Supporting Information

Design Rule for Two-Dimensional van der Waals Heterostructures with Unconventional Band Alignments

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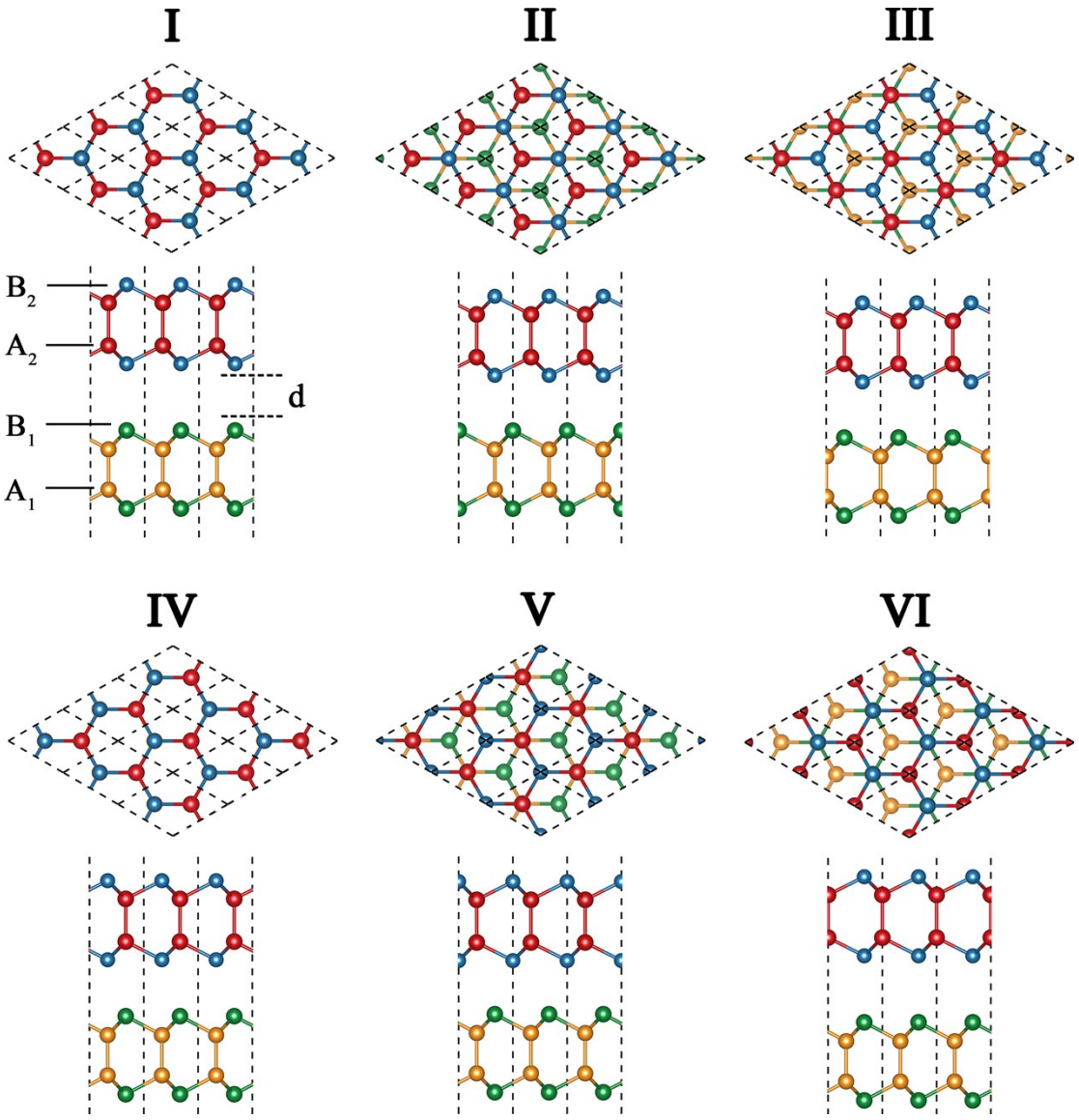

Fig. S1. Stacking patterns of the heterostructures. Top and side views of six different stacking of the group IV-V heterostructures. A and B denote the elements from the group-IV and V, respectively. The unit cells of the monolayer and heterostructure are shown in black dash line.

