Enhanced resistance of single-layer graphene to ion bombardment

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We report that single-layer graphene on a SiO2/Si substrate withstands ion bombardment up to \( \sim 7 \) times longer than expected when exposed to focused Ga\(^+\) ion beam. The exposure is performed in a dual beam scanning electron microscope/focused ion beam system at 30 kV accelerating voltage and 41 pA current. Ga\(^+\) ion flux is determined by sputtering a known volume of hydrogenated amorphous carbon film deposited via plasma-enhanced chemical vapor deposition. © 2010 American Institute of Physics. [doi:10.1063/1.3428466]

I. INTRODUCTION

Graphene, a one atom thick sheet of \( sp^2 \) hybridized carbon atoms arranged in a honeycomb lattice, is highly researched because of its unique and advantageous electronic properties.\(^1\)\(^-\)\(^4\) The combination of its ballistic electron transport,\(^5\) high elastic limit,\(^6\) and the recent achievement of producing macroscale conducting sheets\(^7\) makes its use in graphene’s Raman spectra.\(^8\) It is, therefore, likely that par-tions demonstrate that defects can be introduced into the graphene lattice via electron beam irradiation as manifested by the appearance of a disorder-related D peak and a change in height of both the D peak and zone-center G peak within graphene’s Raman spectrum.\(^8\) It is, therefore, likely that particle bombardment—electronic or ionic—causes varying degrees of damage in graphene. Therefore, in order to design and maintain graphene’s desired characteristics, it is critical to understand its response to electron and ion bombardment. Here we report that a single-layer graphene sheet is approxi-mately seven times more resilient against ion bombardment than expected based on sputtering mechanisms of other carbon-based structures.

II. EXPERIMENT

Graphene samples were obtained by mechanical exfoliation of highly oriented pyrolitic graphite (SPI Supplies) and subsequently transferred onto Si substrates with a 300 nm thick SiO\(_2\) layer by using Nitto Denko tape.\(^9\)\(^,\)\(^10\) Single-layer flakes were first identified by optical microscopy (Nikon Eclipse LV100D) using white light to distinguish the graphene sheets via the added optical path that causes an increase in contrast against the SiO\(_2\)/Si substrate.\(^9\)\(^,\)\(^11\) Figure 1 shows optical and SEM images of such representative single-layer sheets. Once the single-layer flakes were identified, Raman spectroscopy with a Reinshaw spectrometer, operating at room temperature with a holographic notch filter (HNF) 514 nm laser working at \( \sim 1.25 \) mW, was used to confirm their thickness. The Raman spectrum for the sample shown in Fig. 1 with a G peak near 1580 cm\(^{-1}\) and G’ band [also known as 2D] near 2700 cm\(^{-1}\) is provided in Fig. 2. The sample is defect-free as indicated by the lack of a disorder-related D peak near 1350 cm\(^{-1}\). The symmetric shape of the 2D peak confirms that the sample is indeed a single sheet, as demonstrated by Ferrari et al.\(^,\)\(^12\)\(^,\)\(^13\) Fig. 2(b).

Ion and electron beam imaging was performed in a FEI Nova 200 DualBeam System with a Ga\(^+\) liquid metal ion source. The e-beam was operated at an acceleration voltage of 10 kV and beam current of 0.54 nA. During the initial alignment, the graphene sample was exposed to the e-beam for \( \sim 20 \) minutes. The sample was then tilted to the eucentric point at a 52° incline with respect to the e-beam at a working distance of 5.1 mm to allow simultaneous imaging of the region with both columns. Magnifications and beam positions were coupled to ensure that the graphene sample could be reliably imaged without unnecessary exposure to either beam. After taking the initial SEM image of the graphene sheet, a single ion beam frame was taken at an accelerating voltage of 30 kV and beam current of 41 pA (nominally 10 pA) to intentionally sputter away the single-layer region.

![Enhanced resistance of single-layer graphene to ion bombardment](image-url)
SEM and focused ion beam (FIB) scans were iteratively repeated until the graphene sheet could no longer be identified in subsequent SEM images, Fig. 3.

