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To cite this article: A Fukuda et al 2018 J. Phys.: Conf. Ser. 969 012130

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Magnetotransport of Monolayer Graphene with Inert Gas Adsorption in the Quantum Hall Regime

A Fukuda¹, D Terasawa¹, A Fujimoto², Y Kanai³, K Matsumoto³

¹ Department of Physics, Hyogo College of Medicine, 1-1 Mukogawacho, Nishinomiya, Hyogo 663-8501, Japan
² Applied Physics, Faculty of Engineering, Osaka Institute of Technology, Osaka 535-8585, Japan
³ The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

E-mail: fuku@hyo-med.ac.jp

Abstract. The surface of graphene is easily accessible from outside, and thus it is a suitable material to study the effects of molecular adsorption on the electric transport properties. We investigate the magnetotransport of inert-gas-adsorbed monolayer graphene at a temperature of 4.4 K under a magnetic field ranging from 0 to 7 T. We introduce ⁴He or Ar gas at low temperature to graphene kept inside a sample cell. The magnetoresistance change δRₓₓ and Hall resistance change δRₓᵧ from the pristine graphene are measured as a function of gate voltage and magnetic field for one layer of adsorbates. δRₓₓ and δRₓᵧ show oscillating patterns related to the constant filling factor lines in a Landau-fan diagram. Magnitudes of these quantities are relatively higher around a charge neutral point and may be mass-sensitive. These conditions could be optimized for development of a highly sensitive gas sensor.

1. Introduction

Graphene, a two-dimensional monolayer of carbon atoms, has been investigated both theoretically and experimentally, and is a topic of major interest in modern condensed-matter physics [1, 2, 3, 4]. A milestone in the study of graphene is the experimental evidence of an unusual quantum Hall effect (QHE) reported by two different groups [5, 6]. One of the major motivations for the enormous scientific interest in graphene is the technological potential of graphene such as an electric-field effect in graphene, i.e., the possibility of controlling the carrier density in a graphene sheet by application of a gate voltage. Apart from technological applications, another motivation to study graphene in fundamental research is the relativistic physics associated with the massless Dirac fermions. The relativistic QHE is understood in terms of Landau quantization for massless Dirac fermions. In contrast, in low magnetic fields, weak localization (WL) dominates the transport properties of graphene. A negative magnetoresistance as a signature of WL has been reported [7] and theoretically investigated [8]. Recent intensive investigation by our group reveals the clear relationship between universal conductance fluctuations (UCF) and the WL effect in monolayer graphene in terms of the ratio of the elastic intervalley scattering time to the inelastic dephasing time [9].

Another motivation of research on graphene is focused on its another remarkable feature - accessibility to the two-dimensional electron gas (2DEG) from outside. Direct access to the
2DEG using such as an optical or scanning tunnel microscope in conventional semiconductor heterostructures like GaAs/AlGaAs is extremely difficult due to the cap layers. Graphene is a suitable material to address this problem with earlier investigations on the effects of the adsorption or chemical adjunction of various kinds of molecules on its surface[10] and their applications[11]. Therefore, to study the transport properties with an adsorption or chemical modification by external molecules on graphene is intriguing. Shedin et al. show that sensors made from graphene can detect individual events when a gas molecule such as CO, NH$_3$, H$_2$O, or NO$_2$ attaches to or detaches from the surface of graphene[12]. Subsequently, the molecular adsorption has been investigated theoretically with a first-principles study[13]. Elias et al. found evidence of hydrogenated graphene called “graphane”[14], where the QHE is fully controllable by reversible hydrogenation. Their techniques are applied for such as an electrical detecting pH and protein adsorptions[15] or band-gap opening by water adsorption[16]. These works imply that graphene-based devices can be utilized as mass-sensitive or species-sensitive gas sensors with high sensitivity. Adsorption of an inert gas on graphene may result in extremely small changes in the transport properties, which is difficult to detect, and hence has not yet been thoroughly investigated. We previously reported magnetotransport measurements of $^4$He-adsorbed bilayer graphene at low temperatures under a magnetic field ranging from 0 to 4T where even 10 % amount of one saturated layer of $^4$He was detectable associated with the magnetoresistance oscillation due to the WL and UCF in pristine graphene[17].

In this study, we observe the magnetotransport of monolayer graphene at low temperatures, and under a magnetic field $B$ ranging from 0 to 7T. We measure the magnetoresistance $R_{xx}$ and Hall resistance $R_{xy}$, and the differences in the magnetoresistance $\Delta R_{xx}$ and Hall resistance $\Delta R_{xy}$ between pristine graphene and $^4$He or Ar-adsorbed graphene, where the layer number of adsorbed atoms is precisely controlled. We also discuss the possibility of utilizing the graphene device as a highly sensitive sensor for adsorbed gas.

