Strain and electric field effect on arsenene and antimonene heterobilayers

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Abstract
We investigated the electronic properties of arsenene and antimonene heterobilayer under strain and external electric field by the first-principles calculation method. The appropriate biaxial strain ($\varepsilon = -5\%$) and E-field ($E = -1.0$ and $0.07 \text{ V} \text{ Å}^{-1}$) of As/Sb bilayer convert the heterostructure from semiconductor to metal. The transition is caused by the sensitivity of the interlayer coupling and charge distribution on each layer of As/Sb heterobilayer. With the change of biaxial strain, the alterations of the orbital states in each layer present synchronous tendency. In contrast, the electronic occupation under E-field intensities is mostly contributed by the layer of Sb atoms. It is remarkable that a double-peak curve is occurred in band gaps as the function of intensities when negative E-field applied. The mechanism of tuning band structures affected by strain and electric field is also discussed.

1. Introduction

Since black phosphorus reported, a new two-dimensional (2D) material field constituted by group V element has attracted considerable attention [1]. According to recent researches, arsenene and antimonene manifest indirect semiconductors and significant tuning band gaps under strain and electric field [2]. The strain engineering can tune band structure of graphene/BN bilayer by destroying the symmetry of two carbon sublattices in graphene layer [3]. And a small band gap is opened at K point when applying the vertical electric field in germanene [4]. It is necessary for adjustable band structures in many application areas, such as piezoelectric, field effect, storage and transistor technology [5–12]. The typical structure of arsenene monolayer is low-buckled hexagonal configuration and performs strong interlayer coupling in the As block [13]. It has good chemical and physical stability and tunable electronic properties as a result of exceptional structural characteristics. The hexagonal arsenene can transform to a direct-band-gap semiconductor in a tiny biaxial tensile strain and then convert from normal insulator (NI) to topological insulators (TI) at appropriate large strain [14]. Different from arsenene, because of spin–orbit coupling (SOC) effect, strain-induced band inversion and topological nontriviality in the Sb monolayer are raised [15].

The combination of different two-dimensional semiconductors into bilayer systems is also an effective strategy for investigating the novel physical phenomena and functionalities. Vertical stacking of monolayers to create 2D heterostructures, easier to accomplish experimentally, has opened significant possibilities in material science and device design [16]. These bilayers exhibit the prospective van der Waals behavior, with flexible interlayer coupling and small binding energies. The features of each layer maintain to a certain degree when stacking to the bilayer. For instance, a non-zero band gap is induced in graphene bilayer by applying electric field to break the inversion symmetric of the two layers [17]. The research on graphene/black phosphorus suggests that structural and chemical degradation of each layer in the heterostructure still maintain its major electronic characteristics and the carrier dynamics and optical properties of BP can be tuned by the active graphene layer [18].
Motivated by these, we established an arsenene and antimonene vdW heterostructure by stacking the As and Sb monolayers in the form of pattern AB to investigate the extraordinary properties and its mechanism. Appropriate biaxial strain and external electric field are applied on the heterobilayer to modify the electronic properties. The novel characteristics of tuning band structures are revealed in our research for potential applications in semiconductor devices.

2. Calculation method

The electronic properties of arsenene/antimonene heterostructures were calculated by the Vienna *ab initio* simulation package (VASP) [19] with Density Functional Theory (DFT) [20]. Electron exchange and correlation were treated using the generalized gradient approximation (GGA) in the form proposed by Perdew, Burke and Ernzerhof (PBE) [21]. The Becke88 optimization (optB88) method was employed to describe the interlayer interaction of arsenene and antimonene atomic sheets [22]. The energy cutoff of the plane wave was set to 280 eV and atomic positions of the As/Sb heterostructure were relaxed until the maximum force on each atom and convergence criteria of energy were less than 0.01 eV Å and $10^{-5}$ eV, respectively. A Monkhorst-Pack mesh of $13 \times 13 \times 3$ k-points was used to sample the Brillouin zone of the unit cell for geometry optimizations [23]. Phonon dispersion was computed by phonopy code with the method of density functional perturbation theory (DFPT) [24]. The vacuum space was set to at least 15 Å to avoid the effects of adjacent structures.

3. Results and discussion

3.1. Structures and electronic properties of As/Sb heterostructure

Arsenene and antimonene have many allotropes, and their layered structures are stable under ambient conditions. Among them, the average binding energies of $\beta$-phase As and Sb monolayers with buckled honeycomb lattice are higher than others [25]. For the purpose of heterostructures construction, it is necessary to match the lattices of two stacking sheets. According to Hao Lu’s research, we establish a pattern AB $\beta$-arsenene and $\beta$-antimonene layered structure different from their research on $8 \times 8$ arsenene monolayer matched with $7 \times 7$ antimonene [26]. The model of arsenene and antimonene heterostructure after geometry fully relaxed is shown in figure 1.

