Effect of Energetic Electron Irradiation on Graphene

Isaac Childres$^{1,2}$, Romaneh Jalilian$^{1,2}$, Michael Foxé$^4$, Alex Chernyshov$^{1,2}$, Leonid Rohkinson$^{1,2}$, Igor Jovanovic$^4$, Yong P. Chen$^{1,2,3}$

$^1$Department of Physics, Purdue University, West Lafayette, IN, 47907
$^2$Birck Nanotechnology Center, Purdue University, West Lafayette, IN, 47907
$^3$School of Electrical and Computer Engineering, Purdue University, West Lafayette, IN, 47907
$^4$School of Nuclear Engineering, Purdue University, West Lafayette, IN, 47907

Email address: yongchen@purdue.edu

Graphene has been the focus of much research in material science and nanotechnology due to its many unique properties and potentials in device applications. Many reports have been made on graphene’s very high electrical conductivity [1,2] at room temperature, and it is discussed as having potential for use in next-generation transistors [3] and novel nano-sensors [4].

Here we present a study of extended exposure of energetic electrons on graphene and the effect of the exposure on its conductivity and crystal structure. Our interest in the change in graphene, especially its degree of degradation, caused by electron bombardment is threefold: 1) Electron-beams are a commonly used tool in both imaging of graphene, e.g. scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and fabrication of graphene devices using electron-beam lithography; 2) Such studies are important to develop graphene-based radiation-hard electronics which can stand up to, for example, charged particle radiations in space; 3) Our group is currently developing a radiation detector based on a graphene field-effect transistor (figure 1). Radiation excites secondary electrons in the semiconductor substrate supporting graphene, and these electrons could travel through the substrate and reach graphene (figure 2). Therefore, understanding how energetic electrons interact with the graphene is important for the reliability and long-term robustness of such sensors.

We have used micro Raman spectroscopy and electrical characterization to study in detail the effects of electron-beam radiation on pristine single-layer exfoliated graphene to understand how disorder develops in the material through bombardment of energetic electrons.

In our experiments, the graphene was exposed to an electron beam in an EVO 40 SEM system with a 0.15nA beam current at a 30KeV acceleration voltage over a 50um-by-50um area for 5 minutes. This gives a dosage of 112.5e-/nm$^2$. The graphene flakes irradiated were exfoliated from natural graphite using Scotch tape onto a highly doped silicon substrate with a 300nm SiO$_2$ over-layer [1]. The flakes were typically 20-100um$^2$ in size.

A single-layer graphene sample was measured by a confocal DXR Raman system using a 514nm laser at 2mW power. Before exposure, the Raman spectrum showed the signature for pristine single-layer graphene, with a G peak at 1584cm$^{-1}$ and a 2D peak at 2674cm$^{-1}$ [5], with a ratio of the intensities of the G and 2D peaks, I(2D)/I(G), to be 2.62. There were also no signs of D or D’ peaks commonly associated with disorder in graphene (figure 3).
After e-beam exposure, the Raman spectrum showed an emergence of a D peak at 1341cm⁻¹ and a small D’ peak appeared at 1624cm⁻¹ [5]. The peak ratio I(2D)/I(G) shrunk to 2.32, while I(D)/I(G) went to 0.565 and I(D)/I(2D) went to 0.244.

The increase of I(D)/I(G) is attributed to a gradual evolution from the sp²-bonded carbon found in graphene into amorphous carbon with substantial sp³ bonding [5]. Our results are also consistent with similar Raman work done by Teweldebrhan and Baladin [6].

The electrical characterization, performed on three single-layer samples, was 2-terminal conductance measurements under a varying back gate voltage across the Si substrate. A typical graphene device can be seen in figure 4. Graphene is a semimetal, such that, as the back gate voltage is varied, there is a voltage value where the majority charge carrier density shifts from p-type to n-type. This is the point of lowest conductivity, because the average charge density is zero. In addition to measuring an overall change in conductance, we also found a shift in this “charge-neutral point” (CNP) after the e-beam exposure.

Before electron-beam irradiation, we measured CNPs of 24V, 25V and 26.5V for the single-layer samples. These samples typically have a positive CNP because of p-doping caused by environmental impurities such as water. After exposure, the charge-neutral point of all samples shifted toward the negative (14V, 4V, and 5V respectively). In each case, there is also an overall decrease of conductivity, especially at the CNP (figure 5).

We interpret these results as negative doping in graphene, likely due to an excessive presence of electrons. The position of this CNP is time-dependent after the exposure, and CNP will gradually shift back toward the positive, but never go to its original value. The decrease of conductivity is also consistent with the development of disorder peaks in the Raman spectrum, as defects in the carbon lattice can also cause more carrier scattering.

In this study, we have shown evidence of disorder and conductivity reduction caused by energetic electron irradiation of graphene. Disorder and a development toward amorphous carbon can be seen in the Raman spectroscopy taken after the exposure, and the conductivity reduction is evident from the electrical characterization. We conclude that care should be taken when using electron-beam-based lithography or imaging on graphene, as prolonged exposure could cause a degradation of graphene. The study is also relevant for the development of radiation-hard electrons and radiation sensors based on graphene.
Figure 1: Schematic of a graphene field effect transistor used as a radiation detector. Incident radiations (such as gamma rays) ionize part of the undoped, electrically biased semiconductor substrate, creating charge carriers that modify the E-field applied on the graphene. A graphene FET should be able to detect this change in the E-field as a change in its resistance.
Figure 2: CASINO simulation of possible paths of secondary electrons ionized by a 400keV Compton electron (e.g. generated by a gamma ray photon) through a 0.5mm-thick silicon substrate. When using graphene FETs as radiation detectors, energetic electrons produced by gamma or other ionizing radiations could pass through the substrate and interact with the graphene.

![CASINO simulation](image)

Figure 3: Raman spectrum measured by a 514nm laser operating at 2mW on a single-layer graphene sample before and after exposure to electron-beam radiation. Exposure causes a reduction of both the G(1584 cm⁻¹) and 2D(2674 cm⁻¹) peaks while causing an emergence of D(1341 cm⁻¹) and D'(1624 cm⁻¹) peaks. The D and D' peaks are clear indications of disorder in the graphene.

![Raman spectrum](image)
Figure 4: Graphene FET device showing the area of the surface exposed to 112.5e/nm² of 30KeV electron radiation.

Figure 5: Gate voltage ($V_{gs}$) -dependent conductance measurements made on 3 single-layer graphene samples with a 10mV drain voltage ($V_{ds}$) for the first sample (a) and 5mV drain for the others (b,c) both before and after e-beam exposure. Conductance was obtained from the measured 2-terminal current ($I_{ds}$) divided by $V_{ds}$. The conductance at the charge-neutral point decreased from: (a) 5.86*10^-5 ohm^-1 before exposure to 5.00*10^-5 ohm^-1 after exposure; (b) 9.41*10^-5 ohm^-1 to 3.50*10^-5 ohm^-1; (c) 7.40*10^-5 ohm^-1 to 5.25*10^-5 ohm^-1.

References: