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Electronic Supporting Information:

Anisotropic buckling of few-layer black phosphorus

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Thickness determination through quantitative analysis of the transmission mode optical images of the flakes

The determination of the thickness of the black phosphorus flakes studied in the main text has been made by quantitative analysis of the transmission mode optical images of these flakes.

In order to determine the thickness through optical microscopy we acquire transmission-mode microscopy images of several flakes with different thicknesses on the surface of a Gel-Film substrate. Then these flakes are transferred onto a SiO_2 substrate (performing AFM characterization on the Gel-Film substrate is rather challenging because of the large tip-Gel-Film adhesion force) and their thickness is measures with atomic force miscroscopy (AFM). All this process is summarized in Figure S1.

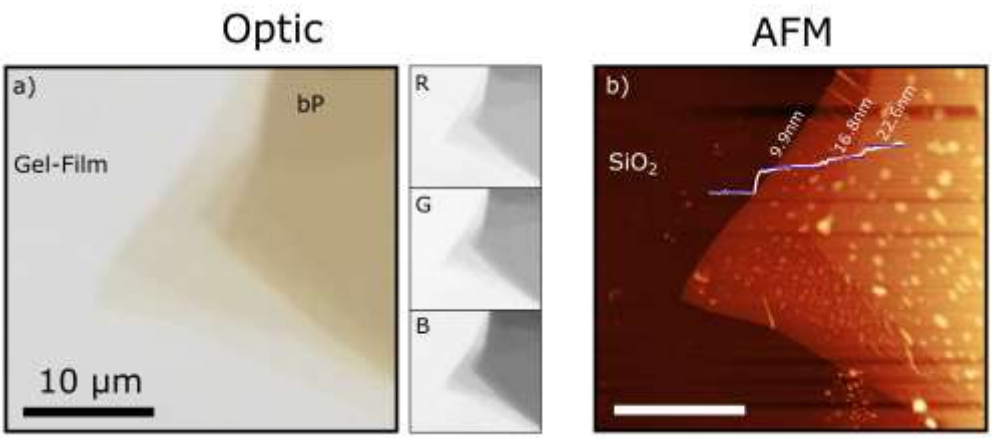

Figure S1. **a)** Optical microscopy image of multi-layer black phosphorus flake. Different RGB channels for the same flake. **b)** AFM image of the same flake in a) after being transferred onto a SiO_2/Si substrate. A topographic line profile over a region with some layers is included.

With the above data collected, a thickness versus normalized transmission graph can be made for the three channels (red R, green G, blue B) of the camera. Then, a polynomial fit to the data is used to obtain a relationship between thickness and transmission. The results are shown in the Figure S2.

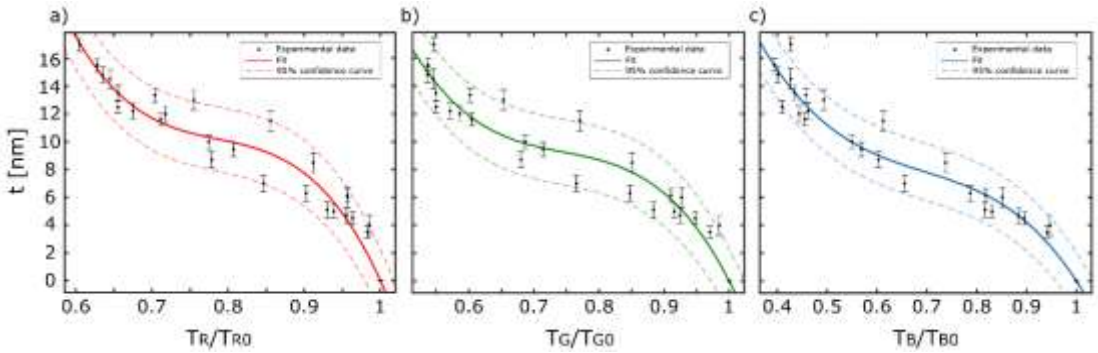

Figure S2. Thickness vs normalized optical transmission graph for some flakes and the polynomial fit with the 95% confidence curves for each channel **a)** Red **b)** Green **c)** Blue

By the graphs of Figure S2 we can obtain the thickness of a flake knowing the value of its normalized optical transmission, which makes this method quite comfortable. The error made by this approach is about ± 2 nm in the thickness.

