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On the mechanism for plasma hydrogenation of graphene

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We report that hydrogenation of mono-, bi-, and trilayer graphene samples via exposure to H₂ plasma occurs as a result of electron irradiation of H₂O adsorbates on the samples, rather than H species in the plasma as reported by [Elias *et al.*, Science **323**, 610 (2009)]. We propose that the hydrogenation mechanism is electron-impact fragmentation of H₂O adsorbates into H⁺ ions. At incident electron energies >60 eV, we observe hydrogenation that is significantly more stable at temperatures >200 °C than previously reported. © 2010 American Institute of Physics.

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Monolayer graphene (MLG), a single layer of *sp*²-bonded C atoms, has recently attracted considerable interest due to its unique structural and electronic properties.¹ Of particular interest has been the hydrogenation of MLG (Refs. 2 and 3) and multilayer graphene⁴ by exposure to H₂ plasma. Fully hydrogenated MLG, graphene, is *sp*³-bonded and predicted to have a band gap of 3.5 eV.⁵ However, hydrogenated MLG has been reported to significantly dehydrogenate at temperatures *T*=100 °C and almost completely revert back to its nonhydrogenated form at *T*=200 °C,³ limiting its applications. It is thought that plasma hydrogenation is due to H ions and radicals in the plasma that react with the graphene surface.^{2,4} It is important to understand the mechanisms for plasma modification of graphene in order to fully utilize this phenomenon. In this paper, we study H₂ plasma hydrogenation of MLG, bilayer graphene (BLG), and trilayer graphene (TLG) while varying sample preparation and bias.

Our samples were made by mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) onto a 300 nm thick SiO₂ layer grown on a Si wafer.¹ The exfoliation was carried out in air at room temperature (RT) and relative humidity of 50%, producing samples that have H₂O adsorbed on the top and bottom from contact with the air and SiO₂. Adsorbates such as H₂O can be removed from MLG by annealing at *T*=150 °C.⁶ We annealed samples at *T*≤400 °C and 400 °C<*T*<645 °C in vacuum at pressures of 10⁻⁶ and 10⁻¹⁰ Torr, respectively. Test samples annealed under such conditions show no damage as inferred from Raman spectroscopy. We did not anneal at *T*>645 °C to avoid desorption of SiO₂ from the substrate. We compared the effects of plasma exposure on MLG, BLG, and TLG regions that were on the same graphite flake to achieve similar exposure conditions. Our plasma system consists of a 50 W, 19–21 MHz rf source that is capacitively coupled to a quartz tube. More detailed descriptions of our sample preparation and plasma system are given in the supplementary materials.⁷

Graphite is characterized by a set of Raman peaks: a *G* peak at 1580 cm⁻¹ due to the in-plane vibrational *E*_{2*G*} mode, and a 2*D* peak at about 2700 cm⁻¹ due to two phonon intervalley scattering.² Hydrogenated graphene shows an addi-

tional sharp *D* peak at about 1340 cm⁻¹ that is activated by defects.^{2–4} For hydrogenated graphene, the integrated intensity of the *D* peak, *I*_{*D*}, saturates at a value two to three times greater than that of the *G* peak, *I*_{*G*}.^{2–4} The disappearance of the *D* peak after annealing at *T*=200 °C is taken as evidence for dehydrogenation³ since HOPG dehydrogenates at these temperatures. Figure 1(a) shows micro-Raman data, taken at an excitation wavelength of 532 nm, for a pristine sample showing no *D* peak and a 2*D* peak with a full-width-at-half maximum of 30 cm⁻¹, indicating MLG. Figure 1(b) shows data for the same sample shown in Fig. 1(a) after exposure to H₂ plasma at 50 mTorr for 10 s with the sample electrically floating. We observe a sharp *D* peak with *I*_{*D*}/*I*_{*G*}=3.2, consistent with hydrogenated graphene, and *D'* and (*D*+*D'*) peaks that have also been attributed to hydrogenation.^{2,4} The dotted

FIG. 1. Monolayer samples. (a) Pristine. (b) Exposed to H₂ plasma. (c) Preannealed then exposed to H₂ plasma. (d)–(f) Preannealed then exposed to N₂, O₂, H₂O, and NH₃ gasses, respectively, then to H₂ plasma. Inset shows spectra of samples exposed to H₂ plasma at biases of -40 and 40 V and dosages of 1.1 and 6.5 mC/cm², respectively, and exposed to He plasma.

