

Adsorption of alkali metal atoms on germanene: A first-principles study



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ABSTRACT

The structural, energetic and electronic properties of alkali metal (AM) atoms (including Li, Na and K) adsorbed germanene with a wide range of coverages are investigated by means of first-principles calculations. All AM atoms we considered prefer to bind on the hexagonal hollow site of germanene. In contrast to graphene, the interaction between adatom and germanene surface is quite strong due to its buckled hexagonal structure. As the increasing adatom coverage, the binding between AM atom and germanene sheet is weakened, due to the enhanced adatom–adatom repulsion while the decreased adatom–germanene attraction at high coverage. As a consequence of heavy charge transfer from AM to germanene, the formed adatom–Ge bonds perform mainly an ionic character. Through adsorption, the semimetallic germanene becomes to be metallic with its Dirac point moving below the Fermi level, thus making germanene behave as n-type doped. In addition, a small band gap can be opened at the Dirac point, and both the band gap and the concentration of charge carriers of AM/germanene system can be tuned by controlling the adatom coverage. The strong binding of AM adatoms to germanene and the rich electronic properties of the AM/germanene systems suggest possible potential applications in germanene based field effect transistor (FET) devices.

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1. Introduction

Two-dimensional (2D) honeycomb network of C atoms, graphene, becomes the fascinating material in physics, chemistry and nanoscience, due to its unique properties, such as “massless” relativistic Dirac fermion behavior [1,2], near-ballistic transport at room temperature [3,4] and high-speed mobility of carriers [5]. Though significant research interests in graphene grow rapidly, the growth of graphene over large areas and its integration in current Si-based nanotechnologies still face important challenges. Ge is an important semiconductor material having well compatibility with Si in conventional semiconductor industry and also higher carrier mobility which offers potential advantages for performance gains in high-speed electronic devices [6]. If the 2D graphene-like Ge, so called germanene, could be grown, its integration into Si-based nanoelectronics would be most likely much favored over graphene. Recent theoretical works pointed out that the stable germanene is a semimetal with linearly crossing bands at the Fermi level like

graphene, but has buckled crystal structure due to mixed sp^2 – sp^3 hybridization [7–9].

It has been demonstrated that the adsorption of metal atoms provides an efficient way to improve the properties of graphene sheets thus widening their applications in many fields. Upon some 3d transition metal atoms adsorption, the semimetallic graphene can become to be a metal with ferromagnetic or anti-ferromagnetic spin alignment, which can be used as spintronic devices [10]. Considering the effect of spin-orbit coupling, for most 3d transition metals adsorbed graphene sheets, Ding et al. found a nontrivial energy gap opens near the Dirac point which leading to the quantum anomalous Hall effect [11]. Using first-principles calculations, Kan et al. found that alkali metal and alkali-earth metal adatoms can easily dope electrons into graphene thus can greatly change its electronic properties [12]. In addition, it is predicted that Li coated graphene has a relative high critical temperature ($T_c = 18$ K), which shows the potential for the development of new superconducting electronic devices using 2D graphene as a basis material [13,14]. Recently, the superconductivity has already been realized in K-doped graphene [15]. It is found that through Li or Ca adsorption, graphene can serve as a high-capacity hydrogen storage medium [16–18]. Moreover, Au-embedded and Fe-embedded

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graphene sheets can also act as catalysts for certain chemical reaction [19,20].

Compared with graphene, germanene has a larger hexagonal lattice parameter and a buckled surface with two sublattices not in the same plane. In addition, the Ge–Ge bond in germanene also shows partial sp^3 hybridization character rather than complete sp^2 hybridization in graphene. It is possible that germanene will exhibit different structural and electronic properties from graphene when interacting with metal adatoms. Therefore, it is worth investigating the properties of metal atom adsorbed germanene.

In this work, we have systematically investigated the structural, energetic, and electronic properties of alkali metal (AM) atoms (including Li, Na and K) adsorbed monolayer germanene for a wide range of coverages, using first-principles methods. We propose that, through surface adsorption of AM, the semimetallic germanene can become to be metallic with a small band gap opening at the Dirac point. It is interesting that both the gap and the concentration of charge carriers of AM/germanene systems can be tuned by controlling the coverage of AM. This implies AM/germanene systems could be of great interest for germanene based nanoscale electronic devices, such as field effect transistors (FETs). The rest of the paper is organized as follows: Section 2 gives a brief description of the computational methods and the relevant parameters used in our calculations. In Section 3, the energetic, geometries and electronic properties of AM adsorbed germanene are analyzed and discussed in detail. Finally, we draw out conclusions in the last section.

