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First-principles simulations on the new hybrid phases of germanene with alkali metal atoms coverage

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ABSTRACT

We present first-principles calculations of a new type hybrid phases composed by buckled germanene with saturated or half-saturated alkali metal atoms adsorption. Our energetics and electronic structure analysis suggests that adsorbed alkali metal atoms (Li, Na, K) can be used as covered adatoms to synthesize germanene-based new phases in two dimensional. The predicted new phases of Ge_2X_2 and Ge_2X_1 (X = Li, Na, K) relative to the single germanene sheet could exist at room temperature. The formation energy of Ge_2Li_2 configuration obtained from complete lithiation is even more favorable than that of germanane. Charge transfer is significant between the alkali metal atoms and Ge, indicating the ionic interactions between them. Furthermore, our charge density analysis indicates that covalent component in some extent exists in Ge_2X_2 and Ge_2X_1 (X = Li, Na, K) 2D phases, which even leads the complete lithiated germanene into a semiconductor with an energy gap of 0.14 eV. We report that 2D phases of Ge_2X_1 (X = Li, Na, K) are metallic with weak polarization on the Fermi level and in unoccupied states. It is found that half-lithiated germanene exhibits local magnetic moments of 0.48 μ_B on the Ge atoms neighbored with Li adatoms.

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1. Introduction

Germanene is a kind of weak buckling germanium nanosheet in two-dimension, which is another graphene-counterpart besides silicene. It is reported that germanene can be grown on metallic substrates, such as (1 1 1) oriented Ag [1], Pt [2], Au [3] and Al [4] surfaces. In silicene, first-principles calculations [5] predicted that silicene hydride and fluoride exhibit different structural conformations, corresponding to direct and indirect band gap in band structure, respectively. Ferromagnetic semiconducting property was found due to half-hydrogenation occurring in one-side of the silicene [6]. Furthermore, metalized silicene by K atoms coverage was predicted to have a high capacity in storage hydrogen [7,8]. By single-side adsorption of alkali metal atoms, a band gap was found opening in silicene due to the bond symmetry breaking in two silicon sublattices [9].

In germanene, functionalizations by H, F, Cl, Br, or I were found changing the nanosheet into large-gap topological insulators [10]. Pang et al. [11] investigated alkali metal atoms adsorbed germanene for a wide range of coverage using first-principles methods and found that the electronic properties can be tuned by controlling the concentration of coverage. Though the structural similarities between lithiated silicene [12] and graphene [13] exist, they correspond to semiconductor and conductor properties upon complete lithiation, respectively. To the best of our knowledge, the stability and corresponding electronic properties of two-sides or one-side lithiated germanene are still unknown. A much larger band gap originated from spin–orbit coupling (SOC) [14] in germanene than that in silicene and graphene may conduct to different electronic properties after forming alkali metal–germanene complexes. The recent progress on the study of graphene-like 2D nanostructures such as silicene and its derivatives stimulate us to investigate new type 2D phases based on buckled germanene sheet. In this paper, based on density functional calculations including SOC, we found that alkali metal atoms, Li, Na and, K, can be covered on a germanene layer alternately in both sides or in one side with lower formation energies than that of germanene itself. The adsorbed alkali metal atoms positioned in the two sides of germanene distort the buckling honeycomb in 2D lattice and form the new metal-germanene phases. These new phases, composed by periodically

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repeating coverage of saturated alkali metal atoms, display metallic properties in electronic structure besides Ge_2Li_2 phase constructed from complete lithiation. An energy gap of 0.14 eV opening is found in Ge_2Li_2 phase, which has potential applications such as field effect transistors based on germanene [15–17]. Furthermore, we found half-hydrogenation in germanene has similar spin-polarization semiconductor property as that in silicene. However, with one-side coverage, alkali metal (Li, Na, K) adsorbed germanene are metallic and possess weak spin polarization.

2. Computational methods

Our density functional theory calculations were performed using Vienna ab initio software package (VASP) [18]. The electron–electron exchange correlation interaction is treated by the functional Perdew–Burke–Ernzerhof (PBE) [19,20] within the framework of Generalized Gradient Approximation (GGA) [21]. The electron–ion interaction is described by the projector augmented wave (PAW) method [22]. The plane wave cut-off energy 450 eV was found sufficient for the convergence in total energy. The separated vacuum space of 20 Å above each 2D sheet is used to eliminate the interactions between the neighbor supercells. K-mesh $25 \times 25 \times 1$ for sampling the Brillouin zone [23] in structural relaxation and three times 2D dense k-points in lateral electronic structure calculations are employed. In this work, SOC is included in all the cases we present our results. Total energy calculations are treated with a criterion of the components of the Hellmann–Feynman force on each atom to be smaller than 0.01 eV/Å. Due to the importance of van der Waals (vdW) interactions [24] between the adsorbates and germanene, vdW interactions have been accounted.

The stability can be evaluated by formation energy E_f, which was calculated as the difference between the total energies

$$E_f = E_{total} - nE_{Ge} - n_X E_X \quad (1)$$

where E_{total} is the total energy of the relaxed Ge_2X_2 or Ge_2X_1 complex. n_{Ge} and E_{Ge} denote the number of Ge atoms in the constructed configuration and the energy of a single Ge atom, respectively. For comparison, we also calculate the two-sides or one-side hydrogenated germanene. n_X and E_X represent for the number of adsorbed X (X = H, Li, Na, K, Rb) atom and the energy of a single X atom, respectively. In our calculations, we calculate the energy of a single Ge atom or a single X atom in the same supercell built for the calculation of germanene. Similar computational method has been used in silicene system and was proved accurate [25]. Phonon frequency calculations [26] were performed using linear response method and compared the results with that using finite displacement method, which is explained in detail in Appendix A.

