

Supplementary information for

Nitrogen induced phosphorene formation on the boron phosphide (111) surface: a density functional theory study

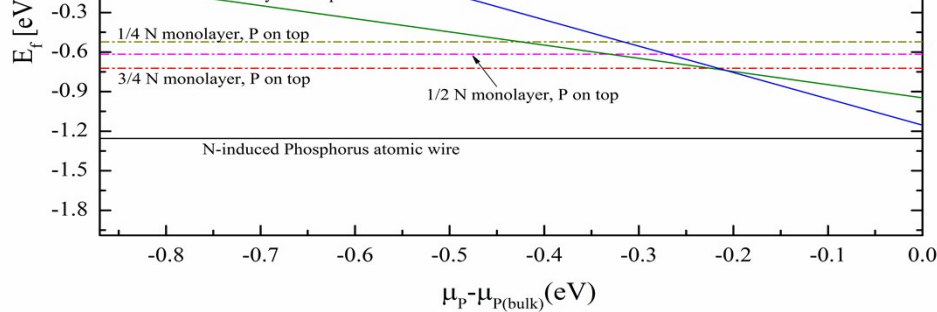
J. Guerrero-Sánchez^{a*}, M. Lopez-Fuentes^b, F. Sánchez-Ochoa^c, Noboru Takeuchi^a and Gregorio H. Cocoletzi^c.

^aCentro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Apartado Postal 14, Ensenada Baja California, Código Postal 22800, México.

^bBenemérita Universidad Autónoma de Puebla, Facultad de Ingeniería Química, Ciudad Universitaria, San Manuel, Puebla, Código Postal 72570, México.

^cBenemérita Universidad Autónoma de Puebla, Instituto de Física “Ing Luis Rivera Terrazas”, Apartado Postal J-48, Puebla 72570, México.

Corresponding author e-mail: guerrero@cnyunam.mx



**Results
Stability
analysis
without**

vdW-DF2 functional

Figure S1. Surface formation energy lines obtained with only PBE exchange and correlation.

From Figure S1, we can observe that surface formation energies of the adsorption of $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ N monolayers on the BP (111) surface can be seen as horizontal lines, with the configuration corresponding to the $\frac{1}{4}$ monolayer being the less stable. As the N coverage increases the structure becomes more stable. At low chemical potentials (B-rich conditions) the surface formation energy indicates that the P atomic wire (induced by incorporation of a N monolayer) on top of the BP (111) surface is clearly more stable than any other geometry. As the P chemical potential increases towards P-rich conditions, the phosphorene structure becomes more stable. However, its surface formation energy is always higher than the surface formation energy of the P atomic wire structure. As explained in the main text, with the inclusion of vdW interactions the SFE lines of the last two described models are almost degenerated (see Figure 2). Then, it is demonstrated that the inclusion of the van der Waals interactions improve the thermodynamic stability of the phosphorene bilayer by describing in a better way the out-of-plane phosphorene-phosphorus wire interactions.

