The excess of dephasing rate in the gas annealed CVD graphene

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Abstract

Graphene was expected to prove useful in the field of spintronics because a long spin relaxation time (few micro second) was theoretically expected. However, experimental results using exfoliated graphene have shown that the spin relaxation time is a few orders of magnitude less than the theoretical prediction. It was discovered that the reason for this unexpected shorter spin relaxation time is the presence of magnetic moments on graphene and magnetic moments exist on most forms of graphene. Many theoretical articles expected these magnetic moments to arise due to graphene defects. However, it is not experimentally clear where and how they arise.

To answer where and how, we investigates it with dephasing rate (phase relaxation rate) monitored via weak localization on graphene, grown by chemical vapour deposition (CVD graphene). The experiments are performed on field-effect devices made from CVD graphene on various substrates under perpendicularly applied magnetic fields at 4.2 K. The samples are thermally annealed under various conditions, which is a commonplace technique used to clean the surface of graphene.

Only the gas annealing induces the additional source of dephasing rate on CVD graphene. However, this could not be seen in before-annealed samples and vacuum annealed samples. Additional experiment confirms that this additional source on gas annealed sample has the magnetic property. The result on this thesis can help answer the origin of magnetic moments on graphene.

Lay summary

Various distinctive properties in graphene, consisting of a single layer of carbon, has been theoretically predicted and verified experimentally. There are also active studies on various applications utilizing these characteristics. Among them, spintronics, which is expected to replace the conventional semiconductor technology, attracted considerable interest early in the discovery of graphene. However, the relaxation time of spin in graphene, which is the core of spintronics, is measured in a short time in actual experiments, compared to theoretical expectation. Hence, graphene is difficult to use it as spintronics.

The finding in this thesis could help explain the short spin relaxation time in graphene. In this thesis, we show that annealing under gases, which is the conventional way to clean the surface of graphene, induces an additional interaction source on graphene grown by Chemical vapor deposition method (CVD). Experiments were carried out with resistance measurements in a perpendicularly applied magnetic field at 4.2 K, before and after annealing under various condition.

Preface

Chapter 4 is based on work conducted in Quantum devices group in University of British Columbia by me and my supervisor, Dr. Joshua Folk, research associate Dr. Silvia Lüscher Folk, and our collaborators at the University of British Columbia, Dr. Ali Khademi, and Dr. Rui Yang. I conducted all experiments and data analysis and developed the interpretation and conclusion of the experiment under the supervision of Dr. Joshua Folk.

All of the sample fabrication processes, such as exfoliation and electron beam lithography, were done by the author. Dr. Ali Khademi provided a test sample made from CVD graphene on SiO_2 substrate. The additional experiment with in-plane magnetic fields on Appendix F was conducted by Dr. Silvia Lüscher Folk. Dr. Silvia Lüscher Folk has the authorship of the results of these additional experiments.Result of this thesis is soon to be submitted for publication.

The following figures were taken and from each corresponding article and modified:

Figure 2.1: Neto AC, Guinea F, Peres NM. Drawing conclusions from graphene. Physics World. 2006 Nov;19(11):33. [1]

Figure 2.2: Neto AC, Guinea F, Peres NM, Novoselov KS, Geim AK. The electronic properties of graphene. Reviews of modern physics. 2009 Jan 14;81(1):109. [2]

Figure 2.3 (a): Novoselov KS, Geim AK, Morozov SV, Jiang DA, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA. Electric field effect in atomically thin carbon films. science. 2004 Oct 22;306(5696):666-9. [3]

Figure 2.3 (b): Novoselov KS, Geim AK, Morozov S, Jiang D, Katsnelson M, Grigorieva I, Dubonos S, Firsov AA. Two-dimensional gas of massless Dirac fermions in graphene. nature. 2005 Nov;438(7065):197. [4]

Figure 2.3 (c): Morozov SV, Novoselov KS, Katsnelson MI, Schedin F, Ponomarenko LA, Jiang D, Geim AK. Strong suppression of weak localization in graphene. Physical review letters. 2006 Jul 5;97(1):016801. [5]

Figure 3.5: Geim AK, Novoselov KS. The rise of graphene. InNanoscience and Technology: A Collection of Reviews from Nature Journals 2010 (pp. 11-19). [6] Preface

Figure 5.1: Chen JJ, Wu HC, Yu DP, Liao ZM. Magnetic moments in graphene with vacancies. Nanoscale. 2014;6(15):8814-21. [7]

Table of Contents

A	ostra	\mathbf{ct} ii	i
La	y su	mmary iv	V
Pr	eface	e	V
Ta	ble o	of Contents	i
Li	st of	Tables	¢
\mathbf{Li}	st of	Figures	K
A	cknov	vledgements	i
1	\mathbf{Intr}	oduction	1
2	The	oretical background	1
	2.1	Graphene	1
		2.1.1 Honeycomb structure in real space and k-space 4	1
		2.1.2 Tight binding model - Energy dispersion in Graphene	3
		2.1.3 Transport properties of graphene	7
	2.2	Weak localization)
		2.2.1 Weak localization in graphene)
	2.3	Various source of the dephasing 12	2
3	\mathbf{Exp}	erimental setup and background	5
	3.1	Sample preparations	3
		3.1.1 CVD graphene on various substrates	3
		3.1.2 Exfoliated graphene on SiO_2)
		3.1.3 Lithography process)
	3.2	Rapid thermal annealing system)
	3.3	Measurement system at 4.2K - Dunker	1
	3.4	4 probes measurement with magnetic fields 23	3

Table of Contents

4	\mathbf{Exp}	erimental result
	4.1	Measurement process 26
		4.1.1 Weak localization fitting
	4.2	CVD graphene on Silicon Oxide
		4.2.1 Before-annealed CVD graphene
		4.2.2 Ar gas annealed CVD graphene
		4.2.3 Vacuum annealed CVD graphene
	4.3	CVD graphene on Hafnium Oxide (HfO_2) substrate 35
	4.4	Air exposure on CVD graphene on Silicon Oxide
	4.5	Comparison experiments to hBN and exfoliated graphene . 40
	4.6	Summary
		4.6.1 The excess of dephasing rate in CVD graphene 41
		4.6.2 Summary
5	Con	clusion
Bi	bliog	\mathbf{graphy}

Appendices

\mathbf{A}	Details of sample fabrication	54
	A.1 Exfoliation	54
	A.2 CVD graphene Transferring	55
в	Weak localization fitting function	56
С	Surface temperature on RTA	58
D	Error bar in fitting process	60
	D.1 Temperature fluctuation	60
	D.2 Conductivity depending on magnetic fields	60
	D.3 Fitting parameters	61
\mathbf{E}	Additional experimental data	62
	E.0.1 CVD graphene on hexagonal Boron Nitride (hBN)	62
	E.0.2 Exfoliated graphene	63
\mathbf{F}	Additional experiment with in-plane magnetic fields	66

List of Tables

3.1	Various types of graphene on various substrates samples	16
C.1	Surface temperature in RTA	59

List of Figures

2.1	Carbon allotrope and graphene structure	5
2.2	Electronic dispersion of graphene	7
2.3	Transport properties in Graphene	8
2.4	Weak localization from the loop	9
2.5	Weak localization in graphene	11
3.1	Various of graphene samples	17
3.2	Device chip carrier	18
3.3	Rapid Thermal Annealing system	20
3.4	Measurement system	22
3.5	Electric field effect in graphene and the schematic sample	24
	geometry	24
4.1	Example of experiment result	27
4.2	Before-annealed graphene result	30
4.3	Ar annealed CVD graphene result	32
4.4	Vacuum annealed CVD graphene result	34
4.5	CVD graphene on HfO2 substrate	35
4.6	Hafnium Oxide sample result	37
4.7	Air and moisture exposure result	39
4.8	The excess of dephasing result	42
5.1	Induced magnetism from the vacancy on graphene	45
A.1	sample fabrication process	54
A.2	CVD graphene transfer process	55
C.1	RTA for surface temperature test	58
E.1	Graphene on hBN result: conductivity changes	62
E.2	Graphene on hBN result: the dephasing rate VS e-e interac-	e o
E.3	Exfoliated graphene result: before and after annealing	63 64

F.1	In-plane magnetic fields data									•										6	6
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Chapter 1

Introduction

Graphene was expected to prove useful in the field of spintronics because a long spin relaxation time was theoretically expected [8]. However, experimental results using exfoliated graphene have shown that the spin relaxation time is a few orders of magnitude less than the theoretical prediction [9–12]. It was discovered that this shorter spin relaxation is due to magnetic moments on graphene [13]. It has further been discovered that these magnetic moments are one of the dominant causes of the suppression of quantum mechanical coherent effects among conduction electrons. This suppression of coherent effect is called dephasing (phase relaxation) [14]. Magnetic moments exist on most forms of graphene, such as exfoliated, epitaxial, and chemical vapour deposited (CVD) graphene [14, 15]. Many theoretical articles expected these magnetic moments to arise due to graphene defects [16–19]. However, experimentally, it has not been made clear where they come from and how they arise. The result of experiments in this thesis can help to answer those questions with respect to CVD graphene.

The work described in this thesis started as an extension of a previous experiment by Dr. M. Lundeberg [14] from the Quantum Devices group at the University of British Columbia (UBC). His work showed, via charge transport measurements, that magnetic moments on exfoliated graphene are a significant source of dephasing. After this publication, the Quantum Devices group compared those exfoliated graphene results to analogous behaviours observed in CVD graphene. It is interesting to compare these two forms of graphene because exfoliated graphene (which is peeled off using adhesive tape) and CVD graphene have many different extrinsic physical properties, such as charge mobility and contamination level, yet in other ways are very similar. Surprisingly, the group found (anecdotally) that the the dephasing rate in CVD graphene was very different before and after annealing. Before annealing, CVD graphene and exfoliated graphene showed the same dephasing rates. After gas annealing, however, CVD graphene showed a drastic change of dephasing rate compared to exfoliated graphene.

The main goals of this thesis were to understand why the dephasing rate in CVD graphene depends so strongly on annealing, and to investigate the properties of this enhanced dephasing. To this end, experiments on fieldeffect devices made from CVD graphene were performed, before and after thermal annealing processes. The dephasing rate was monitored via weak localization and magnetoresistance measurements at 4.2 K. Also, whether the source of the increased dephasing rate has magnetic properties was established through the application of in-plane magnetic fields as an additional experiment.

A crucial part of this work was the extraction of a dephasing rate for graphene via a fitting function of weak localization theory. Weak localization theory is a quantum mechanical conductivity correction, and it is affected by various interactions in graphene, such as inter- or intra-valley scatterings and dephasing [20]. Therefore, scattering rates and the dephasing rate can be extracted using weak localization theory. From this extracted dephasing rate, various interactions can be investigated as sources of dephasing by comparing the behavior as a function of temperature or comparing with interaction rate models [21, 22].

The samples were annealed under various conditions. Annealing is the conventional method used to remove water and chemical residues from graphene and other 2D materials, for example to make better ohmic contact to the sample [23]. Annealing can also improve mobility and other electronic properties [24–26]. However, this annealing could induce some unintentional results [27]. For example, it can cause carbon to be dissolved from graphene to the metal contacts [23] and graphene to be excessively adsorbed into the substrate [24]. Likewise, thermal annealing could in principle induce unintentional effects in CVD graphene, which could activate or create magnetic moments.

By comparing various annealing processes and analyzing based on weak localization theory, the conditions of unusual enhancement of the dephasing rate and its specific properties for CVD graphene were investigated. Specifically, CVD graphene on several different substrates were annealed under various gas conditions, and the dephasing rate was extracted via weak localization fitting. Finally, the unknown source of the increased dephasing rate was investigated through additional experiments involving the application of in-plane magnetic fields, which can confirm the presence of magnetic moments.

As a result, it was demonstrated that thermal annealing in an inert gas dramatically increases the CVD graphene's dephasing rate at a temperature of 4.2 K. This increased dephasing rate shows several distinctive properties, such as a minimum rate at zero gate voltage and the increase as a function of the charge carrier density.

