Journal of Semiconductors
(2020) 41, 080402
doi: 10.1088/1674-4926/41/8/080402

A new single-element layered two-dimensional semiconductor: black arsenic

Mianzeng Zhong and Jun He†

Hunan Key Laboratory of Super-Microstructure and Ultrafast Process, School of Physics and Electronics, Central South University, Changsha 410083, China

Citation: M Z Zhong and J He, A new single-element layered two-dimensional semiconductor: black arsenic[J]. *J. Semicond.*, 2020, 41(8), 080402. http://doi.org/10.1088/1674-4926/41/8/080402

The discovery of graphene, the first two-dimensional material with a thickness of an atomic layer, opened the prelude to the development of other atom-thin two-dimensional layered materials. They are considered to be one of the best candidates to extend Moore's law. However, graphene is a zero-bandgap semimetal, which limits its application in logic circuits[1]. In 2014, Zhang's group from Fudan University reported a new type of elemental 2D material — black phosphorus (b-P) with an adjustable bandgap of ~0.34 to ~2 eV. In addition, few-layer b-P exhibits high carrier mobility about 1000 $cm^2V^{-1}s^{-1}$ and large on–off current ratio $>10^5$[2]. It makes possible to achieve the application of 2D materials in logic integrated. However, as research continued, scientists discovered that b-P is quite unstable under atmospheric environments. The few-layer b-P crystals can be seriously degraded within a few minutes, which directly limits its applications in optoelectronic devices[3].

In contrast to b-P, another group-VA element crystal, arsenic, also has the layered structure. Arsenic usually has three allotropes in nature: gray arsenic, yellow arsenic and black arsenic (b-As). Among them, the most stable and common crystalline state is gray arsenic, which has a double-layer structure composed of interlocking six-membered rings similar to blue phosphorus, and it has a metallic electronic structure. The yellow arsenic is an insulator and has a similar crystal structure of white phosphorus. In contrast, there are limited studies on b-As. B-As, like b-P, has an orthorhombic structure with a layered configuration (ε-As, space group Bmab). Inside a single layer, each arsenic atom is covalently bonded with three adjacent atoms to form a puckered honeycomb network, and the adjacent layers are held together by weak van der Waals interactions (Fig. 1(a))[4, 5]. Recent theoretical studies predicted that it has good stability and extraordinary physical properties. In 2015, Zeng's group of Nanjing University of Science and Technology predicted that the atomically thin arsenene is thermodynamically stable, and it has a wide electronic bandgap and an ultra-high carrier mobility through first-principle calculations[6]. After that, several groups also carried out the theoretical studies on their physical properties in detail[7–10]. According to the results, the bandgap of b-As has a strong layer number dependence. The bulk b-As has a direct bandgap of about 0.3 eV. With the number of layers gradually decreases, the bandgap gradually increases; when the thickness decreases to two-layers, it is still a direct band gap. However, when the thickness continues to decrease to single layer, it changes into an indirect band gap semiconductor, and the calculated band gap value of the monolayer b-As is about 0.73–1.403 eV. This uncertainty of the bandgap is mainly derived from the adopted differences in calculation methods and differences in modelling. More interestingly, the theoretical studies predicted that the carrier mobility of b-As can reach $(5.29–12.32) \times 10^3$ $cm^2V^{-1}s^{-1}$; meanwhile, the conductance and carrier mobility have obvious anisotropy in the direction of the armchair and the zigzag directions[11].

More recently, several groups have experimentally stud-

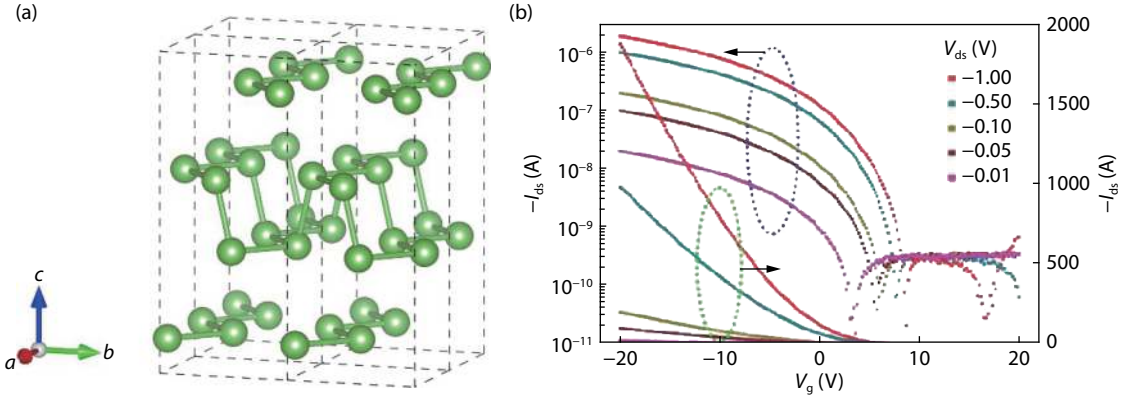

Fig. 1. (Color online) (a) 3D crystal structures of b-As. (b) Transfer characteristics (I_{ds}–V_g) of the monolayer b-As FET[5]. Copyright 2018 John Wiley and Sons.

Correspondence to: J He, junhe@csu.edu.cn

ied the properties of arsenic crystals with different structures. Tsai *et al.* successfully synthesized the multilayer gray arsenic with a rhombohedral structure on InAs substrate using the plasma-assisted process[12]. Chen *et al.* rediscovered the b-As crystals from a natural mineral, and studied its physical properties[4]. The electronic structure of the bulk b-As crystal was measured by the Nano-ARPES. They found that the conductance, carrier mobility, and thermal conductivity of the bulk b-As possesses high anisotropies along AC and ZZ directions. To further explore the application of b-As in electronics and optoelectronics, Zhong *et al.* successfully synthesized the monolayer and few-layer b-As crystals by the traditional micromechanical exfoliation method[5]. The properties of few-layer b-As based field-effect transistors show strong thickness dependence. The obtained highest carrier mobility up to about 59 $cm^2V^{-1}s^{-1}$ and the largest current on/off ratio exceeding 10^5 (Fig. 1(b)). More important, few-layer b-As crystals show a relatively good ambient stability: the few-layer b-As based FET still can work after exposure in air conditions for about one month.

Research on b-As crystals is in the primary stage, and they still face many problems that need to be solved. How to achieve the carrier mobility from experimentally close to the theoretical value? How to improve the environmental stability of crystals? Can we find a suitable method to achieve controllable synthesis of few-layer b-As? All of these issues are obstacles to the development of b-As crystals. We believe that with the deepening of research, all these problems will be solved. B-As crystal will become an important candidate for multi-functional applications in nanoelectronic devices.

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