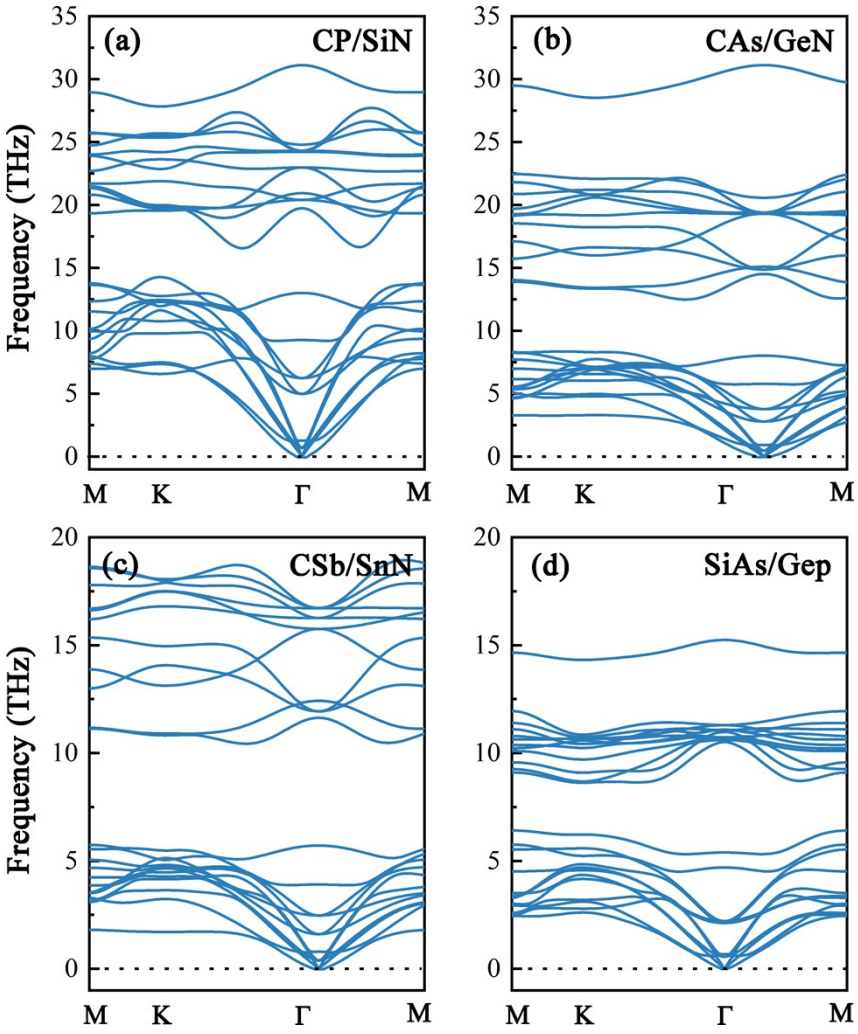

Fig. S2. **Phonon dispersions of four group IV-V heterostructure.** The phonon dispersion curves of (a) CP/SiN, (b) CAs/GeN, (c) CSb/SnN and (d) SiAs/GeP.

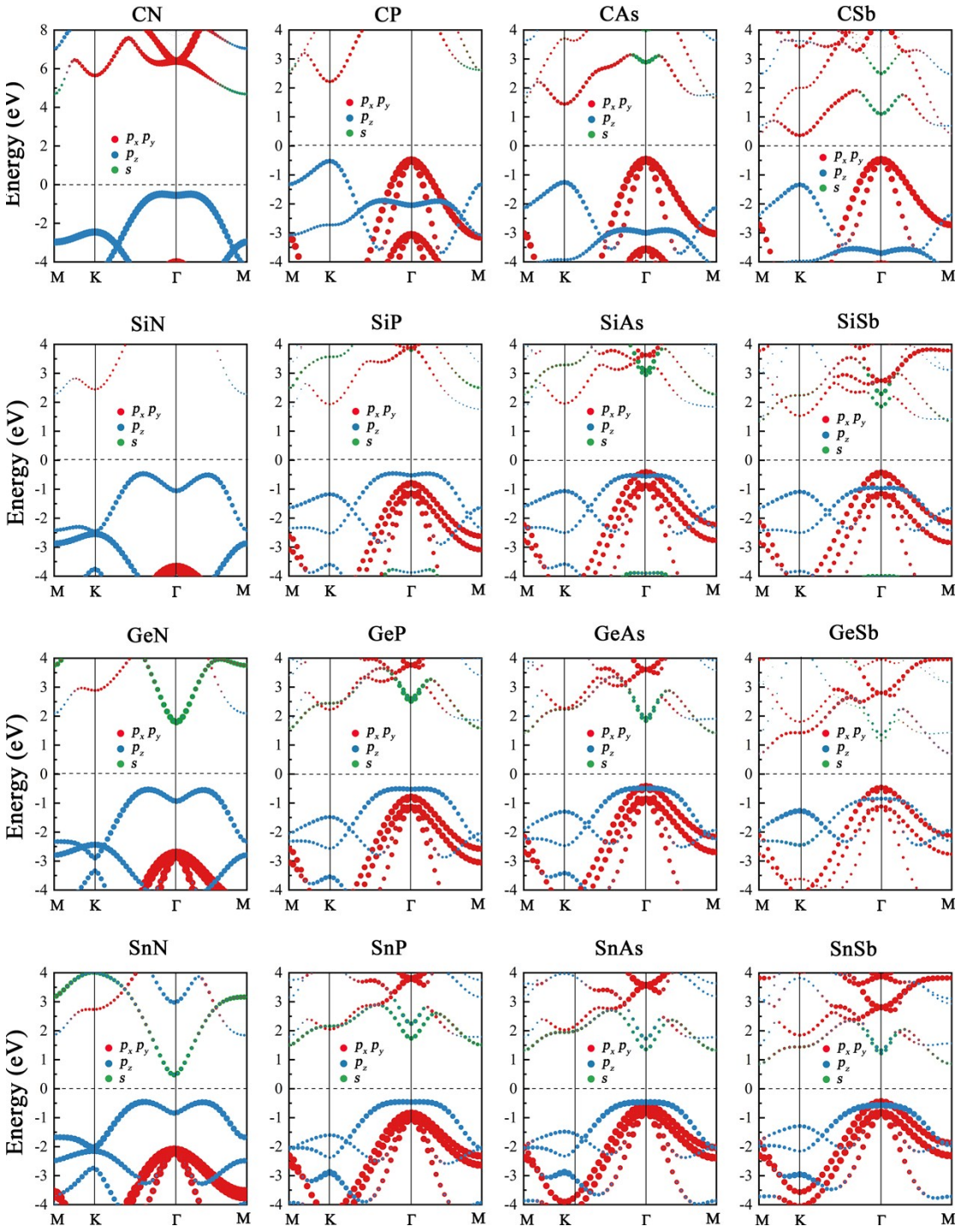

Fig. S3. Electronic structures of group IV-V monolayers. The projected band structures of 16 group IV-V monolayers. The red dots denote the p_x and p_y orbitals, while blue and green dots represent p_z and s orbitals, respectively. Black dash line denotes the Fermi level.

