

Supporting Information

Ultrathin and Flat Layer Black Phosphorus Fabricated by Reactive Oxygen and Water Rinse

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A-B. Evolution of BP flakes upon ambient oxidation

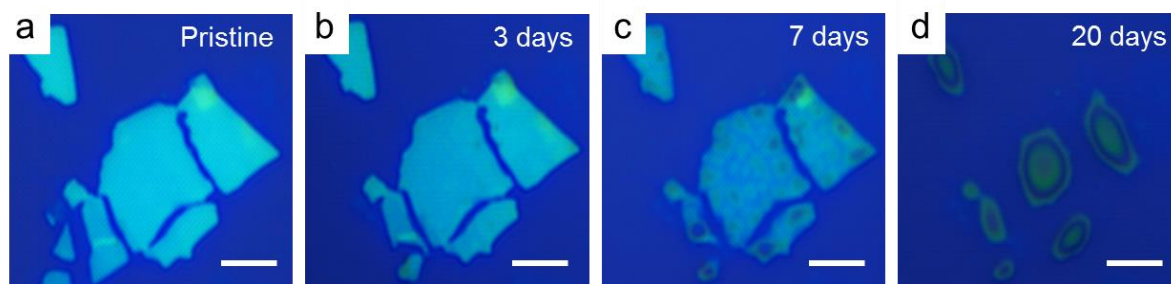


Figure S1. (a-d) Optical images of the BP flakes obtained during the course of ambient oxidation, corresponding to the AFM images of the same area in Figure 1a-d. Scale bars in a-d: 400 nm.

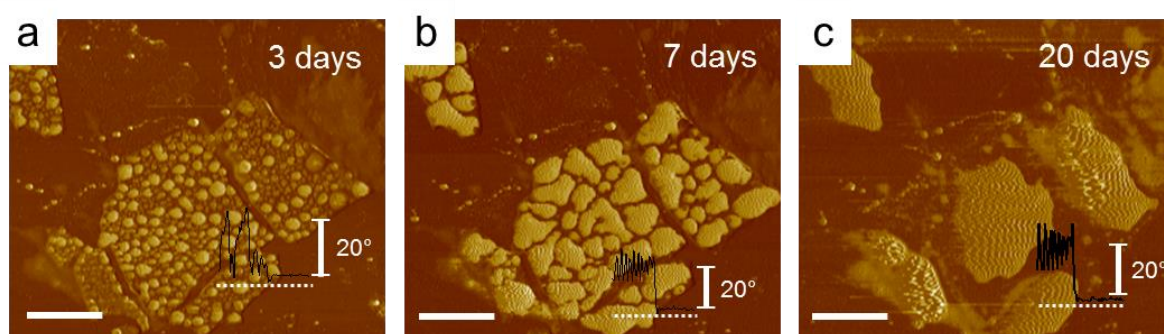


Figure S2. (a-c) AFM phase images of the BP flakes exposed to ambient conditions for varying times: 3 days (a), 7 days (b), and 20 days (c). Phase angle line profiles obtained along the white dotted lines are given in the AFM images. Scale bars in a-c: 400 nm.

C. Water rinsing-induced resistance to ambient oxidation

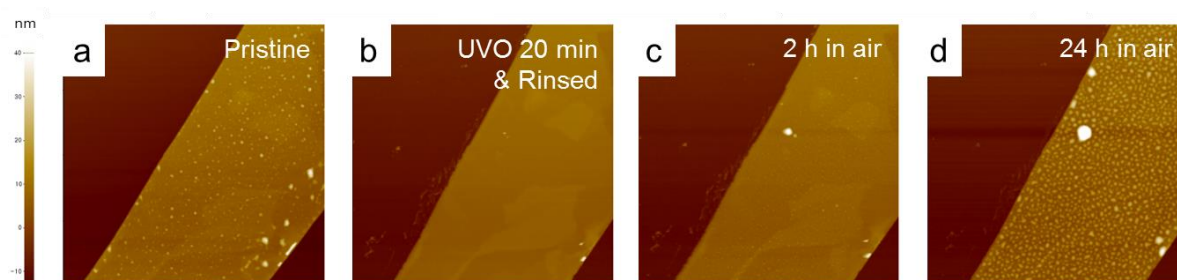


Figure S3. (a-d) AFM topography images of BP flakes exposed to ambient conditions for varying times: pristine (a), UVO 20 min and rinsed (b), 2 h in air (c), and 24 h in air (d). All AFM images were scanned in $10 \times 10 \mu\text{m}^2$.