This thesis consists of four main chapters; In Chapter 2, theoretical backgrounds for graphene, the dephasing mechanism, and weak localization are briefly given. Weak localization theory in graphene is also explained in connection with dephasing. In Chapter 3, graphene sample preparation and fabrication are outlined, as are associated experimental setups, such as the annealing and sample measurement systems. Experimental results for various graphene samples annealed under different atmospheric conditions are shown in Chapter 4. Lastly, Chapter 5 concludes the annealed CVD graphene experiments and discusses possible mechanisms which can create or activate magnetic moments on CVD graphene. In the Appendix, further details of sample fabrications and the fitting functions for use with weak localization theory are explained. Also, the details and results of sample surface temperature measurements in the annealing system are shown. Appendix also contains the results of exfoliated graphene, CVD graphene on hBN, and the additional experiments using in-plane magnetic fields, which can give information on any magnetic moments on annealed CVD graphene.

Chapter 2

Theoretical background

This chapter gives brief theoretical backgrounds for graphene, weak localization and source mechanisms of dephasing. Specifically, the following topics are described in each section.

- Graphene (Section 2.1)
- Weak localization (Section 2.2)
- Various source of dephasing (Section 2.3)

2.1 Graphene

Carbon, which has atomic number 6 with 6 electrons per atom, has many different allotropes as shown in Figure 2.1 (a). Graphene is one of these allotropes, which has a two-dimensional (2D) structure. Specifically, it has a single atomic layer of carbon with 1.1 Å thickness and these carbon atoms form a honeycomb or benzene ring structure. Graphene has many interesting physical properties because of this honeycomb structure. For example, it has linear energy dispersion with Dirac point, and shows distinctive properties in transport measurements [3, 28]. These physical properties make graphene distinct compared to conventional 2D materials. In the following sections, a theoretical background of graphene and details of its physical properties are given.

2.1.1 Honeycomb structure in real space and k-space

In a primitive cell of graphene, two carbon atoms are covalently bonded at a distance of 1.42 Å as shown in Figure 2.1 (b) and (c). These two carbon atoms are named A (filled circle) and B (empty circle). It can be seen that the structure is honeycomb in real and momentum space. Based on this hexagonal structure, the lattice vectors of graphene in real space can be 2.1. Graphene



Figure 2.1: Carbon allotrope: graphene, graphite, carbon nanotube, and fullerene (C60) from top left to bottom right (Taken from Ref. [1]) Graphene lattice structure in (b) real space and (c) momentum space. Carbon atoms site on circles A and B with 1.42Å. The dashed line of rhombus indicates unit cell of graphene and solid arrows indicate lattice vectors.

written as

$$a_1 = \frac{\sqrt{3}}{2}a\hat{x} + \frac{3}{2}a\hat{y}, \ a_2 = -\frac{\sqrt{3}}{2}a\hat{x} + \frac{3}{2}a\hat{y}, \tag{2.1}$$

where $a \approx 1.42$ Å.

These vectors form a rhombus shaped unit cell [Figure 2.1 (b)]. The reciprocal-lattice vectors can be written in a similar way, as shown in Figure 2.1 (c). For a honeycomb structure in momentum space, there are two special points K and K' at the corner of the Brillouin zone. The following section will show why these points are special for graphene. Although a single carbon atom has 4 out of the 6 electrons filling the 2s and 2p orbital states, the outer orbitals $2s, 2p^3$ of the lattice are hybridized into $2sp^2$ and $2p_z$ orbitals between carbon atoms and form a trigonal planar structure in graphene. These hybridized orbitals also form π (conduction band), σ , and π^* (valence band) bonds where the π bond has only one electron due to the Pauli exclusion principle. Since this π state is half-filled and protrudes out of the 2D-plane, most of the electrical transport properties are determined by this half-filled state. Such lattice vectors and hybridized orbitals enable graphene to have distinctive properties from other 2D materials [29, 30]. This can be easier demonstrated in momentum space than real space.

2.1.2 Tight binding model - Energy dispersion in Graphene

In this subsection, distinctive energy dispersion in graphene will be explained. The Hamiltonian for graphene in real space with a hopping term $(t \approx 3 \text{ eV})$, between the nearest neighbor orbitals [A \rightarrow B or B \rightarrow A in Figure 2.1 (a)] which is the half-filled state, is given following Equation 2.2 by [31].

$$H_0 = E_0 - t \sum_r |r, A\rangle \left[\langle r, B | + \langle r - a_1, B | + \langle r - a_2, B | + h.c \right]$$
(2.2)

where a_1 and a_2 are lattice vectors in Equation 2.1 and r indicates the position in the real space. E_0 is the potential energy which is influenced by the orbital binding energy and electrostatic potentials from external fields. Because the physical properties of graphene are represented better by the dispersion relation in momentum space, the energy dispersion relation in momentum space is calculated from the real space Hamiltonian in Equation 2.2:

$$E(k) = E_0 \pm t \sqrt{1 + 4\cos^2\left(\frac{\sqrt{3}}{2}k_xa\right) + 4\cos\left(\frac{\sqrt{3}}{2}k_xa\right)\cos\left(\frac{3}{2}k_ya\right)} \quad (2.3)$$

where a is 1.42 Å, t is the hopping energy, and k_x and k_y are coordinates of momentum space.

At K and K', Equation 2.3 becomes zero when $E_0 = 0$. Moreover, when we use the low energy approximation around K and K', we can find a special energy dispersion relation [30]. That is,

$$\pm E(q) = \pm v_F q \tag{2.4}$$

where v_F is Fermi velocity and q is the momentum measured from the K or K'. Since the energy is zero at q = 0, the so-called Dirac point as shown in Figure 2.2, graphene is classified as a zero bandgap semiconductor or semimetallic [6, 31]. This zero-energy point symmetrically forms the valley at K and K' [Figure 2.2 zoom-in]. In these valleys, intravalley and intervalley scatterings occur and contribute to diverse distinctive properties, such as various interaction sources in weak localization [3, 20, 32]. The details of these interaction scatterings with weak localization will be discussed in Section 2.2.1. Moreover, when spin components including isospin from the sublattice (A and B), pseudospin from the valley (K and K'), and real spin are included in the Hamiltonian of Equation 2.2, graphene has more degrees of freedom and the chirality between sublattice and momentum [29].



Figure 2.2: Electronic dispersion in the honeycomb graphene lattice. Zoom in of the energy bands close to one of the Dirac points: this shows two valleys above and below the Dirac point. (Taken from Ref. [2])

2.1.3 Transport properties of graphene

The motion of electrons in graphene is governed not only by intrinsic properties involving linear energy dispersion described above but also by extrinsic properties. One of the extrinsic properties in graphene is disorder due to impurities, structural defects, and other various reasons [33]. The combined effects of intrinsic properties and extrinsic disorders in graphene can be observed via transport experiments. Thus, the study of transport properties is a powerful tool to study graphene while encompassing intrinsic and extrinsic properties. Various physical properties can be monitored via transport measurements, and here three examples are given: the Dirac point, the quantum Hall effect, and low field magneto-transport property.

When one changes the gate voltage on the graphene device inducing the electric field on graphene, it can also change the charge carrier density and Fermi level of graphene as shown in Figure 2.3 (a). When observing resistance versus applied gate voltage, the resistance gradually increases and reaches a peak and then gradually decreases again. This is because the type of charge carrier is changed from hole to electron due to the applied electric fields. The maximum resistance peak between the transition of two type of charge carriers represents the Dirac point shown in Figure 2.3 (a). This means from the transport measurement with applied electric fields one can



Figure 2.3: . Various transport properties of graphene. (a) Dirac point in resistance measurement, (b) quantum Hall effect, and (c) weak localization. (These figures are taken from [3], [4], [5] and modified to show the purpose clearly).

confirm the Dirac point as the form of a peak in the resistance measurement data.

When strong magnetic fields are perpendicularly applied to graphene and resistance is measured, peaks and steps of plateaus can be observed in ρ_{xx} and σ_{xy} respectively as shown in Figure 2.3 (b). This is because electrons are confined in a 2D system (in the case of graphene), and the energy spectrum splits into discrete energy levels, the so-called Landau levels. This Landau level is shifted as magnetic fields increases, and as a result, it shows the plateaus on σ_{xy} and the peaks on ρ_{xx} . This quantized magneto-transport property is called the quantum Hall effect [34].

If weak magnetic fields are applied to graphene, different phenomena can be observed in magneto-transport measurements as shown in Figure 2.3 (c). As magnetic fields are applied, the resistance is decreased or increased from a peak value at zero magnetic fields. This phenomenon is because the quantum conductivity correction by the various interactions with an electron in the diffusive region can be suppressed by the magnetic fields. This phenomenon under weak magnetic fields is called weak localization or weak anti-localization. Among the various physical properties studied through transport measurements, weak localization is mainly focused on in this thesis to investigate the behavior of dephasing on CVD graphene, before and after the annealing.

2.2 Weak localization

When an electron is moving diffusively, it experiences a series of random scattering events [35]. Because of these random scattering events, the electron propagates randomly and one example of these random propagations is a loop in the clockwise or counter-clockwise direction as shown in Figure 2.5. These loops are said to be paths which are time reversed with respect to one another, and they can interfere constructively or destructively [36]. This interference changes the backscattering probability which affects the electron transport resulting in a conductivity correction. This conductivity correction is called weak localization (increasing the backscattering probability and decreasing conductivity). In other words, this conductivity correction originates from the quantum mechanical interference between pairs of time-reversed paths with self-crossing trajectory.



Figure 2.4: The randomly scattered paths of electron in (a) counter clockwise and (b) clockwise loop. The colored circles represent impurities.

If an electron in a diffusive region collides with other particles inelastically, such as with other electrons, phonons, and impurities during the random scattering events, phase coherence between the loops is randomized with the rate τ_{ϕ}^{-1} . τ_{ϕ}^{-1} is called the dephasing rate (phase relaxation rate) and details the rate at which phase loss events occur [35, 37].

If the phase coherence in these loops is broken for various reasons, the conductivity correction from this phase coherence can be suppressed. For example, when the magnetic fields are applied perpendicularly to the system, the Aharonov-Bohm effect changes the phase difference between the self-crossing paths and suppresses the conductivity correction [36]. This means that applied magnetic fields can suppress the conductivity correction induced by weak localization. Hence, weak localization is most robust at zero magnetic fields, and it becomes suppressed when out of plane magnetic fields are increased.

From the Hikami-Larkin-Nagaoka equation [38], the theoretically modeled quantitative result of weak localization for 2D samples can be seen. Here, only the case for intermediate and low magnetic fields (limit of $B \ll \hbar/(eD\tau_{tr})$, τ_{tr} is the momentum relaxation rate) is used because such low magnetic fields are enough to suppress the weak localization in our graphene experiments [39].

$$\Delta\sigma(B) = \sigma(B) - \sigma(0) \approx -\frac{2e^2}{\pi h} F\left(\frac{\tau_B^{-1}}{\tau_\phi^{-1}}\right)$$
(2.5)

$$\tau_B^{-1} = \frac{4e}{\hbar} DB \tag{2.6}$$

$$\tau_{\phi}^{-1} = \frac{4e}{\hbar} DB_{\phi} \tag{2.7}$$

where $F(z) = \ln z + \psi(0.5 + z^{-1})$, and $\psi(x)$ is the digamma function. τ_B^{-1} is the interaction rate scale of applied magnetic field, τ_{ϕ}^{-1} and B_{ϕ} are dephasing rate and its field scale respectively. D is diffusion coefficient. This equation in low field limit assumes that the dominant interaction in weak localization is dephasing compared to other interactions.

Using this weak localization Equation 2.7, one can make the fitting function and can extract the dephasing rate (τ_{ϕ}^{-1}) from magneto-conductivity measurements. Because dephasing rate is comprised of various interactions, such as electron-electron interaction and electron-phonon interaction, one can investigate the presence of specific interaction or magnitude of interaction rates from this extracted dephasing rate. The details of weak localization for graphene case and dephasing rate details will be discussed in the following Sections.

