Chemistry at graphene edges in the electron microscope

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Abstract

Transmission electron microscopy (TEM) and scanning TEM (STEM) are indispensable tools for materials characterization. However, during a typical (S)TEM experiment, the sample is subject to a number of effects that can change its atomic structure. Of these, perhaps the least discussed are chemical modifications due to the non-ideal vacuum around the sample. With single-layer graphene, we show that even at relatively low pressures typical for many instruments, these processes can have a significant impact on the sample structure. For example, pore growth becomes up to two orders of magnitude faster at a pressure of ca. $10^{-6}$ mbar as compared to ultra-high vacuum (UHV; $10^{-10}$ mbar). Even more remarkably, the presence of oxygen at the sample also changes the observed atomic structure: When imaged in UHV, nearly 90% of the identifiable graphene edge configurations have the armchair structure, whereas armchair and zigzag structures are nearly equally likely to occur when the oxygen partial pressure in the column is higher. Our results both bring attention to the role of the often neglected vacuum composition of the microscope column, and show that control over it can allow atomic-scale tailoring of the specimen structure.

Aberration-corrected [1] scanning transmission electron microscopy (STEM) provides the ultimate spatial control for defect engineering [2, 3] down to the level of individual atoms (see, for example [4–7] and references therein). However, the range of possible structural changes is normally limited by the elastic and inelastic interactions between the energetic imaging electrons and the sample to knock-on damage and radiolysis via electronic excitations [8–10]. While it is known that also chemical changes happen at the sample during microscopy experiments [11], these are often neglected due to the uncontrolled composition of the residual vacuum. It thus remains unknown how large an impact residual vacuum gases can have on the sample during imaging. Additionally, if the atmosphere could be controlled, available parameters for defect engineering inside the microscope would expand from electron energy [12], dose rate [13] and sample temperature [14] to the vacuum level and composition [11], ideally providing chemical control of materials down to the nanoscale.

Chemical effects have been reported for graphene nanopores [12] via the comparison of pore growth rate at different electron acceleration voltages (20 and 80 kV), which ruled out the role of either knock-on damage or radiolysis or other processes arising from electronic excitations. Instead, structural changes at the pore edges were hypothesized to be caused by chemical processes through the interaction of the electron beam and molecules in the residual gases of the microscope column vacuum. Earlier transmission electron microscopy studies [15] have demonstrated a tendency for zigzag (ZZ) edges to form via sputtering under electron irradiation. This is in contrast to a recent environmental TEM study [16], where the formation of armchair (AC) edges was reported during high-temperature oxygen treatment at pressures in the mbar regime, as well as the recent UHV STEM
study where preference for AC edges was similarly reported [17].

Graphene edges are also interesting in the context of graphene nanoribbons (GNRs), for which their control remains a challenge in top-down production. GNRs have a width of just a few nanometers and electronic properties suitable for nanoelectronics applications [18]. Although the competing bottom-up approach using organic precursor molecules has lead to impressive results [19], it tends to be limited to metallic substrates. In the top-down alternative, graphene sheets are cut in the desired width and orientation. For applications, control over the exact edge structure of GNRs is critical since it directly affects their electronic properties [18, 20]. GNRs with edges in the AC crystallographic orientation are semiconducting, whereas those with ZZ edges are metallic. Previous etching experiments with GNRs have been carried out with scanning probe microscopy techniques on a substrate [21–23]. For example, in [21] high temperature oxidation was used to produce sub-5 nm wide GNRs from graphene on a Si/SiO₂ substrate that were imaged through non-atomic-resolution atomic force microscopy. However, no method has until now demonstrated control of different edge types at atomic resolution.