On the arsenene layer, the As-As band length, band angle and bulking height are 2.539 Å, 99.142° and 1.21 Å respectively (2.726 Å, 90.332° and 1.56 Å on the antimonene layer). The lattice constant of the heterostructure is 3.87 Å, with the value between arsenene monolayer (3.76 Å) and antimonene monolayer (4.21 Å), but the band gap of As/Sb bilayer (0.402 eV) is lower than both of them (band gaps are 1.26 eV and 1.08 eV respectively), shown in figure 2 [27]. Relative to the previous single layer structure, the lattice constants of As and Sb layers increase 2.9% and narrow 8.1%, and the As/Sb heterostructure is a narrow-band-gap semiconductor with the possibility of phase transition under the influence of certain conditions [28]. In order to verify the accuracy of the calculation, the band gaps of As or Sb monolayers calculated by several different methods are listed in the table 1 [25]. Tiny differences are caused by computational precision and parameter settings.

Figure 3(a) shows the density of states of As layer, Sb layer and total As/Sb heterostructure. The relaxed As and Sb monolayers have similar structures that leads to the analogous band structures and density of states of As and Sb layers pertaining to the heterostructure, and As and Sb layers have an equal contribution to the band
energy. In order to examine the stability of As/Sb heterostructure, the phonon dispersion spectra is calculated, and no imaginary vibration frequency appeared (shown in figure 3(b)) suggests that the As/Sb bilayer heterostructure has certainly lattice stability [29].

### 3.2. Strain effect on band structures

Strain function is a conventional approach for tuning electronic properties of two-dimensional materials [30]. We apply the biaxial strain by fixing the lattice constant into a series of acceptable values, which are smaller or larger than that of the equilibrium structure, to modify the properties of As/Sb heterostructure and fully relax the atomic positions. The strain is defined as $\varepsilon = (l - l_0) / l_0$, where $l_0$ and $l$ are lattice constants of the original and forced unitcell, respectively [31]. Because of As and Sb buckled configuration, the As/Sb bilayers are more regulatable than planar ones and easier to endure the tolerance caused by applied strain on the As/Sb bilayer structures. Figure 4 shows a series of total energies of strained and unstrained cell change with the increasing biaxial strain from negative (compressive) to positive (tensile) values [32]. It is noticed that at the minimum and maximum strain ($\varepsilon = -5\% \text{ and } 20\%$), the total energies increase by 1.6 eV. Consequently, the flexible warped covalent bonds in As/Sb heterostructures result that the stability of bilayers maintains in this range of strain.

Figure 5(a) shows the electronic band structures of As/Sb heterostructures with biaxial compressive strain from $-7\%$ to $-1\%$. The compressive As/Sb heterostructure is an indirect band gap semiconductor which valence band maximum(VBM) locates near the high-symmetry point $\Gamma$ and conduction band minimum(CBM) is situated in the high-symmetry point $M$. The transition of electrons or holes between energy bands demands not only the absorption of energy but also the change of momentum [33]. Under the strain of $-5\%$, the valence band maximum approaches and crosses the Fermi surface which leads to the characters of As/Sb bilayer transform from the semiconductor to the semimetal. This changeable phase characteristic under strain shows considerable application in semiconductor memory devices [34]. Figure 5(b) displays the band structures of As/
Sb bilayer with biaxial tensile strain from 1% to 7%. Different from compression, at this stage, the bottom of the conduction band migrates from the high-symmetry point M to $\Gamma$. As the biaxial tensile strain increasing, band gaps still grow numerically as former but the electronic band structures of As/Sb bilayers change from an indirect-band-gap semiconductor to direct one.

Further research for the biaxial tensile strain of As/Sb heterostructure, the band structures with strain from 7% to 20% are illustrated in Figure 6(a). Contacted with the biaxial tensile strain range from 1% to 7%, the particular biaxial strain $\varepsilon = 7\%$ separates the band structures of As/Sb heterostructure into two different configurations. And with the increasing strain (7%–20%), band gaps get narrower. The bottom of conduction band located at the high symmetry point $\Gamma$ gradually shifts to the Fermi level and finally interleaves with the VBM, resulting in a transition from semiconductor to semimetal with Dirac-like band structure. The band gap values with the function of biaxial strain are given in Figure 6(b). Ranging from $-7\%$ to 7%, band gaps of As/Sb bilayer keep increasing trend until the transformation of CBM from point M to $\Gamma$. On the contrary, after 7%, the
Figure 5. (a) Band structures of As/Sb heterostructures with biaxial compressive strain from −7% to −1%. (b) Band structures of As/Sb heterostructures with biaxial tensile strain from 1% to 7%.

