Manifestation of unexpected semiconducting properties in few-layer orthorhombic arsenene

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In this letter, we demonstrate that few-layer orthorhombic arsenene is an ideal semiconductor. Owing to the layer stacking, multilayer arsenenes always behave as intrinsic direct bandgap semiconductors with gap values of approximately 1 eV. In addition, these bandgaps can be further tuned in its nanoribbons. Based on the so-called acoustic phonon limited approach, the carrier mobilities are predicted to approach as high as several thousand square centimeters per volt–second and to simultaneously exhibit high directional anisotropy. All these characteristics make few-layer arsenene promising for device applications in the semiconductor industry.

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Mainstream logic device applications depend largely on the high performance of semiconducting materials, and graphene, which exhibits superior carrier mobility, seems to be an ideal candidate. On the other hand, the ability to control the electronic properties of a material by an external field requires a moderate electronic bandgap. Unfortunately, the intrinsic dispersion of graphene is gapless, and thus the scientific community continues to search for novel semiconducting materials. Recently, phosphorene, a monolayer of black phosphorus (BP), has emerged as a promising two-dimensional (2D) semiconductor that might go beyond graphene. Phosphorene holds a high carrier mobility in a wide range of $\sim 10^2–10^4$ cm$^2$V$^{-1}$s$^{-1}$. It simultaneously maintains a considerable bandgap of approximately 2.0 eV. At the same time, phosphorene and its bulk counterpart, BP, are stimulating intense fundamental studies owing to their versatile properties. For instance, they exhibit structural transformation at high pressure, low-temperature superconducting properties, highly anisotropic transport, excellent optical and thermoelectric responses, negative Poisson’s ratio, and strain-induced inversion of conduction bands. These unusual properties make phosphorene a potential material for realization of optoelectronic devices in the post-silicon era.

With five sp electrons in the valence state, As sits below and closest to P in the periodic table. The condensed-state substances of these two elements are most likely similar to each other from a chemical point of view. However, up to now, little has been known about As as compared to black phosphorene. On the other hand, following the success of graphene in experiments, various chemical classes of 2D materials initially considered to exist only in the realm of theory have been synthesized. Taking silicene as an example, it was first proposed using an ab initio method. It was then epitaxially grown on both Ag(111) substrates and diboride thin films in experiments. All these studies provide motivation for a timely study of As in low-dimensional forms, which would be promising for future device applications.

This express reports a large bandgap and high carrier mobility simultaneously in few-layer orthorhombic arsenic based on first-principles calculations. A monolayer of As can be called “arsenene”, which is analagous to “graphene” and “phosphorene”. Although the bandgap of the monolayer structure was reported to be indirect, our results surprisingly show that multilayer arsenenes always behave as intrinsic direct bandgap semiconductors, with proper bandgaps of approximately 1 eV. More importantly, the carrier mobilities are predicted to be as high as several thousand square centimeters per volt–second. All these characteristics make few-layer arsenene intriguing for device applications in the semiconductor industry.

The most stable configuration of As allotropes is the rhombohedral (A7) structure (called gray As). This is a metallic phase as bands near the T point and at the L point largely overlap by approximately 0.5 eV. When As is heated at the boiling point of water (370 K), an orthorhombic phase (arsenolamprite) arises, which is similar in structure to that of BP. Because the orthorhombic phase is less dense than the A7 phase, orthorhombic As is a narrow-band semiconductor with a bandgap on the order of 0.3 eV. In reality, little attention has been paid to crystalline As, in particular the orthorhombic phase. The much spacer amorphous As with a gap of 1 eV or more takes up most of the research interest. In this context, we focused our study on orthorhombic As, as shown in Fig. 1(a). The first Brillouin zone of the primitive cell is displayed in Fig. 1(b). To guarantee that the lattice parameters are used accurately, five functionals are taken in realistic simulations (see the online supplementary data at http://stacks.iop.org/APEX/8/055201/mmedia). The optimized structural parameters are summarized in Table I. In comparison with the experimental results, the revPBE–vdW functional yields reasonable lattice parameters that are slightly larger than the experimental ones. By contrast, the functional of Perdew–Brueke–Emzerhof (PBE) without van der Waals (vdW) correction produces a large error along the layer-stacking direction of as much as 4.1%. This means the vdW correction is of crucial importance in determining the interlayer distance. Generally, pure density functional theory (DFT) underestimates the bandgap of a semiconductor because of improper consideration of the Coulomb interaction. The revPBE–vdW functional gives a near-zero bandgap at the Z point (see the online supplementary data at http://stacks.iop.org/APEX/8/055201/mmedia, Fig. 1), contradicting the experimental measurement. To overcome this problem, the HSE06 hybrid functional is utilized and the resultant band structure is displayed in Fig. 1(c). The figure clearly shows that orthorhombic As is an intrinsic direct bandgap semiconductor with a bandgap of approximately 0.39 eV, which is comparable to the experimental value.

At the Z point, one valence band (VB) and one conduction band (CB) near the Fermi level disperse quite strongly along the Z–Q and Z–T directions [Fig. 1(c)]. As a result, very small effective masses of carriers can be highly expected. Based on the nearly free electron model, the effective mass of a carrier can be evaluated as $m^* = \hbar^2/(\partial^2 E / \partial k^2)$, with $\hbar$, $E$, and $k$...
being Planck’s constant divided by $2\pi$, the band energy, and the crystal momentum, respectively. Using the above equation, almost equal effective masses of 0.13 $m_0$ (where $m_0$ is the free-electron mass) are obtained for both electrons and holes along the Z−Q direction, whereas those along the Z−Γ direction are smaller (0.10 $m_0$) for electrons and larger (0.26 $m_0$) for holes. Relatively larger values are found along the Z−Γ−A′ direction, where the carrier effective masses are 1.26 $m_0$ and 1.70 $m_0$ for electrons and holes, respectively. All these values are consistent with the experimental report. Thus, such small effective masses obtained for orthorhombic As would set a crucial precondition for few-layer arsenene to exhibit a high carrier mobility, as discussed below.

In principle, arsenene can be fabricated by mechanically isolating the orthorhombic bulk counterpart. Here, we validate it by using first-principles calculations, as shown in Fig. 2(a). Arsenene is indeed thermally stable since no imaginary frequency is observed in its phonon dispersion curve (see the online supplementary data at http://stacks.iop.org/APEX/8/055201/mmedia, Fig. 2). In addition, we also checked its stability from the cohesive energy. Although the cohesive energy of the gray As is more stable by approximately 0.15 eV/atom than that of orthorhombic As, a relatively smaller difference of approximately 0.01 eV/atom is obtained for their respective monolayers, indicating the possible existence of orthorhombic arsenene in the experiments. The lattice parameters $a = 4.80$ Å and $b = 3.68$ Å are obtained for arsenene. As compared with the bulk phase, the lattice constant $a$ is elongated by 2.8% in arsenene, whereas $b$ is shortened by 0.8%. As a result, the bond angles $\theta_1$ and $\theta_2$ are changed accordingly, i.e., $\theta_1 = 100.92^\circ$ and $\theta_2 = 94.52^\circ$, leaving the bond lengths $R_1 = 2.49$ Å slightly decreased and $R_2 = 2.51$ Å nearly unchanged. Such modification in the structural parameters stems from the lack of interlayer interactions when transitioning from bulk to monolayer. However, the effect on electronic structure is significant, as discussed below.

