Computational Materials Science 150 (2018) 314–320

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

New two-dimensional allotrope of single layer IV-V semiconductor XBi (X = Si, Ge, Sn)

Chunyan Xu, Mingfeng Zhu, Jianmin Zhang, Wenquan Wang, Yu Yan*

Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), Department of Physics, Jilin University, Changchun 130012, China

ARTICLE INFO

Keywords:
Two dimensional semiconductor
First-principles
Strain
Band structure

ABSTRACT

Using first-principles calculations based on density functional theory, we propose a new two dimensional (2D) tetragonal allotrope of single layer IV-V semiconductor XBi (X = Si, Ge, Sn), which consists of repeated square and octagon rings. The calculated cohesive energy, phonon dispersion and ab-initio molecular dynamics simulations indicate that 2D tetragonal XBi (X = Si, Ge, Sn) are stable at room temperature and have potential to be synthesized in the future. Furthermore, due to the strong spin–orbit coupling (SOC) of Bi atom, the inclusion of SOC alters character of the fundamental band gaps of 2D tetragonal XBi (X = Si, Ge, Sn) and decreases their band gaps. When SOC is include, the electronic band structures show that 2D tetragonal SiBi is a direct band gap semiconductor, while 2D tetragonal GeBi and SnBi are indirect band gap semiconductors. Interestingly, the strain can induce 2D tetragonal XBi (X = Si, Ge, Sn) to undergo a direct to indirect band gap transition or an indirect band gap semiconductor to metal transformation.

1. Introduction

Graphene, a single layer of covalently-bound sp^2-hybridised carbon atoms with honeycomb lattice structure, has attracted much interest due to its extraordinary properties [1–6]. But the absence of band gap in pristine graphene hinders its practical applications in nano-electronic devices. Consequently, a great deal of effort has been devoted to search for atomically thin two-dimensional (2D) semiconductor and many 2D materials with a natural band gap have been proposed by theoretical calculation [7–12]. Recently, several typical 2D semiconductors, such as single- and few-layer black phosphorus [13–16], single layer transition metal dichalcogenides [17,18] and trichacogenides [19–21], and single- and few-layer group III monochalcogenide GaSe [22,23], GaS [24], GaTe [25,26] and InSe [27,28], have been experimentally fabricated. In the search of the 2D semiconductors, Miao et al. [29] used electron-counting rule to propose that if each Mo atom in hexagonal MoS_2 is replaced by two covalently bonded group III elements, the electrons will occupy all the bonding states and leave all antibonding states empty, forming a family of 2D III − VI semiconductors. By extending this structure type to other main group elements, it has been proposed that group IV elements can form similar 2D semiconductors with group V elements [29–32], and group II elements can form 2D semiconductors with group VII elements [29]. Different to MoS_2, which greatly favors the inversion asymmetric structure, these proposed 2D semiconductors can assume both the inversion asymmetric and symmetric structures, respectively. Among these proposed 2D semiconductors, the formation energy of 2D IV-V semiconductors XBi (X = Si, Ge, Sn) relative to their three-dimensional (3D) counterparts are almost equal to or lower than that of single layer SnSe [29]. Recently, a single layer SnSe has been successfully synthesized as a free-standing layer [33,34], thus proposed 2D IV-V semiconductors XBi (X = Si, Ge, Sn) have potential to be synthesized in the future.

On the other hand, the single layer allotropes of many 2D materials have been predicted to be stable and were found to possess fantastic physical properties even superior to their original counterparts. Among the possible single layer allotropes of carbon, it was predicted that a tetragonal graphene [35–43], which consists of repeated square and octagon rings, is stable and exhibits a semimetal with the Fermi surface consisting of one hole and one electron pocket [36]. Inspired by the atomic structures of grain boundaries in normal transition metal dichalcogenides MT_2 (M = Mo, W, Nb; T = S, Se, Te), a tetragonal allotrope of single layer MT_2 (M = Mo, W, Nb; T = S, Se, Te), which consists of repeated square and octagon rings, was theoretically found [44–50]. Interestingly, it was reported that this MoS_2 allotrope possesses both massless Dirac fermions and heavy fermions [44]. Apart from stable single-layer puckered and buckled honeycomb lattice structures of group V elements (P, As, Sb and Bi), it was theoretically proposed that these elements can also form a stable 2D tetragonal allotrope composed of buckled square and octagon rings [51–55], and they are semiconductors with different band gaps from single-layer

