

# Supplemental on-line material for Unusual electronic structure of few-layer gray arsenic: A computational study

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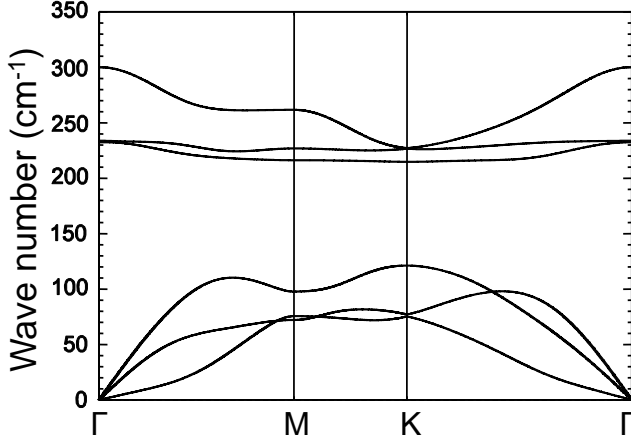


FIG. S1. Vibrational band structure of a monolayer of gray As.

## STABILITY AND THE VIBRATION SPECTRUM OF A MONOLAYER OF GRAY AS

We find the monolayer of gray As to be nearly as stable as its layered bulk counterpart with  $E_{coh} = 2.96$  eV/atom [1]. More important than a high cohesive energy is the vibration spectrum that indicates whether a crystal is or is not resilient under arbitrary deformations. The calculated vibration spectrum of a monolayer of gray As, shown in Fig. S1, does not contain any soft vibration modes that would indicate spontaneous deformation channels. We find the vibration spectrum to be rather isotropic, similar to that of blue phosphorene with the same buckled honeycomb structure [2]. The hardest optical modes occur at  $\Gamma$  at a frequency of  $300 \text{ cm}^{-1}$ , which is rather high in view of the heavy mass of As atoms. We expect this vibration spectrum to be useful to identify monolayers of gray arsenic using Raman or infrared spectroscopy.

## EQUILIBRIUM STRUCTURE OF FEW-LAYER AND BULK GRAY AS

The calculated electronic structure of gray As depends sensitively both on the functional used in density functional theory (DFT) and the optimum geometry obtained using that functional. Whereas the optimum geometry is usually rather independent of the DFT functional in most covalent solids, this is often not the case in lay-

ered materials with a significant van der Waals interlayer interaction. In Figs. S2(a) and S2(b) we show the dependence of the interlayer spacing  $d$  and the in-layer lattice constants  $a = a_1 = a_2$  on the number of layers  $N$  for different types of stacking and different DFT functionals. With the bilayer being an exception, the trends in  $d(N)$  and  $a(N)$  are independent of the DFT functional.

We find that the Local Density Approximation (LDA) [3] as well as the van der Waals-corrected optB86b-vdW DFT functional [4, 5] underestimate the interlayer spacing with respect to the observed bulk value, whereas the Perdew-Burke-Ernzerhof (PBE) [6] functional overestimates this value. Deviations of LDA and PBE results from the observed interlayer distance are expected, since none of these functionals is designed to take into account van der Waals interactions. Much less expected is the error in the interlayer spacing value predicted by the optB86b-vdW functional, which is supposed to treat van der Waals interactions more accurately. In our study of the isoelectronic black phosphorus [7], we also found that optB86b-vdW overestimates the interlayer interaction energy when compared to more precise Quantum Monte Carlo (QMC) calculations. In view of this uncertainty, we present results based on PBE as the default functional in the main manuscript.

Our results in Fig. S2(a) indicate a very weak dependence of  $d$  on the number of layers. The interlayer separations are rather uniform within a given slab, but somewhat larger near the surface, especially in ABC stacked slabs. As expected intuitively, the interlayer spacing in the energetically less favorable AA stacking is generally larger than in the observed rhombohedral or ABC stacking.

While the interlayer interaction may be small, we find that it still changes the in-layer structure, primarily by changing the buckling of the layers. We characterized the degree of non-planarity or buckling by the pyramidalization angle  $\theta_P$ , defined in Fig. S3(a). As seen in Fig. S3(b), increasing the number of layers from a monolayer to the bulk system decreases the pyramidalization angle, but does not change the interatomic bond length noticeably. It is this change of the pyramidalization angle that is chiefly responsible for the dependence of the lattice constants  $a_1 = a_2$  on the number of layers  $N$ , shown in Fig. S2(b). The observed decrease of the pyramidalization angle with increasing  $N$  explains the decrease in the interlayer distance  $d$  with increasing  $N$ , seen in Fig. S2(a), and a corresponding increase of the interlayer interaction.

