Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Intrinsic magnetism and spontaneous band gap opening in bilayer silicene and germanene

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A. Possible structures for bilayer silicene (germanene)

Within silicene (germanene) monolayer, the overlap of p_z orbitals between neighboring Si-Si (Ge-Ge) atoms is much smaller than that of C-C in graphene; therefore, the sp^2 hybridization is dehybridized to be sp^3-like by buckling to regain stability. A silicene (germanene) monolayer can be divided into two halves and each occupies one of the two sublattices (top ***t*** and bottom ***b***, separated by the bucking parameter Δ. As shown in Figure S1, due to the buckling character of silicene (germanene) monolayer, the AA and AB stacking bilayer systems have two and three variants, respectively, i.e., AA with aligned top-top sublattices (AA-α), AA with aligned bottom-top sublattices (AA-β), AB with aligned top-bottom sublattices (AB-α), AB with aligned top-top sublattices (AB-β), and AB with aligned bottom-top sublattices (AB-γ). These five configurations have various symmetries: the AA-α, AB-α, and AB-γ possess the D_{3d} symmetry, while the point group for AA-β is D_{3h}, and AB-β has the lowest symmetry C_{3v} among them. As summarized in Table 1S, the AB-γ configuration has the lowest total energy.

Table 1S. Optimized structural parameters and total energies for the five possible bilayer silicene configurations. Here a (in Å) is the lattice constant, h (in Å) is the interlayer distance, and Δ is the buckling parameter, i.e., the distance between the top and bottom sublattices within one layer. Data in the upper and lower columns for one structure are obtained using PBE and optB86b-vdW functionals, respectively.

Structure	a (Å)	h (Å)	Δ (Å)	Total energy (eV/unit cell)
AA-α	3.770	2.714	0.925	-19.650
	3.733	2.695	0.940	-20.229
AA-β	3.867	3.100	0.652	-19.524
	3.838	3.074	0.653	-20.125
AB-α	3.861	3.933	0.488	-19.172
	3.822	3.389	0.563	-19.737
AB-β	3.818	2.983	0.708	-19.303
	3.782	2.929	0.749	-19.902
AB-γ	3.853	3.189	0.667	-19.658
	3.825	3.150	0.668	-20.248

B. Energy barriers for phase transitions from AA-α or AA-β to AA-planar

We note that under compression, two AA stacking configurations could transform into another geometry (AA-planar with the point group of D_{6h}, see Figure 1S) with all atoms fully bonded. AA-planar has a lower total energy than AA-α and AA-β because of more interlayer bonds. Such phase has already been studied by Bai *et.al.*,[1] which was predicted to be a semimetal with an indirect zero band gap.

We used the climbing image nudged elastic band (CI NEB) method[2,3] to simulate the phase transition from AA-α (AA-β) to AA-planar. As shown in Figure 2S, though AA-α has a total energy 0.124 eV/cell higher than AA-planar, the corresponding energy barrier is 0.20 eV per unit cell. On the other hand, the total energy difference between AA-β and AA-planar is 0.347 eV per unit cell, with an energy barrier of 0.20 eV per unit cell.