The calculated band structure of arsenene is displayed in Fig. 2. It is interesting to note that arsenene is an indirect semiconductor with a bandgap of ~0.90 eV since the valence band maximum (VBM) and the conduction band minimum (CBM) occur at different crystal points $\Gamma$ and $\Gamma$. Our results are consistent with those reported by Kamal and Ezawa, except that our gap value is slightly larger by ~0.05–0.07 eV. This originates from the different structural parameters obtained from different functionals. The indirect bandgap in arsenene contrasts strikingly with phosphorene, which has a direct bandgap. To unveil this difference, we carefully checked the structural parameters between them. Two main changes occur for arsenene: (i) The bond lengths $R_1$ and $R_2$ increase by ~0.2 Å in arsenene, indicating the relatively weak covalent bonding of As–As compared with P–P; to maintain the stability, (ii) the bond angles $\theta_1$ and $\theta_2$ shrink by 1.48–2.59°. We emphasize that this is a natural consequence as the heavier As atom exhibits weaker covalent characteristics as compared to P. This is also confirmed in the similar monolayer of antimony, where the structural parameters change significantly and VB at the $x'$ point significantly exceeds that at the $\Gamma$ point (not shown for brevity), claiming an obvious indirect bandgap. To further understand the underlying physics, we mapped out the respective wavefunctions of VB and CB at the $x'$ and $\Gamma$ points, as shown in Fig. 2(c). Our findings are very insightful. For VBs, the bonding feature appears between the atoms linked by $R_1$ at the $\Gamma$ point [see the first panel of Fig. 2(c)], whereas that at the $x'$ point occurs between the atoms connected by $R_2$ [see the third panel of Fig. 2(c)]. The mutual competition between them dictates the VBM. Obviously, in the case of arsenene, VB at the $x'$ point forms a weaker covalent bond and thus occupies the higher energy level. The opposite situation is found for CBs at the $x'$ and $\Gamma$ points. This is why arsenene is an indirect semiconductor.

Based on the above understanding, a bandgap transition from indirect to direct by changing $R_1$ and $R_2$ is expected. Layer-stacking is demonstrated to be an effective approach in this study. With the addition of more layers, additional bands are introduced near the Fermi energy level. For example, at the $\Gamma$ point, the bands VB1 and CB2 appear, as shown in Fig. 2(d). Owing to the overlap of wavefunctions, VB1 and VB2 (CB1 and CB2) contribute to the bonding and antibonding states, respectively. However, the energy separations between those states are entirely different. At the $\Gamma$ point, the energy separation reaches as high as ~1 eV for the conduction

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**Table 1.** The optimized lattice constants ($a$, $b$, and $c$) and structural parameters ($R_1$, $R_2$, $\theta_1$, and $\theta_2$) for the orthorhombic bulk As under five functionals. The corresponding values in the experiment are given as well.

| Functional          | $a$ (Å) | $b$ (Å) | $c$ (Å) | $R_1$ (Å) | $R_2$ (Å) | $\theta_1$ (°) | $\theta_2$ (°) |
|---------------------|---------|---------|---------|-----------|-----------|----------------|----------------|
| Expt. (Ref. 22)     | 4.47    | 3.65    | 11.00   | 2.48      | 2.49      | 98.5           | 94.1           |
| PBE                 | 4.67    | 3.71    | 11.45   | 2.51      | 2.52      | 99.8           | 95.08          |
| revPBE–vdW           | 4.67    | 3.71    | 11.07   | 2.50      | 2.51      | 100.01         | 95.29          |
| optPBE–vdW           | 4.38    | 3.72    | 10.91   | 2.49      | 2.50      | 98.03          | 96.30          |
| optB88–vdW           | 4.26    | 3.73    | 10.88   | 2.48      | 2.49      | 97.29          | 96.83          |
| optB86b–vdW          | 4.08    | 3.74    | 10.79   | 2.47      | 2.50      | 95.90          | 96.86          |
bands and approximately 0.5 eV for the valence bands, which are obviously much larger than those at the x’ point. This is because the p local orbital directly couples with the neighboring layer at the Γ point but not at the x’ point. Such an overlap of interlayer p local orbitals not only decreases the bonding length R1, it also pushes the CB1 and VB2 bands closer to each other as compared to those at the x’ point. Thus, an indirect–direct bandgap transition is obtained for bilayers or multilayers, extending the potential application of few-layer arsenene. This also explains why orthorhombic bulk As is a direct bandgap semiconductor. Another e

layer arsenene. This also explains why orthorhombic bulk As

is a direct bandgap semiconductor. Another effect of layer-stacking is reflected in the decrease of bandgap, sharing the same mechanism proposed in our previous work.27) As the number of layers increases, the fundamental bandgap decreases from 0.97 eV for the monolayer to 0.16 eV for six layers, as shown in Fig. 2(e). These bandgap values follow the exponential decay law (see the fitting dashed line). The limit bandgap obtained by extrapolation is approximately 0.16 eV [marked as Inf in Fig. 2(e)], which is larger than that obtained for the bulk calculation. This originates from the structural adjustment from bulk to few-layer, as suggested by the changed structural parameters in few-layer arsenene (see the online supplementary data at http://stacks.iop.org/APEX/8/055201/mmedia, Table I). More accurate bandgaps of few-layer arsenene are obtained by the HSE06 hybrid functional, as shown by the red circles and dashed line in Fig. 2(e).

