Electronic Supplementary Material

Crystallographically Selective Nanopatterning of Graphene on SiO_2

Péter Nemes-Incze[1] (✉), Gábor Magda[2], Katalin Kamarás[3], and László Péter Biró[1]

[1] Research Institute for Technical Physics and Materials Science, PO Box 49, H-1525 Budapest, Hungary
[2] Budapest University of Technology and Economics (BME), PO Box 91, H-1521 Budapest, Hungary
[3] Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, PO Box 49, H-1525 Budapest, Hungary

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Annealing and oxidation treatments

The heat treatments were carried out in an electric oven inside a quartz tube reactor, at atmospheric pressure. The oxidation of the graphene samples was carried out at a temperature of 500 °C, for 10–40 min. At this temperature only single layers are oxidized. At 700 °C, in an Ar atmosphere, crystallographic orientation-dependent etching was carried out. For these carbothermal etching reactions, in all cases the quartz tube reactor was flushed for 5 min with Ar, after which the temperature was raised to 700 °C in 20 min, kept at 700 °C for some time (the etching time) and then left to cool to room temperature (see Fig. S-1). In the case of the oxidation

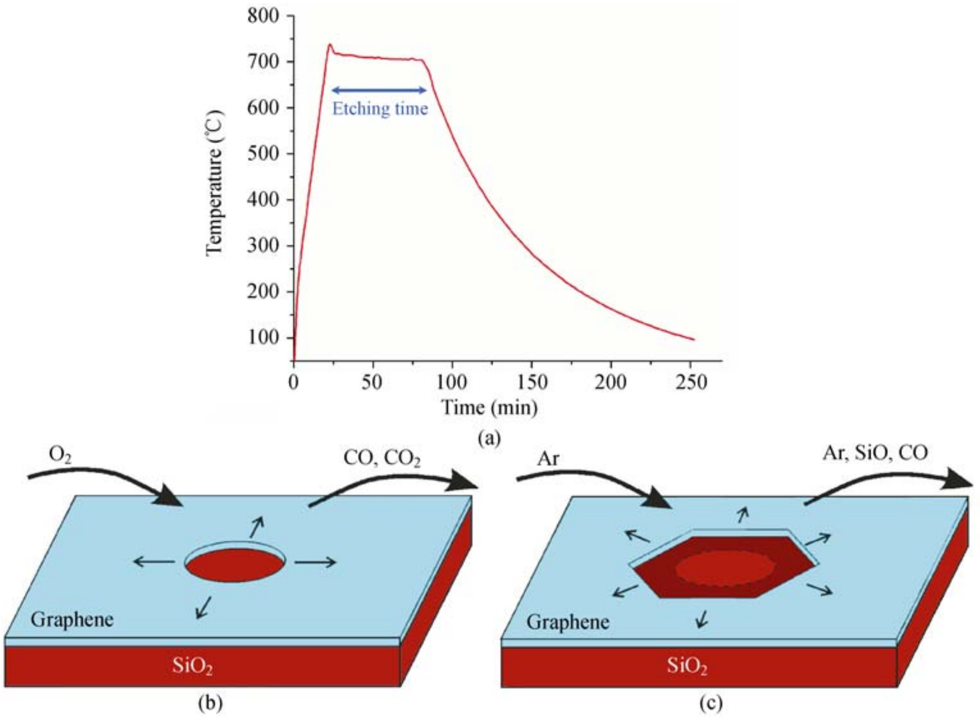

Figure S-1 (a) Graph showing the heating and cooling cycles of our treatments. The etching time referred to in the text is the treatment time at 700 ℃. Schematic illustrations of (b) the oxidation process (at 500 ℃) and (c) subsequent etching process (at 700 ℃)

Address correspondence to nemes@mfa.kfki.hu

reaction, a mixture of high purity O_2 (99.9995%) and N_2 (99.999%) was used, with flow rates of 700 mL/min and 1300 mL/min, respectively. For the carbothermal etching process, Ar gas (99.99%) was employed, with a flow rate of 1000 mL/min. Here, Ar was used instead of N_2, because SiO may form Si_3N_4 in a N_2 atmosphere (Liou, T. H.; Chang, F. W. Kinetics of carbothermal reduction and nitridation of silicon dioxide/carbon mixture. *Ind. Eng. Chem. Res.* **1995**, *34*, 118–127).

STM measurements

For the STM measurements electrical contacts were attached to the samples,using a nano-soldering method, using indium (Girita, Ç. Ö.; Zettl, A. Soldering to single atomic layer. *Appl. Phys. Lett.* **2007**, *91*, 193512). This method of preparing contacts has the added advantage, that is, uses no resist material whatsoever, and therefore leaves no contaminants on the graphene surface which could interfere with STM measurements.

