Supplemental Material: Extreme

Monolayer-Selectivity of Hydrogen-Plasma Reactions with Graphene

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Experimental setup

Figure S1 shows a schematic of our furnace setup. See “Methods” section in main text for details.

Figure S1: Experimental setup for sample processing.

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Monolayer-selectivity of reaction with hydrogen plasma

Figure S2 presents a further sample exposed to hydrogen plasma treatment at 500 °C for 10 minutes, to illustrate the strong monolayer-selectivity of the interaction.

![Graphene sample after hydrogen plasma treatment at 500 °C for 10 minutes. (a) AFM topography of monolayer and multilayer sheets. (b) Magnified AFM topography and (c) phase shift images of monolayer graphene, covering the area indicated by white square in (a). (d) Raman G-band and (e) D-band mapping of the same sample.](image)

Substrate involvement in the reaction

We see evidence that the SiO$_2$ substrate plays a role in the etch reaction of graphene treated with hydrogen plasma. Figure S3a shows an AFM topography image of a sample treated with hydrogen plasma at 400 °C for 3 minutes. The monolayer is heavily etched, while the bilayer is not impacted. An apparent depression into the SiO$_2$ is visible, most clearly next to the bilayer sheet edge. Intriguingly, the AFM phase image also shows an apparent difference in the cantilever phase shift between the “pristine” SiO$_2$ and the “reacted” SiO$_2$ under the etched monolayer and in the trench at the bilayer boundary. On the SiO$_2$ substrate exposed where the monolayer was etched
monolayer, phase shift variations reveal circular patterns that reflect how etching proceeded on the monolayer. Since the AFM phase shift is highly sensitive to chemical differences, we hypothesize that the chemical composition of the reacted substrate, at the surface, is different from that of the pristine substrate, due to participation in the etch reaction. The unusually large apparent height of the remaining portions of the monolayer and the bilayer (2 nm and 3 nm, respectively) is most likely due to chemical contrast. Raman spectroscopy was used to unequivocally confirm the layer assignment prior to plasma treatment.

Figure S3: Additional evidence of the involvement of the substrate in the reaction.

**Localization of the D-band**

In our samples treated with hydrogen plasma, we observe that the D-band is prominent only on the sheet edges and the edges of etch pits, with the unetched portions of the basal planes of sheets being free of appreciable defects, except for occasional trenches that cut through sheets and likely propagated from pre-existing defects. Figure S4 shows a sample treated at 350 °C for 3 minutes. The map of the integrated Raman G-band intensity in Fig. S4a clearly shows large etch pits in the monolayer, and the corresponding integrated D-band intensity map highlights the increased intensity on the edges of sheets and etch pits. The topography image of the same monolayer with etch pits and the surrounding area is presented in Fig. S4c and at higher resolution in Fig. S4d. The
locations of increased D-band intensity inside the monolayer sheet correspond to the edges of the etch pits.

Figure S4: Localization of the D-band on the edges of sheets and etch pits.

**Time dependence of etch rate**

The isotropic etching of monolayer graphene appears to be higher at short times, and then levels off. If plasma exposure at 300 and 350 °C is limited to 30 seconds, we observe apparent etch rates of \( \sim 80 \text{ nm/min} \), a factor of 2 higher than the corresponding etch rates for a longer plasma exposure of 10 minutes plotted in Fig. 2. Generally, there appears to be a very high initial etch rate within the first few minutes, with the rate declining and then remaining constant. Figure S5 illustrates this phenomenon for a series of samples treated at 400 °C for various times. In Fig. S4a, a monolayer treated at this temperature for 30 seconds exhibits holes, from which a rate of \( \sim 90 \text{ nm/min} \) can
be extracted (since continuous nucleation is seen on monolayers treated at any temperature, we calculated etch rates based on the several largest intact holes within a sheet). In Fig. S5b, a sample treated for 3 minutes, substantial etching is seen, but from the intact etch pits that remain, we extract a rate about half that seen at the 30-second mark, or 40 – 45 nm/min. White circles outline the expected size of the largest holes, had the same initial etch rate been maintained. The etch rate after 10 minutes of treatment (Fig. S5c) is approximately the same as that after 3 minutes, suggesting that the etch rate levels off to a constant value, following the initially high reaction rate.

Figure S5: Time dependence of etch rate.

**Power dependence of etch rate**

To study the dependence of the reaction rate on the power dissipated in the plasma discharge, we performed hydrogen plasma etch experiments at RF power levels of 10 W, 20 W, and 30 W, with samples held at 500 °C. We observed that the reaction rate changes monotonically with power: for a 10 minute exposure to a discharge at 10 W, we observed an apparent etch rate of 10 nm/min, compared to an etch rate of ~28 nm/min at 20 W. A plasma treatment at 30 W led to an apparent etch rate of 80 nm/min, after a brief exposure of 15 seconds. At all three RF power levels studied, the etch reaction remains highly selective for monolayers.