Here, we study the pore growth rate and atomic structure of edges in graphene as a function of the oxygen partial pressure in in situ STEM imaging experiments. Nanopores are initially created using a high accelerating voltage of 100 kV, whereas imaging is carried out at 60 kV to minimize direct knock-on damage. The pressure is controlled between near-UHV (10⁻⁶ mbar) and 10⁻⁸ mbar using a leak valve at the microscope column, connected to a gas distribution line [11]. The residual gas composition is additionally measured with a mass spectrometer in the vacuum setup adjacent to the microscope column, connected through a flange facing the sample stage. We show that in near-UHV conditions, pore growth is practically nonexistent over typical experimental time scales, whereas it increases by orders of magnitude when oxygen is introduced into the column. Additionally, the atomic structure of nanopore edges—and more clearly of longer edges—depends on the oxygen atmosphere at the sample. At low pressures, AC edges are clearly preferred over ZZ (nearly 90% of identifiable edges are AC), whereas the two edge types become equally likely at higher pressures.

1. Results and discussion

We begin our experiments by creating nanopores into pristine graphene (commercial samples grown via chemical vapor deposition and transferred onto Quantifoil support grids by Graphenea Inc). Since electron beam damage in pristine graphene is limited to knock-on damage [12, 24], we use a relatively high acceleration voltage of 100 kV for this purpose. The electron beam is placed over a clean area (16 nm²) of the sample, and irradiated for ≈1 min with an approximate beam current of ca. 50 pA. After this, the voltage is changed to 60 kV, the aberration corrector is retuned (the whole process takes about 30 min with the constant current mode of the Nion UltraSTEM 100 in Vienna; see [17] for a description of a similar instrument). We first record image sequences of the created nanopores with a field of view of ca. 3 nm in near-UHV to establish a baseline for the pore growth rate. Next, we introduce oxygen into the column through a leak valve, and repeat the experiment for nanopore growth at higher pressures (up to 2 × 10⁻⁷ mbar). The measured gas composition for three gases with the highest partial pressures and the pore growth data are presented in figure 1.

As can be seen from figure 1(a), the residual vacuum gas contains mainly N₂ (CO has the same mass, but there is little reason to assume it makes a significant contribution) and water with a trace amount of oxygen. Note that the data cannot reach down to the near-UHV pressure that is our normal condition, because the volume with the mass spectrometer has a base pressure of slightly above 10⁻⁹ mbar. When we start to introduce oxygen into the column, its partial pressure rapidly rises and it becomes the most prominent species of the residual vacuum. Overall, the partial pressure of O₂ is consistently an order of magnitude higher than that of chemically inert N₂ and two orders of magnitude higher than that of water. All reported pressures are readings from the objective area gauge of the microscope (OG), unless otherwise mentioned.

The etching rates corresponding to the growth of pores were calculated by measuring the pore area from image sequences at different pressures. This data, plotted against the cumulative electron dose, is shown in figure 1(b) with an example partial sequence of six images shown below. As can be immediately seen, pore growth in near-UHV is very slow (the complete image sequences were much longer than the data shown here, with no changes up to very high doses), while much higher rates are measured under oxygen atmosphere. Etching rates (calculated as the number of atoms lost per second) obtained by linear fits to the data are shown in figure 1(c).

This linearity indicates that the process is limited by the availability of oxygen atoms and not of etching sites. If the rate were proportional to the available edge atoms and not limited by oxygen supply, then the etch rate would depend on the diameter of the holes in the graphene, and would increase during the exposure as the holes grow. However, the rate at which oxygen is dissociated by the beam is expected to stay constant, in agreement with a constant etch rate. The difference in the etching rate between
near-UHV (0.057 atoms s\(^{-1}\)) and 2 \(\times\) 10\(^{-7}\) mbar (4.0 atoms s\(^{-1}\)) is nearly two orders of magnitude, highlighting the importance of the atmosphere on the structural changes in the sample during (S)TEM imaging. After the leak valve is closed, the vacuum recovers quickly (within half an hour) to the near-UHV values, bringing the etching rate back down to the values recorded before the leak valve was opened.