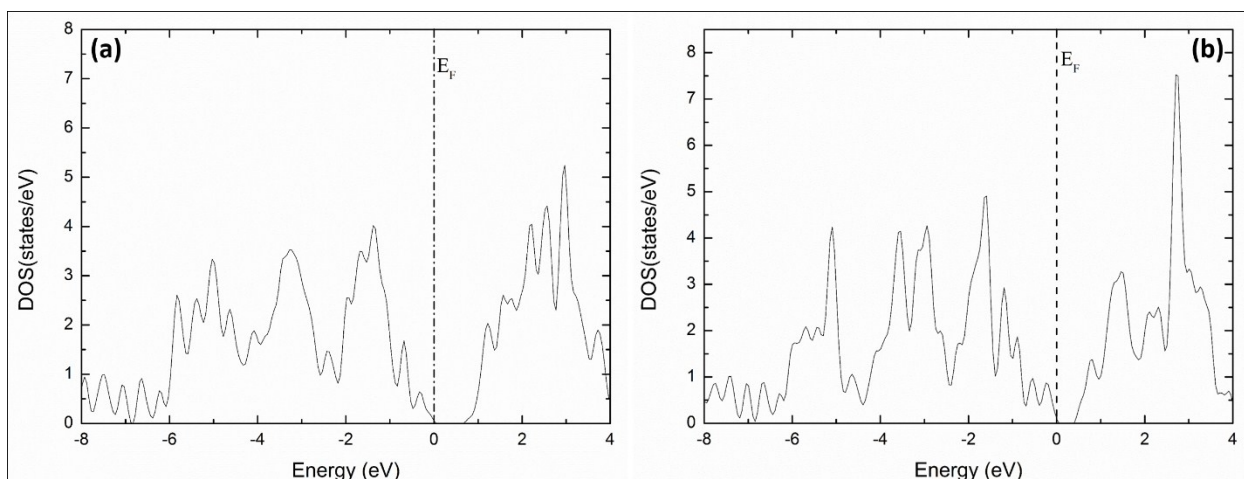


Figure S2. Total density of states of (a) an ideal phosphorene bilayer obtained from the black phosphorus structure, and (b) an elongated phosphorene bilayer as found in the epitaxial growth on BP(111).

From Figures S2 we can see that the density of states is very similar in both cases, but for the elongated phosphorene, the band gap is reduced, showing that band gap engineering can be achieved by straining the phosphorene, in good agreement with a previous report.¹

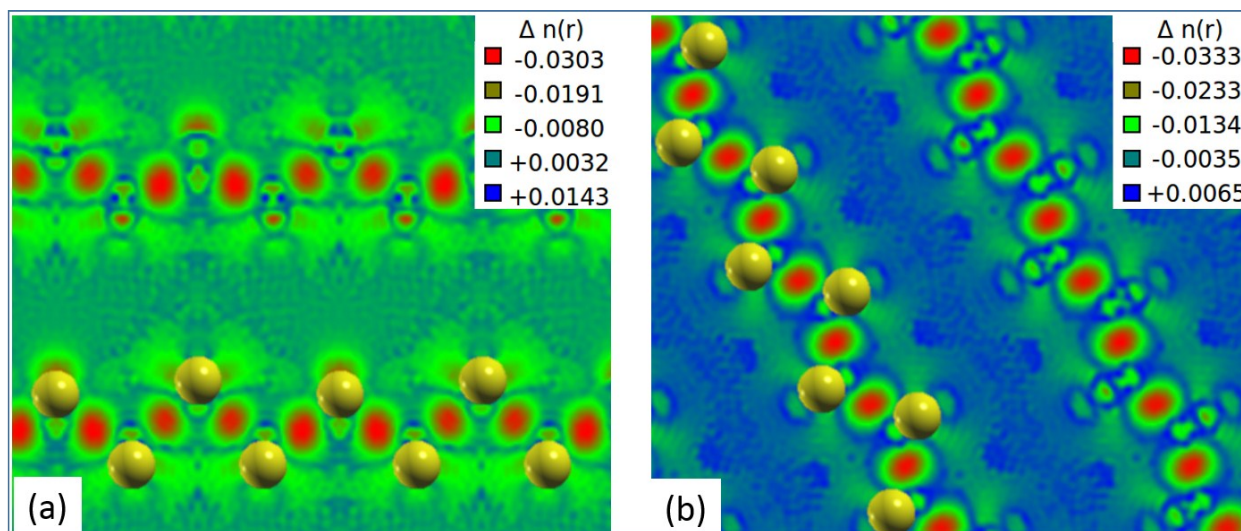


Figure S3 Reduced density gradient plots for the Phosphorus atomic wire (a) and in the phosphorene bilayer (b).

Reduced density gradient plots show charge density accumulation in the phosphorus-phosphorus bond region (Figure S3), supporting the conclusions presented in the paper.

References

1 B. Sa, Y.-L. Li, J. Qi, R. Ahuja, Z. Sun, *J. Phys. Chem. C*, 2014, 118, 26560.