Electronic Supplementary Information for

Raman and Electrical Transport Properties of Few-Layered Arsenic-Doped Black Phosphorus

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1. Synthesis and X-ray crystallography:

Single crystals of As-bP were grown through the cubic-anvil high-pressure and hightemperature technique. Pellets containing the high purity powders of grey arsenic (99.9999 %) and red phosphorus (99.999 %) with molar ratio 30:70 were enclosed in a boron nitride container and placed into a graphite heater. A pressure of 10 kbar was applied at room temperature. Then, by keeping pressure constant the temperature was ramped up to 1050 °C in 3 h, maintained there for 3 h, and after that cooled to 650 °C in 15 h, and finally abruptly quenched to room temperature. Once the pressure was released, the sample was removed. More details about high-pressure instrumentation are given elsewhere [Ref S1, S2]. The structural characterization was performed by means of standard single crystal X-ray diffraction measurements performed at room temperature, which confirmed the single-phase nature of the crystals. At high pressure conditions, AsbP crystallizes in orthorhombic structure with the space group of *Cmca* and the lattice parameters are a = 3.388(2) Å, b = 10.566(9) Å, and c = 4.390(3) Å. Energy-dispersive xray (EDX) spectroscopy was used to analyze the chemical composition of the grown crystals. The EDX analysis performed on several crystals correspond to the As_{0.25}bP_{0.75} chemical composition, see Fig. S2.



Figure S1: Powder X-ray diffraction pattern of a ground $b-As_{0.25}P_{075}$ single crystal as a function of diffraction angle. It reveals not clear evidence for impurity phases.

Table S1.	Crystallographic	data and structure	refinement for	$b-As_{0.25}P_{0.75}$.
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Identification code	shelx	
Empirical formula	As P	
Formula weight	167.83	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Cmca	
Unit cell dimensions	a = 3.388(2) Å	<i>α</i> = 90°.
	b = 10.566(9) Å	β= 90°.
	c = 4.390(3) Å	$\gamma = 90^{\circ}$.
Volume	157.15(19) Å3	
Ζ	2	
Density (calculated)	3.547 mg/m^3	
Absorption coefficient	12.026 mm ⁻¹	
F(000)	156	
Crystal size	0.339 x 0.154 x 0.054 mm ³	
Theta range for data collection	3.857 to 31.751°.	
Index ranges	-5<=h<=5, -15<=k<=15, -6<=l<=6	
Reflections collected	1986	
Independent reflections	156 [R(int) = 0.0667]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.892 and 0.09	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	156 / 0 / 7	
Goodness-of-fit on F2	1.155	
Final R indices [I>2sigma(I)]	R1 = 0.0508, $wR2 = 0.1325$	
R indices (all data)	R1 = 0.0546, $wR2 = 0.1370$	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.862 and -1.268 e.Å-3	

2. Energy Dispersive Analysis of b-As_{0.25}P_{0.75}



Figure S2: Electron dispersive spectroscopy analysis of a $b-As_{0.25}P_{0.75}$ single-crystal grown via the high pressure method. As seen, the material contains only As and P with table below indicating a

composition that is very close x = 0.25 in As. These values correspond to the average of the data collected from 6 points throughout the crystal whose picture is shown in the inset.



3. Air sustainability test for exfoliated b-AsP crystals:

Figure S3: Optical micrograph images of b-AsP exfoliated flakes as a function of time, i.e. from 0 (immediately after exfoliation) to 23 hours. (a) Optical image immediately after exfoliation, (b) after 1 hour, (c) 2 hours, (d) 4 hours, (e) 5 hours and (e) 23 hours.

4. Raman Spectroscopy of encapsulated b-AsP crystal with polymer:

In Figure S4 (a-c) the theoretically calculated Raman spectra (green lines) are plotted together with the experimentally measured ones. (a), (b) and (c) correspond to 50%, 62.5% and 75%, respectively of As doped in black-phosphorus as calculated using the DFT method. (d) Raman Spectroscopy of b-AsP crystal months after exfoliation and encapsulation in CytopTM. The Raman spectrum is similar to the one of exfoliated flakes presented in the main text. This confirms that the intrinsic properties of b-AsP can be preserved for a long time in air when protected by a suitable polymer encapsulation.



