Controllable Atomic Scale Patterning of Freestanding Monolayer Graphene at Elevated Temperature

AUTHOR NAMES

Qiang Xu¹, Meng-Yue Wu¹, Grégory F. Schneider¹, Lothar Houben², Sairam K. Malladi¹, Cees Dekker¹, Emrah Yucelen³, Rafal E. Dunin-Borkowski² and Henny W. Zandbergen¹*

SUPPLEMENTARY INFORMATION:

Contents:

1. Raman spectroscopy of monolayer graphene
2. Discussion of control parameters for destructive STEM sculpting and non-destructive imaging
3. Edge reconstruction at 800 °C
4. Comparison of sculpting at room temperature, 600 °C and 800 °C
5. Mobile configurations at the edges
6. Agglomerates on the graphene and their effect on hole formation
7. Optimization of electron beam energy for imaging and sculpting
8. Contrast comparison in STEM and HRTEM

List of Movies supplied

References

*to whom the correspondence should be addressed, Email: H.W.Zandbergen@tudelft.nl; Telephone: +31 15 278 2266; Fax: +31 15 278 6600
1. *Raman spectroscopy of monolayer graphene*:

The crystallinity and single-layer nature of each graphene flake were confirmed using electron diffraction and Raman spectroscopy (Figure S1).

![Raman spectrum of sample W7M1](image)

**Figure S1.** Typical Raman spectrum acquired from monolayer graphene
2. Discussion of control parameters for destructive STEM sculpting and nondestructive imaging:

One can consider four regimes: 1) nondestructive imaging of defect-free graphene; 2) the start of the sculpting process, which requires the removal of several neighboring atoms; 3) the continuation of the sculpting to form larger structures; 4) nondestructive imaging of sculpted graphene. Regime 2 requires the highest dose because the graphene lattice has the tendency to a complete repair. Once this extended cluster of vacancies is formed, repair to a continuous graphene lattice is much less likely. The lowest dose is required for regime 4. Evidently for regimes 1 and 4 one requires a low probability for vacancy formation, such that self-repair can take place. In this context one should also take into account the tail of the electron beam, which is relatively weak but can still cause vacancy formation. For instance, if one has formed a hole of 1 nm and put the beam with a full width half maximum (FWHM) of 0.1 nm in the centre of this hole, the hole will continue to increase up to 3 nm in several minutes, which is caused by the tail (obviously the final size of the hole will also depend on the speed of self-repair).

The probability of vacancy formation of a given C lattice site depends on the acceleration voltage of the electrons, the atom type, the e-beam current on this C atom and the dose rate. In the experiment the acceleration voltage of the electrons and the atom type are fixed and the e-beam current is relatively difficult to adjust. Other properties of the beam that one has to take into account are the FWHM of the beam and the intensity in the tails of the beam. The easily adjustable parameters are 1) the dwell time, which is the time the beam is kept at one position during the scan, and 2) the step size in the scan, which is the distance between pixels. Note that with a step size that is much smaller than one C atom, the e-beam remains on a given C atom for several dwell times, which increases the effective dose. Also it should be noted that if the
FWHM of the e-beam is smaller than 1 Å, the central part of the beam is not effective in vacancy formation if it is positioned in the centre of a C hexring.

