

2D black arsenic phosphorous

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Citation: J C Liang, Y Hu, L M Ding, and Z Jin, 2D black arsenic phosphorous[J]. *J. Semicond.*, 2024, 45(3), 030201. <https://doi.org/10.1088/1674-4926/45/3/030201>

Since the successful exfoliation of graphene in 2014, two-dimensional (2D) materials have explosively increased in the past few years^[1]. 2D pnictogen materials with intriguing properties beyond graphene are gradually coming into eyesight, such as black phosphorous (BP)^[2], arsenene^[3], antimonene^[4], bismuthine^[5], etc. BP is a star material in 2D materials. It has high carrier mobility and tunable bandgap, and its bandgap locates between that of graphene and transition metal sulfides (TMS), enabling its application in photonic and electronic devices. To further explore the excellent properties of BP and broaden its application, alloying BP with other foreign atoms is an effective strategy to enhance the properties. By alloying BP with different equivalents of arsenic atoms, a series of black arsenic phosphorous (*b*-AsP) can be obtained. It retains the crystal structure of BP but produces tunable bandgap. Thus, many new properties can be found. The pioneering works on *b*-AsP are limited to theoretical calculations and some synthesis methods.

Arsenic phosphorous alloys have been studied since 1980s^[6]. High-quality *b*-AsP crystals were synthesized by chemical vapor transport (CVT) method^[7]. However, layered *b*-AsP came into view in 2015, and it offsets the deficiencies of BP in some respects^[8]. As shown in Fig. 1(a), the arsenic and phosphorus atoms are alternatively distributed with the same valence bond in a single atomic layer of *b*-AsP, forming an orthorhombic lattice with a puckered honeycomb structure. Theoretical calculations predicted that $b\text{-As}_x\text{P}_{1-x}$ can be realized only when $x < 0.83$. Otherwise, the structure of phosphorus-arsenic alloy will be transformed into a gray-arsenic-like structure. The bandgap structure of *b*-AsP is shown in Figs. 1(b) and 1(c), in which the doping of arsenic atoms effectively narrows the bandgap of *b*-AsP. The $b\text{-As}_{0.83}\text{P}_{0.17}$ with the highest arsenic content has a bandgap of 0.15 eV measured from infrared absorption, while the bandgap of BP is 0.3 V. Obviously, the bandgap of *b*-AsP locates at 0.15–0.3 eV. Based on such narrow bandgaps, a series of mid-infrared detectors were fabricated. In 2016, Xie *et al.* demonstrated that monolayer *b*-AsP is a promising donor with a 1.54 eV direct bandgap. Another special feature of *b*-AsP is the high carrier mobility^[9]. As early as 1987, phosphorus-arsenic alloys were found to be superconductive under high pressure^[6]. In 2016, more in-depth research proved that the electron mobility of *b*-AsP could reach $1977 \text{ cm}^2/(\text{V}\cdot\text{s})$ ^[10]. Later, the anisotropic car-

rier migration behavior and bipolar transport properties were reported.

Compared with BP, the dual-composition nature and adjustable ratio make the synthesis of ultrathin *b*-AsP layers much difficult. The CVT method is the most convenient and mature way to prepare high-quality *b*-AsP single crystal (Fig. 1(d)). Unlike BP, the interlayer interactions of *b*-AsP are difficult to overcome by the usual top-down method due to its asymmetric atomic arrangements in the layer. The thinnest 2D *b*-AsP obtained by mechanical exfoliation was reported by Liu *et al.* in 2015^[8]. They prepared 1.3 nm thick *b*-AsP bilayer flake (Figs. 1(e) and 1(f)). However, owing to the impurity and instability of the surface, only 15 nm thick nanosheets were selected for further study of mid-infrared response. The liquid phase exfoliation method can generate a large number of *b*-AsP thin layers, which is suitable for the saturable absorbers (SA) in fiber lasers^[11] (Fig. 2(a)). However, we should note some disadvantages of this method, such as uncontrollable thickness, small lateral scale and many surface defects.

