Negative magnetoresistance in Ti-cleaned single-layer graphene

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Abstract. Symmetric graphene tunneling field-effect transistors (SymFETs) consisting of two independently gated graphene layers separated by a potential barrier have been proposed as a room-temperature resonant tunneling device. In a SymFET, the inelastic-coherent length ($L_\phi$) of the electrons is considered to be one of the important characteristic scattering lengths. Weak localization (WL) is a good tool to estimate $L_\phi$. In this study, the surface of the chemical-vapor-deposited single-layer graphene was Ti cleaned after performing the conventional fabrication processes for graphene transistors. We found that the charge-neutral point ($V_{\text{CNP}}$) shifted to a lower back-gate voltage and the mobility increased owing to Ti cleaning. Ti-cleaned Hall bars were investigated at 0.3 K under magnetic fields of up to 14 T. Negative magnetoresistance (MR) appears because of the WL effect, and the MR increases as the back-gate voltage ($V_G$) approaches $V_{\text{CNP}}$. From a fitting analysis using the theoretical formulation of WL, we found that $L_\phi$ was greater than 100 nm and that $L_\phi$ decreased as $V_G$ approached $V_{\text{CNP}}$ because of electron–hole puddles and electron–electron interaction.

1. Background

Graphene is a promising candidate for future electronic devices owing to the high mobility of its carriers and its perfect two-dimensionality. However, single-layer graphene transistors have a low on–off ratio due to the zero bandgap. Therefore, new transistors using double-layer graphene have been proposed, among which is the bilayer pseudospin field-effect transistor (BiSFET) [1]. In a BiSFET, electrons and holes in respective layers form excitons, and Bose–Einstein condensation occurs. Consequently, the tunnel resistance between two layers reduces and a high on-current is obtained. However, BiSFET operation has not been experimentally demonstrated. Another new type of transistor is the symmetric graphene tunneling field-effect transistor (SymFET) [2, 3], which consists of two independently gated graphene layers separated by a tunnel barrier. The SymFET has been proposed as a room-temperature resonant tunneling device because a large resonant current is produced when the Dirac points of the graphene sheet are aligned by the applied voltage, resulting in negative differential resistance (NDR). This phenomenon requires that the tunneling electrons conserve their lateral momentum, and the inelastic-coherent length ($L_\phi$) of the electrons is considered to be one of the important characteristic scattering lengths. In our previous studies, we fabricated double-layer graphene with h-BN tunnel dielectrics formed using CVD. The conventional tunneling...
characteristics for these devices were equivalent to similar characteristics for exfoliated devices [4, 5]. However, devices fabricated using CVD graphene and h-BN have not yet exhibited a large resonant peak and NDR.

In comparison with exfoliated graphene, chemical-vapor-deposited (CVD) graphene is better for fabricating devices on a large scale. However, the charge-neutral point ($V_{\text{CNP}}$) of CVD graphene appears at a relatively high back-gate voltage because of molecular adsorption [6] and impurities on the graphene surface. One of the challenges with CVD graphene is that the transfer process typically results in contamination, which is very difficult to remove. A good method to overcome this issue is Ti cleaning [7]. Some researchers have reported p-type and n-type graphene produced using the adsorption of Ti. Li et al. [8] reported a p-type graphene FET with titanium oxide on the graphene surface. The conductance ($G$) is not controlled by the back-gate voltage, and the Fermi level is pinned between an electrode and graphene. Iqbal et al. [9] reported an n-type Ti-coated graphene FET and showed that the $V_{\text{CNP}}$ shifts toward a negative back-gate voltage and electron transport becomes dominant.

In this study, by performing Ti cleaning during the graphene Hall bar fabrication process, we improved the graphene surface to observe quantum transport phenomena. In particular, weak localization (WL) measurements were performed to estimate the inelastic and intervalley scattering lengths.

2. Experimental

CVD single-layer graphene on Cu purchased from ACS Material was used. A solution-based transfer process was used to transfer the graphene onto 90 nm or 268 nm SiO$_2$ on Si substrates, and then annealed in forming gas [10]. Back-gated Hall bars were fabricated using conventional photolithography and etching in O$_2$ plasma. Electrodes were fabricated with e-beam evaporation for the deposition of Ni contacts with Au. After patterning CVD-graphene Hall bars, 2 nm of Ti was deposited on the graphene using e-beam evaporation and allowed to oxidize to Ti oxide upon exposure to air. The Ti oxide was then removed with HF, and the graphene surface was cleaned of resist residue.

Four kinds of graphene Hall bars were employed in our measurements as shown in Table 1. Figure 1 shows one of the measured single-layer graphene Hall bars. Two Hall bars, one with (#1) and the other without Ti cleaning (#2), were measured in this study at 77 K. At low temperatures, we examined another two Ti-cleaned Hall bars on 268-nm-thick SiO$_2$ (#3 and #4). #3 and #4 were fabricated on the same die. We employed a 3He cryostat system with a 14 T superconducting magnet for cooling to 0.3 K. At low temperatures, a standard ac lock-in technique was used with an excitation current of 50 nA to prevent Joule heating. Our measurements in the magnetic field were performed for different carrier types and densities controlled using the back-gate voltage ($V_G$).

| Sample No. | SiO$_2$ thickness (nm) | Ti-cleaning |
|------------|------------------------|-------------|
| #1         | 90                     | with        |
| #2         | 90                     | without     |
| #3         | 268                    | with        |
| #4         | 268                    | with        |
3. Results and Discussion

Figure 2 shows the $V_G$ dependence of longitudinal resistance ($\rho_{xx}$) with (#1) and without Ti cleaning (#2) at 77 K. $V_{\text{CNP}}$ decreases to approximately $V_G = 0$ V owing to Ti cleaning, and the mobility increases with Ti cleaning. The graphene Hall bars tended to become $n$-type with Ti cleaning (#1), and this result supported the report by Iqbal et al. [9]. To analyze the data, we employed the constant mobility model proposed by Kim et al. [11]. The graphene transistor’s resistance ($R$) consists of contact ($R_{\text{Cont}}$) and channel resistances ($R_{\text{Channel}}$), in which carrier concentration in the graphene channel is expressed as the square root of the sum of the squares of intrinsic carrier concentration ($n_0$) and carrier concentration ($n_{\text{ind}}$) induced by back-gate voltage ($V_{\text{bg}}$), where $V_{\text{bg}}^* = V_G - V_{\text{CNP}}$. Kim et al. assumed that the mobility ($\mu$) is constant and independent of $V_G$. The resistance is expressed as follows:

$$R = R_{\text{Cont}} + R_{\text{Channel}}$$

$$= R_{\text{Cont}} + \frac{L}{W} \left( n_0^2 + n_{\text{ind}}^2 (V_{\text{bg}}^*) \right) \frac{e \mu}{\sqrt{e \mu}}.$$  

Here, $e$ is the electron charge and $L$ and $W$ are the length and width of the measured device, respectively. Table 2 lists the parameters extracted with a fitting analysis using Kim’s model. By performing Ti cleaning, $\mu$ increases and $n_0$ decreases because of the improvement of the graphene surface. The most important advantage of Ti cleaning is that the $V_{\text{CNP}}$ shifts to a lower $V_G$. On the other hand, $R_{\text{Cont}}$ increases; as we perform the Ti-cleaning after fabricating the electrodes, Ti cleaning seems to negatively affect $R_{\text{Cont}}$. Furthermore, we have checked the electrical properties of various CVD
graphene transistors and confirmed that $V_{\text{CNP}}$ shifts to a lower $V_G$ and $\mu$ improves upon Ti cleaning [7]. On the other hand, Morozov et al. reported that resistivity of doped graphene could empirically be described by two contributions: $\rho_L \propto 1/n$ and $\rho_S$ independent of $n$ due to long- and short-range scatterers, respectively, where $n$ is the carrier concentration [12]. The constant mobility model proposed by Kim et al. is also composed of two terms, which are dependent and independent of $n$. Therefore we need to measure the detailed temperature dependence of resistivity of graphene and discuss our results in the future.

Figure 3 shows the $V_G$ dependence of $\rho_{xx}$ for two Ti-cleaned single-layer graphene Hall bars with a 268-nm-thick SiO$_2$ film at 0.3 K and 0 T. $V_{\text{CNP}}$ appears at +13 V for the two Hall bars, and its value is larger than that of Hall bar #1 because of the SiO$_2$ film. Figure 4 shows $\rho_{xx}$ and Hall resistance ($\rho_{xy}$) of Hall bar #3 at 0.3 K and a magnetic field of 14 T applied perpendicular to the graphene surface. The value of $\rho_{xx}$ appears to oscillate under the magnetic field ($B$) with changing $V_G$, and the sign of $\rho_{xy}$ inverts at $V_{\text{CNP}}$. Furthermore, we calculated $\sigma_{xx} (= \rho_{xx} / (\rho_{xx}^2 + \rho_{xy}^2))$ and $\sigma_{xy} (= \rho_{xy} / (\rho_{xx}^2 + \rho_{xy}^2))$. Figure 5 shows the quantum Hall plateaus, which exhibits a half-integer step ($0.5 \times 4e^2/h$). This indicates that the samples are single-layer graphene [13]. However, $\sigma_{xx}$ is not 0 at the Hall plateaus. In fact, there exists some mixing between $\sigma_{xx}$ and $\sigma_{xy}$. At 0.3 K Hall mobility of Hall bar #3 is $3.6 \times 10^3$ cm$^2$/Vs at $V_G = 0$ V.

Figure 6 shows the $V_G$ dependence of the magnetoresistance (MR) for magnetic fields less than 1 T at 0.3 K. The figure shows three MR curves of Hall bar #3 for $V_G = -60$ V (hole transport region), +13 V (charge neutral point), and +60 V (electron transport region). The vertical axis in figure 6 represents the ratio $\Delta \rho_{xx}(B) / \rho_{xx}(0)$, which is the rate of change of MR to the resistance in the absence of a

### Table 2. Characteristic parameters extracted with a fitting analysis using Kim’s model.

|                  | $R_{\text{cont}}$ (Ω) | $n_0$ (cm$^{-2}$) | $\mu$ (cm$^2$/Vs) | $V_{\text{CNP}}$ (V) |
|------------------|-----------------------|-------------------|-------------------|----------------------|
| With Ti cleaning (#1) | 7.1 x 10$^2$          | 3.0 x 10$^{11}$   | 4.6 x 10$^3$      | -0.6                 |
| Without Ti cleaning (#2) | 4.9 x 10$^2$          | 1.2 x 10$^{12}$   | 7.8 x 10$^2$      | +26                  |
magnetic field. The MR shows a gradual decrease with $B$ and increases as $V_G$ approaches $V_{\text{CNP}} (= +13 \, \text{V}$ for this Hall bar). The negative MR at $V_G = +13 \, \text{V}$ is several times larger than that at $V_G = -60 \, \text{V}$. The negative MR is caused by the WL effect. WL is a constructive quantum interference effect of the scattered electron waves at low temperatures. The WL states for electrons are broken by a magnetic field and inelastic scattering such as phonon scattering, which reduces resistance. The theory of MR due to the WL in single-layer graphene was proposed by McCann et al. [14]. The theory should hold for not only inelastic but also elastic scattering. Elastic scattering that breaks chirality will destroy the interference within each of the two graphene valleys in $k$ space. The theory is expressed as follows:

$$\Delta \rho(B) = \frac{e^2 \rho}{\pi h} \left[ F\left(\frac{B}{B_\phi}\right) - F\left(\frac{B}{B_\phi + 2B_i}\right) - 2F\left(\frac{B}{B_\phi + B_s}\right) \right],$$

(3)

$$F(z) = \ln z + \psi\left(\frac{1}{2} + \frac{1}{z}\right),$$

(4)