2.2.1 Weak localization in graphene

As mentioned in previous section, weak localization in 2D materials and metallic materials is mostly dominated by dephasing interaction, τ_{ϕ}^{-1} . However, other materials like graphene have several other dominant interaction terms in weak localization. In graphene, there are additional elastic scattering terms due to the intervalley and intravalley scatterings at the valleys, Kand K' in Figure 2.2 and Figure 2.5 [20, 22, 32]. Hence, the manifestation



Figure 2.5: The intravalley scattering (τ_*^{-1}) and intervalley scattering (τ_i^{-1}) in momentum space of graphene. The dashed line represents the Brillouin zone of graphene. The solid line trigonal shapes at K and K' represent the Fermi surface at a finite energy in the vicinity of two non-equivalent valleys.

of weak localization in graphene is mainly determined by the following interplay of inelastic and elastic scattering mechanisms; the intravalley scattering rate τ_*^{-1} , the intervalley scattering rate τ_i^{-1} , and the dephasing rate τ_{ϕ}^{-1} [20]. Weak localization or anti-weak localization in graphene are determined by the relative speeds of these interactions.

Through these particular interaction mechanisms and due to the weak spin-orbit interaction in graphene, the general theory of weak localization in Equation 2.5 can be transformed into an equation for graphene with several modifications as following equation shows [20, 29, 40].

$$\Delta \sigma(B) = \sigma(B) - \sigma(0)$$

$$\approx \frac{e^2}{\pi h} \left[F\left(\frac{\tau_B^{-1}}{\tau_\phi^{-1}}\right) - F\left(\frac{\tau_B^{-1}}{\tau_\phi^{-1} + 2\tau_i^{-1}}\right) - 2F\left(\frac{\tau_B^{-1}}{\tau_\phi^{-1} + \tau_*^{-1}}\right) \right]$$
(2.8)

where $F(z) = \ln z + \psi(0.5 + z^{-1})$, and $\psi(x)$ is the digamma function. Compared to the general weak localization theory of Equation 2.5, two additional terms added; intervalley scattering (τ_i^{-1}) and intravalley scattering (τ_*^{-1}) .

Also, in graphene's case, a diffusion coefficient can be defined in Equation 2.7 as

$$D = \frac{\sigma \pi \hbar v_f}{2e^2 \sqrt{\pi n_s}}, \ v_f = 10^6 m/s.$$
 (2.9)

11

where σ is conductivity, n_s is charge carrier density, and v_f is the Fermi velocity of graphene.

This weak localization of Equation 2.8 is modified into a fitting function to extract the respective interaction rates from the measured data [41]. For instance, the linearity term of the measured data and the maximum resistance term are added into the weak localization fitting function. The details of the weak localization fitting function are in given in Appendix B.

From this weak localization fitting function, interaction rates can be extracted and the magnitude of each rate as a function of other external changes, such as a function of charge carrier density and the condition of annealing, can be compared. Particularly, among the interaction rates, the dephasing rate is focused on since the dephasing rate can be caused by various interactions and the behavior of the dephasing rate can allow various interactions such as electron-electron interaction [22] or electron-magnetic impurity interaction [42] to be characterized [35, 37]. The following section will discuss more details of dephasing.

2.3 Various source of the dephasing

Dephasing (phase-relaxation) is the term for when coherent effects between the electrons of various paths is suppressed for any reason [37]. In other words, any events inducing a random phase difference between the electron paths is a dephasing process. Here are the main sources of dephasing:

- Electron-phonon interactions: τ_{e-h}^{-1}
- Electron-electron interactions: τ_{e-e}^{-1}
- Impurities with internal degrees of freedom: τ_{e-i}^{-1}

Dephasing is the result of these various interactions and the dephasing rate τ_{ϕ}^{-1} is the approximate sum of these interaction rates as given in the following equation:

$$\tau_{\phi}^{-1} \approx \tau_{e-p}^{-1} + \tau_{e-e}^{-1} + \tau_{e-i}^{-1}.$$
(2.10)

The first two interactions, electron-phonon and electron-electron interactions, are the intrinsic causes of the dephasing and include a temperature dependence. Additionally, impurities with internal degrees of freedom is the external factors which contribute to the dephasing rate. When an electron interacts with a phonon, an electron-phonon interaction, the phonon changes the phase of the electron randomly with time, and it results in a non-stationary interference pattern [35]. Hence, electronphonon interactions suppress the coherent effect. However, since it is relatively weak at low temperature due to the reduction of the number of phonon, the effect of electron-phonon interactions on the dephasing can be negligible in experiments performed at 4.2 K [21, 43].

In graphene case, electron-electron interactions are more dominant in dephasing because phonon has smaller relaxation rate than electron's at low temperature [21, 22, 44, 45]. This electron-electron interaction does not change the net momentum but changes the phase coherence between the electrons, and this change induces the dephasing. The electron-electron interaction rate in two dimensions can be described by the following equation:

$$\tau_{e-e}^{-1} = \frac{k_B T}{\hbar} \left(\frac{\ln\left(\frac{G}{2}\right)}{G} \right), \ G = \frac{\sigma A}{l}$$
(2.11)

where σ is conductivity, G is conductance, A is the area of the cross section of the sample, and l is its length [21]. This equation tells us that an electronelectron interaction can be represented as a function of conductance and linearly depends on the temperature. More importantly, this equation is not related with dephasing rate or weak localization. Thus, the magnitude of electron-electron interaction rate can be extracted from the conductivity measurement with this equation, regardless of magnitude of dephasing rate or weak localization. If one compares the electron-electron interaction rate from Equation 2.11 with the dephasing rate from Equation 2.8 and Equation 2.7, one can determine how much electron-electron interaction influences the dephasing process.

Impurities which have internal degrees of freedom can also cause dephasing [35]. This is because impurities can change the electron's phase state upon interaction [46]. For example, when the electron interacts with local magnetic moments which have an internal spin fluctuating with time, the phase in the electron varies randomly with time as well. The effect of these impurities can be reduced by changing the external environment, such as the temperature and applying low magnetic fields. For example, when in-plane magnetic fields are applied to the magnetic moments, the spin directions of the magnetic moments are aligned with the direction of the applied fields and these magnetic fields weaken the dephasing mechanism by suppressing the degrees of freedom in impurities. However, if this in-plane field is parallel to the direction of electron's motion, it does not affect the electron transport.

Additionally, when magnetic fields are applied to the system, the phase coherence among the electrons in different paths is changed due to the Aharonov-Bohm effect. Hence, this applied magnetic field can affect coherent effects, such as weak localization as mentioned in previous Section 2.2. The dephasing rate induced by the various sources described above can affect many physical properties seen in various transport measurements. Conversely, the dephasing rate can be extracted from experimental results of transport measurements [47]. We extract the dephasing rate from the magneto-conductivity data using weak localization.

With this extracted dephasing rate via weak localization and its fitting, the source of the dephasing can be verified in various ways, such as by applied in-plane magnetic fields, compared with theoretical models such as Equation 2.11, and observation of the change of the dephasing rate as a function of external parameters. In this thesis, the dephasing rate is compared before and after thermal annealing processes to investigate the effect of annealing. Also, the dephasing rate is compared with the electron-electron interaction rate, which is investigated via the change of conductivity and Equation 2.11, to verify the dominant source and additional sources of dephasing in CVD graphene.

Chapter 3

Experimental setup and background

The goals of the experiments in this thesis were to determine under what conditions the increase of the dephasing rate happens and how it changes when the gate voltage or charge carrier density changes for CVD graphene samples. These goals were founded on the previous experimental result that CVD graphene and exfoliated graphene show similar behavior in dephasing rate before annealing, and CVD graphene shows drastic increase of dephasing rate beyond electron-electron interaction rate after annealing. To conduct these experiments, we mainly prepared CVD graphene samples on several substrates, and additionally exfoliated graphene samples. Because of their different manufacturing methods, their properties, such as mobility, the position of the Dirac point, and the level of surface contamination differ [48]. Also, to investigate the effect of the substrate we used several different substrate materials; silicon oxide (SiO_2) and hafnium oxide (HfO_2) . Thereafter, these graphene samples were processed into the standard Hall bar geometry to measure the conductivity and charge carrier density through charge transport measurements. After sample fabrication, the charge transport properties of the samples were measured under perpendicularly applied magnetic fields at 4.2 K, before and after annealing in a custom-made rapid thermal annealer (RTA). Thermal annealing was performed under various atmospheres, from vacuum to N_2 gas, to investigate any resulting effects.

This chapter has sections, detailing sample fabrication and the experimental measurement setups. Section 3.1 shows the preparation of various graphene samples built on several different substrates. Section 3.2 and Section 3.3 show the custom-made, rapid thermal annealing (RTA) system and the 4.2 K measurement experimental setups respectively. Lastly, Section 3.4 explains the four probes charge transport measurement under applied magnetic fields.

3.1 Sample preparations

CVD graphene was mainly prepared on SiO_2 and HfO_2 , whereas exfoliated graphene was prepared on SiO_2 as shown in Table 3.1 and Figure 3.1. CVD graphene and exfoliated graphene both have a carbon-based mono-layered structure and should have the same physical properties as described in Section 2.1. However, several of their properties will differ as they are fabricated in different ways [48, 49].

Graphene	Substrate	Length	Width	Annealing	Temp.		
\mathbf{type}	Substrate	(μm)	(μm)	\mathbf{type}	(°C)		
				Vacuum	200-350		
CVD graphene				N_2/H_2	300		
from Graphenea	SiO_2	120-300	40-100	Ar/H_2	300		
from Graphenea				N_2	300		
				Ar	300		
	HfO_{2}	120	30	Vacuum	200-350		
CVD graphene	$11JO_2$	120	00	Ar	300		
from ACS	h B N	120	30	Vacuum	200-350		
	nDN	120	50	Ar	300		
Exfoliated	SiO	60.40	20.15	Vacuum	200-350		
graphene	DiO_2	00-40	20-10	Ar/H_2	200-350		

Table 3.1: Various types of graphene on various substrates samples.

CVD graphene is grown via CH_4 gas deposition on copper or nickel foil and then transferred to other substrates such as SiO_2 [50]. During the vapor deposition process on the metal substrate, graphene can have unintended carbon vacancies and multiple domains. Also, during the transfer process, graphene is chemically contaminated because CVD grown graphene needs to be covered by polymers to protect the surface. Thus, CVD graphene typically has structural defects and chemical contaminations. However, This has the advantage of being unlimited in size.

On the other hand, since exfoliated graphene is made from bulk graphite by exfoliation, sample size will be smaller than CVD graphene but also less contaminated. Because of less chemical contamination, exfoliated graphene shows a lower doping effect and has a higher mobility than CVD graphene. Due to these differences, both types of graphene samples were prepared in the experiments of this thesis to compare the results. However, the result of exfoliated graphene is not compared in the main thesis part but in the appendix because exfoliated graphene cases show fitting problems. The



Figure 3.1: CVD graphene (a) on HfO_2 substrate and (b) on hBN. Green area under yellow indicates the hBN flake. (c) Exfoliated graphene on SiO_2 substrate. Yellow colors indicate Ar/Cr electrodes and dashed lines indicate the standard Hall bar geometry of graphene.

details of exfoliated graphene and CVD graphene on hBN will be discussed in Appendix E.

Samples were processed into the standard Hall bar geometry via a conventional electron beam lithography process using Au (80 nm thickness) and Cr (5 nm thickness) electrodes in all samples. Photographic and schematic pictures of the sample geometry are shown in Figure 3.1 and 3.5 (b) respectively. After this fabrication step, the sample was placed on the chip carrier as shown in Figure 3.2. More fabrication details are summarized in the following section and Appendix A.



Figure 3.2: Chip carrier with the graphene sample on the center. The sample (black color) is wire bonded to the chip carrier (yellow color) by gold wires.

