Enhanced band gap opening in germanene by organic molecule adsorption

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HIGHLIGHTS

- We perform a study of germanene adsorbed with several small organic molecules (SOMs).
- The high adsorption energies indicate strong interactions between SOMs and germanene.
- A enhancement of band gap with 3.9—81.9 meV due to the sublattice symmetry breaking.
- The small electron effective mass is expected to result in high electron mobility.

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ABSTRACT

We study the geometric and electronic properties of germanene adsorbed with several small organic molecules (SOMs) by using first-principles calculations. The adsorption energies are found in the range from −0.459 to −0.231 eV, higher than those of SOMs adsorbed on graphene and silicene, indicating strong interactions between organic molecules and germanene. These lead to a large enhancement of band gap of germanene with sizable values of 3.9—81.9 meV due to the sublattice symmetry breaking. Noticeably, the characteristics of Dirac cone with low effective mass and high electron mobility are preserved. These findings provide a possible way to design germanene based optoelectronic devices.

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1. Introductions

Graphene, a two-dimensional (2D) sp^2-hybridized carbon monolayer, has attracted many interests due to its peculiar electronic properties which allow electrons to move freely in its surface with high speed [1—3]. However, it lacks an intrinsic band gap, which makes electronic applications of graphene difficult for electronic devices. The same problem also exists in 2D silicene [4,5], another well-known $sp^2 + sp^3$ hybridized group-IV monolayer, which has most similar remarkable electronic properties to graphene but with buckled honeycomb structures. Recently, the graphene-like Ge nanosheet, which is referred to as germanene [5], has been synthesized from the topochemical deintercalation of $CaGe_2$ compound [6]. Li et al. [7] also reported buckled germanene formation on Pt(111) substrate experimentally. Its band structure is found to be similar to that of graphene, in which the π and π* bands cross linearly at E_F of the Brillouin zone, with a Fermi velocity of 1.7×10^6 m/s, a value comparable to the case of graphene [8]. Remarkably, it reveals several features such as a large spin−orbit gap at Dirac point [9], experimentally accessible quantum spin Hall (QSH) effect, as well as electrically tunable band gap [10—12]. Thus, the germanene will be a good candidate which replace graphene, because of its compatibility to current existing Si-based nanotechnology.

Generally, introducing defects [13], including adsorption and substitution into 2D material is of fundamental importance to enable a wide range of nanoelectronic devices by modulating their electronic properties [14,15]. The adsorption of small organic molecules (SOMs) on graphene is of considerable interest since the SOMs enhance the chemical reactivity of graphene, and thus

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modify the electronic properties of graphene-based systems [13,16–20], which could be relevant for sensing devices [21]. On the other hand, molecules adsorption on silicene are reported to exhibit a significantly higher chemical reactivity than graphene, showing good potential applications on silicene based molecule sensor and detection [22–26]. Similar to silicene, the combination between atoms of germanene is much stronger than graphene, which is mainly caused by the sp^3 hybridization of Ge atom [27]. Recently, there are several group's work demonstrated that the energy gap can be tuned by structural defects [13], functionalization [20] and alkali metal atoms coverage [28].

In this paper, we study the geometric and electronic properties of adsorption of SOMs, including acetone, acetonitrile, ammonia, benzene, methane, methanol, ethanol, toluene, on germanene by using first-principles calculations. The adsorption is found to tune effectively band gap of germanene, changeable in the range of 3.9–81.9 meV for all SOMs. Interestingly, the characteristics of Dirac cone with a small electron effective mass are preserved, which is expected to result in relatively high electron mobility. These findings provide a possible way to design germanene-based electronic devices.

2. Methods

All calculations are performed by using first-principles method as implemented in the Vienna ab initio Simulation Package (VASP) [29]. We use the Perdew-Burke-Ernzerhof (PBE) [30] functional to describe the exchange−correlation interaction, which is developed for the calculations of surface systems. Also, the projector augmented wave (PAW) method [31] is used to describe the electron−ion interaction, and the dipole corrections are included considering the possible charge redistribution in these systems. To properly take into account the van der Waals (vdW) interactions in the structures, the DFT-D2 method [32,33] was used throughout all the calculations. The energy cutoff of the plane waves is set to 400 eV with the energy precision of 10^{-4} eV. The Brillouin zone (BZ) is sampled by using a $5 \times 5 \times 1$ Gamma-centered Monkhorst−Pack grid, and the vacuum space is set to 25 Å to minimize artificial interactions between neighboring slabs, and the methodology for charge calculation is Bader analysis. By 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 eVÅ^{-1}.