Figure S4: Experimental Raman spectra with theoretically calculated ones for 50% As (a), 62.5% As (b) and 75% As (c) doped black-phosphorus. (d) Raman spectra for exfoliated b-AsP flakes, encapsulated in polymer after 6 months in a desiccator and a month under air exposure.

5. Polar plot of polarization Raman study



Figure S5: Angular dependence of the Raman intensity for each Raman mode branch at seven different frequencies. (a) Raman intensity as a function of the polarization angle for the modes at 239 cm⁻¹ and 257.4 cm⁻¹ associated to As-As bonds. (b) Raman intensity as a function of the polarization angle for three peaks at 316 cm⁻¹, 346 cm⁻¹ and 364 cm⁻¹ resulting from the As-P bonds. (c) Raman intensity as a function of the polarization angle for the modes at 426 cm⁻¹ and 456 cm⁻¹ which correspond to the P-P bonds in b-AsP. Dots are the measured values and solid lines are guides to eyes.

As shown in Fig. S5, we analyzed the polarization dependence of all main Raman peaks. All peaks from the three different Raman branches show a polarization-dependent Raman intensity. We have measured polarization dependent Raman studies on 3 different flakes using the same laser source and all three samples show consistent polarization-dependent Raman intensity data. Figures S5a, S5b and S5c show the angular dependence of the Raman intensity at 239 cm⁻¹ and 257.4 cm⁻¹ corresponding to As-As bonds, 316 cm⁻¹, 346 cm⁻¹ and 364 cm⁻¹ and 426 cm⁻¹ and 456 cm⁻¹. If one compares Figs. S4 and S5 with the Raman modes of pristine b-P in Ref. S3 (see its Fig. 3), one can see groups of modes, one at very low frequencies, that is between 235 and 260 cm⁻¹, another one between 300 and 400 cm⁻¹ , and a third one between 400 and 500 cm⁻¹. Table S2 below provides our calculated Raman modes associated with these Raman mode groups for b-AsP. As seen, each Raman mode involves vibrations associated to P-P, As-As, and As-P bonds.

In Fig. S5 one sees a 90° rotation between the angular dependences displayed by the modes of the third group with respect to the groups displaying modes at lower frequencies. B. Liu *et al.*, (Ref. S3) attributed a similar contrasting angular dependence observed in b-As_{0.87}P_{0.13}, to the distinct character of the modes, that is A^{1}_{g} for the lower frequency modes, and B_{2g} for the higher frequency ones. in. In contrast Ribeiro *et al.* Ref. **[S5]** sees twice the periodicity for the B_{2g} modes when compared to the A_{1g} one. This could be attributed to the use of polarized collection, in contrast to the use of unpolarized collection as used by us.

Notice that the Raman mode calculations in Liu *et al.* (Ref. S3) includes only the As-P bonds, and an As fraction x = 0.5. In our calculations, we include all chemical bonds and the actual As configuration for x = 0.25.

As for the contrasting angular dependence observed for the different modes we do not have a solid explanation for it, since our calculations contrast with the previous ones by indicating that all modes are A type. Here, we can only speculate that the As clusters might be preferentially oriented along a certain crystallographic direction. The lower frequency modes involve mainly As-As and As-P bonds, while the higher frequency ones are mainly associated with the P-P bonds that do not display a similar axial asymmetry. Perhaps this might lead to their contrasting anisotropies. Notice that higher As concentrations should lead to As clusters of distinct sizes and geometries naturally leading to distinct frequencies and anisotropies for their Raman modes.

6. Table S2: Calculated Raman modes:

Table S2 shows the frequencies in the left column and middle column represents modes name with image of modes showing in right column. The unit cell of the $b-As_{0.25}P_{0.75}$ structure using P1 symmetry, we calculated 45 Raman active modes. We listed the 15 most intense modes and plot the corresponding atomic displacements in the table. Arsenic atoms are is Green and Phosphorous atoms are in purple. Since the symmetry of the primitive cell is P1, the point symmetry associated with this cell is C1. Therefore, Table S2 shows only modes belonging to one irreducible representation, i.e. "A". This means that all the vibrational modes are Raman active and should be labeled as A.

