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A first-principles study of gas adsorption on germanene

Wenqi Xia,^a Wei Hu,^{ab} Zhenyu Li^{ac} and Jinlong Yang^{*ac}

The adsorption of common gas molecules (N₂, CO, CO₂, H₂O, NH₃, NO, NO₂, and O₂) on germanene is studied with density functional theory. The results show that N₂, CO, CO₂, and H₂O are physisorbed on germanene via van der Waals interactions, while NH₃, NO, NO₂, and O₂ are chemisorbed on germanene via strong covalent (Ge–N or Ge–O) bonds. The chemisorption of gas molecules on germanene opens a band gap at the Dirac point of germanene. NO₂ chemisorption on germanene shows strong hole doping in germanene. O₂ is easily dissociated on germanene at room temperature. Different adsorption behaviors of common gas molecules on germanene provide a feasible way to exploit chemically modified germanene.

Since the successful identification of graphene from mechanically exfoliated graphite and the subsequent discovery of unusual properties,¹ graphene has attracted enormous experimental and theoretical interest.^{2,3} Because of the high surface area, low electrical noise and extremely high electron mobility, graphene is highly sensitive to changes in its chemical environments, making it suitable for applications as a gas sensor.⁴ However, the physisorption of common gas molecules on pristine graphene limits its immediate potential.⁵ Introducing defect and substitutional doping are effective ways of enhancing the reactivity of gas molecules to graphene.^{6–8}

Recently, silicene and germanene, analogues to graphene of silicon and germanium, have also attracted increasing attention. In experiments, silicene was successfully grown on Ag,^{9–12} Ir¹³ and ZrB₂¹⁴ substrates. Most recently, germanene was also successfully grown on Pt(111).¹⁵ Germanene, multilayer hydrogen-terminated germanene, has also been synthesized and then mechanically exfoliated to a single layer onto SiO₂/Si surface.¹⁶ Silicene and germanene show the most outstanding properties similar to those of graphene such as high carrier mobility,¹⁷ ferromagnetism,¹⁸ half-metallic,¹⁹ quantum hall effect²⁰ and a topological insulator.²¹ However, silicene on metal substrates does not exhibit these properties, and the properties of silicene on low dimensional materials, e.g. graphene, is considerably closer to pristine silicene.²²

Interestingly, because of its buckled honeycomb structure,²³ silicene exhibits a significantly higher chemical reactivity than graphene, showing a much stronger adsorption of atoms^{24–30}

and molecules^{31–35} than graphene with good potential applications on new silicene based nanoelectronic devices,²³ Li-ion storage batteries,²⁷ hydrogen storage,²⁸ catalysts,²⁹ thin-film solar cell absorbers,³⁰ helium³² and hydrogen³³ separation membranes, molecule sensor and detection.^{34,35} Recently, atom adsorption on germanene is also studied.^{36,37} Similar to silicene, atoms bind much stronger to germanene than graphene, which is mainly caused by the sp²–sp³ hybridization of Ge atom. However, little attention has been focused on molecule adsorption on germanene.

In this study, a systematic investigation of common gas molecules' adsorption behavior on germanene is performed with density functional theory calculations. The results show that N₂, CO, CO₂ and H₂O are physisorbed on germanene but NH₃, NO, NO₂ and O₂ are chemisorbed on germanene. The moderate adsorption of NH₃ and NO₂ makes germanene a potential material for gas sensing. Strong adsorption of NO₂ and O₂ indicates that they can be used for modifying the electronic structures of germanene.

We perform density functional theory (DFT) calculation implemented in VASP (Vienna ab initio Simulation Package)³⁸ with the generalized gradient approximation (GGA)³⁹ of Perdew, Burke, and Ernzerhof (PBE) functional. The van der Waals (vdW) correction proposed by Grimme (DFT-D2)⁴⁰ is chosen to describe the long-range interaction.^{41–49} As a benchmark, DFT-D2 calculations give a good bilayer distance of 3.25 Å and binding energy of –25 meV per carbon atom for bilayer graphene, which is in complete agreement with the previous experiments^{50,51} and theories.^{52,53} The energy cutoff is set to 450 eV. The vacuum space in the Z direction is about 15 Å to separate the interactions between the neighboring slabs. For a 4 × 4 supercell, 3 × 3 × 1 *k*-points in Brillouin zone are sampled for geometry optimization and 7 × 7 × 1 *k*-points for static total energy and band structure calculation. The energy and force convergence