To put these numbers into context, let us consider an ideal gas at 300 K. The impingement rate at a pressure of 2 \(\times\) 10\(^{-7}\) mbar is \(\sim\)1 nm\(^2\) s\(^{-1}\). Assuming a mean residence time of \(\sim\)5 \(\times\) 10\(^{-10}\) s (using an adsorption energy of 0.16 eV for an O\(_2\) molecule on graphene [25]), the surface concentration of oxygen molecules should be \(\sim\)1 \(\times\) 10\(^{-9}\) nm\(^{-2}\), which is obviously too low to explain the observed etching rates. Note that even at the limit of the ballistic regime (\(\sim\)1 \(\times\) 10\(^{-4}\) mbar), surface concentration would remain below \(\sim\)5 \(\times\) 10\(^{-7}\) nm\(^{-2}\). Such estimates are typically used to argue that the vacuum level in microscopes (often ca. 10\(^{-7}\) mbar) is sufficient to prohibit significant structural changes caused by chemical processes arising from the residual vacuum composition. As our results show, this is clearly incorrect. Moreover, the values we report here are consistent with recent literature. For example, analysing the data provided in [12, 15] leads to etching rates of 0.15 atoms s\(^{-1}\) and 0.4 atoms s\(^{-1}\), respectively, in non-UHV instruments with assumed vacuum conditions similar to our high-pressure experiments. In these studies it was noticed that etching tends to slow down over time, which is consistent with the depletion of oxygen from the hydrocarbon-based contamination, as we described previously [11]. The overall etching rates between 0.05 and 5 atoms/s, depending on the oxygen partial pressure, are consistent with the simple kinetic model of ideal gases (see the supplementary information (available online at stacks.iop.org/2DM/8/035023/mmedia) for details), but only if a significant fraction of O\(_2\) molecules close to the imaged area have been dissociated through radiolysis before landing on the sample.

We next turn to the detailed atomic structure of the pore edges during the experiments. Taking only knock-on damage into account, atomistic simulations [26] showed in 2012 that the removal of atoms from a graphene edge is determined by the dynamics of the edge atoms after they are hit by an electron. Armchair edges were found to be more stable against such damage than zigzag edges due to their higher displacement threshold energy (energy required to displace an atom from its site in the structure). This is in contrast to the experimental findings from 2009 showing mostly zigzag edges under irradiation with 80 keV electrons [15], carried out at a typical vacuum level of \(\lesssim\)10\(^{-7}\) mbar.

We classify the atomic structures at the pore edges in our images into five different categories: AC, most likely AC (may not be identified with total certainty due to local image contrast), ZZ, most likely ZZ, and ‘other’ (figure 2(a); see also supplementary information for examples of many of the ‘other’ configurations). We then compared the prevalence of AC and ZZ configurations by calculating the ratio of AC to all identified AC or ZZ configurations at each oxygen partial pressure. The results, normalized to the corresponding unit cell length, are shown in figure 2(b) (full symbols). Although the results are quite similar at all pressures (ranging from ca. 0.56 \(\pm\) 0.03 in near-UHV to 0.42 \(\pm\) 0.03 at 2 \(\times\) 10\(^{-7}\) mbar), there is a clear trend for the AC edges to become less prominent as the oxygen partial pressure increases.

As was also pointed out in [26], the circular shape of the pores may play a role in the observed

![Figure 1. Pore growth rates at different pressures: (a) partial pressures of three selected gases as a function of the objective gauge (OG) pressure. (b) Pore growth for series at different pressures. For the UHV series, after 20 images only every 20th image (dose of \(\sim\)1 \(\times\) 10\(^9\) electrons) was included in the analysis due to slow changes. (c) Number of atoms lost per second as a function of pressure. (1)–(6) Selected images of a 3 \(\times\) 10\(^{-7}\) mbar etching series.](image-url)
To bring light to this question, we turn to density functional theory simulations (see section 3). Due to the large number of possible reactions, our aim here is only to provide plausible mechanisms in support of our experimental findings. First, to understand the diffusion of atomic oxygen towards the zigzag edge, we studied the stability of O adatoms at nearby bridge (epoxide-like bonding) adsorption sites (figure 3). Carbonyl-like bonding (oxygen bound to one carbon atom) at the edge is by far the energetically most favored bonding configuration, one that is also reached without a barrier if an O atom is placed on the bridge site next to the edge (red circle in figure 3(a)). The threshold energy for knocking out a C edge atom bound to the O is about 10 eV, thus slightly weakening the zigzag edge against electron irradiation. Placing an O on the next-nearest bridge site (red square in figure 3(a)) results in another barrierless reconstruction: a C chain partly detaches from the edge to allow out-of-plane carbonylic bonding for the O atom. Only the third-nearest bridge site (red cross in figure 3(a)) results in a stable adatom configuration. However, the relative energetics of the stable absorption sites clearly indicate the preference for O to bind directly to the edge.

