The effect of residual gas scattering on Ga ion beam patterning of graphene

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The effect of residual gas scattering on Ga ion beam patterning of graphene

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The patterning of graphene by a 30 kV Ga⁺ focused ion beam (FIB) is studied by *in-situ* and *ex-situ* Raman spectroscopy. It is found that the graphene surrounding the patterned target area can be damaged at remarkably large distances of more than 10 μm . We show that scattering of the Ga ions in the residual gas of the vacuum system is the main cause of the large range of lateral damage, as the size and shape of the tail of the ion beam were strongly dependent on the system background pressure. The range of the damage was therefore greatly reduced by working at low pressures and limiting the total amount of ions used. This makes FIB patterning a feasible alternative to electron beam lithography as long as residual gas scattering is taken into account.

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Graphene, a two-dimensional atomically flat material, has attracted much attention mostly because of its excellent electrical properties.^{1–3} Graphene can be mechanically exfoliated from graphite crystals (forming only few small flakes at random), or synthesized over very large areas by chemical vapour deposition (CVD).^{4,5} Although mechanical exfoliation still delivers the highest quality graphene,³ CVD is currently the most promising synthesis method for high-end electronic applications such as RF devices. To fabricate many individual devices out of large area graphene, it must first be patterned to isolate small device areas from the bulk of the graphene. Patterning is typically performed by electron beam lithography (EBL) followed by reactive ion or plasma etching,^{6,7} which requires the graphene to be coated by a resist film. The removal of these resist films after processing is challenging and a thin layer of residue is known to remain on the graphene, influencing the electrical properties of devices.⁸ Furthermore, uncontrolled under-etching and delamination of the graphene during lift-off is common.⁹

An alternative to lithography is direct-write ion beam patterning, in which a focused ion beam (FIB) defines the desired pattern by locally removing the graphene via milling or sputtering. Using a FIB, the graphene can be patterned directly and the use of resist coatings can be avoided. Ga⁺ ion beams are commonly used to pattern graphene;^{10–14} however, it has been found that these ion beams can damage the graphene up to tens of micrometers away from the intended target area.^{10,11,14} For example, Archanjo *et al.* briefly noted a small amount of lateral damage after patterning exfoliated graphene when using ion doses high enough to remove the graphene.¹⁰ Chen *et al.* measured a large reduction of the field-effect mobility after removing large areas of graphene by Ga⁺ FIB,¹¹ but attributed this to damage during transfer of the graphene to the SiO₂ substrate. However, it is possible that damage due to the large lateral range of the ions played a role as well. More recently, Liao *et al.* reported in detail on

the large lateral range of the damage observed in graphene after Ga⁺ FIB exposure.¹⁴ The effect was attributed to ions in the tail of the intrinsically Gaussian beam shape of the FIB. However, the lateral range over which the damage was reported is much larger than the typical intrinsic beam shape of an FIB.¹⁵ Their observation that the lateral damage decreases using a higher beam current (which would actually increase the intrinsic beam size^{16–18}), points towards the direction that other factors besides the intrinsic beam size also play an important role in damaging the graphene in areas away from the targeted area. It is clear that this large range of lateral damage is not well understood and sometimes overlooked in literature, even though it could be a limiting factor in the use of ion beams for patterning of devices.

In this work, we use *in situ* and *ex situ* Raman spectroscopy to reveal that the large lateral range of damage in graphene after Ga⁺ FIB patterning is mainly caused by scattering of the ions in the residual gas of the vacuum system. With this in mind, the processing conditions were optimized to reduce scattering and we found that patterning of graphene devices with Ga⁺ beams is a feasible alternative to the EBL patterning. Furthermore, the Raman D peak of graphene turned out to be an excellent probe for determining the Ga ion beam diameter and shape.

Graphene samples were grown by chemical vapor deposition (CVD) on copper foil and transferred to 90 nm SiO₂ on Si wafers using a standard polymethyl methacrylate (PMMA) transfer process.¹⁹ An FEI Helios 650 DualBeam system was used for Ga ion beam milling and *in situ* Raman measurements of the graphene sample. The DualBeam system combines an electron beam and Ga FIB allowing for simultaneous milling and imaging by SEM. In addition, a Raman laser (785 nm wavelength) is present in the same vacuum chamber,²⁰ enabling Raman measurements of the graphene immediately after FIB exposure. The substrate stage can be tilted and moved back and forth a known distance between the FIB (52° tilt) and Raman laser, without losing focus in either position, to quickly switch between FIB exposure and Raman measurement of the same sample area.

