Electronic Supplementary Information

Potential SiX (X = N, P, As, Sb, Bi) homo-bilayers for visible-light photocatalysts application

Radha N Somaiya[1], Deobrat Singh[2,*], Yogesh Sonvane[1,*], Sanjeev K. Gupta[3,*], and Rajeev Ahuja[2,4]

[1]Advanced Materials Lab, Department of Physics, Sardar Vallabhbhai National Institute of Technology, Surat 395007, India

[2]Condensed Matter Theory Group, Materials Theory Division, Department of Physics and Astronomy, Uppsala University, Box 516, 75120 Uppsala, Sweden

[3]Computational Materials and Nanoscience Group, Department of Physics, St. Xavier's College, Ahmedabad 380009, India

[4]Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology (KTH), S-100 44 Stockholm, Sweden

Tables Caption:

Table. S1 Calculated lattice parameters for the hexagonal SiX bilayers with different stacking configurations.

Table. S2 Calculated parameters for the hexagonal SiX homo-bilayers with different stacking configurations via GGA-PBE.

Table. S3 Calculated parameters for the hexagonal SiX homo-bilayers with different stacking configurations via DFT-D2.

Table. S4 Indicating the calculated carrier mobilities of group IV-V SiX monolayers at 300 K along the x- and y- direction with PBE functional.

Table. S5 Calculated values of the electronegativities, energy band gap, valence band and the conduction band potentials of SiX monolayer.

Table. S6 Indicates the adsorption energies (ΔE_{ad}) in eV of intermediates O*, OH*, and OOH* on SiP and SiAs homo-bilayer at different sites.

Figures Caption:

Fig. S1 Indicates the orthogonal supercell for stable SiX homo-bilayers to study the transport properties along x- and y-directions with the corresponding Brillouin zone for orthorhombic lattice.

Fig. S2 Phonon dispersion spectrum of group-IV and V homo-bilayers viz. (a) SiN, (b) SiP, (c) SiAs, (d) SiSb, and (e) SiBi for five different stackings plotted at high symmetric points in the Brillouin zone.

Fig. S3 Molecular dynamics simulations indicating evolution of total energy vs time and the snapshots of the top views of the structures initially at 0 K and optimized structure at 300 K for (a) SiN, (b) SiP, (c) SiAs, (d) SiSb, and (e) SiBi homo-bilayers respectively for five different stackings. Green and purple balls indicate Si and X (X=N, P, As, Sb, Bi) atoms respectively.

Fig. S4 Indicates the electronic band structures and the projected density of states of group IV-V homo-bilayers of (a) SiN, (b) SiP, (c) SiAs, (d) SiSb, and (e) SiBi calculated with both PBE functional (solid blue line) and HSE06 hybrid functional (solid red line) for the unstable stackings S-II and S-IV.

Fig. S5 Energy shift of VBM and CBM for homo-bilayers (a) SiN, (b) SiP, (c) SiAs, (d) SiSb, and (e) SiBi w.r.t. uniaxial compressive and tensile strains applied along the x- and y- directions for all the stable stacking configurations.

Fig. S6 Depicts the strain energy difference between the total energy of unstrained and strained homo-bilayers (a) SiN, (b) SiP, (c) SiAs, (d) SiSb, and (e) SiBi w.r.t. uniaxial compressive and tensile strains applied along the x- and y- directions for all the stable stacking configurations.

Fig. S7 The optimized structures of the adsorption of intermediates O*, OH*, and OOH* on the SiP homo-bilayer. The Si, X, O, and H atoms are represented by green, purple, red, and gray respectively.

Fig. S8 Indicates the calculated relaxation time for the studied homo-bilayers at different temperatures.

Fig. S9 Indicates the power factor plotted as a function of chemical potential at different temperatures.

Table S1

System	Stacking	I	II	III	IV	V
SiN	No-vdW	2.899	2.899	2.899	2.899	2.899
	DFT-D2	2.895	2.894	2.894	2.894	2.895
	DFT-D3	2.889	2.887	2.887	2.887	2.888
SiP	No-vdW	3.529	3.529	3.529	3.529	3.529
	DFT-D2	3.520	3.520	3.522	3.520	3.521
	DFT-D3	3.497	3.497	3.502	3.497	3.499
SiAs	No-vdW	3.696	3.696	3.697	3.696	3.696
	DFT-D2	3.688	3.688	3.690	3.688	3.689
	DFT-D3	3.664	3.661	3.668	3.661	3.664
SiSb	No-vdW	4.017	4.015	4.019	4.014	4.018
	DFT-D2	4.014	4.026	4.019	4.018	4.016
	DFT-D3	3.978	3.993	3.995	3.993	3.983
SiBi	No-vdW	4.171	4.169	4.179	4.168	4.176
	DFT-D2	4.171	4.188	4.179	4.174	4.175
	DFT-D3	4.132	4.148	4.146	4.129	4.139