2. Experiments

The monolayer graphene device is fabricated by the mechanical exfoliation method[18] from kish graphite onto the surface of SiO$_2$, 300 nm apart from the n$^+$ doped Si substrate. Optical microscope image of the exfoliated graphene device is shown in Fig.1(a). We choose a large natural monolayer graphene flake that has an almost rectangular shape. We fabricate a Hall bar with the following dimension: 5$\mu$m-long for the source - drain electrodes, 3$\mu$m-long for the longitudinal voltage electrodes, and 2$\mu$m-wide for the Hall voltage electrodes. The contact pattern is depicted using electron beam lithography. The ohmic contact materials (10-nm-thick
Pd followed by 100-nm-thick Au) are deposited by thermal evaporation followed by liftoff in warm 1-methyl-2-pyrrolidone. The number of layers is determined from the Raman shift spectra[19], which is displayed in Fig. 1(b). Using the 632.8 nm He-Ne laser, we observe two intense peaks - a G band peak at 1580 cm^{-1} and a 2D band peak at 2640 cm^{-1}. Good Lorentzian fit and higher intensity of the 2D band peak ensures that the sample is a monolayer. The sample is first annealed at 700 K in a H2 atmosphere for 30 minutes.

An overview of our cryostat for the transport measurements of graphene with gas adsorption is presented in our previous paper[17]. The sample is placed in a vacuum-tight cell with an external heater and a grafoil sheet having large effective areas of 1.2 m2. The grafoil sheet is utilized to regulate and determine the precise number of layers of adsorbed molecules. The heater inside the sample cell enables in situ annealing even at low temperatures. The sample is annealed using the heater for several hours at 410 K. However, there is a concern that repeated thermal annealing may induce disorders and degrade the sample quality. Resistances are measured by a standard ac lock-in technique of 4-terminal measurements with a frequency of 37 Hz. Carrier densities are controlled by the back-gate voltage \( V_g \) applied between the graphene sheet and the substrate. A helium-free Gifford-McMahone (GM) refrigerator is used to cool down the sample as well as the superconductor magnet with a maximum magnetic field of 8 T. A magnetic field up to 7 T is applied in this experiment.

Fig. 1(c) presents the \( V_g \) dependence of the zero-field resistance \( R_{xx} \) in the monolayer graphene device at 4.4 K. Initially, the charge neutral point (CNP) is located at approximately \( V_{\text{CNP}} = 16.9 \) V. The relationship between the carrier density \( n \) and the gate voltage is given by the equation \( n = (C/e) \cdot \left| V_g - V_{\text{CNP}} \right| = 7.2 \times 10^{10} \cdot \left| V_g - V_{\text{CNP}} \right| \) cm^{-2}, where \( C \) denotes the capacitance between the graphene sheet and the substrate and \( e \) denotes the elementary charge. The carrier mobility differs slightly from the electron side \( \mu_e (V_g > V_{\text{CNP}}) \) to the hole side \( \mu_h (V_g < V_{\text{CNP}}) \), where \( V_{\text{CNP}} \) is the gate voltage at the charge neutral point. Fitting of the 4-terminal resistance for \( V_g < V_{\text{CNP}} \) and \( V_g > V_{\text{CNP}} \) at room temperature and zero magnetic field gives \( \mu_e = 0.25 \) m^{2}V^{-1}s^{-1} and \( \mu_h = 0.40 \) m^{2}V^{-1}s^{-1}, respectively. This behavior may be due to the invasive contacts with Pd [20]. It is also noteworthy that the resistance oscillation near the CNP emerges prominently due to UCF.

3. Results and discussion

Initially, we cool down the device of monolayer graphene to approximately 4.4 K in the vacuum-tight cell and investigate the magnetotransport properties of the pristine graphene. Figure 2(a) shows an image plot of the magnetoresistance \( R_{xx} = R_{xx}^{\text{pristine}} \) as a function of gate voltage \( V_g \) and magnetic field \( B \) up to 7 T. The data are taken for the sweep of \( V_g \) at various constant values of \( B \). The bright yellow area indicates the high-resistance state mainly emerging around the CNP. In high magnetic fields, oscillation in \( R_{xx} \) manifests itself, though it is not perfectly quenched in the QHE due to the degradation of the sample by thermal annealing. The equi-resistance lines generally seem to be aligned along the equi-Landau filling factor \( \nu \) lines, \( B \propto |V_g - V_{\text{CNP}}| \), from \( B = 0 \) T to \( B = 7 \) T almost linearly, which forms the so-called Landau-fan diagram.