D. Wavelength dependence of UVO etching

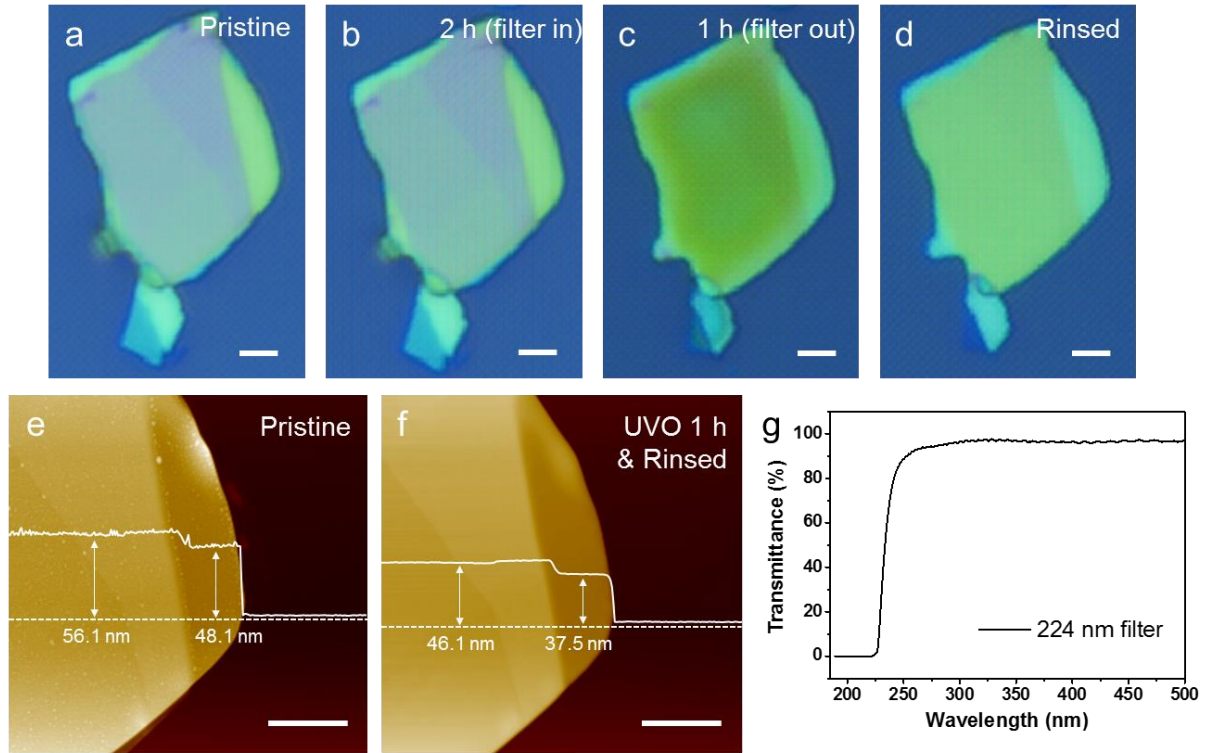


Figure S4. Effects of wavelength-selected UV irradiation on BP. (a-d) Optical images obtained for a BP flake during a series of UV irradiation tests: without any treatment (a), after 2 h irradiation with a long wave pass filter ($\lambda_{\text{threshold}} = 224$ nm) inserted in the beam path (b), after 1 h irradiation without the filter (c) and after rinsing with DI water (d). (e and f) AFM height images obtained for the pristine (e) and UVO and rinsed (f) sample. The height line profiles were obtained from the dashed lines. Scale bars in a-f: 2 μm . (g) Optical transmission spectrum of the filter employed in (b).

