Tuning the electronic and magnetic properties of germanene by surface adsorption of small nitrogen-based molecules

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ABSTRACT

The structural, energetic and electronic properties of germanene adsorbed with small nitrogen-based molecules, including N_2, NH_3, NO_2 and NO, have been investigated by using first-principles calculations. The results show that all nitrogen-based molecules considered bind much stronger to germanene than to graphene due to the hybridized sp^2-sp^3 bonding of Ge atoms. The N_2, NO and NO_2 molecules all act as an acceptor, while the NH_3 molecule donates electrons to germanene. We also found sizable band gaps (2–158 meV) are opened at the Dirac point of germanene through N_2, NH_3, and NO_2 adsorptions, but with only slightly destroying its Dirac cone shape. The NO_2 molecule also shows a heavy p-type doping character and makes germanene to be metallic. Moreover, when adsorbed by NO molecule, the germanene can change to be a ferromagnetic half-metal with 100% spin-polarization at the Fermi level. Overall, the different adsorption behaviors of small nitrogen-based gas molecules on germanene provide a feasible way to exploit chemically modified germanene for a wide range of practical applications, such as field-effect transistors, gas sensors and spintronic devices.

1. Introduction

In the last two decades, thin two-dimensional (2D) honeycomb materials have gradually gained broad attention from researches. Among these 2D materials, graphene is the most prominent one due to its fascinating properties which shows potential applications in many fields, such as field-effect transistors (FETs) [1–4], gas sensors [5,6] and capacitors [7,8] etc. However, in current Si-based nanotechnologies, it is still difficult to integrate graphene over large areas because of its finite compatibility with Si. In addition, the absence of a suitable energy gap in graphene also hinders its application in the actual FETs devices.

The success of graphene also inspires the studies for other group IV elements with similar structures, such as silicene (2D honeycomb silicone) and germanene (2D honeycomb germanium). Theoretical studies indicate silicene and germanene prefer a low-buckled structure rather than a planar one because of strong sp^2-sp^3 hybridization in Si–Si or Ge–Ge bonds. Whereas, they all show similar electronic band structures to graphene with linearly crossing at the *K* point [9,10]. Silicene has been fabricated in both metallic [11–14] and semiconducting substrates [15], and its buckled structure and Dirac cone behavior have also been demonstrated. Recently, Li et al. firstly fabricated buckled germanene on Pt(111) substrate and found strong covalent

bonds existing throughout the Ge layer [16]. Till now, germanene has also been obtained by epitaxial growth on other metallic substrates, such as Au [17] and Al [18]. Silicene and germanene also have many other unique properties. Compared to graphene, silicene and germanene will be well compatible with the current Si-based semiconductor industry. Using first-principles calculations, Liu et al. predicted that spin-orbit coupling effect can open much larger energy gaps in silicene and germanene than in graphene. Especially for germanene, the energy gap can reach to ~23.9 meV which is much higher than the liquid nitrogen temperature, indicating the quantum spin Hall effect can be easily observed in germanene experimentally [19]. By applied a vertical electric field, it can also open an energy gap in silicene and germanene, and the size of the band gap increases linearly with the increment of the electric field strength. This provides an avenue to fabricate dual-gated FETs using pristine silicene and germanene [20]. Moreover, Ye et al. recently predicted that the intrinsic carrier mobility of germanene can reach to 6×10^5 cm²–V⁻¹–s⁻¹, much larger than that of graphene [21].

Owing to the thin thickness and high surface/volume ratio, the electronic and magnetic properties of 2D materials can be easily tuned by hetero adsorbates thus widening their applications. Small gas molecules are know to be ubiquitously present on 2D materials surfaces. By first-principle calculations, Leenaerts et al. found that NO and NO_2 adsorption can introduce magnetism into graphene [22].

Zhou et al. reported interactions between gas molecules (O_2, CO, NO_2 and NH_3) and graphene can be enhanced by embedded transition metal elements, and the rich electronic and magnetic properties for these adsorption systems also have potential application in gas-sensing and spintronics [23]. Single molecule F_2 adsorption can introduce energy gap at K point in graphene and bilayer graphene with the gap value being controlled by the atomic arrangement of adsorbate relative to surface [24]. Xu et al. reported that not only F_2, but also Cl_2, Br_2 and I_2 adsorptions can open energy gaps in graphene, which can be also tuned by the thickness and the stacking order of graphene layers [25].

