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In-situ observation and atomic resolution imaging of the ion irradiation induced amorphisation of graphene

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Ion irradiation has been observed to induce a macroscopic flattening and in-plane shrinkage of graphene sheets without a complete loss of crystallinity. Electron diffraction studies performed during simultaneous in-situ ion irradiation have allowed identification of the fluence at which the graphene sheet loses long-range order. This approach has facilitated complementary ex-situ investigations, allowing the first atomic resolution scanning transmission electron microscopy images of ion-irradiated graphene defect structures together with quantitative analysis of defect densities using Raman spectroscopy.

The engineering of the physical and electronic properties of two dimensional materials requires control over sheet conformation as well as atomic scale lattice defects 1–6. For example, there is often a reduction in carrier mobility for defective graphene material 2 and introducing point defects by ion irradiation can induce spin-half paramagnetism 6. It is clear that for the remarkable properties of graphene to be effectively harnessed, the nature and extent of defects must be carefully controlled. Correlating physical property variations with ion-induced structural changes requires direct characterisation of defect structures. Transmission electron microscope (TEM) imaging provides a powerful means of observing both types of structural feature. Macroscopic bending produces characteristic bend contours in conventional bright-field (BF) images while aberration-corrected TEM and scanning transmission electron microscopy (STEM) are almost unparalleled in their capabilities for achieving atomic resolution in the imaging of defective free-standing graphene 7–16. Coupled with electron energy loss spectroscopy (EELS), STEM can provide information on local bonding environments 17–19 and the presence of individual atomic impurities 20–24. To date, the majority of (S)TEM studies of defective graphene have relied on defects induced either during the growth process 5,8,15 or by imaging with high energy electrons 7,16,25,26 with only a few recent papers reporting high-resolution TEM imaging of ion irradiated graphene 12–14.

In this paper we demonstrate that ion irradiation could provide a simple means for ironing out macroscopic corrugations in suspended graphene sheets. In addition, we report the first atomic resolution imaging of defect structures produced in single-layer graphene using ion irradiation with the corresponding average defect densities evaluated via Raman spectroscopy.

Results

Ironing out macroscopic corrugations in suspended graphene sheets. The low magnification bright field TEM images in Figs. 1a(i) and 1b(i) show the macroscopic morphology of a few-layer graphene sheet suspended on a Quantifoil TEM grid before a(i) and after b(i) ion irradiation with 30 keV He ions to a fluence of 8.0 × 1014 ions cm−2. A sample thickness of ~10 graphene layers was estimated from the optical image contrast of the flake on a SiO2/Si substrate before it was transferred to the Quantifoil TEM grid 27. Fig. 1a(i) shows bend contours due to the presence of macroscopic wrinkles/corrugations in the suspended graphene before irradiation. During ion irradiation the bend contours are observed to gradually disappear until at a fluence of 8.0 × 1014 ions cm−2 they are completely removed suggesting a flattening of the graphene sheets (Fig. 1b(i)). Similar loss of bend contours has been observed for thicker samples irradiated with 30 keV He ions and for fewer layer graphene irradiated with 6 keV Ar ions (further details in supplementary materials Figs. S1 and S2).

The loss of bend contours in the graphene sheets as a result of modest ion irradiation could be produced from a significant loss of crystallinity in the graphene sheets. To investigate this possibility, we have recorded comple-
in-plane contraction of the graphene which is pinned at the edges phenomenon that occurs, at least in part, due to gradual irradiation-induced macroscopic corrugations of the free-standing sheets—a phenomenon illustrated in Fig. 1. Instead we conclude that the crystallinity is not likely to be responsible for the disappearance of intensity scale.

In-situ diffraction patterns for irradiated single-layer graphene are displayed with the same patterns acquired before irradiation (a(ii)) and after irradiation (b(ii)) are displayed to the right of the BF TEM images. These were acquired under identical diffraction conditions and are both displayed with the same intensity scale.

