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Electronic and magnetic properties of germanene: Surface functionalization and strain effects

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ABSTRACT

The surface functionalization and strain effects on the structural, electronic, and magnetic properties of full-/half-passivated germanenes are investigated systematically by the first-principle calculations within density functional theory. It is found that the germanenes with full-passivation have different band structures. i.e., the band-gap of GeH is larger than that of GeF and GeCl. Interestingly, when surface passivation and strain are utilized, germanenes go through a transformation from semiconductor to semi-metal. Moreover, germanenes with half-passivation present different magnetic characters, i.e,. Ge_2H is a ferromagnetic semiconductor, while Ge_2F and Ge_2Cl are anti-ferromagnetic semiconductors. The stability of magnetic coupling of Ge_2Xs can be modulated by external strain. Our calculations indicate that the electronic and magnetic properties of passivated-germanenes strongly depend on their surface functionalization and strain effects.

1. Introduction

Since monolayer graphene have been exfoliated mechanically [1], two-dimensional (2D) nano-materials have attracted more and more attention due to their unique properties. Graphene, a single atomic layer honeycomb structure, has been found possessing many remarkable physical and chemical properties, such as high carrier mobility, quantum Hall effect, and high optical transparency [2]. Nevertheless, there are still several vital problems with graphene, i.e., graphene is incompatible with modern mature Si-technology. Germanene is the analog of graphene, and Ge is in the same column with carbon in periodic table, therefore, germanene might share the same novel properties with graphene. What is more, germanene is compatible with Si-technology, which makes it a potential candidate for the next generation of semiconductor materials. Very recently, Bianco et al. have successfully synthesized full-hydrogenated germanene (GeH) of millimeter-scale, and single atomic layer hydrogenation germanene was mechanically exfoliated from few layer GeH. Synthesized GeH has high stability and high oxidation resistance in ambient condition, which is a good base for further application of germanene [3].

To realize the widely application, more excellent properties of germanene are needed. Germanene is an entirely surface area structure, which might provide many methods to tune its electronic and magnetic properties, such as finite nanostructures [4], surface functionalization [5], and interaction with substrates [6]. Among the methods mentioned above, surface functionalization is a powerful and widely-used way to tune the performance of germanene. In past few years, great theoretical efforts have been made to surface functionalization. For example, Lew Yan Voon et al. [7] theoretically reported that the full-hydrogenated germanene opens a band-gap with ~3 eV from semi-metal for bare germanene. Based on first-principle calculations, Wang et al. [8] found that ferromagnetism can be induced on the one-side half-hydrogenation germanene. Besides hydrogenation, halogenation is also a common strategy to tailor electronic property of 2D materials, such as grapheme [9], silicone [10], and germanene [11], due to strong electronegativity of halogen atoms. Cheng et al. [12] demonstrated a reversible fluorinated graphene with a wide band-gap. Ding et al. [13] reported Z-line fluorinated silicene, which open a narrow band-gap, is stable. But apart from Ma et al.'s [11] theoretical reports about the robust quantum spin Hall states of halogenated germanenes, few works have been done on halogenated germanene.

Strain engineering is another useful method for 2D materials to obtain richer nature of germanene. Guinea et al. [14] showed that strain engineering can open band-gap and can create topological insulator state in graphene. Qin et al. [15] also theoretically reported a semimetal-metal shift of silicene under biaxial stress. He et al. [16] even demonstrated the electronic structure of few layers MoS_2 is continuous tuned by a uniaxial tensile strain. These studies proved that strain engineering is a powerful and important

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way of changing the properties of 2D materials. However, synthesis and application of 2D materials are usually on substrates, for example, silicene could be synthesized on Ag(111), Ir(111) [17], and ZrB_2(0001) surface [18]. The mismatch of lattice constants between substrate and 2D materials may result in unintentional strains, which might lead to some trouble while put strain engineering into practice. Therefore, synthesis and applications of germanenes probably face the same problems caused by these two kinds of strains.

In this paper, in order to examine how the surface functionalization and strain will affect on the electronic and magnetic properties of the surface functionalized germanenes, and to shed some light on the corresponding mechanisms, we have made comprehensive first-principle calculations to study the structural and electronic properties of surface functionalized germanenes with different strains.