^a Hefei National Laboratory for Physical Sciences at Microscale,
University of Science and Technology of China, Hefei, Anhui 230026, China.
E-mail: jlyang@ustc.edu.cn

^b Computational Research Division, Lawrence Berkeley National Laboratory,
Berkeley, CA 94720, USA

^c Synergetic Innovation Center of Quantum Information and Quantum Physics,
University of Science and Technology of China, Hefei, Anhui 230026, China

are 10^{-5} eV and 0.01 eV \AA^{-1} , respectively. Charge transfer is obtained based on Bader analysis.⁵⁴ The optimized lattice constant of a unit cell is 4.058 \AA , which agrees with the previous studies.^{55,56}

To evaluate the stability of the adsorption of gas molecules on germanene, the adsorption energy is defined as

$$E_a = E_{\text{gas/germanene}} - E_{\text{gas}} - E_{\text{germanene}},$$

where E_{gas} , $E_{\text{germanene}}$ and $E_{\text{gas/germanene}}$ are the total energy of the gas molecule, germanene and gas molecule adsorbed on germanene, respectively.

The most stable adsorption configurations for the adsorption of gas molecules on germanene are plotted in Fig. 1, and the corresponding adsorption properties are listed in Table 1. We find that N_2 , CO, CO_2 and H_2O are physisorbed on germanene *via* van der Waals interactions. N_2 and CO prefer to adsorb on the hollow site, while CO_2 is adsorbed on the valley site. H_2O is adsorbed on the top site with two hydrogen atoms pointing toward the surface. The adsorption energies of N_2 , CO, CO_2 and H_2O are -0.13 , -0.16 , -0.10 and -0.22 eV, respectively. Therefore, germanene is also chemically inert to these gas molecules, similar to graphene⁵ and silicene.³³ The adsorption energy of water molecule cluster is calculated to find whether germanene is hydrophobic or not. For a cluster with five water molecules, the total adsorption energy is -0.11 eV per H_2O molecule, which is smaller than the binding energy of the water cluster

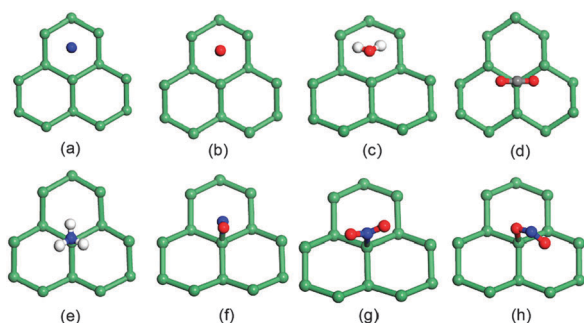


Fig. 1 Atomic structures of the adsorption of gas molecules in the most stable configuration on germanene. (a) N_2 , (b) CO, (c) H_2O , (d) CO_2 , (e) NH_3 , (f) NO, (g) NO_2 (N-Ge), (h) NO_2 (O-Ge). The white, blue, gray, red and green balls denote hydrogen, nitrogen, carbon, oxygen and germanium atoms, respectively.

Table 1 E_a : the adsorption energy. ρ : the charge transfer from germanene to gas molecule. $d_{\text{Ge-X}}$: the shortest distance of the atom in the molecule to the germanene surface. E_g : the band gap opened at the Dirac point of germanene

Model	E_a/eV	ρ/e	$d_{\text{Ge-X}}/\text{\AA}$	E_g/meV
N_2	-0.13	0.05	3.54	4
CO	-0.16	0.10	3.32	11
CO_2	-0.10	0.05	3.54	3
H_2O	-0.22	0.03	2.99	21
NH_3	-0.44	-0.12	2.33	82
NO	-0.51	0.24	2.34	95
NO_2 (N-Ge)	-0.90	0.58	2.14	161
NO_2 (O-Ge)	-1.08	0.66	2.02	170

(-0.37 eV per hydrogen bond). Thus, germanene is hydrophobically similar to graphene.⁵⁷