**Doping of monolayer graphene**

In a study of the reactivity of graphene at elevated temperature, it is informative to study the evolution of graphene’s post-treatment Raman spectrum as a function of treatment temperature.
Figure S6a summarizes our observations of blue-shifts of the G-band (squares) and 2D-band (triangles), from Raman spectra acquired \textit{ex-situ} on monolayer graphene samples, in comparison to the unprocessed samples. Blue-shifts of the G- and 2D-lines are typical signatures of p-type doping in graphene samples\textsuperscript{S1}, and samples treated in hydrogen plasma at temperatures between 300 – 700 °C, after oxidative pretreatment at 500 °C, have a constant blue-shift 21 ± 5 cm\textsuperscript{-1}. Since this blue-shift is typical also for samples that have been annealed at 500 °C in inert atmosphere, without any plasma exposure, we assign the observed p-type doping in our samples to heat-treatment (and subsequent air exposure) alone. Consistent with this understanding, a sample exposed to hydrogen plasma at room temperature without any pretreatment is not p-type doped (see arrow); the small red-shift of the G- and 2D bands in this sample (2 – 3 cm\textsuperscript{-1}) is likely insignificant.

Figure S6: (a) p-type doping of monolayer graphene induced by treatment at elevated temperature. (b-e) Effect of hydrogen plasma exposure at room temperature.
Hydrogenation

In previous work, remote treatment of monolayer graphene with hydrogen radicals at room temperature resulted in hydrogenation, evidenced by a sharp D-band in the Raman spectrum due to $sp^3$-bond formation. This effect was observed to be reversible by heating the samples to temperatures above $200 - 250 \degree C$. In our experiments, away from the edge of etch pits, we do not observe significant D-band intensity within the basal plane of monolayer sheets after 10 minutes of hydrogen plasma treatment at elevated temperature, to the limit of our Raman spatial resolution ($\sim 400$ nm). Similarly, after a 10 minute plasma treatment at room temperature, the graphene Raman spectrum is indistinguishable from the spectrum of the pristine sample.

For a longer plasma exposure at room temperature lasting 60 minutes, figures S6b and c show Raman G- and D-band maps for monolayer and few-layer graphene sheets. Within the basal plane, the D-band intensity is significant for monolayers, but very small for bilayer and trilayer sheets. High-resolution AFM topography and phase images (figures S6d and e) provide evidence that this D-band is at least partly due to numerous small etch pits in the monolayer sheet, with diameters up to $\sim 50$ nm (two etch pits marked by circles). We conclude that at the experimental conditions discussed in this work, we observe no clear evidence for hydrogenation of graphene monolayer sheets.

Control experiments

See “Methods” section of main text for discussion.

Plasma treatment of graphene on mica

Hydrogen plasma treatment of graphene on mica exhibits the same main features as that on $\text{SiO}_2$: selectivity of the reaction for monolayers, and isotropic etching. Figure S9a shows a pristine monolayer graphene sheet deposited on cleaved muscovite mica. After treatment with plasma at $500 \degree C$ for 10 minutes, the topography image becomes much richer, as shown in Fig. S9b,c. Water
Figure S7: Absence of etch phenomena after a control experiment consisting of the oxidative pre-treatment only (10% O₂ in Ar at 500°C, for 1 hour), without exposing the sample to hydrogen plasma. (a) G-band and (b) D-band mapping of a monolayer and few-layer graphene sample. The D-band intensity is very low across the entire monolayer sheet, indicating that the oxidative pre-treatment does not lead to etching. Increased D-band intensity appears at sheet edges and steps (for example, in several places close to the right edge of the scan). (c) Raman spectrum of monolayer graphene (integration time of 5 sec), acquired at the location indicated by a cross in (a) and (b). The arrow marks the wavenumber where a D-band would be situated (∼1350 cm⁻¹). (d) AFM topography of monolayer and multilayer graphene. No etch pits are visible in the graphene sheets.

Figure S8: Etch phenomena are identical whether or not the sample is exposed to oxidative pretreatment before hydrogen plasma treatment. (a) Raman G-band mapping and (b) AFM topography image, after hydrogen plasma exposure at 500°C for 10 minutes, without oxidative pretreatment. Monolayers feature round etch pits, while multilayer sheets are unetched, with the exception of several trenches that span long sections of the graphene flake. Due to the omission of the oxidative pretreatment, the AFM image shows the presence of particles that stem from preexisting hydrocarbon contamination, such as adhesive residue from the exfoliation process.
Figure S9: Hydrogen plasma treatment of graphene on muscovite mica at 500 °C.
adlayers trapped between the mica and the monolayer segregate into small islands and channels. The etched holes are most clearly seen in the corresponding phase image, Fig. S9d, in which numerous round holes and a trench are seen. The phase shift in the holes and trench is similar to that on the mica substrate (light blue in false color), showing that these features are holes in the monolayer. Due to chemical contrast, height inversion can sometimes be observed in AFM tapping-mode topography images: depressions can have an apparent positive height. Such height inversion can be seen in Fig. S9c, in which the etched holes appear to have a slightly positive height. The occurrence of a noticeable D-band on the monolayer after etching (Fig. S9e,f) is further evidence of the etch process. Figures S9g,h demonstrate the selectivity of the reaction for monolayers. The phase image shows that the etch holes only appear on monolayers.

For this treatment, we selected a monolayer that was largely free of the frequently-seen trapped water adlayers,\(^4\) as seen by AFM after exfoliation on mica. AFM images of the monolayers after plasma treatment, however, reveal the presence of sizeable amounts of water, appearing as a network of water channels and islands trapped between the mica substrate and the graphene. The presence of water underneath graphene sheets that did not appear to have water adlayers before treatment is a typical outcome that we see on samples that have undergone a thermal treatment at 500 °C, even without a subsequent plasma exposure. It is conceivable that the local curvature induced by these adlayers influences the reaction and enhances the etching of graphene, such that the effective substrate roughness is significantly greater than the ultraflat nature of water-free mica.

References