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Raman line-scans were measured by an *ex situ* Raman laser (Renishaw inVia confocal Raman microscope, 514 nm wavelength). The ion beam acceleration voltage was typically chosen at the highest setting of 30 kV. Areas of interest on the graphene sample were not imaged before ion beam exposure to prevent beam damage in the graphene. The background pressure of the chamber is typically $\sim 10^{-5}$ mbar under regular working conditions just after sample loading, but can be reduced to below 10^{-6} mbar by increasing the pumping time.

Before investigating the lateral range of the Ga^+ FIB, we first investigate the behaviour of the graphene while under ion bombardment. This allows us to determine the relevant ion dose range in which the graphene is removed from the substrate without significantly milling the substrate itself. An *in situ* Raman laser was used inside the same vacuum chamber as the FIB to investigate how the Raman spectrum of graphene changes as it is exposed to Ga ions. The use of the *in situ* Raman laser allows observation of the same graphene area for each measurement. This eliminates the influences of variations of the graphene quality from one area to the next and prevents the irradiated graphene from being oxidized or otherwise affected by the ambient before measurements. Figure 1(a) shows how the Raman spectrum of the graphene changes after consecutive exposures to Ga ions. The same $20 \times 20 \mu\text{m}^2$ area was irradiated and moved between the Ga beam and the *in situ* Raman laser for each spectrum. A large D peak appears at a very low dose of only $\sim 10^{12}$ ions/ cm^2 , which indicates that the graphene is already getting damaged at a relatively low dose of ions (compared to the areal density of carbon atoms in graphene of 3.8×10^{15} atoms/ cm^2). Furthermore, it confirms that Raman spectroscopy is sensitive even to small amounts of defects, as has been shown for graphite,²¹ and Raman spectroscopy is therefore an ideal tool to investigate the influence of small amounts of scattered ions. After 10^{13} ions/ cm^2 the D and G peaks start to broaden and merge together into a single broad feature, indicative of amorphous carbon. After approximately $3\text{--}6 \times 10^{15}$ ions/ cm^2 (not shown), both peaks are no longer discernible and the Raman signal of the bare SiO_2 substrate appears, indicating that the graphene has been

removed. Therefore, on average 1–2 carbon atoms are removed per incident Ga ion which is consistent with simulations.¹² At this ion dose, it is possible that there are still some carbon species remaining below the detection limit of Raman.²² The electrical conductance through the milled area is however already negligible at a lower ion dose, as shown in the supplementary material.²³

The ratio between the D and G peak intensities (I_D/I_G ratio) is typically used as a measure of the defect density in graphene. Figure 1(b) shows the I_D/I_G ratio as a function of the ion dose (the peak intensity I is defined here as the maximum height of a Gaussian fit through the baseline-corrected peak). The ratio increases from almost 0 (pristine graphene) to ~ 3.5 for a dose of 10^{13} ions/ cm^2 at which point the graphene is highly damaged. At even higher doses, the D and G peaks start broadening and merging causing I_D/I_G to decrease again. This behaviour follows the typical amorphization trajectory of graphene, where pristine graphene is first transformed into nanocrystalline graphene with defects (stage 1 disorder), and then further into amorphous carbon (stage 2 disorder). It is also commonly observed for exposures to Ar^+ ions,^{24,25} He^+ ions,^{26–28} or even electrons.²⁹ However, the small mass of the He^+ ions and electrons results in less efficient momentum transfer and lower sputtering yield, therefore the dose at which the transition from stage 1 to stage 2 occurs is consequently much higher. The mechanism of graphene removal by the FIB can therefore be summarized as (1) quick initial amorphization of the graphene by a low dose of ions (until about $10^{13}\text{--}10^{14}$ ions/ cm^2), followed by (2) milling of the remaining amorphous carbon during prolonged ion exposure (until 6×10^{15} ions/ cm^2).

After the FIB patterning, a large Raman D peak was sometimes observed in the graphene even micrometers away from the patterned areas (see Figure 2(a)), indicating that some ions were unintentionally damaging the graphene far away from their intended target. The micrometer scale at which the graphene becomes damaged is remarkably large. Moreover, we found that it is independent of beam current and focusing conditions. This suggests that it is not caused by ions in the tail of the intrinsically Gaussian beam shape (as suggested by Liao *et al.*¹⁴) or poor focusing of the beam.