Evolution of the Raman spectra for irradiated graphene. Raman spectroscopy is complementary to TEM imaging and diffraction, ideally suited to obtaining lower spatial resolution information concerning the number of graphene layers and identifying the presence of defects. In order to quantify the defect density induced in our single-layer graphene samples, Raman spectroscopy was performed before and after irradiation to different ion fluences (Fig. 3a). The Raman spectra before irradiation exhibit a behaviour typical of suspended single-layer graphene with one sharp double-resonant peak (2D peak) and a first-order Raman peak (G peak) with the intensity of latter being significantly lower than that of the former. The absence of a prominent D peak in our graphene samples before ion irradiation suggests that the material is largely defect free, as this peak is known to be activated by the presence of defects in the material. This absence of defects in the pristine samples is in agreement with our TEM and STEM observations of the unirradiated material. The G peak frequency observed for the graphene sample prior to irradiation was ~1580 cm⁻¹ suggesting no significant doping in the sample. As shown in Fig. 3a, increasing ion irradiation produced additional D, D’ and D + D’ peaks in the Raman spectra, the presence of which is known to be associated with defects in graphene.

Lucchese et al. have proposed a model to aid the interpretation of Raman spectra obtained from defective graphene (Fig. 3b). They proposed that activation of the D peak requires not only defective graphene (indicated by the red circles in Fig. 3b) but also a surrounding region of crystalline graphene (indicated by the green areas in Fig. 3b). The intensity of the D peak is proportional to the total area of crystalline graphene that is locally-activated by the defects and not to the area of the defective regions themselves. Therefore, when the average defect distance (Lυ) is greater than twice the radius of the activated crystalline regions surrounding each defect (Rυ), the intensity ratio of the D peak to G peak (I(D)/I(G)) increases in direct proportion to the increasing number of defects (Fig. 3b(i)). However, if the defect density becomes sufficiently high that neighbouring...
Figure 2 | Electron diffraction patterns recorded in-situ for single-layer graphene as a function of 30 keV He ion irradiation. (a) BF TEM image and (b) electron diffraction pattern for the single-layer graphene sheet before ion irradiation. (c)–(g) Show a sequence of selected area electron diffraction patterns acquired during in-situ irradiation of the single-layer graphene sheet with 30 keV He ions after fluences of (c) $3.0 \times 10^{15}$ ions cm$^{-2}$, (d) $6.0 \times 10^{15}$ ions cm$^{-2}$, (e) $9.6 \times 10^{15}$ ions cm$^{-2}$, (f) $9.9 \times 10^{15}$ ions cm$^{-2}$ and (g) $1.2 \times 10^{16}$ ions cm$^{-2}$. Selected area region used to acquire diffraction data (b)–(g) is indicated by the dashed circle in (a). (h) BF TEM image after $1.2 \times 10^{16}$ ions cm$^{-2}$ of irradiation. (i)–(k) Show the reduction in diffraction peak intensity as a function of irradiation dose for a line scan taken: (i) through (0–110) perpendicular to the reciprocal lattice vector; (j) through (1–210) perpendicular to the reciprocal lattice vector; and (k) through (1–210) parallel to the reciprocal lattice vector.

Figure 3 | The evolution of Raman spectra of irradiated single-layer graphene. (a) Raman spectra of single-layer graphene after irradiation with 30 keV He ions at the fluences labelled. (b) Schematic showing situations with b(i) low defect-density ($L_D > 2R_N$) and b(ii) high defect-density ($L_D < 2R_N$). D peak activated regions (perfect graphene) are indicated by the green areas and D peak inactive regions (defective graphene) are indicated by the red circles. (c) $I(D)/I(G)$ as a function of ion fluence. The fitting method used to calculate the intensity ratio ($I(D)/I(G)$) is outlined in the supplementary information (Fig. S3).
activated regions begin to overlap (Fig. 3b(ii)), the ratio of I(D)/I(G) decreases with increasing defect density. As shown in Fig. 3c, our samples followed the expected amorphisation trajectory in that I(D)/I(G) initially increased and then decreased for fluences greater than \(9.6 \times 10^{10}\) ions cm\(^{-2}\). Ferrari et al. have interpreted the amorphisation trajectory of carbon materials as being described by three stages with the fraction of sp\(^3\) bonds increasing from stage 1 to stage 3. Comparing their results to our measurements (Fig. 3c), we assign the Raman spectra of irradiated graphene shown in Fig. 3a to various stages of the amorphisation process. In particular, a fluence of \(6.0 \times 10^{15}\) ions cm\(^{-2}\) is consistent with the start of stage 2 where the bonding begins to change from sp\(^3\) to sp\(^2\) configurations. The result is in good agreement with the evolution of the diffraction patterns in Fig. 2, as any significant sp\(^3\) bonding will produce nanoscale buckling which will in turn lead to streaking of the diffraction spots as observed in Fig. 2d–g to occur at a similar fluence of \(\sim 10^{15}\) ions cm\(^{-2}\).

