Supplemental on-line material for Semiconducting layered blue phosphorus: A computational study

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S1. EQUILIBRIUM GEOMETRY AND BINDING IN THE BULK LAYERED BLACK AND BLUE PHOSPHORUS ALLOTROPES

Density functional calculations based on the Generalized Gradient Approximation, such as the PBE functional used here, often overestimate the interlayer distances and, unless augmented by van der Waals interaction corrections, underestimate the interlayer interaction in layered systems such as black and blue phosphorus. We find that the observed interlayer distance of 5.24 Å in black phosphorus is reproduced rather well by the PBE value of 5.55 Å and the value of 5.09 Å based on the local density approximation (LDA). In the postulated blue phosphorus structure, the interlayer distance based on PBE is 5.63 Å, somewhat larger than the LDA value of 4.79 Å. The calculated interlayer interaction energy in black phosphorus is 20 meV/atom according to PBE and 100 meV/atom according to LDA. The PBE value for the interlayer interaction energy in blue phosphorus is 6 meV/atom, smaller than the LDA value of 38 meV/atom.

S2. BULK BAND STRUCTURE OF BLACK AND BLUE PHOSPHORUS

The calculated bulk band structures of black and blue phosphorus are presented in Fig. S1. There is a strong band dispersion normal to the layers. The origin of this band dispersion is the interlayer overlap of states close to the Fermi level, which are shown in Fig. 3(c) of the main manuscript. Inspecting the band structure along high symmetry lines normal to the layers, we find that the band dispersion varies throughout the Brillouin zone and may amount up to ≈1 eV. We should point out at this point that the band dispersion of states near E_F, which dominate transport, is rather independent of the weak inter-layer interaction. A very similar behavior occurs in graphite, where the 1 eV band dispersion along the $K-H$ line in the Brillouin zone does affect the character of frontier orbitals imaged in scanning tunneling microscopy[1], but is independent of the weak inter-layer bonding.

S3. FLEXURAL RIGIDITY OF BLACK AND BLUE PHOSPHORUS

In 2D systems such as phosphorus monolayers, one of the acoustic modes is the ZA mode with a vanishing speed of sound and band dispersion $\omega{\propto}k^2$ for $k{\to}0$. It has been shown that the dispersion of the ZA mode near $k=\Gamma$ can be quantified using continuum elasticity theory[2]. We obtain the expression

$$\lambda^{-1}(k) = \epsilon k^2 \quad \text{for} \quad k{\to}0 \tag{1}$$

for the spectroscopic wave number λ^{-1}, where

$$\epsilon = \frac{1}{2\pi c}\left(\frac{D{\cdot}A}{m}\right)^{1/2} . \tag{2}$$

Here, D denotes the flexural rigidity, c is the speed of light in vacuum, A is the area per atom and m is the atomic mass. The spectroscopic wave number is always given in unit of cm^{-1} and sometimes called by the confusing name 'frequency ω'.

D can be extracted from total energy calculations of nanotubes with different diameters. Continuum elasticity theory calculations[3], which describe the deformation energy well, provide an expression for the strain energy per area A in a nanotube or radius R

$$\Delta E_s = \frac{D}{2R^2} . \tag{3}$$

By comparing the total energy of planar sheets and nanotubes of blue and black phosphorus monolayers with different diameters, we have estimated $D = 1.51$ eV for black phosphorus along the a_1 direction and $D = 0.84$ eV for blue phosphorus along the armchair direction, specified in Fig. 1 of the main manuscript. The band dispersion of the ZA modes close to Γ obtained using Eqs. (1)-(2) is in good agreement with the calculated vibration spectra in Fig. 2 of the main manuscript.

S4. TRANSITION FROM BLACK TO BLUE PHOSPHORUS

The conversion process from black to blue phosphorus, including energy estimates, is discussed in Fig. 4 of the main manuscript. Since our main objective is to estimate if a transformation would be energetically feasible, we did not attempt to determine the precise optimum transformation path between the two allotropes using the nudged

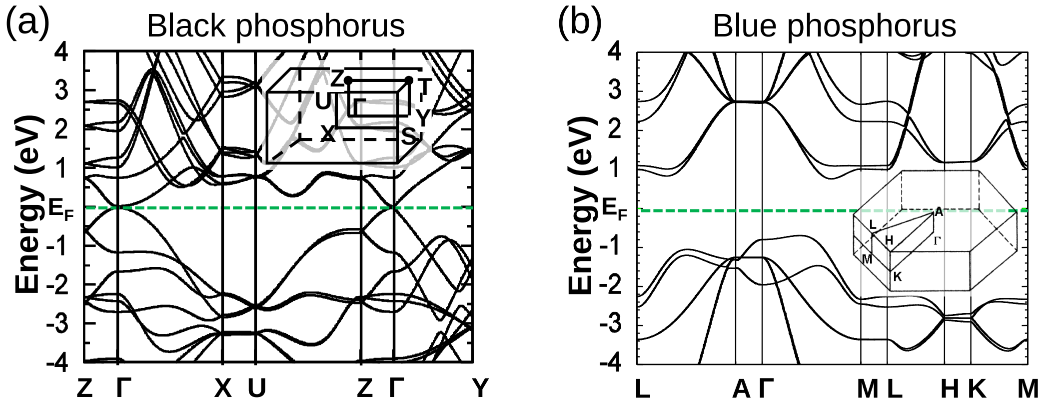

FIG. S1. Bulk band structure of (a) black and (b) blue phosphorus, based on PBE density functional calculations. The Brillouin zones in the insets show the location of the special k-points.