As the carbothermal etching process also takes place at grain boundaries in the sample, extra care was taken during the STM measurements to take atomic resolution data from the same grain as that where the hexagonal holes were located. STM measurements were performed on the samples prepared by AFM indentation.

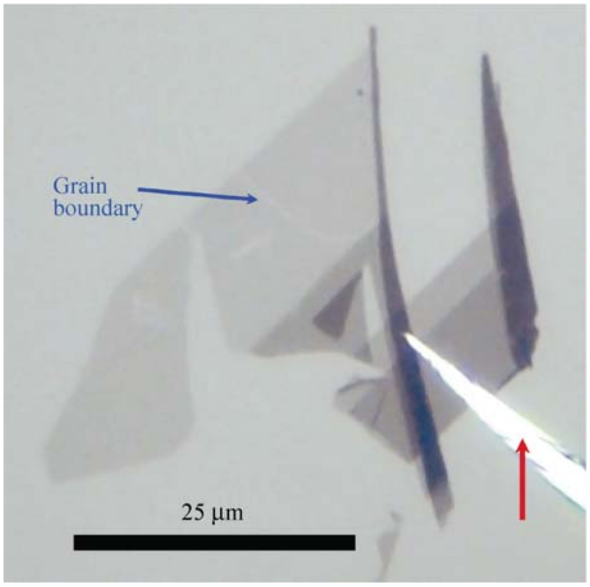

Figure S-2 Optical micrograph of the patterned graphene sample contacted by an indium spike (red arrow)

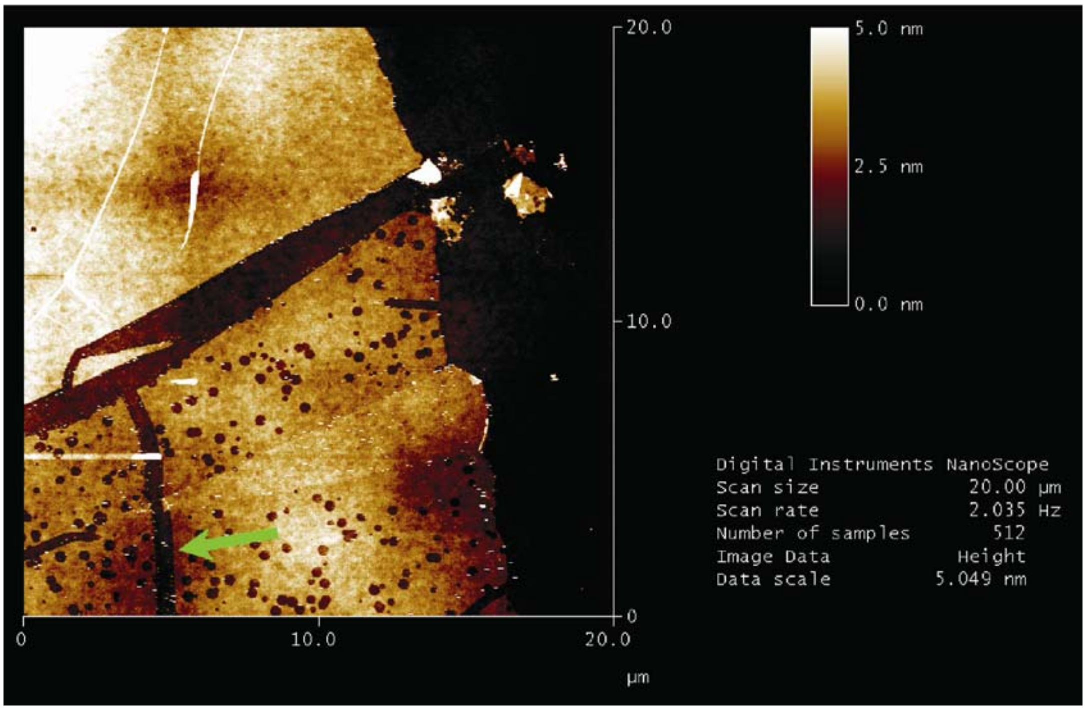

Figure S-3 AFM image of another etched sample, showing an etched out grain boundary, shown by the green arrow

The AFM images of the hexagonal holes were matched to the atomic resolution STM images by imaging the graphene flake in both AFM and STM at low magnifications, using specific sites on the sample as markers. By this technique the orientational relationship between the STM and AFM images could be established.