3.1.1 CVD graphene on various substrates

In these experiments, three different types of substrates are used with CVD graphene: 295 nm SiO_2 , 30 nm HfO_2 to investigate the effect of the substrates [Figure 3.1]. These substrates were chosen for the following reasons: 1. SiO_2 is the common substrate used for all types of graphene. 2. As HfO_2 is grown by atomic layer deposition (ALD), this substrate is single crystal structure and one can compare the effect of substrate type. Additionally hBN was used as a substrate for CVD graphene because hBN is known as a better substrate than SiO_2 and because it shows high mobility [51, 52]. In Appendix E the result of CVD graphene on hBN is shown.

Commercial CVD graphene on SiO_2 from Graphenea [53] was used for SiO_2 substrate experiments. In the case of HfO_2 and hBN, CVD graphene on filtered paper manufactured by ACS materials was used and transferred onto these substrates [54]. CVD graphene transfer process details are ex-

plained in Appendix A.

3.1.2 Exfoliated graphene on SiO₂

The exfoliated graphene is exfoliated from bulk graphite on a SiO_2 substrate in a similar way to the hBN exfoliation [Figure 3.1 (c)]. Further details of the exfoliation process are given in Appendix A. Only exfoliated graphene was used on SiO_2 unlike in the CVD graphene case. This is because we already discerned that the increase of dephasing occurs in CVD graphene on SiO_2 hence it was only necessary to confirm whether this increase occurs in exfoliated graphene. If the same result is observed in both graphene samples, then this increase is a common phenomenon in both CVD and exfoliated graphene. If it is not, then this effect should be specially activated only in CVD graphene because of the specific characteristics of CVD graphene.

3.1.3 Lithography process

In order to pattern the Hall bar geometry on the samples, electron beam lithography process was carried out in five (CVD graphene sample cases) or four (exfoliated graphene cases) steps. CVD graphene sample cases need an extra step to remove some part of graphene covered area on the substrate to make the bonding pads at the beginning. During each step, the 650nm thickness of double layered PMMA (C4 and A2) was used as electron beam resists. 5 nm thickness of Cr and 80 nm thickness of Au were thermally evaporated and deposited on the substrate and graphene as wire-bonding pads and electrodes. Cr was deposited before Au deposition on the substrate because Au does not stick well to SiO_2 .

The first step was making wire-bonding pads (100 μ m by 100 μ m) and alignment marks, 500-1000 μ m away from the graphene flake. The second step was making the leads from wire-bonding pads to near the graphene flake. The third step was connecting the graphene flake and the lead. The last step was making the rectangular Hall bar geometry with oxygen plasma etching as shown in Figure 3.1.

After this electron beam lithography process, the sample was attached on the chip carrier by silver paste as shown in Figure 3.2. Au wire-bonding pads on the graphene sample were wire bonded to a chip carrier.

3.2 Rapid thermal annealing system

Annealing is important in the experiments of this thesis to investigate the source the increasing of the dephasing rate. A custom-made rapid thermal annealer (RTA) was used (as shown in Figure 3.3) to anneal the sample under a vacuum and various gases (Ar, N_2 , and H_2/N_2 mixture). It is known that annealing in different atmospheres has different effects on the samples. For example, annealing in Ar is better for removing contaminations than annealing in a vacuum [26, 55, 56]. Hence, the effect of annealing under different gases was studied by comparing the magneto-conductivity measured data and the change of dephasing.



Figure 3.3: Custom-made Rapid Thermal Annealer (RTA) in (a) the real picture and (b) schematic figure of RTA. (c) Schematic map of RTA and pumping system. Setup in dashed line is only for high vacuum annealing.

This custom-made RTA contains a halogen light bulb covered with a copper sheath, a gas line for releasing various gases, and a quartz glass cover to isolate the RTA from the external environment. Moreover, this RTA was connected to vacuum pumps to remove other unwanted gases which might affect the sample. Only a dry scroll pump was used in gas annealing cases, and dry scroll pump and turbo pump were used in high vacuum annealing cases as shown in Figure 3.3.

In the gas annealing case, the RTA was degassed for 15 minutes using

a dry scroll pump and the annealing system was purged with the relevant gas at least five times. The purging process removes unwanted gases from the RTA through a connected gas cylinder. After this process, the gas was released following a specific recipe to make an equal gas flow rate in every gas annealing case. A stable pressure level (200 mmHg) was observed during the gas annealing process after 1 hour and after 5 hours of annealing. This means that other unwanted gases barely trespassed into the RTA and affected the sample during the gas annealing process so any effect from other unwanted gases including oxygen could be ruled out for the experimental results. After the gas purging and releasing process, the RTA was turned on and the sample annealed under various temperature conditions from 200 $^{\circ}C$ to 350 $^{\circ}C$.

In vacuum annealing cases, firstly degassing was performed for periods of 1 hour to 5 hours using the dry scroll pump and the turbo pump as shown in Figure 3.3 (c). The vacuum level of the RTA was kept below 5×10^{-3} mbar, which is the minimum pressure level Pirani gauge can read. After this degassing procedure, the RTA was turned on and the sample annealed under various temperature conditions, from 200 °C to 350 °C.

In addition to these annealing processes under vacuum and gas, further experiments were conducted to compare the surface temperature of each annealing condition. The results show similar surface temperatures for the gas and vacuum annealing cases. This fact confirms that the experimental results in this thesis do not result from a temperature difference. Details of the sample-surface temperature comparison experiment under gas and vacuum are shown in Appendix C.

3.3 Measurement system at 4.2K - Dunker

After these annealing processes, the RTA was cooled to room temperature and the sample was immediately moved to the 4.2 K dunker measurement system [Figure 3.4 (b) and (c)], less than one minute with minimal air exposure. The minimal air exposure is important in this experiment because moisture and gases in the atmosphere may have an effect on the annealing or create unintended effects on the graphene, such as inducing a doping effect.

The 4.2 K dunker has a chip carrier holder at the end [Figure 3.4 (b)] and copper wires are connected from this chip carrier holder to the breakout box and the lock-in amplifier measurement system, which allows us to apply voltage source and to measure the nano scale current. After the sample is placed on the dunker and covered by the stainless steal tube as shown in



Figure 3.4: (a) Measurement system - dunker in liquid Helium dewar. The magnet in the dewar (orange color) induces perpendicular magnetic fields on the device. (b) Zoom-in figure shows the chip carrier (left - schematic picture, right - real picture) at the end of dunker covered by stainless steel. (c) chip carrier holder in dunker without (left) and with the device (right).

Figure 3.4 (c), this measurement system was degassed for 20 minutes using the turbo pump, and helium gas was added to the dunker to facilitate heat exchange between the liquid helium and the sample. Liquid helium keeps the temperature close to 4.2 K in the dunker.

After degassing and the helium gas adding process were finished, the dunker was placed into the liquid helium dewar as shown in Figure 3.4 (a) and then all the experiment setups are ready to be measured. The liquid helium dewar has a magnet at the bottom as shown with orange color in Figure 3.4 (a). This magnet can induce perpendicular magnetic fields on the sample and is variable to allow sweeping of the magnetic fields from a strength of zero up to a few Tesla. The dunker was placed where the magnetic field is at its maximum strength in order to conduct more accurate experiments and to avoid different magnitude between real magnetic fields and reading fields. If the dunker is placed on wrong position, the magnitude between the applied magnetic field and read magnetic field is different and it could lead experimental error and weak localization fitting error.

3.4 4 probes measurement with magnetic fields

In transport experiments, many physical properties can be investigated by measuring the current or voltage changes with applied electric or magnetic fields as mentioned in Chapter 2.3. Figure 3.5 (a) shows the resistance change as a function of gate voltage (main image) and the change of Fermi level (inset images) in graphene. As shown in this figure, one can investigate the physical properties below the Dirac point (hole charge carrier region) and above the Dirac point (electron charge carrier region) by applying transverse electric fields [29].

To do this transport measurement in different charge carrier density regions of graphene, the standard hall bar geometry was made with a back gate underneath of the substrate as shown in Figure 3.5 (b). From this geometry, the conductivity $\sigma_{XX} = \frac{g*I}{V_{XX}} (\rho_{xx} = \frac{V_{XX}}{g*I})$ can be extracted, where I is the applied current and g is geometric ratio of width to length between V_{XX} (longitudinal voltage change) and V_{XY} (transverse voltage change).

Additionally, the charge carrier density can be calculated from a V_{XY} measurement with applied magnetic fields. To extract the charge carrier density, the low magnetic field approximation can be used and it gives $n_s = \frac{I/e}{dV_{XY}/dB}$ [35]. Through this charge carrier density n_s and resistivity ρ_{xx} from the above, the mobility $\mu = \frac{1}{|e|n_s\rho_{xx}}$ and the diffusion coefficient $D = \frac{\sigma\pi\hbar v_f}{2e_x^2/\pi n_s}$ (v_f =Fermi velocity) can also be obtained [35, 57].



Figure 3.5: (a) Resistivity as a function of applied gate voltage at 4 K. The dashed line indicates the Dirac point, and the small side peak on the right side is the experimental noise. (b) Simplified device geometry and measurement setup of CVD graphene on HfO_2 substrate. Blue indicates CVD graphene and yellow indicates Au (80nm)/Cr (5nm) electrodes, I indicates applied current, and B indicates perpendicularly applied magnetic fields. (c) Real picture of CVD graphene on HfO_2 substrate. Dashed line indicates Hall bar geometry of graphene.

In addition, when the gate voltage (V_G) is applied through the back gate on the sample, electric fields can be applied onto the substrate, inducing a capacitor effect on graphene and changing the Fermi level as shown in Figure 3.5 and the charge carrier density also. Moreover, weak localization can be confirmed by applying perpendicular magnetic fields [indicated as B in Figure 3.5 (b)] and observing the change in conductivity, as the magnetic fields suppress the conductivity correction. The confirmation of weak localization in graphene will be described in Section 4.1

Ideally, graphene is at its Fermi level under zero gate voltage as shown in Figure 2.3 (a) [6], which means that the Dirac point can be seen at zero gate voltage and graphene shows zero conductivity at zero gate voltage. However, in real experimental graphene samples, one can rarely see the lowest conductivity or highest resistance, which are the signal of Dirac point,
at the zero gate voltage because of various factors. Especially on CVD graphene as described in Section 3.1, chemical contaminations from the CVD growth process or the lithography fabrication process induce the doping effect on graphene. As a result, the Dirac point in most experiments is not at the zero gate voltage as shown in Figure 3.5 (a). As the CVD graphene samples of this work show the hole doped effect (voltage of the Dirac point, V_{DP} , is above zero.), the hole doped region ($E < E_F$ and $V_G < V_{DP}$) is mostly focused on.

Also, since most of the before-annealed samples and air exposed samples have very high Dirac points ($V_{DP} > 80 V$) and extremely high gate voltages cannot be applied on the samples, the Dirac point is estimated by using a linear relation between the charge carrier density (n_s) and applied gate voltage (V_G); $n_s = \alpha(V_G - V_{DP})$ with $\alpha = \epsilon_{substrate}/(ed_{substrate})$ which is a capacitance and experimentally extracted. From the fact that theoretical value of n_s at the V_{DP} is zero, the Dirac point can be estimated [2].

Chapter 4

Experimental result

With graphene samples before and after the annealing process, transport measurement experiments were conducted at 4.2 K under application of perpendicular magnetic fields and application of back gate voltage. Physical properties including various interaction rates were extracted from the measured data via weak localization fitting. The effect of annealing at different temperatures and different atmospheres was investigated by comparing the change of conductivity as a function of the applied gate voltage or as a function of the applied magnetic fields. The dephasing rate extracted using Equation 2.8 and the electron-electron interaction rate from Equation 2.11 are also compared. From the comparison of experimental results with various samples, the creation or activation condition and the properties responsible for increasing the dephasing rate were investigated.

Section 4.1 shows the steps to measure the conductivity as a function of the applied gate voltage and details the extraction of the interaction rate. Section 4.2 shows the results of the CVD graphene sample on SiO_2 substrate annealing under various atmospheres. Section 4.3 shows the results of CVD graphene on HfO_2 substrate annealing under the same conditions. Based on these two substrates experiments, Section 4.4 shows the additional experimental results focusing on air and moisture exposure. Section 4.5 briefly describes the reason why the results of exfoliated graphene and CVD graphene on hBN are not compared with CVD graphene on SiO_2 and HfO_2 results. Lastly, Section 4.6 summarizes the experimental results.