Effect of the environmental degradation on the buckling of black phosphorus

It has been thoroughly reported that black phosphorus tends to degrade upon environmental exposure by photo-induced oxidation.[1–3] This environmental degradation have been found to have an impact on the mechanical properties of black phosphorus but previous reports could not test the mechanical properties along different crystal orientations of the black phosphorus lattice.[4]

We have employed the buckling metrology method to test the effect of environmental exposure on the mechanical properties (and on its anisotropy) of black phosphorus. Figure S3(a) shows a sequence of transmission mode optical microscopy images of a buckled black phosphorus flake as a function of time. Figure S3(b) shows the line profile along the blue lines in (a) where the time evolution of the rippling can be easily observed. The degradation of the flake can be readily observed from the change in the flake transmittance as the generation of a phosphorus oxide crusts on the surface will reduce the optical absorption (while black phosphorus has a narrow gap, phosphorus oxides are wide band gap semiconductors). Figure S3(c) shows the line-profiles along the red lines in (a) where the time-dependent transmittance can be seen. Figure S3(d) summarizes the time evolution of the ripple wavelengths and transmittance measured in different spots of the sample.

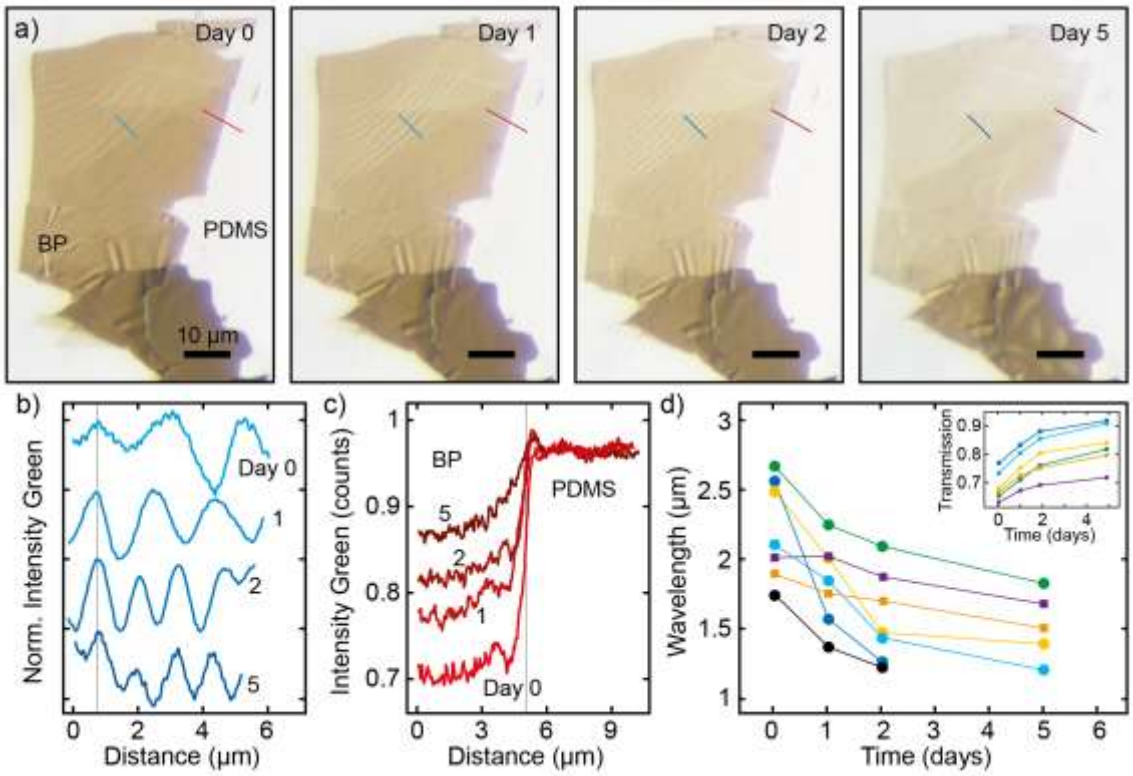