Table S2

System	Stacking	I	II	III	IV	V
SiN	a (Å)	2.899	2.899	2.899	2.899	2.899
	d (Å)	3.917	4.489	4.273	4.547	4.241
	ΔE (meV)	0	1.65	1.22	1.71	0.46
SiP	a (Å)	3.529	3.529	3.529	3.529	3.529
	d (Å)	4.372	4.888	4.564	4.929	4.358
	ΔE (meV)	0	1.27	0.20	1.26	0.12
SiAs	a (Å)	3.696	3.696	3.697	3.696	3.696
	d (Å)	4.184	5.091	4.372	4.959	4.169
	ΔE (meV)	0.40	1.61	0	1.88	0.16
SiSb	a (Å)	4.017	4.015	4.019	4.014	4.018
	d (Å)	4.203	5.150	3.893	5.115	4.016
	ΔE (meV)	5.61	11.64	0	12.80	2.61
SiBi	a (Å)	4.171	4.169	4.179	4.168	4.176
	d (Å)	3.824	5.113	3.497	5.081	3.655
	ΔE (meV)	17.96	32.98	0	34.91	7.99

Table S3

System	Stacking	I	II	III	IV	V
SiN	a (Å)	2.895	2.894	2.894	2.894	2.895
	d (Å)	3.026	3.476	3.233	3.4994	3.112
	ΔE (meV)	0	44.05	24.13	45.33	11.27
SiP	a (Å)	3.520	3.520	3.522	3.520	3.521
	d (Å)	3.356	3.939	3.342	3.939	3.333
	ΔE (meV)	0.75	46.95	1.73	47.49	0
SiAs	a (Å)	3.688	3.688	3.690	3.688	3.689
	d (Å)	3.412	4.004	3.335	4.012	3.376
	ΔE (meV)	5.29	57.02	0	57.39	2.05
SiSb	a (Å)	4.014	4.026	4.019	4.018	4.016
	d (Å)	3.665	5.105	3.430	4.539	3.568
	ΔE (meV)	17.98	74.61	0	71.84	8.94
SiBi	a (Å)	4.171	4.188	4.179	4.174	4.175
	d (Å)	3.250	5.055	2.983	4.116	3.105
	ΔE (meV)	52.89	194.84	0	164.87	25.21

Table S4

System		m_x^* (m_0)	m_y^* (m_0)	C_x^{2D} (N/m)	C_y^{2D} (N/m)	E_d^x (eV)	E_d^y (eV)	μ_x $(10^4 cm^2 V^{-1} s^{-1})$	μ_y $(10^4 cm^2 V^{-1} s^{-1})$
SiN	e	0.041	0.127	299.48	299.44	9.196	3.465	2.56	5.82
	h	0.006	8.133	299.48	299.44	3.286	4.073	44.72	0.02
SiP	e	0.064	1.374	135.11	135.07	5.370	1.434	0.53	0.35
	h	0.103	0.495	135.11	135.07	1.016	3.867	12.03	0.17
SiAs	e	0.116	0.640	111.68	111.53	1.759	2.112	2.44	0.31
	h	0.079	0.310	111.68	111.53	1.483	0.124	8.78	319.57
SiSb	e	0.091	2.139	84.04	83.98	5.479	3.015	0.15	0.02
	h	0.114	0.194	84.04	83.98	2.128	2.723	2.34	0.84
SiBi	e	0.110	0.676	68.70	69.40	0.583	3.465	14.40	0.07
	h	0.093	0.269	68.70	69.40	0.159	4.073	394.85	0.21

Table S5

| System	χ	E_g	E_{CB}	E_{VB}
SiN	5.902	2.711	0.047	2.758
SiP	5.173	2.186	-0.420	1.766
SiAs	5.033	2.261	-0.598	1.664
SiSb	4.813	1.756	-0.565	1.191
SiBi	4.430	1.151	-0.646	0.506

Fig. S1

Fig. S2

Fig. S3(a)

T=0 K   T=300 K

g. S3(b)

Fi

T=0 K   T=300 K

SiAs-I

SiAs-II

SiAs-III

SiAs-IV

SiAs-V

Fig. S3(c)

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T=0 K   T=300 K

Fig. S3(d)

T=0 K   T=300 K

SiBi-I

SiBi-II

SiBi-III

SiBi-IV

SiBi-V

g. S3(e)