---

* Corresponding author.
E-mail address: yanyu@jlu.edu.cn (Y. Yan).

https://doi.org/10.1016/j.commatsci.2018.04.016
Received 7 November 2017; Received in revised form 30 March 2018; Accepted 8 April 2018

puckered and buckled honeycomb counterparts. Remarkably, tetragonal Bi allotrope was predicted to be 2D topological insulator with a sizable band gap about 0.41 eV [51,55], which is larger than the gap of the Bi (1 1 1) bilayer and is the largest among reported elemental 2D topological insulators. Therefore, the new allotrope of 2D materials provides a good opportunity for exploring unique physical properties of 2D materials.

At present, the allotrope of single layer IV-V semiconductors XBi (X = Si, Ge, Sn) have not been explored. In this work, we propose a new 2D tetragonal allotrope of single layer XBi (X = Si, Ge, Sn), which consists of repeated square and octagon rings, and investigate their stability, structure and electronic properties by using first-principle calculations. Furthermore, we also explore the effect of strain on the structure and electronic properties of 2D tetragonal XBi (X = Si, Ge, Sn) allotrope.

2. Computational details

Our first-principle calculations were performed by using the projector-augmented wave (PAW) method as implemented in Vienna ab initio Simulation Package (VASP) [56–60]. The Perdew-Burke-Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA) was adopted to describe the exchange-correlation energy [61]. The atomic positions and lattice constant were fully relaxed in structural optimizations using the conjugate gradient method, until the residual force on each atom was less than 0.01 eV/Å and total energy was converged to 1×10^{-7} eV. It was known that GGA functional normally underestimates the band gaps of semiconductors, while the nonlocal Heyd-Scuseria-Ernzerhof (HSE06) [62] hybrid functional can significantly improve the result by using GGA [53,63]. Therefore, we calculated the electronic band structure of the unstrained 2D tetragonal XBi (X = Si, Ge, Sn) by using HSE06 hybrid functional as implemented in the VASP to check the results by using GGA. Spin-orbit coupling (SOC) was taken into account in the self-consistent calculation of electronic band structure. The energy cutoff for the plane wave basis was set to 500 eV. The convergence of the total energy of 2D tetragonal XBi (X = Si, Ge, Sn) with respect to the number of k-point were tested and the results shown that a 9 × 9 × 1 k-point mesh was sufficient to converge the total energy to required accuracy. Since structural optimization was computational more involved than self-consistent calculation, a 9 × 9 × 1 k-point mesh was employed for structural optimization and 15 × 15 × 1 k-point mesh was used for self-consistent calculations with and without SOC to obtain more accurate results. A vacuum space of more than 20 Å was adopted in the direction perpendicular to the plane of 2D tetragonal XBi (X = Si, Ge, Sn) to eliminate the interaction between periodic replicas. Moreover, to examine the thermal stability of 2D tetragonal XBi (X = Si, Ge, Sn), ab initio molecular dynamics (MD) simulations at 300 K were performed with the VASP. For the MD simulations, the canonical ensemble (*NVT*) was adopted and the simulation time was limited to 10.0 ps with a time step of 1.0 fs. The Nosé-Hoover method was applied to control the temperature at 300 K. Additionally, Phonon dispersion curves were obtained by using the PHONOPY code [64] based on the finite displacement method from VASP calculations.

3. Results and discussion

Fig. 1(a) and (b) display the optimized crystal structure of 2D tetragonal XBi (X = Si, Ge, Sn). It can be seen from Fig. 1 that the lattice of 2D tetragonal XBi (X = Si, Ge, Sn) can be viewed as repeated square and octagon rings in both *x* and *y* directions and the unit cell comprises eight X and eight Bi atoms. Similar to their original counterpart, 2D tetragonal XBi (X = Si, Ge, Sn) can be also viewed as four sublayers stacking in the order of Bi-X-X-Bi, wherein two covalently bonded X atoms are sandwiched between layers of Bi atom, as shown in Fig. 1(b), and each X atom is bound to three neighboring Bi atoms. The optimized structural parameters, including lattice constant (a_0), the X-Bi bond length that constitutes the square (l_1), the X-Bi bond length that connects two squares (l_2), the X-X bond length (l_3) and the vertical distance between top and bottom Bi layers (d), are listed in Table 1. Similar to tetragonal graphene [36] and MoS_2 [44], the X-Bi bond length that constitutes the square is slightly larger than that connecting the squares. Notably, all of the listed structural parameters in Table 1 increase with increase of the atomic indices of X from Si to Sn.

