Supplement Information for "Quantum Spin Hall effect in tilted penta silicene and its isoelectronic substitutions"

Lijin Zhan,[1,*] Yimei Fang,[1,*] Ruotong Zhang,[1] Xiancong Lu,[1]
Tie-yu Lü,[1] Xinrui Cao,[1,2] Zi-zhong Zhu,[1,2] and Shunqing Wu[1,†]

[1]*Department of Physics, OSED, Key Laboratory of Low Dimensional Condensed Matter Physics (Department of Education of Fujian Province), Jiujiang Research Institute, Xiamen University, Xiamen 361005, China*
[2]*Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, Xiamen 361005, China*

GEOMETRIC STRUCTURES AND STABILITIES OF LOW-ENERGY 2D SILICON ALLOTROPES FROM AGA SEARCH

We briefly discuss here the geometric and stabilities of the other two silicon structures obtained from our AGA search, named tilted Tetra-hex (*tTetra-hex*) silicene and tilted hexagon (*tHex*)silicene. The geometric configurations of *tTetra-hex* silicene and *tHex* silicene are depicted in Fig. S1(a)(b) and Fig. S1(e)(f), while their lattice constants are listed in Table 1. It is shown that both *tTetra-hex* silicene and *tHex* silicene look similar to *tPenta* silicene from side view. However, the pentagonal nanoribbons in *tPenta* silicene are replaced by tetragonal-hexagonal stripes in *tTetra-hex* silicene, while there only exists hexagonal stripes in *tHex* silicene. From Fig. S1(c)(d), we can see that the atoms (labelled by 1, 2, 3, and 4 in Fig. S1(a)) that compose the tetragonal rings in the tetragonal-hexagonal stripes are lying on the plane while the other two atoms (atom 5 and 6) are slightly deviated from the plane. The tilted angle θ of tetragonal-hexagonal nanoribbons are 32.19°, which is close to that of tPenta silicene. Nevertheless, these two allotropes are found to be unstable.

TABLE I: The geometrical parameters a, b, and γ for *tPenta* silicene, *tTetra-hex* silicene, and *tHex* silicene, respectively. The tilted angle for pentagonal and tetragonal-hexagonal nanoribbons with respect to the *ab* plane are represented by θ.

System	a(Å)	b(Å)	γ (Deg)	θ (Deg)
tPenta silicene	4.231	5.546	90	33.25
tTetra-hex silicene	5.034	5.034	66.88	32.19
tHex silicene	3.776	5.301	72.33	/

Another five silicene allotropes which have lower energies with respect to silicene are shown in Fig. S2. Although the these configurations are energetically more favorable than silicene, they are dynamically and thermaldynamically unstable.

STABILITIES OF *TPENTA* SILICENE

The dynamical and thermaldynamical stability of the *tPenta* silicene are verified by our phonon calculations and ab initio molecular dynamics (AIMD) simulations. A 3×5 supercell was used to perform the phonon calculations. From the phonon spectra shown in Fig S3 (a), we see that there is no imaginary modes in the entire Brillouin zone, indicating that the *tPenta* silicene is dynamically stable. A 4×4 supercell is constructed to conduct the AIMD simulations at temperatures of 300 K, 500 K, and 700 K with a time step of 2 femtoseconds (fs). As shown in Fig S3(b), during the whole heating process, the total potential energies only fluctuate around a constant value, suggesting that the *tPenta* silicene have good thermaldynamical stability and can withstand a high temperature of 700 K.

tPenta $Si_{0.333}Ge_{0.667}$ AND *tPenta* $Si_{0.333}Sn_{0.667}$

The optimized geometries of *tPenta* $Si_{0.333}Sn_{0.667}$ is displaced in Fig. S5 (a). It is shown that the geometrical configuration of *tPenta* $Si_{0.333}Sn_{0.667}$ is nearly unchanged compared with *tPenta* silicene and *tPenta* $Si_{0.333}Ge_{0.667}$. Based

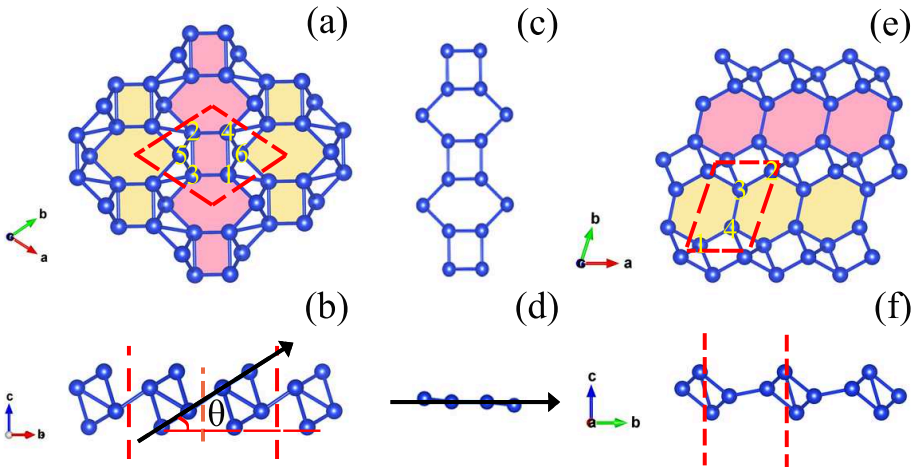

FIG. S1: Geometric configurations of *tTetra-hex* silicene and *tHex* silicene. The red dashed rhomboids represent the unit cells. Top (a) and side (b) view of *tTetra-hex* silicene. Top (c) and side (d) view of tetragonal-hexagonal nanoribbons in the *tTetra-hex* silicene. θ denotes the tilted angle. The six silicon atoms in the unit cell of *tTetra-hex* silicene are indicated by arabic numerals 1, 2, 3, 4, 5 and 6, respectively. Top (e) and side (f) view of *tHex* silicene. The four silicon atoms in the unit cell are indicated by arabic numerals 1, 2, 3, 4, respectively.

on phonon spectra (Fig. S5 (c)) and AIMD simulations(Fig. S5 (e)), we demonstrate that the *tPenta* $Si_{0.333}Sn_{0.667}$ also exhibit good dynamical and thermodynamical stabilities. To better describe the electronic structure of *tPenta* $Si_{0.333}Sn_{0.667}$, we also perform the band structure calculations using the HSE06 functional, the result is shown in Fig. S5 (f). The indirect band gap calculated from HSE06 approximation is 44.0 meV (without SOC) and 94.3 meV (with SOC), which are an order of magnitude larger than the corresponding band gap of PBE.

* These authors contributed equally to this work
† Electronic address: wsq@xmu.edu.cn