Although arsenene is of fundamental importance, practical applications involving this material may require only a small piece of it or a flake, not a large amount. In this respect, arsenene ribbons on a nanometer scale with a well-defined shape may be crucial for device applications. It has been found that several armchair arsenene nanoribbons possess improved and tunable direct bandgaps following the quantum confinement effect (see the online supplementary data at http://stacks.iop.org/APEX/8/055201/mmedia, Fig. 3, for more details).

In the following, we restrict our attention to carrier mobilities in few-layer arsenene. Based on the so-called acoustic phonon limited approach,29) the carrier mobility is given as

\[
\mu_{2D} = \frac{e\hbar^2 C_{2D}}{k_B T m^* (E_i)^2}.
\]

where e is the electron charge, \( \hbar \) is Planck’s constant divided by 2\( \pi \), \( k_B \) is Boltzmann’s constant, and T is the temperature. \( m^* \) (\( m_0^* \) or \( m_0^\perp \)) is the effective mass in the transport direction and \( m_0 \) is the averaged effective mass determined by \( \frac{1}{m_0} = \frac{1}{m_0^*} + \frac{1}{m_0^\perp} \). \( E_i \) is the deformation potential constant of VBM for holes or CBM for electrons along the transport direction, defined by \( E_i = \Delta V_l / (\Delta l / l_0) \). Here, \( \Delta V_l \) is the energy change of the \( l \)th band under proper cell compression and dilatation, \( l_0 \) is the lattice constant in the transport direction, and \( \Delta l \) is the deformation of \( l_0 \). The elastic modulus \( C_{2D} \) of the longitudinal strain in the propagation directions (both x and y) of the longitudinal acoustic wave is given by \( E = E_0 \), \( S_0 = C_{2D} (\Delta l / l_0)^2 / 2 \), where \( E \) is the total energy and \( S_0 \) is the lattice volume at equilibrium for a 2D system.

Besides the effective mass, two other properties of the deformation potential and the 2D elastic modulus are also involved in the calculation of carrier mobility, as described in Eq. (1). First-principles calculations based on the revPBE–vdW functional are taken to yield these properties, together with the carrier mobility, as illustrated in Table II. Since the VBM of the monolayer is located at the x’ point but not at the Γ point [Fig. 2(b)], we neglect the discussion of electron mobility as listed in Table II for the monolayer. In the bilayer, the electron mobility exhibits a value of (0.26–0.40) × 10^3 cm^2 V^{-1} s^{-1} along the Γ–X direction, which is approximately four times higher than that along the Γ–Y direction. This triggers a strongly directional anisotropy, mainly caused by the relatively small effective mass and deformation potential. In addition, as the number of layers further increases, the electron mobility monotonically increases and reaches...
2.17–2.66 (0.45–0.51) \times 10^3 \text{cm}^2 \text{V}^{-1} \text{s}^{-1} along the \Gamma–X (Y) direction at six layers. The directional anisotropy remains nearly unchanged. In the case of holes, in a monolayer, the hole mobility of the \Gamma–Y direction is slightly larger than that of the \Gamma–X direction. However, in a multilayer structure, the \Gamma–X direction holds much higher hole mobilities, reaching as high as \sim 4 \times 10^3 \text{cm}^2 \text{V}^{-1} \text{s}^{-1} at five layers. This is a huge value if one remembers typical carrier mobilities of 200–500 \text{cm}^2 \text{V}^{-1} \text{s}^{-1} in MoS_2.30) Such a high hole mobility in few-layer arsenene benefits from the smaller deformation potential. The deformation potential reaches as low as \sim 1.7 \text{eV} at four layers, which is approximately two times smaller than the value of 3.9 \text{eV} in MoS_2.30) It is also noticed that approximately 1–2 orders of magnitude smaller hole mobilities are obtained along the \Gamma–Y direction, resulting in a large directional anisotropy of hole mobility. It is well known that the higher carrier mobility plays a crucial role in the performance of devices. Thus, few-layer arsenene structures with proper bandgaps and high carrier mobilities are potential materials for practical applications in the semiconductor industry.