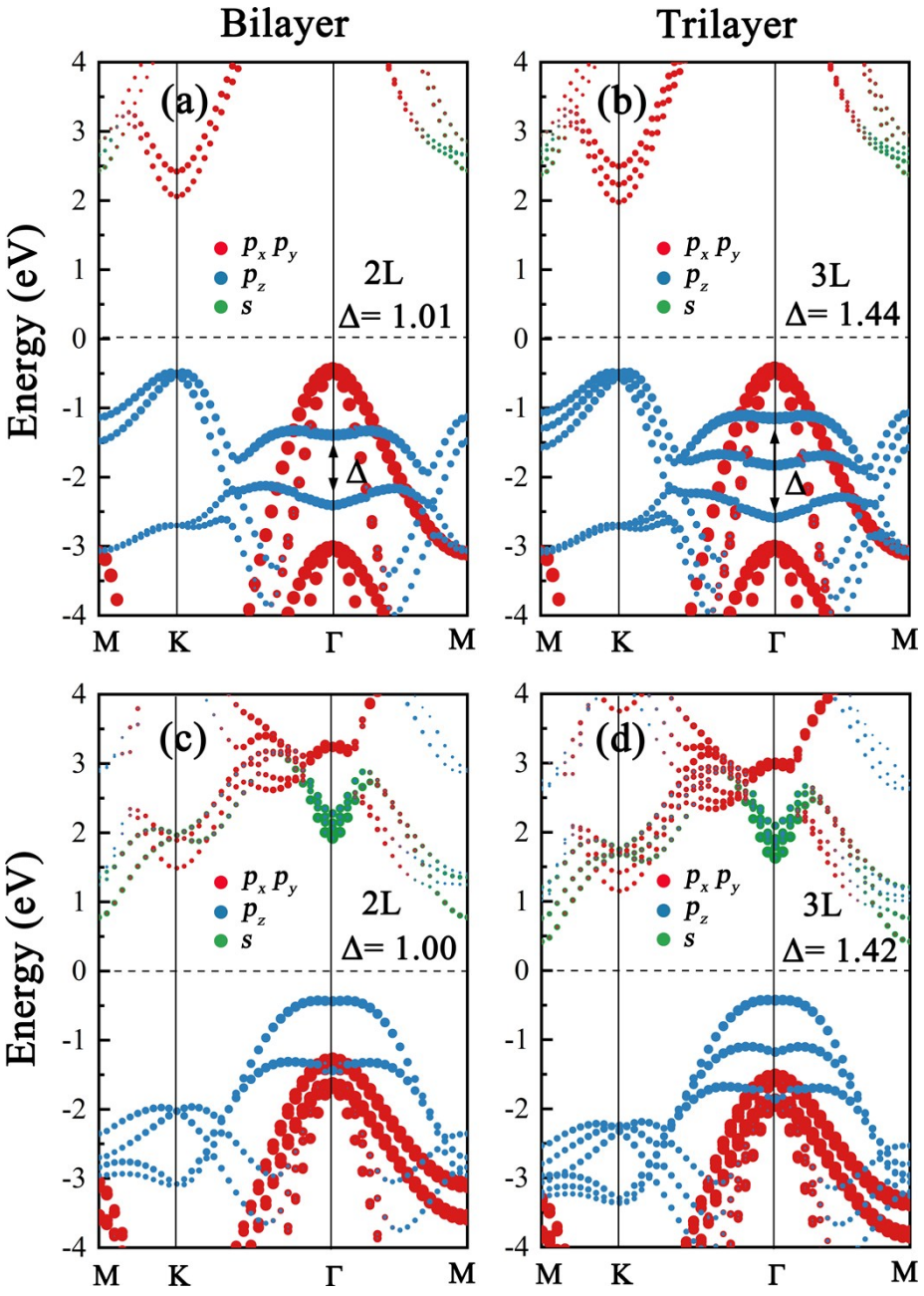

Fig. S4. Electronic structures of multilayer CP and GeP. Projected band structures of bilayer and trilayer of (a,b) CP and (c,d) GeP, respectively. The red dots represent the p_x and p_y orbitals, while blue and green dots represent p_z and s orbitals, respectively. Black dashed line represents the Fermi level. Δ (eV) is the energy difference between the QB with highest and lowest energy at Γ point.

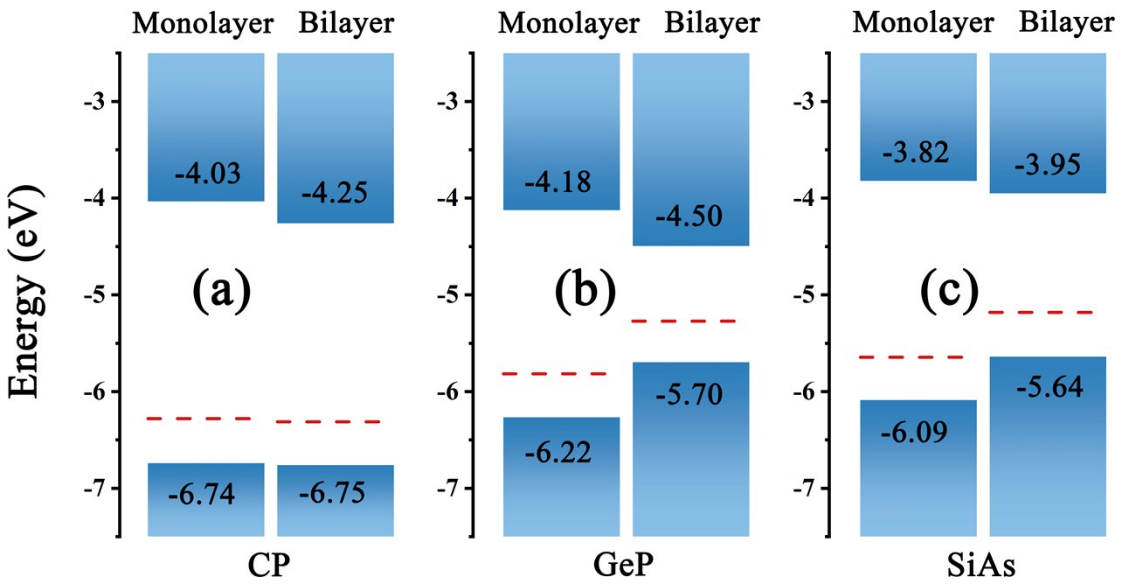

Fig. S5. Schematic diagrams of band alignment of three group IV-V semiconductors. Band edge positions of (a) CP (b) GeP and (c) SiAs monolayer and bilayer, respectively. The vacuum level is set to 0 eV. The red dashed line represents the Fermi level.

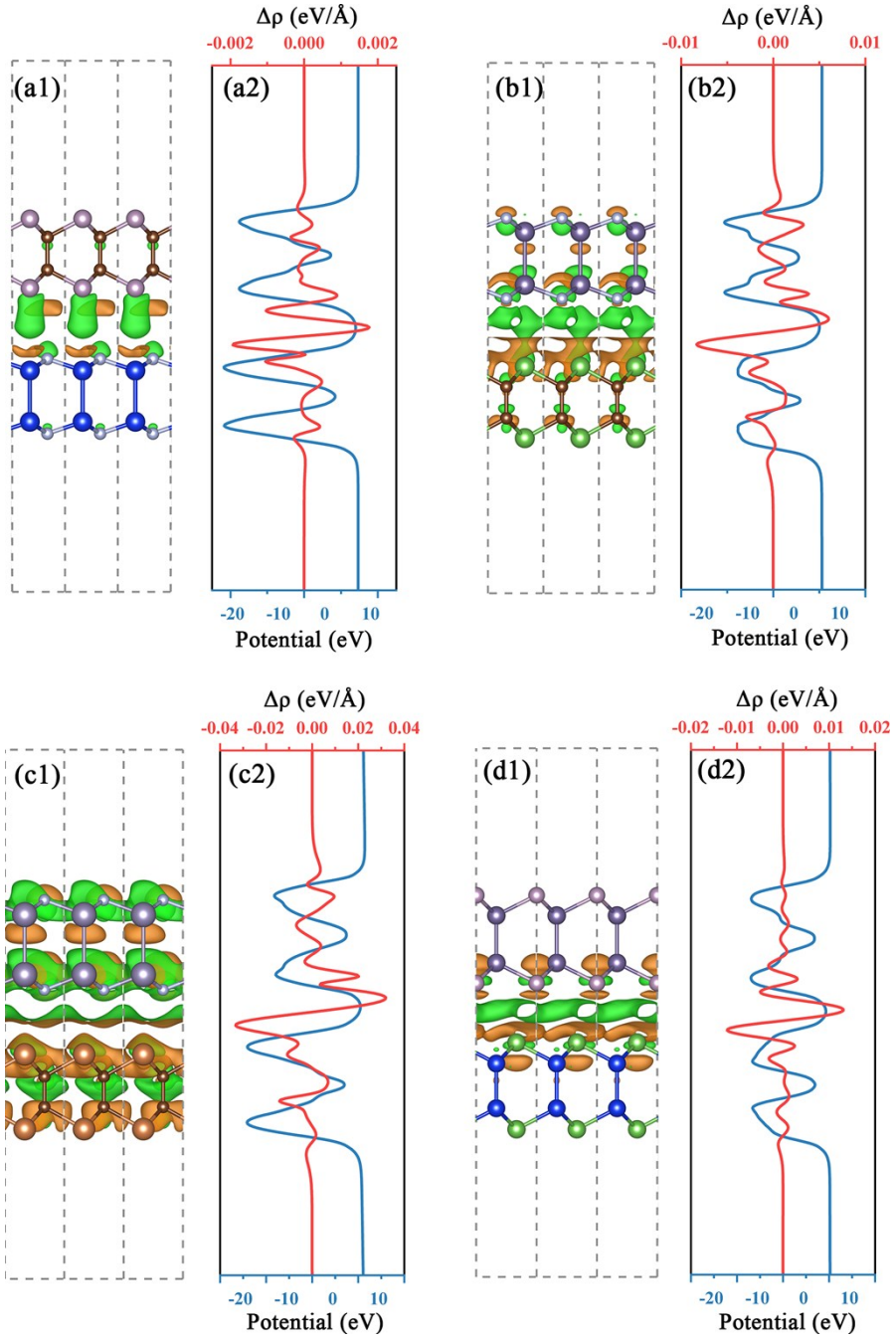

Fig. S6. The interfacial charge transfer for the group IV-V heterostructures (a1-d1) Charge density difference of (a1) CP/SiN, (b1) CAs/GeN, (c1) CSb/SnN and (d1) SiAs/GeP heterostructures with the isovalue of 0.007 e/Å^3. The bottom of the AB (A_1B_1/A_2B_2) heterostructure is A_1B_1 layer, while the upper is A_2B_2 layer. Green and orange block represent electron accumulation and depletion in the space. (a2-d2) The corresponding profiles of planar averaged charge density difference (red line) and planar averaged self-consistent electrostatic potential (blue line) displayed.

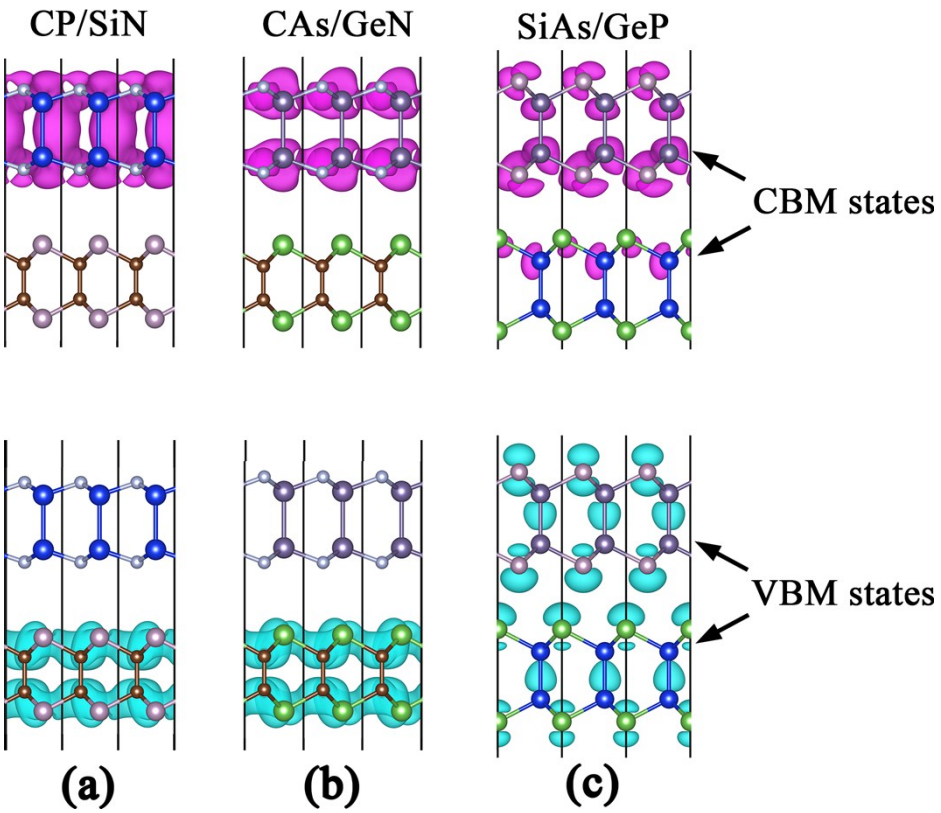

Fig. S7. Distributions of the band edge orbitals of group IV-V heterostructures. Charge distributions of VBM states (blue) and CBM states (pink) of (a) CP/SiN, (b) CAs/GeN and (c) SiAs/GeP heterostructures with an isovalue of 0.005 e/Å^3. The bottom of the AB (A_1B_1/A_2B_2) heterostructure is A_1B_1 layer, while the upper is A_2B_2 layer.

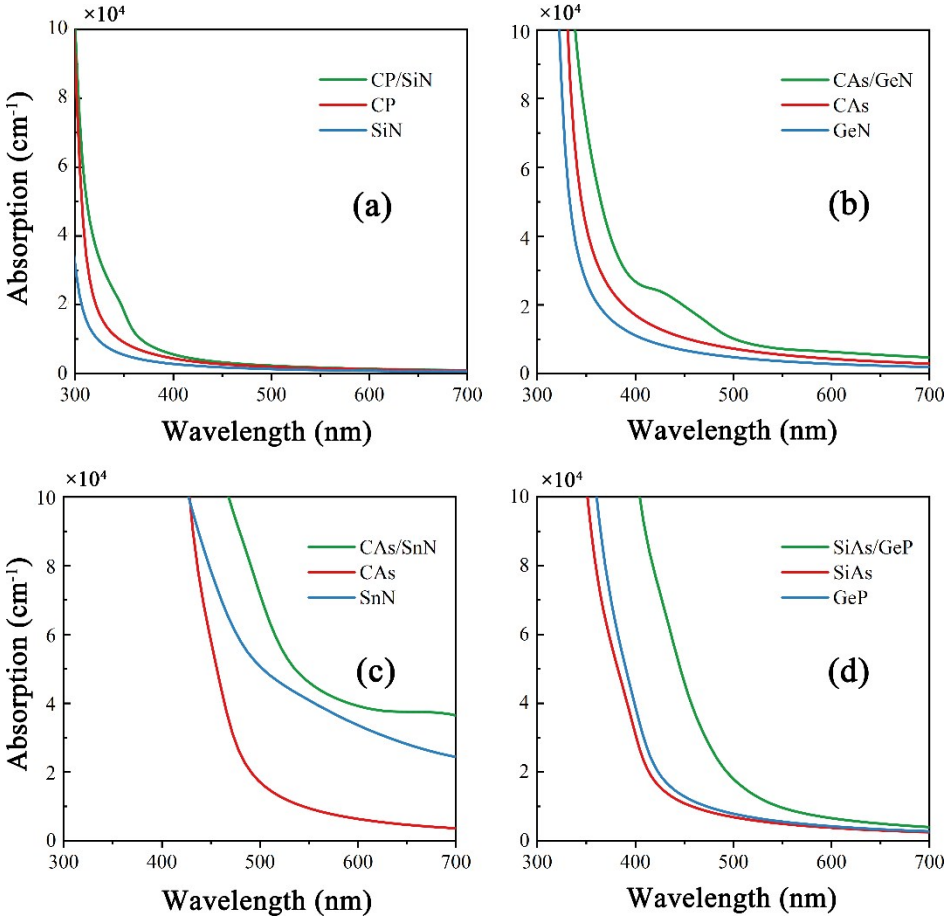

Fig. S8. Optical properties of group IV-V heterostructures. The absorption spectrums of (a) CP/SiN, (b) CAs/GeN, (c) CSb/SnN and (d) SiAs/GeP heterostructures and corresponding monolayers. The green, red and blue lines represent the AB (A_1B_1/A_2B_2) heterostructure, A_1B_1 layer and A_2B_2 layer, respectively.

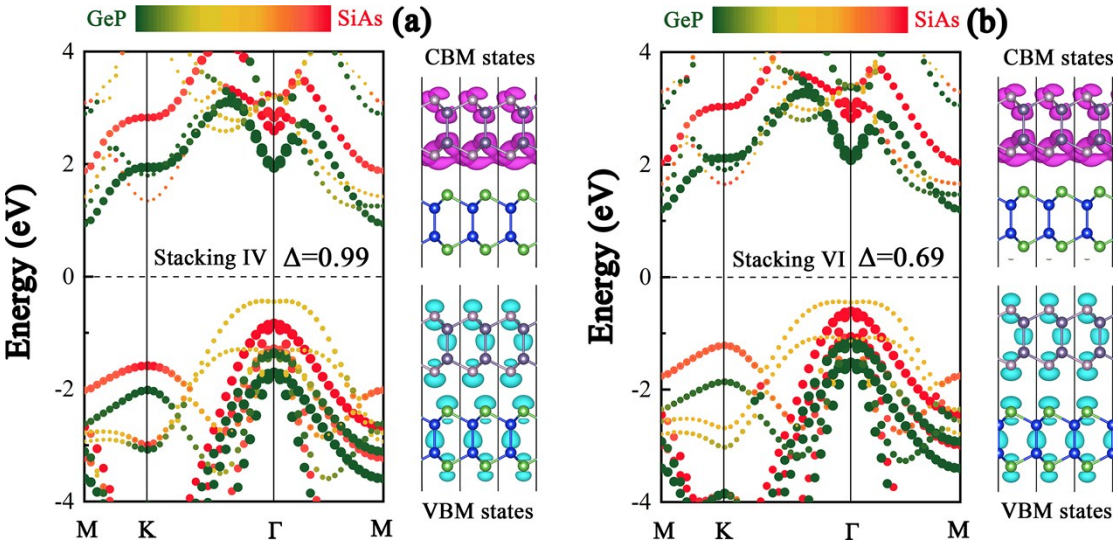

Fig. S9. Effects of different stacking patterns on electronic structure of SiAs/GeP heterostructure. (a,b) Projected band structures (left panel) and corresponding charge distributions (right panel) of VBM states (blue) and CBM states (pink) of (a) stacking IV and (b) VI of SiAs/GeP heterostructure. The upper of the heterostructure is GeP layer, and the bottom is SiAs layer. The isovalues of charge distributions are 0.005 e/Å^3.

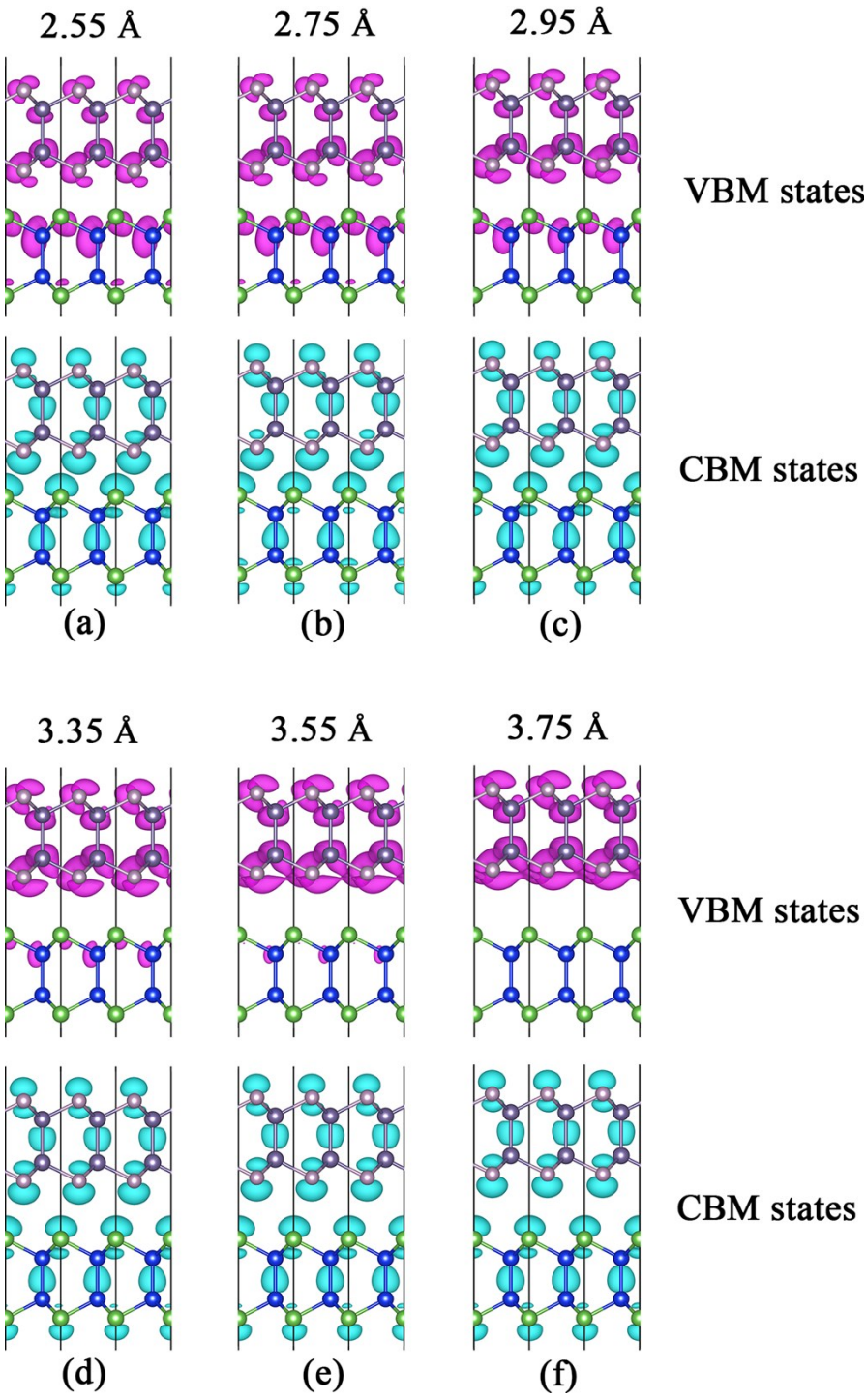

Fig. S10. Effects of vertical strain on the distributions of the band edge orbitals of SiAs/GeP heterostructure. The charge distribution of VBM states (blue) and CBM states (pink) for (a-c) decrease and (d-f) increase of interlayer distance. The upper of the heterostructure is GeP layer, and the bottom is SiAs layer. The isovalues of charge distributions are 0.005 e/Å^3.

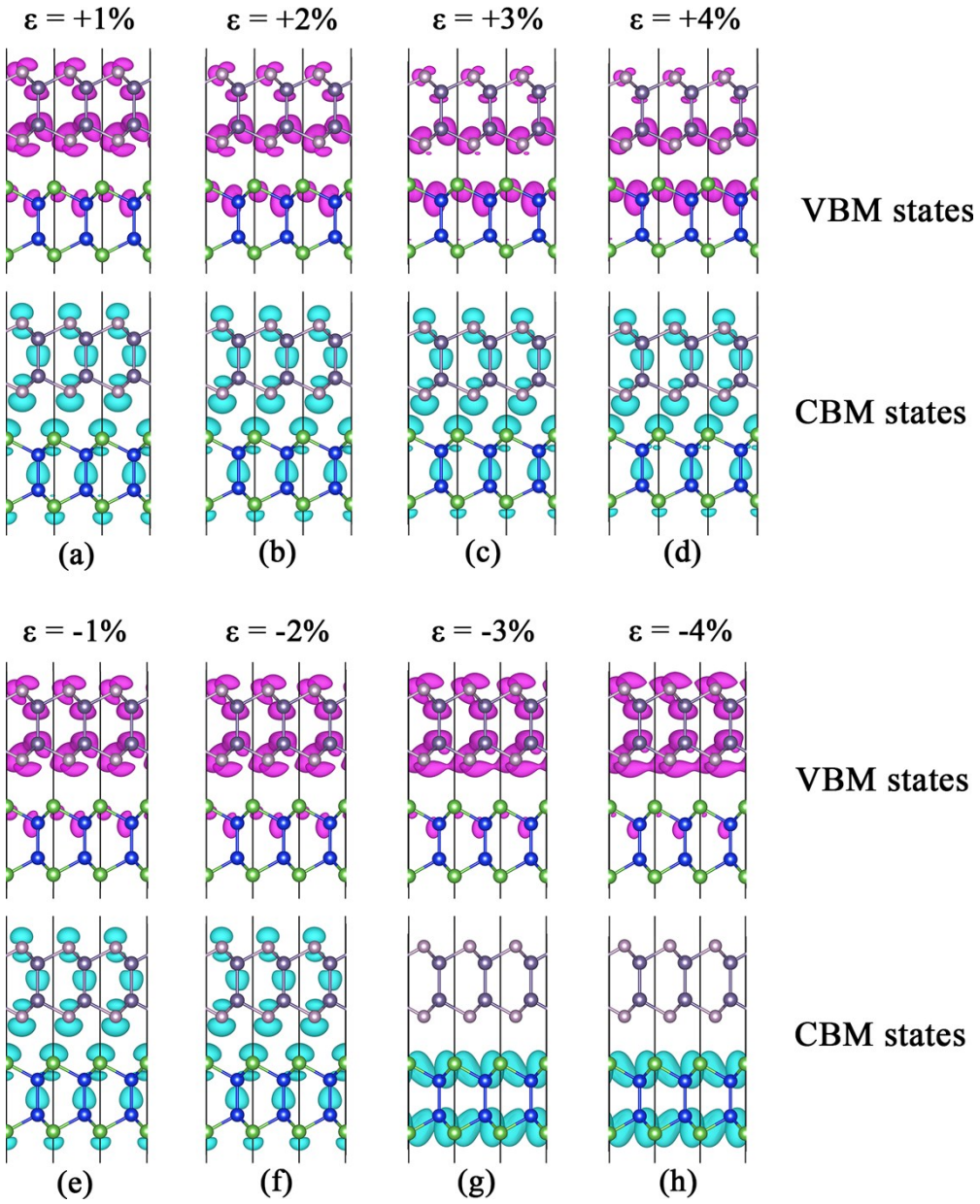

Fig. S11. Effects of biaxial strain on the distributions of the band edge orbitals of SiAs/GeP heterostructure. The charge distribution of VBM states (blue) and CBM states (pink) for (a-d) tensile and (e-h) compressive biaxial strain. The upper of the heterostructure is GeP layer, and the bottom is SiAs layer. The isovalues of charge distributions are 0.005 e/Å^3.

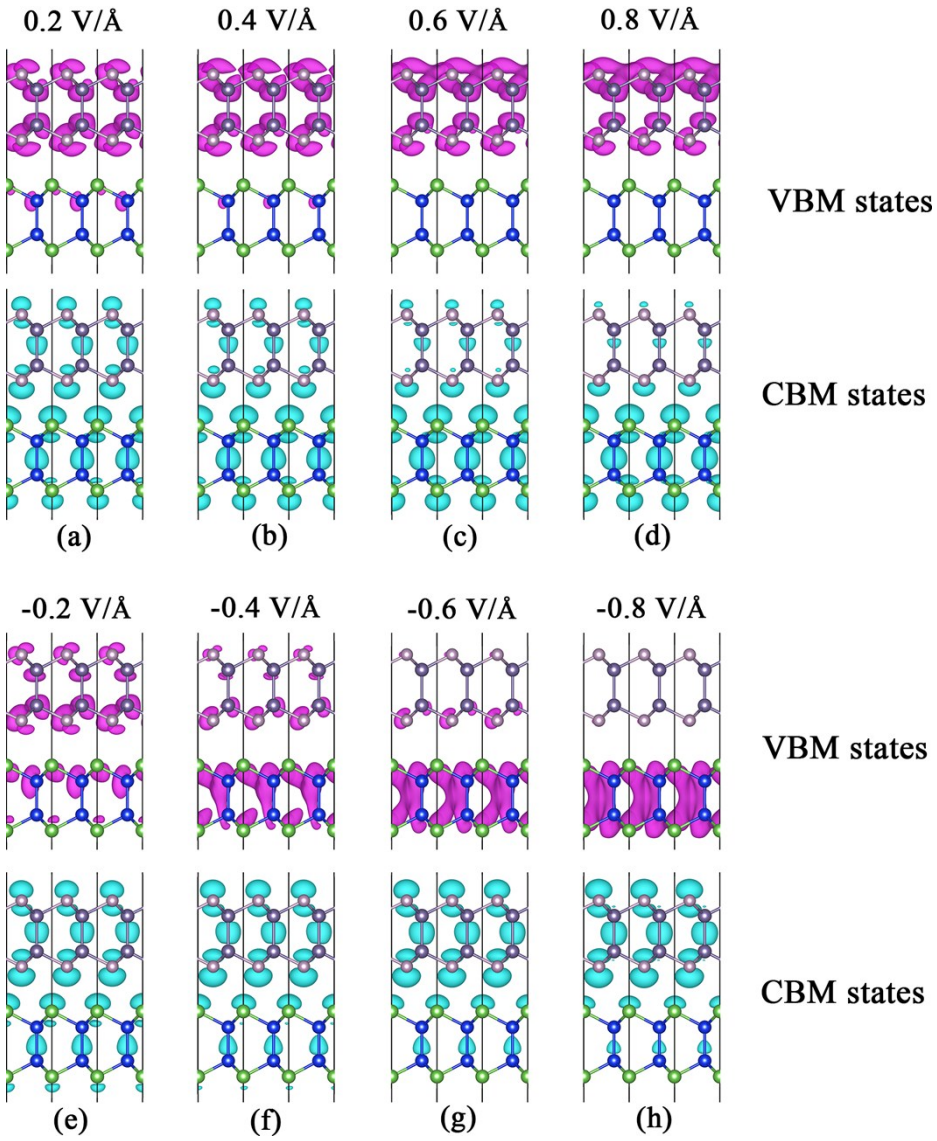

Fig. S12. Effects of electric field on the distributions of the band edge orbitals of SiAs/GeP heterostructure. The charge distribution of VBM states (blue) and CBM states (pink) for (a-d) positive and (e-h) negative electric field. The upper of the heterostructure is GeP layer, and the bottom is SiAs layer. The isovalues of charge distributions are 0.005 e/Å^3.

Table S1. Calculated lattice constant (Å) and band gap E_g (eV) for group IV-V AB monolayers.

Monolayer	a (Å)	E_g (eV)
CN	2.37	5.18
CP	2.88	2.71
CAs	3.10	1.91
CSb	3.39	0.83
SiN	2.89	2.74
SiP	2.22	2.22
SiAs	3.69	2.27
SiSb	4.01	1.77
GeN	3.09	2.33
GeP	3.65	2.04
GeAs	3.81	1.84
GeSb	4.11	1.17
SnN	3.41	0.94
SnP	3.94	1.97
SnAs	4.07	1.79
SnSb	4.37	1.31

Table S2. The energy difference ΔE (meV) for six stacking configurations of group IV-V AB vdW heterostructures.

Heterostructure	I	II	III	IV	V	VI
CP/SiN	30.22	2.53	6.52	0	10.05	29.60
CAs/GeN	39.73	5.12	2.00	0	5.81	39.63
CSb/SnN	56.66	6.73	1.36	0	4.71	57.30
SiAs/GeP	71.79	3.70	7.63	11.16	0	71.60

Table S3. Calculated lattice constant a (Å) and equilibrium interlayer distance d_0 (Å) of four group IV-V heterostructures obtained for different functionals.

Heterostructure	PBE+D3		optPBE-vdW		optB86b-vdW		optB88-vdW	
	a (Å)	d_0 (Å)	a (Å)	d_0 (Å)	a (Å)	d_0 (Å)	a (Å)	d_0 (Å)
CP/SiN	2.89	3.36	2.91	3.40	2.89	3.39	2.91	3.40
CAs/GeN	3.10	3.30	3.12	3.29	3.10	3.29	3.10	3.31
CSb/SnN	3.40	3.21	3.43	3.21	3.40	3.20	3.43	3.20
SiAs/GeP	3.67	3.15	3.70	3.12	3.66	3.10	3.68	3.12

Table S4. The interfacial charge transfer for four group IV-V heterostructures. The positive values and negative values represent charge accumulation and depletion, respectively.

Heterostructure	Charge transfer (e)	
	A_1B_1	A_2B_2
CP/SiN	-0.005	0.005
CAs/GeN	-0.011	0.011
CSb/SnN	-0.056	0.056
SiAs/GeP	-0.007	0.007