PAPER

Electron transport tuning of graphene by helium ion irradiation

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Abstract

This article reviews charge carrier transport phenomena in single-layer graphene, in which crystalline defects are generated by helium-ion-beam irradiation using a helium-ion microscope. Crystalline defects work as electron scatterers, and the conductivity drastically decays as ion dose increases. Moreover, real-time conductivity monitoring during ion beam scans over the graphene surface is demonstrated. In cryogenic measurements under magnetic fields, defective graphene exhibits negative magnetoresistance, suggesting that strong localization occurred in this two-dimensional electron system, which survived even at room temperature. The localized state contributes to inducing a transport gap around the Dirac point, where the density of states is at its minimum, and it enables field-effect control of the carrier transport by tuning the carrier density. The fabrication and operation of field-effect transistors with defective graphene channels are demonstrated.

Introduction

Two-dimensional (2D) electron system in graphene, a 2D sheet of carbon atoms [1], is unique because of its band structure with two degenerated Dirac cones at the Fermi level. Due to its atomic level thinness, electron transport in graphene is subject to strong modulation even by a weak perturbation of electrostatic potential, including graphene lattice imperfection, surface-attached molecules, or physical stimulation of the surface. This feature of 2D materials contributes to sensor applications with high sensitivity. Electron scattering in graphene is also unique, with either inter or intravalley scattering, and this difference has considerable impact on electron localization states. This review investigates the effects of such electron scattering in graphene using intentionally induced scatterers.

As a result of scattering with impurities, electrons could return to the original place and form a closed trajectory. Quantum interference can enhance the probability of this event in systems with time-reversal symmetry. This phenomenon is known as Anderson localization, and its precursor, weak localization (WL) [2–5]. Breaking the time-reversal symmetry by applying a magnetic field causes destructive interference, which is observed as negative magnetoresistance (MR) [6, 7]. Therefore, magnetotransport is a sensitive probe for the quantum interference of electron wavefunctions. In graphene, the backscattering of electrons is suppressed due to the Berry phase of \( \pi \), ‘delocalization’ [8, 9]. This effect is attributed to weak antilocalization (WAL) and experimentally observed as positive MR. The interference effects in graphene depend on phase-breaking inelastic scattering and intravalley scattering, which leads to the cancellation of WAL, and inter-valley scattering, which mixes the states of two valleys, resulting in the occurrence of WL in graphene [9].

On the other hand, strong localization (SL) was observed in defective graphene. The electrical conductance is determined by hopping transport between localised states in the SL regime. Similar to the WL, the time-reversal symmetry breaking leads to destructive interference and orbital effects between the localized states, increasing the hopping probability [10–12], resulting in negative MR [13, 14].
Previous studies have introduced potential perturbation in the 2D electron system in graphene through various means. One typical method uses oxygen \([15–21]\), including ozone, to modify the lattice of carbon atoms. When oxygen atoms are attached to graphene, which is occasionally referred to as graphene oxide (GO), the carrier conduction properties in GO are modified according to the degree of oxidation. In this case, the potential disorder is caused by local sp\(^{3}\) hybridization, resulting in carrier localization \([15]\). Another method is the hydrogenation of graphene \([22–26]\), known as graphene. Hydrogenation, in this case, is a reversible process in which conduction can be changed from metallic to insulating. Here the potential perturbation is also caused by attributed to local sp\(^{3}\) hybridization. One interesting work on the hydrogen process in graphene is hydrogen-plasma etching, which forms hexagonal nanopits with zigzag-edged straight lines \([26]\). Instead of using oxygen or hydrogen, the surface modification process was also investigated by chlorination \([27, 28]\) or fluorination \([29, 30]\).

Another method to modulate the 2D electron system is irradiating graphene with accelerated ions to remove some carbon atoms from the graphene lattice. This method enables control of the irradiation area using the focused ion beam (FIB) technique, commonly used for sample etching. Gallium is a typical ion for the FIB technique. It was adopted for graphene modification \([31, 32]\) to investigate the carrier conduction tuning by defects. Instead of large ions like gallium, much smaller ions like carbon have also been used to generate defects \([33–36]\). To explore electron transport in defective graphene, the size of defects should be as small as possible because the area of disordered graphene would affect electron scattering. The adsorption of molecules from the ambient to the activated dangling bonds and their surrounding areas have also been investigated, illustrating the capturing of molecules from air \([36]\).