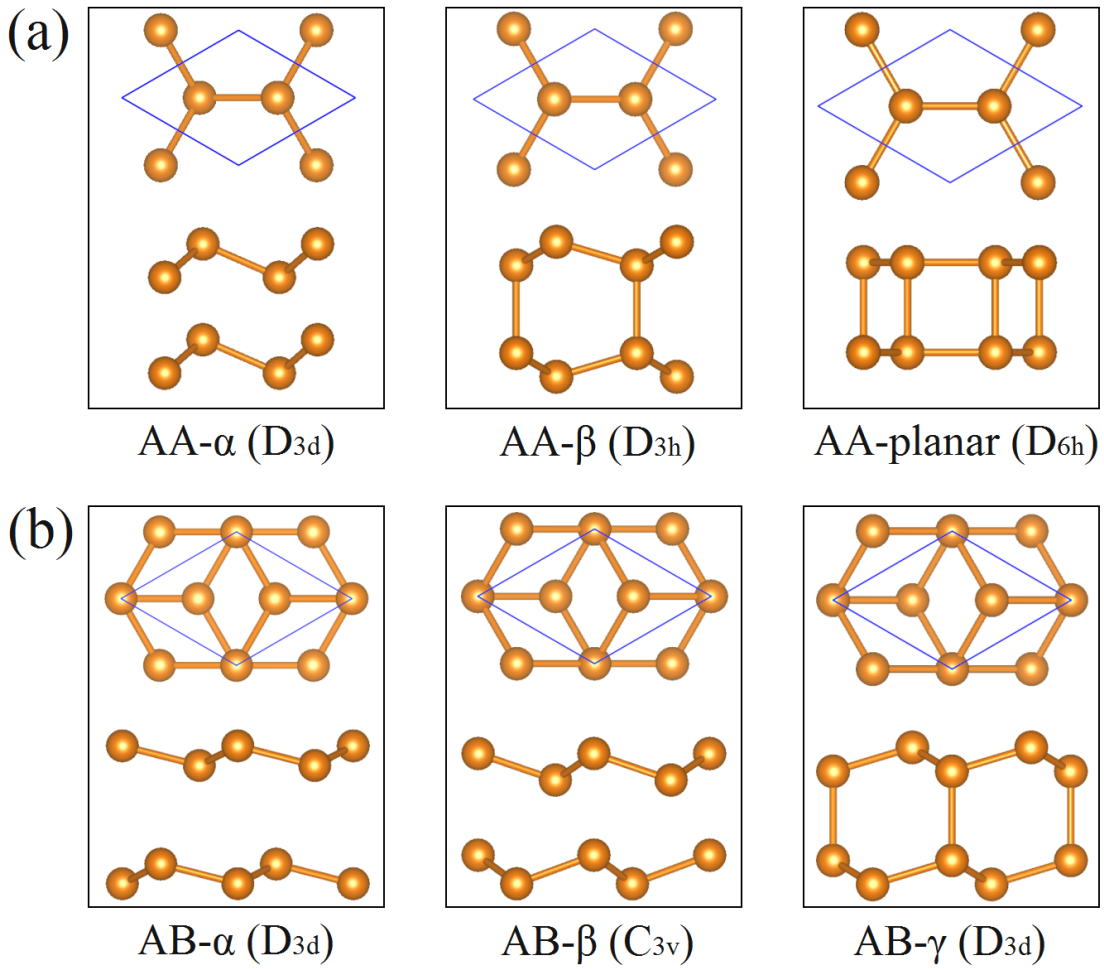

Figure 1S. The variants for (a) AA stacking and (b) for AB stacking of bilayer systems. In panel (a) both AA-*α* and AA-*β* can transform into a planar structure of AA-planar with the D_{6h} symmetry.

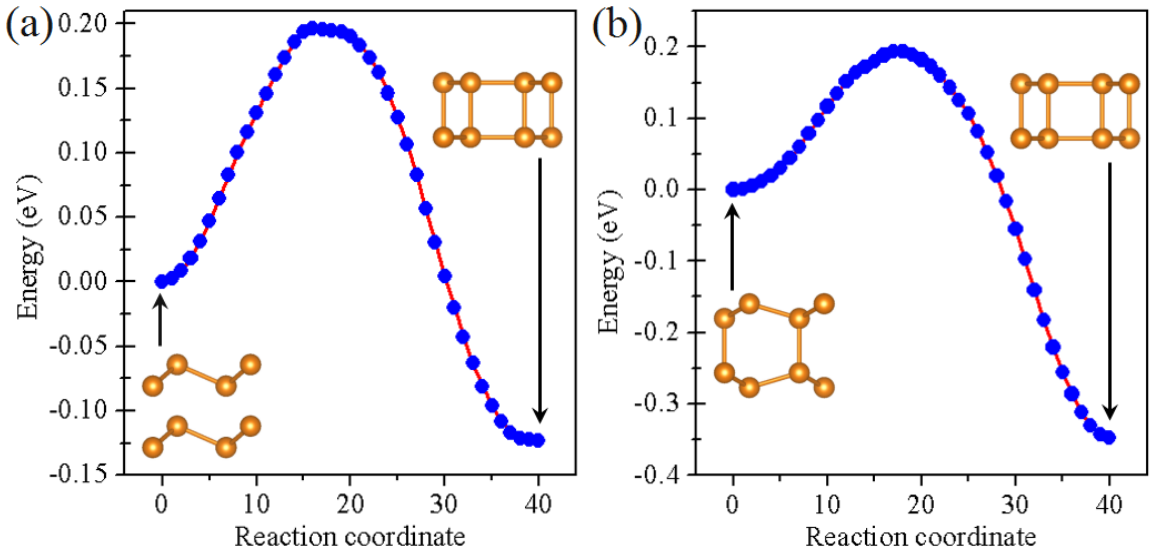

Figure 2S. Relative total energy per unit cell versus reaction coordinate for the phase transition from AA-*α* (a) and AA-*β* (b) to AA-planar.