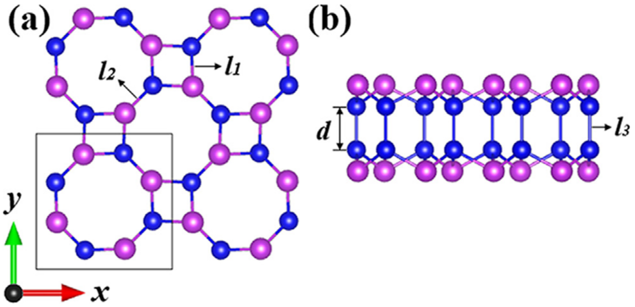

Fig. 1. Top view (a) and side view (b) of crystal structure of 2D tetragonal XBi (X = Si, Ge, Sn). The unit cell is denoted by solid line square. l_1 represents the X-Bi bond length that constitutes the square. l_2 represents the X-Bi bond length that connects two squares. l_3 represents the X-X bond length, and d represents the vertical distance between top and bottom Bi layers. The pink and blue balls indicate Bi and X (X = Si, Ge, Sn) atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Cohesive energy (E_c), lattice constant (a_0), X-Bi (X = Si, Ge and Sn) bond lengths (l_1 and l_2), X-X (X = Si, Ge and Sn) bond length (l_3) and the vertical distance between top and bottom Bi layers (d) of 2D tetragonal XBi (X = Si, Ge, Sn).

System	E_c (eV/atom)	a_0 (Å)	l_1 (Å)	l_2 (Å)	l_3 (Å)	d (Å)
SiBi	3.227	8.198	2.740	2.718	2.351	4.941
GeBi	2.896	8.406	2.805	2.777	2.495	5.128
SnBi	2.697	8.910	2.977	2.951	2.864	5.680

In order to examine the stability and formation possibility of 2D tetragonal XBi (X = Si, Ge, Sn), we calculate the cohesive energy of 2D tetragonal XBi and corresponding 2D allotropes from the following equation

$$E_c = (nE_X + nE_{Bi} - E_{XBi})/2n$$

where E_{XBi}, E_X and E_{Bi} are the energy of unit cell of 2D tetragonal XBi (X = Si, Ge, Sn) (or corresponding 2D allotropes), one free X atom and one free Bi atom, respectively. n is the number of X or Bi atoms in the unit cell. As listed in Table 1, the calculated cohesive energies for 2D tetragonal SiBi, GeBi and SnBi are 3.227, 2.896 and 2.697 eV/atom, respectively, which are almost equal to 3.30 eV/atom for phosphorene, 3.277 eV/atom for single layer SnSe and 2.81 eV/atom for single layer GaSe and are slightly larger than 2.57 eV/atom for single layer InSe [10,65,66], implying that 2D tetragonal XBi (X = Si, Ge, Sn) are stable. Recently single layer phosphorene [15,16], GaSe [22,23], SnSe [33,34] and InSe [27] have already been synthesized, thus 2D tetragonal SiBi, GeBi and SnBi have potential to be synthesized in the future. Also the energy differences between 2D tetragonal XBi (X = Si, Ge, Sn) and the corresponding 2D allotrope are about 0.101, 0.103 and 0.094 eV/atom for 2D tetragonal SiBi, GeBi and SnBi, respectively, which are not only smaller than that between 2D tetragonal graphene and its 2D allotrope [35–37,41] but also smaller than that between tetragonal transition metal dichalcogenides MT_2 (M = Mo, W; T = S, Se) and the corresponding 2D allotrope [50]. Furthermore, the dynamical and thermal stabilities of 2D tetragonal XBi (X = Si, Ge, Sn) are investigated by performing phonon dispersion calculations and Ab initio MD