Comment on "Modification of graphene properties due to electron-beam irradiation" [

Appl. Phys. Lett. 94, 013101 (2009)

]

J. D. Jones, P. A. Ecton, Y. Mo, and J. M. Perez

Citation: [Appl. Phys. Lett. 95](#), 246101 (2009); doi: 10.1063/1.3272954

View online: <http://dx.doi.org/10.1063/1.3272954>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v95/i24>

Published by the [American Institute of Physics](#).

Related Articles

Effect of e-beam irradiation on graphene layer grown by chemical vapor deposition

[J. Appl. Phys. 111](#), 084307 (2012)

Structure of Si-capped Ge/SiC/Si (001) epitaxial nanodots: Implications for quantum dot patterning

[Appl. Phys. Lett. 100](#), 141603 (2012)

Modeling electric charge distribution on insulator under electron bombardment: Case of rectangular surface implantation

[AIP Advances 2](#), 012190 (2012)

Low energy electron beam induced vacancy activation in GaN

[Appl. Phys. Lett. 100](#), 122105 (2012)

Pressure-induced changes in the dielectric response of polymer relaxors

[Appl. Phys. Lett. 100](#), 052904 (2012)

Additional information on Appl. Phys. Lett.

Journal Homepage: <http://apl.aip.org/>

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: <http://apl.aip.org/authors>

ADVERTISEMENT

ACCELERATE AMBER AND NAMD BY 5X.
TRY IT ON A FREE, REMOTELY-HOSTED CLUSTER.

LEARN MORE

Comment on “Modification of graphene properties due to electron-beam irradiation” [Appl. Phys. Lett. 94, 013101 (2009)]

J. D. Jones, P. A. Ecton, Y. Mo, and J. M. Perez^{a)}

Department of Physics, University of North Texas, Denton, Texas 76203, USA

(Received 23 September 2009; accepted 19 November 2009; published online 17 December 2009)

[doi:10.1063/1.3272954]

In their recent letter, Teweldebrhan and Balandin¹ reported modification of graphene properties due to electron-beam irradiation at energies of 5–20 keV from a scanning electron microscope (SEM). After irradiation, they observe the appearance of a strong disorder D peak at around 1345 cm⁻¹ and a drastic increase in electrical resistance. They state that their findings follow the known stages of amorphization of the crystalline graphite lattice into the nanocrystalline state and then, upon further irradiation, into the amorphous state. In this comment, we would like to point out that the appearance of the D peak and increase in resistance with electron irradiation reported in Ref. 1 results from reversible hydrogenation of graphene into graphane or partially hydrogenated graphene,^{2,3} instead of amorphization. Graphane is graphene with an H atom attached to each C atom above and below the C atom in an alternating manner, and is a stable crystalline structure.^{2,4} Partially hydrogenated graphene has H atoms attached to C atoms on only one side of the graphene layer, and is stabilized by ripples in graphene that facilitate *sp*³ bonding with H.^{2,3} The crucial observation we have made that led us to this conclusion is that the D peak that appears after irradiation almost completely disappears after the sample is annealed at low temperatures of 270 °C for 30 min. This reversible appearance of the D peak is the characteristic signature of graphane and partially-hydrogenated graphene.^{2,3}

In our experiments, graphene samples were prepared in air at 50% relative humidity and room temperature by mechanical exfoliation of highly oriented-pyrolitic-graphite onto a 300 nm thick SiO₂ layer grown on a Si wafer.⁵ Graphene samples were identified using optical microscopy,⁵ and micro-Raman spectroscopy that can be used to distinguish single-layer graphene from multi-layer graphene samples by inspection of the full-width-at-half-maximum (FWHM) of the overtone of the D (2D) peak at about 2700 cm⁻¹.⁶ The FWHM is ~30 cm⁻¹ for graphene and ~60 cm⁻¹ for multilayer samples. The micro-Raman system used was a Thermo Electron Alpha XR with a spot size of 0.6 μm², a laser power of 6 mW and a spectral resolution of 2 cm⁻¹. The electron irradiation was carried out using a high-resolution FEI Nova 200 NanoLab SEM system with a sample chamber at a pressure of 10⁻⁶ Torr, and also an electron gun in an ultrahigh vacuum (UHV) chamber at a pressure <10⁻¹⁰ Torr. Postannealing of irradiated samples was carried out using a tube furnace at a pressure of 10⁻⁴ Torr.

Figure 1(a) shows micro-Raman spectroscopy data of a pristine graphene sample that has not been irradiated. Figure

1(b) shows data of the same sample shown in Fig. 1(a) after irradiation for 2 min at an energy of 30 keV using a beam current of 9.5 nA and scanning area of 1.2 × 10³ μm². The resulting electron dosage on the graphene sample was 5.2 × 10¹⁷ e⁻/cm². In Fig. 1(b), we observe a strong and sharp D peak similar to that reported in Ref. 1. In Fig. 1(b), the ratio of the integrated intensity of the D peak, *I*_D, to the integrated intensity of the G peak at about 1580 cm⁻¹, *I*_G, is *I*_D/*I*_G=2.7. This value is similar to the literature value for graphane of about three.² Figure 1(b) also shows D' and (D+D') peaks, which like the D peak, require a defect for activation.² A decrease is observed in *I*_{2D}/*I*_G, where *I*_{2D} is the integrated intensity of the 2D peak at about 2660 cm⁻¹. Also, a slight broadening of the 2D peak is seen in comparison to that of the pristine sample shown in Fig. 1(a). All of these effects are seen in hydrogenated graphene.² After post

