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ADVANCED MATERIALS

Supporting Information

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Black Arsenic–Phosphorus: Layered Anisotropic Infrared Semiconductors with Highly Tunable Compositions and Properties

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*Bilu Liu1, Marianne Köpf2, Ahmad A. Abbas1, Xiaomu Wang3, Qiushi Guo3, Yichen Jia3, Fengnian Xia3, Richard Weihrich4, Frederik Bachhuber4, Florian Pielnhofer4, Han Wang1, Rohan Dhall1, Stephen B. Cronin1, Mingyuan Ge1, Xin Fang1, Tom Nilges2, Chongwu Zhou1**

Dr. B. Liu, A. Abbas, Prof. H. Wang, R. Dhall, Prof. S. B. Cronin, M. Ge, X. Fang, Prof. C. Zhou
Ming Hsieh Department of Electrical Engineering, University of Southern California, Los Angeles, California, 90089, USA
E-mail: chongwuz@usc.edu

M. Köpf , Prof. T. Nilges
Technische Universität München, Department of Chemistry, Lichtenbergstraße 4, Garching b. München 485748, Germany

Dr. X. Wang, Q. Guo, Y. Jia, Prof. F. Xia
Department of Electrical Engineering, Yale University, New Haven, Connecticut 06511, USA

Prof. R. Weihrich, F. Bachhuber, F. Pielnhofer
Institut für Anorganische Chemie, Universität Regensburg, Universitätsstraße 31, Regensburg 93040, Germany

Supplementary Information

Black Arsenic-Phosphorus: Layered Anisotropic Infrared Semiconductors with Highly Tunable Compositions and Properties

Bilu Liu[1], Marianne Köpf[2], Ahmad A. Abbas[1], Xiaomu Wang[3], Qiushi Guo[3], Yichen Jia[3], Fengnian Xia[3], Richard Weihrich[4], Frederik Bachhuber[4], Florian Pielnhofer[4], Han Wang[1], Rohan Dhall[1], Stephen B. Cronin[1], Mingyuan Ge[1], Xin Fang[1], Tom Nilges[2], Chongwu Zhou[1*]

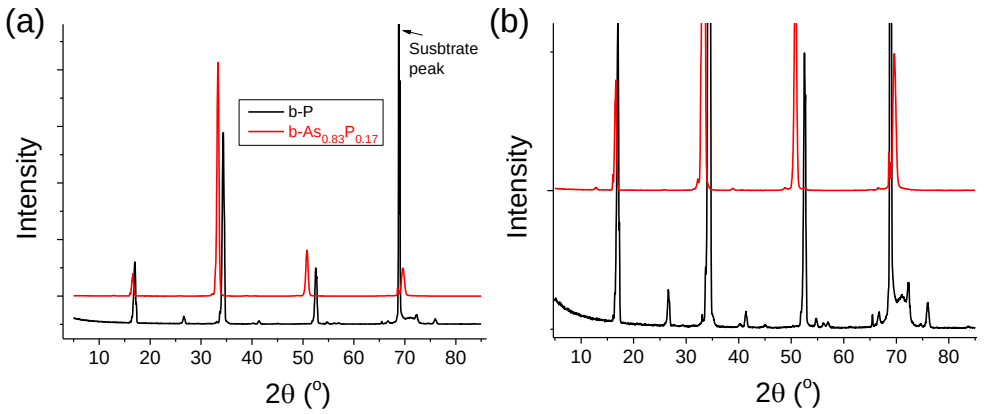
1. Ming Hsieh Department of Electrical Engineering, University of Southern California, Los Angeles, California, 90089, USA

