SUPPLEMENTARY INFORMATION

Environmental Effects in Mechanical Properties of Few-layer Black Phosphorus

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SI1. SAMPLE PREPARATION

Suspended black phosphorus flakes were prepared by deterministic placement over substrates of Si/SiO₂ (300 nm) with predefined wells of different shapes created by reactive ion etching (RIE) on the SiO₂. Figure S1 shows a SEM image of the pattern of the holes. The diameter of the circular wells are between 0.5 and 3 microns and the depth is 300 nm, as the SiO₂ thickness.

Drumheads were prepared by deterministic all-dry transfer with a PDMS stamp, as described in references [1, 2]. There are two main advantages of using this preparation method with respect to standard microexfoliation [3] for this experiment: the first one is its higher yield covering circular wells, and the second one is that 2D material layers stamped over the holes present a very uniform and low pretension.

Figure S1. SEM image of the substrate after all the processes and a zoom in one of the holes to appreciate the verticality of the walls.
SI2. AFM TIPS

In order to have a constant and well defined contact geometry, we use commercial tips from NanoScience Instruments with hemispherical geometry and low wear coating of tungsten carbide with nominal final tip radius of 60 nm. The cantilever spring constants were calibrated by Sader method [4] and yielded values between 25-35 N/m.

![Figure S2. SEM image of the AFM tip used for the measurements (scale bar 200 nm).](image)

SI3. F(δ) CURVES

Indentation experiments were performed using a Nanotec AFM with the WSxM software [5] package. All the measurements presented here were obtained at the same loading/unloading rate of 100 nm/s. We checked that results are independent of the variation of this parameter within our experimental range.

In order to use Equation [1] in the main text, indentation has to be accurately estimated. Indentation is not a direct experimental measure; it is calculated from the differences of the relative displacement of the samples and the tip on the non-deforming SiO₂ substrate. This is illustrated in figure S3.
Figure S3. (a) Scheme illustrating the experimental procedure to extract the indentation ($\delta$) of the membrane from the displacements of the cantilever ($d$) and a reference substrate ($\Delta z$). (b) Force vs. sample displacement curve acquired on the SiO$_2$ substrate (black) and on the center of a suspended sheet (red). Panel (c) depicts a zoom of the same curve in the green rectangle. Here we can appreciate that, due to the flat character of the curves near the zero force level, we have an experimental accuracy of 2-5 nm in determining the position of zero deflection.

In order to calculate the indentation it is then critical to fix the zero displacement point, or zero force level: inaccuracy of 2-5 nm in this point leads to a 10% error in the final calculated $E_{2D}$. According to our previous experience in analyzing indentation curves [6] the protocol followed for these curves was: we find an initial zero force level for the curve as the point where the horizontal line cuts the curve (zero cantilever deflection). A zoom in this region shows the experimental noise of the curve. To avoid noise as much as possible we find the zero by a purely instrumental fitting of the data to a high order polynomial (3rd order). To this end we take about 20 experimental points to the left and about 70 to right of the initial zero. The elastic modulus is then estimated according to Equation [1] in the main text.

The fitting errors for this equation for the measurements in vacuum were under 20%. In contrast for the measurements in air, the fitting error increased with time of exposure to atmospheric conditions, see figure S4. This figure also shows the decrease of the error once the sample is cleaned in vacuum through annealing (data inside a black circumference in figure S4). This suggests that the increase of the error can be caused
by the layer of adsorbed water that hinders the determination of the zero indentation point of the membrane. For these cases we used a complete third order polynomial to fit the indentation curves that gives lower fitting error as it can be expected. The elastic modulus was then obtained merely from the third order term. This type of analysis had been previously used in graphene membranes very effectively [6].

Figure S4. Error of the fitting of the indentation curves to a full third polynomial vs. the time of exposure. The data plotted at 0 hours correspond to measurements in high vacuum (before exposure), and the ones plotted inside a black circumference correspond to data acquired after the entire exposure and the subsequent heating of the sample in high vacuum.