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FIG. 2. (a) and (b) Bi- and trilayer samples, respectively. Exposure dosages of electrons at 40 V and ions at -40 V were 6.5 and 1.1 mC/cm², respectively.

curve in Fig. 1(b) shows data after we have postannealed a hydrogenated sample having $I_D/I_G=3$ at 220 °C for 1 h. The D peak nearly disappears, as in previous reports.³ Figure 1(c) shows data for a pristine MLG sample that is preannealed within the plasma chamber at 400 °C for 1 h to remove adsorbates, and then exposed to the same H₂ plasma conditions as in Fig. 1(b). We observe a shift in the G peak of roughly 20 cm⁻¹ from the pristine to preannealed sample. This effect has been previously reported and attributed to hole-doping from exposure to O₂ in the atmosphere.⁸ A D peak is not observed, indicating that adsorbates rather than H species in the plasma are responsible for the D peak. To identify the adsorbates, we preannealed MLG samples at 400 °C for 1 h, exposed them *in situ* to N₂, O₂, H₂O, and NH₃ gases at RT and 20 Torr for 1 h, and then exposed them to the same H₂ plasma conditions as in Fig. 1(b) with the sample floating. As shown in Figs. 1(d)–1(g), samples exposed to H₂O and NH₃ showed significantly higher $I_D/I_G=1.2$ and 0.8, respectively, than those exposed to N₂ and O₂ that showed $I_D/I_G=0.1$ and 0.2, respectively. The dotted curves in Figs. 1(f) and 1(g) refer to Raman spectra after the gas dosing, but before the H₂ plasma exposure. Since H₂O and NH₃ adsorb on MLG (Ref. 6) and contain H, these results lead us to hypothesize that the D peak, due to hydrogenation, is caused by fragmentation of H species from these adsorbates. We note that pristine samples are exposed to adsorbates on both sides, whereas preannealed samples are only exposed on the top surface due to the lack of diffusion under the layer. The smaller values of I_D/I_G for samples exposed to H₂O and NH₃ versus those for pristine samples in Fig. 1(b) are attributed to exposed samples having adsorbates on only the top. We conclude that the D peak in Fig. 1(b) is primarily due to H₂O adsorbates from the air and SiO₂.

To study the effects of electron and ion irradiation on the formation of the D peak, we biased samples at voltages V relative to the chamber during plasma exposure. Since electrons typically have energies of about 2 eV, a bias of V results in incident electron energies of $V \pm 2$ eV. By measuring the current density between the substrate and chamber,

FIG. 3. (Color online) (a)–(c) Monolayer samples exposed to H₂ plasma at biases of 60, 100, and 150 V and dosages of 11.9, 15.7, and 23.2 mC/cm², respectively, and then postannealed at 245 °C. Inset shows monolayer I_D/I_G vs annealing temperature T , for 40, 60, 100, and 150 V biases at dosages of 6.5, 11.9, 15.7, and 23.2 mC/cm², respectively.

the electron and ion dosages on the substrate are determined. If we assume a uniform current density on the substrate, this dosage is the same as that on the graphene sample. The inset in Fig. 1 shows data for a MLG sample exposed to H₂ plasma at 75 mTorr for 10 s with a sample bias of -40 V, which repels electrons and attracts positive H ions from the plasma. Observed is a small D peak with $I_D/I_G=0.1$. However, under the same plasma conditions and a bias of 40 V, which attracts electrons and repels positive ions, we observe a D peak with $I_D/I_G=2.8$. Annealing the sample at 220 °C results in a significant decrease of the D peak to $I_D/I_G=0.1$, as shown by the dotted curve in the inset. Similar results were observed for BLG and TLG samples, as shown in Fig. 2. Thus we conclude that electron irradiation of H₂O adsorbates is required for the formation of the D peak. This conclusion is supported by the top curve in the inset in Fig. 1 that shows data for MLG exposed to He plasma, which contains electrons but no H species, at 75 mTorr for 60 s with the sample floating. A D peak is still observed with $I_D/I_G=2.5$, comparable to the D peak in Fig. 1(b) after H₂ plasma exposure. As shown by the dashed and dot-dashed curves in the inset, I_D/I_G decreases to 0.9 and 0.2 after annealing at $T=350$ and 590 °C, respectively.