2. Technische Universität München, Department of Chemistry, Lichtenbergstraße 4, Garching b. München 485748, Germany

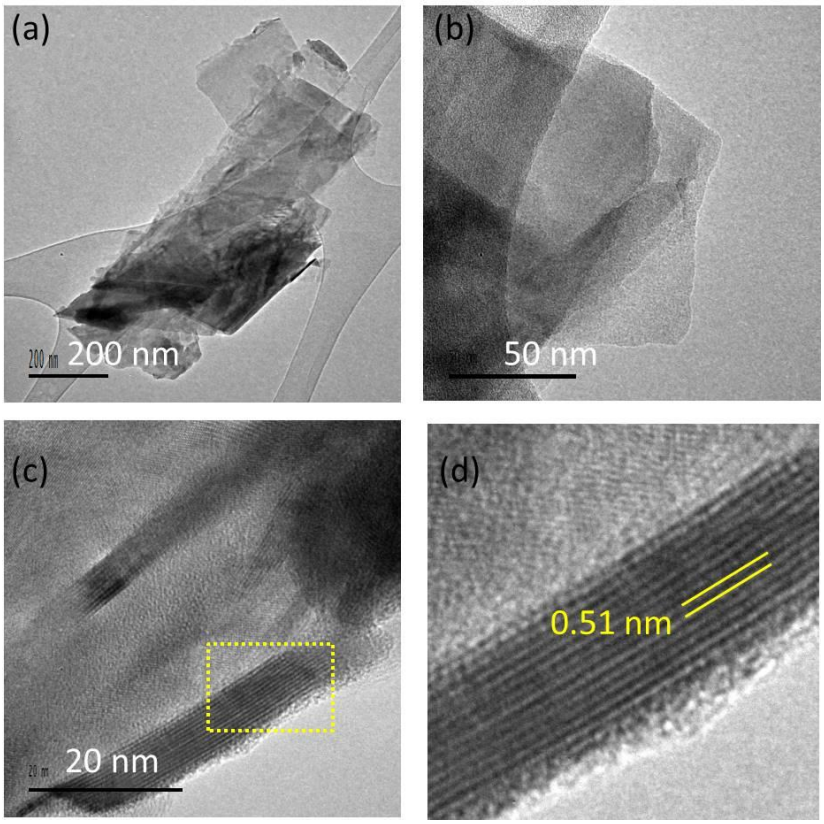
3. Department of Electrical Engineering, Yale University, New Haven, Connecticut 06511, USA

4. Institut für Anorganische Chemie, Universität Regensburg, Universitätsstraße 31, Regensburg 93040, Germany

E-mail: chongwuz@usc.edu



Supplementary Figure S1 XRD patterns of b-P and b-$As_{0.83}P_{0.17}$ bulk crystals. Plot b is a zoom-in plot of a. The results show that b-AsP has orthorhombic structure, similar to b-P. This result is consistent with our early publication.[1] The XRD patterns were collected using a Rigaku Ultima IV powder/thin-film diffractometer with Cu Kα line.