The situation for the armchair edge is significantly more complicated (see supplementary information for an illustration). Again, O adatoms preferentially bind in carbonyl-like bonding to one of the edge C atoms. This configuration can with a negligible energy barrier turn into an intermediate state that can be further modified by the addition of O bridge adatoms. This leads to a step-by-step unraveling of the edge structure, leading to configurations that can be easily sputtered by the electron beam. O atoms adsorbed on bridge sites near the edge result in no reconstructions such as that observed for the zigzag edge, and the energies of the different configurations are within a few hundred meV. We further estimate that even with absorbed oxygen, the thermal...
Figure 3. Density functional theory (DFT) modeling of zigzag edge oxidation. (a) Oxygen adatoms diffusing towards the edge may bond at C–C bridge sites at varying distances from it (circle, square, cross). (b) Absorption of O at the bridge closest to the edge results in a barrierless reconstruction of the O to bind laterally to one edge C atom in the lowest energy state. (c) Absorption on the next-nearest C–C bridge results in a barrierless reconstruction of a C chain, 3.2 eV higher in energy. (d) Adsorption on the furthest C–C bridge results in a stable adatom configuration that is 5.1 eV higher in energy than the lateral edge absorption site.

Figure 4. Atoms bound to graphene edges. (a)–(c) STEM-MAADF images of atoms attached to graphene edges. (d)–(g) Image simulations of the energetically most favourable configurations obtained through DFT simulations when attaching a single or multiple carbon/oxygen atom(s) to a graphene ZZ edge. Oxygen forms Klein-like edges whereas carbon tends to dimerize. Dissociation of CO from the zigzag edge has a barrier of about 4.0 eV, and about 3.3 eV from the armchair edge. Thus both edges are expected to be stable under ambient conditions, and the electron beam must be involved in the etching process through a chemically assisted knock-on process.

Experimental images recorded at high pressures appear to confirm the simulation results, at least for the ZZ edges. Indeed, we can see both carbon chains as well as individual oxygen atoms bound at the edges (similar to figures 3(b) and (c), respectively). Unfortunately, due to the electron-beam sensitivity of the structures, spectroscopic identification of the oxygen atoms proved impossible. To identify the atomic species protruding from the ZZ edges, DFT simulations were performed to obtain the energetically most favourable bonding sites for a single or for multiple carbon or oxygen atom(s). Figure 4 contains representative experimental images of atoms at the edge as well as multislice image simulations [28] for DFT-relaxed configurations. The DFT simulations show that for oxygen, it is more favourable to bond in a Klein-like configuration (lower in energy by 1.60 eV, see figure 4(d)), whereas for carbon, bivalent bonding is preferred (by 0.45 eV, see figure 4(e)). Additionally, Klein edges seem to be only stable for oxygen atoms (figure 4(f)), as carbon edge atoms gain a significant amount of energy by dimerization (figure 4(g)). Comparing the simulated images to the experimental ones thus indicates that most of the atoms observed protruding from the edge should be oxygen, since such geometries do not correspond to ground-state configurations for carbon.
This conclusion is supported by intensity analysis. Our MAADF-STEM image simulations show that the intensity for a singly-coordinated carbon atom at a ZZ edge decreases compared to its neighbor (down to 92%), whereas for oxygen it would increase (up to 158%). In the experimental images (figures 4(a)–(c)), the intensities of the attached atoms are always higher than their neighbors (for some up to 120%), which can not be explained by carbon atoms. These values, although lower than the simulated ones, are consistent with oxygen, especially considering that the atoms at the edge tend to move during image acquisition, as seen from the streaked scan lines.

