d (distance of impurity to the graphene plane) equal to 1 nm. This deviation qualitatively indicates the incomplete screening by graphene predicted in [11]. That d is somewhat larger than the expect potassium-graphene distance of 0.3 nm may indicate that the self-consistent approximation is not strictly quantitatively correct. Note that the temperature-dependent conductivity data used to probe correlations (Figure 2) were taken at doping levels $n_K \geq n_{imp}$. For the highest doping levels $n_K \approx 10 n_{imp}$ and it is reasonable to neglect n_{imp} in our fits to the correlated impurity theory. That the theory also works well for $n_K \approx n_{imp}$ indicates that the single additional parameter (r_c) describes well the correlations of the mobile impurity population (n_K), however we might expect r_c to be different in the absence of the additional potential imposed by n_{imp}.

Figure 4 shows the temperature dependence of σ_{min}. σ_{min} varies only slightly with potassium doping, as previously observed [22]. Within the self-consistent theory [11], $\sigma_{min} = n^* e \mu$, where n^* is the residual (puddle) carrier density, and μ the mobility. Interestingly, the temperature dependence of σ_{min} is weak, and is very similar to the undoped case ($\Delta V_{g,min} = 0$). This is surprising, given the large increase in mobility; it

suggests a large decrease in the effective (puddle) carrier density at the minimum point for correlated disorder. More work is needed to understand this behavior.

The fact that impurity correlations always produce sublinear $\sigma(n)$ prompts us to revisit the interpretation of equation (1). While experimental evidence for long range scattering (μ_L) prevails [14-16,22], the source of the proposed weak short range scattering (ρ_s) is mysterious. In particular STM measurements have found that point defects in graphene lattice are extremely rare [15,16], and symmetry-breaking point defects are expected to give rise to resonant scattering [32] which experimentally gives a linear $\sigma(n)$ [7]. Meanwhile, it is quite likely that the long range scatterers are correlated to some degree. We find that correlations in long-range scatterers alone can explain the observed sub-linearity in $\sigma(n)$ without invoking point disorder.

In the right inset of Fig.1 we refit $\sigma(n)$ for the pristine graphene sample to the theory for correlated charged impurities, and the result is shown as the blue dashed curve; fit parameters are impurity density n_{imp} = 4.6 (3.9) $\times10^{11}$ cm^{-2} and r_c = 6.1 (7.0) nm for electrons (holes). The fit is almost indistinguishable from equation (1). This is not surprising; for small argument of the Bessel function in equation (2) i.e. $\pi n r_c^2 \lesssim 1$, $\sigma(n)$ is well approximated [20] by equation (1), with $\mu_L = \mu_0/(1 - \alpha)$ and $\rho_s = 290 \ \Omega \times \alpha^2$ where μ_0 is the mobility for uncorrelated charged impurities, $\alpha = \pi n_{imp} r_c^2 < 1$ [25]. This is consistent with the range of observed ρ_s of 50-100 Ω on SiO$_2$ [3,13] and h-BN [21]. Charges are known to be mobile on the surface of SiO$_2$ on a timescale of seconds at room temperature [33]. Assuming that the SiO$_2$ mobile surface charges correspond to a

nondegenerate plasma frozen at a temperature T_0 [17], the correlation length $r_c = \kappa k_B T_0 / n_{imp} e^2 \sim 6$ nm predicts $T_0 \sim 170$ K which is a plausible temperature for freezing the oxide trapped charge configuration. More experiments are needed to understand the degree of correlation of disorder in various substrates used for graphene devices, but intentional correlation of disorder e.g. by control of charge trap distributions or by rapid thermal annealing and quenching should be a powerful tool to increase mobility in graphene devices.

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Figure captions:

FIG. 1 (color online) Potassium deposition on graphene. The main panel shows the low temperature (20 K) gate voltage dependence of the conductivity for the pristine device (black) and successive depositions of potassium (colored). Potassium density for each curve (see below in Fig.3 inset) is indicated (unit: 10^{12} cm^{-2}). The top left inset shows an optical microscope image of the monolayer graphene device used in this experiment, with a schematic of the measurement circuit. The scale bar is 3 μm. The right inset shows the carrier-density-dependent conductivity of the pristine graphene device. The red curve is a fit to equation (1), and the blue curve is a fit to the correlated charged impurity model (see text for fit parameters and discussion).

FIG. 2 (color online) Carrier-density dependence of graphene conductivity at various temperatures for three different potassium doping levels. (a) $\Delta V_{g,min}$ = 78 V. The temperatures are 21.8, 42.5, 100, 116.5, 130.1, 146.3, 156.6, 162.6 K. (b) $\Delta V_{g,min}$ = 41V. The temperatures are 19.4, 50.1, 94.9, 112.8, 126.8, 141.9, 158.5 K. (c) $\Delta V_{g,min}$ = 10V. The temperatures are 20.7, 132.7, 141.9, 150.4, 162, 177.2 K. For each set the curves are ordered from lowest to highest conductivity; the lowest and highest temperatures are also indicated in each panel. The dashed lines are fits to equation (3). The densities of potassium used as global fit parameters are shown for each panel.

FIG. 3 (color online) Fit parameters for data in Fig. 2 to theory of correlated impurity scattering. The main panel shows the correlation length r_c as a function of temperature for

the seven sets of data at different potassium densities reflected in the shift of the minimum conductivity point $\Delta V_{g,min}$ indicated in the legend. The inset shows in log-log scale $\Delta V_{g,min}$ dependence of the potassium densities n_K obtained from the fits. The red dots correspond to the seven sets of temperature dependence data and the grey squares are for other potassium doping levels measured at base temperature only. The lines are theoretical predictions discussed in the text [11].

FIG. 4 (color online) Temperature dependence of the minimum conductivity. Black circles are for pristine graphene and colored symbols are for various potassium densities given by the shift of minimum conductivity point $\Delta V_{g,min}$ indicated in the legend.

Inset (top left): circuit diagram with labels V, I_{sd}, BG, V_g, C_g

Inset (top right):
- long and short range scattering (red)
- correlated charged impurity (blue dashed)
- experiment (black)

$\sigma\ (e^2/h)$ vs $n\ (\times 10^{12}\ cm^{-2})$

Main plot labels:
$\sigma\ (e^2/h)$ vs V_g (V)

T = 20K

0

0.37

1.0

2.1

n_K=3.3