Electronic Supporting Information: Tunable gap in stable arsenene nanoribbons opens the door to electronic applications

A. García-Fuente,^a J. Carrete,^b A. Vega^c and L. J. Gallego^d

^aDepartamento de Física, Universidad de Oviedo, E-33007 Oviedo, Spain; ^bInstitute of Materials Chemistry, TU Wien, A-1060 Vienna, Austria; ^cDepartamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, E-47011 Valladolid, Spain; ^dDepartamento de Física de la Materia Condensada, Facultad de Física, Universidad de Santiago de Compostela, E-15782 Santiago de Compostela, Spain

1. Computational method

We performed calculations of the structural and electronic properties of As 2D sheets and AsNRs using the projector-augmented-wave (PAW) formalism^{1,2} as implemented in VASP.^{3,4} The PBE⁵ parametrization of GGA was used for the exchange-correlation potential. However, since band gaps are underestimated by standard DFT, we applied a correction to the PBE results using the screened hybrid functional HSE06,^{6–9} that mixes a 25 % of the Hartree-Fock exact exchange with 75 % of the PBE exchange. 12 k points were included along the periodic directions, which were found to be enough to converge the energies to meV precision. The electronic wave functions were expanded in a plane wave basis set with a cutoff energy of 400 eV, and the structures were relaxed until all forces were smaller than 0.005 eV/Å. A Gaussian smearing technique with a smearing width of 25 meV was used to determine partial occupations of the electronic states. The sheets and AsNRs were simulated inside a supercell that was repeated periodically, with a minimum distance between periodic images of 15 Å. For the metallic AsNRs, we also simulated AsNRs with two unit cells in the simulation box to check if a Peierls distortion could happen, but no distortion was found in any case.

Phonon spectra were calculated using a real-space finite-displacement method. The Phonopy package¹⁰ was employed to generate a minimal set of displaced supercell configurations for each nanoribbon, from which a sufficiently complete set of harmonic interatomic force constants (IFCs) can be reconstructed. VASP was again used to obtain the forces on each atom in each of those configurations. In this case the force criterion was changed to 10^{-5} eV/Å to guarantee the accuracy of the phonon spectra. We used supercell sizes of 8 unit cells for zz-b-AsNRs, 6 unit cells for zz-p-AsNRs, 5 unit cells for ac-b-AsNRs, ac-p-AsNRs and ac-s/o-AsNRs, and 4 unit cells for t-s/o-AsNRs, and kept the number of k points per reciprocal atom in each DFT run constant with respect to the minimization step. From those IFCs we calculated the dynamical matrix at each point in reciprocal space, and obtained the phonon frequencies and wave functions from its eigenvalues and eigenvectors. Hence, our phonon dispersions correspond to those of the truly infinite nanoribbons at points of the Brillouin zone commensurate with each supercell, and to a Fourier interpolation at any other point.

		E_g -PBE	E_g -HSE
b	d	1.95(1.94)	2.60(2.73)
	i	1.60(1.59)	2.20(2.25)
р	d	0.89(0.90)	1.48(1.48)
	i	0.77(0.77)	1.32(1.43)
s/o	d	1.71(1.79)	2.37(2.47)

Table 1. Fundamental band gaps (in eV) of the b, p and s/o 2D arsenene structures, as computed in this paper using the PBE and HSE functionals. Results obtained in Refs. 12 and 13 using the same approaches are given in parenthesis. 'd' and 'i' refer to direct and indirect band gaps, respectively.

2. Atomic and electronic structures of arsenic 2D phases

The AsNRs investigated in this work were constructed by cutting strips out the b, p and s/o arsene structures along the directions indicated in Figure 1. These structures were obtained in Ref. 11 using the PBE form of the GGA, and their main geometrical features can be found in that reference. Figure 2 shows the electronic band structures of the three 2D arsenene sheets calculated with PBE and the hybrid HSE functional. In Table 1 we compare our predicted band gaps with the results obtained in Refs. 12 and 13.



