Effect of current annealing on electronic properties of multilayer graphene

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Abstract. While ideal graphene has high mobility due to the relativistic nature of carriers, it is known that the carrier transport in actual graphene samples is dominated by the influence of scattering from charged impurities, which almost conceals the intrinsic splendid properties of this novel material. The common techniques to improve the graphene mobility include the annealing in hydrogen atmosphere and the local annealing by imposing a large biasing current. Although annealing is quite important technique for the experimental study of graphene, detailed evaluation of the annealing effect is lacking at present. In this paper, we study the effect of the current annealing in multilayer graphene devices quantitatively by investigating the change in the mobility and the carrier density at the charge neutrality point. We find that the current annealing sometimes causes degradation of the transport properties.

1. Introduction

Graphene, a single atomic layer of graphite, is expected to take important roles both in fundamental physics and in industrial applications. In fundamental physics, single layer graphene (SLG) attracts a lot of attentions, because an electron in SLG behaves as a massless relativistic particle, called a Dirac fermion, due to the linear energy dispersion. On the other hand, graphene is expected to be applied to future nano electronic devices due to its possible high mobility, reaching 200,000 cm\textsuperscript{2}/Vs at room temperature.

In spite of such expectations, the mobility achieved in actual graphene devices has been limited to one-tenth of the intrinsic value. Possible scattering factors behind the decrease in the mobility include (1) phonons in graphene itself and in the SiO\textsubscript{2} substrate, (2) the structural defects and ripples in the graphene, and (3) the charged impurities originated from the contamination of residual resist, adsorbed gas molecules, and the SiO\textsubscript{2} substrate. We can expect that the influence of factor (2) is relatively small, since it is known that graphene films obtained with the commonly-used micromechanical cleavage technique\cite{2} has a nearly perfect crystal structure over several micrometer range.\cite{3} On the other hand, factor (3) seems to be quite serious since by using a scanning single electron transistor (SET) microscope, Martin \textit{et al.} observed spatial fluctuations of the carrier density, called electron and hole puddles, even at the Dirac point, at which no carrier is supposed to be present.\cite{4} Besides, theoretical study\cite{5} has shown that the charged impurities is the origin of the linearly increasing conductance as a function of the gate voltage, which is commonly observed in experiments.\cite{6} Thus, the charged impurities dominates the transport properties in graphene at low temperatures, concealing the intrinsic relativistic physics.
Annealing is generally known as a method to remove such charged impurities. Two types of annealing methods are used commonly. In the first, graphene on a Si/SiO$_2$ substrate is annealed around 300 °C in Ar/H$_2$ atmosphere. The second is the so-called current annealing by applying a large biasing current to graphene at low temperatures.[7] Although these methods are widely used to remove contamination and adsorbed molecules, how they works has not been investigated in detail so far. In this paper, we study the effect of the current annealing using two techniques: evaluation of the carrier density by the transport measurement and observation of the graphene surface by an atomic force microscope (AFM).

2. Results and discussion

Multilayer graphene (MLG) films were obtained by the standard micromechanical cleavage technique of Kish graphite.[2] Four current and voltage leads are connected to an MLG film by using the electron beam lithography and the deposition of Cr/Au. The highly-doped Si/SiO$_2$ substrate was used as a back gate. Figure 1 shows an optical micrograph of a sample. The samples were set in a low temperature probe stations, and cooled to 4 - 10 K. Current-voltage characteristics were measured as a function of the gate voltage while the temperature rose to room temperature. Conductance was calculated from the current-voltage characteristics. After the first measurement finished, we cooled the sample again without taking it out of the vacuum chamber. Current annealing was performed with a current density around $1 \times 10^8$ A/cm$^2$ for 10 - 20 minutes just before the second measurement started (4 K).

Here, we compare electrical transport before and after the current annealing. Figures 2(a) and 2(b) show the conductance of sample 1 as a function of the gate voltage, $\sigma(V_{\text{gate}})$ for several temperatures before and after the current annealing, respectively. $\sigma(V_{\text{gate}})$ takes a minimum value $\sigma_{\text{min}}$ at a gate voltage corresponding to the charge neutrality point. From the linear part of $\sigma(V_{\text{gate}})$ seen at large $|V_{\text{gate}}|$, we calculated the field effect mobility $\mu$. By using the Drude formula and the relation between the carrier density and the gate voltage, $\mu$ is given by,

$$\mu = \frac{1}{\alpha e} \frac{d\sigma}{dV_{\text{gate}}},$$  \hspace{1cm} (1)

where $\alpha = 7.2 \times 10^{10}$/cm$^2$V is the induced carrier density by the gate voltage change of 1 V. Note that $\mu$ is defined both for electrons and holes. The minimum carrier density $n_0$ corresponding to the charge neutrality point is calculated from the minimum conductivity $\sigma_{\text{min}}$, as follows:
Figure 2. Gate voltage dependence of the conductivity before (a) and after (b) annealing in sample 1. Minimum carrier density as a function of temperature before and after the current annealing for sample 1(c) and sample 2(d).

\begin{equation}
  n_0 = \frac{\sigma_{\text{min}} \cdot 2}{e \cdot (\mu_h + \mu_e)},
\end{equation}

where \(\mu_h\) and \(\mu_e\) are the hole and electron mobilities, respectively.

Figure 2(c) shows the minimum carrier density \(n(0)\) before and after the annealing for sample 1. By the current annealing, the mobility rises and the minimum carrier density decreases for all temperature range; the hole mobility changes from 3,500 to 4,300 cm\(^2\)/Vs, and the carrier density from 6.9 \times 10^{12} to 5.2 \times 10^{12}/cm\(^2\) at 4 K. This result suggests that the number of charged impurities were decreased by the current annealing. Sample 2, however, shows the opposite result: the mobility decreases and the minimum carrier density increases by the current annealing, as shown in Figure 2(d): the mobility changes from 8,500 to 5,300 cm\(^2\)/Vs and the carrier density changes from 5.3 \times 10^{12} to 6.3 \times 10^{12}/cm\(^2\) at 4 K. This result indicates the increase of the charged impurities despite of the current annealing. So far we have examined seven samples; four samples behaved like sample 1: the current annealing increased the mobility and decreased the minimum carrier density. On the other hand, three samples were similar to sample 2: the current annealing decreased the mobility and increased the minimum carrier density.

To investigate the origin of the contradicting effects of the current annealing on the transport properties of graphene, we observed the surface of the samples after the current annealing with the AFM. The results are shown in Fig. 3. Sample 1 (Fig. 3(a)) has a flat surface with asperity below 1
nm. In contrast, sample 2 has rough surface near the electrodes with roughness from several nanometers to several 10 nm. At present, the origin of this rough surface is not clear, but we have confirmed that the formation of rough surface is closely related to the current annealing and that the degradation of the mobility and the increase of the minimum carrier density are seen only in samples with rough surfaces induced by current annealing. The details will be published elsewhere.

3. Conclusion
We have studied the effect of current annealing in graphene by transport measurements and AFM observation. The results are classified into two categories; in the first, the current annealing removes contamination as expected, and increases the mobility and decreased the carrier density by the order of $10^{12}/\text{cm}^2$. On the contrary, in the second case, the current annealing accumulates the contamination, suppresses the mobility and increases the carrier density. To improve the transport properties of graphene using the current annealing, we need to optimize the annealing conditions.

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Figure 3. AFM image of sample 1 (a) and sample 2 (b) after annealing.