4.1 Measurement process

After the sample preparation described in Chapter 3, the measurement in the dunker at 4.2 K is performed before and after annealing process under application of perpendicular magnetic fields and the back gate voltage.

First, back gate voltages are applied to the sample through the substrate over wide range as shown in Figure 4.1 (a) to investigate the change of conductivity as a function of the applied gate voltage and to find the position of Dirac point.



Figure 4.1: The example of experimental procedures in this thesis. (a) Measurement of conductivity change as function of applied gate voltage. This is the case of Ar annealed CVD graphene with $V_G = \text{from } -80 \text{ V to } 30 \text{ V}$, and $V_G = 18 \text{ V}$. Magneto conductivity data measured at 4.2 K in (b) long range magnetic fields ($\pm 100 \text{ mT}$) and (c) shot range magnetic fields ($\pm 10 \text{ mT}$) and its weak localization fitting. These two field ranges are measured separately.

Second, perpendicular magnetic fields are swept over ranges of $\pm 100 \text{ mT}$ and $\pm 10 \text{ mT}$ ranges [Figure 4.1 (b) and (c)] at each gate voltage with a step based on the variation of charge carrier density. Because each field range has a different dominant interaction mechanism based on its interaction rate, the measurements with different magnetic field ranges allow one to extract more accurate fitting parameters. For example of CVD graphene case, in 100 mT range, intravalley scattering rate dominantly affects weak localization fitting, and in 10 mT range, dephasing rate dominantly affects the fitting. Additionally, these magneto-transport measurements begin 20-15 V below from the Dirac point V_{DP} , which is the hole charge carrier region. This is because one can reduce the effect of electron-hole puddles [22, 32].

With this measured magneto-conductivity data, the dephasing rate is extracted using the weak localization fitting function from Equation 2.8, and the electron-electron interaction rate is calculated via conductivity and Equation 2.11. This fitting function is briefly described in the following section, and further details are given in Appendix B. Next, these extracted rates are compared as a function of charge carrier density and applied gate voltage. If the dephasing rate and electron-electron interaction rate are equal, this means that the main source of the dephasing in graphene is the electron-electron interaction as mentioned in Section 2.3. If not, other interactions can be expected to be additional sources of the dephasing as well as the electron-electron interaction.

4.1.1 Weak localization fitting

The weak localization theory for graphene in Equation 2.8 is modified to be used as a fitting function in the following equation and the fitting results are shown in Figure 4.1 (b) and (c).

$$f(B) = L * (B - B_0) + R_0 - R_0^2 \left(\frac{e^2}{\pi h} \left[F(z_1) - F(z_2) - 2F(z_3)\right]\right) * g \quad (4.1)$$

$$F(z) = ln(z) + \psi \left(0.5 + \frac{1}{z} \right)$$
 (4.2)

$$z_1 = \frac{|B - B_0|}{B_\phi}, \ z_2 = \frac{|B - B_0|}{B_\phi + 2B_i}, \ z_3 = \frac{|B - B_0|}{B_\phi + B_*}$$
(4.3)

In this fitting function, the followings are the fitting parameter: L is linearity of measured data, B is the perpendicularly applied magnetic fields, R_0 is the maximum resistance, B_0 is magnetic field where R is the maximum, g is geometric ratio (width/length), and ψ is digamma function. $B_{\phi,i,*}$ are the magnetic field scale of each interaction rates. More details of this fitting function are given in Appendix B

This fitting function is used to extract interaction rates in terms of magnetic field scale from the magneto-conductivity data at each charge carrier density with ± 100 mT and ± 10 mT magnetic fields ranges. Then, one can calculate interaction rates; $\tau_{\phi,i,*}^{-1} = \frac{4e}{\hbar}DB_{\phi,i,*}$ as desribed in Section 2.2.1.

Because this weak localization fitting process cannot perfectly fit on the measured data and extract interaction rates due to the various reasons, we used the error bar on the extracted rates to compensate this imperfection of fitting process. The details of this error bar are described in Appendix D.

4.2 CVD graphene on Silicon Oxide

The first experiment was conducted with CVD graphene on SiO_2 substrate. For these samples, commercial CVD graphene from Graphenea [53] is used after fabrication steps described in previous Chapter 3. These samples were annealed at temperatures from 200 °C to 350 °C in vacuum or under presence of Ar, N_2 , or a $N_2\&H_2$ mixture. Since a significant change of dephasing rate in the 200 °C and 250 °C annealed samples could not be seen, only the 300 °C annealed samples are compared in this chapter.

4.2.1 Before-annealed CVD graphene

First, CVD graphene samples, after lithography process and before any annealing process, are measured. Because applying extremely high voltage could damage the device, we only applied up to 60 V and estimated the Dirac point based on a linear relation as described in 3.4. The Dirac points for these samples are located between 88 V to 114 V. The case of $V_{DP} = 88$ V is described in this Section and the results are shown in Figure 4.2.

Figure 4.2 (a) shows the change of charge carrier density as a function of applied gate voltage. The linear fit in this figure (a) indicates the position of Dirac point at 88 V. The conductivity in Figure 4.2 (b) increases linearly with $\frac{d\sigma}{dV} = -0.46 \ e^2/hV$ as the applied gate voltage changes from 60 V to -40 V. This slope (which is related to field-effect mobility, $\mu \propto \frac{\sigma}{V_G}$) and curvature of $\sigma(V_G)$ near the Dirac point can tell inhomogeneity and the level of charged impurity [58, 59]. This result will be compared with Ar annealed and vacuum annealed cases.

Figure 4.2 (c) compares the magneto-conductivity in ± 10 mT range results at each charge carrier density. $\Delta \sigma$ in ± 10 mT does not saturate, but continuously increases as the charge carrier density increases from $2 \times 10^{12}/\text{cm}^2$ to $9 \times 10^{12}/\text{cm}^2$ (red to black color). This means that the conductance correction due to the weak localization is larger as charge carrier density increases. This also shows that the dephasing rate is getting slower as carrier density increases [22].

The dephasing rate, which is extracted from weak localization Equation 2.8, and electron-electron interaction rate, which is calculated via conductivity and Equation 2.11, are quantitatively compared in Figure 4.2 (d). Even these two rates are extracted from two different sources with each equation, these rates are equally decreased within the error as a function of charge carrier density. Therefore, before annealing, it can be confirmed that the main mechanism of the dephasing in CVD graphene at 4.2 K is the electron-electron interaction.

Furthermore, intervalley scattering rates (τ_i^{-1}) are higher than 300 /ns, and intravalley scattering rates (τ_*^{-1}) are higher than 10 /ps for all charge carrier density ranges. This result made less fitting error in dephasing rate



Figure 4.2: Before-annealed CVD graphene (a) Hall bar measured hole charge carrier density as a function of applied gate voltages. Dashed lines represents the linear line fit as a extension of measured data from -40 V to 60 V. (b) change of σ as a function of applied gate voltages from -40 V to 60 V. Solid line represents the σ_{xx} measurement, swept gate voltage from 0 V to 60 V. Markers represents the. (c) $\Delta \sigma$ in magnetic field. Dashed line represents the measured data and the solid line represents the weak localization fitting. (d) extracted rates as function of charge carrier density (dashed line: τ_{ϕ}^{-1} (dephasing rate), solid line: τ_{ee}^{-1} (electron-electron interaction rate)). Each color represents each charge carrier density from $2 \times 10^{12}/\text{cm}^2$ to $9 \times 10^{12}/\text{cm}^2$.

because variation of one parameter did not affect others during the fitting process.

4.2.2 Ar gas annealed CVD graphene

After before-annealed samples were measured, those samples were annealed under various type of gases to investigate the effect of gas annealing on dephasing. The Dirac points in gas annealed CVD graphene on SiO_2 cases are located between 18 to 40 V. This Section and Figure 4.3 show the result of Ar annealed CVD graphene sample, which was used in previous Section 4.2.1. This sample was annealed for 1 hour at 300 °C under 99.999 % purity Ar gas and it has the Dirac point at 18 V.

When the conductivities before-annealed sample in Figure 4.2 (b) and Ar annealed sample in 4.3 (b) are compared, conductivity change as a function of the applied gate voltage is only shifted close to zero voltage without a significant change. Also, $\frac{d\sigma}{dV}$ is -0.43 e^2/hV (green dashed line) in the gate voltage range from 0 V to -90 V, which is close to the before-annealed case (-0.46, blue dashed line) except near the Dirac point. The slope and the sharp curvature of $\sigma(V_G)$ near the Dirac peak indicate less impurity and inhomogeneity in Ar annealed CVD graphene sample compared to before-annealed sample.

Figure 4.3 (c) compares the magneto-conductivity data measured at each carrier density. One of the most significant changes is that $\Delta\sigma$ in different charge carrier densities fold on top of each other when the charge carrier density is larger than $3 \times 10^{12}/\text{cm}^2$, although σ keeps increasing as shown in (b). This fact is distinct from the before-annealed case shown in Figure 4.2 (c), which the curvature of $\Delta\sigma$ keeps changing. This shows that the conductivity correction due to weak localization is maintained even the charge carrier density increases.

When the dephasing rate from WL fitting and electron-electron interaction rate from conductivity are quantitatively compared in Figure 4.3 (d), these two rates are no longer the same. The difference between these two rates becomes larger as the charge carrier density increases. To be specific, although the electron-electron interaction rate decreases, the dephasing rate is maintained indicating the effects from additional sources of dephasing would increase as the charge density increases. Interestingly, this phenomenon also occurs even when annealing under different gases, i.e. under N_2 and under a H_2/N_2 mixture, and this fact indicates that gas annealing induces additional source of dephasing on CVD graphene.



Figure 4.3: Ar-annealed CVD graphene (a) Hall bar measured hole charge carrier density as a function of applied gate voltages. Dashed line (red) represents the linear fit. (b) change of σ as a function of applied gate voltages from -80 V to 30 V. Two dashed lines represents the linear line fits from before-annealed one from Figure 4.2 (blue color) and Ar annealed one data (green color). Before-annealed case is shifted by 70 V, which is V_{DP} difference. (c) $\Delta \sigma$ in magnetic field and (d) extracted rates as function of charge carrier density (dashed line: τ_{ϕ}^{-1} , solid line: τ_{ee}^{-1}) Each color represents each carrier densities.

4.2.3 Vacuum annealed CVD graphene

To confirm whether annealing under any condition could induce the additional source of dephasing on CVD graphene, the similar experiments were conducted with vacuum annealed CVD graphene sample. Before experiments were conducted, similar result was expected as was seen with the Arannealed sample experimental result, because Ar with 99.999% purity is an inert gas, close to vacuum.

First, the fresh CVD graphene on SiO_2 sample was measured before annealing and it showed similar behavior of conductivity and dephasing rate as was observed in before-annealed sample, Figure 4.2. The dephasing rate and electron-electron rate were the same in error range as shown for the before-annealing case in Figure 4.2 (d). After this measurement, this CVD graphene sample was annealed for 1 hour at 300 °C under a vacuum condition below 5×10^{-3} mbar. These vacuum annealed cases shows the Dirac point between 42 to 114 V. Figure 4.4 shows the result of $V_{DP} = 114 V$ case.

In this vacuum annealed case, the Dirac point was estimated from the linear relation between charge carrier density and applied gate voltage as described in Section 3.4 and it is shown in Figure 4.4 (a). $\frac{d\sigma}{dV}$ is -0.4 e^2/hV and the conductivity changed similarly to the above two measurements as shown in Figure 4.4 (b). Although we could not compare near the Dirac point, the slope shows that annealing under vacuum or gas does not affect the changing of the conductivity significantly. When the charge carrier density increases, $\Delta\sigma$ continues to increase without any overlap as shown in Figure 4.4 (c). This is similar to the case of the before-annealed experiment.