For a given e-beam intensity, on the one hand the dwell time and the step size determine the vacancy formation and on the other hand the self-repair speed determines its annihilation. Only in the case that self-repair does not dominate one can use dwell time and step size as adjustable parameters to choose between sculpting and imaging. Thus when the electron beam is scanned over a sample, dwell time, step size and the speed of self-repair will influence the e-beam induced damage. In sculpting mode, the step size should be smaller than the FWHM to avoid creating a series of discrete holes (Figure S2a). In imaging mode, the step size can be considerably bigger than the FWHM of e-beam probe. If this is the case, one will not image the individual C atoms or C hex-rings. In case one still wants to obtain atomic resolution HRSTEM, imaging each atom needs to be oversampled to achieve the resolution. Oversampling of an atom causes the electron beam to be repeatedly exposed to the same atom (Figure S2b). For instance, atomic-resolution HRSTEM imaging of graphene (Figure S3) at 300 kV was achieved by using a longer dwell time of 240 µs to obtain a good signal to noise ratio and a scanning resolution of ~0.015 nm/pixel. Each carbon atom is nearly sampled by 10 pixels and thus is exposed by e-beam 10 times. The effective exposure time is thus 10 times the dwell time, ~2 ms. This is nearly 100 times longer than that for normal non-destructive STEM imaging (~10 µs) and comparable to that used for sculpting (~10ms). Figure S3 shows an example of the resulting increased electron beam damage. In this experiment, a series of atomic resolution STEM images of graphene recorded at 700 °C using a 300 kV electron beam show defect-free graphene in the first few scans but visible defects after 4-5 scans.
**Figure S2.** Schematic diagram illustrating the influence of scanning resolution $d_s$ on sculpting and imaging. (a) Discrete sculpting of holes due to a large scan-resolution setting; (b) Smaller scan pixel size results in an overlapping region where the atoms are multiple times.

**Figure S3.** High-resolution STEM imaging of graphene at 700 °C using 300 kV electrons with a dwell time of 240 µs and a scanning resolution of 15pm/pixel. (a) 2nd scan showing a nearly defect-free graphene lattice. (b) 5th scan showing visible defects induced by the electron beam.
3. **Edge reconstruction at 800 °C**:

At ~800 °C, we observed that a curved edge of graphene reconstructed into several straight armchair edges (Figure S4), suggesting the possibility of using heat treatment to control edge type and to improve edge sharpness.

![Figure S4](image)

**Figure S4.** (a, b) Annular dark-field STEM images of holes in graphene recorded at (a) 700 and (b) 800 °C. Imaging the graphene at 800 °C for 5 mins was observed to lead to the growth and faceting of holes to form armchair edges. (c) shows (b) with overlaid white lines, highlighting the reconstructed edges. (d) Defocused high-resolution TEM image acquired at 800 °C showing armchair edges, some of which are highlighted with white lines.
4. *Comparison of sculpting at room temperature, 600 °C and 800 °C:*

Self-repair and beam induced contamination are strongly temperature related. In Figure S5a and Movie S2, one can see that by increasing temperature, one can enhance self-repair to compensate electron beam damage, such that sculpting cannot be carried. At room temperature (See Figure S5b), the electron beam induces contamination, also resulting in the failure of sculpting. Note that the adatoms density on the graphene surface is another factor to influence on the speed of self-repair, however, cannot be controlled so far.

![Figure S5](image)

**Figure S5.** Temperature effect on STEM sculpting. (a) by increasing temperature from 600 °C to 800 °C, self-repair is accelerated such that one cannot drill a hole (outlined by a dash white lines) under the same electron beam conditions that are used for sculpting at 600 °C (outlined by red lines). (b) at room temperature, scanning electron beam on graphene induced contamination even after sample was *in situ* heated up to 800 °C in the microscope.
5. *Mobile configurations at the edges:*

Figure S6 shows a series of HREM images taken with 80 kV electrons with the specimen at 600 °C. Black dots can be observed on the edges of the graphene. Comparisons of the images in the series show that the black dots change position in both and intensity. They are most stable on armchair edges.

**Figure S6.** Series of images showing black dots on the edges of graphene, many of which are mobile. Red arrows indicate the positions of black dots in the first image.
6. **Agglomerates on the graphene and their effect on hole formation:**

Figure S7 shows a HREM image at 80kV with a few agglomerates on top of monolayer graphene. We observed that sometimes formation of a hole occurs at such agglomerate. After the initiation of a hole, it continues to grow with the removal of graphene occurring only at the position of the agglomerate, while the rest of the edge of the hole remains unchanged. We speculate that these agglomerates may contain metal atoms and that the damage to the graphene is associated with a metal-catalyzed reaction and not solely by electron irradiation.\(^2\)

![Figure S7. An image showing various agglomerates (indicated by arrows) of unknown composition](image-url)
7. **Optimization of electron beam energy for imaging and sculpting:**