SI4. PRE-STRESS INFLUENCE IN $k_{\text{flake}}$ vs. $t^1/R^2$

Equation [2] of the main text assumes that the flakes used to calculate the elastic modulus have the same pre-tension $\sigma_0$. As we apply this expression to different flakes, we relax this condition which can result in a source of error. In order to quantify the possible error introduced by this assumption, we have numerically simulated indentations curves for 30 flakes in the low indentation regime (see figure S5(a)). The drumheads have random thicknesses between 4 and 30 nm. Each of these nanosheets has an elastic modulus of 52 GPa (value experimentally obtained by this method) and a pre-tension that can randomly vary between 0 and 0.3 N/m (the maximum pre-tension obtained from Equation [1] in the main text). As it can be seen in figure S5(b), the noise induced by the set of random pretensions have a similar dispersion to that of the experimental data. In fact, the error of $E_{3D}$ and $\sigma_0$ obtained from simulated data and experiments have the same value (±6 GPa and ±0.02 N/m for the elastic modulus and the pre-tension respectively). This suggests that the main source of noise in our data comes from the random pretensions among the different flakes.
Figure S5. (a) Simulated force vs. indentation plots in the low indentation regime for flakes with growing thickness. The lines are spanned by random pre-tensions. (b) Plot of the stiffness of the flakes, calculated as the slopes of the lines in figure (a), vs. $t^2/R^2$. For constant pre-tension this plot should be a perfect straight line. The noise reflects the contribution of the random pre-tensions, which is similar to our experimental noise.

SI5. AFM TOPOGRAPHIC IMAGES OF FLAKES: IN HIGH VACUUM, AIR-EXPOSED AND ANNEALED IN HIGH VACUUM

During the exposure of few-layer BP flakes to atmospheric conditions, oxidized phosphorus species and water adsorption occur. The latter (at least) seems to be somehow dependent on the flake thickness. This is shown in figure S6, where the flake show different topographic features depending on its thickness. Before exposure, the thickness of the flake was around 6 nm in the area covered by blobs while the flat part of the flake was 4.5 nm thick. Therefore, during exposure to air, the measure of the real thickness of BP flakes by AFM becomes infeasible.

Figure S6. AFM topography of a flake after being exposed 120 hours to atmosphere (temperature around 22°C and average relative humidity of 47 %). Previous to the exposure, the flake was imaged by AFM showing a thickness of 6 nm in the area covered by blobs while the rest of the flake had a thickness of 4.5 nm. The drumhead was spontaneously broken during the exposure to air.

In order to measure by AFM the real thickness of the flakes after the exposure to ambient conditions, the samples were annealed in high vacuum. This allows the removal of adsorbed water. The total time of exposure to ambient conditions was nearly 200 hours. Annealing of the samples was performed in high vacuum at 230°C during 15
hours. Afterwards, the topography of the samples were measured by AFM at room temperature maintaining the vacuum environment. Figure S7 shows the topography AFM images and profiles of a flake before the exposure and after exposure and pumping/heating. According to the profiles, the thickness of the flake has not experienced noticeable changes, while the topographic images show the appearance of some left-over residues.

Figure S7. Topographic changes in BP flakes after nearly 200 hours of exposure to ambient conditions and annealing at high vacuum. (a) Topography AFM image (the same image as figure 1(b) in the main text) of a BP flake in high vacuum, before the exposure to atmosphere. (b) Topography AFM image of the same flake shown in (a), acquired also in high vacuum but once the sample has been in contact to air for almost 200 hours, and subsequently heated in high vacuum. Both membranes appear broken due to indentations experiments performed until rupture in high vacuum before exposure to air. (c) Topographic profiles along the blue and cyan lines in (a) and (b). (d) Topographic profiles along the black and green lines in (a) and (b).

SI6. PASSIVATION MODEL

For the purpose of understanding the different environmental effects in the values obtained for $E_{3D}$ in thin (< 6 nm) and thick (> 7 nm) drumheads, we propose an elementary model of the passivation process. It is based in the following assumptions (see figure S8(a)):

(i) The total thickness of every BP flake during the entire exposure time is constant and equal to the initial thickness of the BP flake measured in high vacuum before the passivation process starts ($t_{BP}^{ini}$):

$$t_{BP}^{ini} = t_{pass}(\tau) + t_{BP}(\tau) = const.$$  

where $\tau$ is the exposure time, $t_{pass}$ the thickness of the outer passivated BP and $t_{BP}$ the thickness of the underlying pristine BP flake. This assumption is supported by the experimental preservation of flakes’ height shown in figure S7.

(ii) The growth of the passivation layer takes place at a speed that exponentially decays with time, in other words, the passivation process experiences saturation, having a maximum passivation depth, $t_{pass}^{max}$. This is suggested by the data of thicker flakes at advanced exposure in figure 4 in the main text. This leads to the following relations:

$$t_{pass}(\tau) = t_{pass}^{max} \cdot \left(1 - \exp\left(-\frac{\tau}{\tau_c}\right)\right)$$

$$t_{BP}(\tau) = t_{BP}^{ini} - t_{pass}(\tau)$$
where \( \tau_c \) is a passivation characteristic time.