Figure 4.4 (d) shows that the dephasing rate and electron-electron interaction rate decrease with a similar slope as a function of charge carrier density. However, there is a maintained difference ($\sim 4 / ns$) between the dephasing rate and electron-electron interaction rate. In other words, unlike with gas annealing, the main source of the dephasing in vacuum annealed CVD graphene is still the electron-electron interaction. However, since the two interaction rates do not have the same value and the difference is maintained for all charge carrier densities, the creation or activation of additional interactions for the dephasing is also expected in the vacuum annealed case. Otherwise, these differences can be simply a systematic error because these are within the error range.

In addition to this 1 hour vacuum annealing experiment, there was still no overlap of $\Delta \sigma$ even with the 5 hours vacuum annealing case. However, the maintained difference between the dephasing rate and electron-electron



Figure 4.4: Vacuum-annealed CVD graphene (a) Hall bar measured hole charge carrier density as a function of applied gate voltages. Dashed lines (red) represents the linear line fit. (b) change of σ as a function of applied gate voltages from -20 V to 60 V. Dashed line (black) represents the change of conductivity in before- annealed case from Figure 4.2 with the offset along V_G . (c) $\Delta \sigma$ in magnetic fields and (d) extracted rates as a function of charge carrier density (dashed line: τ_{ϕ}^{-1} , solid line: τ_{ee}^{-1}). Each color represents each carrier density from $3.5 \times 10^{12}/\text{cm}^2$ to $8.6 \times 10^{12}/\text{cm}^2$.

interaction rate is slightly larger ($\sim 8.5 / ns$) than the 1 hour vacuum annealing case ($\sim 4 / ns$). From the fact that this increase in 5 hours annealing is beyond the error range, one can confirm that vacuum annealing induces additional source of dephasing, which is maintained in all charge carrier densities unlike the case of Ar annealing.

4.3 CVD graphene on Hafnium Oxide (HfO_2) substrate

As the change of dephasing rate in gas annealed CVD graphene on SiO_2 substrate is confirmed in previous chapter, one can suspect gas annealing or the SiO_2 substrate as the cause of dephasing change. For this reason, here CVD graphene on HfO_2 substrate samples were used. We also measured three different types of annealing cases: before-annealed, vacuum annealed and gas annealed. The Dirac points in these cases were located near 0 V unlike the cases of CVD graphene on SiO_2 . Nonetheless, those CVD graphene on HfO_2 experiments show the similar results in change of interaction rates as CVD graphene on SiO_2 shows above.



Figure 4.5: Ar-annealed CVD graphene on HfO_2 substrate. (a) Hall bar measured hole charge carrier density as a function of applied gate voltages. (b) change of σ as a function of applied gate voltages from -100 V to 20 V. Dashed line indicates Ar annealed CVD graphene on SiO_2 substrate with offset along V_G . (c) $\Delta\sigma$ as a function of magnetic fields. Each color represents each carrier density.

Figure 4.5 shows the result of Ar annealed CVD graphene on HfO_2 . Compared to Ar annealed on SiO_2 substrate case, graphene on HfO_2 shows two significant differences; charge carrier density and conductivity slowly change as a function of applied gate voltage with $\frac{d\sigma}{dV} = -0.25e^2/hV$, and the position of Dirac points are close to zero gate voltage. This is because HfO_2 has higher dielectric constant than SiO_2 , $\kappa = 25$ (κ for $SiO_2 =$ 3.9), and much thinner than SiO_2 (60 nm in HfO_2 and 285 nm in SiO_2). However, $\Delta\sigma$ as a function of magnetic fields in Figure 4.5 (c) shows the similar overlap at higher charge carrier density region as Ar annealed SiO_2 substrate shows. The overlap of $\Delta\sigma$ in both substrates cases indicates that the sample on HfO_2 also has the additional source of dephasing after gas annealed.

For the detailed quantitative comparison of dephasing rate and electronelectron interaction rate, Figure 4.6 shows the change of dephasing rate and electron-electron interaction rate as a function of charge carrier density before, and after annealing in vacuum or under gas, in case of HfO_2 and SiO_2 substrates. In case of before-annealing shown in Figure 4.6 (a), the dephasing rate and the electron-electron interaction rate are almost equally decreased for all charge carrier density ranges. The slight difference between the dephasing rate and electron-electron rate at the lowest carrier density can arise from the electron-hole puddle [58]. After the annealing in vacuum shown in Figure 4.6 (b), the interaction rates are of a similar range to the before-annealed case, and the difference between the dephasing rate and electron-electron interaction rate is maintained as ~4.5 /ns for all charge carrier densities.

After new sample was annealed under Ar gas, as shown in Figure 4.6 (c), both interaction rates are increased compared to the before-annealed case, to around 15 /ns for the electron-electron interaction rate and 20 /ns for the dephasing rate. The difference between the dephasing rate and electronelectron interaction rate continues to increase as a function of charge carrier density.

When HfO_2 cases in Figure 4.6 (a), (b), (c) are compared with SiO_2 cases in (d), (e), (f), it is confirmed that there is no significant difference in the change of the dephasing rate between CVD graphene on SiO_2 and HfO_2 substrates. Only noticeable difference between these two cases is at the low carrier density region. HfO_2 cases show the significant discrepancy in dephasing rate and electron-electron interaction at low density region. For this reason, electron-hole puddle can be suspected.

Furthermore, as the unusual increase of the dephasing rate due to the additional sources after gas annealing occurs in both CVD graphene samples on oxide substrates, these results can be interpreted so: the induction of additional source of dephasing could be an effect from the oxide substrate, or not affected by the type of substrate.



Figure 4.6: The results of CVD graphene on HfO_2 substrate in three annealing cases. Extracted rates as function of charge carrier density are in (a) before-annealed, (b) vacuum annealed, and (c) Ar annealed sample. To make comparison with SiO_2 substrate, the figures from the experiment above with SiO_2 are used; (d) before-annealing, (e) vacuum annealing, (f) Ar gas annealing. Both substrate cases show the similar behavior in dephasing rate (τ_{ϕ}^{-1}) and electron-electron interaction rate (τ_{ee}^{-1}) at each annealing process.

4.4 Air exposure on CVD graphene on Silicon Oxide

Along with the above experiments, another experiment was conducted to see how the position of Dirac point and the air exposure affect the change of dephasing rate. The reason for this experiment was there are significant differences in the position of Dirac point V_{DP} between before-annealed, gas annealed, and vacuum annealed samples. This position difference could induce the difference in the additional source of dephasing. This experiment was also to verify whether the dephasing rate returns to the electron-electron interaction rate which can indicate the unknown interaction effect for dephasing disappears.

As the increase of dephasing and the difference between the dephasing rate and electron-electron interaction rate was observed for all oxide substrates cases, these experiments were conducted only with the samples, CVD graphene on SiO_2 .

First, the new CVD graphene sample was annealed under H_2/N_2 and measured [Figure 4.7, ①]. Then, this sample was intentionally exposed to air [Figure 4.7, ② - ④]. The effect of this intentional exposure to air is to introduce a hole-doping effect on graphene [60]. Specifically, each number indicates the step of treatments on the sample; ① : 1 hour annealing in H_2/N_2 mixture, ② - ④: air exposure, ⑤ : additional 1 hour annealing in gas. Accordingly, after these air exposures, the Dirac points in ② – ④ are shifted to a higher positive voltage ($\Delta V_{DP} > 0$). The results of the following treatments on the same graphene sample are summarized in Figure 4.7.

When the Dirac point of the gas annealed sample [(1) in Figure 4.7] is shifted away due to the air exposure [(2) - (4) in Figure 4.7], the overall dephasing rate decreases in the low carrier density region and then increases again in the higher charge carrier density region. However, the electronelectron interaction rates only decrease without other significant changes. This sample is further annealed under gas at 300 °C for 1 hour, and the Dirac point is shifted back to 70 V [(5)]. In this case, the Dirac point and the dephasing rate are larger than the initial annealing case (1) ($V_{DP} = 60 V$). However, the electron-electron interaction rates are within the same range similar to the case of (1), which indicates that there is no relation between the magnitude of the dephasing rate and the position of the Dirac point.

To thoroughly compare the quantitative changes between the dephasing rate and the electron-electron interaction rate, Figure 4.7 (b) shows the excess of the dephasing rate, which is subtracting the electron-electron



Figure 4.7: (a) Dephasing rate (solid lines) and electron-electron interaction rate (dashed lines), and (b) the excess of the dephasing rate $(\tau_{\phi}^{-1} - \tau_{e-e}^{-1})$ as a function of charge carrier density. Arrow denotes the minimum value. $(V_{DP}: 1=60 \text{ V}, 2=92 \text{ V}, 3=109 \text{ V}, 4=140 \text{ V}, 5=70 \text{ V})$

interaction rate from dephasing rate $(\tau_{\phi}^{-1} - \tau_{e-e}^{-1})$ and only indicates the additional source, as a function of charge carrier density. After only 1 hour of gas annealing cases [①-④], although the Dirac point has shifted away significantly, the excess of the dephasing rates in these cases are maintained between 10 /ns and 30 /ns in a shape consistent with a minimum. This suggests that the effect from gas annealing is preserved even after the sample is exposed to air for a long time, while it is shifted to higher carrier density region. Also, considering the remarkable increase of the excess of dephasing of in the extra annealed case (5), it is expected that additional annealing under gas conditions would induce more additional source of the dephasing and further increase the excess of dephasing. This means that the annealing under gas would keep creating or amplifying the unknown source of the

dephasing.

Another interesting feature in Figure 4.7 (b) is that every case of the excess of dephasing rate has the minimum excess rate (marked with arrows), when the applied gate voltage is zero. This fact suggests that the applying gate voltage on the sample could play a significant role in switching on the effect of the additional source on dephasing rate. However, how the gate voltage affects the dephasing rate could not be clearly answered. Theoretical model by [61] could help to answer this, which suggests applied gate voltage could affect the orbital of graphene. Another explanation can be given as follows: because the minimum excess rate in gas annealed cases is not negligible compared to the before-annealed cases, the mechanism of increasing the excess rate can be divided into two types. One can cause the fixed extra increment of the dephasing rate regardless of the applied gate voltage as observed in vacuum annealed cases. The other type can cause the proportional increment as a function of the applied gate voltage as observed in gas annealed cases only.

4.5 Comparison experiments to hBN and exfoliated graphene

Experiments with CVD graphene on hBN and exfoliated graphene on SiO_2 were also conducted. However, experimental results of these samples are not compared with the above experimental results. This section briefly describes why these results are not compared with CVD graphene on oxide substrate results. The details of experimental result and the reason shows in Appendix E.

In case of CVD graphene on hBN, electron-electron interaction rates are higher than dephasing rates in all annealed cases and we could not observe any significant effect of annealing in vacuum and under gases. In exfoliated graphene on SiO_2 samples, intravalley scattering rate and intervalley scattering rate and dephasing rate are comparable, which are close to 50/ns. These similar magnitudes made significant error during the weak localization fitting process. Also, it has no drastic difference between gas annealing and vacuum annealing for the dephasing rate.

Due to these reasons, we decided that the experiments conducted with hBN and exfoliated graphene does not give the meaningful data and results. More details of these experiments are explained in Appendix E.

4.6 Summary

4.6.1 The excess of dephasing rate in CVD graphene

When the values excluding the electron-electron interaction rate from the dephasing rate $(\tau_{\phi}^{-}1 - \tau_{ee}^{-}1)$, which is the excess of dephasing rate as a function of charge carrier density and as a function of applied gate voltage are compared, very interesting results are observed as shown in Figure 4.8. In this figure, all the gas annealed cases are annealed at 300 °C for 1 hour and the vacuum annealed samples are annealed for 1 hour and 5 hours.

First, when the applied gate voltage is zero, all the gas annealed cases have the minimum excess of the dephasing rate except in the HfO_2 substrate case. A possible reason that HfO_2 has an exception at $V_G = 0$ is because its Dirac point is close to zero volts so weak localization in this sample might be affected by electron-hole puddles. Also, all gas annealed cases have a similar excess of the dephasing rate at similar charge carrier densities. These are increased with a similar slope, $\left(\frac{\tau_{\phi}^{-1} - \tau_{ee}^{-1}}{n_s}\right)$, in a similar rate range.