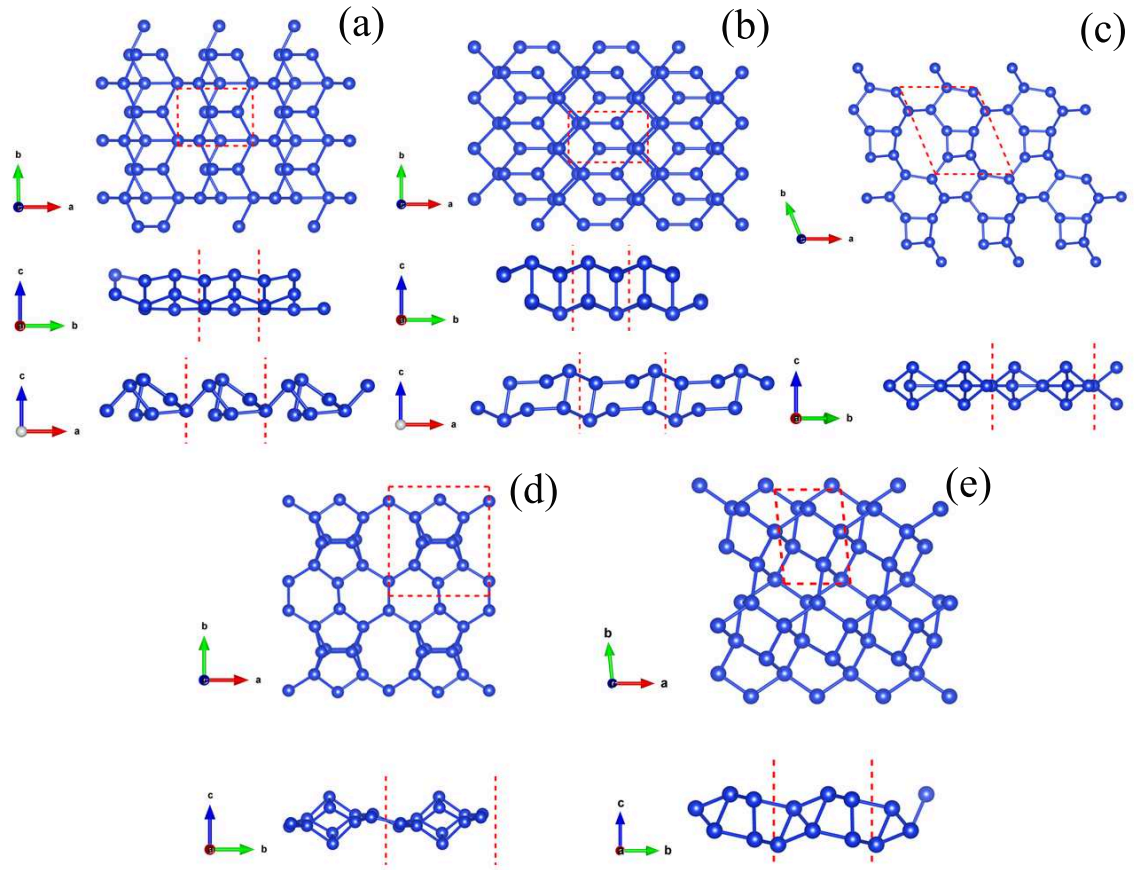

FIG. S2: Geometric configurations of silicene allotropes that have lower energies with respect to the honeycomb silicene.

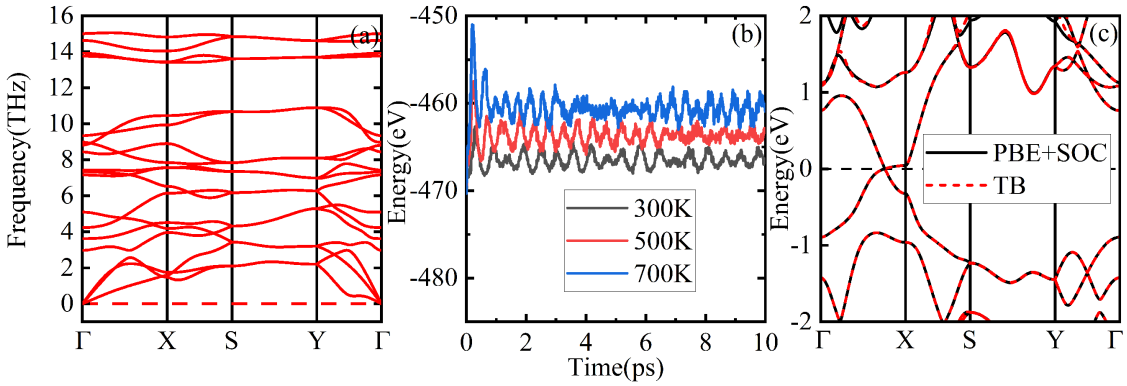

FIG. S3: The phonon spectra (a) and the fluctuation of total potential energies during the AIMD simulation (b) of *tPenta* silicene. (c) The band structure of the *tPenta* silicene with SOC, the black solid lines indicate the PBE result and the red dashed lines represent the fitted one by wannier90.