We calculate the scan time per frame of 2.7 s by multiplying the total number of pixels in a single ion beam image (1024 × 884) by the beam dwell time per pixel (3 μs). The graphene sheet was then iteratively sputtered away with each scan. The final step, Figs. 3(d) and 3(i), shows that the region originally covered by single-layer graphene became the same hue as the underlying SiO2. The total time to sputter away this sheet was 57 s, a surprisingly high value for a single-atom-thick material.

To determine whether this etch time was reasonable, we performed a similar experiment on a hydrogenated amorphous carbon (a-C:H) film with an average thickness of 125 nm, Fig. 4(d). Sputtering of this film was also used to calculate the incident Ga+ ion flux and subsequently determine the sputtering time of these carbon-based structures. The a-C:H was deposited on a Si substrate via plasma-enhanced chemical vapor deposition with a methane/hydrogen/argon containing plasma. The amorphous and hydrogenated nature of the film was confirmed with Raman spectroscopy under the same conditions as used for graphene. Using a two-peak Gaussian fit for the deconvolution of the D and G peaks, we determined the relative fractions of sp2 and specific position of the G peak we determined the weighted average of the sp3 and sp2 bonds in the film and the reported sputter yields for different carbon allotropes under Ga+ ion bombardment: 2.3, 2.55, and 2.7. The sputter yields at 30 kV are assumed to be the same as those experimentally determined at 50 kV due to flattening out of the yield curve as a function of accelerating voltage at energies of 30 keV and higher. Figure 4(a) shows the a-C:H film before its exposure to the ion beam, and Fig. 4(c) shows the selected 2.15 × 2.06 μm2 area (4.33 μm2) in the film that is completely sputtered away after 45 s of exposure to the same ion beam conditions as in the graphene experiments.

Generally, experimentally-determined values for a-C:H sputter yield fall between 2.3 to 2.8 carbon atoms per incident ion at an acceleration voltage of 50 kV. Theoretically determined values for carbon sputter yield, however, range from 1.2 to 1.7 at an acceleration voltage of 30 kV, with the former obtained by transport of ions in matter (TRIM) simulations and the latter through use of the linear cascade collision (LCC) model developed by Sigmund. We refrain from using the computationally determined sputter yields due to the limitations associated with these models. For example, the TRIM simulations do not take into account any orientation dependent phenomena such as the channeling of Ga+ ions through the graphene lattice. The LCC model, whose underlying assumptions require ample material volume and an amorphous structure, is also unlikely applicable in estimating the sputtering yield of graphene due to its 2D nature and highly ordered lattice. Furthermore, we find that even if the theoretically determined sputter yields were taken into account, they would have marginal influence on our subsequent calculations for the estimated graphene sputter time.

III. RESULTS AND DISCUSSION

We estimate the sputter yield of this a-C:H film to be 2.63 C atoms/incident Ga+ by utilizing the determined
We determine the Ga⁺ ion flux incident on the a-C:H film (and, therefore, on graphene) by calculating the total number of sputtered carbon atoms from a selected area, and then dividing it by both the sputter yield and the time required to fully etch away the film in that area. First, by assuming the mass density of the a-C:H film to be 2 g/cm³, as widely reported for amorphous carbon films,19 we determine the number of sputtered C atoms, Ns, from the 125 nm thick a-C:H film to be \( \frac{1.254 \times 10^{18} \text{ C atoms/cm}^2}{m_c} \) by utilizing Eq. (1)

\[
N_S = \frac{\rho_c \times N_A \times d}{m_c},
\]  

(1)

where \( \rho_c \) is the mass density of the a-C:H film, \( N_A \) is Avogadro’s Number, \( m_c \) is atomic mass of carbon, and \( d \) is the film thickness. Using the experimentally-determined etch time, \( t_{etch} \), required to entirely remove the film in the 4.33 \( \mu \text{m} \) area, we calculate the sputter rate (\( R_S \)) to be 2.786 \( \times 10^{16} \text{ atoms/cm}^2 \text{s} \) by using Eq. (2)

\[
R_S = \frac{N_S}{t_{etch}}.
\]  

