Tuning of Graphene Properties via Controlled Exposure to Electron Beams

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Abstract—The controlled modification of graphene properties is essential for its proposed electronic applications. Here, we describe a possibility of tuning electrical properties of graphene via electron-beam (e-beam) irradiation. We show that by controlling the irradiation dose one can change the carrier mobility and increase the resistance at the minimum conduction point in the single layer graphene. The bilayer graphene is less susceptible to the e-beam irradiation. The modification of graphene properties via irradiation can be monitored and quantified by the changes in the disorder D peak in Raman spectrum of graphene. The obtained results may lead to a new method of defect engineering of graphene physical properties. They are also important implications for fabrication of graphene nanodevices, which involve scanning electron microscopy and e-beam lithography.

Index Terms—Defects in graphene, Raman spectroscopy, disordered graphene, electron-beam (e-beam) irradiation, graphene devices.

I. INTRODUCTION

GRAPHENE is a single sheet of sp²-bound carbon atoms with many unique properties. It reveals extraordinary high room temperature (RT) carrier mobility of up to \(\sim 15,000 \text{ cm}^2/\text{Vs} \) [1]–[3] and an extremely high “intrinsic” thermal conductivity exceeding \(\sim 3000 \text{ W/mK} \) near RT for large flakes [4]–[6]. Recent experiments with the modification of graphene surface via hydrogenation [7], [8], potassium doping [9], ions irradiation [10], and the adsorption of individual gas molecules (\(\text{NO}_2, \text{NH}_3, \text{etc.} \)) [11] have shown that graphene’s properties can be altered and tuned for specific applications. However, little is known about the effect of the electron-beam (e-beam) irradiation on graphene or graphene-based devices. The focused beams of electrons, which are commonly used in scanning electron microscopy (SEM) and device fabrication, are known to induce changes to the properties of carbon allotropes and nanostructures including graphite, fullerenes, and carbon nanotubes [12]. Recently, it was also shown that graphene exposure to the e-beams results in the modification of its surface [13], [14]. We have demonstrated that electron irradiation leads to the appearance of the disorder D peak at \(\sim 1350 \text{ cm}^{-1} \) in the Raman spectra of irradiated graphene [13].

In this paper, we report how electrical properties of the single-layer graphene (SLG) depend on the irradiation dose, and correlate the current–voltage characteristics with the evolution of Raman spectrum of irradiated graphene. We also investigate the response of bilayer graphene (BLG) on the e-beam irradiation and compare it with that of SLG. It is known that BLG reveals a band gap when subjected to electrical field, and as a material might be more promising for electronic applications [3]. Our finding that BLG is less susceptible to e-beam irradiation, conventionally used in SEM characterization and device fabrication, adds extra motivation for the BLG device applications.

II. FABRICATION AND MEASUREMENTS

The graphene flakes were prepared by the standard micromechanical exfoliation from the high-quality graphite. The flakes were transferred to the silicon substrate with 300-nm-thick layer of silicon oxide. The Raman spectroscopy was used to verify the number of layers and check their quality. The details of our Raman inspection procedures were reported by us elsewhere [15]–[18]. The SLG and BLG samples were selected via deconvolution of the Raman 2-D band and comparison of the intensities of the G peak and 2-D band. The graphene back-gate devices were fabricated with the e-beam lithography (EBL). We defined the source and drain regions and then followed with evaporation of Cr/Au with thickness of 10 and 60 nm, respectively. The heavily doped silicon substrate was used as the back gate to tune the Fermi level of graphene.