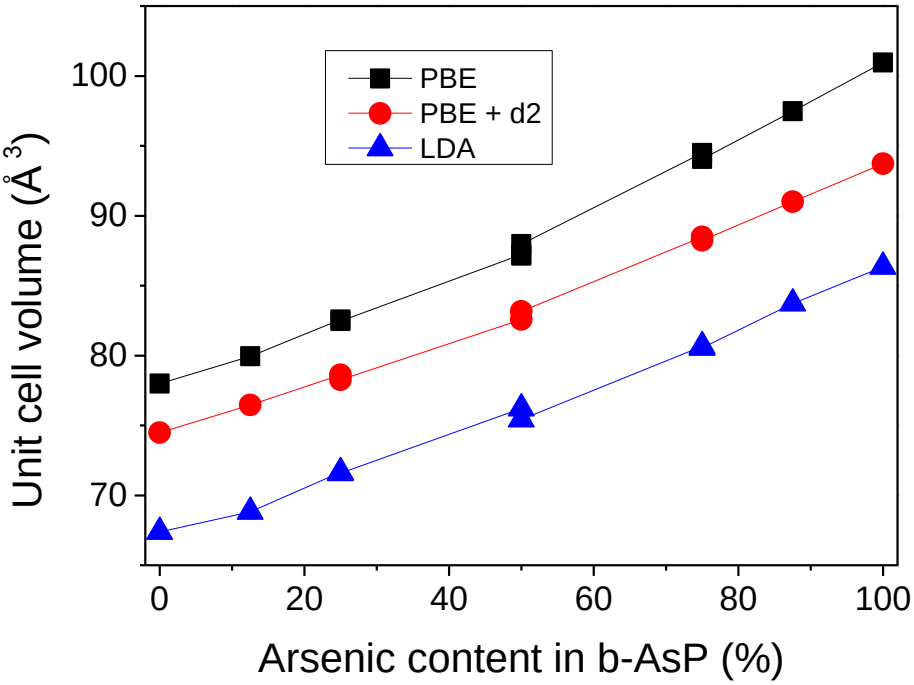


Supplementary Figure S2 TEM characterization of b-$As_{0.83}P_{0.17}$ samples. (a) (b) Low magnification TEM images show thin flakes of b-$As_{0.83}P_{0.17}$. (c) A HRTEM image shows the edge of a flake. (d) Zoom-in image of the yellow box highlighted area in image c, showing a ~13 layer b-$As_{0.83}P_{0.17}$ flake. The layer distance was measured to be 0.51 nm. For TEM sample preparation, the b-AsP flakes were first exfoliated on scotch tape, followed by gently attached the tape onto a TEM grid. After separation of the tape with TEM grid, some b-AsP flakes left on TEM grid were used for subsequent TEM characterization.

DFT calculations

First principles calculations were performed within the framework of DFT with GGA-PBE functionals and Grimme D2 corrections for van-der-Waals interactions, to calculate the geometrical structure, band gap, and vibrational properties of black arsenic-phosphorus (b-AsP) system. This combination provides the best results based on our recent investigations on phosphorus allotropes (see Figure S3 and reference [1]). Here, full structure optimizations and calculations of vibrational frequencies were performed as implemented in the CRYSTAL14 code.[2, 3] For phosphorus and arsenic, all electron basis sets with triple-zeta valence were applied.[4] Additional electronic structure calculations were performed with the full potential local orbital code FPLO14 in the scalar relativistic mode.[5, 6] For the graphical representation of vibrational frequencies, the j-ice was applied.[7]

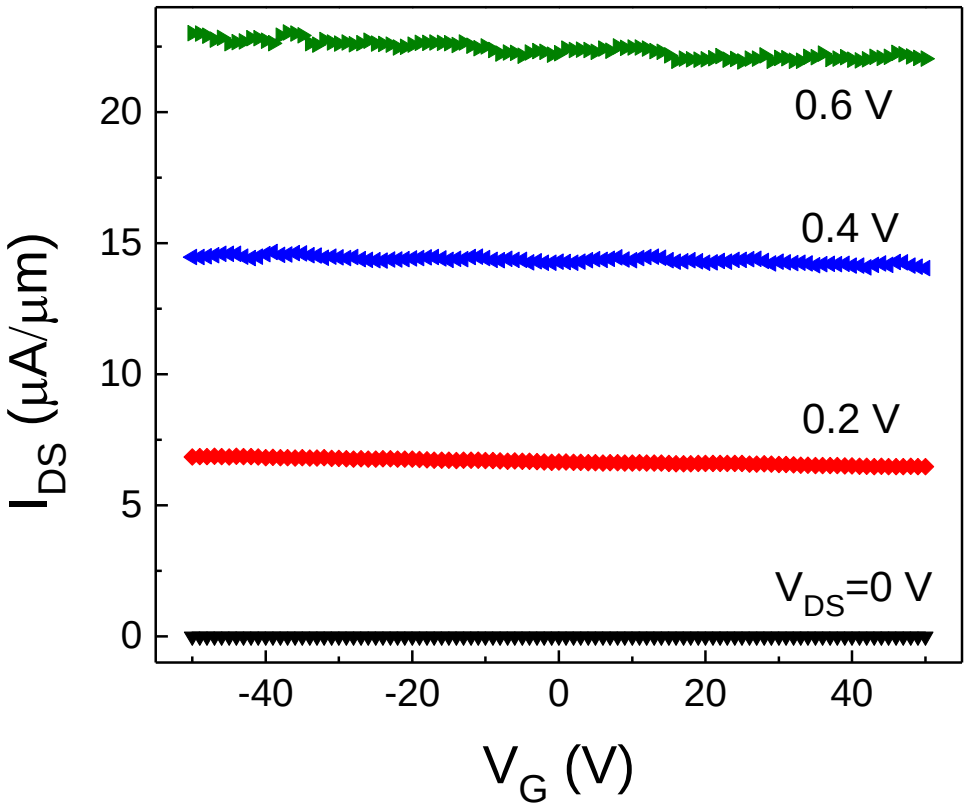
The calculated band gaps for b-As_xP_{1-x} are listed in Table S1. Systematical underestimated band gaps are due to the GGA functional as known from literature. Nevertheless, the general trend is confirmed as also found from test calculations with the B3LYP and HSE hybrid functionals that overestimate the band gaps. We also find that the calculated electronic structure further depends strongly on distortions in the structure related to the van der Waals interactions. From a shortening of interlayer distances (sample thickness increases), a smaller band gaps are observed, i.e., monolayer b-AsP would exhibit larger band gaps than the bulk. Moreover, with shorter inter-layer distances, the direct band gap is systematically shifted from the Y k-point towards U, due to van der Waals interactions.



