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Formation, Stability, Geometry and Band Structure of Organically Surface-Modified Germanane

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Surface modification may be an effective means for controlling the properties of germanane, i.e., hydrogenated germanene. In this work, we investigate the formation, stability, structure and electronic properties of surface-modified germanane that results from the hydrogermylation, alkoxylation, aminization or phenylation of germanane. By assuming the typical organic surface coverage of ~33%, we have compared organically surface-modified germanane with germanene and germanane in the framework of density functional theory. It is found that organically surface-modified germanane may all stably exist despite the endothermic nature of organic surface modification. Organic surface modification leads to the decrease of the Ge–Ge bond length and the Ge–Ge–Ge bond angle of germanane, while causing the buckling distance of germanane to increase. Hydrogenation makes germanene change from a semimetal to a direct-bandgap semiconductor. Organic surface modification further impacts the band structure of the resulting germanane. Hydrogermylated/alkoxylated germanane is a direct-bandgap semiconductor, while aminated/phenylated germanane is an indirect-bandgap semiconductor. All the organic surface modification gives rise to the increase of the bandgap of germanane.

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1. Introduction

Two-dimensional layered materials have been attracting great interest^[1–7]. Among all kinds of two-dimensional layered materials, germanene holds great promise given its compatibility with current silicon-based microelectronics and strong spin-orbital coupling^[8]. It is significant that germanene has already been grown on Pt(111), Au(111), and Al(111) substrates^[9–13]. However, germanene is a nearly zero-bandgap semimetal, impeding its application in electronics. A variety of methods have been employed to turn on the bandgap of germanene, including the application of a vertical electric field and the surface adsorption of alkali metal^[4,14]. It has been realized that surface modification is one of the most important approaches to tune the bandgap of germanene^[15–18]. Bianco et al. and Jiang et al. have found that the surface of germanene may be passivated by hydrogen, leading to the formation of germanane^[16,17]. Germanane is a direct-bandgap semiconductor. It has been demonstrated that organic surface modification may be carried out for hydrogen-passivated silicene (i.e., silicane)^[19–21]. In principle, organic surface modification should also apply for germanane. As the first

attempt, Jiang et al. have managed to modify the surface of germanane by using methyl groups^[17]. The methyl-based organic surface modification resulted in the increase of the bandgap of germanane.

In this work we consider four potentially popular organic surface modification schemes (hydrogermylation, alkoxylation, aminization and phenylation) for germanane in the framework of density functional theory (DFT). We assume a typical organic surface coverage of ~33%, which has been experimentally identified for organically surface-modified silicane^[19–21]. It is found that the organic surface modification of germanane is endothermic. The resulting organically surface-modified germanane is stable. Organic surface modification reduces the Ge–Ge bond length and the Ge–Ge–Ge bond angle of germanane while causing the buckling distance of germanane to increase. The bandgap of germanane increases after hydrogermylation, alkoxylation, aminization or phenylation. Hydrogermylated germanane and alkoxyated germanane are direct-bandgap semiconductors. However, aminated germanane and phenylated germanane are indirect-bandgap semiconductors.

2. Model and Method

Fig. 1 shows the optimized structures of germanene, germanane (hydrogenated germanene) and hydrogermylated germanane,

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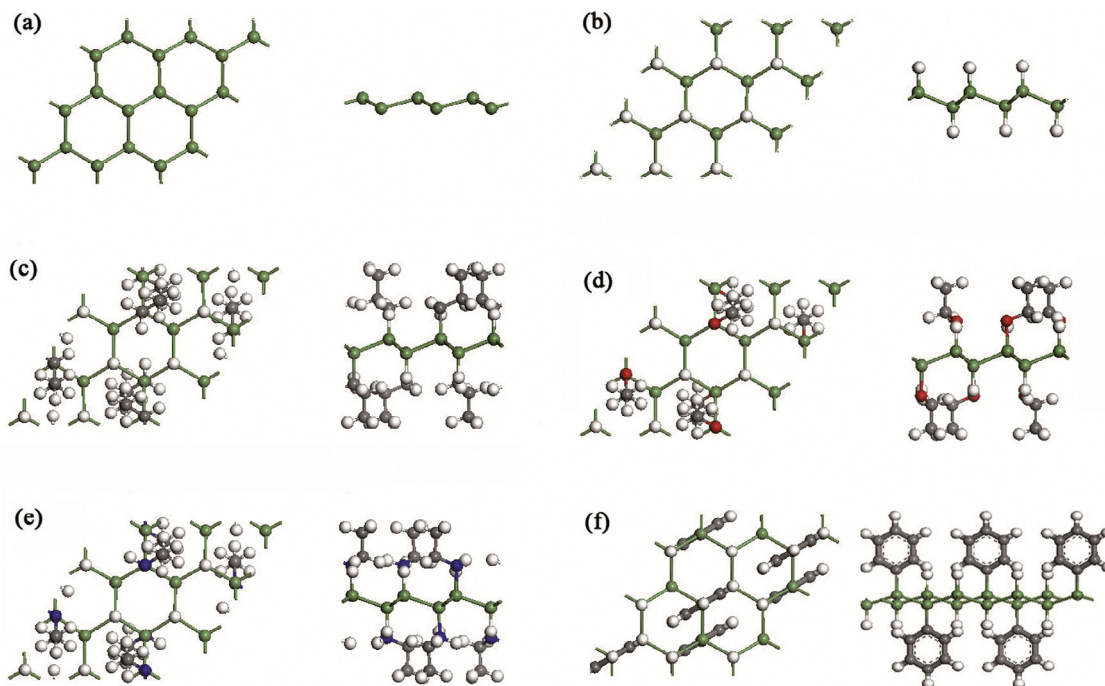