**Figure 4.** $\rho_{xx}$ and $\rho_{xy}$ as functions of $V_G$ of Hall bar #3 at 0.3 K and 14 T.

**Figure 5.** $\sigma_{xy}$ as a function of $V_G$ calculated with $\rho_{xx}$ and $\rho_{xy}$.

**Figure 6.** Back-gate voltage ($V_G$) dependence of MR at 0.3 K.
The first term in equation (3) is responsible for WL, while the other terms express weak anti-localization (WAL). Here, $\rho$ is the resistivity, $h$ is the Planck’s constant, $\psi(x)$ is the digamma function, $D$ is the diffusion constant, and $\tau_*^{-1} = \tau_w^{-1} + \tau_i^{-1} + \tau_z^{-1}$. $\tau_w$, $\tau_i$, and $\tau_z$ are the inelastic, intervalley, and intravalley scattering times, respectively. $\tau_w$ is the effect of trigonal warping. One can see that the curve for $V_G = +13 \text{ V}$ in figure 6 has a steeper upward turn, indicating the greater importance of the second and third terms (WAL) in equation (3) for magnetic fields above 0.3 T. On the other hand, the curves for $V_G = -60 \text{ and } +60 \text{ V}$ show only negative MR, indicating the importance of the first term (WL) in equation (3). In this study, we focus on the negative MR below 0.1 T. We confirmed that $\tau_w$ and $\tau_i$ did not contribute to our MR data by performing the fitting analysis. That is, the effect of trigonal warping and intravalley scattering are suppressed in our Hall bars. Therefore, we performed the fitting analysis with the assumption $B_i = B_w$. Figures 7 and 8 show the results of the fits for $V_G = +13 \text{ V}$ and $+60 \text{ V}$ for Hall bar #3, respectively. The black circles represent the experimental data, and the black solid lines represent the fitting results.

$$B_w = \frac{h}{4D\tau_w}, \quad B_i = \frac{h}{4D\tau_i}, \quad B_z = \frac{h}{4D\tau_z}. \quad (5)$$

Figure 7. Fitting result for $V_G = +13 \text{ V}$ for Hall bar #3 below 0.1 T. Black circles represent the experimental data, and the black solid line is the fitting result.

Figure 8. Fitting result for $V_G = +60 \text{ V}$ for Hall bar #3 below 0.1 T. Black circles represent the experimental data, and the black solid line is the fitting result.

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Figure 9 shows the gate-voltage dependence of the inelastic-coherent ($L_\phi$) and intervalley scattering lengths ($L_i$) extracted from the MR analyses for Hall bars #3 and #4. At a temperature of 0.3 K, $L_\phi$ is greater than 100 nm. $L_\phi$ is also observed to decrease as $V_G$ approached $V_{\text{CNP}}$. Although the average carrier concentration vanishes at $V_{\text{CNP}}$, electrons and holes may form electron–hole puddles. Electrons and holes inelastically scatter more frequently because of the electron–hole puddle and electron–electron interaction [15]. On the other hand, $L_i$ is nearly constant with respect to $V_G$, but $L_i$ is always less than $L_\phi$. The mechanism of intervalley scattering is considered to be the significant fluctuations in potential energy in the atomically sharp defects. The atomically sharp defect is known to strengthen the intervalley scattering [16]. In our Hall bars, the atomically sharp defects might originate from dislocations and some domains in our CVD graphene.
4. Conclusions

Ti cleaning was performed after the conventional fabrication of CVD single-layer graphene Hall bars in order to clean the surfaces. $V_{\text{CNP}}$ appeared at a lower back-gate voltage and the mobility increases because of the Ti cleaning. At 0.3 K, negative MR appears because of the WL effect. As $V_G$ approaches $V_{\text{CNP}}$, the negative MR increases. By performing a fitting analysis using the theoretical expression, $L_\phi$ was observed to decrease as $V_G$ approaches $V_{\text{CNP}}$ because of electron–hole puddles and electron–electron interaction. On the other hand, $L_i$ is nearly constant with respect to $V_G$, and $L_i$ is always less than $L_\phi$, indicating that atomically sharp defects might influence the intervalley scattering. In order to examine the origins of the inelastic scattering at $V_{\text{CNP}}$ and the other scattering mechanisms, a detailed investigation of the $V_G$ and the temperature dependences of the MR is required. Our results will stimulate further investigations on the physics of graphene and applications such as SymFET.

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