# Response to "Comment on 'Modification of graphene properties due to electron-beam irradiation'" [Appl. Phys. Lett. 95, 246101(2009)]

D. Teweldebrhan and A. A. Balandin[a)]
*Department of Electrical Engineering and Materials Science and Engineering Program, University of California—Riverside, Riverside, California 92521 USA*

Jones Ecton, Mo, and Perez (JEMP)[1] reported an experimental study of graphene under the electron-beam irradiation. In their Comment,[1] JEMP reproduced our results for irradiated graphene,[2] thus providing an independent confirmation for our visible (VIS) Raman spectroscopy data. JEMP then annealed an unspecified number of samples for 30 min, and observed a disappearance of *D* peak. Based on this observation *alone*, they speculated that graphene irradiation in vacuum ($10^{-6}$ Torr) for 2 min leads to its conversion to *graphane*, i.e., hydrogenated graphene. This hypothesis differs from our suggestion that mostly defects, residual carbon, and lattice disorder induced by irradiation are behind the observed Raman spectrum changes.[2] In this reply we show that JEMP's conclusion is based on wrong assumptions and is not supported by either the data provided in their Comment[1] or available literature. Moreover, our ultraviolet (UV) Raman spectroscopy, electrical resistivity, and energy dispersive x-ray spectroscopy data show that JEMP hypothesis is not valid.

JEMP's conjecture that 2 min electron-beam (e-beam) irradiation in vacuum leads to graphene's transformation to graphane is based entirely on appearance of the disorder *D* peak, followed by its disappearance after annealing for 30 min at temperature T~600 K. No electrical resistivity or microscopy data were provided to support this claim. No explanation was given on where a sufficient amount of hydrogen required for graphene transformation to graphane would come in vacuum environment used for irradiation. For comparison, Elias *et al.*[3] had to subject their graphene samples to 2 h of hydrogen-argon mixture with dc plasma to transform graphene to graphane. They needed 24 h of annealing at ~750 K to restore graphene's metallic state. Ryu *et al.*[4] had to coat graphene with 30 nm thick hydrogen silsesquioxane and irradiate it in order to generate hydrogen atoms needed for graphene transformation to graphane. Thus, the physics behind JEMP's suggested hydrogenation is not clear.

In the discussion of disappearance of *D* peak after annealing JEMP make an assumption that the thermodynamics properties of two-dimensional (2D) graphene and three-dimensional (3D) graphite should be the same. JEMP further assume that only the high-temperature annealing ($\geq$1300 K) can be used for the lattice damage removal in graphite. Both these assumption are not valid. Thermodynamic and other properties of 2D and 3D systems are distinctively different. A recent investigation of graphene under

soft x-ray irradiation conducted by Berkeley group[5] has shown that graphene can be transformed to *nanocrystalline* form while bulk graphite does not undergo *any* modifications under the same radiation levels. The authors offered several possible mechanisms of $sp^2$ bond-breaking in exfoliated graphene, which are absent in graphite.[5] The low-energy e-beam irradiation is known[6,7] to produce substantial damage, including bond breaking, in carbon nanotubes (in Ref. 7, 1 keV electrons with the dose up to $8 \times 10^{17}$ cm$^{-2}$ were used). In graphite, some of the radiation defects can be removed after low temperature treatment. For example, Niwase[8] studied the irradiation-induced amorphization of graphite and reported that many defects were repaired at temperature ~473 K.

It is well known[9] that UV Raman (excited at 325 nm or below) is sensitive to $sp^3$ C–C and C–H bonds while visible Raman spectra are dominated by $sp^2$ phase due to resonant enhancement even in graphane.[3] As stated by Elias *et al.*,[3] the majority of carbon bonds in hydrogenated graphene should acquire $sp^3$ hybridization. We carried out detail UV Raman study of the samples described in our letter[2] as well as of additional irradiated samples. Details of our UV Raman measurement procedures were reported elsewhere.[10] We did not observe peaks characteristic for C–H bonds or C–C $sp^3$ phase in any of our e-beam irradiated graphene samples (inset of Fig. 1). In addition, we performed detail energy dispersive x-ray spectroscopy investigation of all e-beam irradiated graphene samples. No traces of hydrogen were observed in the spectra while characteristic C, O (from the
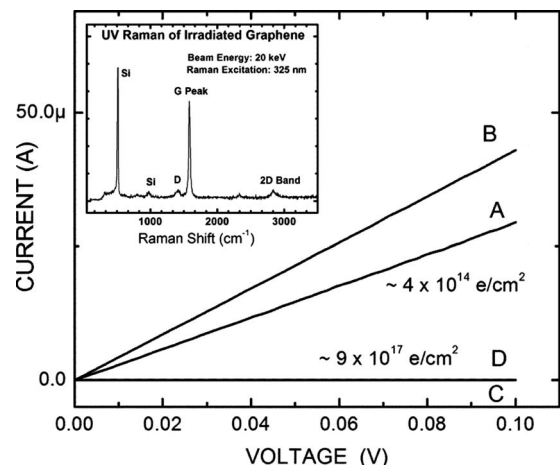


FIG. 1. Electrical current vs applied voltage in graphene after a low irradiation dose (a), after annealing (b), after a high irradiation dose (c), and after annealing (d). No signatures of $sp^3$ C–C or C–H are observed.