Fig. 1. Optimized structures of (a) germanene, (b) germanane, (c) hydrogermylated germanane, (d) alkoxyate germanane, (e) aminated germanane and (f) phenylated germanane. Both top (left) and side (right) views of these structures are shown. Ge, H, C, O and N atoms are denoted by green, white, grey, red and blue balls, respectively.

alkoxyated germanane, aminated germanane and phenylated germanane with both top and side views. A 3×3 supercell is used to sufficiently optimize each structure. Image-image interaction between adjacent atomic layers is avoided by setting a distance of 20 Å. The most energetically stable chair-like configuration is chosen for germanane as a starting point^[22]. Propylene ($\text{CH}_2=\text{CH}-\text{CH}_3$), ethanol ($\text{CH}_3-\text{CH}_2-\text{OH}$), ethylamine ($\text{CH}_3-\text{CH}_2-\text{NH}_2$) and phenylmagnesium bromide ($\text{C}_6\text{H}_5-\text{MgBr}$) are representatively chosen to enable the hydrogermylation, alkoxylation, amination and phenylation of germanane, respectively. Please note that a typical organic surface coverage of ~33% is assumed for each organic surface modification scheme. The organic surface coverage of ~33% corresponds to the fact that the ratio of the number of Ge-H to that of Ge-X ($X = \text{C}$ for hydrosilylation, O for alkoxylation, N for amination and Ph for phenylation) is 2, as shown in Fig. 1(c-f).

All the calculations in this work have been performed in the framework of DFT, which is implemented in the Vienna ab initio Simulation package (VASP) with the projector-augmented wave (PAW) method^[23,24]. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential is employed at the generalized gradient approximation (GGA) level. All the calculations proceed until the changes in energy are less than 1×10^{-6} eV per cell. The force

convergence on each atom is set at 1×10^{-5} eV/Å. A $(9 \times 9 \times 1)$ special Monkhorst-Pack k-point mesh is used in the Brillouin zone during both the geometry optimization and density-of-states (DOS) calculation^[25,26]. When band structures are calculated, thirty points between neighboring high symmetric k-points are considered. We would like to point out that PBE-based DFT calculations underestimate the bandgap of a semiconductor because of quasiparticle and excitonic effects^[27,28]. However, the underestimation does not affect the relative order of the bandgaps^[28].

3. Results and Discussion

Table 1 shows the structural parameters of germanene, germanane, hydrogermylated germanane, alkoxyated germanane, aminated germanane and phenylated germanane. For germanene, the bond length of Ge-Ge is 2.44 Å. The bond angle of Ge-Ge-Ge is 112°. The buckling distance is 0.69 Å. After hydrogenation, the bond length of Ge-Ge does not change, while the bond angle of Ge-Ge-Ge decreases to 109°. The buckling distance increases to 0.81 Å. These changes indicate the transition from mixed sp^2/sp^3 hybridization in germanene to sp^3 hybridization in germanane for Ge atoms. Please note that the current structural properties of

Table 1 Formulas, structural properties, binding energies (E_b), formation energies (E_f) and bandgaps (E_g) of germanene, germanane and organically surface-modified germanane. The structural properties include the buckling distance (Δ), the Ge-Ge bond length ($\langle \text{Ge-Ge} \rangle$) and the Ge-Ge-Ge angle ($\angle(\text{Ge-Ge-Ge})$). The superscripts of i and d stand for the indirect and direct bandgaps, respectively

	Germanene	Germanane	Hydrogermylated germanane	Alkoxyated germanane	Aminated germanane	Phenylated germanane
Formula	Ge_{18}	$\text{Ge}_{18}\text{H}_{18}$	$\text{Ge}_{18}\text{C}_{18}\text{H}_{54}$	$\text{Ge}_{18}\text{C}_{12}\text{O}_6\text{H}_{42}$	$\text{Ge}_{18}\text{C}_{12}\text{N}_6\text{H}_{42}$	$\text{Ge}_{18}\text{C}_{36}\text{H}_{42}$
$\langle \text{Ge-Ge} \rangle$ (Å)	2.44	2.44	2.42 (0.8%)	2.42 (0.8%)	2.42 (0.8%)	2.41 (1.2%)
$\angle(\text{Ge-Ge-Ge})$ (°)	112	109	109	106-108	107-108	105-106
Δ (Å)	0.69	0.81	0.90 (11.1%)	0.93 (14.8%)	0.90 (11.1%)	0.95 (17.3%)
Ge-X (Å)	-	1.59	1.99	1.96	1.96	1.99
E_f (eV)	-	-4.4	48.7	37.0	39.6	74.4
E_b (eV)	-	3.7	4.8	4.8	4.8	5.5
E_g (eV)	0	0.9 ^d	1.8 ^d	1.2 ^d	1.6 ⁱ	1.1 ⁱ

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