Full Length Article

Characterization of point defects in monolayer arsenene

Xiongyi Liang [a], Siu-Pang Ng [a], Ning Ding [a,b], Chi-Man Lawrence Wu [a,b,*]

[a] Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong SAR, People's Republic of China
[b] Key Laboratory for Applied Technology of Sophisticated Analytical Instruments, Shandong Academy of Sciences, Qilu University of Technology, Jinan 250014, People's Republic of China

ABSTRACT

Topological defects that are inevitably found in 2D materials can dramatically affect their properties. Using density functional theory (DFT) calculations and *ab initio* molecular dynamics (AIMD) method, the structural, thermodynamic, electronic and magnetic properties of six types of typical point defects in arsenene, i.e. the Stone-Wales defect, single and double vacancies and adatoms, were systemically studied. It was found that these defects were all more easily generated in arsenene with lower formation energies than those with graphene and silicene. Stone-Wales defects can be transformed from pristine arsenene by overcoming a barrier of 2.19 eV and single vacancy defects tend to coalesce into double vacancy defects by diffusion. However, a type of adatom defect does not exhibit kinetic stability at room temperature. In addition, SV defects and another type of adatom defect can remarkably affect the electronic and magnetic properties of arsenene, e.g. they can introduce localized states near the Fermi level, as well as a strongly local magnetic moment due to dangling bond and unpaired electron. Furthermore, the simulated scanning tunneling microscopy (STM) and Raman spectroscopy were computed and the types of point defects can be fully characterized by correlating the STM images and Raman spectra to the defective atomistic structures. The results provide significant insights to the effect of defects in arsenene for potential applications, as well as identifications of two helpful tools (STM and Raman spectroscopy) to distinguish the type of defects in arsenene for future experiments.

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1. Introduction

Two-dimensional (2D) atom-thick materials [1,2] such as graphene [3], silicene [4], hexagonal boron nitride (*h*-BN) [5], transition metal dichalcogenides (TMDs) [6] and phosphorene [7] have attracted numerous scientific interests due to their extraordinary electronic, magnetic, optical and chemical properties. In particular, although graphene shows excellent carrier mobility due to free electrons on its surfaces, the zero band gap nature limits its applications in optoelectronic devices and transistors. Silicene and germanene [8] (i.e. a single layer of germanium) also faces the same restriction, which has novel electronic properties and periodically buckled topology..

Recently, a new 2D material, arsenene (i.e. a monolayer of grey arsenic), has been theoretically predicted [9,10]. The results reveal that monolayer arsenene is kinetically stable and possible to be isolated from bulk arsenic. In addition, arsenene exhibits proper large band gap and tunable electronic band structures under

biaxial strain, which provides feasibility of applications in arsenene-based transistors, optoelectronic devices operating under the blue and ultraviolet range or mechanical sensors due to its strain sensitive band gap [11–13].

It is well known that the defects, especially point defect, can dramatically affect the electronic, magnetic, thermodynamic and optical properties of 2D materials, which may significantly influence the performance of arsenene-based devices. However, defects may also enable innovative applications [14–18]. In the fabrication and processing of 2D materials, point defects are inevitable and the most typical point defects found in other 2D materials are Stone-Wales defects (SW), single vacancy (SV), double vacancies (DV), and adatoms (Adatom) [19–22]. For example, Chen et al. found that SV and DV can open a small band gap in graphene [23]. Furthermore, a theoretical study by Wei et al. showed that local magnetic moments can be introduced in phosphorene by SV and the band gap can be widened by DV [21]. Thus, it is very important to understand the effects of these defects on arsenene properties and characterization of defects in arsenene. Such understanding would also help creating ideas to control the defects to prepare new arsenene-based materials with novel properties. In general, in situ scanning tunneling microscopy (STM) [24–27] and Raman spectroscopy

[28–31] are the most widely used and well-established techniques to investigate the atomistic structure of 2D materials and identify the topological defects. It would therefore be useful to demonstrate how these two techniques can characterize arsenene defects.

In this work, structural, electronic, magnetic and thermodynamics properties of a series of typical point defects in arsenene, such as SW, SV, DV and adatom defects, were systematically studied using density functional theory (DFT) and Car–Parrinello molecular dynamics (CPMD). The formation energies and cohesive energies of these defects were calculated. Besides, CPMD simulations at finite temperatures and diffusion barriers were studied to investigate their thermal stabilities. The effects of defects on electronic and magnetic properties were also discussed. STM images were predicted, to demonstrate the feasibility of visualizing these point defects with STM. Similarly, Raman spectra were simulated, to show that characterization of these defects in arsenene using Raman spectroscopy is feasible. The results in this study provide fundamental knowledge to defects in arsenene, so as to make good use of these defects. They also serve as guidance for identification of defects in arsenene for future experiments.

2. Computational methods and models

All the first principle calculations were performed using spin-polarized DFT based on ultrasoft-pseudopotentials [32], as implemented in QUANTUM ESPRESSO [33]. Generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional [34] was selected to describe the exchange-correlation interaction. Van der Waals (vdW) interactions were considered using the Grimme's DFT-D2 method [35]. The kinetic energy cutoff for wavefunctions and density were 30 Ry and 240 Ry given by standard solid state pseudopotentials [9,36]. The convergence threshold of 10^{-5} Ry/Borr for total energy and 10^{-4} Ry for total force were used.