We conducted e-beam irradiation using Leo SUPRA 55 EBL system, which allows for accurate control of the exposed area and irradiation dose. Special precautions have been taken to avoid additional unintentional e-beam irradiation. The alignment program in the utilized EBL system offers a way to scan only the alignment marks without exposing other locations. We used the gold alignment marks located more than 30 \(\mu\text{m} \) away from the graphene device to avoid unintentional irradiation during the scanning steps. For our experiments, we selected the accelerating voltage of 20 keV and the working distance of 6 mm (the same as in EBL process). The area dosage was calculated and controlled by the nanometer pattern generation system (NPGS). NPGS allowed us to control the scanning distance from point to point and set the dwelling time on each point. The beam current, used in calculation of the irradiation dose, was...
measured using a Faraday cup. The beam current for all the irradiation experiments in this paper was 30.8 pA. The experiments were conducted in the following sequence. First, the back-gated graphene devices were irradiated with a certain dose of electrons. Second, the irradiated graphene devices were examined using micro-Raman spectroscopy to detect any changes with the Raman signatures of graphene. Third, the current–voltage (I–V) characteristics were measured to examine the changes of electrical properties. After I–V data were collected, the irradiation dose was increased and all the steps were repeated.

The e-beam irradiation was performed inside the SEM vacuum chamber with a low pressure ($10^{-7}$ torr), whereas the Raman spectroscopy and electrical measurements were carried out at ambient conditions. We used a Reinshaw InVia micro-Raman spectrometer system with the laser wavelength of 488 nm. The electrical measurements were performed with an Agilent 4142B instrument. Fig. 1(a) shows an optical image of a typical SLG graphene device. Fig. 1(b) illustrates the irradiation process showing the exposed and shielded regions of the device under test. The devices and irradiation process were intentionally designed in such a way that only graphene channel is exposed to the e-beam, while the metal contacts are not irradiated. The latter allowed us to avoid any possible changes in metal contact resistance after the irradiation. We tested three SLG and three BLG devices.

III. RESULTS AND DISCUSSION

A. Single-Layer Graphene Devices

We started by measuring the electrical resistance between the source and drain as a function of the applied gate bias. Fig. 2(a) shows the evolution of the electrical characteristics of SLG device after each irradiation step. The electron irradiation dose for each step is indicated in the figure’s legend. As one can see, the ambipolar property of graphene is preserved after irradiation within the examined dosage range. The observed up shift of the curves indicates increasing Resistivity of graphene over a wide range of carrier concentration. The increase is especially pronounced after the fourth step with a higher irradiation dose (1280 $\mu$C/cm$^2$).

In order to analyze the results and rule out the role of the contact resistance, we used the following equation to fit our
resistance data [19], [20]:

\[ R_{ds} = R_{\text{Cont}} + \frac{L}{W} \left( \frac{1}{e\mu\sqrt{n^2 + n_{BG}^2}} \right) \]  

(1)

where \( R_{\text{Cont}} \) is the contact resistance, \( \mu \) is the mobility, \( e \) is the elementary charge, and \( L \) and \( W \) are the length and width of the channel, respectively. In (1), \( n_0 \) is the background charge concentration due to random electron–hole puddles [14], and \( n_{BG} \) is the charge induced by gate bias calculated from the following:

\[ n_{BG} = \frac{C_{BG} |V_{BG} - V_{BG,\text{min}}|}{e} \]  

(2)

where \( C_{BG} \) is the gate capacitance per unit area taken to be 0.115 mF for 300-nm SiO\(_2\) substrate.

The inset to Fig. 2(b) shows the result of the fitting with (1) and (2) of the data for SLG device before e-beam irradiation. Note that the fitting does not cover the interval close to the charge neutrality point because this region is characterized by a large uncertainty in the data. The fitting was separately conducted for the negative and positive gate bias regions. For simplicity, we consider the fitting results from the p-type branch. The fitting gives the contact resistance of 446 \( \Omega \), the initial mobility \( \mu = 5075 \text{ cm}^2/\text{Vs} \), and the charge impurity concentration of \( 2.13 \times 10^{11} \text{ cm}^{-2} \), which are very close to the typical values for clean graphene samples [21]. During the experiments, the irradiated regions excluded the contacts. For this reason, the contact resistance should not change during the measurements, and we can estimate the resistance of the irradiated graphene channels by subtracting the contact resistance from the total resistance. To fit our results for irradiated graphene devices, we modified (1) by adding the term \( R_{\text{irrad}} = (L/W)\rho_{\text{irrad}} \), which is the resistance increment induced by e-beam irradiation. 