This review presents a novel method to generate point defects in graphene using a helium-ion microscope (HIM) to apply helium ion beam to graphene sheets \([37–39]\). Localization phenomena of 2D electrons in defective graphene are investigated via the negative magnetotransport effect, which is detected even at room temperature. In addition, such localization generates a transport gap around the Dirac point, enabling carrier transport tuning by electrostatic carrier density control. Transistor operations based on the transport gap in defective graphene are also demonstrated.

**Transport tuning by helium-ion irradiation**

When a large-sized ion, such as gallium, forms a defect in graphene, even if a high electric field accelerates the ion, the ion will be stopped at the graphene surface (or the insulating substrate such as SiO\(_2\)), leaving a big ‘crater’ instead of a point defect in graphene \([37, 38]\). The electron scattering process in a disordered region around such a crater is complicated, thus making it unsuitable for exploring the localization phenomena. On the other hand, helium-ion irradiation could form point defects because of its small ion size. The helium-ion beam was first applied to graphene to curve it into nanoribbons using HIM \([37]\). This technique is based on the atomic level spatial resolution due to helium ions’ strongly focused ion beams accelerated by a high voltage of 30 keV. The small size of helium ion enables its penetration in the substrate, leaving a point defect in graphene without forming a crater on the surface. The effect of the substrate on the ion irradiation process is an important point in the present technique of carrier transport tuning, particularly in terms of the backscattering of ions from the substrates. It should be explored more precisely by changing the substrate. Here, the positive charge of the helium ions remains close to the surface of the sample. To eliminate the effect of positive charge on the electron transport properties, the charge is neutralized by applying the electron shower after the ion irradiation process with a flood gun equipped with HIM.

However, etching graphene on an insulator surface requires a large ion dose (typically \( > 10^{17}\) ions cm\(^{-2}\)). This causes swelling at the surface of the silicon dioxide, inducing strain and a disordered lattice around the bombardment centre \([40]\). Therefore, the nanoribbons should be formed in suspended graphene \([37]\).

On the other hand, it was observed that an ion dose less than \(10^{16}\) ions cm\(^{-2}\) could significantly modulate the electronic transport properties without swelling \([40]\). Here, we demonstrate how ion irradiation causes current modulation in graphene \([39]\). In figure 1, we show the real-time monitoring of ion-irradiation-induced current modulation. A single layer of graphene, placed on a SiO\(_2\) substrate, is attached with metal electrodes to measure the current flowing in the graphene between the electrodes. The sample is placed on HIM’s sample stage. Subsequently, the in situ monitoring of current flowing in graphene during helium-ion-beam irradiation is enabled (figure 1(a)). Around the centre of this sample, called the channel, some rectangular regions are irradiated with a high dose of \(2.0 \times 10^{16}\) ions cm\(^{-2}\) to form highly resistive regions, as shown in the HIM image in figure 1(b). Before and after the high dose irradiation process, we performed certain HIM observations with a low ion dose of \(5.0 \times 10^{15}\) ions cm\(^{-2}\) for obtaining images like figures 1(b) and (d). Figure 1(c) shows the in situ monitoring of the current flowing between the two electrodes at a bias of 1 mV during irradiation. Even with a low ion dose, each observation process here leads to a sharp drop in current. Next, the channel (1 \(\mu\)m\(^2\)) is
irradiated with three 100 nm width lines at different ion doses, as shown in figure 1(d). Here, each scan is with 1 nm spacing of beam spots, scanned from left to right across the channel. Figure 1(e) shows the monitored current flowing between electrodes at 100 mV bias. Followed by the sharp drop in current by the first shot of irradiation 1, the current decay is 'exponential' to the processing time in Irradiation 2 and 3. Here, the irradiation time is proportional to the width of the irradiated area. Therefore, the current decay is exponential to the length of the irradiated region, which is the hallmark of electron localization.