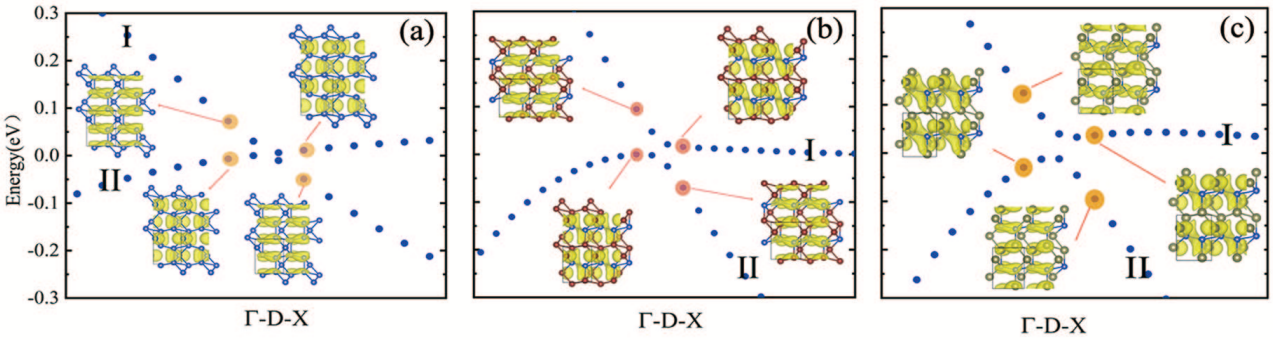

FIG. S4: Charge density distributions near the distorted Dirac cone for *tPenta* silicene (a), $Si_{0.333}Ge_{0.667}$ (b), and $Si_{0.333}Sn_{0.667}$ (c). Fermi level has been set to zero.

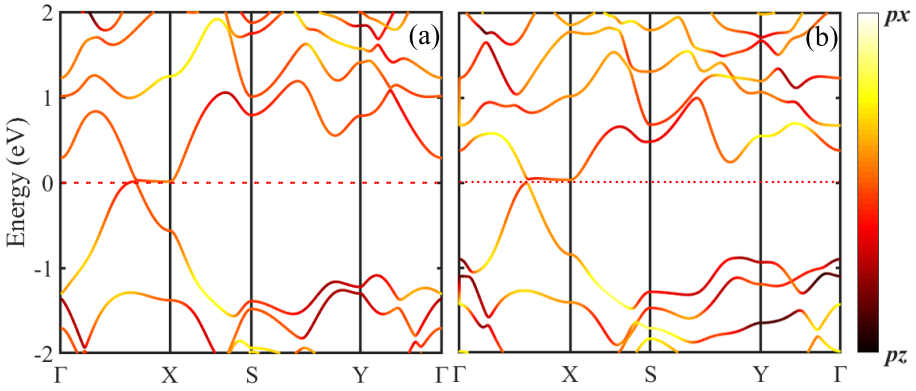

FIG. S5: Orbitally resolved electronic structure of *tPenta* $Si_{0.333}Ge_{0.667}$ (a), and $Si_{0.333}Sn_{0.667}$ (b). Fermi level has been set to zero.