Next, we introduce 4He gas to the sample cell through a thin capillary of 0.6 mm diameter from a 4He tank with a constant volume at room temperature, monitoring the decrement of the gas pressure of the tank, which is translated to the amount of substance into the cell. The adsorption energy of a 4He atom on graphite is approximately 12.2 K[21]. Although the exact binding energy of a 4He atom on graphene has not yet been experimentally measured, theoretical calculation indicates that the adsorption energy on the monolayer graphene is approximately 13.4 K[22]. At our working temperature of \( T = 4.4 \) K, it is reasonable that almost all 4He atoms are homogeneously adsorbed on the grafoil together with the graphene sample, and we are able to estimate the layer number of adsorbed 4He atoms. Here we introduce the 1.0 layer 4He atoms on graphene. After equilibrium is reached, we measure \( R_{xx}^{\text{He}} \) as a function of \( V_g \) and \( B \) again.
Figure 2. (a) Image plot of the magnetoresistance $R_{xx}$ as a function of gate voltage $V_g$ and magnetic field $B$ with equi-resistance lines. (b) Image plot of the magnetoresistance change $\Delta R_{xx}$ of the monolayer graphene adsorbing one-layer $^4$He gas from the pristine one as a function of $V_g$ and $B$. Green lines indicate the equi-Landau filling factor $\nu$ lines.

Figure 3. (a) Hall resistance $R_{xy}$ of the pristine graphene. (b) Hall resistance change $\Delta R_{xy}$ of the graphene adsorbing one-layer $^4$He gas from the pristine one. (c) Normalized Hall resistance change $\Delta R_{xy}/R_{xy}$. (d) Normalized magnetoresistance change $\Delta R_{xx}/R_{xx}$ as a function of $V_g$ for $B = 6.0 \, T$ and $6.5 \, T$.

The resistance change $\Delta R_{xx} = R_{xx}^{\text{He}} - R_{xx}^{\text{pristine}}$ is demonstrated as an image plot for $B$ and $V_g$ in Fig. 2(b). Blue and red colors represent the sign of $\Delta R_{xx}$. Maximum amplitude of the change ratio $|\Delta R_{xx}/R_{xx}|$ is approximately 4.0% at high magnetic field and near the CNP. Regions of each color emerge alternatively and their pattern also seems to be aligned along the equi-$\nu$ lines. It should be noted that this behavior is completely different from the bilayer case[17]. This may be because the effect of the adsorbate on the magnetotransport is larger in the monolayer adsorbent than in the bilayer one.

To investigate the effects of the $^4$He adsorption in detail, especially in the QHE region, we
adsorbing one layer Ar gas from the pristine one, respectively, as a function of
for the development of a highly sensitive gas sensor for heavier atoms.
grades of samples is required, the results imply that the monolayer graphene device is promising
investigation into the effects of disorder or impurities on the magnetotransport using various
Fig. 4(a) and (b) demonstrate the magnetoresistance
oscillating structure around the CNP due to the UCF effects. The values of
R
xy
oscillations are observed than in the case of
R
xx
and its change \( \Delta R_{xy} \). In contrast, \( \Delta R_{xy} \) is relatively small in
pristine graphene, which affect the transport properties. Consideration of disorder or impurities may be
may increase the disorder, and evacuations of the sample cell may introduce impurities on the
is achieved up to several tenths of a percent. However, repeated thermal cycles of the sample
may increase the disorder, and evacuations of the sample cell may introduce impurities on the
graphene, which affect the transport properties. Consideration of disorder or impurities may be
essential to the variation in \( R_{xx} \) or \( R_{xy} \). Though the data are still primitive, and further careful
investigation into the effects of disorder or impurities on the magnetotransport using various
grades of samples is required, the results imply that the monolayer graphene device is promising
for the development of a highly sensitive gas sensor for heavier atoms.

In conclusion, we have carried out the magnetotransport measurements of \(^4\)He or Ar-adsorbed

\[ \text{Figure 4. (a) Magnetoresistance } R_{xx} \text{ and (b) magnetoresistance change } \Delta R_{xx} \text{ of the graphene adsorbing one layer Ar gas from the pristine one.} \]

study Hall resistance \( R_{xy} = R_{xy}^{\text{pristine}} \). Fig. 3(a) presents the \( V_g \) dependence of \( R_{xy} \) for \( B = 6.0 \, \text{T} \)
and 6.5 T. Non-perfect Hall plateaux are found, which may be affected by the disorders or
impurities. Fig. 3(b) also indicates the Hall resistance change \( \Delta R_{xy} = R_{xy}^{\text{He}} - R_{xy}^{\text{pristine}} \), where
\( R_{xy}^{\text{He}} \) denotes the Hall resistance of the graphene adsorbing one layer \(^4\)He gas. \( \Delta R_{xy} \) has an
oscillating structure around CNP due to the UCF effects. The values of \( V_g \) that yield the
large amplitude of \( \Delta R_{xy} \) are distributed around \( V_{\text{CNP}} \). In contrast, \( |\Delta R_{xy}| \) is relatively small in
the quantum Hall regime; for instance, \( 2.1 \, \text{V} < V_g < 7.0 \, \text{V} \) for \( B = 6.0 \, \text{T} \), or \( 1.4 \, \text{V} < V_g < 5.7 \, \text{V} \)
for \( B = 6.5 \, \text{T} \), which is reasonable due to the invariance of \( R_{xy} \) in the quantum Hall plateau.