We have estimated the average defect density, \(\sigma\), assuming \(\sigma = 1/ L_0^2\) and using the method described in Ref. 39. As summarized in supplementary Table S1, the values of \(\sigma\) for our samples are typically 2–3 orders of magnitude lower than the total ion fluence which is in good agreement with the theoretical predictions of molecular dynamics simulations. The simulations suggest that only \(\sim 1/100\)th of incident ions will interact with single-layer graphene under these irradiation conditions. The Raman spectra obtained from ion-irradiated graphene were found to be stable for several weeks at room temperature. However, after annealing at 100°C in vacuum for 5 hours we have found that the intensity ratio I(D)/I(G) decreased from 1.06 to 0.42 (supplementary Fig. S4). According to the quantification method in Ref. 39 this change corresponds to an increase in \(L_0\) from 12 nm to 20 nm. This behaviour is similar to the hysteresis cycle described by Ferrari et al. which suggests some defects were removed after annealing - although we cannot rule out the possibility that this result is associated with changes of the surface contamination.

**Atomic resolution images of irradiated graphene.** To better understand the amorphisation process and the character of the defects induced during ion irradiation, we have performed high-resolution high-angle annular dark field (HAADF) STEM imaging of our irradiated samples at different ion fluences (Figs. 4–6). In all cases, the electron beam exposure prior to high-resolution image acquisition was minimized to reduce the possibility of electron-beam induced structural changes. The D peak observed in the Raman spectra for a fluence of \(3.0 \times 10^{15}\) ions cm\(^{-2}\) (Fig. 3a) suggests that defects are present at this fluence. However, despite extensive time spent imaging single-layer graphene samples irradiated with fluences of up to \(3.0 \times 10^{15}\) ions cm\(^{-2}\) no structural defects were observed in these samples (Fig. 4a). Therefore the presence of the D peak in the corresponding Raman spectra may be simply a result of the presence of adatom-type defects associated with surface contamination or it could be that surface contamination obscured defective regions such that they could not be observed in the STEM. The different spatial resolution of the two techniques makes it difficult to draw firmer conclusions. At a slightly higher fluence of \(6.0 \times 10^{15}\) ions cm\(^{-2}\), corresponding to the onset of streaking in the electron diffraction data, a limited number of structural defects were observed. Only when imaging samples that had been irradiated to a fluence of \(\sim 10^{16}\) ions cm\(^{-2}\) were structural defects consistently detected in the majority of regions that were sufficiently free from surface contamination to facilitate their clear observation using HAADF STEM (Fig. 4b–d). The observed defects consisted of multiple pentagon-heptagon (5–7) pairs which are known to be produced during structural relaxation after vacancy formation. This type of vacancy creation followed by structural relaxation represents a loss of material from the two dimensional lattice, and an in-plane shrinkage will therefore be required in order to prevent large holes being produced in the graphene sheets. This in-plane shrinkage is consistent with the loss of bend contours that was observed in low-magnification TEM images during in-situ ion irradiation (Fig. 1 and supplementary information Fig. S1). Modelling of these types of topological defect using density functional theory has suggested that they are associated with a localised buckling of the graphene sheet. Pentagon-heptagon (5–7) pairs, a unit cell of the haeckelite structure, Stone-Thrower-Wales defects and Inverse-Stone-Thrower-Wales defects are observed in (b), (c) and (d), respectively. Images have been filtered based on the method as reported in Ref. 48 to improve clarity (raw images are given in supplementary material Fig. S5).