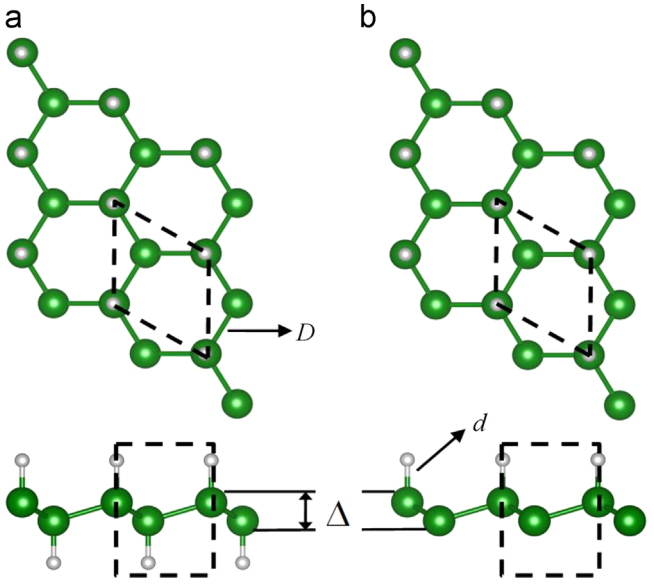

Fig. 1. (Color online) Top (upper panel) and side (lower panel) view of the geometric structures of (a) full-passivated, (b) half-passivated germanene. The dash line area denote calculated unit cell. The green and gray balls represent germanium and adatoms X, respectively.

Table 1
Summary of formation energies of X passivated germanenes. The energies are given in eV/atom.

E_f	Hydrogenation	Fluorination	Chlorination
Full-X	−0.254	−3.220	−1.628
Half-X	0.254	−1.287	−0.477

2. Computational details

All calculations in this paper are performed by employing the Vienne ab inito package(VASP) [19] within the density-functional theory frame. The interaction between valence electrons and ion cores is described by the projected augmented wave method (PAW) [20]. The exchange-correlation potentials are approximated by the generalized gradient approximation(GGA) using the Perdew–Burke–Ernzerhof(PBE) functional [21]. A plane-wave basis set with energy cutoff is set to 400 eV. The Brillouin-zone is sampled by the Monkhorst-Pack *k*-point mesh of 15 × 15 × 1 [22] which is found to achieve sufficient accuracy. All atoms were relaxed in the geometry optimization until the force acting on each atom is less than 10^{-2} eV/Å.

The three different adatoms X (X=hydrogen, fluorine and chlorine) full-passivated and half-passivated germanene configurations were studied, named as GeX, and Ge_2X, respectively. These configurations are schematically shown in Fig. 1. Full-/half-passivated germanene is generated by one/two side(s) adatoms-terminated single (111) sheet of germanium.

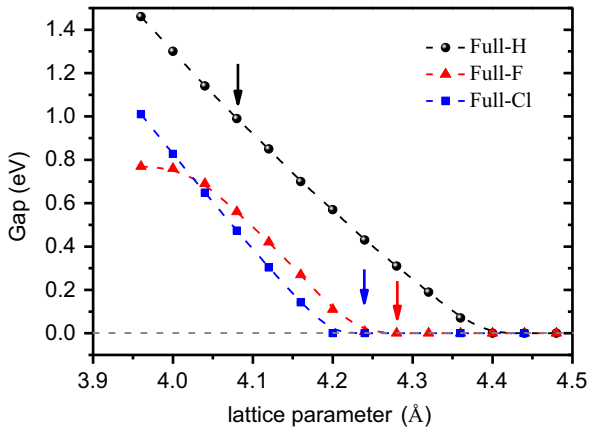

Fig. 3. Band gaps of full-passivated germanenes with hydrogenated (spheres), fluorinated (triangles), and chlorinated (rectangles) as a function of planer lattice constant. The three arrows represent equilibrium lattice constants for GeH, GeF, and GeCl, respectively. The gray dash line represents 0 eV.

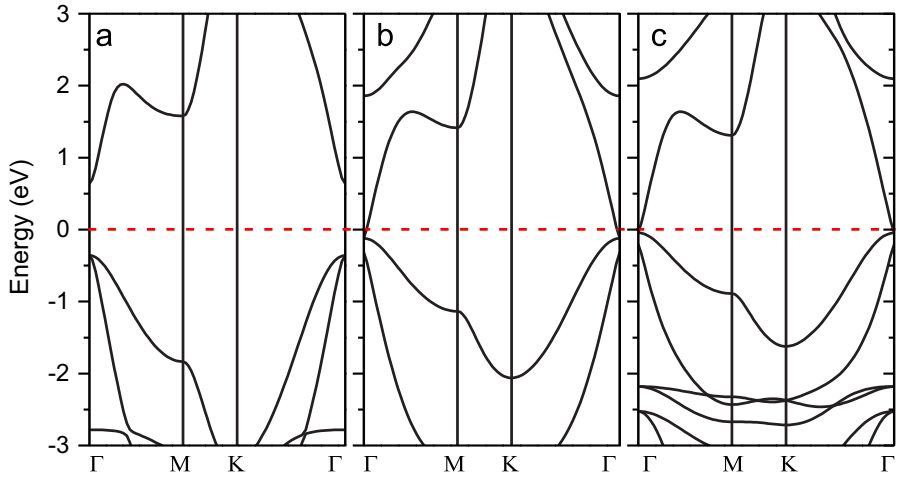

Fig. 2. Band structures of full-passivated germanenes (a) hydrogenation, (b) fluorination, (c) chlorination, respectively.