First, the primitive cell of arsenene was fully variable-cell relaxed. Then, a 5×5 hexagonal supercell with a sufficiently vacuum slab of 25 Å was built and SW, SVs, DVs and Adatoms were introduced to study the effect of point defects on the properties of arsenene. For sampling the Brillouin zone, Monkhorst-Pack k-point [37,38] was set as $8 \times 8 \times 1$, and a larger $16 \times 16 \times 1$ k-point was used to investigate the electronic properties. As it had been reported that PBE functional would underestimate the band gaps in semiconductors, the hybrid functional Heyd-Scuseria-Ernzerhof (HSE) [39] was employed to obtain more accurate description of the band structure.

Ab initio molecular dynamics (AIMD) calculations, implemented in the Car–Parrinello (CPMD) method [40,41], were performed to explore the thermal stability of defects in arsenene. The electronic structure was also described by the PBE functional with vdW correction. All the CPMD simulations were performed for 3 ps with a time step of 0.1 fs at 300 K and 500 K controlled by the standard Nosé thermostat [42,43]. In addition, climbing-image nudged elastic band (NEB) method [44,45] was used to investigate the diffusion of defects in arsenene. The NEB calculations were performed with a total of 10 images between the initial and final points to search for the diffusion path and energy barrier [46].

3. Results and discussion

3.1. Structures of defective arsenene and the simulated STM images

The optimized atomic structures of the pristine arsenene and six typical point defects in arsenene are shown in Fig. 1. In order to help recognizing these defects with intuitive images for future

experiments, Fig. 1 also represents simulated STM images of pristine and defective arsenene at +1.0 V and −1.0 V bias.

From Fig. 1(a), it is clear that arsenene has honeycomb lattice and buckled structure. The calculated lattice constant, the buckling height, As-As bond length and As-As-As bond angle are 3.60 Å, 1.39 Å, 2.50 Å and 92.04°, respectively, which agree well with previous theoretical reports [9,10,47]. From the predicted STM images of pristine arsenene at both ±1.0 V bias, it is easy to recognize and correlate them with the corresponding atomistic structure. Note that the distribution of dark spots at +1.0 V and bright rings at −1.0 V is regular and symmetrical with a distance of 3.60 Å, which is equal to the lattice constant. In general, due to height variation of As atoms resulted from the buckled structure of the arsenene sheet, only half of the atoms can be clearly observed in the STM images [22].

In order to obtain SW defects in arsenene, two adjacent As atoms were rotated by 90° before structural optimization, and the optimized structure is shown in Fig. 1(b). In the predicted STM images at 1.0 eV, the pattern is asymmetric and there are three bright spots appearing in the defect center, which correspond with the out-of-plane distortion of the SW defect. However, from the predicted STM images at −1.0 eV, only the three out-of-plane distortion atoms can be identified, in which there are only three bright spots in the defect center.

As shown in Fig. 1(c), SV is obtained from structural relaxation of a pristine arsenene that had lost one As atom. It is found that SV is centrosymmetric, where three edge atoms are equivalent and move toward the vacancy center by the same distance. The distance between any two of these three edge atoms is 3.49 Å. Obviously, the STM image at positive bias reveals that SV has three dangling atoms, while the negative bias STM image can also directly show the SV defect in arsenene by missing one spot in an asymmetric spots array.

Two types of DV defects can be observed in arsenene, as shown in Fig. 1(d) and (e). The DV1 defect is formed by two pentagons and one octagon, while the DV2 defect contains three pentagons and three heptagons. These two defects can be mutually transformed by rotating a bond, which will be discussed later. In Fig. 1(d), the STM image of DV1 at + 1.0 V shows four very bright spots, suggesting strongly localized electronic density around this defect, which is similar to that of silicene [22] and phosphorene [21]. In addition, DV1 can be easily recognized at -1.0 V bias. On the other hand, DV2 is easy to distinguish at the positive bias STM image, but not so at negative bias, such that there are only some bright spots around the defect region.

It is noted that there are two adsorption configurations of an As atom on an arsenene surface. One configuration has the As atom located on top of the center of arsenene hexagon, namely Adatom1, while the other structure, which is called Adatom2, has the As atom on top of one of the As atoms. As shown in Fig. 1(f) for Adatom1, the distance between the As adatom and each of the three adjacent atoms is equal to 2.77 Å. Thus, the pattern in the STM images is centrosymmetric and can easily be characterized. On the other hand, for the Adatom2 configuration, the atom in the arsenene immediately below the As adatom slightly moves down and forms a bond with As adatom with a length of 2.32 Å, as shown in Fig. 1(g). Noticeably, the As adatom bond is not perpendicular to the arsenene surface. Nevertheless, the structure is axis-symmetric, which is well recognized in the negative bias STM images.

3.2. The thermodynamic properties and mobility of defective arsenene

To investigate the thermal stability of these defects in arsenene, the formation energies of various defective arsenene are calculated by