Quantitative analysis of the defect density using high-resolution STEM imaging was impossible due to the increased level of contamination observed for all samples after ion irradiation (Fig. 5, Fig. 6, and supplementary videos S1 and S2). The origin of the increased contamination in the irradiated case is unclear but it is known that the defective material acts as an energetically favourable site for attracting atoms or molecules onto graphene. Electron energy loss spectroscopy measurements suggest that this contamination (brighter white/grey regions in Fig. 5) consists of mainly hydrocarbons with silicon and metal impurities (all are known to be frequently present in these materials from the graphene TEM sample preparation). With increased fluence, the level of contamination was found to increase and the clean areas of graphene (dark areas visible in Fig. 5) became smaller. The observation of the increased contamination further suggests that the surface contamination may account for the higher estimated topological defect densities found via Raman spectra (Fig. 3) compared to those observed in atomic resolution images.
For the high-resolution imaging conditions used in this work, pristine graphene (Fig. 4a) is found to be stable over several hours of imaging. However, this is not the case for defective graphene as the activation energy for bond rotation is considerably lower (4–10 eV compared to ~18–20 eV for knock-on damage of pristine material7). Fig. 6 demonstrates the instability of the topological defects during extended imaging (full videos available in supplementary videos S1–S2). Fig. 6a illustrates a 90° bond rotation for the adjoined heptagons in a Stone-Thrower-Wales defect that occurred over ~7 seconds of imaging. However, other highly defective regions were more stable, demonstrating only limited reconstruction after ~30 seconds of imaging as shown in Fig. 6b.

**Conclusion**

In conclusion, we have observed in-situ the macroscopic shrinkage of graphene sheets produced by 30 keV He or 6 keV Ar ion irradiation. Raman spectroscopy measurements for the irradiated material are consistent with a higher fraction of sp³ bonding in the irradiated graphene and allow a quantitative estimation of defect density. Atomic resolution imaging of the irradiated material has shown that the irradiation-induced defects consist of many 5–7 pairs. This type of defect is known to be associated with a localised buckling of the structure which is consistent with the streaking observed in diffraction patterns and with the changes observed in the Raman spectra obtained from irradiated material. Our first STEM observation of the atomic structures of these defects in ion irradiated graphene supports previous theoretical predictions regarding ion irradiation induced damage processes8 and will be beneficial towards the goal of tuning electronic and magnetic properties via irradiation-induced modifications of graphene materials26 as well as for the optimisation of graphene processing with focused ion beams. Furthermore, the direct visualisation of the defects and morphological changes leading to amorphisation in a single atomic plane provides valuable fundamental insight into the irradiation induced damage sequence of bulk layered materials such as nuclear graphite and sheet silicate minerals.

**Methods**

In-situ ion irradiation experiments were performed using the MIAMI in-situ ion irradiation TEM facility at the University of Huddersfield, UK. This instrument consists of a JEOL JEM-2000FX TEM modified to allow the sample to be ion irradiated while microstructural changes can be continuously monitored via TEM imaging and diffraction53. In the current study 30 keV He or 6 keV Ar ions beams were used at an angle of 30° to the imaging electron beam. The diameter of the ion beam is ~1 mm and care was taken to ensure that the ion beam is coincident with the centre of the TEM grid so that the full field of view is irradiated uniformly. The TEM was operated at 80 kV and with a low current density to reduce the likelihood of knock-on radiation damage from the electron beam7. Selected area electron diffraction patterns were acquired using a selected area aperture with a diameter on the sample of ~1 μm. Suspended graphene TEM samples were prepared by transferring micromechanically cleaved graphene from SiO₂/Si substrate onto Quantifoil TEM grids with perforated carbon films according to the method in Ref. 54. Repeat experiments were performed for differing sample thicknesses and ion flux and the in-
situ ion irradiation was halted at various ion fluences between $10^7$ and $10^9$ ions cm$^{-2}$ to allow complementary ex-situ analysis of defect formation using atomic resolution STEM imaging and Raman spectroscopy. Ex-situ Raman measurements were performed using a Renishaw 1000 Raman system with a laser of 514 nm and a ~2 μm spot size. The laser power was limited to ~0.25 mW to avoid sample heating. Raman spectra from identical regions before and after ion irradiation have been compared in order to confirm the expected ion fluence and likely defect density. Atomic resolution STEM imaging was achieved using an aberration corrected Nion UltraSTEM100 with a probe size of 1.1 Å and a beam current of ~45 pA. The instrument was operated at an accelerating voltage of 60 kV in order to reduce the likelihood of knock-on damage even in defective single-layer graphene and the near-ultra-high vacuum of the microscope (less than 5 x 10$^{-10}$ Torr at the sample) also contributed to reducing the likelihood of contamination.