(2)

We then determine the Ga⁺ flux (\( J_{Ga^+} \)) to be 1.059 \( \times 10^{16} \text{ Ga}^+ \text{ ions/cm}^2 \text{s} \) through Eq. (3)

\[
J_{Ga^+} = \frac{R_S}{Y_{a-C:H}}.
\]  

(3)

We then use the carbon-carbon bond length of 1.42 Å and the geometry of the graphene lattice, Fig. 5, to calculate the aerial density of graphene (\( A_p \)) to be 3.818 \( \times 10^{15} \text{ atoms/cm}^2 \). If the sputtering mechanism in graphene is similar to that in other carbon-based structures, the theoretical time (\( t_{theo} \)) to remove a single graphene sheet of a certain area in its entirety can be calculated by

\[
t_{theo} = \frac{A_p}{A_{a-C:H} \times J_{Ga^+} \times Y_{a-C:H}}.
\]  

(4)

here \( A_{a-C:H}/A_S \) is the ratio between the exposed area of the a-C:H film (\( A_{a-C:H}=4.33 \mu \text{m}^2 \)) and the total area (\( A_S \)) of the image depicting a graphene monolayer sample. This scaling takes into account the frequency with which the ion beam rasters over the exposed area. For the graphene monolayer presented in Fig. 3(a) (sample 1), \( A_{S1}=290.1 \mu \text{m}^2 \), and \( t_{theo}=8.96 \text{ s} \), resulting in the ratio between \( t_{exp} \) and \( t_{theo} \) to be 6.362. For the second graphene monolayer studied here (sample 2), \( A_{S2}=34.3 \mu \text{m}^2 \), \( t_{theo}=1.06 \text{ s} \), and \( t_{exp}=8.15 \text{ s} \). Using the \( t_{exp}/t_{theo} \) ratios for these two samples, we calculate that average \( t_{exp} \) is \( \sim 7.03 \text{ times longer than } t_{theo} \) for a single sheet of graphene (Table I). This \( t_{exp} \) surpasses any expectations for a carbon-based material under ion bombardment.

We believe that this resilience stems from the 2D nature of graphene. Since graphene is only one atom thick, it eliminates the volume in which sputtering cascade collisions occur in bulk materials and minimizes the interactions with recoiling atoms from the underlying substrate and graphene lattice.17,20,21 The absence of cascade collisions near the surface would greatly reduce the number of ejected carbon atoms from the graphene lattice. It is also possible that C atoms in graphene act as an intermediary in transferring the kinetic energy to the underlying substrate without being readily displaced from the lattice, acting like a system of billiard balls where energy is completely transferred to the substrate underneath. Graphene’s relatively open and ordered atomic structure may also facilitate Ga⁺ ion channeling through its lattice.17,22 This would limit the number of primary ion collisions, thus reducing the number of carbon atoms sputtered away. Ultimately, Ga⁺ ions that are not back-scattered by the graphene lattice come to a halt in the underlying SiO₂ after losing their kinetic energy through elastic and inelastic collisions. Since SiO₂ is an insulator, Ga⁺ ions may be implanted into the substrate surface, causing a net positive charge to build up in the region exposed to ion bombardment, forcing the subsequent incoming ions to be electrostatically repelled.18 These considerations should be taken into account when developing a more thorough understanding of graphene’s ability to withstand a prolonged ion beam exposure.

Further investigations, involving the substitution and elimination of the substrate, will help shed light onto the specific mechanisms operating during sputtering of graphene by removing any effects that the substrate has on the cascade collision process. Elimination of the substrate will ensure that mechanisms inducing the sputtering of graphene will be solely from elastic and inelastic collisions with incident ions.

**IV. CONCLUSION**

In summary, we convincingly demonstrate the ability of a single-atom-thick graphene layer to withstand approximately seven times higher ion bombardment than expected. Our findings reaffirm the wide range of science that is yet to be done on this unique single-atom thick material.
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19CRC Handbook of Chemistry and Physics (CRC, Cleveland, 1979).