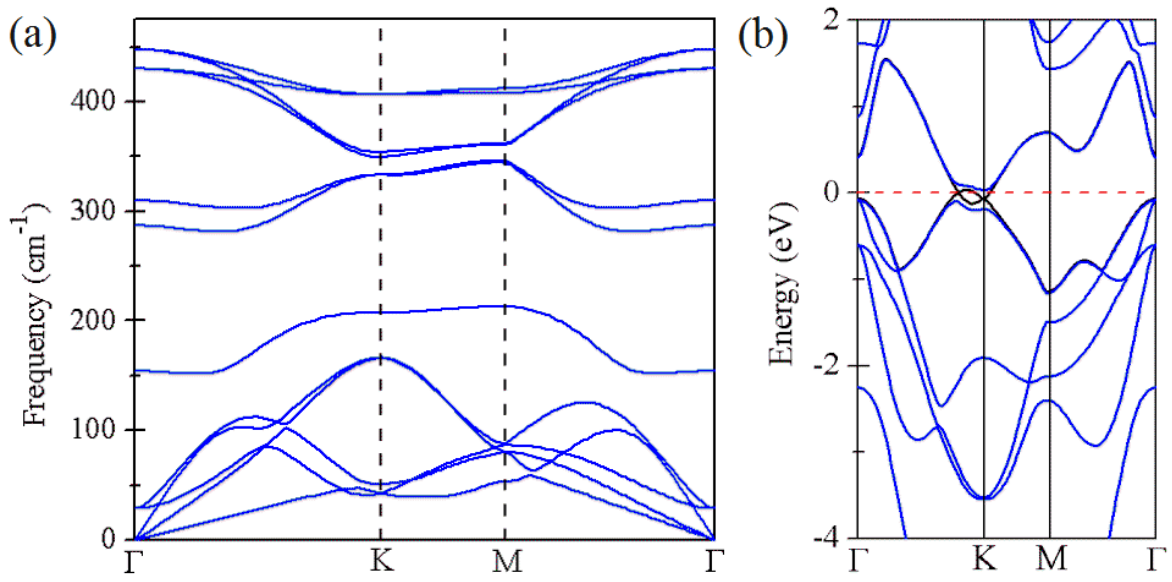

Figure 3S. (a) Phonon dispersion in bilayer germanene of the AB-*γ* configuration. (b) Electronic band structure for spin-polarized state (in blue) of the bilayer germanene. We also plotted two bands (in black) near the Fermi level (red dashed line) for the non-spin-polarized state.

C. Phonon dispersion and electronic band structure of bilayer germanene

Due to the similarity between silicene and germanene as well as the significance for germanium of being an important semiconductor material, we also studied the bilayer germanene. When two germanene monolayers are attached together, they can also form the AB-*γ* configuration. Figure 3S (a) shows its phonon dispersion without imaginary branches; therefore it is dynamically stable. Its highest optical branch locates at Γ, which belongs to a doubly degenerate mode with a frequency of ω_Γ = 450 cm^{-1}, much lower than 521 cm^{-1} in bilayer silicene.

We plot the electronic band structures of bilayer germanene in Figure 3S (b). The system is metallic at the non-spin-polarized state; however, upon including the spin degree of freedom, a band gap of 0.13 eV appears, and it is further increased to 0.32 eV using the *GW* approximation. It should be specified that, its conductive band minimum is located near K, while its valence band maximum is moved to Γ rather staying along Γ-K as that of bilayer silicene.

Reference:

(1) Bai, J.; Tanaka, H.; Zeng, X. C. Nano Res. **2010**, 3(10), 694.
(2) Sheppard, D; Xiao, P; Chemelewski, W.; Johnson, D. D.; Henkelman; G. J. Chem. Phys. **2012**, 136, 074103.
(3) Sheppard, D; Henkelman, G J. Comp. Chem. **2011**, 32, 1769.