elastic band method, which would be a significant undertaking, but rather estimate likely intermediate structures. We considered the layer to lie in the xy plane. To estimate changes in the atomic arrangement during the conversion process, we considered a 4-atom unit cell consistent with both structures. Of these four atoms, we selected two atoms A and B, for which we know the optimum geometry in the black phosphorus structure ‘1’ and the blue phosphorus structure ‘8’. To get structures ‘2’-‘7’, we interpolated the positions of atoms A and B between ‘1’ and ‘8’ and fixed their z-coordinates. With only this constraint, structures ‘2’-‘7’ were generated by an optimization of the remaining degrees of freedom with a constrained unit cell size. We expect that the estimated transition path may deviate slightly from the optimum path. Consequently, we expect the precise geometry of the transition state to deviate slightly from our structure ‘4’ and the activation barrier to be even lower than the present estimate.

S5. STABILITY OF BLUE PHOSPHORUS MONOLAYERS AT HIGH TEMPERATURES

To study the structural stability of a blue phosphorus monolayer, we performed canonical molecular dynamics simulations of a periodic layer structure and a free-standing finite flake and present our results in Fig. S2. At room temperature, the infinite layer undergoes only minimal changes. The flake exhibits reconstruction at the edge, but otherwise keeps the structure in the middle of the layer intact. The higher temperature of 1500 K is well above the melting point of phosphorus ($T_M = 863$ K for red phosphorus). Our results indicate significant structural changes, which are somewhat suppressed in the infinite lattice structure. There is, however, no indication of a preferential structural change to the atomic arrangement found in black phosphorus.

S6. MOVIES OF BLUE PHOSPHORUS MONOLAYERS AT HIGH TEMPERATURES

The following movies are part of the Supplemental Information:

- `lattice-300K.avi` represents the infinite monolayer at $T = 300$ K in top view;
- `lattice-1500K.avi` represents the infinite monolayer at $T = 1500$ K in top view;
- `flake-300K.avi` represents a flake at $T = 300$ K in top view;
- `flake-1500K.avi` represents a flake at $T = 1500$ K in top view.

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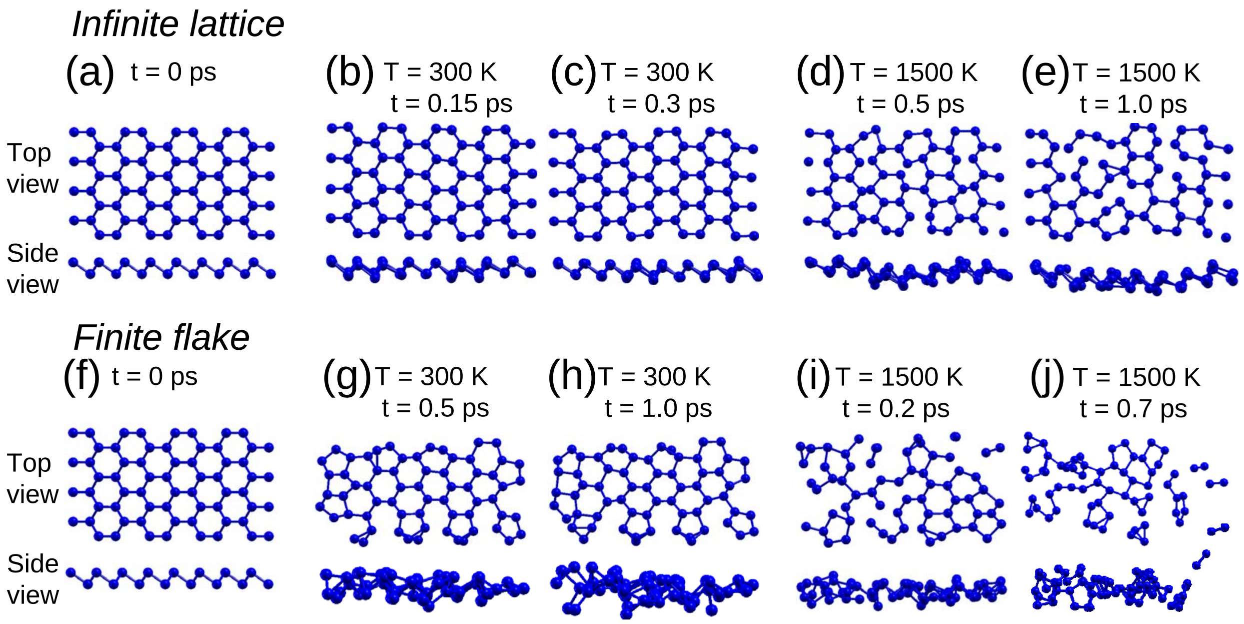

FIG. S2. Snap shots of canonical molecular dynamics simulations depicting structural changes in (a-e) a contiguous monolayer and (f-j) a free-standing, finite flake of blue phosphorus at different temperatures. The unit cell of the lattice and the flake contain 64 P atoms. The initial geometries are shown in (a) and (f).