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Oxidation of Suspended Graphene: Etch Dynamics and Stability Beyond 1000 °C

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Keywords: Graphene, oxidation, reactivity, TEM, edge roughness

ABSTRACT

We study the oxidation of clean suspended mono- and few-layer graphene in real-time by *in situ* environmental transmission electron microscopy. At an oxygen pressure below 0.1 mbar we observe anisotropic oxidation in which armchair-oriented hexagonal holes are formed with a sharp edge roughness below 1 nm. At a higher pressure, we observe an increasingly isotropic oxidation, eventually leading to irregular holes at a pressure of 6 mbar. In addition, we find that few-layer flakes are stable against oxidation at temperatures up to at least 1000 °C in the absence of impurities and electron beam-induced defects. These findings show first that the oxidation

behavior of mono- and few-layer graphene depends critically on the intrinsic roughness, cleanliness and any imposed roughness or additional reactivity from a supporting substrate; and second, the activation energy for oxidation of pristine suspended few-layer graphene is up to 43 % higher than previously reported for graphite. In addition we have developed a cleaning scheme that results in the near complete removal of hydrocarbon residues over the entire visible sample area. These results have implications for applications of graphene where edge roughness can critically affect the performance of devices, and more generally highlights the surprising (meta)stability of the basal plane of suspended bilayer and thicker graphene towards oxidative environments at high temperature.

Edge roughness, charged impurities and the properties of the supporting substrate are key sources of disorder in devices made from two-dimensional materials.^{1, 2} Edge roughness in particular is critical to device performance as devices approach ballistic limits,³ and changing the edge roughness can lead to suppression of carrier mobility,^{4, 5} thermal conductivity,^{6, 7} or a complete change in the physics of a device: for example the recently demonstrated suppression of quantization in the quantum Hall effect in narrow graphene constrictions with smooth edges.³ As argued by Geim and Novoselov, graphene nanoribbons with widths of about 10 nm are needed to obtain technologically relevant band gaps at room temperature.⁸ While such small dimensions no longer present a significant hurdle for modern lithographic technologies,⁹ the true bottleneck is now in defining structures in graphene with a sufficiently controlled crystallographic orientation and degree of edge roughness.^{10, 11}

Graphene is typically patterned by electron beam lithography (EBL) to define an etch resistant mask and subsequent oxygen plasma or reactive ion etching. Such techniques typically provide a

mask with an edge roughness of approximately 3-5 nm^{12, 13} which limits the edge roughness that can be achieved in resulting devices¹⁴ and leaves behind a contamination layer of residual resist which degrades the electronic properties of graphene.¹⁵ These are significant drawbacks and typically require subsequent processing steps to mitigate their impact, for example annealing in inert atmospheres¹⁶. Such strategies are normally applied with the intention of removing surface residues, which are by nature easier to study than atomic scale edge roughness.

Anisotropic or crystallographic etching of graphene or graphite with a partial pressure of oxygen shows promise for low edge roughness resist-less structuring as well as control of edge chirality.¹⁷ To date however, different groups have variously reported the process to result in holes with armchair,¹⁸ zigzag¹⁹⁻²² or isotropically etched edges.²³⁻²⁵ The substrate in particular has been shown to affect the morphology of the etched structures. In one study (Ref. 19) etching graphene at high temperature in a partial pressure of oxygen, anisotropic etching with zigzag-oriented edges was demonstrated when the graphene was placed on SiO₂, but etching was isotropic when placed on an intermediate layer of hexagonal boron nitride on SiO₂, implying a strong dependence on roughness and/or charged impurities. Furthermore, the lowest temperature at which oxidation is reported varies between 450-600 °C for graphite and 400-570 °C for graphene.^{18, 23, 24, 26} These differing observations together suggest that the oxidation process is very sensitive to the experimental conditions.

In this work, we study anisotropic etching of clean suspended graphene by oxidation in an environmental transmission electron microscope (ETEM). In contrast to previous studies, etching dynamics can be monitored in real-time. We investigate the effect of layer number, oxygen pressure, temperature, and electron beam current density on the initiation, etch rate, and edge roughness obtained in the graphene. We find that the lowest edge roughness of < 1 nm is

obtained at oxygen pressures of less than 0.1 mbar, resulting in hexagonal holes with armchair edges. We also extract an activation energy for the rate limiting step of the reaction of 2.11 ± 0.12 eV.