FIG. 1. (a) Evolution of the Raman spectrum of the irradiated graphene after increasing doses of Ga ions (spectra are offset for clarity; dose increases from bottom to top). A large D-peak at $\sim 1300 \text{ cm}^{-1}$ appears after less than 10^{12} ions/ cm^2 , which then broadens and merges with the G-peak at $\sim 1600 \text{ cm}^{-1}$ indicative of amorphous carbon. (b) The ratio of the D- and G-peak intensity as a function of ion beam dose shows the typical amorphization trajectory. The ratio increases quickly to a maximum, indicating transformation from pristine graphene to nanocrystalline graphene (stage S1), and then decreases as the D- and G-peak merge indicating transformation to amorphous carbon (stage S2).

FIG. 2. (a) Raman line-scan measurements (ratio of I_D/I_G as a function of the lateral distance r) for four different system background pressures. The location of the FIB pattern is indicated by the dark bar on the left. The inset shows the mean lateral range of the exponential tail of the damage as a function of the system background pressure. (b) The same data from (a) transformed to show the beam profile (ion dose as a function of lateral distance). The lines are numerical fits to the data with the expected r -dependence of $r^{-2.55}$. The pressures indicated in the legend hold for both graphs (a) and (b).

Furthermore, Liao *et al.* showed that reducing the exposure time (while keeping the ion dose the same by increasing the beam current) reduces the range of the damage. However, higher beam currents would normally lead to an increase in beam size,^{16–18} causing more lateral damage. This contradiction points to the possibility of another cause for the damage, such as scattering of the ions in the residual gas of the vacuum system. Residual gas consists typically of water, oxygen, and hydrocarbons, and its influence on Ga^+ ion beams has been reported previously,^{15,30–32} though mostly on Si or other substrates less sensitive than graphene. It is thought to remain dominant over other beam broadening effects until pressures drop below 10^{-7} mbar,^{15,32} which is rarely achieved in commercial FIB tools. Residual gas scattering could therefore explain inconsistencies in previously reported results if the system background pressure, and hence the degree of scattering, has varied during or in between experiments.

Under normal vacuum conditions (background pressure $< 5 \times 10^{-5}$ mbar) the mean free path of the ions is on the order of 1 m and direct collisions with residual gas molecules is unlikely.³¹ However, the distance from ion source to sample is typically also large; on the order of 50 cm through the ion beam column (where the pressure is low), and a further 1–2 cm through the chamber itself. The ion beam column will typically see a pressure gradient from about 10^{-7} mbar at the source to about 10^{-6} – 10^{-5} mbar in the chamber. Even when taking into account only scattering in the chamber itself and ignoring scattering in the lower pressure ion beam column, a scattering angle of only 0.015° already results in a lateral range of $5 \mu\text{m}$ on the sample. In addition, graphene is very sensitive to energetic ions and even a small dose of unintended ions is enough to cause damage, as was shown in Figure 1.

To investigate the influence of residual gas scattering, several identical thin lines ($1 \mu\text{m}$ wide) were patterned by Ga^+ FIB at a dose of 10^{16} ions/ cm^2 , using an acceleration voltage of 30 kV, and a beam current of 40 pA. The lines were patterned at irregular time intervals in the timespan of several hours while the system was being pumped down from initial working conditions ($\sim 5 \times 10^{-5}$ mbar) to a pressure of 2×10^{-6} mbar in order to investigate the effect of the

residual gas pressure. Raman line-scans were measured perpendicular to the patterned lines to measure the I_D/I_G ratio as a function of the lateral distance to each line.

Figure 2(a) shows scans of four representative FIB patterns. Note that it is expected that the dose of scattered ions (and therefore the damage in the graphene) will be highest near the FIB pattern and decrease at further distances in the direction away from the FIB pattern. The I_D/I_G ratio initially increases from about 1 to ~ 3.5 in the first 2–4 μm , and then decreases again exponentially away from the intended target over tens of micrometers. The shape of these graphs can be counter-intuitive, but can be explained by the two stages of disorder shown in Figure 1(b). The exponential decrease far away from the FIB pattern (at a low dose of scattered ions) is due to stage 1 disorder where the I_D/I_G ratio simply increases for increasing ion doses. However, the initial increase of the I_D/I_G ratio close to the FIB pattern is due to stage 2 disorder, where the I_D/I_G ratio actually decreases for higher ion doses (closer to the pattern) due to amorphization of the graphene. Using this knowledge, we can visualize this data in a more intuitive way by plotting the ion dose (instead of the I_D/I_G ratio) as a function of the lateral distance. To this effect, the I_D/I_G ratio in each measurement point can be correlated with the corresponding ion dose that the graphene received by using the relation in Figure 1(b). By fitting the data in Figure 1(b) with an analytical expression,²⁴ any I_D/I_G ratio can be numerically inverted to find the corresponding ion dose. Note that because the expression is not one-to-one (for example, an I_D/I_G ratio of 2 can mean a low ion dose during stage 1 disorder, or a high ion dose during stage 2 disorder), careful inspection of each result is required to choose the ion dose that corresponds to the correct stage of disorder. More information about this procedure can be found in the supplementary material.²³