We note that these results are not in contradiction with [29], because the TEM data provided there does not allow for elemental identification and was not recorded in UHV. In that study, both Klein edges and dimerized edges were observed, consistent with configurations containing both carbon and oxygen atoms. In [30], electron energy-loss near-edge spectroscopy was used to identify a single carbon atom in a Klein configuration, with no trace of oxygen. It is possible that the metastable carbon configuration has appeared due to strain or other influence of the surrounding structure. However, as noted above, we were also not able to detect oxygen signal at the edges, which we attribute to the high mobility of the atoms at the edge (in contrast to stationary oxygen atoms embedded inside the graphene basal plane, for which detection is possible [31]).

2. Conclusions

Electron-beam induced chemical processes potentially affect all materials, given a suitable composition of residual gases in the vacuum. Although these effects are typically neglected due to the unknown residual vacuum composition, they can play a crucial role in determining the stability of the sample in the microscope, but also affecting its atomic structure. In this work, we demonstrated that at oxygen partial pressures typical for non-UHV microscopes, the etching rate of graphene edges is up to two orders of magnitude faster than in near-UHV, where the process is so slow to be practically non-existent over experimental time scales. Additionally, while graphene armchair edges are significantly more resistant against knock-on damage due to their higher displacement threshold energy than zigzag edges, they are effectively destabilized under oxygen atmospheres. Thus there exists an active competition between physical and chemical processes in the electron microscope that can be tuned via acceleration voltage (high voltage leads to more elastic scattering and thus physical changes) and the sample atmosphere (chemical processes depend on the availability of suitable molecules). Due to the importance of atomically defined edges in applications with graphene nanoribbons, our results may also provide new ways to create nanostructured samples with unprecedented spatial resolution. Although our results were obtained with the atomically small electron probe inside a microscope, the same physical principles are active also for electron irradiation with an unfocused beam. Indeed, the edges in a sample previously patterned for example with an ion beam [32] could be turned into (mostly) armchair configuration through high-energy electron irradiation in ultra high vacuum, whereas the same treatment in an oxygen atmosphere should increase the prevalence of zigzag edges. Naturally, the possible material modifications through this method are not limited to etching but can be extended to any chemical manipulation where the end structure is sufficiently tolerant of electron irradiation. Overall, the method presented here demonstrates the possibilities of spatially controlled chemistry of materials, opening the way for a number of exciting new experiments.

3. Methods

Experiments were conducted with the aberration-corrected scanning transmission electron microscope Nion UltraSTEM 100 [1] at acceleration voltages of 60 kV and 100 kV with a beam current of ca. 50 pA. The convergence semi-angle of the beam was 30 mrad. The probe size of the instrument at 60 kV is on the order of 1 Å, which together with the scan area are important for limiting the electron beam effects to only the desired sample position. For acquiring images, a medium angle annular dark field (MAADF) detector with semi-angular range of 80–200 mrad was used. The MAADF detector was selected for this study over the high-angle annular dark field detector due to its higher contrast for light elements. Original version of all images used for the analysis are available through the repository of the University of Vienna [33]. The vacuum level in the sample chamber that can be reached with the instrument in Vienna [34] is \(~2 \times 10^{-10}\) mbar (i.e. ultra-high vacuum, UHV). We point out that all pressures mentioned here are readings from the gauge in the objective area. The actual pressure at the sample is expected to be five to six times higher due to the geometry of the objective area of the microscope [11].

The instrument is equipped with a leak valve system that adds the possibility to introduce gases into the sample chamber in the range of \(10^{-9}\)–\(10^{-6}\) mbar without affecting atomic resolution imaging [11] or causing noticeable changes in pressures measured in the neighboring volumes (i.e. the actual pressure remains below ballistic flow). The partial pressures of various gases as a function of pressure in the objective area when leaking in oxygen was measured with a mass spectrometer (Pfeiffer Prisma QME200). In the pressure range of the conducted experiments (\(10^{-8}\)–\(10^{-6}\) mbar) the measured oxygen partial pressure (by the mass spectrometer) starts slightly higher than...
were carried out with the GPAW package. The partial pressure of other prevalent gases is always at least one order of magnitude (N2/CO, Ar) lower than oxygen. The partial pressures of water, hydrogen and carbon dioxide are two orders of magnitude lower. Detailed results are shown in the supplementary information.