Fi

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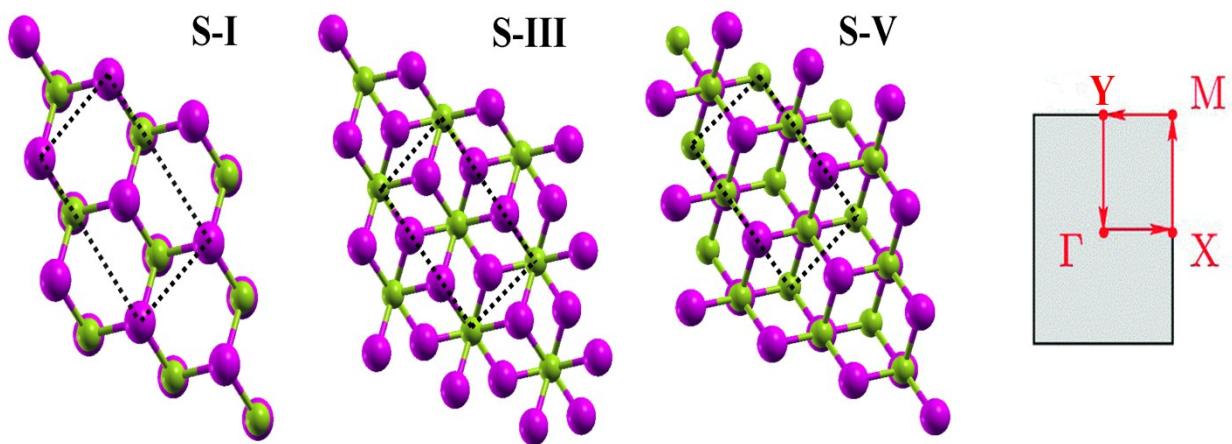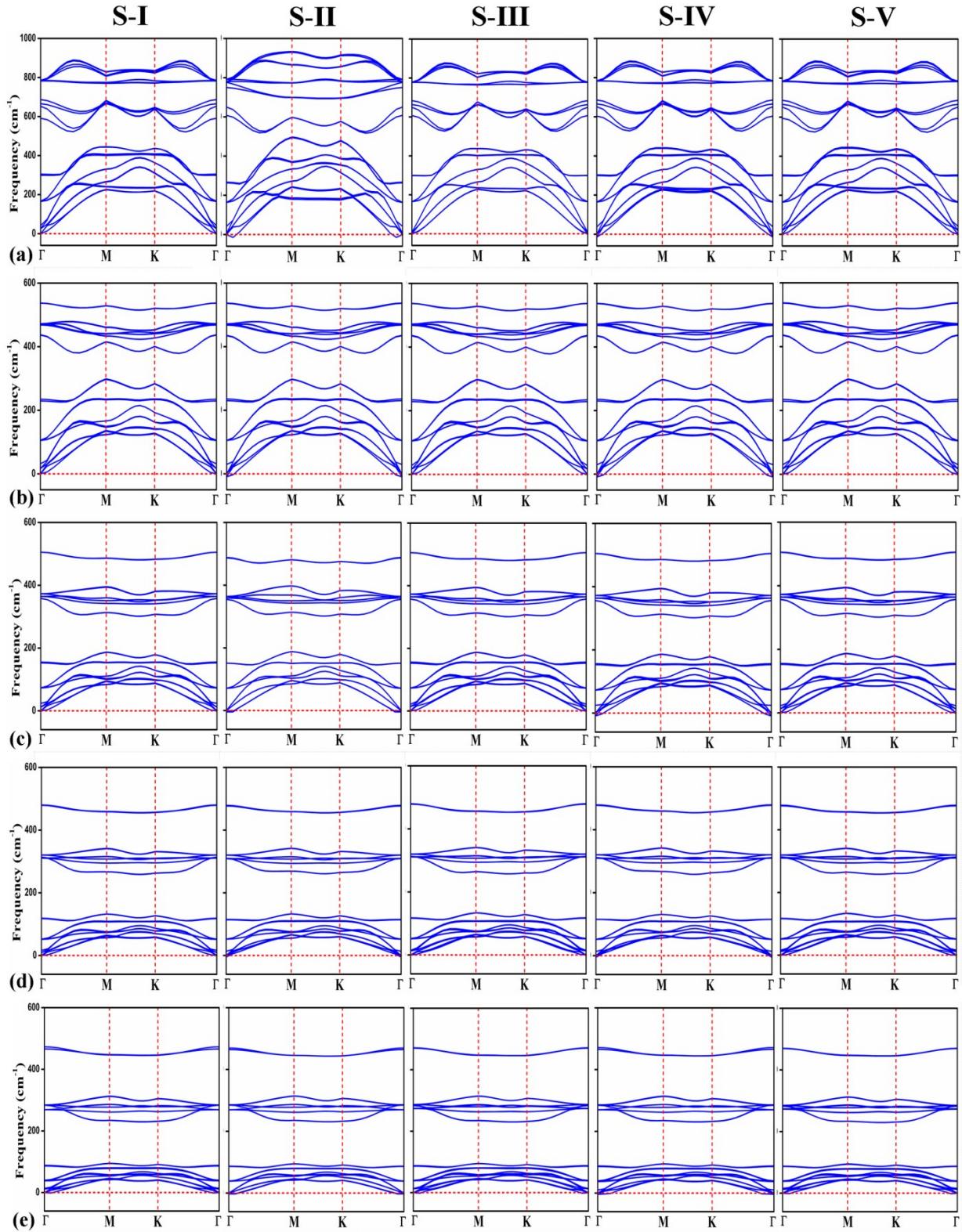