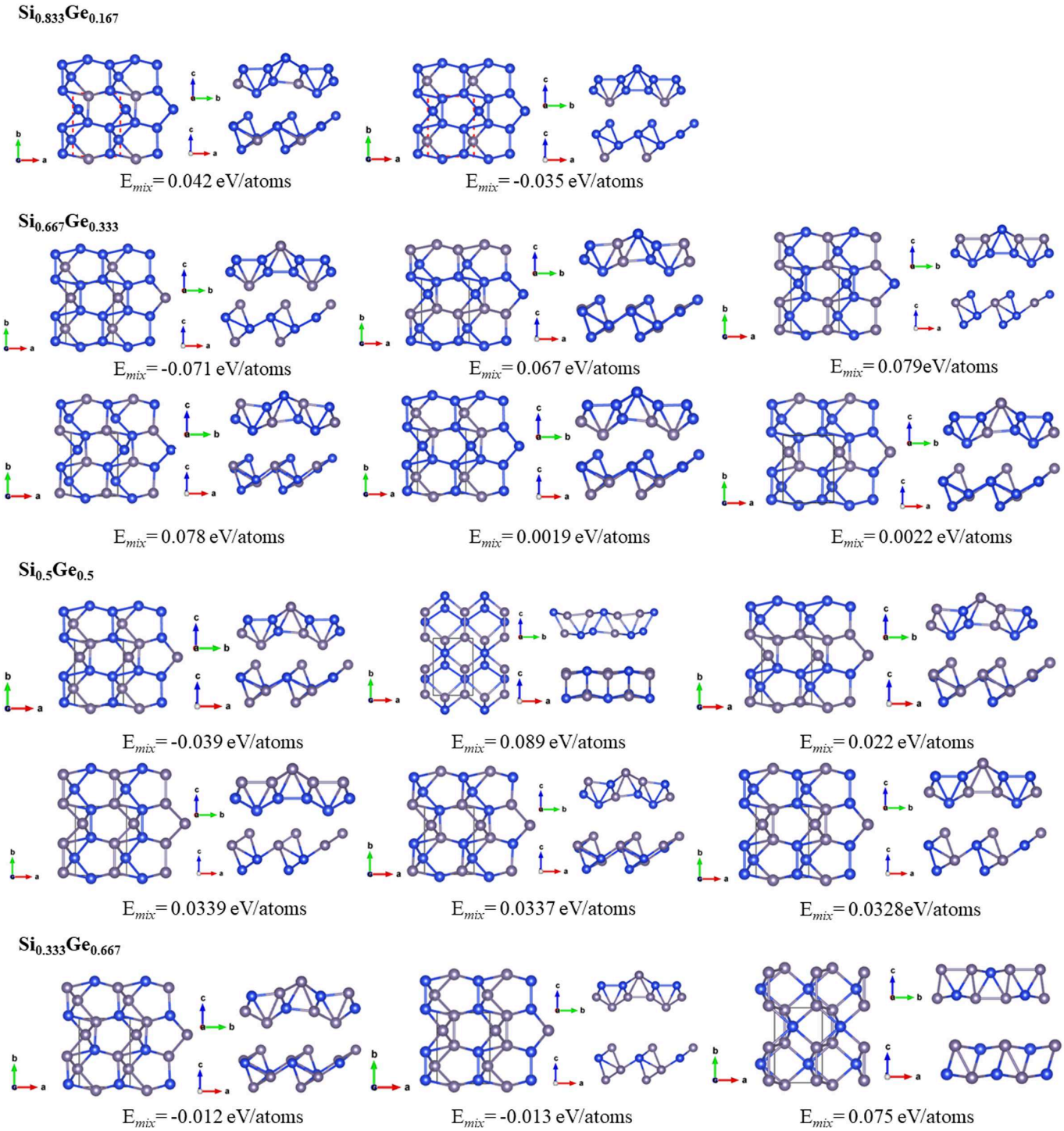

FIG. S6: All 22 configurations of *tPenta* Si_xGe_{1-x} -1.