**Carrier localization in helium-ion-irradiated graphene**

The carrier localization of helium-ion-irradiated graphene was systematically investigated by measuring the electrical resistance and its dependence on the carrier density, magnetic field, temperature and ion dose [41]. Monolayer graphene devices were fabricated using the conventional process, including the mechanical exfoliation method and electron beam lithography. We defined the effective channel as the region between Cr/Au electrodes with controlled mild dose irradiation (the light blue region in figure 2(a)). Other regions were insulated by irradiation with a high dose (the red region in figure 2(a)). To minimise the effect of the non-irradiated graphene region, the electrode width (W_E) and the non-insulating region width (W) are almost equal, and the effective channel length (L) and the distance between the electrodes (L_gap) are almost the same.

For the results of MR measurement for various temperatures, as shown in figure 2(b), the negative MR was observed in the entire temperature (T) range, up to 300 K. The absolute value of the MR ratio (∆R/R_0) increased under a perpendicular magnetic field (B) and is not saturated even at 6 T. The observed negative MR can be attributed to hopping transport in the SL regime as discussed below [10–12, 15, 41–44]. ∆R/R_0 as a function of B at T = 10 K for each hole density (n_h). |∆R/R_0| is maximized at the charge neutral point (CNP) to be ~0.51 and decreased with increasing n_h.

When SL is dominant, the transport mechanism, including magneto transport, is expected to be hopping conduction [10–12]. In the 2D-variable range hopping (VRH) model [45], the T dependence of the resistance (R) is described by R ~ exp[(T_0/T)^1/3]. Here, T_0 is the characteristic temperature of VRH, expressed as T_0 = 3/(k_b N(E_f)^0.5), where k_b is the Boltzmann constant, N(E) is the density of states (DoS) at energy E [45], and ξ is the localization length. These characteristics can be confirmed in our devices, as shown in figure 3, indicating that the SL regime is the dominant transport mechanism in the helium-ion-irradiated graphene. The estimated
localization lengths are independent of the carrier density, while the localization length is sensitive to the ion dose.

Figure 4 (a) summarises $\Delta R/R_0$ at the CNP for various $T$. The negative MR is observed for all $T$. (c) $\Delta R/R_0$ versus $B$ plot at $T = 10$ K for various $n_h$. The inset depicts the optical image of one of the multichannel devices in this study. The scale bar corresponds to 10 mm. Reprinted from [41] © 2020 Elsevier Ltd. All rights reserved.

Figure 3. $R$ versus $T^{-1/3}$ semilogarithmic plot of the device with a channel size of $L = W = 1.0$ mm and a dose of $0.5 \times 10^{15}$ ions cm$^{-2}$. The symbols represent the experimental data. The solid lines and $T_0$ values are the fitting results with $R \sim \exp((-T_0/T)^{1/3})$. Reprinted from [41] © 2020 Elsevier Ltd. All rights reserved.

localization lengths are independent of the carrier density, while the localization length is sensitive to the ion dose.

Figure 4(a) summarises $\Delta R/R_0$ at the CNP and $B = 6$ T for various doses. The devices with $\geq 2.0 \times 10^{15}$ ions cm$^{-2}$ dose show small $|\Delta R/R_0|$ and/or unstable characteristics. The VRH fitting analysis shows that the localization length decreases with an increased dose, as shown in figure 4(b). This modulation could be associated with an interval distance ($d$) between point defects. We derive $d$ by considering the scattering probability of helium ions with carbon atoms in graphene [38, 41].

Figure 4(b) shows that $\xi$ and $d$ are slightly correlated. However, this correlation is unclear for the dose $\geq 2 \times 10^{15}$ ions cm$^{-2}$, where the data have relatively large error bars of $\xi$ due to the smaller/unstable $\Delta R/R_0$. The unstable characteristics could be attributed to small $\xi$ and $d$, close to the order of the distance between carbon atoms in graphene. Thus, large defects might be formed in the highly dosed devices owing to point defect percolations, destroying graphene crystalline integrity and the interference effect.
Graphene transistor with helium-ion-irradiated graphene channel

Graphene was expected to be used as the channel material in field-effect transistors (FETs) because of its extremely high carrier mobility, with the prospect of overcoming the short-channel effect in the scaled-down transistors because of its atomic size thinness [46]. However, despite the significant development efforts [47–49] in graphene nanoribbons or bilayer graphene, the lack of a band gap has been a limitation for transistor applications.