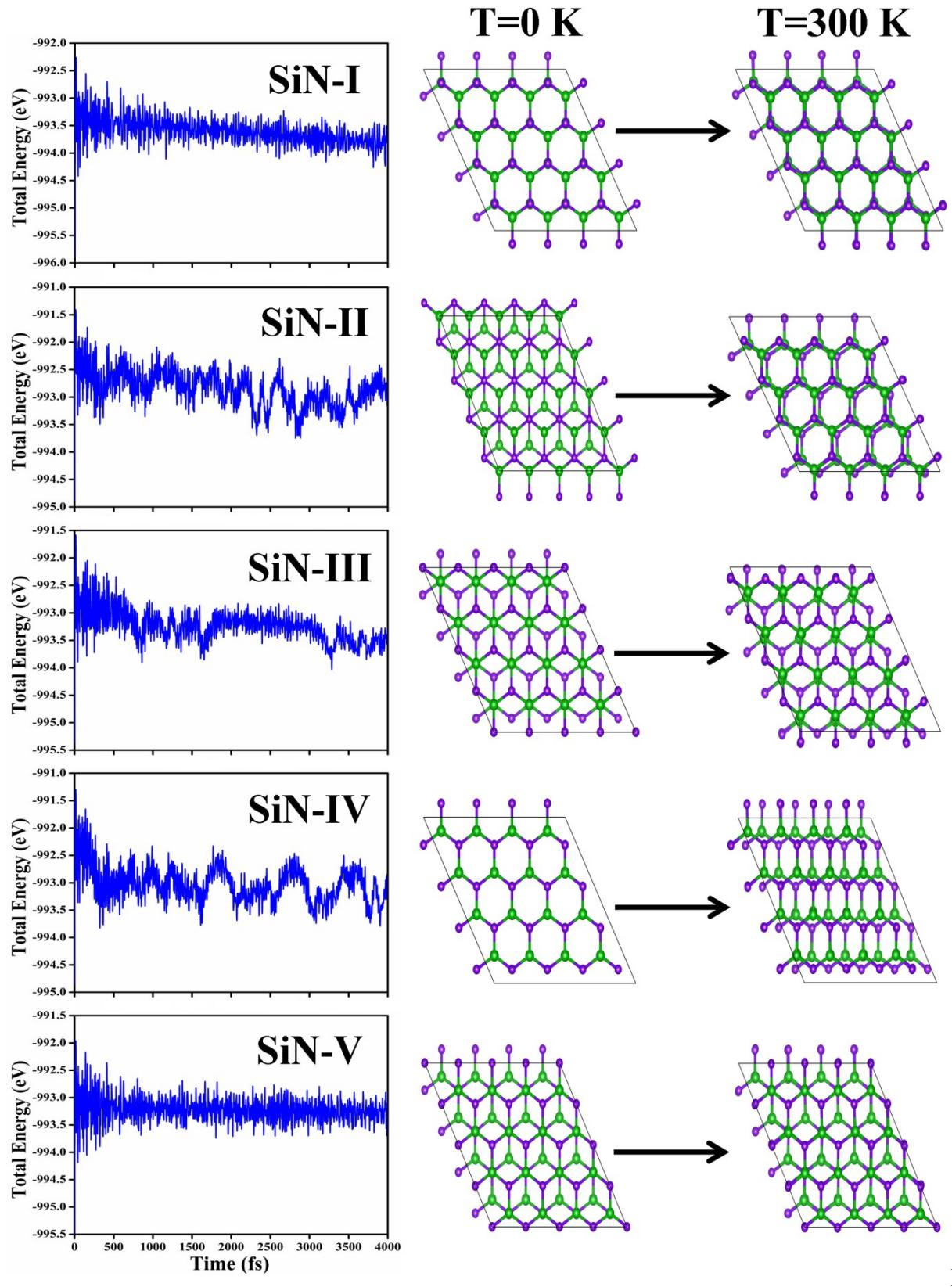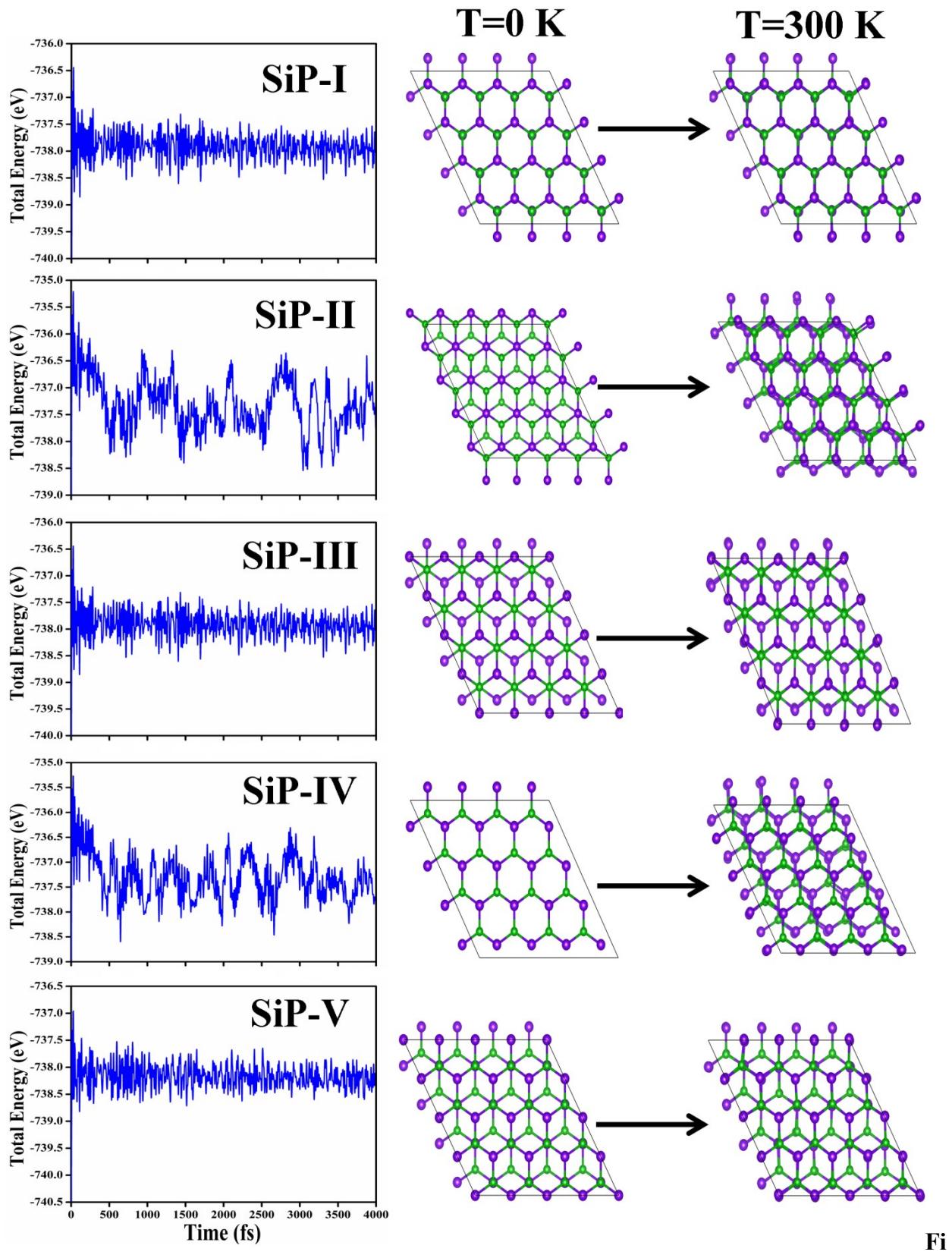