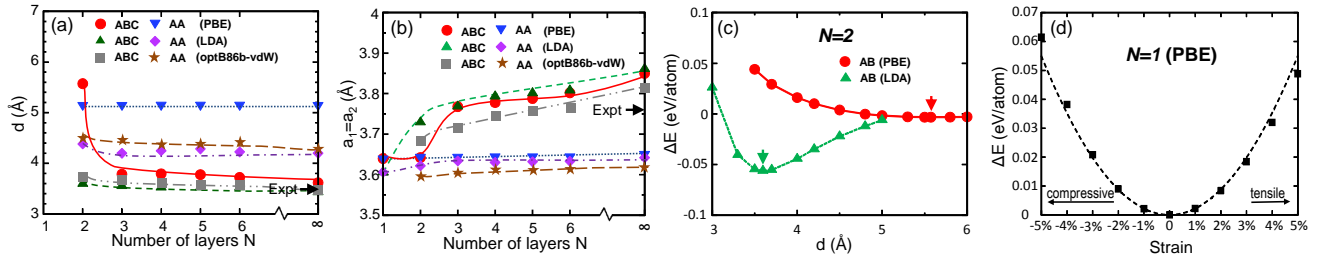


FIG. S2. (Color online) (a) The interlayer spacing  $d$  and (b) the in-layer lattice constant  $a_1 = a_2$  of gray arsenic slabs as a function of the number of layers  $N$ . Presented results, obtained using different DFT functionals, consider both the energetically favorable ABC and the less stable AA stacking. (c) Energy dependence of an AB stacked As bilayer on the interlayer spacing  $d$  as determined by PBE and LDA. Equilibrium geometries are indicated by arrows and  $\Delta E = 0$  refers to two isolated gray arsenic monolayers. (d) Energy dependence of a monolayer on in-layer strain, based on PBE. The dashed line represents harmonic behavior.

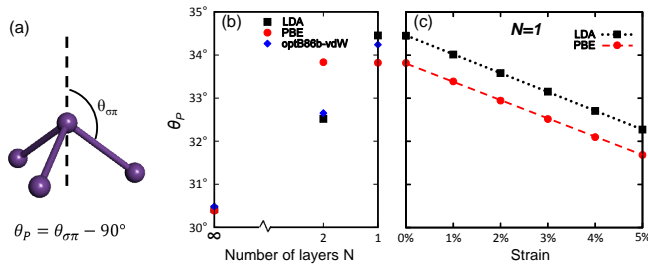


FIG. S3. (Color online) (a) Definition of the pyramidalization angle  $\theta_p$  in a buckled monolayer of arsenic with  $sp^3$  hybridization. The  $\sigma$  orbitals extend along the interatomic bonds, and the direction of the  $\pi$  orbital is indicated by the dashed line. Dependence of the pyramidalization angle on (b) the number of layers in a thin film and (c) in-layer tensile strain in a monolayer, as obtained using the PBE, LDA and optB86b-vdW functionals. The dashed lines in (c) serve as guides to the eye.

As seen in Fig. S2(b), the in-layer lattice constant shows a much stronger dependence on the number of layers in the favorable ABC stacking than in the less favorable AA stacking. The changes are significant, amounting to a 5% reduction in the in-layer lattice constant in the monolayer with respect to the bulk structure.

As common in DFT calculations using nonlocal exchange-correlation functionals including PBE, the interlayer interaction is underestimated and the interlayer distance larger than in LDA. This contrast is particularly large in layered gray arsenic structures, as evidenced in the bilayer results in Figs. S2(a) and S2(c).

As mentioned above, the PBE value (in contrast to the LDA value) of the interlayer distance in the AB stacked bilayer does not follow the trend of  $d(N)$  for  $N > 2$ . To make sure that this is not an artifact of the optimization, we present in Fig. S2(c) the energy of the bilayer as a function of the interlayer separation  $d$ . Both LDA and PBE indicate the presence of a well-defined single optimum structure. In a similar way, we find that the deformation energy  $\Delta E$  of a gray arsenic mono-

layer subject to in-layer strain, presented in Fig. S2(d), shows no deviation from the expected near-parabolic behavior, suggesting that the buckled structure represents a single optimum geometry. As seen in Fig. S3(c), also the pyramidalization angle in a stretched monolayer decreases uniformly with tensile strain, with no indications of a structural bistability.