In conclusion, we have investigated the electronic properties of few-layer arsenene from first-principles calculations. Our results show that few-layer arsenene possesses carrier mobilities as high as several thousand square centimeters per volt–second, which exhibits a high anisotropy. Combining such superior carrier mobility with tunable bandgaps of approximately 1 eV, few-layer arsenene is an ideal semiconductor material for device applications in the semiconducting industry.

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Table II. Carrier mobilities in few-layer arsenene. Types “e” and “h” denote the “electron” and “hole”, respectively. \( m^*(m^*) \) (in units of \( m_0 \), with \( m_0 \) being the static electron mass) represents the effective mass along the \( \Gamma–X (Y) \) direction. \( E_{1\text{G}} (E_{1\text{L}}) \) (in units of eV) is the deformation potential along the \( \Gamma \) point along the \( \Gamma–X (Y) \) direction. \( C_{\text{\parallel 2D}} \) and \( C_{\text{\perp 2D}} \) (in units of \( 10^3 \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \)) along the \( \Gamma–X (Y) \) direction was calculated by using Eq. (1), together with \( T = 300 \text{K} \).

| Type | \( N_L \) | \( m^*/m_0 \) | \( m^*/m_0 \) | \( E_{1\text{G}} \) | \( E_{1\text{L}} \) | \( C_{\text{\parallel 2D}} \) | \( C_{\text{\perp 2D}} \) | \( \mu_{\text{\parallel 2D}} \) | \( \mu_{\text{\perp 2D}} \) |
|------|--------|------------|------------|--------|--------|------------|------------|--------|--------|
| e 1  | 0.23   | 1.22       | 0.81 ± 0.17| 3.74 ± 0.04| 28.99  | 74.69      | 5.29–12.32| 0.17–0.18|        |
| e 2  | 0.25   | 1.38       | 5.56 ± 0.68| 6.75 ± 0.56| 56.74  | 147.35     | 0.26–0.40| 0.07–0.11|        |
| e 3  | 0.33   | 1.39       | 3.67 ± 0.21| 5.21 ± 0.12| 83.98  | 218.55     | 0.92–1.16| 0.21–0.23|        |
| e 4  | 0.22   | 1.40       | 4.24 ± 0.20| 5.24 ± 0.05| 109.5  | 266.64     | 0.97–1.18| 0.26–0.27|        |
| e 5  | 0.19   | 1.41       | 5.13 ± 0.17| 5.38 ± 0.11| 136.90 | 362.37     | 1.06–1.21| 0.35–0.38|        |
| e 6  | 0.18   | 1.41       | 4.17 ± 0.11| 5.24 ± 0.17| 164.61 | 436.75     | 2.17–2.66| 0.45–0.51|        |
| h 1  | 0.19   | 1.77       | 4.06 ± 0.05| 1.88 ± 0.05| 28.99  | 74.69      | 0.33–0.35| 0.42–0.47|        |
| h 2  | 0.21   | 4.49       | 1.96 ± 0.24| 2.01 ± 0.06| 56.74  | 147.35     | 1.13–1.89| 0.13–0.14|        |
| h 3  | 0.20   | 7.54       | 2.71 ± 0.09| 5.15 ± 0.09| 83.98  | 218.55     | 0.93–1.08| 0.08–0.019|       |
| h 4  | 0.20   | 10.08      | 2.43 ± 0.04| 5.53 ± 0.05| 109.5  | 266.64     | 1.35–1.44| 0.012–0.013|      |
| h 5  | 0.18   | 11.44      | 1.70 ± 0.05| 5.79 ± 0.04| 136.90 | 362.37     | 3.68–4.19| 0.013–0.014|      |
| h 6  | 0.16   | 11.44      | 3.09 ± 0.21| 6.36 ± 0.11| 164.61 | 436.75     | 1.49–1.94| 0.014–0.015|      |