Assuming that the D peak is due to hydrogenation, we propose that the mechanism is electron-impact fragmentation of H₂O adsorbates. The cross-section σ for fragmentation of H₂O into H⁺ ions varies from about 1 to 3×10^{-17} cm² for electron energies from 30 to 1000 eV, with a broad maximum at about 100 eV.⁹ The probability for fragmentation of an adsorbate is $P=(1-e^{-N\sigma})$, where N is the number of incident electrons per cm². For a dosage of 6.5 mC/cm² we have $N=4.1 \times 10^{16}$ /cm². Using $N=4.1 \times 10^{16}$ /cm² and $\sigma=1-3 \times 10^{-17}$ cm², we have $P=0.34-0.71$. The cross-section σ

FIG. 4. (Color online) (a)–(d) Mono-, bi-, and trilayer I_D/I_G vs annealing temperature T , for 40, 60, 100, and 150 V biases at dosages of 6.5, 11.9, 15.7, and 23.2 mC/cm^2 , respectively.

for fragmentation of H_2O into H^- ions and H radicals is about one-fifth and one-tenth of that into H^+ ions, respectively.⁹ Thus we propose that hydrogenation is mainly due to H^+ ions. Most of the ejected H^+ ions have energies of 0–5 eV for electron energies of 35–400 eV.¹⁰

Figures 3(a)–3(c) show data for pristine MLG samples exposed to H_2 plasma at 75 mTorr for 10 s and biases of 60, 100, and 150 V, respectively, and then postannealed at $T = 245^\circ\text{C}$ for 1 h. Biases greater than 150 V were not used because they resulted in arcing. In Figs. 3(a)–3(c), the resulting current densities were 1.2, 1.6, and 2.3 mA/cm^2 , respectively. These combinations of energies and current densities are about two orders of magnitude lower than those reported to cause damage in graphene.¹¹ Observed in Figs. 3(a)–3(c) are D peaks with $I_D/I_G = 2.2$, 3.1, and 3.2, respectively. These values are significantly greater than those previously reported;³ these authors found that I_D/I_G nearly disappeared after annealing at $T = 200^\circ\text{C}$. The inset in Fig. 3 shows I_D/I_G as a function of T for MLG samples biased at 40, 60, 100, and 150 V. For samples biased at 100 and 150 V, I_D/I_G is about 2 after annealing at $T = 400^\circ\text{C}$. Figures 4(a)–4(d) show I_D/I_G as a function of T for MLG, BLG, and TLG samples exposed under the same plasma conditions as Fig. 3 and biases of 40–150 V. For Figs. 4(a)–4(d), each set of curves at a given bias was collected from the same flake. For MLG, BLG, and TLG, the temperature stability of the D peak is observed to be greater at higher biases. We attribute

the greater stability to an increase in the hydrogenation probability due to higher current densities. In addition, the higher electron energies lead to an increase in σ . Recent scanning tunneling microscopy studies of graphene on SiC have shown that, at low H coverage, H monomers and dimers form with monomers having a lower binding energy.¹² At high H coverage, large hydrogen clusters form, and nearly complete dehydrogenation is observed after annealing at $T = 800^\circ\text{C}$.¹² We propose that at higher biases, larger H clusters form that require a higher T for removal. In Fig. 4, the average value of I_D/I_G at RT over all biases for MLG, BLG, and TLG is 2.8 ± 0.5 , 2.0 ± 0.5 , and 1.8 ± 0.2 , respectively. The lower values for BLG and TLG are attributed to the additional C layers in these materials.

In conclusion, we have shown that hydrogenation of MLG, BLG, and TLG using H_2 plasma results from electron irradiation of H_2O adsorbates. The temperature stability of the hydrogenation significantly increases at sample biases > 60 V. Irradiation of adsorbates may provide a useful technique for modifying these materials.

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⁷See supplementary material at <http://dx.doi.org/10.1063/1.3524517> for details on sample preparation and plasma apparatus.

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