In contrast to the cases with gas annealing, vacuum annealing cases have a near-zero increment of the dephasing rate ($\sim 4 / ns$ for 1-hour annealing and $\sim 8.5 / ns$ for 5 hours annealing). These increases are maintained irrespective of the charge carrier densities and the applied gate voltages. From these results, one can expand the possible explanation of the two different mechanisms responsible for increasing the dephasing rate, as described in Section 4.4. The mechanism causing the fixed extra increment in the dephasing rate regardless of the applied gate voltage might occur in both gas annealing and vacuum annealing, but the effect in vacuum annealing is weaker than in gas annealing. Also, the source causing the proportional increment as a function of the applied gate voltage (charge carrier density) is only created or activated by the gas annealing. The details for the error bar in Figure 4.8 are described in Appendix D.

4.6.2 Summary

From the results of the experiments with CVD graphene on oxide substrates, the following statements can be concluded.

First, the excess of the dephasing rate is arisen in both vacuum annealing and gas annealing cases [Figure 4.4 and 4.3]. However, in the case of vacuum annealing [Figure 4.4], the excess rate is very small (4 /ns) compared to gas annealing cases and is maintained irrespective of the charge carrier densities and the applied gate voltages. On the other hand, in the case



Figure 4.8: The excess of dephasing rate $(\tau_{\phi}^{-1} - \tau_{e-e}^{-1})$ as function of applied gate voltage (a) and of charge carrier density (b) on various annealing conditions. The cases of CVD graphene on HfO2 before annealing and vacuum annealed are excluded due to the similarity to CVD graphene on SiO_2 cases. (before-annealed: $V_{DP} = 90$ V, Vacuum in 1 hour $V_{DP} = 115$ V, in 5 hours 30 V, Ar: $V_{DP} = 18$ V, N_2 : $V_{DP} = 31$ V, $H_2\&N_2$: $V_{DP} = 60$ V, HfO_2 on Ar: $V_{DP} = 5$ V)

4.6. Summary

of gas annealing, the excess of the dephasing rate keeps increasing as the charge carrier density increases with the minimum rate at zero gate voltage. Therefore, the excess of the dephasing rate produced by these two annealing processes should come from the two different mechanisms or sources. One induces the maintained increment of dephasing rate regardless of applied gate voltage. The other induces the increment of the dephasing rate which increases as a function of applied gate voltage. Vacuum annealing only induces the first mechanism due to the constant increment of extra dephasing rate in all applied gate voltages. Whereas gas annealing induces both mechanisms due to the shape of the minimum excess of dephasing rate at zero gate voltage.

Moreover, since both annealing cases show a similar surface temperature [Appendix C], the temperature difference of the sample surface as the cause of the dephasing rate increase can be ruled out. Because the pressure level is maintained at 200 mmHg during gas annealing, we could rule out the effect from unwanted gases such as oxygen or moisture.

Second, the additional experimental result in Appendix F that the excessive dephasing rate caused by gas annealing is reduced by the in-plane magnetic fields [Figure F.1] can suggest the following statements; magnetic moments are induced or activated by the gas annealing, and it causes the additional dephasing source for graphene. The effect of this additional dephasing source disappears when in-plane magnetic fields "freeze" the magnetic moments. Moreover, since all the gas annealed cases have a minimum of the excess of dephasing rate at 0 V and this excess of dephasing rate keeps increasing with the applied gate voltage, the applied gate voltage could trigger the magnetic moments, and the additional dephasing source.

In addition, since SiO_2 and HfO_2 show similar trends of the increment of the dephasing rate after annealing under different gases, this effect can be caused by the interaction between graphene and the oxide substrate. To clearly confirm whether this effect is from the oxide substrate, similar experiments with CVD graphene on other substrates, such as SiC and Al_2O_3 , are necessary under the same annealing and experimental conditions.

Chapter 5

Conclusion

The goals this thesis were to understand why the dephasing rate in CVD graphene shows certain unexpected behaviors and how the increase of dephasing rate happens, and to investigate the properties of the increased dephasing. Another supplementary goal was to verify whether this source has magnetic properties. To achieve these research goals, weak localization theory for graphene and thermal annealing experiments under various conditions were used. CVD graphene on different oxide substrates samples were measured at 4.2 K using perpendicularly applied magnetic fields.

As a result, it was found that the excess of the dephasing rate, where the electron-electron interaction rate is excluded from the dephasing rate, has several interesting findings. When the CVD graphene sample was annealed under gas, the dephasing excess had a turning point shape with the minimum rate at zero gate voltage and it increases as a function of applied gate voltage. Also, all the gas annealed CVD graphene on oxide substrates had a similar excess of dephasing rates at similar charge carrier density regions. When the CVD graphene sample was annealed under a vacuum, the dephasing excess is maintained in all charge carrier densities at 4 /ns for 1 hour vacuum annealing and 8.5 /ns for 5 hours vacuum annealing. Both maintained rates in the 1 hour and 5 hours vacuum annealing cases are smaller than the minimum rate in the gas annealing cases.

From these findings, it can be concluded that there are two mechanisms for the dephasing excess. One causes the constant increment of the dephasing rate regardless of the applied gate voltage. The other causes the difference in the dephasing rate which increases as a function of the applied gate voltage. Vacuum annealing only induces the afore-mentioned mechanism as there is a constant increment for all applied gate voltages. Gas annealing induces both mechanisms as there is a turning point shape with the minimum at zero gate voltage.

In the additional experiment, when the in-plane magnetic fields are applied to the gas annealed CVD graphene on SiO_2 , the dephasing rate is decreased from 66 /ns to 23 /ns. This result indicates that in-plane magnetic fields "freeze" the additional source of dephasing. Thus, the gas annealing

should cause or activate the magnetic moments on CVD graphene on oxide substrates.

From the dephasing rate derived by combining weak localization theory and the experimental results with CVD graphene, the conditions for creating or activating the magnetic moments as a source of the dephasing rate are given as: Annealing CVD graphene on SiO_2 or HfO_2 substrates under gases, such as Ar, N_2 , and H_2/N_2 mixture, at temperature above 300 °C. The properties of this enhanced dephasing are:

- It has the minimum at zero gate voltage.
- It has the similar excess of dephasing rate at the similar charge carrier density.
- It decreases when in-plane magnetic fields are applied on the sample.



Figure 5.1: Theory simulations of local magnetic moments in graphene with vacancies. Optimized atomic structure and charge distribution for spin up and spin down states (a) with one vacancy and (b) with two A sublattice vacancies and one B sublattice vacancy, where green balls and red balls indicate the A sublattice atoms and B sublattice atoms, respectively. (Adapted from Ref. [7])

Here, an additional possible explanation for how magnetic moments are

created or activated via gas annealing is proposed: firstly, because it is reported that the vacancies, defects, and impurities in graphene can create magnetic moments [Figure 5.1] [7, 16, 62–64], gas annealing might create the vacancies or impurities on graphene as the source of magnetic moments. Otherwise, as gas annealing could remove the impurities that were placed in the carbon vacancies, magnetic moments could be activated due to the restored carbon vacancies. It also may induce magnetic moments underneath graphene because annealing in gas could break the dangling bond of the oxide substrate [65, 66]. Adatoms, such as hydrogen or oxygen from the annealing process, could be the possible reason for magnetic moments on CVD graphene, because it is theoretically and experimentally proven that hydrogenated graphene has magnetic properties [67-71]. Also, the fact that oxidation on graphene has the magnetic property is theoretically shown [72]. However, since hydrogenation on graphene needs much different condition than our annealing, such as using hydrogen plasma reactor or few GPa pressure on the graphene, hydrogenation is unlikely.

Also, orbital hybridization induced by applied gate voltage on graphene vacancy could induce the local magnetic moments. The reason for this is that the results we have confirmed are partially consistent with the theoretical model in [61].

To verify the effect of the oxide substrates, additional experiments with CVD graphene on different substrates, such as Al_2O_3 or SiC, are necessary. To verify the effect from the impurity vacancy or applied gate voltage, one could conduct the experiment with STM (scanning tunneling microscope) to investigate graphene in microscopic level. Additionally, because the amount of magnetic moments should be independent of the charge carrier density, (which conflicts with the experimental results of this work - the dephasing rate increases with charge carrier density) more experiments are needed to investigate the relation between the induced magnetic moments and charge carrier density.

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Appendix A Details of sample fabrication

A.1 Exfoliation



Figure A.1: Mechanical exfoliation process. Cleaning the SiO_2 substrate (a) in the 60 °C Acetone and (b) in the Oxygen plasma for 20 minutes. (c) Exfoliated graphite flakes on the blue tape. (d) The tape with flakes on the cleaned SiO_2 . (e) Baking process at 100 °C hot plate.

We follow the steps in Reference [73] to exfoliate graphene and hBN. First, we prepare the clean SiO_2 substrates. We cut the bulk substrate into 3 cm × 3 cm size and submerge this in Acetone, then we put this into the ultrasonic cleaner for 3 minutes and the hot plate for 15 minutes at 60°C [Figure A.1 (a)]. These processes remove all the organic contaminations and dust on the surface. We conduct next procedures in the clean room to prevent the contaminations from air. We conduct the oxygen plasma on silicon oxide for 20 minutes to remove the remained contamination and make the surface flat [Figure A.1 (b)]. For the exfoliation, we use the nitro tape because this nitro tape makes less residue on the substrate when we tested many tapes. We put the bulk hexagonal boron nitride (hBN) or graphite on the tape, and exfoliate several times [Figure A.1 (c)]. Then, we place this tape on oxygen plasma conducted SiO_2 and bake this substrate at 100°C for 1 minute, and remove this tape from the substrate [Figure A.1 (d) and (e)].

After finding the proper size and thickness of hBN or graphene through the microscope, we cleave the substrate into 5 mm × 5 mm to put this substrate onto the chip carrier [Figure 3.2]. Also, we make the standard Hall bar geometry pattern by the conventional electron beam lithography process and evaporate the Cr(5 nm)/Au(80 nm) on the sample as the electrodes [Figure 3.5 (b) and 3.1]. After connected Au wires between electrodes and chip carrier, exfoliated sample is prepared to be measured.

A.2 CVD graphene Transferring



Figure A.2: CVD graphene on center of the filtered paper. Deionized water drops are on four corners of filtered paper to wet the paper. After this wet process, this graphene is transferred on hBN or HfO_2 substrates.

We use commercial CVD graphene manufactured by ACS company for transferring process [54]. Based on their technical data sheet, this CVD graphene is produced by conventional chemical vapor deposition process on the copper foil substrate and transferred onto the filtered paper [Figure A.2]. We follow the procedure that ACS provides and transfer this graphene onto the hBN or HfO_2 substrates. After this transfer process, we remove the chemical residue polymers by Acetone and make the standard Hall bar geometry on this sample.

Appendix B

Weak localization fitting function

To extract τ_{ϕ}^{-1} and other interaction rates via magnetotransport measurement, we make the fitting function from weak localization theory for graphene as described in Section 2.2.1

$$\Delta \sigma(B) = \sigma(B) - \sigma(0)$$
(B.1)
= $\frac{e^2}{\pi \hbar} \left[F\left(\frac{\tau_B^{-1}}{\tau_{\phi}^{-1}}\right) - F\left(\frac{\tau_B^{-1}}{\tau_{\phi}^{-1} + 2\tau_i^{-1}}\right) - 2F\left(\frac{\tau_B^{-1}}{\tau_{\phi}^{-1} + \tau_*^{-1}}\right) \right]$

Our fitting function of weak localization is following.

$$f(b) = L * (b + b_0) + R_0 - R_0^2 \left(\frac{e^2}{\pi h} \left(F_1 - F_2 - 2F_3\right)\right) * g$$
(B.2)

$$F_1 = ln(z_1) + \psi\left(0.5 + \frac{1}{z_1}\right), \ z_1 = \frac{|B - B_0|}{B_\phi}$$
 (B.3)

$$F_2 = ln(z_2) + \psi\left(0.5 + \frac{1}{z_2}\right), \ z_2 = \frac{|B - B_0|}{B_\phi + 2 * B_i}$$
(B.4)

$$F_3 = ln(Z_3) + \psi \left(0.5 + \frac{1}{z_3} \right), \ z_3 = \frac{|B - B_0|}{B_\phi + B_*}$$
(B.5)

where L is linearity of measured data, b is the perpendicularly applied magnetic fields, R_0 is the maximum resistance, B_0 is magnetic field where R is the maximum, g is geometric ratio (Width/Length), and ψ is digamma function $\psi(x) = \frac{d}{dx} ln(\Gamma(x))$. In order to use this fitting function, we need to set the initial values. We set L and B_0 as zero, and R_0 as the maximum value of magneto conductivity data. Also, we fix the g = 1 because we already consider the width and length ratio of samples when we process the raw data into conductivity or resistance.