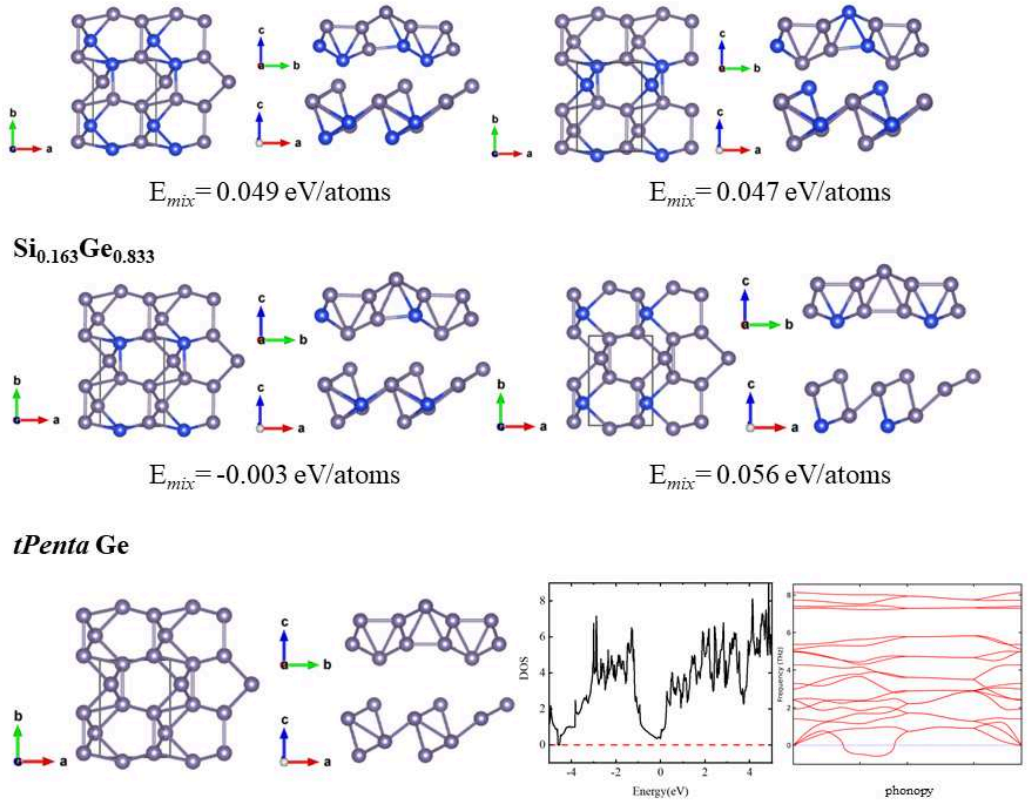

FIG. S7: All 22 configurations of *tPenta* Si_xGe_{1-x} -2. The density of states and the dynamical stability of *tPenta* Ge are shown, respectively.