E. Effects of UV irradiation in vacuum

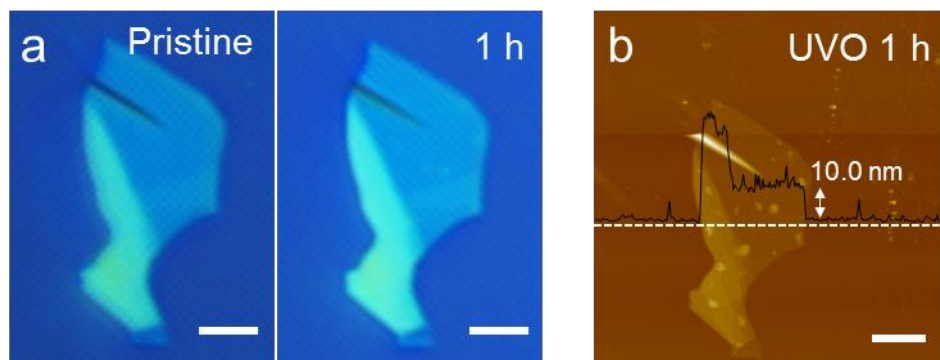


Figure S5. Effects of UV irradiation without O₂. (a) Optical images of a BP flake before and after UV irradiation for 1 h in high vacuum (10^{-6} Torr). No significant optical contrast change was observed. (b) AFM height image obtained after the UV irradiation but without rinsing. The height line profile was obtained from the dashed line. Unlike UVO etching (Figure 2e), irradiation in vacuum does not generate large PA droplets, indicating no UV-induced etching. The small bumps are due to ambient oxidation. Scale bars in a and b: 3 μ m.

F. Confirmation of ozone as the major etchant

To determine the contribution of the major UVO species, O atoms and O₃ molecules, we monitored an etching reaction of a BP flake in the dark induced by migrated UVO species. One sample was mounted with upside down in the optical cell and the backside of the substrate was exposed to the incident UV light. As shown in Figure S4, the BP flake was etched as much as the direct irradiation cases (Figure 2).

Considering the geometry of the cell, the UV-generated species need to diffuse at least 0.5 cm before reaching the BP flake shown in Figure S4. Since the association reaction of O and O₂ to form O₃ is highly efficient, the typical lifetime of O atoms in atmospheric conditions is on the order of 10⁻⁵ s,¹ whereas that of O₃ is ~1 h which is limited by.² The average diffusion distance of each species can be estimated from the root-mean-squared diffusion distance, $x_{\text{rms}} = (2Dt)^{1/2}$, where D and t are diffusion coefficient and lifetime, respectively. As shown in the table below, $x_{\text{rms}}(\text{O})$ and $x_{\text{rms}}(\text{O}_3)$ are respectively two orders of magnitude shorter and longer than the required travel length of 0.5 cm. The concentration of O atoms ([O]) generated by the thermal decomposition of O₃ in the dark region is negligibly small, $\sim 1.5 \times 10^{-9}$ times of [O₃].² These considerations led us to conclude that the major oxidant in the UVO etching is O₃.

	D (cm²/s)*	t (s)	x_{rms} (cm)
O	(0.49)**	1x10 ⁻⁵	0.0031
O₃	(0.15 ± 0.02) ³	3600	33
O₂	(0.176) ⁴	-	-

*At 25 °C and 1 atm; O and O₂ in air; O₃ in O₂

**The diffusion coefficient of O atoms was estimated from that of O₂, assuming that the collision cross section of O atom is twice smaller than that of O₂.