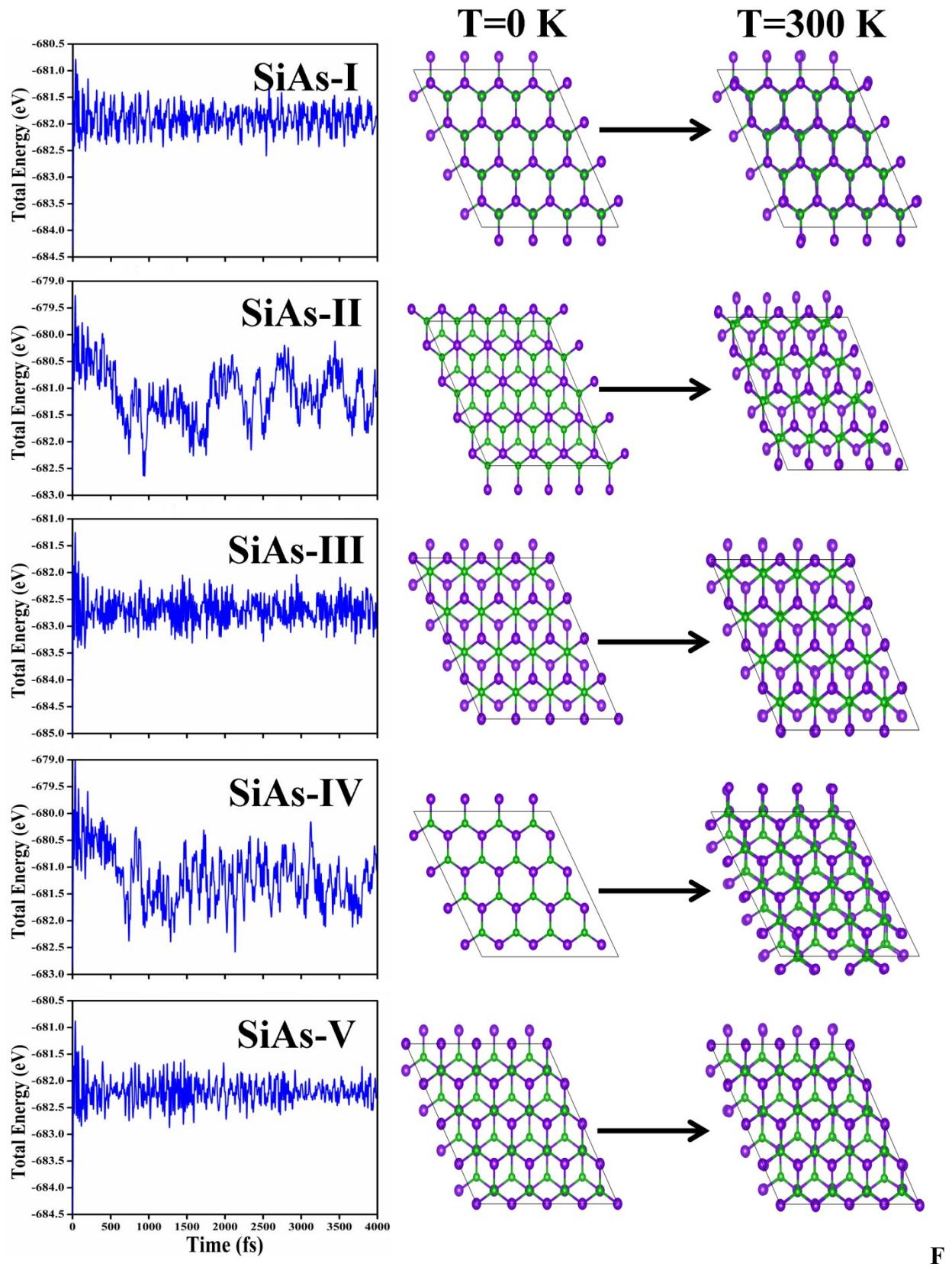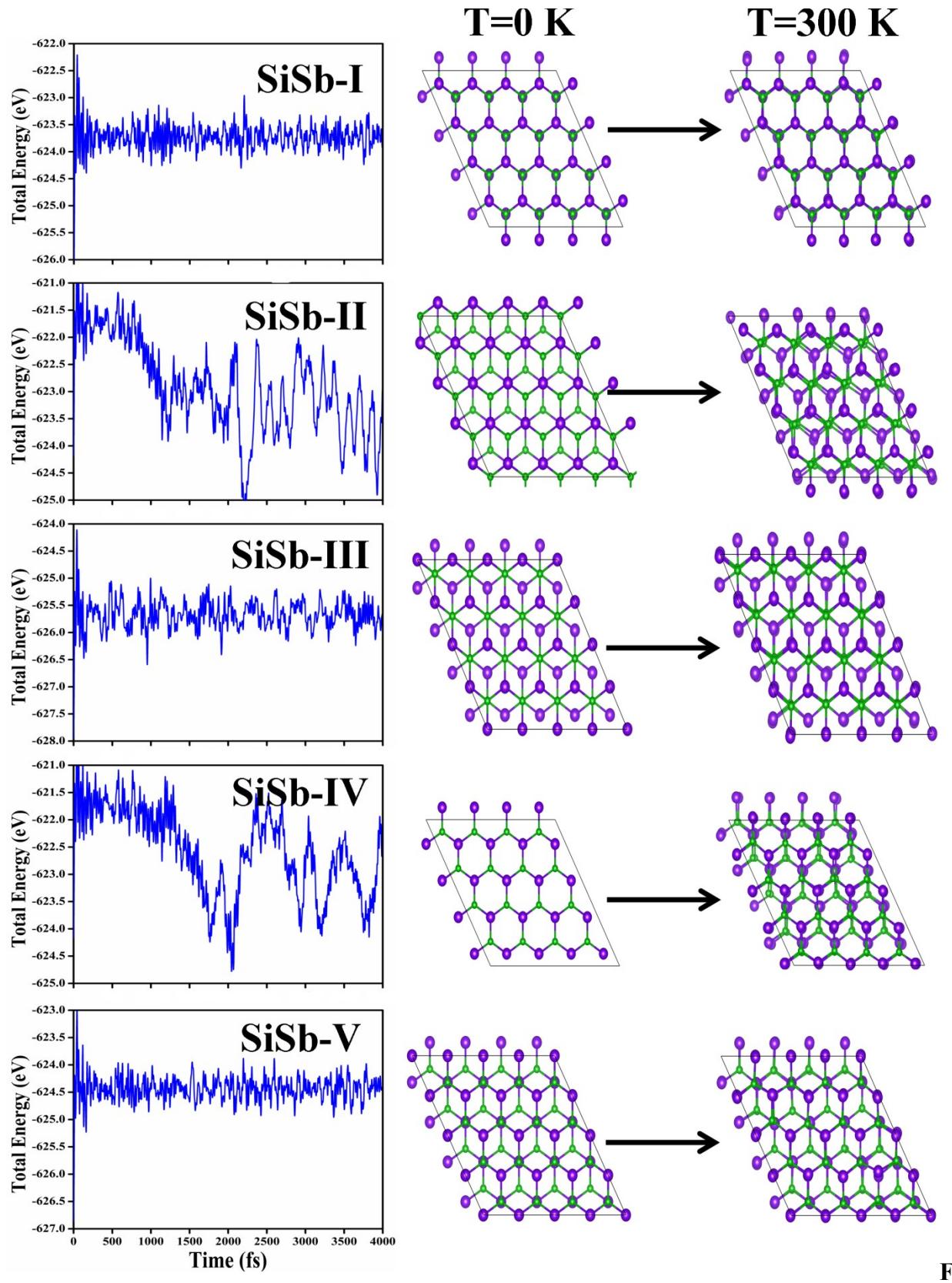