Here, as one of the methods to overcome this limitation, the helium-ion-irradiated graphene was applied to a FET’s channel material. In defective graphene, depending on the channel’s defect density, carrier localization could cause a transport gap around the Dirac point where the density of state attains its minimum value. Therefore, the turning of carrier conduction is expected by adjusting the Fermi level around the transport gap by gate biasing. Low carrier mobility is one of the limitations of this conduction tuning method. Therefore, the channel length should be designed as short as possible. Accordingly, the device structure is shown in figure 5(a) [50]. Here, the device has two independent top gates with a 20 nm gap between them. The spatial resolution of the e-beam lithography and lift-off process of forming a split-gate structure determines the gap between the top gates. The graphene channel between these two gates is irradiated helium ions at a controlled dose of 8.7 × 10^{15} ions cm^{−2}. This device’s channel width is 30 nm, determined by irradiation with heavy-ion dose, as shown in the schematic and HIM image in figure 5(b) and (c), respectively. The two top gates independently control the carrier type and concentration. When the gate bias of one of the top gates is fixed to be positive, inducing electrons underneath, this transistor assumes the ON-state when another top gate is positively biased and OFF-state for negative gate bias, working as an n-type transistor (figure 5(d)). Here, the maximum ON/OFF ratio is nearly three orders of magnitude, and the ON current is 7 × 10^{−11} A, which corresponds to 2 nA μm^{−1}. If the fixed gate bias is negative, the device acts as a p-type transistor (figure 5(e)), with the maximum ON/OFF ratio nearly two orders of magnitude and the ON current of 2 × 10^{−11} A (0.7 nA μm^{−1}). This indicates that the device works as a polarity-reversible transistor, which means that the transistor polarity (n-type or p-type) is defined by electrostatic control. The transistor polarity in conventional silicon is determined by impurity doping and it can never be dynamically changed. It was observed that this new type of dynamically reconfigurable device with a renewed circuit architecture enables a power consumption reduction of 59% [51].

As a demonstration of the polarity-reversible transistor, inverter devices are fabricated by a wafer-scale top-down process on a single-layer graphene sheet grown using the chemical vapour deposition method (figure 6(a)) [52]. Here, an inverter has three gates and two irradiated channels in one device (figure 6(b)), which is constructed by a combination of two polarity-reversible transistors shown in figure 5(a). When the two outer-top gates are biased with opposite polarity to each other, the device works as an inverter when sweeping the centre gate bias (figure 6(c), (d)); this is also a polarity-configurable device. The potentials at V_{1g} and V_{2g} can be flipped by flipping the polarities of V_{tg1} and V_{tg2}. Once the two outer-top gates’ biases are fixed, the inverter could be operated with a single gate charging/discharging process, which can reduce the number of consumed charges compared to the conventional silicon transistors that require two transistors.
Summary

This article reviews the carrier transport properties of defective graphene, in which point defects are generated by helium-ion-beam irradiation using a HIM. Even when obtaining a HIM image with a low ion dose, the electrons’ conductivity rapidly decays as the ion dose increases. It is thus determined that point defects in graphene induce electrons backscattering, which is suppressed in pristine graphene, leading to the SL regime. Magnetoresistance measurements illustrate the occurrence of the SL regime under high magnetic field conditions. Surprisingly, negative magnetoresistance is observed even at room temperature. Additional study is required to precisely identify the type of defects generated by helium-ion-beam irradiation, e.g., using scanning tunnelling microscopy. Moreover, the transistor applications of the defective graphene have been demonstrated. Here, the localization of electrons generates a transport gap around the Dirac point where DoS attains its minimum value and can control between ON and OFF states of the current flowing through the defective graphene channel. The HIM technique, with its high spatial resolution of sub-nanometer scale and the dose control, is expected to be used in various devices.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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