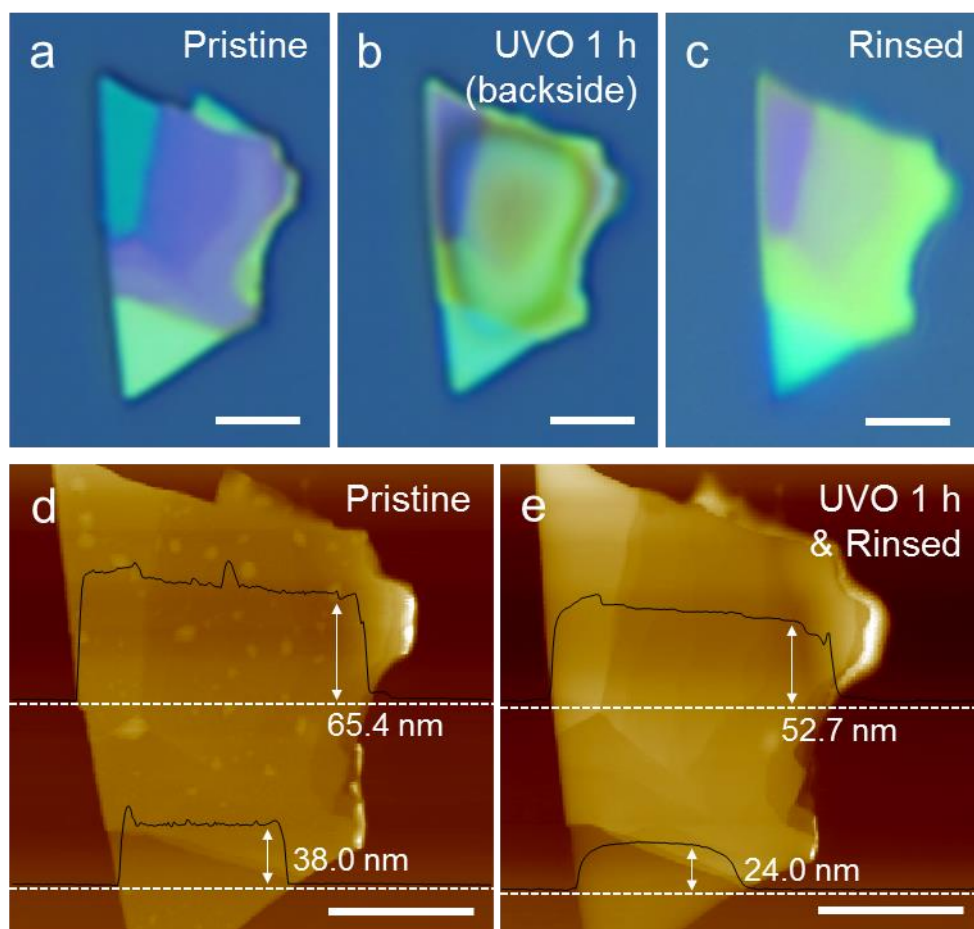


Figure S6. Etching of BP in the dark by migrated UVO species. (a-c) Optical images obtained for a BP flake before and after indirect UV irradiation: without any treatment (a), after 1 h irradiation on the backside of the SiO₂/Si substrate to avoid direct illumination on the BP flake (b), after rinsing with DI water (c). (d and e) AFM height images obtained for the pristine (d) and UVO and rinsed (e) sample. The height line profiles were obtained from the dashed lines. Scale bars in a-e: 3 μm.

