Design of half-metallic ferromagnetism in germanene/silicene hybrid sheet

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ABSTRACT

In this theoretical work, we perform first-principles calculation to study the geometric, electronic, and magnetic properties of the two-dimensional germanene and silicene hybrid sheet (GeSiHS) saturated with brominate atoms (Br). Although the pristine GeSiHS is semi-metallic, half-saturation on only a single side of Si atoms with Br results in the localized and unpaired electrons in unsaturated Ge atoms, showing long-range ferromagnetic (FM) properties with a high Curie temperature. Interestingly, half-brominated GeSiHS exhibits half-metallic character with 100% spin-polarized currents at the Fermi level. These findings provide the possibility of GeSiHS as promising building blocks for spintronic devices.

1. Introduction

Graphene, a two-dimensional (2D) honeycomb lattice of sp^2-bonded carbon atoms [1], has generated an exceptional amount of interest in recent years, both for its electronic properties and for its promise in materials science [2]. Geometric or chemical modifications make 2D graphene an ideal platform for nanotechnology [3]. For instance, graphene has been predicted to become an FM semiconductor upon hydrogenation on the single side with a high Curie temperature [4]. It opens an approach for the minimization of electronic devices to explore 2D graphene systems. Nevertheless, it is facing many challenges such as toxicity, difficulty in processing, and incompatibility with current Si-based electronic technology.

The elements Si and Ge, similar to carbon counterparts, belong to group-IV of the periodic table, both of which have similar s^2p^2 valence electron configurations. Although the C atoms can form a layered graphite structure, the graphite-like Si or Ge allotrope does not exist naturally. Fortunately, silicene [5–10] and germanene [11,15] has been recently predicted theoretically and synthesized experimentally. Noticeably, their band structure is similar to the case of graphene, in which the π and π^* bands cross linearly at the Fermi level (E_F) of the Brillouin zone (BZ), forming the so-called Dirac cone [10–14]. It also reveals several remarkable features such

as a large spin–orbit gap at Dirac point [14], experimentally accessible quantum spin Hall effect [16], as well as electrically tunable band gap [17].

Recent works demonstrate that surface saturation with halogen elements is an effective way to modulate the electronic properties of Si nanowires [18]. Yaya et al. [19] also studied bromination in graphene and graphite, and predicted their intriguing electronic properties. In our recent works, by breaking the extended π-bonding network of Si on a single side of silicene [20,21], we find an interesting half-metallic character with 100% spin-polarized current at E_F in Br decorated silicene. Stimulated by the advances on 2D silicene and germanene, in the present work, we propose the two-dimensional germanene and silicene hybrid sheet (GeSiHS) from mixing Si and Ge atoms in an alternating arrangement in a chair conformer, as shown in Fig. 1(a). Our aim is to extend group-IV based nanostructures to allow the combination of ideas developed for GeSiHS allotropes with the silicon technology. We investigate whether the GeSiHS can be brominated with favorable formation energy and whether the half-brominated GeSiHS is half-metallic and supports room-temperature ferromagnetism.

All the calculations are performed within DFT under the generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE) [22]. The Vienna Ab-initio Simulation Package (VASP) is used to perform all calculations [23,24], and ion cores are modeled with projector augmented wave (PAW) potentials [25]. A plane-wave basis set with maximum plane-wave energy of 450 eV is used for the valence electron wave functions, and a set of $(9 \times 9 \times 1)$ k-point sampling is used for BZ integration.

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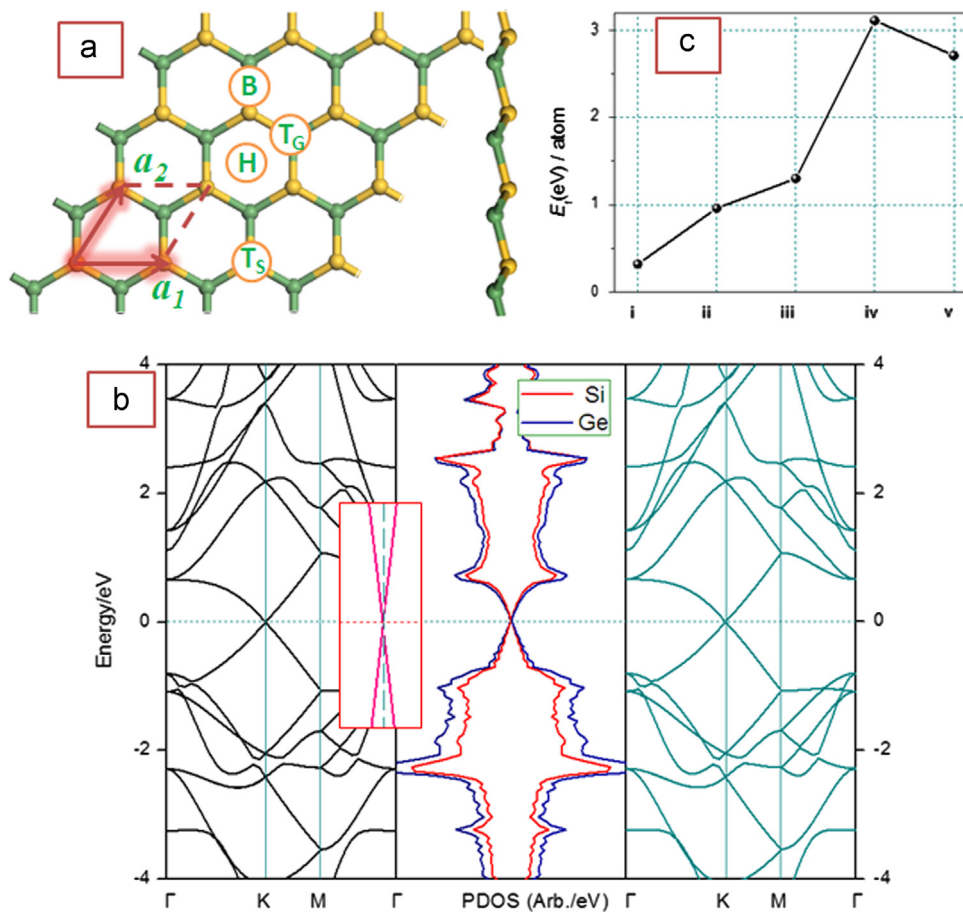 *E-mail address:* zhchwsd@163.com (C.-w. Zhang).