The bottom-up method is the most promising method for preparing monolayer *b*-AsP. With the help of thin-film deposition systems, the synthesis of monolayer *b*-AsP with different element ratios could be realized by precisely controlling the growth temperature and the source material weight ratio. In 2018, Eric *et al.* first synthesized wafer-scale *b*-AsP material with a thickness of 6 nm via molecular beam deposition (MBD), which demonstrates the feasibility of bottom-up synthesis of 2D *b*-AsP materials^[12] (Fig. 2(b)). However, there is still no feasible method to make monolayer *b*-AsP by using bottom-up method. Making monolayer *b*-AsP on a substrate needs to overcome many difficulties. First, a suitable substrate is required to induce the epitaxial growth of monolayer arsenic phosphorous crystals. Second, the decomposition of phosphorus sources and arsenic sources needs to overcome high energy barriers. So far, the research works on monolayer *b*-AsP still stagnate at the stage of theoretical calculations. Breaking through the thickness limit of *b*-AsP materials is still a challenge.

b-AsP has some applications. The air-stable mid-wave infrared photodetector made of *b*-AsP offered a responsivity of 190 mA/W for 3.4 μm incident light^[13] (Figs. 2(c) and 2(d)). Field-effect transistors made of *b*-AsP had a high hole mobility of $307 \text{ cm}^2/(\text{V}\cdot\text{s})$ at a drain voltage of 0.01 V^[14]. Besides, the anisotropic carrier migration behavior and bipolar transport properties of *b*-AsP were also demonstrated by FET devices^[15]. *b*-AsP can also be used as the anode in Li-ion batteries^[16].

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Received 17 JANUARY 2024.

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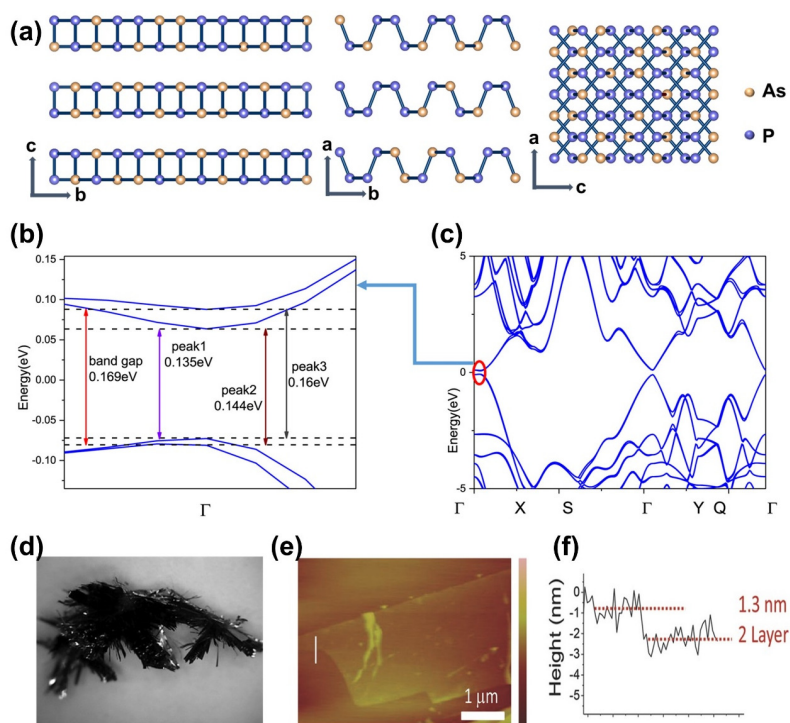


Fig. 1. (Color online) (a) $b\text{-As}_x\text{P}_{1-x}$ crystal. (b) The band structure of multilayer $b\text{-AsP}$. (c) Enlarged image of the energy band in (b), in which the band has been split into four sub-bands. Reproduced with permission^[17], Copyright 2018, IOP Publishing. (d) $b\text{-As}_{0.83}\text{P}_{0.17}$ crystal synthesized by CVT. Reproduced with permission^[7], Copyright 2015, WILEY-VCH. (e) AFM image for an exfoliated bilayer $b\text{-As}_{0.83}\text{P}_{0.17}$ flake. (f) Height profile for the exfoliated bilayer $b\text{-As}_{0.83}\text{P}_{0.17}$ flake with a thickness of ~ 1.3 nm. Reproduced with permission^[8], Copyright 2019, Optical Society of America.