G. *In situ* dissolution of phosphorus oxides

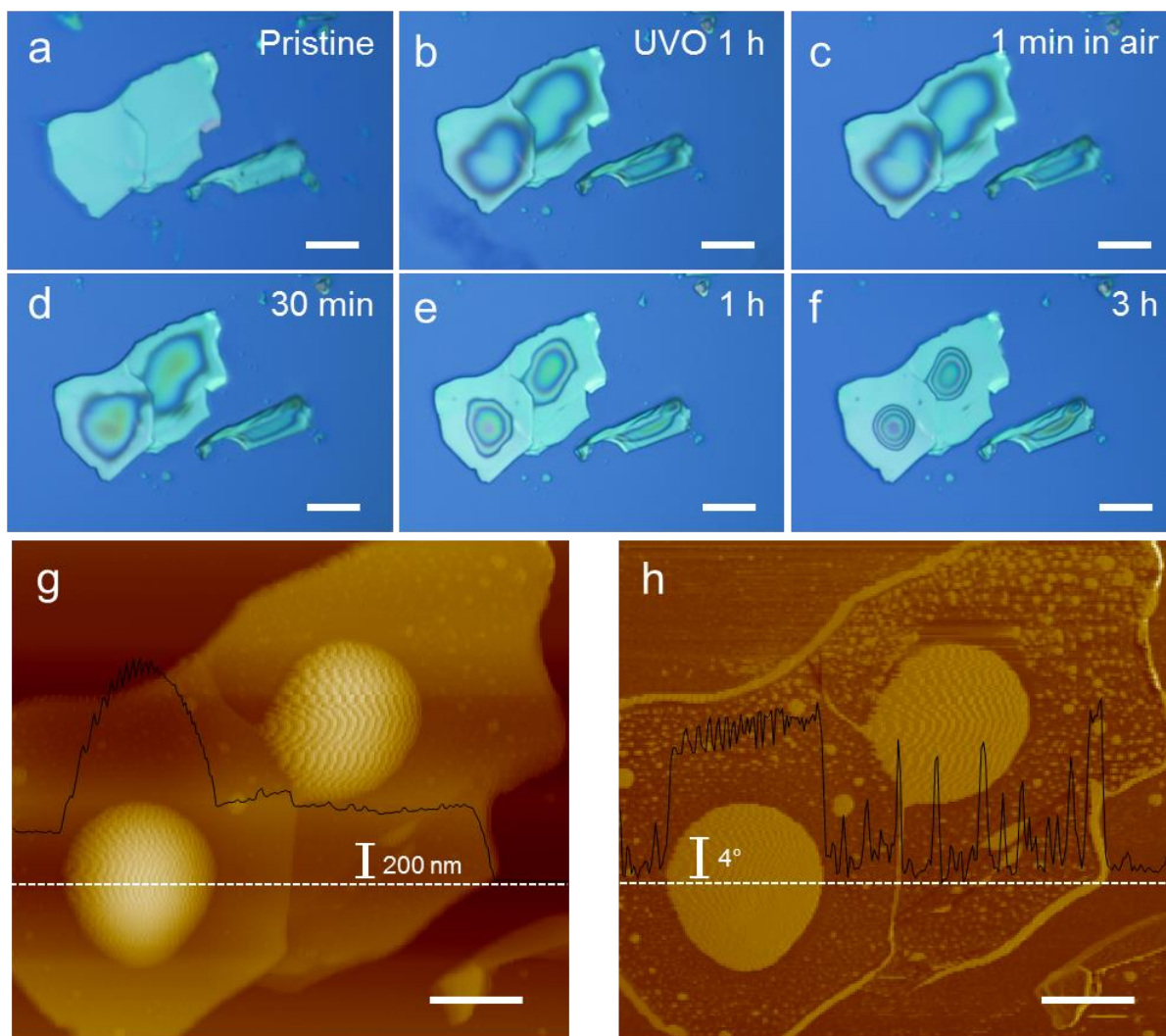


Figure S7. (a and b) *In situ* optical images of BP flakes in the optical cell obtained before and after UVO etching: before etching but in O_2 flow (a), right after 1 h etching but in the presence of O_2 flow (b). (c-f) Optical images obtained ~1 min (c), 30 min (d), 1 h (e) and 3 h (f) after the optical cell was opened to the ambient air. (g and h) AFM height (g) and phase (h) images obtained after f. Scale bars in a-f and g-h, respectively: 10 μm and 5 μm . The contrast change localized at the center of the flakes (b) reveals that UVO-generated phosphorus oxides possibly dissolved into phosphoric acid droplets (g and h) by absorbing residual moisture contained in O_2 gas (99.995%) flow. Assuming 1 ppm ($\sim 10^{-3}$ Torr) water impurity in the O_2 gas, an exposure for 1 h would correspond to 3.6×10^6 Langmuir, which is enough to form an $\sim 10^6$ nm thick water film on the substrate with a sticking probability of unity.