2. Methods

The spin-polarized total energies and electronic structures calculations are implemented on VASP code [21], based on the density-functional theory (DFT) method. The electron exchange and correlation energies are calculated with the Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA) [22]. The projector-augmented wave (PAW) potentials [23] are used with kinetic energy cutoff of 450 eV. For the germanene unit cell, the Brillouin zone (BZ) is sampled by using a $(15 \times 15 \times 1)$ Monkhorst–Pack [24] grid for relaxation calculations and a $(25 \times 25 \times 1)$ one for static calculations. These samplings are scaled according to the size of supercell. The supercell geometry with periodic boundary conditions is adopted and a sufficiently

large vacuum of 15 \AA is inserted in the direction perpendicular to the germanene plane (Z direction) in order to prevent artificial interactions. During relaxations, the positions of all atoms are allowed to fully relax until the force on each atom is less than 0.01 eV/\AA between two ionic steps and the convergence of the electronic self-consistent energy is less than 10^{-5} eV . Considering AM adatom results in a net electrical-dipole in the Z direction, the dipole correction technique is also implemented to eliminate the artificial electrostatic field between the periodical images.

3. Results and discussion

The optimized atomic structure of germanene by DFT-GGA is shown in Fig. 1(a). For convenience, we denote the sublattice with a smaller Z coordinate as sublattice A, and the other one as sublattice B. The equilibrium hexagonal lattice constant a and the buckling height δ are 4.059 and 0.689 \AA , respectively. The values are in good agreement with those obtained by Garcia et al. from DFT-GGA [9], while are slightly larger than the values obtained from DFT-LDA [7,8]. The electronic band structure of the germanene unit cell is shown in Fig. 1(b), it can be seen that germanene is a semimetal with linearly π and π^* bands (originate from the perpendicular p_z orbitals of Ge atoms) crossing near K symmetric point in the BZ, thus charge carriers in germanene can behave like “massless” Dirac fermions. The calculated energy band gaps at M and Γ symmetric points are 1.83 and 0.86 eV , respectively. At the Γ point, the valence band (VB) is composed of p_x and p_y orbitals, while the conduction band (CB) is contributed by the hybridization of p_z and s orbitals. These results coincide well with those obtained by Cahangirov et al. previously [7].

To get the most preferable site for AM atoms adsorption on germanene, we firstly choose a (4×4) germanene supercell as the simulation model, in which the distance between neighboring AM adatoms is 16.236 \AA . The interaction between adatoms is rather weak, therefore, the AM/germanene system can be considered to be an isolated AM adatom on germanene approximately. As shown in Fig. 2, three different adsorption sites are considered: (1) the hollow site above the center of a hexagon (**Hol**), (2) the valley site above a Ge atom of sublattice A (**Val**), (3) the top site above a Ge atom of sublattice B (**Top**). When AM atoms are initially placed above the midpoint of a Ge–Ge bond (bridge site), they always move to the

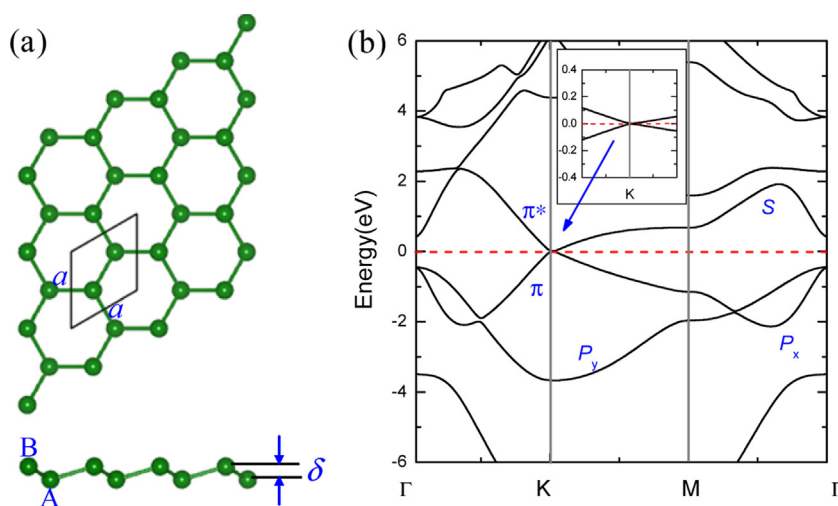


Fig. 1. (a) The top and side views of the germanene sheet with its unit cell indicated by a black parallelogram. The sublattices A and B, the hexagonal lattice constant a , and the buckling height δ are labeled. (b) The band structure of germanene unit cell with Fermi level set to zero energy and indicated by the red-dashed line. The π and π^* (p_z), s , p_x and p_y orbital character of bands are also marked out. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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