However, NH_3 , NO, NO_2 and O_2 are chemisorbed on germanene *via* strong covalent (Ge-N or Ge-O) bonds. NH_3 prefers to adsorb on the top site of germanene with a moderate adsorption energy of -0.44 eV and a Ge-N bond of 2.33 \AA . For NO, spin-polarized calculation is used because it is a molecule with net magnetic moment. NO also prefers to adsorb on the top site and keeps its magnet moment. The adsorption energy is -0.51 eV and the Ge-N bond length is 2.34 \AA . There is little charge transfer between germanene and these two molecules. The electron is transferred from NH_3 (electron donor) to germanene and then from germanene to NO (electron acceptor). Furthermore, the charge transfer of NH_3 and NO is distinctly larger than those (-0.03 and -0.02 e) on graphene.⁵ Meanwhile, the adsorption energy is moderate, and it is possible to desorb them simply by heating. Therefore, germanene may act as a potential material for the gas sensor of NH_3 and NO.³⁴ Although it is paramagnetic,⁵⁸ charge transfer in NO adsorption mainly occurs through orbital overlap.

For NO_2 chemisorption on germanene, we find two stable configurations, namely N-Ge and O-Ge, as shown in Fig. 1g and h with strong adsorption energies of -0.90 and -1.08 eV, and strong covalent Ge-N and Ge-O bonds of 2.14 and 2.02 \AA , respectively. The NO_2 molecule lost its magnet moment in both configurations. A large amount of the charge transfers from germanene to NO_2 , as listed in Table 1.

The effect of the adsorbed molecules on the electronic structures of germanene is also studied, and the corresponding electronic band structures are plotted in Fig. 2. The linear Dirac-like dispersion relation of germanene $E_k = \pm \hbar v_F |k|$ around the Fermi level, where v_F is the Fermi velocity, remains

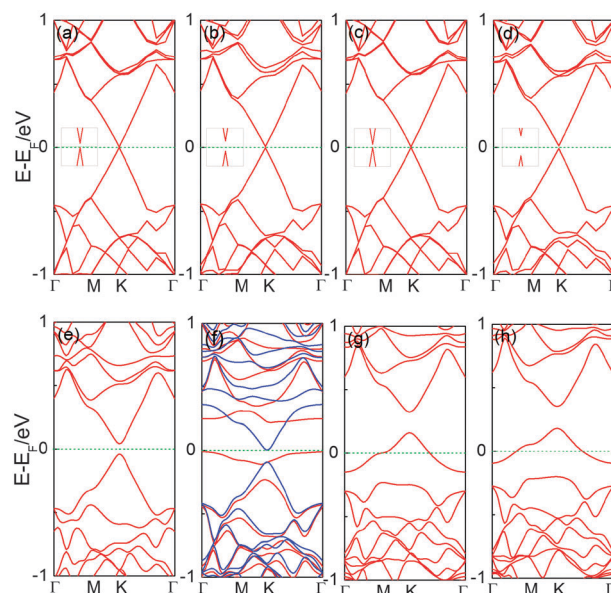


Fig. 2 Electronic band structures of (a) N_2 , (b) CO, (c) CO_2 , (d) H_2O , (e) NH_3 , (f) NO, (g) NO_2 (N-Ge) and (h) NO_2 (O-Ge) adsorption on germanene. The red and blue lines represent spin-up and spin-down states, respectively. The Fermi level is set to zero and is marked by the green dotted line.

almost unaffected by the physisorption of N_2 , CO , CO_2 and H_2O on germanene. Tiny band gaps (3–21 meV) are opened at the Dirac point of silicene, which are lower than thermal fluctuation (about 25 meV) at room temperature, similar to graphene.⁵ However, sizable band gaps of (82–170 meV) are opened at the Dirac point of germanene for the chemisorption of NH_3 , NO , NO_2 and O_2 on germanene, which would slightly lower the Fermi velocity of germanene.³⁴ The large charge transfer from germanene to NO_2 can also be confirmed in their band structures, as shown in Fig. 2g and h, as the Dirac point is moving above Fermi level, resulting in strong p-type doping of germanene.

Recent calculations³¹ show that O_2 is very reactive on silicene and can be easily dissociated into two O atoms, which is different from O_2 physisorption on graphene. Here, we study the adsorption behavior of O_2 on germanene. For O_2 , we consider two common initial orientations, namely side-on and end-on mode. The most stable configuration is shown in Fig. 3, and is marked IS. The O–O bond in the O_2 molecule interacts with the Ge–Ge bond, forming a four-membered ring. The O–O bond is parallel to germanene. The adsorption energy is -0.90 eV. The O–O bond is elongated to 1.471 Å, indicating that the O_2 molecule is very reactive. The triplet O_2 molecule lost its magnet moment. To further explore the dissociation process of O_2 on germanene, climbing image nudged elastic band (CI-NEB) is performed. The final state is a state with two O atoms adsorbed on germanene separately, marked as FS in Fig. 3. The adsorption of O atom breaks the Ge–Ge bond. The MEP is shown in Fig. 3. We can see there is a 0.57 eV barrier for O_2 to dissolve into two O atoms. It is quite moderate compared to O_2 dissociation on graphene. Thus, germanene is not very stable in air and chemically modified germanene is possible by O_2 adsorption.