3. Results and discussions

We first consider the energetics of the Ge_2X_2 and Ge_2X_1 systems, which are constructed by X (X = H, Li, Na, K, Rb) atoms two-sides or one-side adsorption on germanene. The formation energies we have calculated along with their structural parameters are listed in Table 1. From Table 1, we can find that the formation energies of all the adsorbed systems besides Ge_2Rb_2 and Ge_2Rb_1 are lower than that of monolayer germanene. This indicates that the energies of Ge_2X_2 and Ge_2X_1 (X = Li, Na, K) are favorable to form new 2D phases in certain conditions. Ge_2Li_2 phase constructed from complete lithiation behaves lowest formation energy. Its energy even lower about 0.2 eV than that of Ge_2H_2 configuration which we called hydrogenated germanene or germanane. We note that germanane was proved stable in 2011 by the study of HSE hybrid functional as well as the GW approximation [27]. Moreover, the H saturated germanene has already been fabricated by Bianco et al. [28] in 2013. We further calculated the phonon structure of Ge_2Li_2 phase as shown in Fig. S1. As indicated, Ge_2Li_2 phase shows stability based on the absence of imaginary phonons eigenfrequencies. This character in phonon structure is same with that of lithiated silicene predicted from first principles in the literature [12]. Therefore, the Ge_2Li_2 phase may be stable exist. However, the formation energies of Ge_2X_1 (X = Li, Na, K) with alkali metal atoms one-side adsorbed on germanene are all higher than that of Ge_2H_1 half-saturated hydrogenated configuration, which indicates the relative instability of new phases Ge_2X_1 when compared with one side hydrogenated configuration of germanene. Table 1 also indicates that the formation energies weaken down the periodic table in alkali metal hybrid germanene configurations Ge_2X_2 and Ge_2X_1 (X = Li, Na, K). This is related to the different buckled structures obtained from alkali metal atoms adsorption on germanene and the bonding character, which we will discuss in details as below.

Fig. 1 represents the relaxed configurations of Ge_2Li_2 and Ge_2Li_1 composed by 2D germanene hybrids with lithium. For comparison, we also show the results of corresponding hydrides Ge_2H_2 and Ge_2H_1. In Fig. 1, a 4×4 supercell in the left panel of each figure is chosen to indicate an overall structure of top view. In the right panel, the unit cell is used to exhibit the side view along with the charge density (top side) and charge density difference (bottom side). In Fig. 1(a), we can find the configuration of germanene adsorbed with lithium alternately on each side. From the top view, it is found that this conformation is very similar with that of complete lithiated graphene [13] or silicene [12]. We emphasize that the Ge_2Li_2 configuration with complete lithiation possesses higher stability than germanane. In addition, their structures have large difference. As indicated in the right panel of Fig. 1(a) and (b), the buckling height h is enlarged from 0.75 Å in germanane to 1.21 Å due to the attached lithium alternately on both sides of germanene.

Table 1
The calculated results of germanene and its new phases Ge_2X_2 and Ge_2X_1 (X = Li, Na, K, Rb). E_f (eV): formation energy, a (Å): lattice constant, d_{Ge-Ge} (Å): bong length of Ge–Ge, d_{Ge-X} (Å): bond length of Ge–X, $\alpha_{X-Ge-Ge}$ (°): bond angle of X–Ge–Ge, h(Å): buckling height between two Ge plane, $\rho^X(e)\rho^X$: the number of transferred electrons ("+" means gain electrons and "−"means lose electrons, respectively), Δ (eV): band gap, where M represents "metal". In the table, Germanene means its configuration in unit cell.

Structure	E_f (eV)	a (Å)	d_{Ge-Ge} (Å)	d_{Ge-X} (Å)	$\alpha_{X-Ge-Ge}$ (°)	h (Å)	ρ^{Ge} (e)	ρ^X (e)	Δ (eV)
Germanene	−6.79	3.48	2.42	/	/	0.70	/	/	0.0244
Ge_2H_2	−11.91	3.49	2.44	1.56	107.77	0.75	−0.29	+0.29	1.08
Ge_2Li_2	−12.12	3.35	2.54	2.63	61.58	1.21	+0.82	−0.82	0.14
Ge_2Na_2	−10.73	3.39	2.53	3.09	63.26	1.14	+0.66	−0.66	M
Ge_2K_2	−10.01	3.54	2.58	3.45	65.88	1.06	+0.49	−0.49	M
Ge_2Rb_2	−6.71	3.43	2.49	3.52	67.01	0.97	+0.37	−0.37	M
Ge_2H_1	−8.75	3.05	2.49	1.58	107.69	0.76	−0.19	+0.26	M
Ge_2Li_1	−8.15	3.47	2.42	2.54	107.19	0.72	+0.50	−0.50	M
Ge_2Na_1	−7.94	3.45	2.42	2.95	107.84	0.74	+0.26	−0.27	M
Ge_2K_1	−7.86	3.52	2.45	3.29	106.84	0.71	+0.26	−0.28	M
Ge_2Rb_1	−5.29	3.54	2.46	3.39	106.56	0.70	+0.24	−0.27	M

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