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The electronic properties of bare and alkali metal adsorbed two-dimensional GeSi alloy sheet

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In this paper, the structural and electronic properties of both bare and alkali metal (AM) atoms adsorbed two-dimensional GeSi alloy sheet (GeSiAS) are investigated by means of first-principles calculations. The band gaps of bare GeSiAS are shown slightly opened at Dirac point with the energy dispersion remain linear due to the spin-orbit coupling effect at all concentrations of Ge atoms. For metal adsorption, AM atoms (including Li, Na and K) prefer to occupy the hexagonal hollow site of GeSiAS and the primary chemical bond between AM adatom and GeSiAS is ionic. The adsorption energy has an increase tendency with the increase of the Ge concentration in supercell. Besides, single-side adsorption of AM atoms introduces band gap at Dirac point, which can be tuned by the Ge concentration and the species of AM atoms. The strong relation between the band gaps and the distribution of Si and Ge atoms inside GeSiAS are also demonstrated. The opened band gaps of AM covered GeSiAS range from 14.8 to 269.1 meV along with the effective masses of electrons ranging from 0.013 to 0.109 m_e, indicating the high tunability of band gap as well as high mobility of carriers. These results provide a development in two-dimensional alloys and show potential applications in novel micro/nano-electronic devices.

1. Introduction

Because of the ultra-low resistivity, high thermal conductance, high fracture strength and a series of peculiar properties, two-dimensional(2D) materials become promising candidates in micro/nano-electronics since 2004 [1–3]. Two kinds of group-IV 2D materials, silicene and germanene, have received wide attention around the world due to that Si and Ge are acting as the foundation of current information industry [4–6]. Theoretical studies have shown that they are massless Dirac Fermi systems like graphene [5,7,8]. Both of silicene and germanene have honeycomb structure but unlike graphene, they prefer low-buckled (LB) structure due to the mixture of sp^2 and sp^3 hybridization whereas graphene is planar [9]. Because of the LB structure, the band gap can be opened more easily. In addition, silicene and germanene have stronger spin-orbit coupling (SOC) effect which introduces direct band gaps of 1.55 meV and 23.9 meV at Dirac point respectively [10,11]. Furthermore, Yan et al. have recently found that SOC in silicene can be tuned by the biaxial strain and then lead to topological quantum phase transition [12]. Till now, silicene has been experimentally synthesized on Ag(1 1 1) [13–15], Ir(1 1 1) [16] and

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ZrB_2 [17] substrates. Less successful fabrication of germanene have been reported, but still came through on Pt(1 1 1) [18], Au(1 1 1) [19] and Al(1 1 1) [20] substrates.

Previous studies indicated that the adsorption of metal atoms provided a path to change the structural and electronic properties of silicene and germanene for applications in batteries, catalysis and transistors [21]. Owing to the LB structure, the adsorbed metal atoms have strong combination with silicene and germanene substrates. Upon the alkali metal (AM) adsorbed on silicene, the band gap at Dirac point can be opened and tuned by the coverage and variety of the metal adatoms, which can apply to high-speed logic devices [22]. Furthermore, Cu-, Ir- and Pt-adsorbed silicenes respectively behave as n-type, p-type and neutral type doped systems, hence it can be used to build p-i-n junction and tunneling field effect transistor (TFET) [23]. As for germanene, adsorption of different metal atoms also exhibits semiconductor, half-metallic and metallic behavior [24]. Ti and Cr coated germanene displays metallic states as well as antiferromagnetic ordering and V covered germanene exhibits quantum anomalous Hall effect, which have vast perspectives in spintronic devices [25]. Moreover, SiGe alloying in micro/nanostructures such as quantum wells, nanowires and quantum dots gradually becomes a very important topic due to the accessibility of the mixture of Si and Ge atoms [26–30]. Recently, Padilha et al. have shown that disordered 2D SiGe alloy, which determined by special quasirandom structure (SQS) method, can become nontrivial topological insulators same as pristine silicene and germanene [31]. However, lack reference can be found for metal covered SiGe alloyed 2D material where Ge/Si concentration can play as another important role and design freedom in determining the electronic properties.

In this paper, by orderly substituting Si(Ge) atoms by Ge(Si) atoms in silicene(germanene), the two-dimensional ordered GeSi alloy sheet (GeSiAS) is demonstrated. We systematically investigate the impact of Ge concentration on energy, structural and electronic properties of the bare GeSiAS as well as the AM atoms (Li, Na and K) adsorbed GeSiAS by using first-principles calculations. As expected, the energy band of GeSiAS can be opened at Dirac point by SOC effect and unilateral adsorption of AM atoms. The band gap is regulable by controlling the alloy concentration and larger band gaps than AM absorbed silicene and germanene are observed.

2. Methods

Based on density-functional theory (DFT) method, all the calculations of geometry optimization and electronic properties are implemented on VASP code [32–34]. The projector augmented wave (PAW) pseudopotentials [35] are adopted to replace the actual potential in ion cores and the exchange correlation functions are set as the Perdewe-Burkee-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) [36]. After the convergence test, the maximum kinetic energy cutoff of the plane wave basis set is chosen 450 eV and the k-point sampling for Brillouin zone integration is $9 \times 9 \times 1$. By using the Quasi-Newton method, the optimizing of atomic positions and cell dimension are carried out until the force on each atom becomes less than 0.01 eV/Å. The energy convergence criterion of self-consistent calculations is set less than 10^{-4}eV between two continuous steps. In order to analyze the charge transfer, Bader charge method is used [37]. A vacuum layer of 15 Å is built in the Z direction of one AM atom covered (2×2) GeSiAS supercell to avoid periodic interactions. The SOC effect is included in all calculations. By means of semi-empirical DFT-D2 method, the van der Waals (vdW) interaction is taken into consideration [38,39]. In addition, dipole moment correction is included for AM-covered GeSiAS [40].

3. Results and discussion

3.1. Bare GeSiAS

The first GeSiAS supercell is a (2×2) primitive silicene cell which contains 8 Si atoms with periodic boundary condition. Then, we introduce Ge atoms to orderly replace Si atoms one by one from the bottom sublattice under the condition of

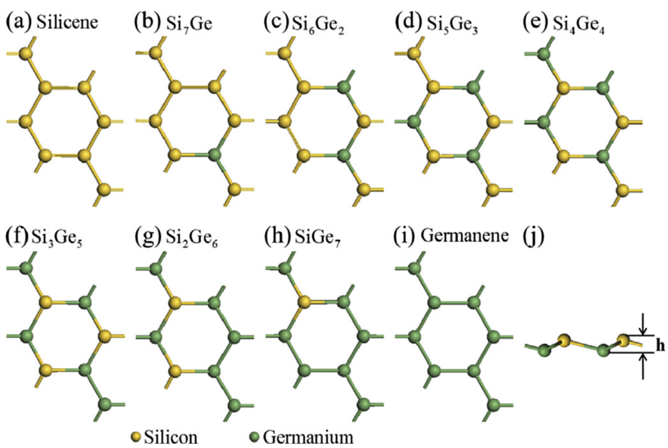

Fig. 1. The structure of 2×2 GeSiAS supercell. The Ge concentration of in supercell N = 0%(a), 12.5%(b), 25%(c),37.5%(d), 50%(e),62.5%(f),75%(g), 87.5%(h),100%(i), respectively. (j) The side view of the Si_4Ge_4 supercell. h: buckling height of the GeSiAS supercell.