Here, we reveal the origin of the (N_2 , CO , CO_2 , H_2O) physisorption and (NH_3 , NO , NO_2 and O_2) chemisorption of gas molecules on germanene. Their densities of states (DOS) are plotted in Fig. 4 and show that the frontier orbitals (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)) of NH_3 , NO , NO_2 and O_2 are close to the Dirac point (or the Fermi level) of germanene. Thus, these gas molecules have higher reactivity to germanene than the

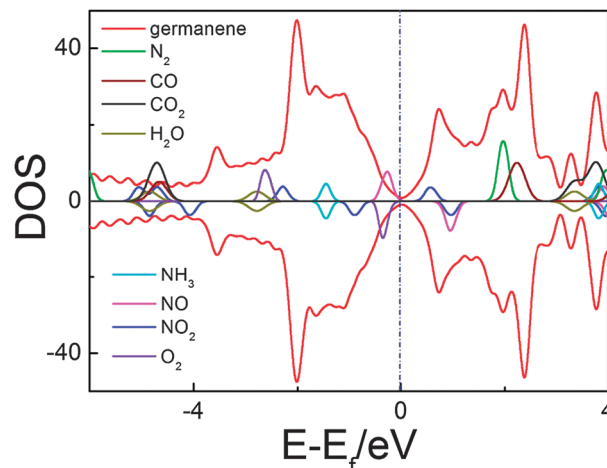


Fig. 4 Density of states (DOS) of N_2 , CO , CO_2 , H_2O , NH_3 , NO , NO_2 , O_2 and germanene. The positive and negative values represent spin-up and spin-down states, respectively. The Fermi level of germanene is set to zero, and other molecules are referenced to the vacuum level of germanene.

physisorption of other common gas molecules (N_2 , CO , CO_2 , H_2O) on germanene, which is similar to adsorption of these molecules on silicene.^{31–35} The adsorption of these molecules is weaker compared to silicene because of the larger radius and electro-negativity of the Ge atom.

In conclusion, we investigate the adsorption of N_2 , CO , CO_2 , H_2O , NH_3 , NO , NO_2 , O_2 on germanene on the basis of density functional theory calculations. We find that N_2 , CO , CO_2 and H_2O are physisorbed on germanene, whereas O_2 , NH_3 , NO and NO_2 are chemisorbed on germanene. NH_3 and NO chemisorption on germanene have moderate adsorption energies and few electrons transfer in different directions, making germanene a candidate for the gas sensing of NH_3 and NO . For NO_2 chemisorption on germanene, a strong chemical bond is formed, and a large amount of charge is transferred to the molecule, resulting in heavier p-type doping than NH_3 and NO . O_2 adsorption is very strong, and the molecule is activated and is easily dissociated into two O atoms.

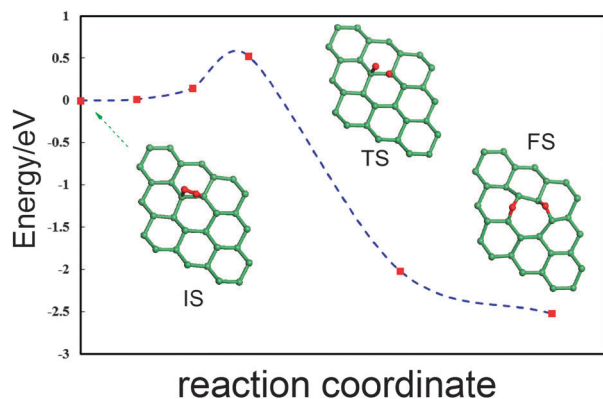


Fig. 3 Minimal energy path (MEP) of O_2 dissociation on germanene. The initial state (IS), transition state (TS) and final state (FS) are shown in the inset. The green and red balls represent Ge and O atom, respectively.

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