Next, we discuss the sensitivity of a monolayer graphene device for use as a gas sensor
working at low temperatures and in high magnetic fields. To evaluate the resistance variation
in more detail, we evaluate the normalized Hall resistance \( r_{xy} = \Delta R_{xy}/R_{xy} \) as a function of
\( V_g \) in Fig. 3(c) together with the normalized magnetoresistance \( r_{xx} = \Delta R_{xx}/R_{xx} \) in Fig. 3(d).
In the case of \( r_{xy} \), enormous enhancement of \( |r_{xy}| \) appears at \( V_g \approx 19.7 \, \text{V} \), which is near the
point where \( R_{xy} = 0 \), in contrast to the broad enhancement of \( r_{xx} \) around \( V_{\text{CNP}} \). Although the
significance of the absolute resistance change or the normalized one is controversial, selectivity
among \( \Delta R_{xx} \), \( \Delta R_{xy} \), \( r_{xx} \) or \( r_{xy} \) is beneficial for obtaining higher sensitivity as the situation
demands for various parameters such as magnetic fields, temperatures, or gate voltages.

Finally, we present preliminary results regarding the mass effects on magnetotransport.
Fig. 4(a) and (b) demonstrate the magnetoresistance \( R_{xx} \) and its change \( \Delta R_{xx} \) of the graphene adsorbing one layer Ar gas from the pristine one, respectively, as a function of \( V_g \) for \( B = 6.0 \, \text{T} \)
and 6.5 T. These data are taken after thermal annealing of the sample \textit{in situ}; therefore, CNP
moves to approximately 0 V. In Fig. 4(a), imperfect quantum oscillations originating in the
QHE are also visible, as is the case with the initial state. Broader and larger-amplitude \( \Delta R_{xx} \)
oscillations are observed than in the case of \(^4\)He adsorption. The magnitude of \( |\Delta R_{xx}/R_{xx}| \)
is achieved up to several tenths of a percent. However, repeated thermal cycles of the sample
may increase the disorder, and evacuations of the sample cell may introduce impurities on the
graphene, which affect the transport properties. Consideration of disorder or impurities may be
essential to the variation in \( R_{xx} \) or \( R_{xy} \). Though the data are still primitive, and further careful
investigation into the effects of disorder or impurities on the magnetotransport using various
grades of samples is required, the results imply that the monolayer graphene device is promising
for the development of a highly sensitive gas sensor for heavier atoms.

In conclusion, we have carried out the magnetotransport measurements of \(^4\)He or Ar-adsorbed
monolayer graphene with disorder or impurities at a temperature of 4.4 K under a magnetic field $B$ ranging from 0 to 7 T. The magnetoresistance difference $\Delta R_{xx}$ and the Hall resistance difference $\Delta R_{xy}$ from the pristine graphene oscillate with the gate voltage $V_g$ and $B$ for one layer of $^4$He or Ar-adsorbed graphene, and this behavior is related to the Landau filling factor. Magnitudes of both quantities strongly depend on $V_g$ and are generally larger in the region around the CNP while being smaller in the QHE regime. The results obtained in this study indicate that mass effects of inert atoms may facilitate development of highly sensitive gas sensors.

Acknowledgments

We acknowledge A. Sawada and H. Yayama for the experimental setup at low temperature and high magnetic field with a helium-free cryostat. We thank T. Nakajima for machining the cryostat parts and the electronics of the experiments. We are thankful to T. Terashima and S. Sasaki for permitting us to use the clean room facilities in the LTM center of Kyoto University. This research was performed under the Cooperative Research Program of ”Network Joint Research Center for Materials and Devices” (Grant No. 2011A10, No. 2013A18, No. 20161202, and No. 20161210). This work was supported by the ”Topological Quantum Phenomena” (No. 25103722) Grant-in Aid for Scientific Research on Innovative Areas from the MEXT of Japan, JSPS KAKENHI Grant Number 25870966 and No. 15K05135, Grants-in-Aid for Basic Science Research Projects from the Sumitomo Foundation (Grant No. 100711).

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