1. Novoselov, K. S. et al. A roadmap for graphene. Nature 490, 192–200 (2012).
2. Chen, I.-H., Cullen, W., Jiang, C., Fuhler, M. & Williams, E. Defect Scattering in Graphene. Phys. Rev. Lett. 102, 236805 (2009).
3. Lehtinen, O., Kotakoski, J., Krasheninnikov, A. V. & Keinonen, J. Cutting and controlled modification of graphene with ion beams. Nanotechnology 27, 157306 (2016).
4. Lehtinen, O. et al. Effects of ion bombardment on a two-dimensional target: Atomic simulations of graphene irradiation. Phys. Rev. B 81, 153401 (2010).
5. Lahiri, J., Lin, Y., Bozkurt, P., Oleynik, I. I. & Batzill, M. An extended defect in graphene as a metallic wire. Nat. Nano. 5, 326–329 (2010).
6. Nair, R. R. et al. Spin-half paramagnetism in graphene induced by point defects. Nat. Nano. 5, 199–202 (2010).
7. Kotakoski, J., Krasheninnikov, A. V., Kaiser, U. & Meyer, J. C. From Point Defects to Graphene to Two-Dimensional Amorphous Carbon. Phys. Rev. Lett. 106, 105505 (2011).
8. Warner, J. H. et al. Dislocation-Driven Deformations in Graphene. Science 337, 209–212 (2012).
9. Huang, P. Y. et al. Grains and grain boundaries in single-layer graphene atomic patchwork quilts. Nature 469, 389–392 (2011).
10. Meyer, J. C. et al. Direct Imaging of Lattice Atoms and Topological Defects in Graphene Membranes. Nano Lett. 8, 3582–3588 (2008).
11. Girit, C. O. et al. Graphene at the Edge: Stability and Dynamics. Science 323, 1705–1708 (2009).
12. Russo, C. J. & Golovchenko, J. A. Atom-by-atom nucleation and growth of graphene nanoribbons. Proc. Natl. Acad. Sci. 109, 5953–5957 DOI:10.1073/pnas.1119827109 (2012).
13. Wang, H. et al. Probing Monolayer Graphene with Single Atom Substitutions. Nano Letters 12, 141–144 (2012).
14. Lehtinen, O. et al. Non-invasive transmission electron microscopy of vacancy defects in graphene produced by ion irradiation. Nanoscale 6, 6569 (2014).
15. Angelova, P. et al. A Universal Scheme to Convert Aromatic Molecular Monolayers into Functional Carbon Nanomembranes. ACS Nano 7, 6489–6497 (2013).
16. Eder, F. R., Kotakoski, J., Kaiser, U. & Meyer, J. C. A journey from order to disorder — Atom by atom transformation from graphene to a 2D carbon glass. J. Phys. Cond. Mat. 24, 335301 (2012).
17. Ramasse, Q. M. Probing the Nature of Defects in Graphene by Raman Spectroscopy at Low kE Imaging and Analysis at Ultimate Detection Limits. Nanoscale 14305–14312 (2012).
18. Ramasse, Q. M. et al. Doping Monolayer Graphene with Single Atom Substitutions. Nano Letters 12, 141–144 (2012).
19. Lehtinen, O. et al. Non-invasive transmission electron microscopy of vacancy defects in graphene produced by ion irradiation. Nanoscale 6, 6569 (2014).
20. Ferraro, A. C. Raman spectroscopy of graphene and graphite: Disorder, electron–phonon coupling, doping and nonadiabatic effects. Phys. Rev. B 80, 235407 (2009).
21. Ziegler, J. F., Ziegler, M. D. & Biersack, J. P. SRIM – The stopping and range of ions in matter (2010).
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