The mass spectrometer was calibrated to the total chamber pressure as measured with the Vacum BARION(R) hot cathode ionization gauge. However, since the gauge itself was not calibrated specifically for these measurements, certain uncertainty remains regarding the absolute values of the partial pressures. Nevertheless, since the pressure increase in the microscope objective directly correlates with the gas leaked into the column, their differences provide a reliable estimate of the real change in the gas composition around the sample. Finally, an additional uncertainty in the measurement arises from the differing total pressure of the objective area of the microscope and the adjacent volume containing the mass spectrometer, which may also reflect some differences in the vacuum composition.

Both the microscope column and the adjacent volume where the mass spectrometer is contained are only rarely (less often than once a year) exposed to air, because the samples are introduced into the system through a load lock which is separated from this area by four different vacuum volumes. Additionally, after each air exposure both volumes are kept at an elevated temperature for at least one day to reduce the water concentration in the residual vacuum. Partial pressure of water in vacuum systems is known to decrease over time [35], which is consistent with the low values measured in our setup.

Unless otherwise specified, the samples were commercial freestanding monolayer graphene (Graphenea Inc) with a natural isotope concentration grown via chemical vapor deposition on Quantifoil TEM grids. The samples were baked at 150 °C in a separate vacuum system or a chamber connected to the column for at least 10 h before being introduced into the microscope.

Our density functional theory (DFT) simulations were carried out with the GPAW package [36] using the Perdew–Burke–Ernzerhof exchange-correlation functional [37]. The model systems were six rows wide zigzag (48 °C atoms and four passivating H atoms on one side of the ribbon) and five rows wide armchair (60 °C and 6 H) graphene nanoribbons with 9 k-points along the periodic direction of the ribbon and at least 10 Å of lateral and vertical vacuum between the periodic images. Spin polarization was included in all calculations with a fixed total magnetic moment. After relaxing the structures [38] with a force convergence criterion of 0.01 eV Å−1, we placed one or more atoms of oxygen or carbon at or near the ribbon edges to find the most favorable bonding sites, as well as any direct changes in the edge structure upon oxidation.

To further study the effect of oxidation on the electron-beam stability of the edges, we conducted molecular dynamics (MDs) simulations to determine the displacement threshold energies of selected edge atoms following our established methodology [24, 39]. We considered in the simulations AC, ZZ, and ZZ-57 edge configurations. The simulated displacement threshold energies for the configurations are, in agreement with earlier computational results [26], 18.75–19.00 eV (AC), 12.00–12.50 eV (ZZ) and 20.00–20.25 eV (ZZ-57), and the pristine graphene value is 21.75–22.00 eV as calculated with the same method.

STEM image simulations were carried out using the multislice method within the abTEM package [28], with a spherical aberration coefficient of 1.5 μm, a focal spread of 5 nm, and MAADF detector angles and illumination semiangle set to the experimental values.

Data availability statement

All the data generated or analysed in this study are included in this article and its supplementary information.

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Author contributions

G T L carried out most microscopy experiments and grew and prepared the 13C sample. T S carried out the DFT simulations. J C M participated in the initial experiments. C M participated in the experiments and established the gas line for the experiments. J K participated in microscopy experiments, measured the residual gas composition with C M, carried out the image simulations, supervised the study and carried out the analysis together with G T L. G T L and J K wrote the article with contributions from all authors.
Conflict of interests
The authors declare no competing interests.

Additional information

Supplementary information contains results obtained with heavy graphene, additional observed atomic configurations at graphene edges, DFT modeling of oxygen etching at AC edges, mass spectrometer measurements of the vacuum composition and details about the edge type analysis. References [27, 40] are cited in the supplementary information. Additionally, original microscopy images for all shown figures are provided as supplemental material.

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