FIG. 1. Micro-Raman spectra of graphene. All the curves are normalized to have the same G peak intensity. (a) Pristine graphene sample that has not been irradiated. (b) Sample shown in (a) after irradiation at 30 keV to a dosage of 5.2×10^{17} e⁻/cm². A large and sharp D peak is observed with *I*_D/*I*_G=2.7 indicating graphane has been formed. (c) Same sample shown in (b) after postannealing at 270 °C for 30 min. No D peak is observable indicating the sample has reverted back to its original state. (d) Graphene sample that is preannealed in UHV at 590 °C for 1 h and then irradiated at a dosage of 7.4×10^{15} e⁻/cm² at 5 keV. A small D peak having *I*_D/*I*_G=0.07 is observed, indicating that little or no hydrogenation occurred.

^{a)}Electronic mail: jperez@unt.edu.

annealing the sample shown in Fig. 1(b) at 270 °C for 30 min, the D peak almost completely disappeared, as shown in Fig. 1(c). The nearly complete disappearance of the D peak after annealing at temperatures of 100–400 °C is a unique characteristic of graphane and partially hydrogenated graphene.^{2,3} These temperatures are significantly lower than those for removal of lattice damage in graphite that are typically >1000 °C. Therefore, we propose that the D peak observed after irradiation is due to hydrogenation instead of amorphization. We note that graphane and partially hydrogenated graphene were shown to be insulating,^{2,3} consistent with the findings of high resistance reported in Ref. 1.

We observed the appearance of a reversible D peak by irradiating samples over a range of parameters: with the SEM at energies from 2 to 30 keV and dosages from 7.8×10^{15} to 7.8×10^{18} e⁻/cm², and with the electron gun in UHV at energies of 100 eV–5 keV and dosages of 5.4×10^{15} to 1.8×10^{16} e⁻/cm². In addition, we annealed graphene samples at 590 °C for 1 h in the UHV chamber to remove adsorbates. The samples were then irradiated *in situ* in UHV with the electron gun at an energy of 5 keV and dosage of 7.5×10^{15} e⁻/cm². As shown in Fig. 1(d), these samples exhibited values of I_D/I_G of about 0.07, indicating that little or no hydrogenation occurred. Therefore, we propose that hydrogenation is due to adsorbates such as H₂O on graphene from which H is dissociated by the incident electrons.

Figure 2(a) shows micro-Raman spectroscopy data for a pristine double-layer (DL) graphene sample that has not been irradiated. Figure 2(b) shows data for the same sample after irradiation using the SEM at an energy of 30 keV and dosage of 2.6×10^{18} e⁻/cm². A small D peak with $I_D/I_G=0.27$ is observed. This result is also consistent with hydrogenation, since one would expect I_D/I_G for DL samples to be within a factor of a half of I_D/I_G for graphene if the D peak were due to amorphization. This is because one expects at least the top layer of a DL sample to be amorphized. The small D peak in DL samples has been attributed to less partial hydrogenation due to the significantly fewer number of ripples in DL versus single-layer graphene samples.^{2,3} As shown in Fig. 2(c), the D peak for DL graphene also disappears after post-annealing.

FIG. 2. Micro-Raman spectra of DL graphene. (a) Pristine DL sample that has not been irradiated. (b) Sample shown in (a) irradiated at 30 keV to a dosage of 2.6×10^{18} e⁻/cm². A D peak is observed with $I_D/I_G=0.27$, indicating significantly less hydrogenation than for single-layer graphene samples. (c) Same sample in (b) after postannealing at 270 °C for 30 min, showing that a D peak is not observable.

In summary, we claim that the appearance of the D peak in graphene after electron irradiation is due to hydrogenation instead of amorphization as reported in Ref. 1. This conclusion is primarily based on the almost complete disappearance of the D peak after annealing the sample at temperatures of 270 °C for 30 min. In addition, our conclusion is supported by a decrease in I_{2D}/I_G and slight broadening of the FWHM of the 2D peak, and a significantly reduced value of I_D/I_G for double layer samples after irradiation.

This work was supported by the Faculty Research Grant Program and the Center for Advanced Research and Technology of the University of North Texas. We thank Joshua Wahrmond for useful discussions.

¹D. Teweldebrhan and A. A. Balandin, *Appl. Phys. Lett.* **94**, 013101 (2009).

²D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, and K. S. Novoselov, *Science* **323**, 610 (2009).

³S. Ryu, M. Y. Han, J. Maultzsch, T. F. Heinz, P. Kim, M. L. Steigerwald, and L. E. Brus, *Nano Lett.* **8**, 4597 (2008).

⁴J. O. Sofo, A. S. Chaudhari, and G. D. Barber, *Phys. Rev. B* **75**, 153401 (2007).

⁵K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. L. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, *Nature (London)* **438**, 197 (2005).

⁶A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim, *Phys. Rev. Lett.* **97**, 187401 (2006).