3. Results and discussion

The SOM/germanene systems are modeled in a 4×4 germanene supercell with periodic boundary conditions as shown in Fig. 1. The primitive cell of germanene is a parallelogram with two Ge atoms. We consider four different high symmetry adsorption sites of SOM on germanene: the hollow (H) site at the center of a hexagon, the bridge (B) site at the midpoint of a Ge−Ge bond, the top (T) site directly above the upper Ge atom, and the valley (V) site directly above the low Ge atom. The adatom height (d) is defined as the difference in z coordinate of the SOM and nearest neighboring Ge atoms in germanene. The band structure of 4×4 germanene supercell is showed in Fig. 1(c), and indicated it's a semimetal with the energy gap is 0 meV. To check their stability, we calculate the adsorption energies of the adsorbed systems written as

$$E_{ads} = E(M@Ge) - [E(Ge) + E(M)]$$

Where $E(Ge)$, $E(M@Ge)$ and $E(M)$ are the total energies of pristine germanene, system with the SOMs adsorbed to the germanene, and free-standing SOMs, respectively, and the values are listed at Table 1, while these values are adsorption energy of the most stable

adsorption site. For instance, the adsorption energies is −0.459, −0.452, −0.447 and −0.449 eV on T, V, B and H sites, respectively, in the case of ammonia. Therefore, the optimal adsorption is T site. Among the adsorption sites of eight systems, the adsorption energy of ammonia on T site is the largest, while methane on H site is the smallest. Also, we have checked the other possibilities by rotating the SOMs and find that the rotated structures are energetically less favorable. As can be seen from Fig. 2, ammonia, methanol, and ethanol molecules are all energetically favorable to attach on T site, while acetonitrile and benzene on B site, methane and toluene on H site, as well as acetone on V site, respectively. Here, the adsorption position of SOMs is relative, depending on the composition of SOMs, and thus we highlight adsorption place by small black arrow in Fig. 2. Furthermore, most of the adsorption energies are larger as compared to silicene [25], indicating that these SOMs are more strongly bound to germanene. This is attributed to the more outer electrons in Ge atom than Si atom. The adsorption energy is moderate, and it is thus to desorbs them simply by heating. As for ammonia, it is far more strongly adsorbed on germanene with an adsorption energy of −0.459 eV, which is more robust than the case of graphene (0.112 eV) [34] and silicene (−0.293 eV) [25], and it is consistent with previous works [35]. The difference of energy sequence in calculation formula decided the positive and negative values. This indicates that germanene is an extremely good candidate compared to graphene to detect or act as sensor for harmful gases.

Fig. 2 displays the most stable adsorption configurations for the eight organic molecules on germanene. Upon adsorption of SOMs on germanene, the averaged buckling height between Ge atoms (h), the hexagonal angle between two planar Ge and one out of plane Ge (θ), as well as Ge−Ge bond lengths in germanene alters significantly. The h varies from 0.43-0.96 Å to 0.62−0.79 Å for ammonia to acetone, respectively, as shown in Table 2, which is lower than the cases of alkali metal atoms coverage [28]. Similarly, the angle and Ge−Ge bond lengths as a result of adsorption of the SOMs are found to be 109.95−112.83° to 112.31−112.40° and 2.44−2.46 Å to 2.44 Å for ethanol to methane, respectively. Furthermore, the C−C bond length in SOMs are found to be 1.51, 1.45, 1.40, 1.51, and 1.42 Å for acetone, acetonitrile, benzene, ethanol, and toluene, respectively, consistent with that of the free-standing SOMs. To check the interaction of germanene adsorbed with SOMs, we choose acetone as the representative, and find that the length of O−Ge bond is 3.28 Å, demonstrating a weakly binding of acetone with the host germanene with slight structural reconstruction, and thus a O−C bond length of 1.23 Å is similar to the free-standing acetone. Noticeably, It is larger than O−Si bond length of 1.69 Å in acetone adsorbed silicene, indicates a stronger binding of acetone to silicene with significant structural reconstruction of silicene close to the adsorbed region [27]. Similarly, a N−C bond length of 1.17 Å has been obtained for acetonitrile, a N−H length of 1.03 Å for ammonia, a C−O length 1.44 Å and O−H length 0.98 Å for methanol, a O−C length 1.45 Å and O−H length 0.98 Å in ethanol. The distance (d) between the host germanene and SOMs varies from 2.04 to 3.03 Å, which is similar to experimental and theoretical reports for graphene [27] and silicene [29]. Thus, these geometric modification significantly changes the electronic properties of germanene.

Fig. 3 displays the band structures for eight SOMs adsorbed on germanene sheets. In the cases of acetone, acetonitrile, and methane, the linear Dirac-like dispersion relation of germanene, $E_k = \pm h v_k |k|$, around the Fermi level, where v_k is the Fermi velocity, remains almost unaffected by the weakly interaction of SOMs with germanene. Thus, a small band gap of (3.9−4.6 meV) is achieved (Table 1). For the benzene and toluene adsorbed systems, due to locally distorted Ge atoms around the SOM areas, band gaps of 10.6 and 13.7 meV are obtained. Noticeably, these gaps opened here are