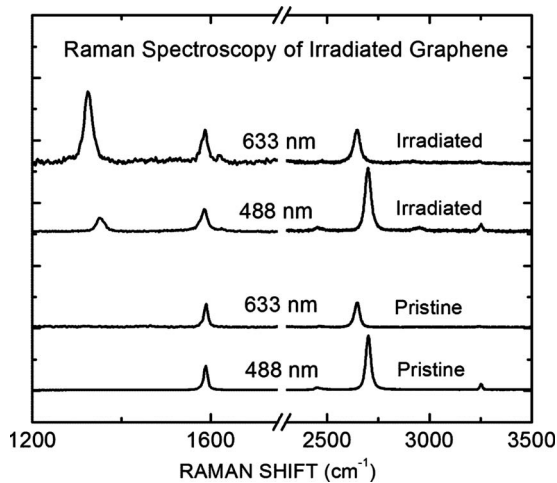a)Electronic mail: balandin@ee.ucr.edu.

FIG. 2. Raman spectra of graphene before and after e-beam irradiation under 488 and 633 nm laser excitation.

oxide layer) and Si (from the substrate) peaks were clearly seen.

JEMP's hypothesis further implies that e-beam irradiated samples always return to the conducting state after annealing. The graphene samples described in our letter[2] did not recover their current conducting ability after annealing at $\sim 600-700$ K for more than 30 min. An extended study, completed by us well before Comment,[1] indicates that the changes in irradiated graphene follow a more complex pattern than the one offered by JEMP. We established that if the e-beam dose is kept at minimum [before stage II (Ref. 2) is reached], graphene can be returned to the electrically conductive state by annealing. If the irradiation dose exceeds the threshold, irradiated graphene does not return to conductive state. In Fig. 1 we present data for new graphene samples irradiated in $\sim 10^{-6}$ Torr vacuum (electron gun is kept at $6 \times 10^{-10}$ Torr) with the constant beam current 0.15 nA, electron energies of 20 and 30 keV, and the radiation dose varying from $\sim 4.3 \times 10^{14}$ to $9.3 \times 10^{17}$ $e^-/cm^2$. The electrical current after a small irradiation dose (curve A) increases after annealing (B). Conduction is strongly inhibited after extended irradiation (C) and does not recover after annealing (D).

Finally, we point out at other deficiencies in Comment,[1] which complicate data analysis. JEMP used high laser excitation intensity (6 mW), above of what is considered to be safe for graphene. Since the data accumulation time was not provided it is not clear if laser damage was a factor. Even moderate laser excitation (1 mW) for prolonged time can lead to C–C bond breaking and graphene transformation to nanocrystalline form.[11] JEMP's manuscript provided to us did not contain information on the excitation wavelength (we can only estimate it from the 2D peak position). For this reason, discussion of $I_D/I_G$ ratio in the Comment does not have much meaning due to ratio's dependence on the wavelength (see Fig. 2). JEMP's indication that they based their conclusion about the number of atomic layers in the samples on the 2D-peak width instead of 2D-peak deconvolution, and the peak energy and symmetry analysis creates an ambiguity. Indeed, 2D band in their Fig. 2(a) (Ref. 1) appears to belong to multilayer rather than bilayer graphene.

In summary, we are pleased that our first report[2] on e-beam irradiated graphene generated follow-up work. At the same time, we are of the opinion that JEMP,[1] while successfully reproducing our Raman spectra, presented interpretation, which is purely speculative and not supported by the experimental data or theoretical considerations.

[1]J. D. Jones, P. A. Ecton, Y. Mo, and J. M. Perez, Appl. Phys. Lett. **95**, 246101 (2009).

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

[3]D. 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).

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

[5]S. Y. Zhou, C. O. Girit, A. Scholl, C. J. Jozwiak, D. A. Siegel, P. Yu, J. T. Robinson, F. Wang, A. Zettl, and A. Lanzara, Phys. Rev. B **80**, 121409(R) (2009).

[6]S. Suzuki, K. Kanzaki, Y. Homma, and S. Fukuba, Jpn. J. Appl. Phys., Part 2 **43**, L1118 (2004); A. Vijayaraghavan, K. Kanzaki, S. Suzuki, Y. Kobayashi, H. Inokawa, Y. Ono, S. Kar, and P. M. Ajayan, Nano Lett. **5**, 1575 (2005).

[7]S. Suzuki and Y. Kobayashi, NTT Tech. Rev. **4**, 25 (2006).

[8]K. Niwase, Phys. Rev. B **52**, 15785 (1995).

[9]A. C. Ferrari and J. Robertson, Phys. Rev. B **61**, 14095 (2000); C. Baron, S. Ghodbanea, A. Deneuvillea, E. Bustarreta, L. Ortegab, and F. Jomard, Diamond Relat. Mater. **14**, 949 (2005).

[10]I. Calizo, I. Bejenari, M. Rahman, G. Liu, and A. A. Balandin, J. Appl. Phys. **106**, 043509 (2009).

[11]B. Krauss, T. Lohmann, D. H. Chae, M. Haluska, K. Von Klitzing, and J. H. Smet, Phys. Rev. B **79**, 165428 (2009).