Fig. 1. (Color online) Relaxed structure of the GeSiHS hybrid in (a) top view and side view. Si atoms and Ge atoms are represented by yellow and green colors, respectively. The side view confirms the planar structure of GeSiHS hybrids. (b) shows the band structure versus high-symmetry lines in the hexagonal BZ for GeSiHS. The corresponding formation energies of five possible adsorbed structures in GeSiHS are presented in (c).

The convergence criterion of our self-consistent calculations for ionic relaxations is 10^{-5} eV between two consecutive steps. Using the conjugate gradient method, all atomic positions and the size of the unit cell are optimized until the atomic forces are less than 0.02 eV Å^{-1}.

The total-energy optimization of GeSiHS yields a buckled honeycomb-like structure ($\Delta=0.598$ Å) with two threefold-coordinated Si and Ge atoms in the hexagonal unit cell [Fig. 1 (a)], similar to the cases of silicene and germanene, whose stable configuration is also buckled. The low buckling GeSiHS is more stable in energy than the highly buckling one. The optimized buckled height in the z direction of the former is 0.12 Å lower than the latter one. Table 1 lists the lattice bond lengths, calculated bond lengths, buckling parameters, cohesive energies, and band properties for GeSiHS, the Br atoms occupy the ontop positions of all the Si sites (T_S), and fully-brominated sheets (GeSiHS:2Br), respectively. For the partially sp^3-bonded GeSiHS, we find a bond length $d_{Si-Ge}=2.379$ Å, which is intermediate between the Si–Si bond length in silicene of 2.28 Å [9] and distance of the Ge–Ge bond in silicene of 2.46 Å [14]. In order to determine the stability of free-standing GeSiHS, we calculate the formation energy defined by

$$E_f = [2E(\text{GeSiHS}) - E(\text{Ge}) - E(\text{Si})]/2$$

where $E(\text{Si})$, $E(\text{Ge})$, and $E(\text{GeSiHS})$ are the total ground-state energy per unit cell of silicene, germanene, and GeSiHS, respectively. As a result, a negative value of E_f should indicate a more stable system. We find that the energy gain E_f in forming GeSiHS with respect to germanene and silicene is -4.12 eV, suggesting

Table 1
Calculated structural parameters of the pristine, T_S, and fully brominated sheets. The a is the lattice bond length, the buckling parameter (Δ), d_{Si-Ge} and d_{Si-Br} are the bond lengths of Si–Ge and Si–Br, respectively (in Å). The formation energy E_f in eV/atom, and band properties are given for different structures.

Structure	a	Δ	d_{Si-Ge}	d_{Si-Br}	E_f	*Band properties*
GeSiHS	3.954	0.598	2.379	–	-4.12	Semi-metal
T_S	3.987	0.687	2.427	2.015	-5.27	Half-metal
GeSiHS: 2Br	4.013	0.984	2.514	2.171	-3.89	Semiconductor

the possibility of experimental synthesis. To further check its stability, we also performed the molecular dynamics simulation on a 2×2 GeSiHS supercell at room temperature ($T=300$ K) with a time step of 1 fs. After running 1800 steps, the geometry structure of the GeSiHS is kept, and thus it is possible to synthesize in experiments.

The band structure versus high-symmetry lines in the hexagonal BZ for GeSiHS is depicted in Fig. 1(b). Consistent with the band character of silicene and germanene, the newly constructed GeSiHS is also a gapless semiconductor, with the bonding π and antibonding π^* bands crossing only at K points in the hexagonal BZ. Qualitatively, the band structures are similar to the graphene monolayer [26].

To modulate GeSiHS magnetic properties, we consider the single-sided bromination in GeSiHS, as shown in Fig. 2. We construct five possible adsorbed configurations in GeSiHS; (i) T_S, the Br atoms occupy the ontop positions of all the Si sites, (ii) T_G, those of all the Ge sites, (iii) H, all the hollow sites, and (iv) B, half