Figure S3. **a)** Sequence of transmission optical microscopy images of a buckled black phosphorus flake upon time exposure. **b)** Line profiles along buckling-induced ripples at different time exposures. **c)** Time evolution of the transmission of the black phosphorus flake. **d)** Summary of the time evolution of the ripple wavelength and the transmission (of the green channel) measured at different locations of the black phosphorus flake upon air exposure. Note: average relative humidity 20% during the experiment.

To get a deeper insight into the effect of the environmental induced degradation on the mechanical properties of black phosphorus we compare the results of the controlled buckling experiments (where the compression is applied in a controlled way along the ZZ and the AC directions) on pristine black phosphorus flakes and on aged flakes (after 9 days of air exposure). Figure S4(a) shows optical microscopy images of an aged black phosphorus flake (after 9 days of air exposure with an average relative humidity 20%) compressed along both AC (blue) and ZZ (red) directions. A direct comparison between the ripples profiles measured on a pristine flake and on the aged flake shown in Figure S4(a) is displayed in Figure S4(b). A summary of the anisotropy measured on pristine flakes and on two different aged black phosphorus flakes is shown in Figure S4(c).

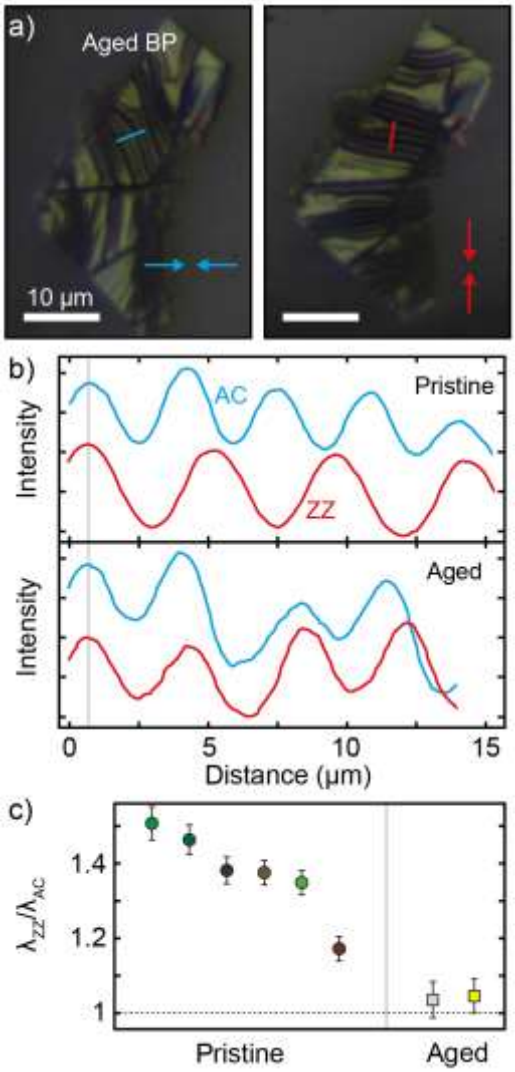

Figure S4. **a)** Optical microscopy images of an aged black phosphorus flake (after 9 days of air exposure with an average relative humidity 20%) compressed along both ZZ (red) and AC (blue) directions. **b)** Comparison between the ripples profiles measured on a pristine flake and on the aged flake. **c)** Comparison between the buckling anisotropy measured on pristine flakes and on two aged black phosphorus flakes.

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