Frequency (cm ⁻¹)	Name	Image	

231.8	A(20)	
242.46	A(21)	
249.59	A(22)	
259.12	A(24)	
309.84	A(25)	
312.45	A(26)	
329.9	A(27)	
384.17	A(33)	
423.02	A(39)	200

430.47	A(40)	
432.33	A(41)	
433.3	A(42)	
438.49	A(43)	
440.43	A(44)	
449.16	A(45)	

7. Calculated electronic band structure for 25% As doped black phosphorus:



Figure S6: (a) Configuration of As (green atom) and P (purple atoms) that would yield the experimental Raman modes observed for $b-As_xP_{1-x}$ where x = 0.25 according to our DFT calculations. (b) Band structure calculations, total density of states (DOS) and *p*-subshells DOS of the As contributing in the total DOS using the UDFT-HSE06-D2 DFT method (or HSE06-D for short) for monolayer b-As_{0.25}P_{0.75} in panel (a).

We performed electronic band structure calculations for single layer, bi-layer, tri-layer and bulk crystals of b-As_{0.25} $P_{0.75}$ following the particular As configuration that according to the DFT calculations would describe the observed experimental Raman spectra. The estimated size of the gap for monolayer, 2L, 3L and bulk are 1.558 eV, 1.123 eV, 0.84 eV and 0.21 eV respectively. In general the band gaps are smaller than those calculated for pristine b-P, see ref. [S4]. In this plot the bands are normalized (i.e. the Fermi energy E_F was subtracted from the each band energy).

Table S3: Lattice constants (a, b, c), band gap and the position of Fermi energy (E_F) are reported.

Materials	Symmetry	a in Å	b in Å	c in Å	Band	Fermi
	(Space group				Gap (Eg)	Energy (E _F)
	or layer				in eV	Level in eV
	group no.)					
Bulk	СМСА	3.336	10.210	4.393	0.324	-2.449
Structure	(64)					
Pristine bP						
Bulk	РМС21	3.423	10.299	4.397	0.210	-2.620
Structure b-	(26)					
AsP						
1Layer b-	<i>P1</i>	3.400	4.548	NA	1.558	-5.336
AsP	(1)					
2Layer b-	<i>P1</i>	3.398	4.506	NA	1.123	-5.303
AsP	(1)					
3Layer b-	<i>P1</i>	3.398	4.486	NA	0.840	-5.272
AsP	(1)					

8. Electrical transport at T = 4 K for the FET presented in main text.



Figure S7. Electrical transport properties of a $As_{0.25}bP_{0.75}$ FET at T = 4K. (a) and (b) I_{ds} as a function V_{bg} for $V_{ds} = 5$ mV, 10 mV and 15 mV in a linear scale measured *via* 2-terminal and 4-terminal configurations. (c) and (d) the same data but plotted in a semi-logarithmic scale indicating ON/OFF current ratios ranging from ~10⁴ to 10⁵.

9. I_{ds} as a function of V_{ds} at T = 2K for the As-bP FET presented in main text.

In Figure S8 we plot the low temperature I_{ds} as a function V_{ds} for the b-AsP device presented in the main text. These measurements indicate that at even at low temperatures, the I_{ds} as a function of V_{ds} looks ohmic like despite having a large contact resistance between the b-AsP and the Ti metal. The current measured using the 4-terminal configuration still is much higher than the one obtained through the 2-terminal method.



Figure S8: 2-terminal (left) and 4-terminal (right) drain-to-source current measured under several values of the applied gate voltage at a temperature T=2 K displaying nearly ohmic like behavior.

10. I_{ds} as a function of V_{bg} for the b-AsP FET presented in the main text at T = 50 K and 25 K.

Figure S9 (left) and (right) displays I_{ds} as a function of V_{bg} for a b-AsP FET in a semilogarithmic scale and for two temperatures 50 K and 25 K, respectively. The data shows an improved ON to OFF current ratio and subthreshold voltage swing at low temperatures compared to room temperature. This FET shows a ~10⁵ ON/OFF current ratio at a small applied $V_{ds} = 15$ mV.