The large buckled surfaces endow silicene and germanene with higher reactivity than graphene. Therefore, they are more suitable for adsorption of heteroatoms and molecules. For silicene, Sahin et al. found that the alkali, alkali-earth and the transition metal atoms all binding stronger on silicene than on graphene [26]. In the context of keeping high carriers mobility of silicene, Quhe et al. found that alkali metal atoms adsorption can open a band gap in silicene which can be enlarged to the required value of FETs devices by controlling adatom coverages [27]. Du et al. predicted the band gap of silicene can also be tuned by the amounts of oxygen adatoms [28]. Feng et al. systematically studied the properties of several gas molecules (SO_2, O_2, NH_3, NO and NO_2) on silicene, and found silicene not only can be used as a good sensor for detecting NO and NH_3, but also a well catalyst for certain chemical reactions [29]. Kaloni et al. predicted that sizable band gaps (6–350 meV) with only slightly lower the Fermi velocity, can be obtained in silicene by adsorbing different organic molecules (C_3H_6O, C_2H_3N, C_6H_6, CH_4, CH_3OH and CHOH etc.) [30]. For germanene, it is found that both fully hydrogen-termination and halogen-termination can result in a much larger spin-orbital coupling gap in germanene [31,32]. Wang et al. predicted that the one-side hydrogen termination can make germanene a ferromagnetic semiconductor [33]. Similar ferromagnetic behavior has also found in semi-terminated germanene with alkali metal atoms [34]. Nevertheless, both hydrogen-termination and halogen-termination destroy the Dirac cone shape, which results in a significant decrease in the carrier mobility of germanene. In addition, metal atom (including alkali, alkali-earth and the transition metals) adsorption has also proved to be a efficient way to opening gap in germanene and tuning its electronic properties [35–38]. Recently, the adsorption characteristics of gas molecules on functionalized germanene nanosheets have been investigated by Chandiramouli et al. using first-principles [39,40], and their results suggest the hydrogenated/fluorinated, as well as the In/P substituted germanene nanosheets can be used to detect the presence of gas molecules, such as NH_3 and NO_2.

To our knowledge, the investigation on the electronic and magnetic properties about adsorption of small gas molecules on the surface of germanene is still lacking. Therefore, in this paper, we have systematically investigated how nitrogen-based gases (including N_2, NH_3, NO and NO_2) interact with monolayer germanene, and hope our results could have practical interest in the applications of FETs and gas sensors. The structural, energetic, and electronic properties of N_2, NH_3, NO and NO_2 on germanene are all considered by using the first-principles methods based on the density-functional theory.

2. Methods

The total energy and electronic structure calculations were performed by using projector-augmented wave (PAW) method [41] which implemented in VASP code [42]. The electron-electron interaction was considered by the generalized gradient approximation (GGA) [43] in form of Perdew-Burke-Ernzerhof (PBE) exchange-correlation function. A plane wave basis set with energy cutoff 500 eV and a $15\times15\times1$ Monkhorst-Pack grid [44] in Brillouin zone (BZ) were used for the structural optimization and total energy calculations. The supercell geometry with periodic boundary conditions was adopted and a void region of 15 Å was included in the direction perpendicular to the germanene plane (Z direction) to ensure that the wave functions vanish smoothly at the edge of the cell as would be required in an isolated system. The Gaussian smearing method with a width of 0.05 eV was used for partial occupations. During relaxation, the positions of all atoms were allowed to fully relax until the force on each atom was less than 0.01 eV/Å and the convergence of the electronic self-consistent energy less than 10^{-5} eV.

The optimized hexagon lattice constant of monolayer germanene and the buckling height of germanene are 4.059 and 0.689 Å, respectively. These values are in good agreement with previous theoretical researches [9,10]. Here, we only consider a single gas molecule on a (4×4) germanene supercell (32 germanium atoms), in which the distance between neighboring gas molecules is large enough to eliminate their interaction. The adsorption energy for gas/germanene system can be defined as:

$$E_a = E_{Gas} + E_{Ge} - E_{Gas+Ge} \quad (1)$$

in which E_{Gas}, E_{Ge}, and E_{Gas+Ge} are the total energies of the gas molecule, germanene supercell, and gas/germanene system, respectively.

3. Results and discussion

We have considered several possible high symmetric sites of germanene surface, including gas molecule above the center of buckled hexagon, the Ge atom at either top or bottom Ge sublattice, etc. The results (including adsorption energies E_a, the X-Ge bond length d_{X-Ge}, the charge transfer from molecule to germanene ΔQ calculated by Bader program [45], as well as the band gap opening at the Dirac point E_g) base on the lowest energy configurations are shown in Table 1. For comparison, the adsorption energies for molecules on graphene calculated by Leenaerts et al. [22] are also listed in the third column. From the table, we can clearly see that, due to the sp^2-sp^3 hybridization in Ge atoms, all nitrogen-based molecules bind much stronger on germanene than on graphene. Our calculations suggest that N_2, NH_3 and NO_2 adsorbed germanene are all nonmagnetic, while the NO adsorbed germanene prefers to be ferromagnetic.

3.1. N_2 adsorption

For N_2 adsorption, the most stable binding configuration is shown in Fig. 1a. The N_2 molecule locates above the center of the buckled Ge hexagon with N–N bond being aligned the direction perpendicular to

Table 1

The adsorption energies (E_a), the X–Ge bond length (d_{X-Ge}), the charge transfer from molecule to germanene (ΔQ), and the band gap opening at the Dirac point (E_g) of the lowest energy configurations of gas/germanene systems. The adsorption energy of gas/graphene systems ($E_{a,graphene}$) in reference [22] is also listed for comparison.

Molecules	E_a (meV)	$E_{a,graphene}$ (meV)	d_{X-Ge} (Å)	ΔQ (e)	E_g (meV)	Donor/Acceptor
N_2	40	/	4.000/4.582	−0.021	2	Acceptor
NH_3	271	31	2.342	0.084	78	Donor
NO	303	29	2.343	−0.253	133/80	Acceptor
NO_2(N-Ge)	710	67	2.139	−0.939	154	Acceptor
NO_2(O-Ge)	859	/	2.015	−0.963	158	Acceptor