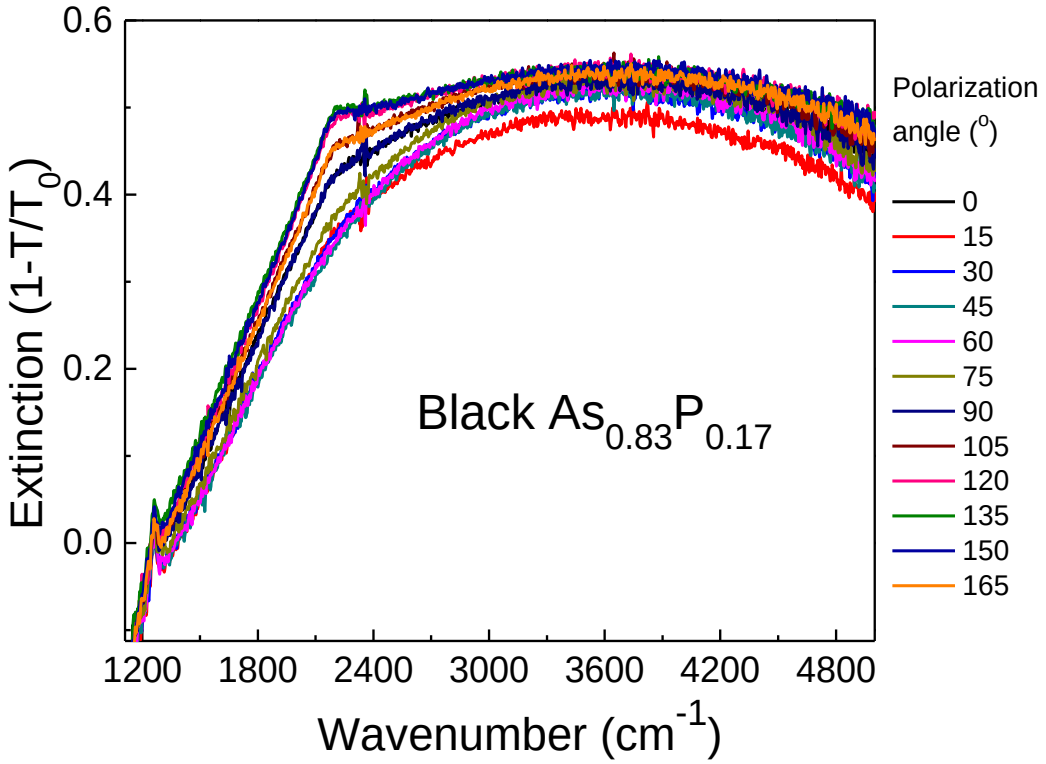
Supplementary Figure S3 Cell volumes for b-As_xP_{1-x} calculated with PBE, PBE+d2, and LDA functionals. The PEB and LDA results are from previous studies[1] and used as comparisons here.

Supplementary Table S1 Calculated band gaps for b-AsP using GGA method.

