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A first-principles study of n-type and p-type doping of germanium carbide sheet

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ABSTRACT

We present our study on the adsorption of C, Si and Ge adatoms on binary compound germanium carbide (GeC) honeycomb structure based on density functional theory using the generalized gradient approximation. We found that C atom is bound at bridge site, while Si and Ge prefer to adsorb to top site above the top of carbon. The electronic and magnetic properties of GeC can be modified by the adsorption of these adatoms. Nonmagnetic semiconductor GeC is either metal or narrow band gap semiconductor depending on the adatoms coverage. One of the reason of this effect is the bonding combination of adatom-p and GeC-sp^2 orbitals. All the adatom adsorptions on GeC have zero net magnetic moment, except Ge adsorption at low coverage, which has a net magnetic moment of $\mu = 2.0\mu_B$ per cell. Our results also indicate that because of the charge transfer, the adsorption of C and Si/Ge on a GeC surface allow us to obtain p- and n-type doping, respectively. Therefore, adatom covered GeC can serve as an interesting alternative for the nanodevice applications.

1. Introduction

Graphene, a monoatomic layer of carbon atoms arranged in a two-dimensional (2D) honeycomb lattice, was first isolated from bulk graphite by Novoselov et al. [1]. Graphene exhibits outstanding electronic, thermal, optical and mechanical properties, such as massless Dirac fermions [2], high thermal conductivity [3,4], half-integer Hall conductance [5,6], high optical transmittance [7,8], high carrier mobility at room temperature [9], high chemical stability, ambipolar electric field effect [10] and extraordinary stiffness [11]. All these exotic properties of graphene have led to investigation of other 2D honeycomb lattices such as hexagonal boron nitrides [12], zinc oxide [13] and transition metal dichalcogenides [14]. Especially, graphene-like buckled honeycomb structures of silicene and germanene [15] have attained significant interest due to their nonmagnetic semimetallic behavior with linearly crossing π and π^* bands at Fermi level which is similar to graphene and due to their compatibility with silicon-based micro-electronic industry. In addition, two-dimensional silicon carbide (SiC) and germanium carbide (GeC) honeycomb structures have been reported theoretically as stable [16–19]. In contrast to the zero band gap of honeycomb lattices of group-IV elements, monolayer honeycomb structures of group-IV binary compounds such as 1H-GeC and 1H-SiC are direct and indirect band gap semiconductors, respectively [17]. As a result of direct band gap properties, 1H-GeC can be promising material for digital circuits and light-emitting diodes. After determining its 2D honeycomb structure as stable [17], the mechanical [20] and electronic [21,22] properties of GeC were investigated. It was found that the electronic properties of 1H-GeC can be modified by introducing various strained conditions [23]. Another study on semifluorinated and semihydrogenated GeC sheets showed that by controlling the adsorption atoms, the electronic and magnetic properties can be modulated [24]. Earlier studies dealing with functionalization of graphene [25,26], silicene [27] and germanene [28] have shown that the electronic and magnetic properties of graphene and silicene can be remarkably changed upon adatom adsorption as well. In our previous study [25,29], we found that Si, Ge and C are bound to graphene with significant binding energies, and hence these adatoms give rise

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to important changes in the electronic and magnetic properties of graphene. Therefore, the investigation of adsorption properties of isovalent C, Si and Ge atoms on GeC monolayer will be important.

In this study, we present ab initio calculations of the adsorption of C, Si and Ge on germanium carbide at different level of coverage. We found that the electronic and magnetic properties of monolayer GeC can be modified through foreign atom adsorption. Bare hexagonal monolayer GeC, which is a nonmagnetic semiconductor, becomes either nonmagnetic metal or narrow band gap semiconductor depending on adatom–adatom distance. Especially at $\theta = 1/32$, it becomes a spin-polarized semiconductor upon the coverage of Ge with a net magnetic moment of $2.0\mu_B$ per cell.

2. Calculation methods

The processes of adsorption of C, Si and Ge atoms on a monolayer honeycomb structure of germanium carbide have been investigated by means of first-principles spin-polarized and spin-unpolarized plane-wave calculations within density functional theory (DFT) using projector augmented wave (PAW) potentials [30]. The exchange-correlation potential is approximated by generalized gradient approximation (GGA) using Perdew–Burke–Ernzerhof (PBE) parameterization [31]. All numerical results have been obtained by using Quantum Espresso software [32]. A plane-wave basis set with the kinetic energy cutoff $\hbar^2(\mathbf{k}+\mathbf{G})^2/2m = 500$ eV is used. Pseudopotentials with $2s^2 2p^2$, $3s^2 3p^2$ and $4s^2 3d^{10} 4p^2$ valence electron configurations for C, Si and Ge atoms were used, respectively. All structures are treated using periodic boundary conditions. To investigate the C, Si and Ge adsorption on 1H-GeC, we considered two different levels of one-sided periodic adatom coverage on the (2×2) and (4×4) cells of monolayer hexagonal GeC corresponding to $\theta = 1/8$ and $\theta = 1/32$, respectively. The Brillouin zone has been sampled by $(15\times15\times1)$ and $(7\times7\times1)$ special mesh points in **k**-space by using Monkhorst–Pack scheme [33] for (2×2) and (4×4) GeC cells, respectively. All atomic positions and lattice constants are optimized by using BFGS quasi-Newton algorithm [34] where the total energy and forces are minimized. The convergence criteria for energy is chosen as 10^{-8} Ry between two consecutive steps. The maximum Hellmann–Feynman forces acting on each atom is less than 0.001 Ry/au upon ionic relaxation. The maximum pressure on the unit cell is less than 0.5 kbar. Gaussian type Fermi-level smearing method is used with a smearing width of 0.1 eV. To prevent the interaction between periodically repeating GeC layers, vacuum spacing is chosen as 20 Å. The charge at the adatom ρ_L or ρ_B is obtained by Löwdin [35] or Bader [36] charge population analysis. The excess charge of adatom is calculated as $\rho_X^{ex} = Z_A - \rho_X$. Here, Z_A is the valance charge of the adatom; ρ_X is the charge at adatom (where X indicates Löwdin or Bader charge population analysis). The isosurfaces of difference charge density are calculated by the following equation:

$$\Delta\rho = \rho_{total} - \rho_{GeC} - \rho_A \quad (1)$$

where ρ_{total}, ρ_{GeC} and ρ_A are the charge of GeC + adatom system, bare GeC structure and adatom, respectively. All charge density plots are generated using the VESTA [37] program with the isosurface values of 0.001 electrons/Å^3. The cohesive energy of GeC per unit cell is obtained from $E_{coh} = E_{Ge} + E_C - E_{GeC}$, where E_{Ge}/E_C are the total energy of single free Ge/C atoms and E_{GeC} is the total energy for GeC monolayer. The adsorption energy of adatom on GeC is defined as

$$E_b = E_{GeC+A} - E_{GeC} - E_A \quad (2)$$

where E_{GeC}, E_A and E_{GeC+A} are the total energy for GeC, the isolated adatom and GeC + adatom system, respectively.

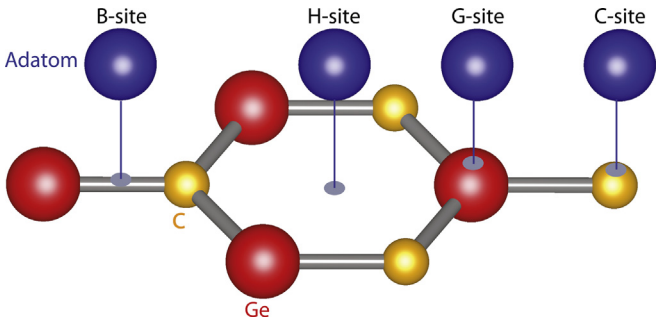

Fig. 1. The schematic representation of possible adsorption sites on (2×2) cell of 1H-GeC. The bridge site (B): the adatom is initially placed on top of Ge—C bond of 1H-GeC. The hollow site (H): the adatom is located on above the center of hexagons. G site: the adatom is placed on top of Germanium atoms. C site: the adatom is placed on top of Carbon atoms of 1H-GeC.

3. Results and discussion

3.1. Properties of two dimensional GeC

We present a brief discussion of the structural and electronic properties of bare 2D honeycomb germanium carbide. The cohesive energy of 1H-GeC is calculated as 11.96 eV per Ge—C pair. The lattice constants of optimized hexagonal structure in equilibrium are $a = b = 3.24$ Åand the bond distance between Ge and C atoms is $d_{Ge-C} = 1.87$ Å. The ground state of monolayer 1H-GeC is nonmagnetic semiconductor with direct band gap which is calculated to be $E_G = 2.10$ eV at the K point. All results are in good agreement with previous local density approximation (LDA) calculations [17,21,23].

3.2. Adsorption on two dimensional GeC

3.2.1. Structural properties and binding energy

Adsorption sites of a single atom are determined by placing the adatom in various adsorption sites above GeC: the bridge (B) site above the Ge—C bond, the carbon top (C) site on top of carbon atoms, the germanium top (G) site on top of germanium atoms and the hollow (H) site above the center of hexagons as shown in Fig. 1. In Table 1, we present relevant structural parameters, such as the lattice constant, the length of the adatom-C and adatom-Ge bond, binding energies, electronic properties, charge transfer and magnetic moments. For both coverages ($\theta = 1/8$ and $\theta = 1/32$), we have predicted that C atom is bound at the B-site as in graphene [25,29], whereas Si and Ge atoms prefer to adsorb to the C-site of 1H-GeC as illustrated in Figs. 2 and 3. The binding of adatom to GeC is confirmed by examining the charge difference isosurfaces indicated in Figs. 2 and 3. For $\theta = 1/8$ coverage, carbon atom adsorbed on B-site can break the Ge—C bond and the underlying adatom C increases its coordination number from 3 to 4, resulting a local reconstruction due to Jahn–Teller distortion [38]. Finally, the distance between Ge and C atom changes from 1.87 to 2.50 Å. The binding energy of C to monolayer GeC is $E_b = -4.56$ eV, which is characterized by the formation of a Ge—C—C bridge bond with the bond lengths of $d_{Ge-C} = 1.91$ Åand $d_{C-C} = 1.31$ Å. The binding energies (E_b) for the adsorption of Si and Ge those have relatively larger atomic radius compare to C are found to be -2.82 and -2.41 eV, respectively. These values are smaller than the binding energy of C adatom because of larger Si—C and Ge—C bond length. Such a behavior was occurred for metal adsorption on graphene [39].

On the (4×4) supercell, the binding energy of C adsorption at the B-site is higher by 67 meV than the energy of highest coverage given in Table 1. In the coverage of $\theta = 1/32$, Si and Ge adatoms placed initially to the B-site move to the C-site upon relaxation. This causes a small change in the Ge—C bond underlying adatom, so that