When $|B-B_0|$ is zero $(B = B_0)$, ln(z) and $\psi(0.5+1/z)$ are not defined in this fitting function. In Igor program we used, as these undefined parameters

show zero, fitting function $f(B = B_0)$ has only R_0 part, which indicates the maximum resistance when weak localization of graphene is not suppressed. With these fitting parameters we can extract $B_{\phi,i*}$ at each measured data and calculate $\tau_{\phi,i,*}^{-1}$ with using Equation 2.7 and 2.10.

To be specific for the fitting process, R_0 and B_0 are fixed at the first step because these values are clearly seen as a peak in measured data under applied magnetic fields. After these parameters are fixed, weak localization fitting function is applied to long range magnetic field scan (± 100 mT) because $\tau_{i,*}^{-1}$ are dominant in this long range and these rate can be extracted accurately compared to τ_{ϕ}^{-1} . After this long range fitting process, short range fitting (± 10mT) is processed with fixing $\tau_{i,*}^{-1}$ extracted from long range fitting, and this process enables to extract more accurate τ_{ϕ}^{-1} .

Appendix C

Surface temperature on RTA



Figure C.1: Test sample in RTA with k-type thermocouple on its surface

When we confirmed the different behavior of dephasing rate between the gas annealed experiment and vacuum annealed experiment, we suspect that the increase of dephasing rate can occur if the temperature of the sample surfaces differ between gas annealing and vacuum annealing processes. Hence, we conduct experiment with measuring the sample surface temperature by attaching the extra k-type thermocouples during thermal annealing process on RTA [Figure C.1]. Two thermocouples are mounted on the surface of the sample and copper sheath to measure the temperature on the bottom and surface of the sample. For the sample surface, we use the very thin

k-type thermocouple from Omega company (diameter: 0.002 inches) to prevent external heat being transferred to the sample. When we measure the temperature at room temperature, copper sheath and the surface of sample show 1 °C difference. And then, we turn on the power on RTA to increase temperature from 100 °C to 325 °C, and measure the temperature under each atmosphere condition. As shown in the Table C, vacuum annealed and gas annealed show the similar temperature variation, which is 71 % of temperature on the copper sheath, bottom of the sample.

From this result, we confirm that there is no temperature difference on the sample surface between vacuum annealing and gas annealing. Thus, surface temperature difference is not responsible for the increase of dephasing rate.

Copper T	Vacuum surface T	Copper T	Gas surface T
100 °C	75 °C	125 °C	85 °C
300 °C	210 °C	175 °C	127 °C
311 °C	220 °C	298 °C	218 °C
325 °C	229 °C	300 °C	220 °C
Surface T \approx 71.4 % of copper T		Surface T \approx 71.8 % of copper T	

Table C.1: Surface temperature in RTA

Appendix D

Error bar in fitting process

There are several factors which can contribute the experimental error. In this thesis, only the following experimental errors are mainly considered through the error bar. The details of these errors are explained in this Appendix D

- Temperature fluctuation
- Conductivity depending on magnetic fields
- Fitting parameters

D.1 Temperature fluctuation

Our measurement system is dunked in liquid helium dewar [Figure 3.4], which is 4.2 K. Thus, the temperature of our system should be maintained at 4.2 K. However, there might be the temperature fluctuation because measurement system cannot be totally isolated from room temperature atmosphere. Also, the heat from the outer system can be transferred to our measurement system. If there is temperature fluctuation (T=4.2 K $\pm \Delta$), electron-electron interaction rate in Equation 2.11 is also fluctuating. However, in our experiments, since we assume that the temperature fluctuation Δ is negligible compared to the temperature 4.2 K in our measurement system and the effect of this fluctuation is negligible compared to other error factors, we do not consider this temperature fluctuation in error bar.

D.2 Conductivity depending on magnetic fields

When we apply and increase the perpendicular magnetic fields from 0 mT to 100 mT, conductivity keeps increasing until the weak localization effect is totally suppressed. Therefore, there are small differences in electron-electron interaction rate, diffusion coefficient $(D = \frac{\sigma \pi \hbar v_f}{2e^2 \sqrt{\pi n_s}})$, and the dephasing rate $(\tau_{\phi}^{-1} = \frac{4e}{\hbar} DB_{\phi})$, when we use the minimum conductivity at 0 mT or the maximum conductivity at 100 mT. However, as the maximum conductivity
is up to 3 % higher than the minimum conductivity, the interaction rates and diffusion coefficient in these extreme conductivities show negligible differences. Thus, the error from conductivity difference is negligible compared to the fitting parameters error described in the following section.

D.3 Fitting parameters

When we use the weak localization fitting, we need to determine the geometric ratio (width/length) as described in Appendix B. The geometric factor during the fitting process should be fixed to 1 because we already divide the pure voltage measured data by the width and length ratio (1 - 1.5) of the sample in Figure 3.1 and the applied currents in the process of calculating the conductivity. However, this process with geometric factor of 1 does not make the best fitting results in every cases, which means the χ^2 is not always the minimum when geometric factor is fixed to 1. For this reason, we need to adjust the geometric factor within the \pm 5 % of χ^2 , which gives usually geometric factor placed between 0.9 - 1.1, and extract the dephasing rate during the adjustment processes. With these dephasing rates from the adjustment process, we define the experimental error bars.

Also, we conduct the same adjustment process with changing intervalley scattering rate τ_i^{-1} , and intravalley scattering rate τ_*^{-1} . However, when we change these rates, the magnitude of error bar is negligible compared to error bar from geometric factor except for the exfoliated graphene cases.

Appendix E

Additional experimental data

In this appendix, the results of non compared experimental data from CVD graphene on hBN substrate and exfoliated graphene on SiO_2 are described.

E.0.1 CVD graphene on hexagonal Boron Nitride (hBN)



Figure E.1: CVD graphene on hBN substrate. change of R_{XX} (top) and σ (bottom) as a function of applied gate voltages from -80 V to 20 V. The Dirac point is positioned at -5 V.

We measure CVD graphene on hBN substrate before and after annealing under the same atmosphere conditions as used in previous experiments. Unlike other CVD graphene on oxide substrates experiments, these samples have a very sharp Dirac point shown in Figure E.1 and this is similar to other graphene-hBN experimental results [51, 52]. However, when it goes away from the Dirac point, it shows very flat conductivity changes, $\frac{d\sigma}{dV}$ =



Figure E.2: CVD graphene on hBN. Change of the dephasing rate and electron-electron interaction rate as a charge carrier density (a) before annealing, (b) vacuum annealing, and (c) gas annealing cases. All cases show that electron-electron interaction is higher than the dephasing rate. Also, all cases have the similar dephasing rate between 70 /ns and 25 /ns.

-0.1 e^2/hV . Also, when the conductivity is compared between hBN and silicon oxide substrates, it shows 34 $e^{2/}h$ at -80 V and 23 $e^{2/}h$ at -40 V in CVD graphene on hBN but it shows 54 $e^{2/}h$ at -80 V and 40 $e^{2/}h$ at -40 V in CVD graphene on silicon oxide substrate.

This hBN substrate sample shows unexpected results in before-annealed, vacuum annealed, and gas annealed cases, shown in Figure E.2. In all cases, electron-electron interaction rates are higher than the dephasing rates, which is not observed in other CVD graphene sample experiments. Additionally, the dephasing rates in all cases have a similar value range even after gas annealing, i.e. an effect of annealing in CVD graphene on hBN sample is not observed. More specifically, gas annealing does not induce the additional source of dephasing in hBN substrate samples. From the results of this work it is hard to define the main source of changing the dephasing rate in graphene on hBN samples. Due to these reasons, CVD graphene-hBN experiments are not compared with other CVD graphene experiments.

E.0.2 Exfoliated graphene

The same annealing process and measurements were performed on the exfoliated graphene on SiO_2 samples. There are two significant experimental differences between exfoliated graphene and CVD graphene on oxide substrates. The first is that the Dirac point of before-annealed exfoliated graphene is close to zero voltage when compared to the case of CVD graphene. In other words, there are less chemical contaminations on the



Figure E.3: Exfoliated graphene result: (a) before annealing and (b) after gas annealing.

surface of exfoliated graphene than for CVD graphene and a lesser doping effect. This is because of the omission of a transfer process in contrast to with CVD graphene.

The second significant difference is the magnitude of the intervalley and intravalley scattering rates. In the case of CVD graphene, the intravalley scattering rate is much higher than the intervalley scattering rate and the dephasing rate. However, in the case of the exfoliated graphene, the three interaction rates are comparable. Due to the similar scattering rates, there is no dominant interaction in the used range of magnetic fields. Hence, if one interaction rate is modified during the weak localization fitting process, the other rates also vary significantly. This difference should come from the sample size difference between CVD graphene (length: $100 - 150 \ \mu m$, width: $30 - 50 \ \mu m$) and exfoliated graphene (length: $40 - 60 \ \mu m$, width: $13 - 20 \ \mu m$) or the level of surface contamination. Specifically, when the device dimensions are comparable to the phase coherence length or the level of contamination is different, other disorder can affect interaction rates and results in different magnitudes of the interaction rate.

Moreover, even if gas annealed exfoliated graphene shows a tendency of an increase of the dephasing rate as shown in Figure E.3, it cannot be stated that the main mechanism of dephasing is not electron-electron interaction because the increment in the excess of the dephasing rate is not so significant and not proportional to the charge carrier density (applied gate voltage) unlike with CVD graphene on oxide substrates samples.

For these reasons, the experimental results for exfoliated graphene are

not compared with the results of CVD graphene on oxide substrates samples.

Appendix F

Additional experiment with in-plane magnetic fields



Figure F.1: Magnetoconductivity in $B_{\perp} = \pm 10$ mT with $B_{\parallel} = 0$ mT (red, triangle) and 700 mT (purple, circle), and its WL fitting (solid lines) at T= 100 mK. After applied $B_{\parallel} = 700$ mT, the dephasing rate is decreased from 66 /ns to 23 /ns (inset: differential of MC)

Figure F.1 shows the results of additional experiments using a dilution refrigerator conducted by Dr. Silvia Lüscher Folk. The dilution refrigerator is used to measure the sample below 4.2 K. The fresh CVD graphene samples on SiO_2 are annealed under the same gas conditions are used in the experiment Section 3.4. The experiment is performed at 100 mK and the perpendicular magnetic fields are scanned within a ± 10 mT range with the same methods as described in Section 3.4. In this experiment, additional 700 mT in-plane magnetic fields are applied to investigate the presence of magnetic moments which have an internal degree of freedom and can be the

source the dephasing, as described in Section 3.4. The reason for the application of in-plane magnetic fields is that these in-plane magnetic fields can "freeze" the motion of magnetic moments on the CVD graphene samples. Thus, it is expected that the excess of the dephasing rate would decrease if there are magnetic moments and in-plane magnetic fields freeze those. When in-plane magnetic fields are applied at $n_s = 4.8 \times 10^{12}/\text{cm}^2$, the change of $\Delta \sigma$ is increased and the dephasing rate decreases from 66 /ns (red) to 23 /ns (purple) as shown in Figure F.1. This result indicates that the effect of increasing the dephasing rate is induced by the magnetic moments and these magnetic moments are caused or activated by gas annealing.