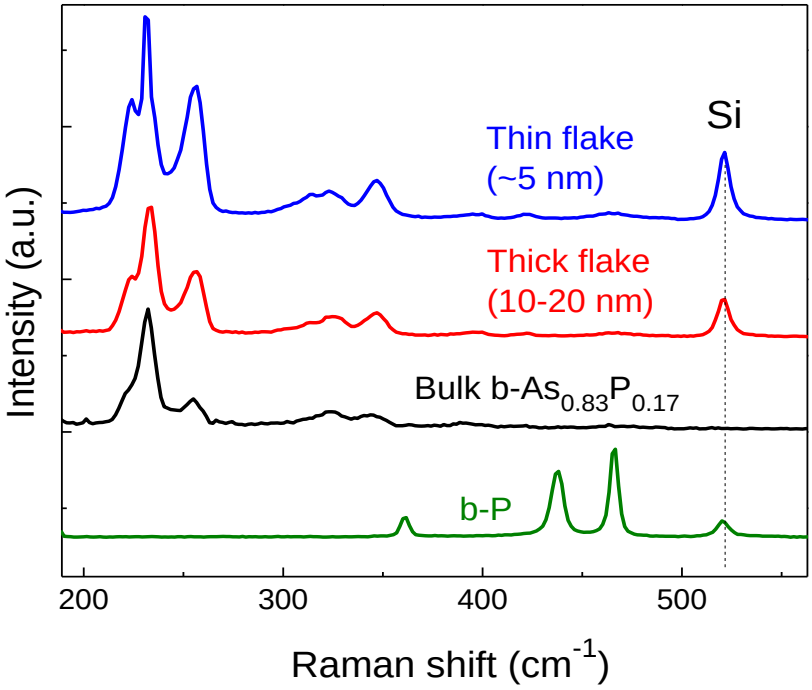
Materials ($b\text{-}As_xP_{1-x}$)	$b\text{-}As_0P_1$ (pure b-P)	$b\text{-}As_{0.25}P_{0.75}$	$b\text{-}As_{0.5}P_{0.5}$	$b\text{-}As_{0.75}P_{0.25}$	$b\text{-}As_1P_0$ (pure b-As)
Band gaps (eV)	0.16	0.13	0.11	0.052	0.05



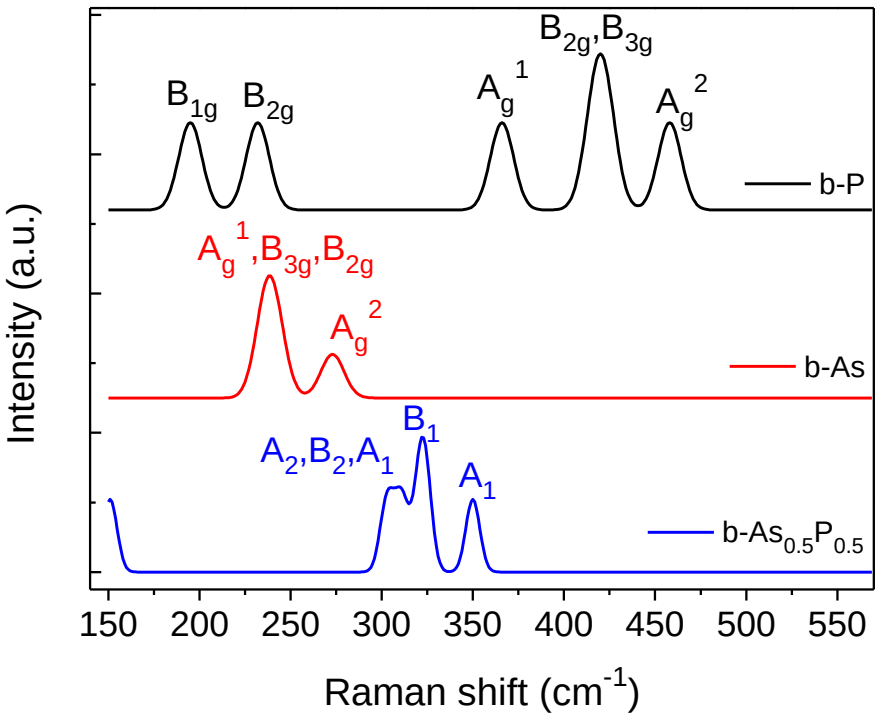
Supplementary Figure S4 I_{DS}-V_G characteristics of a representative thick black arsenic-phosphorus flake (b-$As_{0.83}P_{0.17}$). The thickness of the flake is around 60 nm based on AFM measurements. The sample is highly conductive and there is nearly no gate dependence for such thick flakes due to screening effect.