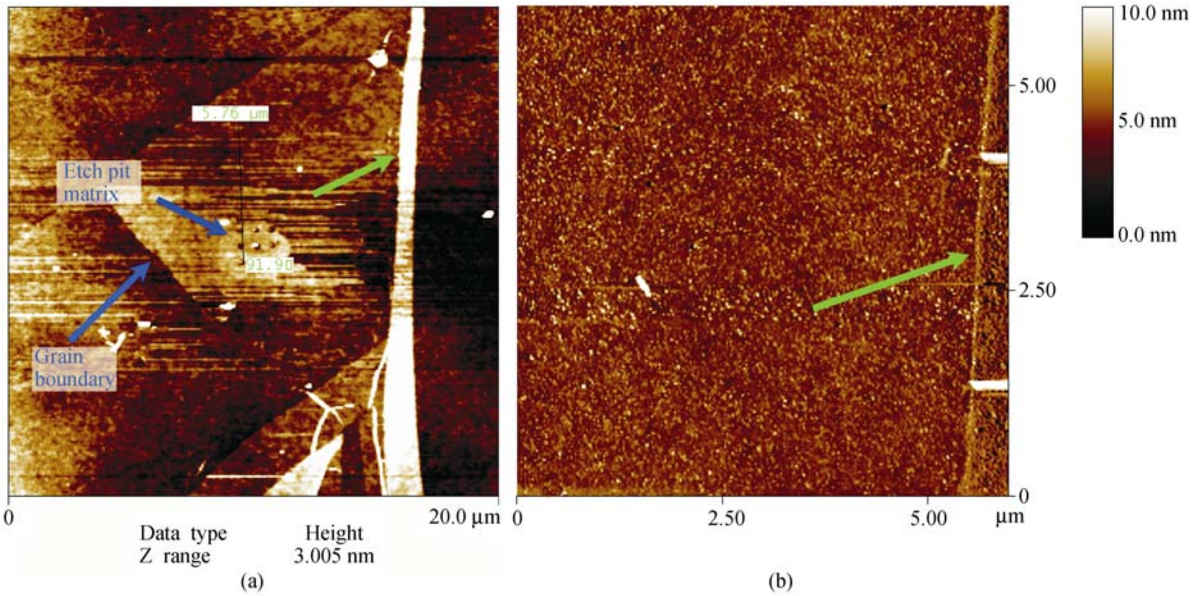

Figure S-4 (a) AFM and (b) STM images of the same graphene sample. The folded back edge of the sample (shown with green arrows) serves as a marker to match the orientations of the AFM and STM images. Blue arrows show an etched out grain boundary (also seen on the optical microscopy image in Fig. S-2) and the hexagonal hole matrix. The atomic resolution STM images were obtained in the vicinity of the etch pit matrix, in the area shown in the STM image

AFM imaging of the annealed samples

A Multimode Nanoscope AFM from Veeco, with a IIIa controller, was used in tapping mode to characterize the samples, under ambient conditions. Silicon scanning tips used in tapping mode were purchased from Nanosensors (model: PPP-NCHR). AFM measurements were carried out taking into consideration our previous results on measuring graphene on SiO_2 (Nemes-Incze, P.; Osváth, Z.; Kamarás, K.;.Biró, L. P. Anomalies in thickness measurements of grapheme and few layer graphite crystals by tapping mode atomic force microscopy. *Carbon* **2008**, *46*, 1435–1442).

AFM indentation experiments

For the AFM indentation experiments diamond-like carbon coated indentation tips were used, type: Tap300DLC, purchased from Budget Sensors (mean force constant: 40 N/m).

Raman measurements

The Raman spectra were recorded using a Renishaw 1000 MB Raman microscope. The excitation source was the 488 nm line of an Ar^+ laser with incident power in the mW range in order to avoid excessive heating of the sample, using a laser spot with a diameter of 2 µm.

We observed strong upshifts of the G and 2D peak frequencies after oxidation and/or carbothermal etching of our samples. By comparing the observed Raman shifts with the electrochemical doping results of Das et al. (Ref. 25 in the main text) we can conclude that the shift is the result of strong p-type doping of the graphene.

Furthermore from the value of the G peak shift we can estimate the doping level of our graphene sample. The changes in the relative intensities of the two peaks (I_{2D}/I_G) are also in good agreement with the values obtained by Das et al.

Table S-1 Frequency shifts (top) and the change in the relative intensities (bottom) of the G and 2D peaks for the sample presented in Fig. 2(b) in the main text. Values are in cm^{-1}

	G	2D	G shift	2D shift
Pristine sample	1580.23	2693.08		
Oxidized at 500 ℃	1599.9	2712.3	19.67	19.22
Etched at 700 ℃	1600.1	2710.47	19.87	17.39

	I_G	I_{2D}	I_{2D}/I_G
Pristine sample	703	2600	3.69
Oxidized at 500 ℃	1914	2518	1.31
Etched at 700 ℃	1459	2453	1.68