Figure 2(b) shows the resulting beam profiles (ion dose as a function of lateral distance r) for the same FIB patterns as shown in Figure 2(a) and shows the expected monotonic decrease of the ion dose at further distances from the target. When residual gas scattering is significant, the ion dose is expected to depend on the distance r as about $r^{-2.55}$ as modelled by Ishitani *et al.*³⁰ The lines in the graph are numerical fits to the data with this expected r -dependence and show

that the data follows this model well (see supplementary material for more details²³). This clearly demonstrates the effect of residual gas scattering and shows that the beam size increases for higher background pressures. The dose of scattered ions ranges from about 10^{14} ions/cm² close to the pattern down to 10^{12} ions/cm² after several microns, which is a factor 10^2 – 10^4 lower than the dose of 10^{16} ions/cm² in the patterned area. The amount of scattering is therefore very low as expected, however it is still high enough to significantly damage the graphene, which demonstrates that Raman spectroscopy on the graphene substrates is an ideal tool to measure ion beam profiles.

As an additional demonstration, the exponentially decaying part of the I_D/I_G ratio in Figure 2(a) can be used to visualize the effect of the background pressure by plotting the $1/e$ mean distance (obtained from exponential fits) as a function of the background pressure, see the inset of Figure 2(a). The range of the damage decreases quickly as the system background pressure decreases, which confirms that scattering in the residual gas is indeed a major cause of the lateral damage.

To prevent damaging the graphene close to those regions that are patterned, the ion scattering must therefore be reduced as much as possible. This can be done by three strategies: (1) First of all, reducing the distance between the ion column and sample would reduce the lateral range of scattered ions. However, this is not practical in existing systems due to geometrical constraints (e.g., the tilting sample stage should not hit other system components in close proximity), but could be kept in mind in the design of new systems. (2) Second, the system background pressure should be as low as possible to reduce the amount of residual gas. This can be achieved by working at very low base pressures and using load-lock systems to prevent breaking vacuum. (3) Finally, the size of the patterned area should be reduced as much as possible. This can be achieved by patterning only small cuts to isolate sections of graphene instead of removing very large areas. For a small area, the total amount of ions needed to achieve a sufficient ion dose to remove the graphene is reduced, and therefore, the amount of ions that scatter will also be reduced.

By combining strategies (2) and (3) (e.g., working at low pressures and patterning only small areas), thin cuts of 100 nm width can be patterned in graphene with very minimal damage due to scattered ions. Figure 3 shows a Raman line-scan over a series of the FIB cuts of varying ion dose and a corresponding SEM image above the graph. The I_D/I_G ratio is high when the Raman laser is on top of a cut, but decays down to the base level (non-damaged graphene) within a distance of 2–3 μm , which is limited by the resolution of the Raman laser spot size. This result shows that the FIB patterning of graphene is feasible when residual gas scattering is taken into account.

We have demonstrated that residual gas scattering is the main cause of the large range of lateral damage typically seen in graphene after Ga^+ FIB patterning. Using *in situ* and *ex situ* Raman spectroscopy, we investigated how the diameter and shape of the FIB is influenced by the background pressure of the vacuum system. When the background pressure is lowered, the lateral range of the ions in the tail of the

FIG. 3. A Raman line-scan with a step-size of $0.33 \mu\text{m}$ measuring the I_D/I_G ratio along a line perpendicular to small FIB cuts created with varying ion doses. A high I_D/I_G ratio is measured when the laser is on top of a cut due to the damage on the edges of the cut, while a low I_D/I_G ratio (the same as the base level far from the cuts) is measured in between, indicating no damage to the graphene. The I_D/I_G ratio signal decays down to the base level within 2–3 μm . This value is limited by the size of the Raman laser spot. The FIB cut patterned with the dose required to remove the graphene (6×10^{15} ions/cm²) is indicated by the darker background.

FIB becomes smaller and the ion dose in the area surrounding the target is reduced. The range of the lateral damage in the graphene was therefore greatly reduced by working at low pressures and limiting the total amount of ions used. With these insights, we conclude that FIB patterning could be a feasible alternative to EBL when residual gas scattering is reduced.

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