Figure S9: Semi-logarithmic plot of the source-to-drain current at T = 50 K and 25 K for several values of the applied V_{ds} . An enhanced ON to OFF current ratio of ~10⁵ is observed under a small $V_{ds} = 15$ mV.

11. Temperature dependent transport properties of 2nd As-FET device:

Figure S10 displays the I_{ds} as a function of V_{ds} for a 2nd b-AsP FET measured at 300 K showing a very linear or ohmic like response. Figure S10(b) shows the linear scale plot of I_{ds} as a function of V_{bg} measured at several temperatures and for $V_{ds} = 40$ mV. The inset shows the optical micrograph image of the device having six contacts. Figure S10(c) plots the same data in b but in semi-logarithmic scale. The temperature dependent data shows a change in threshold gate voltage from 60 V to 20 V when lowering the temperature from 250 K to 2 K. The ON/OFF current ratio also increases as a function of decreasing temperature. The extracted field-effect mobility, calculated using the MOSFET transconductance formula, is shown in Fig. S10(d). The value of the mobility measured at 250 K is ~165 cm²/Vs, it slightly increases when cooling to ~100 K, and then slowly decreases saturating to ~148 cm²/Vs below 30 K. This is similar to the data for the device displayed in the main text using the 2-terminal configuration.



Figure S10: Transport properties of a 2nd b-AsP FET. (a) I_{ds} as a function of V_{ds} measured at room temperature. (b) Linear scale plot of I_{ds} as a function of V_{bg} under a bias voltage $V_{ds} = 40$ mV and measured at several temperatures from 250 K to 2 K. Inset: optical image of the device with Ti/Au (5/80 nm) contacts. The channel length between source and drain contacts is 12.2 µm and the width of the channel is 5.3 µm. (c) I_{ds} as a function V_{bg} in a semi-logarithmic scale. (d) The extracted mobilities from the linear fits of the traces collected at each temperature (panel (b)) as a function of the temperature.

12. Room temperature transport properties of a 3rd b-AsP-FET:

Figure S11 illustrates the *p*-type FET behavior of a 3rd b-AsP-FET measured at room temperature. Figures S11(a) and S11(b) correspond to the I_{ds} as a function of V_{ds} measured through 2- and 4-terminal configurations respectively, and for several values of the applied back gate voltage (V_{bg}). Inset in Figure S11(a) shows the optical image of the device with 6 deposited contacts. The FET characteristic (I_{ds} as function of V_{bg}) is shown in Figure S11(c) and S11(d) for 2- and 4-terminal measurements, respectively. The device shows ON to OFF current ratio > 10³ at 275 K.



Figure S11: (a) I_{ds} as a function of V_{ds} measured at room temperature through a 2-terminal configuration using source (S) and drain (D) terminals under several values of the applied back gate voltage. Inset: Optical micrograph image of a few-layered b-AsP FET. (b) I_{ds} as a function of V_{ds} measured through a 4-terminal configuration on the same device shown in (a). The channel length between source (S) and drain (D) contacts is $L = 5.9 \,\mu\text{m}$ and width $W = 2.5 \,\mu\text{m}$. The length between two voltage contacts V_1 and V_2 is $l = 2.5 \,\mu\text{m}$. (c) and (d) I_{ds} as a function of V_{bg} in a semilogarithmic scale for several bias voltages using 2- and 4-terminal configurations, respectively.

13. Resistivity as a function of the temperature for b-AsP:

Figure S12 displays the resistivity as a function of temperature showing metallic behavior $\left(\!\frac{d\rho}{dT}\!>0\right)$

from room temperature to ~ 100 K where it saturates to a nearly constant value.



Figure S12: Resistivity as a function of temperature under $V_{bg} = -60$, $V_{ds} = 15$ mV.

14. Anisotropy transport on 2nd device of b-AsP:

Figure S13 displays the I_{ds} as a function of V_{ds} measured at room temperature indicating that the anisotropy in electrical transport between currents flowing along the AC and the zig-zag directions is ~ 1.8 . Figure (a) shows a micrograph of the device and (b) display the I-V characteristics. For this device we have not measured T-dependence of its anisotropy.



Figure S13: b-AsP device with several anisotropy contacts using Cr/Au and I_{ds} vs V_{ds} graph.

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