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Dynamical Stability of Supported Black and Blue Phosphorus

Bulk black phosphorus (BP) is an attractive material for applications in nanoelectronic and photonic devices due to its high carrier mobility and anisotropic in-plane properties. Similar to graphite, BP is made of layers which are held together by weak interlayer van der Waals (vdW) forces. Recently, single-layer BP has been obtained by mechanical exfoliation and single-layer blue phosphorus (bP) has been synthesized on a Au(111) substrate by molecular beam epitaxy [1,2]. Theoretical works have predicted a phase transition between single-layer BP and bP [3], but it has not yet been observed experimentally. In addition, to study the stability of two interacting continuous materials, such as BP or bP adsorbed onto an Au(111) substrate, vibrational modes must be taken into account. Based on density functional theory (DFT) calculations, we demonstrate the importance of including the vdW interaction to accurately describe the properties of BP and bP allotropes. The temperature dependent Helmholtz free energy, lattice constants and linear thermal expansion coefficients of BP and bP have been studied using the quasiharmonic approximation. We find that a phase transition between these materials appears around 168 K using a semi-local exchange-correlation (xc) functional. However, single-layer BP is found to remain the most energetically stable phase regardless of temperature when a non-local vdW xc functional is used. To gain insight into how one phase transforms into another, we used the climbing image nudged elastic band (cNEB) method to show that BP must overcome an energy barrier of 0.48 eV/atom to transform into bP. This value is ~10% higher than that obtained without including any vdW interactions. Finally, we extend this study of energetics by adsorbing single-layer BP and bP onto an Au(111) substrate. We propose an improvement of the frozen phonon method to include the vibrational modes located at the interface between these materials. Breathing and shearing modes emerge which contribute to the stability of a surface adsorbed on a substrate.

References

[1] L. Likai *et al.*, *Nat. Nanotech.*, 12 (2017) 21
[2] J.L. Zhang *et al.*, *Nano Lett.*, 16(8) (2016) 4903
[3] Y. Aierken *et al.*, *Phys. Rev. B*, 92 (2015) 081408

Figures

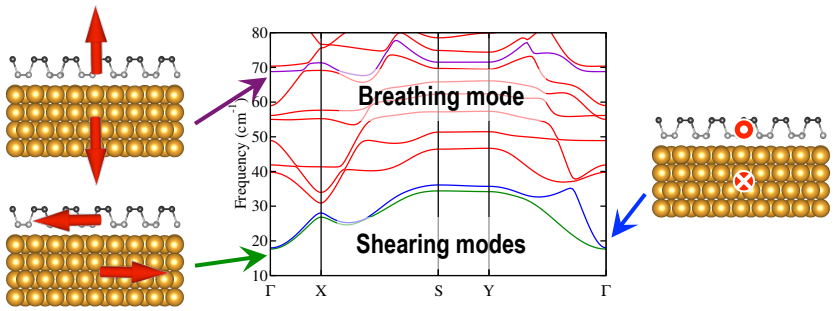

Figure 1: Phonon dispersion of black phosphorus on an Au(111) substrate.