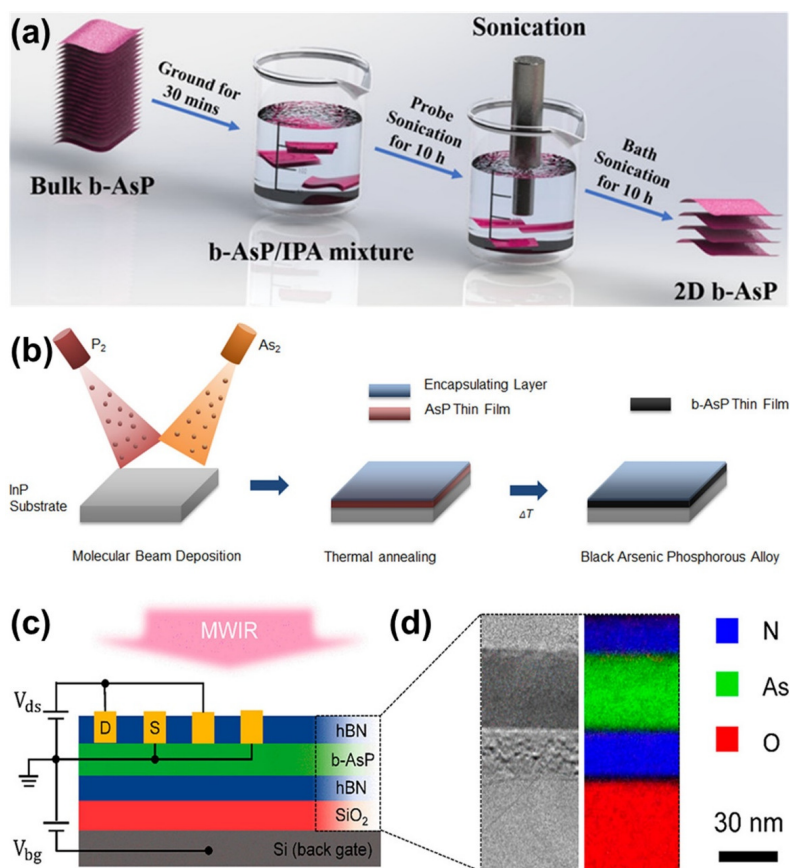


Fig. 2. (Color online) (a) The preparation of 2D $b\text{-AsP}$ nanosheets by the liquid-phase exfoliation method. Reproduced with permission^[11], Copyright 2020, American Chemical Society. (b) The MBD synthesis of $b\text{-AsP}$ alloys. Reproduced with permission^[12], Copyright 2018, American Chemical Society. (c) The $\text{hBN}/b\text{-As}_{0.83}\text{P}_{0.17}/\text{hBN}$ heterostructure photodetector. (d) The cross-section of the device by TEM is shown on the left. The elemental mapping is shown on the right. Reproduced with permission^[13], Copyright 2018, American Chemical Society.

In short, *b*-AsP is a new member of 2D layered pnictogen materials. The property of *b*-AsP changes with As/P ratios. This 2D material may find new applications in the near future.

Acknowledgements

We thank the National Natural Science Foundation of China (22022505 and 21872069), the Fundamental Research Funds for the Central Universities of China (020514380266, 020514380272, and 020514380274), the Scientific and Technological Innovation Special Fund for Carbon Peak and Carbon Neutrality of Jiangsu Province (BK20220008), the Scientific and Technological Achievements Transformation Special Fund of Jiangsu Province (BA2023037), the International Collaboration Research Program of Nanjing City (202201007 and 2022SX00000955), and the Gusu Leading Talent Program of Scientific and Technological Innovation and Entrepreneurship of Wujiang District in Suzhou City (ZXL2021273). L. Ding thanks the National Key Research and Development Program of China (2022YFB3803300, 2023YFE0116800), and Beijing Natural Science Foundation (IS23037).

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