H. UVO etching of a thick BP flake probed by Raman spectroscopy

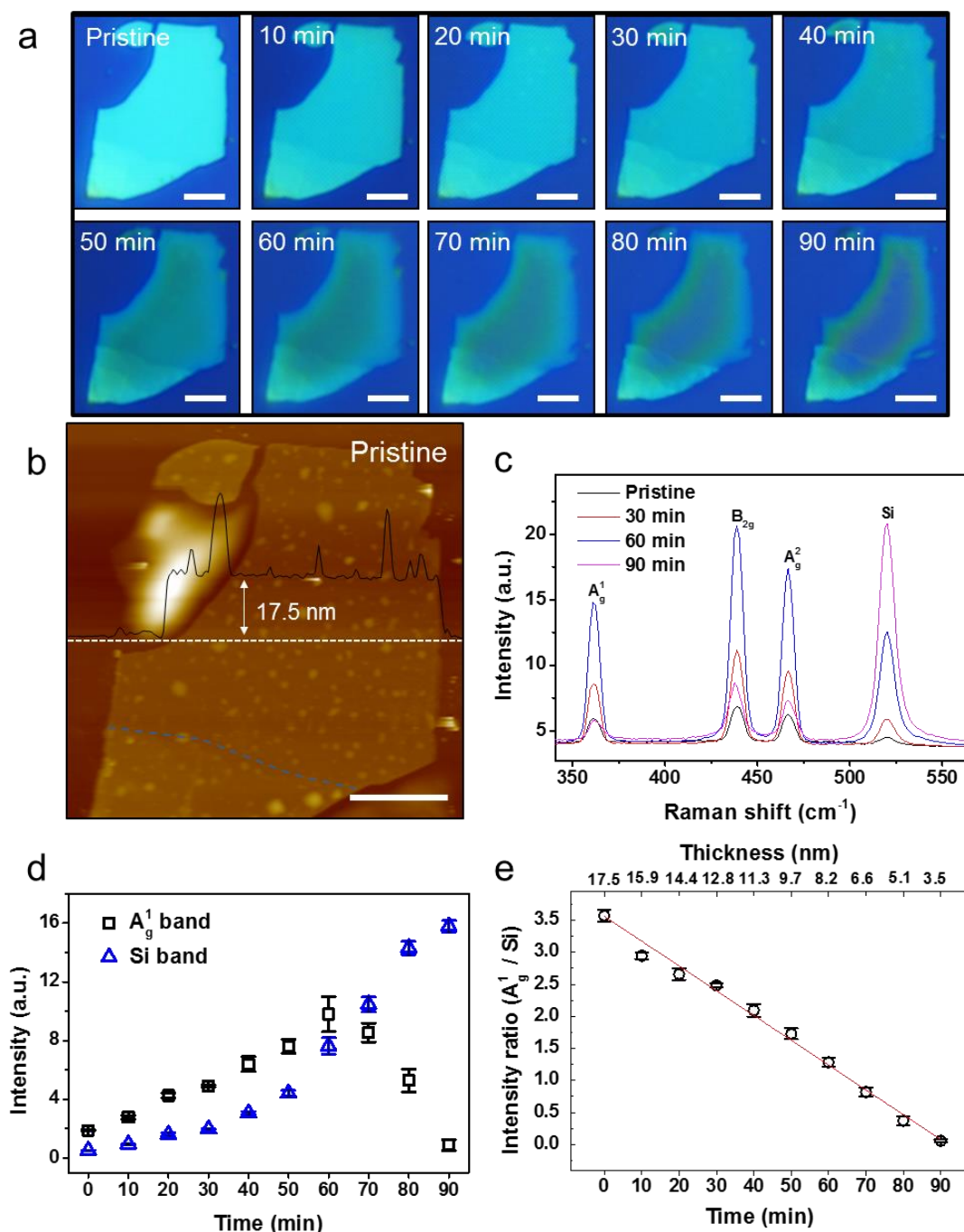


Figure S8. Raman spectroscopy-assisted stepwise UVO etching of a thick BP flake. (a) Optical images of the BP flake obtained in a series of UVO etching reactions. As the accumulated etching time indicated in each image increased, the optical contrast of the BP

flake decreased. (b) AFM image of the pristine BP flake. The height line profile along the dashed line shows that the flake is 17.5 nm thick. Scale bars in a and b: 4 μm . (c) Raman spectra of the BP flake for varying etching times. (d) Peak intensities of the A_g^1 and Si (520 cm^{-1}) peaks given as a function of etching time. (e) Intensity ratio of A_g^1/Si given as a function of etching time. Etching rate: 10 nm/h (pristine 17.5 nm, 3.5 nm 90 min, of which AFM height is 3.5 nm).

I. References

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