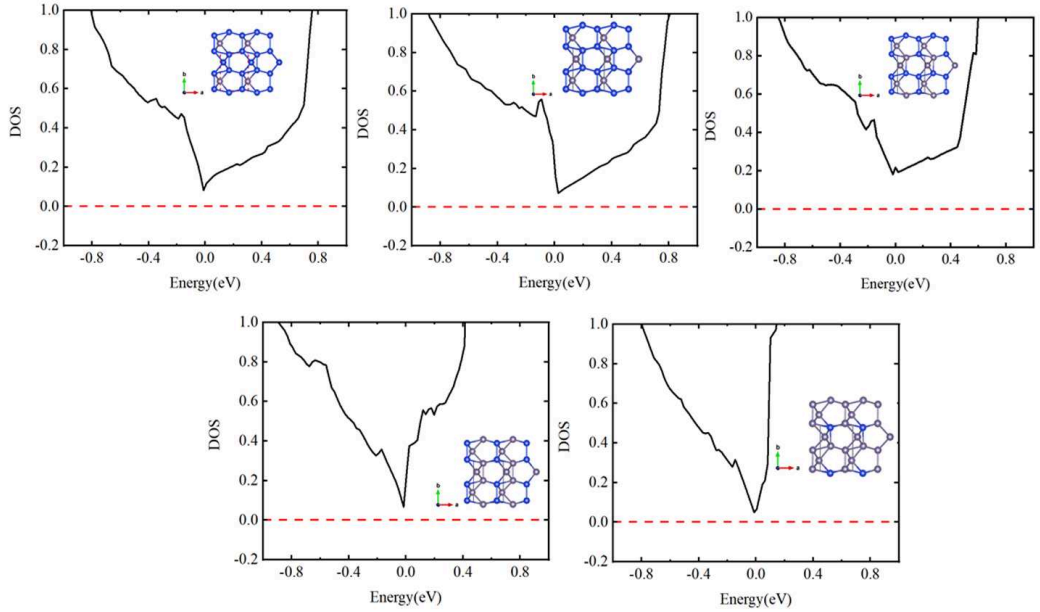

FIG. S8: The density of states of the equilibrium phases and the metastable phases we selected.

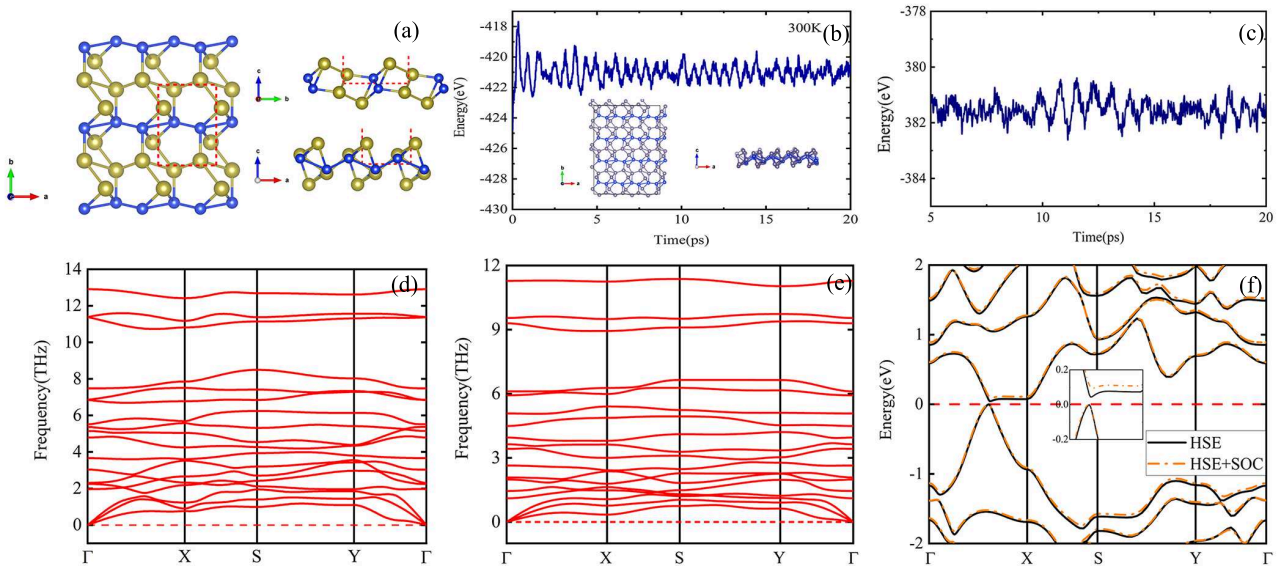

FIG. S9: Top and side (a) geometric views of *tPenta* $Si_{0.333}Sn_{0.667}$, where the claybank and blue balls represent Sn and Si atoms, respectively. The red dashed rectangle represents the unit cell. The thermal (b)(c) and dynamical (d)(e) and stabilities of *tPenta* $Si_{0.333}Ge_{0.667}$ and *tPenta* $Si_{0.333}Sn_{0.667}$, respectively. (f) Band structures calculated without (balck solid lines) and with (orange dashed lines) SOC using the HSE06 functional of *tPenta* $Si_{0.333}Sn_{0.667}$.