(iii) The elastic moduli of the pristine and passivated BP are constant with time and equal to \( E_{3D}^{BP} \) and \( E_{3D}^{pass} \) respectively, being \( E_{3D}^{pass} = \alpha \cdot E_{3D}^{BP}, \alpha < 1 \). According to [7] a value of \( \alpha = 0.66 \) is expected for phosphorene, considering the average of the elastic modulus of both in-plane directions at two stages: when the oxidation ratio is 0% and 100%.

\[
E_{3D}^{pass} = \alpha \cdot E_{3D}^{BP}
\]

\( \text{Passivated BP:} \)

\[
E_{3D}^{pass} = \alpha \cdot E_{3D}^{BP}
\]

\( \text{Pristine BP:} \)

\[
E_{3D}^{BP}
\]

**Figure S8.** (a) Diagram of the passivation model proposed herein. (b) Temporal evolution of the elastic modulus of few-layer BP flakes under exposure to ambient conditions. The symbols correspond to experimental data (blue solid and empty triangles for drumheads thicker than 7 nm, and red circles for drumheads thinner than 6 nm). Blue line corresponds to the fit of the blue solid triangles to the proposed model and the dashed red line depicts the model for the thinner flakes.

Considering the mentioned assumptions, the fact that the \( E_{2D} \) of a layered material is the sum of the \( E_{2D} \) of each layer \( (E_{2D} = E_{2D}^{BP} + E_{2D}^{pass}) \), and that the magnitude that is obtained from our measurements is \( E_{2D} = E_{3D}^{BP} \cdot t_{BP}(\tau) + E_{3D}^{pass} \cdot t_{pass}(\tau) \), the elastic modulus measured during the exposure time is:

\[
E_{3D}^{measured}(\tau) = \frac{E_{3D}^{BP}}{t_{BP}} \left( t_{BP}^{ini} - t_{pass}^{max} \cdot [1 - \exp(-\tau/\tau_c)] \right)
\]

The initial increase in the elastic modulus of the thicker flakes in figure 4 of the main manuscript is in agreement with the evolution of \( E_{3D} \) of phosphorene under oxidation process according to Hao et al. [7]. In this reference an increase of \( E_{3D} \) in the armchair
direction until an oxidation ratio of 25% is ascribed to small relaxations of phosphorene that occur due to chemisorbed oxygen atoms. This increase is not observed in our data of the thinner flakes, probably because it took place in the short exposure prior to the measurements in high vacuum.

Figure S8(b) shows the evolution of the elastic modulus of exposed drumheads with the exposure time. There are two sets of data. One corresponds to the flakes thicker than 7 nm of figure 4, whose average thickness is 7.6 nm, plotted with blue empty and solid triangles. The second set comprises the data of the flakes thinner than 6 nm of figure 4, with an average thickness of 4.9 nm, plotted with red dots. In order to fit the data to the suggested model, firstly, only the data of the thick drumheads are considered, since they present a longer evolution. The data acquired in the first 10 hours (empty triangles) are discarded to avoid the aforementioned increase of $E_{3D}$ at low oxidation rates. Hence, the solid triangles are fitted to the exponential decay expression of $E_{3D}^{\text{measured}}(\tau)$ given above. The following values are fixed: $t_{\text{BP ini}} = 7.6$ nm and $\alpha = 0.66$. This fitting, depicted with a blue line in figure S8(b), yields $E_{3D}^{\text{BP}} = 46\pm5$ GPa, $t_{\text{pass max}} = 9\pm5$ nm and $\tau = 60\pm20$ hours. The value for elastic modulus of pristine BP coincides with the one given in the paper in vacuum environment. For the thinner flakes, we use the obtained values for $t_{\text{pass max}}$ and $\tau$ and $t_{\text{BP ini}} = 4.9$ nm, $E_{3D}^{\text{BP}} = 27$ GPa (provided by the intercept of the linear fit of the first seven data) and $\alpha = 0.66$ again. In this case the red dashed line in figure S8(b) is obtained.

The proposed model and the characteristic values obtained from it, result in some important consequences. Firstly, all the flakes considered in this section, after a long enough exposure, would be completely oxidized, considering that their thicknesses are lower than the maximum passivation depth. Secondly, and more important, every few-layer BP nanosheet thicker than 9 nm would undergo a passivation process until the passivated layer reaches that thickness, similarly to the natural passivation of some other materials such as stainless steel, aluminum, cooper, etc. However, this expected behaviour could deviate from some other actual tendencies due to the dispersion of our data. In fact, this model would not apply for very thick BP flakes (around 100 nm or more), in which water ends covering the BP surface causing a layer-by-layer etching as was reported in [8] and confirmed by us through some optical images of flakes thicker than 100 nm. Moreover, the presented model does not consider the likely circumstance of having passivation on the surface of the membrane facing down, nor simultaneously passivation and etching processes. This later situation was not reflected by our experimental results in few-layer BP flakes.

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