Fig. 2(b) shows the evolution of the mobility due to e-beam irradiation for three SLG devices. We note that the mobility decreases almost linearly and drops by 50–60% over the examined irradiation dose.

We carefully examined the Raman spectrum of the graphene devices after each irradiation step. One can see from Fig. 3(a) that the pristine graphene has typical signatures of SLG: symmetric and sharp 2-D band (\( \sim 2700 \text{ cm}^{-1} \)), and large \( I(2-D)/I(G) \) ratio. The absent or undetectably small D peak at 1350 \( \text{ cm}^{-1} \) indicates the defect-free high-quality graphene. The disorder D peak appears after the e-beam irradiation. Initially, the intensity of the D grows with increasing dosage after each irradiation step. The trend reverses after the irradiation dose reaches a certain level. We used the intensity ratio \( I(D)/I(G) \) to characterize the relative strength of the D peak [13], [22]. The ratio \( I(D)/I(G) \) reveals a clear and reproducible nonmonotonic dependence on the irradiation dose [see see Fig. 3(b)]. This behavior was observed in all devices in our experiments. It is consistent with our earlier studies [13]. A similar trend was reported for graphite, where the ratio \( I(D)/I(G) \) was also increasing with the irradiation dose. Such dependence was attributed to the crystal structure change from crystalline to nanocrystalline and then to amorphous form [22]. The bond breaking in such cases is likely chemically induced, since the electron energy is not sufficient for the ballistic knock out of the carbon atoms [13].

Other factors contributing to the growth of the disorder D band can be contaminant molecules or water vapor, which dissolve under irradiation and may form bonds with the carbon atoms of the graphene lattice.

The change in the G peak position under the e-beam irradiation is shown in Fig. 3(b). The G peak position shifts to higher wave numbers with increasing irradiation dose (with exception for the second step). But after certain dose (step four), the peak position starts to move to the lower wave numbers. A similar trend was also observed in graphite [22]. It is reasonable to believe that e-beam irradiation leads to disorder in graphene’s crystal lattice via formation of defects and sp\(^3\) bonds.

In addition to the D peak, we also observed the appearance of other peaks in Raman spectrum of irradiated graphene. The peak at \( \sim 1620 \text{ cm}^{-1} \), referred to as D’, was detected after the second step of irradiation. This peak was attributed to the intravalley double-resonance process in the presence of defects [7]. The e-beam irradiation also results in the appearance of the D + D’ peak around 2950 cm\(^{-1}\). This peak, unlike the 2-D and 2D’ bands, is due to a combination of two phonons with
Fig. 4. Evolution of SLG resistivity with irradiation dose. The inset shows the effect of e-beam irradiation on the charge density for three SLG devices, represented by red, green, and black data points, respectively.

A slight broadening of the 2-D band and decrease of the $I(2D)/I(G)$ ratio were also observed. The decrease of the $I(2D)/I(G)$ ratio was previously attributed to the increasing concentration of charged defects or impurities [23]. Our electrical measurements are consistent with this interpretation indicating a growing density of the charged impurities with increasing irradiation dose (see inset to Fig. 4).

Fig. 4 shows evolution of the resistivity near the charge neutrality point with the irradiation dose. One can see a clear trend of increasing $\rho_{\text{max}}$ with the irradiation dose. Since the contacts were not irradiated during the experiment, the overall increase of device resistance is due to the increasing resistivity of the irradiated graphene. This can be understood by the induced defects that create an increasing number of scattering centers in the graphene lattice. Note that the $\rho_{\text{max}}$ increases by a factor of $\sim 3$–7 for SLG devices.

We also found that the irradiation-induced changes in the properties of SLG are reversible to some degree. The $I$–$V$ characteristics can be at least partially recovered by annealing or storing the devices over a long period of time in a vacuum box. The annealing may help to repair the bonds and clean the surface from the organic residues, while keeping devices in vacuum may lead to the loss of the irradiation-induced charge. The latter suggests that the e-beam irradiation results in the creation of the charged defects, which are more efficient in carrier scattering than neutral defects.