Figure 6. (a) Band structures of As/Sb heterostructures with biaxial tensile strain from 7% to 20%. (b) Band gaps with the function of biaxial strain and schematic diagram of band structures near Fermi surface with biaxial tensile strain from 7% to 20%.
heterostructure turns into a direct band gap semiconductor with decreasing values of band gaps similar to the research for strain effect on As or Sb monolayers about Quantum spin hall insulators and tunable topological electronic [35].

In order to explore the mechanism of biaxial strain on As/Sb heterojunction, the charge density difference and relevant partial density of states and are calculated (shown in figure 7). As the biaxial strain increasing, the

Figure 7. Charge density difference and partial density of states of As/Sb heterostructures with the biaxial strain of (a) −5%, (b) 7%, (c) 20%. 
alterations of the orbital occupies in each layer of the heterostructure present synchronous changes until a semiconductor-metal transition occurred. As is shown in partial density of states, p orbits of As and Sb dominant the band levels near Fermi surface representing the migration of CBM and VBM and perform the similar transfer, which can be observed in charge density difference of each layer. It is indicated that the biaxial strain has an identical influence on As layer and Sb layer part of the As/Sb heterobilayer.

3.3. Electric field on electronic properties
The phase transmutation with exterior electric field is also investigated as a result of the narrow band gap of As/Sb heterostructure. As is shown in figure 8, we apply external electric field with values from $-1.0$ to $0.2 \text{ V Å}^{-1}$ to manager the alterable indirect band gap. The positive and negative values of the intensity represent the direction of the electric field respectively [36]. It is noticed from band gaps with the function of several electric field intensities that the semiconductor As/Sb heterobilayer has a tendency to semimetal trait as the absolute value of intensities increasing [37]. When a negative electric field is applied, the band gap increases rapidly at a small electric field intensity with the value of $-0.1 \text{ V Å}^{-1}$ approximately, and decreases with the continuously increasing E-field intensity. The similar circumstance appears near the intensity of $-0.7 \text{ V Å}^{-1}$. Under the intensity of $-1.0 \text{ V Å}^{-1}$, the top of valence band penetrates Fermi surface witch is analogous to p-type doping [38]. The band gap narrows to zero suggests that a semiconductor-metal transition is generated by exterior electric field modification. In this process, the applied electric field has an obvious influence on the VBM and CBM near the K point and the Γ point. On the contrast, when in a positive electric field, the bottom of conduction band shifts toward Fermi surface similar to n-type doping, and the intensity($0.07 \text{ V Å}^{-1}$) of the positive external E-field can reduce the band gap until it disappears [39]. It is implied that the variation is caused by the difference between the influence of electric field on CBM and VBM.

The partial density of states and charge density difference under a set of electric field intensities are displayed in figure 9 for the further research on electronic properties with electric field effect. Under negative E-field with the values of intensities from $-0.1 \text{ V Å}^{-1}$ to $-1.0 \text{ V Å}^{-1}$, the energy band levels near the Fermi surface are mainly occupied by s and p orbits of Sb layer while those of As layer have little contribution to the band level, which is different from the strain effect on As/Sb heterostructure. But with the values of intensities from $-0.1 \text{ V Å}^{-1}$ to $0.1 \text{ V Å}^{-1}$, as band gaps decreasing, orbital occupancy of the band near the Fermi level transforms from Sb-leading type to As-leading type. The special vicissitude in the band structure under electric field implies that As and Sb layers show different sensitivities under certain electric field intensities, as a result of the appearance of

![Figure 8](image-url)
two peaks on the function of band gaps with E-field intensities. The particular electronic structures under electric field and rapidly semiconductor to metal transformation under tiny positive E-field imply significant application potential in various sensor and 2D nanoelectronic field effect devices [40].

**Figure 9.** Partial density of states and charge density difference of As/Sb heterostructures under electric field with values of (a) $-0.92 \text{ V Å}^{-1}$, (b) $-0.77 \text{ V Å}^{-1}$, (c) $-0.10 \text{ V Å}^{-1}$, (d) $0.07 \text{ V Å}^{-1}$. 
4. Conclusion

Combining arsenene and antimonene monolayers, the As/Sb vdW heterostructures are established to explore their novel physical and chemical properties. It is shown that a semiconductor-metal transformation is occurred under appropriate biaxial strain and electric field. We also reveal the mechanism of tuning band structures affected by strain and electric field in As/Sb bilayers. It is noteworthy that the transitions of the orbital states in As and Sb layers present synchronous tendency with biaxial strain changing. On the contrary, the layer of Sb atoms makes more contribution to the electronic distribution under electric field. And a double-peak curve is appeared in the function of band gaps with E-field intensities suggests the different sensitive dependence of each layer on intensities. The heterobilayers not only maintain the characteristics of each As and Sb layers, but possess the particular band structures which indicates significant application potential in two-dimensional nanoelectronic devices.

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