#### DEPENDENCE OF THE ELECTRONIC STRUCTURE OF A MONOLAYER AND A BILAYER OF GRAY ARSENIC ON THE EXCHANGE-CORRELATION FUNCTIONAL

It is well known that the fundamental band gap is usually underestimated in DFT calculations. Even though the proper way to determine the electronic band structure involves advanced methods such as GW or QMC, we have not used these approaches, as they are computationally very demanding. We rather made use of the HSE06 hybrid functional [8, 9], which is believed to reproduce the fundamental band gap correctly.

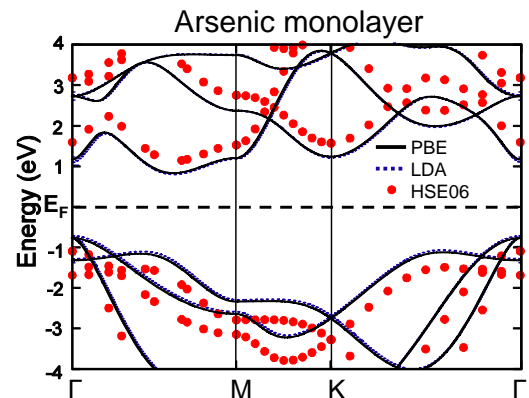


FIG. S4. (Color online) Electronic band structure of a gray arsenic monolayer obtained by DFT calculations using the LDA, PBE and HSE06 functionals.

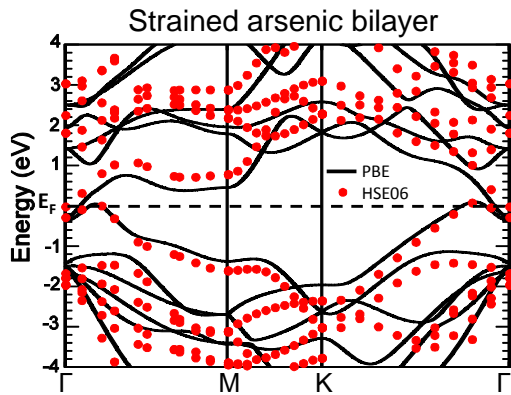


FIG. S5. (Color online) Electronic band structure of a bilayer of gray arsenic subject to 7% tensile strain obtained by DFT calculations using the PBE and HSE06 functionals.

We compare the electronic band structure of a relaxed gray As monolayer, obtained using LDA, PBE and HSE06, in Fig. S4. For the sake of fair comparison, we use the identical geometry, namely that of a PBE-optimized monolayer, in the three sets of results obtained using the VASP code [10]. Our results indicate that both LDA and PBE give a nearly identical band structure with a fundamental band gap near 1.6 eV, in close agreement with SIESTA results [11] quoted in the main manuscript. HSE06 opens up the band gap to about 2.0 eV by essentially rigidly shifting the conduction band up with respect to the valence band. Results based on HSE06 suggest that also a relaxed bilayer is a semiconductor. According to HSE06, relaxed gray arsenic structures with more than two layers are either semimetallic or metallic.

To better estimate the strain required to induce a metal-semiconductor transition in a bilayer of gray arsenic, we performed HSE06 hybrid functional calculations and compared them to PBE results. Both PBE and HSE06 results indicate that the fundamental band gap decreases upon stretching the monolayer and bilayer. Similar to the monolayer, we find the HSE06 functional to increase the band gap value by essentially rigidly shifting the conduction states up, thus delaying the closure of the fundamental gap in the strained system. As seen in Fig. S5, the fundamental band gap closes as the arsenic bilayer is stretched by 7% according to HSE06, very close to the 5% value based on PBE. This small numerical difference between vastly different functionals indicates that a metal-insulator transition in a stretched bilayer should be observable at moderate strain values.

## EXPERIMENTAL REALIZATION OF HIGH IN-LAYER STRAIN LEVELS

Experimental validation of the predicted metal-semiconductor transition in a bilayer of gray arsenic requires in-layer stretch by 5 – 7%, much higher than the typical strain values < 3% obtained by bending a graphene monolayer on a flexible Si/SiO<sub>2</sub> wafer [12]. We first note that such a high strain requires less stress in buckled gray arsenic than in the planar graphene structure. Ultimately, the desired large change in the lattice constant causing a specific change in electronic structure may be achieved by epitaxial growth on selected substrates, as mentioned in the main manuscript. As an alternative, since isolated monolayers of gray arsenic are expected to be stable, we can imagine suspending them across a cavity on a substrate. If this cavity has the form of a deep trench, bending the substrate like a break junction may increase the gap at the top of the trench sufficiently to provide the desirable large strain. Suspending a thin film across a pit on the surface may provide a drum-like geometry. In both types of film suspension geometries, strains of  $\lesssim 15\%$  have been achieved by loading suspended graphene membranes by an AFM tip [13, 14].

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