Strikingly, we find that suspended bilayer and thicker flakes are completely resistant to oxidation of the basal plane at temperatures up to 1000 °C and O₂ pressures up to 3.8 mbar, whereas monolayers display etching of the basal plane at 800 °C. Finally, we show that electron beam illumination can be used to nucleate etching on the basal plane.

By eliminating the influence of substrate and impurities, we demonstrate that oxidation has the potential to be used in the resist-less fabrication of graphene-based devices, which require controllable edge roughness and controlled chirality, and have identified a surprising resistance to oxidation of the basal plane of graphene.

Results and Discussion

Exfoliated graphene/graphite flakes of various thicknesses - Fig. 1(a) - were transferred by wedging transfer²⁷ to TEM sample carriers (DENS Nano-Chip XT), with built-in resistive heating capabilities from room temperature up to temperature, $T = 1300$ °C, Fig. 1(b). Oxidation experiments were performed in an FEI Titan ETEM operated at 80 keV. Prior to imaging, the samples were annealed in the TEM column under high vacuum (pressure $p < 10^{-6}$ mbar) at 500 °C for > 1 hour to remove adlayers of polymeric residues from the transfer process. This anneal results in near complete removal of these commonly observed contaminants over the observable suspended graphene area, Fig. 1(c) (see also Fig. S1 and Ref. 28). It is critical that the sample is not imaged with the electron beam prior to this cleaning step for two reasons. First, exposure to the beam results in crosslinked polymer residues that are far more difficult to remove under our

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3 conditions. Second, exposure to the beam results in the introduction of defects in the basal plane
4 through knock-on damage, or chemical etching with either polymer residues from the sample or
5 gas species from the TEM column. After cleaning, the sample can be imaged briefly to confirm
6 the presence of graphene/graphite. The beam is turned off while the desired temperature is set,
7 and O₂ gas is introduced into the microscope.
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11 First, we investigate graphene's resistance to oxidation by annealing the sample in O₂ without
12 simultaneous imaging. Fig. 1(c) shows a sample consisting both of a mono- and few-layer region
13 before O₂ annealing. After brief imaging, the sample is annealed in 3.8 mbar O₂ at 800 °C for 1
14 hour. After annealing, the O₂ flow is stopped and the microscope is pumped down to $p < 10^{-6}$
15 mbar before re-initiating imaging. The inset of Fig. 1(c) shows the sample after annealing. The
16 monolayer region has been completely etched away, while the few-layer has been etched only
17 from the free edges, forming terraces in the process, while the basal plane is intact. No etching is
18 observed in the pristine basal plane of few-layer graphene, even with an O₂ pressure up to 3.8
19 mbar and temperatures up to 1000 °C for 1 hour. In contrast, monolayer graphene is etched in O₂
20 at these temperatures. At 1000 °C we observe that etching occurs only near residues on the
21 sample, see Fig. 1(d) and Fig. S2. In order to check for the introduction of defects on the basal
22 plane, we performed a Raman spectroscopic map of the suspended region of a few-layer sample
23 annealed in 3.8 mbar O₂ at 1000 °C for 1 hour. No D-peak was observed anywhere in the Raman
24 spectral map, indicating an absence of oxidation-induced defects, and that the limited etching
25 occurring near residual polymer is isotropic and does not lead to a visible D-peak. An example
26 spectrum is shown in Fig. 1(e), with full maps presented in the Supporting Information Figures
27 S4 and S5. TEM images of the characterized sample is shown in Fig. S2(e, f). At higher
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temperatures of 1050-1100 °C we instead see complete etching of the sample within 45 minutes, see Fig. S3.

Figure 1: Sample preparation and oxidation resistance. (a) Optical image of graphene flake consisting of a mono- and few-layer region exfoliated on a SiO₂/Si surface, (b) the same flake as shown in (a) transferred to a TEM sample carrier. The dotted line shows the outline of the monolayer region and the white box corresponds to the area shown in (c). (c) Overview TEM image of the sample before annealing. The inset shows a high magnification TEM image of the border region between the monolayer and few-layer graphene after annealing in 3.8 mbar O₂ at 800 °C for 1 hour, scale 10 nm. The monolayer has been etched away and the few-layer

graphene region is etched from the side in terraces. (d) TEM image of a few-layer sample annealed in 3.8 mbar O₂ at 1000 °C for 1 hour, with etching of the basal plane occurring near contamination (indicated). The red dotted lines highlight the edge of the etched layer. (e) Raman spectrum from a different few-layer sample annealed in 3.8 mbar O₂ at a temperature of 1000 °C for 1 hour.

Next, we investigate the dynamics of hole formation in the samples. Illuminating a clean region with an electron beam current density j at temperatures of $800\text{ °C} < T < 1300\text{ °C}$ and O₂ pressures between $10^{-3} < p < 6$ mbar results in the formation of visible holes both in monolayers and thicker samples. Holes in bi- and few-layer graphene are etched in one of the outermost layers and do not immediately propagate through the layers. Instead, after a hole has formed, etching of a new hole can begin in the exposed region of the graphene layer below. A plot of the hole perimeter length as a function of time for an etched hole is shown in Fig. 2(a) together with selected images at various points in time in Fig. 2(b-e) (see also Supporting Video 1). Edges of graphene monolayers become readily visible in TEM images taken at slight de-focus through Fresnel diffraction, creating an enhanced contrast at the edges. As seen in Fig. 2(a), the onset (time = 0) of a constant rate of growth of the hole perimeter is preceded by a short period of no growth where the hole remains small but visible (Fig. 2(b)), of in this case about 50 s (discussed below). The etch rate in the constant growth phase is determined by fitting a straight line for perimeter > 10 nm. The left side of the inset in Fig. 2(b) is a fast Fourier transform of the image showing lattice periodicities. The right side of the inset is a schematic of a real-space lattice with orientation corresponding to the Fourier transform, showing that that the edges of the hole in Fig. 2(c-e) are armchair oriented. The structure of the edges during etching is quite dynamic, and

variation in the edge roughness is observed during the etching process, as seen in Supporting Video 1 and 2.

Figure 2: Etching dynamics. (a) Perimeter of a hole as a function of time. The data points indicated by (b)-(e) correspond to the TEM images shown in (b)-(e). Scale bars are 5 nm. The arrow in (b) points to the hole in the beginning stages. The left part of the inset is a fast Fourier transform of the image with Bravais-Miller indices, and the right part of the inset is a schematic of the real-space lattice in the same orientation as the Fourier transform with distance between

the main atomic lines indicated. $T = 800\text{ }^{\circ}\text{C}$, $p = 0.1\text{ mbar}$, electron beam current density, $j = 1.49 \cdot 10^5\text{ e}^{-}\text{s}^{-1}\text{nm}^{-2}$.

We find that the etch rate scales with increased temperature, pressure and electron beam current density, in each case with a constant etch rate over time (Fig. 3). To eliminate possible variations between samples and microscope conditions, the effects of the temperature, pressure and electron beam current density are always compared within the same sample (discussed below). In Fig. 3(a) we show that higher pressure leads to a higher etch rate, in this case from 0.14 to 1.70 nm/s for $p = 0.08$ and 6.3 mbar, respectively. Fig. 3(b) shows that for $p = 0.01\text{ mbar}$ and $T = 900\text{ }^{\circ}\text{C}$, increasing j by a factor of 5.9 (from $2.2 \cdot 10^5$ to $1.3 \cdot 10^6\text{ e}^{-}\text{s}^{-1}\text{nm}^{-2}$) increases the etch rate by a factor of 2.1 (from an average of 0.37 to 0.79 nm/s). Finally, in Fig. 3(c) we plot the etch rate as a function of $1/T$. From the Arrhenius relation we find an activation energy of $2.11 \pm 0.12\text{ eV}$ (or $204 \pm 11\text{ kJ/mol}$). We note that in the absence of oxygen, the electron beam alone results in an etch rate less than 1% of that seen in the presence of oxygen. We ascribe this non-zero etch rate to knock-on damage of edge atoms (see Supporting Information and Fig. S6 for details).

Figure 3: Etch rate dependence on process parameters. (a) Perimeter vs. time at different O_2 pressures with $T = 800\text{ }^{\circ}\text{C}$ and a current density of $j = 1.6 \cdot 10^5\text{ e}^{-}\text{s}^{-1}\text{nm}^{-2}$. (b) Perimeter vs. time for different current densities as indicated (unit: $\text{electrons s}^{-1}\text{nm}^{-2}$) at an O_2 pressure of 0.01

mbar and $T = 900\text{ }^{\circ}\text{C}$. (c) Arrhenius plot of rate of perimeter increase as a function of $1/T$. This data is obtained with $p = 0.01\text{ mbar}$ and $j = 1.1 \cdot 10^5\text{ e}^{-}\text{s}^{-1}\text{nm}^{-2}$. In (a) and (b) lines are guides for the eye.

Regarding the etching anisotropy, we find that the overall shape of a hole is closer to a regular hexagon at lower pressures ($<0.1\text{ mbar}$), while the hole morphology displays an increasingly irregular aspect at higher pressures ($>2\text{ mbar}$), as shown in Fig. 4. At low pressures it is possible to identify edges that are apparently straight, *e.g.* Fig. 4(a)(I). This implies that the edge roughness here is smaller than the image resolution, conservatively less than 1 nm (see Supporting Information and Fig. S7 for details on edge roughness quantification of edges denoted (I) and (II) in Fig. 4(a) and Fig. 4(b), respectively). Furthermore, the nucleation density of holes increases with increasing pressure.

Figure 4: Etching anisotropy at various pressures. Scale bars are 20 nm . See Supporting Videos 3-6. Note that the image set presented here is not a series, and comes from different samples.

Comparing the etch rates of holes etched in a monolayer and in a bilayer allow us to gain further insight into the etch mechanism. Fig 5(a) is a TEM image from the start of an etching experiment (see Supporting Video 7 and 8) with a low O_2 pressure of 0.01 mbar , $T = 900\text{ }^{\circ}\text{C}$, with holes growing in a bilayer region. Fig. 5(b) is a TEM image from a later instant in the experiment. The hole marked with a black dotted line in Fig. 5(b) has grown in the monolayer

region exposed by the hole marked with a red dotted line in Fig. 5(a). This enables a comparison of the etch rate of a hole growing in a mono- and bilayer region directly under otherwise identical conditions. Fig. 5(c) is a plot the perimeter of these holes as a function of time. We find that the hole in the monolayer region has an etch rate about twice that of the hole in the bilayer region. See Fig. S8 and Supporting Video 9 and 10 for additional data on the etch rate difference of mono- and bilayer at low pressure.

Fig. 5(d, e) shows representative TEM images from a similar experiment but with a high O₂ pressure of 3.8 mbar. The full data set consisting of 40 measured etch rates in 3 different samples is shown in the Supporting Information (Table S1). The hole outlined with a red dotted line in Fig. 5(d) is growing in one layer of a bilayer. In Fig. 5(e) it has merged with neighboring holes to expose a large monolayer region. A new hole in this region has formed, outlined in a black dotted line. In Fig. 5(f) we plot the corresponding perimeters as a function of time, and again see that the monolayer etches about twice as fast as the bilayer. This finding is consistent for the 40 measured etch rates in 3 different samples.

Figure 5: Thickness-dependent etching kinetics. (a, b) TEM images of a sample with holes growing in a bilayer region (a) and a monolayer region (b), with $p = 0.01$ mbar, $T = 900$ °C, $j = 1.33 \cdot 10^6$ e⁻s⁻¹nm⁻². (c) The perimeter of the holes shown in (a, b) as a function of time. The black and red data points come from the holes with the same color dotted line outlining the hole edges in (a, b). (d, e,) TEM images of a sample with holes growing in a bilayer region (d) and a monolayer region (e), with $p = 3.8$ mbar, $T = 900$ °C, $j = 5.5 \cdot 10^4$ e⁻s⁻¹nm⁻². (f) The perimeter of the holes shown in (d, e) as a function of time. The black and red data points come from the holes with the same color dotted line outlining the hole edges in (d, e).

We now turn to a discussion of our results above. The anisotropically etched edges in our work are consistently armchair-oriented, in contrast to the zigzag-oriented edges or isotropic holes reported previously for oxidative graphene etching¹⁹⁻²⁵ and remote hydrogen plasma etching.^{30, 31} Vacuum annealing graphene at high temperatures *in situ* in the TEM has previously been reported to result in primarily armchair edges.^{32, 33} At lower pressures where we obtain more regular hexagons, the conditions are more similar to the high vacuum conditions of these reports, and carbon oxidation here might occur at a rate low enough to allow carbon atoms to re-arrange to form armchair edges. In this scenario, annealing rather than etching is responsible for the anisotropy seen. Oxygen-terminated armchair edges have also been reported to be more stable than oxygen-terminated zigzag edges,^{34, 35} and armchair edges have lower free energy per atom compared to zigzag edges³⁶ which may provide an additional or alternative explanation.

Previous reports on graphite oxidation showed that at temperatures above 450 °C holes form at pre-existing defects in the sample,^{22, 25} but can be initiated anywhere when the temperature is higher than 700 – 875°C.^{37, 38} In contrast, we find instead that the basal plane of few-layer graphene is not etched over hour timescales at temperatures up to 1000 °C in the absence of

contamination or electron beam illumination. In order to explain this unexpected oxidation resistance and stability of few-layer graphene, we note that graphene reactivity has been reported to increase with roughness^{23, 39, 40} and depend on substrate charged impurities.⁴⁰⁻⁴³ Monolayer graphene supported on SiO₂ has been shown to display roughness values of 224 to 350 pm^{20, 44-46} while suspended monolayer graphene has been shown to display roughness values of 114 pm,²⁸ so suspended graphene layers are typically flatter than their SiO₂-supported counterparts. Furthermore, charged impurities are eliminated in our case by high vacuum annealing. Under these conditions, suspended few-layer samples have sufficiently low reactivity towards oxygen that they are not etched unless the electron beam is used to introduce defects. With electron beam illumination, oxidation-susceptible defects in the graphene are generated.⁴⁷ Additionally, the electron beam is known to ionize gas during ETEM experiments and increase the resulting reactivity,^{48, 49} which may also contribute to etching of the graphene basal plane at temperatures between 800-1000 °C.

Monolayers, on the other hand, are etched at temperatures between 800-1000 °C without the need for electron beam exposure. Similar thickness-dependent etching resistance has previously been reported - albeit occurring at lower temperatures - and has been attributed to charge inhomogeneity and increased roughness as compared to bilayer and thicker samples.^{23, 31, 41} In these reports, the graphene/graphite samples were placed on SiO₂, where thicker samples should allow for better screening from the charged inhomogeneities of the SiO₂. We do not see a difference in cleanliness for mono- vs. few-layer samples, which leads us to believe that without a substrate, charge inhomogeneity cannot account for the reactivity differences seen here. On the other hand, suspended monolayers are known to have higher roughness than bilayers,^{50, 51} and in

our case this roughness alone results in increased reactivity of the monolayer in the absence of dopants.

Our results show that higher pressure results in a higher etch rate, indicating that this reaction is diffusion-limited. Increasing the beam current density also increases the etch rate, which is attributed to the generation of more reactive gas species, as discussed above.

From the temperature dependence of the etch rate, we extract an activation energy of 204 ± 11 kJ/mol which is higher than the activation energy of 143 kJ/mol found in Ref. 37, but in agreement with the 180 ± 20 kJ/mol from Ref. 19. In Ref. 19 the graphene was placed on a SiO_2 substrate, which the authors state might decrease the reaction barrier due to larger roughness.

The smallest observed ‘holes’ in graphene layers appear to be more stable against oxidation before the onset of a constant etch rate. The size of such structures in our images of about 1 nm at our defocus values and environment-limited resolution suggests that they represent defects such as Stone-Wales or divacancies.⁵² These defects are known to be particularly stable and therefore more etch resistant than a larger hole in a graphene layer, whilst still providing a site of preferential etching compared to the pristine basal plane. Finally, smaller holes also have fewer sites for reactions to occur, which limits their growth rate initially due to the Poisson statistics of the atomistic removal acting on a smaller population of atoms. In other words: until the expectation value of atomic removal is sufficiently high, the etch rate is limited by the availability of sites, and not diffusion limited as observed at later times.

We find that holes in monolayers are etched nearly twice as fast as holes in bilayers across our entire tested pressure range. The doubling of the etch rate for monolayers *versus* bilayers can be seen as a consequence of the fact that oxygen adsorbed on both sides of a monolayer sheet can reach a reaction site, while for thicker samples only oxygen adsorbed on the side where a hole is

etched can contribute to the etching. The doubling of the rate for monolayers *versus* bilayers also supports our conclusion that the etching is diffusion limited over this pressure range.

We note that the absolute value of the observed etch rates under identical nominal conditions of p , T and j can vary between samples and different locations on the same sample. We can ascribe such variations to inhomogeneities in temperature arising from exact location on the heater⁵³ and/or imperfect thermal contact - nevertheless the ratios and trends described are consistent at a given location within a given sample.

Finally, we note that our graphene displays very low levels of polymer residue after annealing: through the use of cellulose acetate butyrate (CAB) as transfer polymer almost completely clean suspended graphene can be obtained, in contrast to earlier reports.^{16, 54}

Conclusions

We have studied in real-time the oxidation of single and few-layer suspended graphene flakes by *in situ* ETEM. Surprisingly, we find cleaned few-layer graphene to be stable over long periods of time under oxygen atmospheres at temperature up to 1000 °C, but that the monolayer is readily etched under these conditions. Without nucleating defects by electron beam imaging and in the absence of chemical impurities, few-layer suspended graphene displays exceptional resistance to oxidation – *i.e.* it will not burn. This stability may be explained by the elimination of charged impurities, and the decreased roughness of our samples as compared to samples supported by SiO₂. It also suggests that the deliberate deposition of hydrocarbon ‘residues’ may provide an as yet unexplored route for patterning of graphene by oxidative etching.

We find that in electron-beam initiated holes that the oxidation is diffusion limited as evidenced by the similar etch rates of the mono- and bilayer under these conditions and a

dependence of etch rate on pressure. We find that the resulting edge roughness is also correlated with the oxygen pressure, with pressures below 0.1 mbar producing armchair-oriented hexagonal holes with straight edges to within the achievable *in-situ* imaging resolution of < 1 nm. The low edge disorder is attributed to the combined effects of oxidative removal of carbon atoms from the edge and continuous thermal annealing. This edge roughness is a significant improvement over that which can be achieved by EBL, typically around 3-5 nm.^{12, 13} Taking into account the considerable technological efforts taken to reduce the line edge roughness in EBL, this result is very encouraging, and this oxidative etching process may be useful intermediate step for defining armchair oriented nanoribbons which have a width-dependent bandgap⁵⁵ and have recently been shown to have topological states.^{56, 57}

In addition, we have described a scheme based on existing techniques for producing and cleaning suspended graphene monolayers and thicker samples which results in samples where commonly observed hydrocarbon residues are almost entirely absent.

These results point towards oxygen and high vacuum annealing at high temperature as a means of improving the structural perfection of graphene and other 2D materials for improved technological performance, increasing charge carrier mobility and thermal conductivity. In addition, when few-layer graphene is free from significant contaminants, defects and substrate induced roughness it demonstrates high resistance to oxidation at high temperatures and in pure oxygen environments showing refractory properties beyond those commonly expected. This surprising finding might enable high temperature micro-reactor applications or other micro- and nano-refractory systems.

Methods

Graphene was obtained by exfoliation of natural graphite flakes (NaturGrafrit GmbH) onto oxygen plasma pretreated SiO₂ substrates using 3M Magic™ scotch tape at room temperature. Suitable mono- and few-layer flakes were identified by their contrast in optical microscopy and transferred to commercially available TEM sample carriers capable of heating (DENS Nano-Chip XT) using wedging transfer.²⁷ In brief, the crystals were detached from the substrate through the use of a hydrophobic polymer handle of CAB, and water, and transferred to the TEM sample carriers before removal of CAB and critical point drying - see Fig. 1(a, b). To improve adhesion, samples were baked overnight at 130 °C under vacuum (0.3 atm).

For annealing and etching of hexagonal holes, an aberration-corrected FEI Titan environmental TEM operated at 80 keV was used. The temperature of the sample, is controlled by the TEM sample carrier from room temperature to 1300 °C. The O₂ pressure is controlled in the range 10⁻⁵ to 10 mbar by adjusting the flow of gas and the pumping on the column. The electron current density can be controlled by changing the beam and spot size, and is measured by multiplying the number of counts on the CCD camera by a known conversion factor, pixel areal density and frame acquisition rate.

Videos are analyzed using image analysis software (ImageJ). The frame time is known and from a given image the hole perimeter is recorded. From these values, we extract the average perimeter growth rate which we refer to as the "etch rate".

Raman spectral maps were obtained in a Thermo Fisher DXR Raman spectrometer using a 455 nm laser source at a power of 1 mW. Raman spectra were analyzed as described in Ref. 58. Each of the spectra was assessed for the characteristic graphene Raman peaks, including the D-peak associated with sp³ bonds by fitting of Lorentzian peaks, an example is shown in Supp. Fig S5.

Supporting Information. The supporting information includes further information on (1) the graphene cleaning process, (2) graphene oxidation without simultaneous imaging in the temperature range 800-1100 °C, (3) Raman map and peak fitting procedure edge roughness quantification, (4) a control experiment investigating the etch rate when graphene is only subjected to the electron beam and high temperature (no oxygen), (5) details on edge roughness measurements, (6) additional data on the etch rate difference between mono- and bilayer, and finally, (7) information regarding the Supporting Videos. 12 videos are available showing various experiments referred to in the main text and in the Supporting Information. This material is available free of charge *via* the Internet at <http://pubs.acs.org>. (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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