Supplementary Figure S5 Polarization-resolved infrared absorption spectra of a black-$As_{0.83}P_{0.17}$ flake at different polarization angles of 0 to 165 degrees with a step of 15 degree. Figure 3a in the main text uses part of the spectra (45, 75, 105, and 135 degrees) shown here.



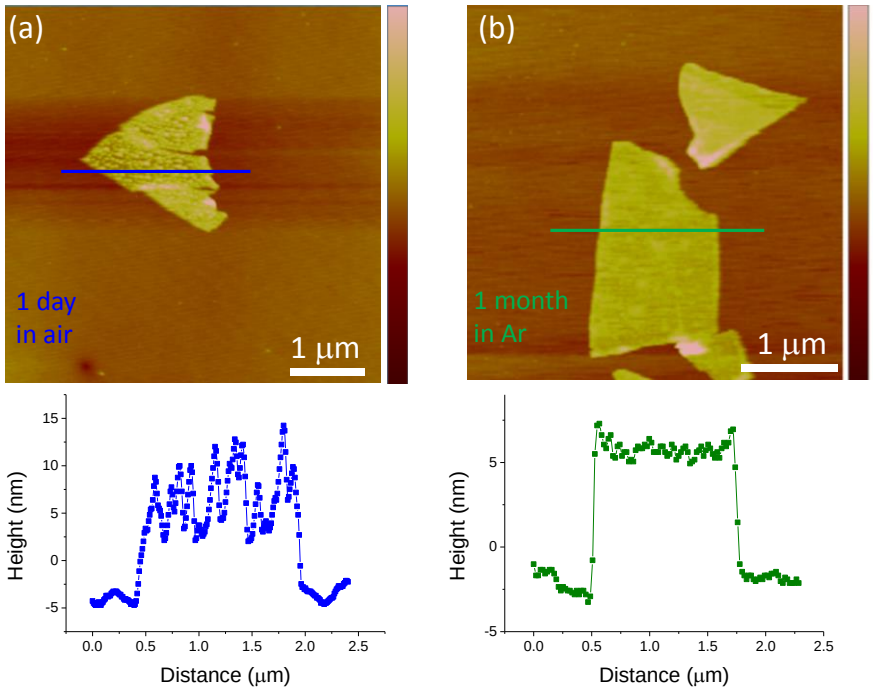
Supplementary Figure S6 Raman spectra of bulk (black), thick flake (red), and thin flake (blue) of b-$As_{0.83}P_{0.17}$. The Raman spectrum of pure b-P (i.e., b-As_0P_1) is also shown as green curve for comparison. The spectra were vertically shifted for clarify.



Supplementary Figure S7 Calculated Raman spectra of black phosphorus (b-P, black), black arsenic (b-As, red), and black arsenic-phosphorus (b-$As_{0.5}P_{0.5}$, blue, model contains arsenic-phosphorus bonds only). The calculation method is PBE-d2.

Supplementary Table S2 Calculated Raman shift for b-P, b-As, and b-AsP

Modes	A_g^2 (cm^{-1})	B_{3g}	B_{2g}	A_g^1	B_{2g}	B_{1g}
b-P	458	422	417	365	232	195
	A_g^2	B_{2g}	A_g^1	B_{3g}	B_{2g}	B_{1g}
b-As	273	241	237	237	121	103
	B_1	A_1	B_1	A_2	B_2	A_1
b-$As_{0.5}P_{0.5}$	372	350	324	320	310	302



Supplementary Figure S8 Stability of b-$As_{0.83}P_{0.17}$ samples. (a) AFM image of a flake after air exposure for 1 day. (b) AFM image of another flake after stored in Ar glove box for about 1 month. The vertical bars are 40 nm for both images. The flake thicknesses are ~10 nm for both flakes. The bottom plots show height profile along the blue line in image a and green line in image b. The results show that b-$As_{0.83}P_{0.17}$ flakes underwent severe degradation in air, while remained stable in Ar atmosphere.

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