As discussed in the main text, non-destructive imaging facilitates accurate control of the sculpting process, which can be automated. The resolution that can be achieved during imaging may then influence the precision of the sculpting process. Although fast-scan STEM imaging of graphene at 300 kV can be regarded as non-destructive, the longer dwell time and finer scanning resolution, which are required to achieve atomic resolution STEM imaging, increase the electron radiation dose by a factor of 100. The damage cannot then be effectively repaired by self-healing. A decrease in the probability of knock-on damage for atomic resolution STEM imaging can be achieved either by decreasing the cross-section for C knock-on damage or by improving the imaging efficiency by increasing the cross-section for STEM imaging. Since the electron scattering cross-section depends on the energy of the incident electrons, the high voltage of the electron microscope can be chosen to optimize STEM imaging while minimizing knock-on damage. The cross-sections for knock-on damage and STEM imaging as a function of accelerating voltage are shown in Figure S8, following the description of Zobelli *et al.*

In the latter study, the theoretical threshold energy for knock-on damage of graphene was calculated to be \(~113\) keV. This energy has been measured experimentally to be between 80 and 100 keV, suggesting either that the calculated value may be an overestimate or that adatoms or lattice vibrations may accelerate knock-on damage. By considering different possible values for the threshold energy of 100 and 140 keV for illustrative purposes, the knock-on cross-section as a function of accelerating voltage can be estimated. The total-cross-section for STEM imaging can be estimated by integrating the theoretical cross-section for a relativistic electron incident on a C atom based on the Mott formula, in the form
\[ \sigma_{\text{STEM}} = \int_{0}^{\beta} \left( \frac{Ze_e^2}{4\pi\varepsilon_02m_0c^2} \right)^2 \cdot \frac{1 - \beta^2}{\beta^4} \cdot \csc^4 \theta \cdot \left( \frac{1}{2} - \frac{\beta^2}{2} \cdot \sin^2 \frac{\theta}{2} + \frac{\pi Ze_e^2}{\hbar c} \cdot \beta \sin \frac{\theta}{2} \cdot (1 - \sin^2 \frac{\theta}{2}) \right) \, d\theta \]

Where, \( \beta = v/c \), \( Z = 6 \) for C and \( \theta \) is the scattering angle of the electrons. In our case, we collected scattered intensity using the STEM detector over an angular range of \( \lambda/2 < \theta < 3\lambda \), where \( \lambda \) is the electron wavelength in Å. The results of these calculations are shown in Figure S8.

**Figure S8.** Calculated cross-sections for graphene knock-on damage and STEM imaging. Two threshold voltages 140 kV (red line) and 100 kV (black line) are used for the calculation for knock-on damage.
From Figure S8, it can be seen that the recorded intensity in STEM images can be improved by a factor of 3 by decreasing the high tension of the electron microscope from 300 to 140 or by a factor of 6 from 300 to 100 kV respectively. The probability of knock-on damage can be decreased dramatically down to, for instance, 1 barn, when the incident electron energy approaches the threshold energy for knock-on damage. Therefore, at a low accelerating voltage, a longer dwell time can be used to achieve atomic resolution STEM imaging without significant beam damage. Optimization of the various parameters (accelerating voltage, specimen temperature, dwell time, use of different acceleration voltages) such that one can create and control artificial defects on graphene at the atomic level, needs further investigation.

8. Contrast in STEM and HRTEM

A HRTEM image of graphene has very low contrast on a high background, especially when the electron dose is limited for defect free imaging. Dark-field STEM imaging provides much better contrast, since electrons that have either been scattered to small angles or not scattered, and non-scattered electrons result in a high background in an HRTEM image, do not contribute to the recorded signal. The difference between the two imaging modes can be seen in Figure S9.
Figure S9. Contrast comparison of (a) Dark-field STEM and (b) bright-field HRTEM images were recorded using the same total exposure time of 2s. Intensity profiles extracted from the images are shown in (c) and (d), taken from the regions marked in (a) and (b). DF-STEM shows much better contrast between the graphene and vacuum region.

LIST OF MOVIES SUPPLIED:

Movie S1: In situ STEM sculpting of free-standing graphene.

Movie S2: Temperature-dependent self-repair effect on graphene sculpting.
REFERENCES:


