Supplementary information for

“Electron-beam induced nano-etching of suspended graphene”

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We have also studied the nano-etching of graphene supported on SiO$_2$. The results will be presented in the following supplementary information.

Supplementary information 1: High-resolution etching of supported graphene layers on SiO$_2$

Figure S1 shows high-resolution nano-etching of supported graphene on SiO$_2$ with a schematic diagram of the etching process in Fig. S1(a). The etching process has been performed using an electron beam with a diameter of ~0.9 nm that was focused on the graphene layer while, in addition, water vapor has been injected by a gas-injection needle onto the graphene layer. Figure S1(b) shows an SEM image of four different line-cuts into single layer graphene, deposited on SiO$_2$, after focused-electron-induced etching for different conditions. Depending on the electron dose (see Fig. S2), the resolution for the different line-cuts improves from 35 nm to approximately 15 nm, while the edge roughness stays below 5 nm. Hence, the smallest line-cut with 15 nm resolution represents the best resolution that we have obtained for supported graphene with this patterning method.
Figure S1(c) shows an SEM image of a graphene flake with a single, a double, and a multi-layer (marked as n layers) of C-atoms. The transition between areas with different number of layers is determined by atomic force microscopy (not shown) and indicated by white dashed lines. It is clearly visible that the etching through the two-layer graphene flake stops after \(\sim 500\) nm, an effect observed several times at the borders of graphene flakes with different layer thicknesses. The graphene etching is most effective at the edges where normally hydrogen passivation is present and less effective in the middle of a flake, where the sp2-hybridized orbital bonding between the carbon atoms is still intact. In the exposed but not fully etched part of the line, an elevation of the graphene can be seen. The material starts to bend upward and forms an arching (see Fig. S1(d)). We have repeatedly observed such behavior, for a low electron dose even on single layer graphene. Exposing a graphene flake to the electron beam without an additional injection of the precursor gas for the nano-etching process has no visible effect on the graphene, the arching of the graphene seems to be a preliminary stage of the etching process.

**Figure S1.** Nano-etching of graphene layers on SiO\(_2\). (a) Schematic picture of the electron-beam induced etching process, where water vapor is injected by a gas-injection needle directly onto the graphene layer. The electron beam is focused onto the surface and locally etches the carbon lattice. (b) Line-cuts into single layer graphene for different etching conditions (see supplementary information 2), where the resolution can be adjusted from 35 nm down to 15 nm. (c) SEM image of an area with different number of graphene layers and an etched line-cut having a 30 nm resolution through the single and double layer graphene. The etching was performed with an electron acceleration voltage of \(V = 20\) kV, a beam current of \(I = 0.69\) nA and an electron dose of \(D = 32\) \(\mu\)C/\(\mu\)m\(^2\). (d) Zoom-in to the white dashed area in (c), where the graphene layer bends upwards and forms an arching.
Supplementary information 2: Etching dose conditions for graphene layers supported on SiO₂

A minimal electron dose is needed to etch graphene. Below the minimal dose D we either see an upwards-bending (arching) of the graphene layer (see Fig. S1(d)) or the line-cut stays incomplete, i.e. there is still material left which connects the two parts of the graphene. The minimal dose as a function of the beam acceleration voltage V can be seen in Fig. S2(a) for a single layer graphene. The minimal dose and therefore the etching time increases with the acceleration voltage V. This can be explained by the dissociation cross section of electrons interacting with the water molecules. The dissociation cross section decreases for increasing kinetic energy of the electrons, a behavior that has been observed for different kinds of gas molecules.¹,²,³ However, the minimal dose needed to etch bilayer or trilayer graphene increases not as expected by a factor of two or three. Rather, for each additional layer it increases by approximately an order of magnitude. Therefore, we could not succeed in etching more than three layers of graphene on SiO₂ so far.

Figure S2(b) depicts the width b of the line-cuts through single layer graphene flakes as a function of the dose D for a different acceleration voltages V of 5, 10, 15 and 20 kV. Clearly visible is that the width b of the etched line-cut depends only on the electron dose D while it is unaffected by the acceleration voltage.

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**Figure S2.** Parameters for etching supported graphene on SiO₂: (a) Minimal electron dose needed to successfully etch single layer graphene as a function of the acceleration voltage V. (b) Width b of the line-cuts through single layer graphene as a function of the dose D for different acceleration voltages V. All line-cuts for this analysis were etched with a beam current of I = 0.69 nA.
V, a situation that has been observed before if focused-electron-induced etching or deposition is mainly stimulated by the primary electron beam.\(^4,5\) If secondary electrons are involved, a strong dependence of the etching or deposition on the acceleration voltage has been observed.\(^4,6\) The increasing width \(b\) of the etched line-cuts with increasing electron dose, and accordingly increasing etch duration, is caused by lateral etching that can be explained by backscattered electrons. They can dissociate surface-adsorbed molecules also in the nominally unexposed area of the surface, and by the diffusion of the dissociated water molecules (the reactive hydrogen). Effects of different beam currents on the etching behaviour for the same dose \(D\) were not observed.

**Supplementary references**

1. Roediger, P., Hochleitner, G., Bertagnolli, E., Wanzenboeck, H. D. & Buehler, W. Focused electron beam induced etching of silicon using chlorine. *Nanotechnology* **21**, 285306 (2010).
2. Randolph, S. J., Fowlkes, J. D. & Rack, P. D. Focused electron-beam-induced etching of silicon dioxide. *J. Appl. Phys.* **98**, 034902 (2005).
3. Ganczarczyk, A., Geller, M. & Lorke, A. XeF\(_2\) gas-assisted focused-electron-beam-induced etching of GaAs with 30 nm-resolution. *Nanotechnology* **22**, 045301 (2011).
4. Utke, I., Hoffmann, P. & Melngailis, J. Gas-assisted focused electron beam and ion beam processing and fabrication. *J. Vac. Sci. Technol. B* **6**, 1197-1276 (2008).
5. Fowlkes, J. D., Randolph, S. J. & Rack, P. D. Growth and simulation of high-aspect ratio nanopillars by primary and secondary electron-induced deposition. *J. Vac. Sci. Technol. B* **23**, 2825-2832 (2005).
6. Hoyle, P. C., Cleaver, J. R. A. & Ahmed, H. Ultralow energy focused electron beam induced deposition. *Appl. Phys. Lett.* **64**, 1448-1450 (1994).