Figure 1. Top, front and side views of each of the 2D arsenene structures considered in this paper. The unit cells are shaded in light blue and delineated with dotted lines.

3. Band gaps of the AsNRs considered in this paper using PBE

Figure 3 shows the band gaps of the AsNRs as functions of their widths, obtained using PBE. Comparing these results with those obtained with HSE (lower panels of Figure 3 of the main text), it can be seen that the effect of the HSE correction is merely to displace the PBE band gaps to larger values.



Figure 2. Energy band structures of each of the 2D arsenene structures considered in this paper calculated with PBE (continuous red lines) and HSE (dashed blue lines).

4. Transmittances, carrier densities and mobilities of the AsNRs

Figures 4-6 confirm the electronic character inferred from the band-structure calculations and illustrate its consequences. Specifically, Figure 4 concerns itself with the ballistic regime and contains the electronic transmittance of the AsNRs represented in Figure 1 of the main text, obtained as the number of electronic bands compatible with each value of the energy for each spin channel. Figure 5 shows the charge carrier density obtained for each value of the chemical potential in the rigid band approxima-



Figure 3. Direct band gaps of the non-passivated and hydrogen-passivated AsNRs as functions of their widths, calculated with PBE; the dashed lines correspond to the direct band gaps for the periodic, infinitely extended, p, b and s/o arsenene sheets.

tion. To obtain the accurate approximation to the one-dimensional electronic density of states required for this kind of calculation, we first interpolated the electronic bands using non-self-consistent VASP runs from a dense $31 \times 1 \times 1$ k-point grid to an even denser $97 \times 1 \times 1$ k-point-grid, and then employed the analytic third-order integration method developed in Ref. 14. Adding a uniform-mean-free-path hypothesis, which is reasonable when charge carrier transport is limited by nanostructural features of the sample, we also estimated the carrier mobility defined as the proportionality constant between the drift velocity of carriers and the applied electric field. Its value per unit of mean free path is shown in Figure 6.

References

- [1] P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953–17979.
- [2] G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.
- [3] G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, 47, 558–561.
- [4] G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169–11186.
- [5] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865–3868.
- [6] J. Heyd, G. E. Scuseria and M. Ernzerhof, J. Chem. Phys., 2003, 118, 8207–8215.
- [7] J. Heyd, G. E. Scuseria and M. Ernzerhof, J. Chem. Phys., 2006, 124, 219906.
- [8] J. Paier, M. Marsman, K. Hummer, G. Kresse, I. C. Gerber and J. G. Ángyán, J. Chem. Phys., 2006, 124, 154709.
- [9] J. Paier, M. Marsman, K. Hummer, G. Kresse, I. C. Gerber and J. G. Ángyán, J. Chem. Phys., 2006, 125, 249901.



Figure 4. Electronic transmittance for the AsNRs shown in Figure 1 of the main text, as calculated with PBE (continuous red lines) and HSE (dashed blue lines).



Figure 5. Carrier densities for the AsNRs shown in Figure 1 of the main text. The chemical potential is represented by the symbol g.

- [10] A. Togo and I. Tanaka, Scr. Mater., 2015, 108, 1–5.
- [11] J. Carrete, L. J. Gallego and N. Mingo, J. Phys. Chem. Lett., 2017, 8, 1375–1380.
- [12] D. Kecik, E. Durgun and S. Ciraci, *Phys. Rev. B*, 2016, **94**, 205409.
- [13] F. Ersan, E. Aktürk and S. Ciraci, Phys. Rev. B, 2016, 94, 245417.
- [14] J. Carrete, B. Vermeersch, A. Katre, A. van Roekeghem, T. Wang, G. K. Madsen and N. Mingo, *Comput. Phys. Commun.*, 2017, 220, 351–362.



Figure 6. Mobilities per unit mean free path (MFP) of the charge carriers in the uniform-MFP approximation for the AsNRs shown in Figure 1 of the main text. The chemical potential is represented by the symbol g.