B. Bilayer-Graphene Devices

In order to compare SLG with BLG under e-beam irradiation, we conducted the same experiments with the back-gated BLG devices. The only difference was a higher dose of irradiation for BLG than for SLG. The first step was $1600 \mu C/cm^2$ compared to $320 \mu C/cm^2$ in the first step for SLG. We expected that a larger dose would be required for BLG from the analogy with the multi-wall carbon nanotubes (CNTs), which were found to be less susceptible to e-beam irradiation than the single-wall CNTs [8].

We again used Raman spectroscopy to monitor the evolution of the material properties revealed by I-V measurements.

![Fig. 4](image1.png)

**Fig. 5.** (a) Evolution of the transfer characteristics of BLG with increasing irradiation dose. The irradiation dose after each step is indicated in the legend. (b) Carrier mobility of BLG devices as a function of the irradiation dose for three BLG devices, shown by pink, cyan, and blue data points, respectively. Note that the for two devices with higher mobility, the dependence has a turning point at the dose of about $12,000 \mu C/cm^2$, but for the device with lower mobility, the decrease is approximately linear. The inset shows the electrical resistivity as a function of the irradiation dose.

We observed substantially different irradiation-induced effects in BLG as compared to SLG devices. Fig. 5(a) shows evolution of the transfer characteristics for a typical BLG device with increasing irradiation dose. The total electron irradiation dose shown for BLG is $27,200 \mu C/cm^2$, while that for SLG is only $4480 \mu C/cm^2$. In Fig. 5(b), we present the effect of irradiation on the charge carrier drift mobility in BLG devices. One can see that the overall trend is similar to the SLG case, but the mobility decrease rate is quite different. Our data indicate that the BLG is much less susceptible to e-beam irradiation than SLG. Indeed, if we look at the irradiation dose below $4480 \mu C/cm^2$, we see that the mobility drop is smaller than $25\%$ for BLG compared with $\sim 50\%$–$60\%$ drop for SLG. At the irradiation dose above $12,000 \mu C/cm^2$, the mobility decrease rate also reduces for the two high-mobility devices, but for low-mobility devices, the mobility decrease rate is roughly constant within the examined range. This is a similar behavior to the one revealed by SLG devices, but requires much higher irradiation doses to be observed.

The resistivity $\rho_{\text{max}}$ increases by a factor of $\sim 1.6$ over the entire range for BLG devices, as seen in the inset to Fig. 5(b). Up to the dose of $\sim 4480 \mu C/cm^2$, $\rho_{\text{max}}$ of BLG changes only by
~14% compared to ~300%–700% in the case of SLG. This difference is reflected by the $I(D)/I(G)$ ratio in the Raman spectra for SLG and BLG.

The inset to Fig. 6 shows the Raman spectrum of a typical BLG device after several e-beam irradiation steps. Unlike in SLG, the disorder-induced Raman D peak in BGL does not reveal a pronounced growth with irradiation dose even over a much larger dose range. No detectable D' or D + D' peaks appear in the Raman spectrum of BLG. The absence of these peaks suggests that e-beam irradiation over the examined dose range does not create limited amounts of defects in BLG.

IV. CONCLUSION

We carried out a detailed investigation of the electrical and Raman spectroscopic characteristics of graphene and BLG under the e-beam irradiation. It was shown that the SLG is much more susceptible to e-beam irradiation than BLG. The appearance of the disorder-induced D peak in graphene Raman spectrum suggests that e-beam irradiation can induce defects in graphene lattice. The mobility and electrical resistivity of graphene can be varied by the e-beam irradiation over a wide range of values. The obtained results may lead to a new method of defect engineering of graphene properties. The results also have important implications for fabrication of graphene nanodevices, which involve SEM and EBL.

REFERENCES