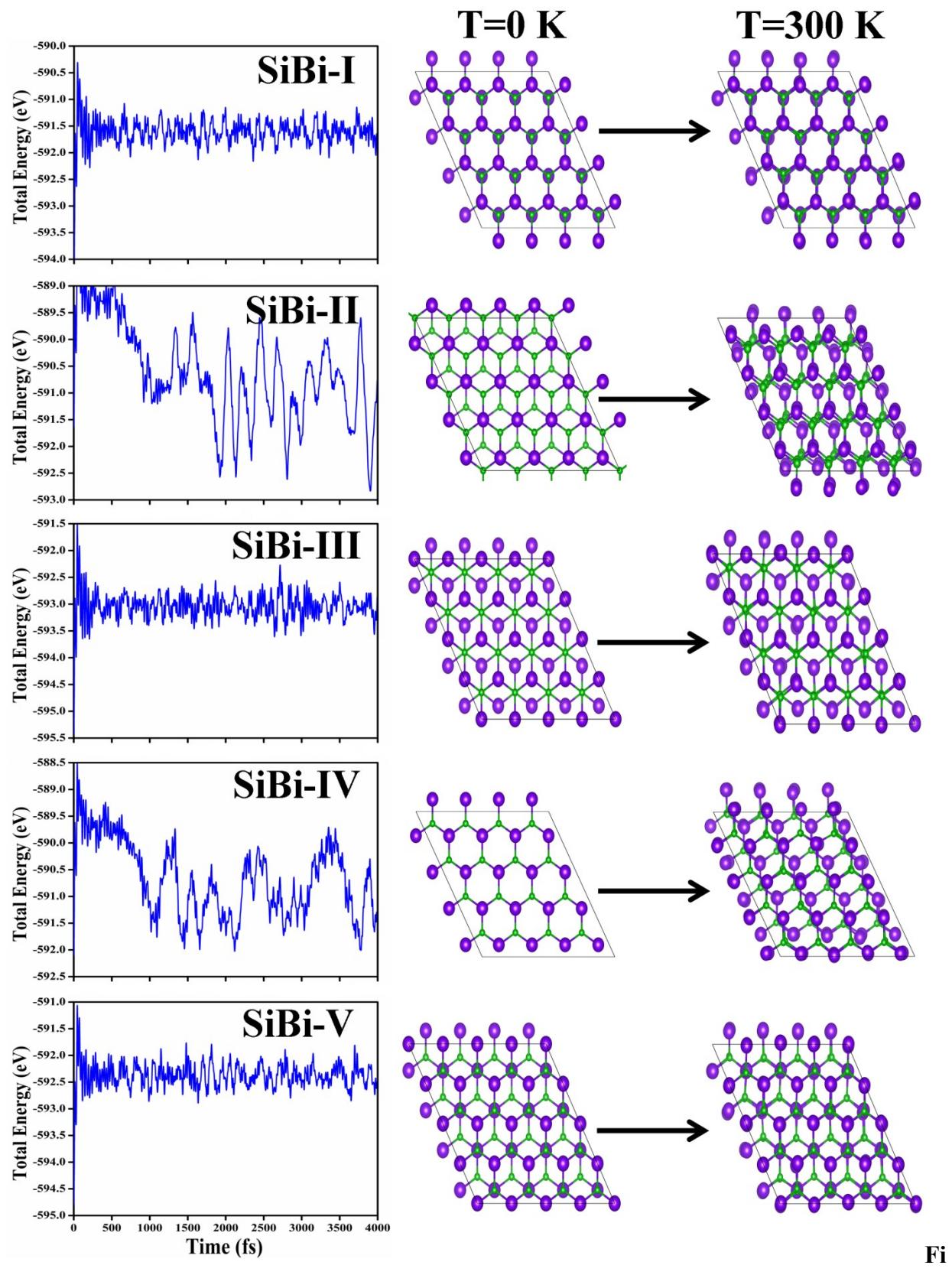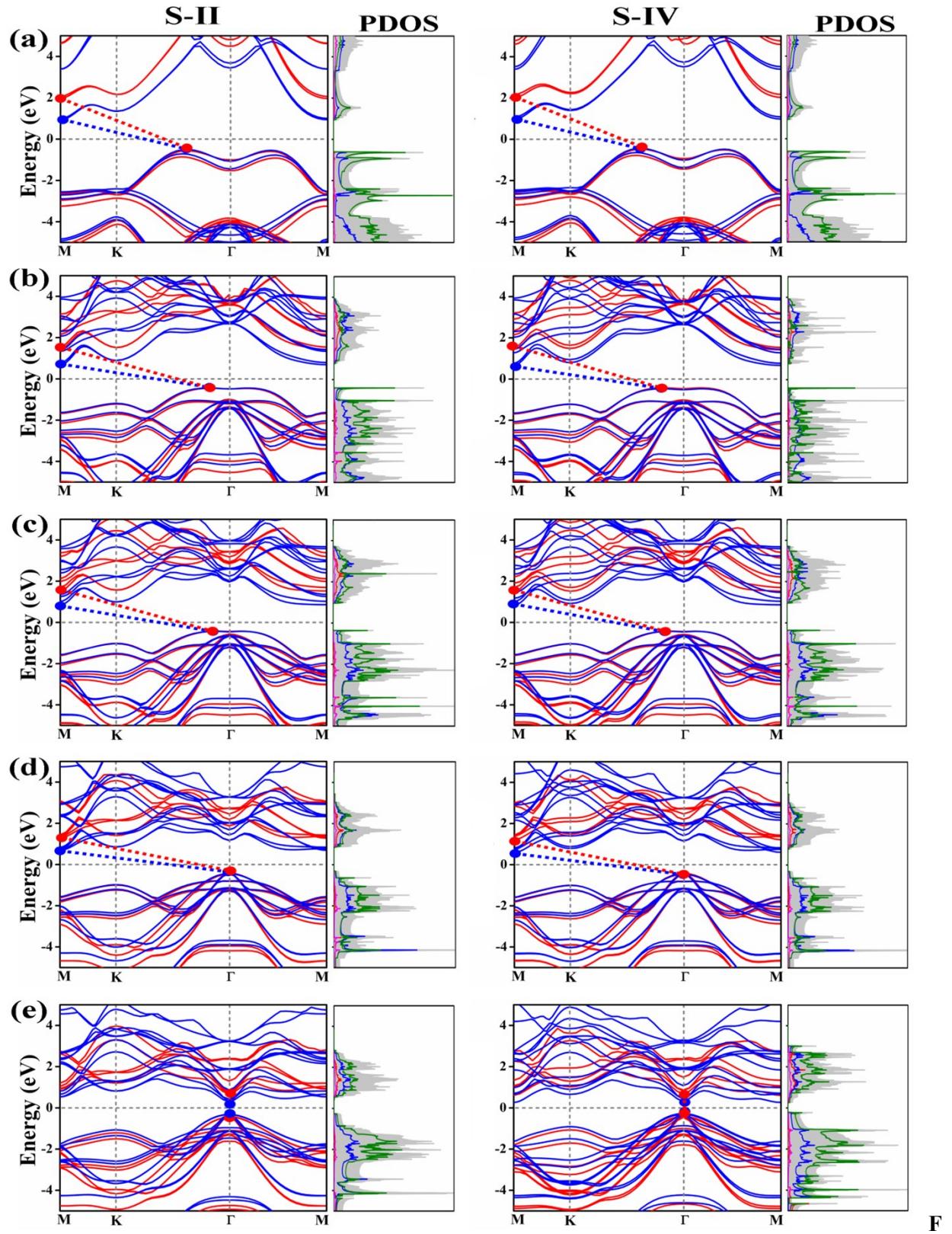
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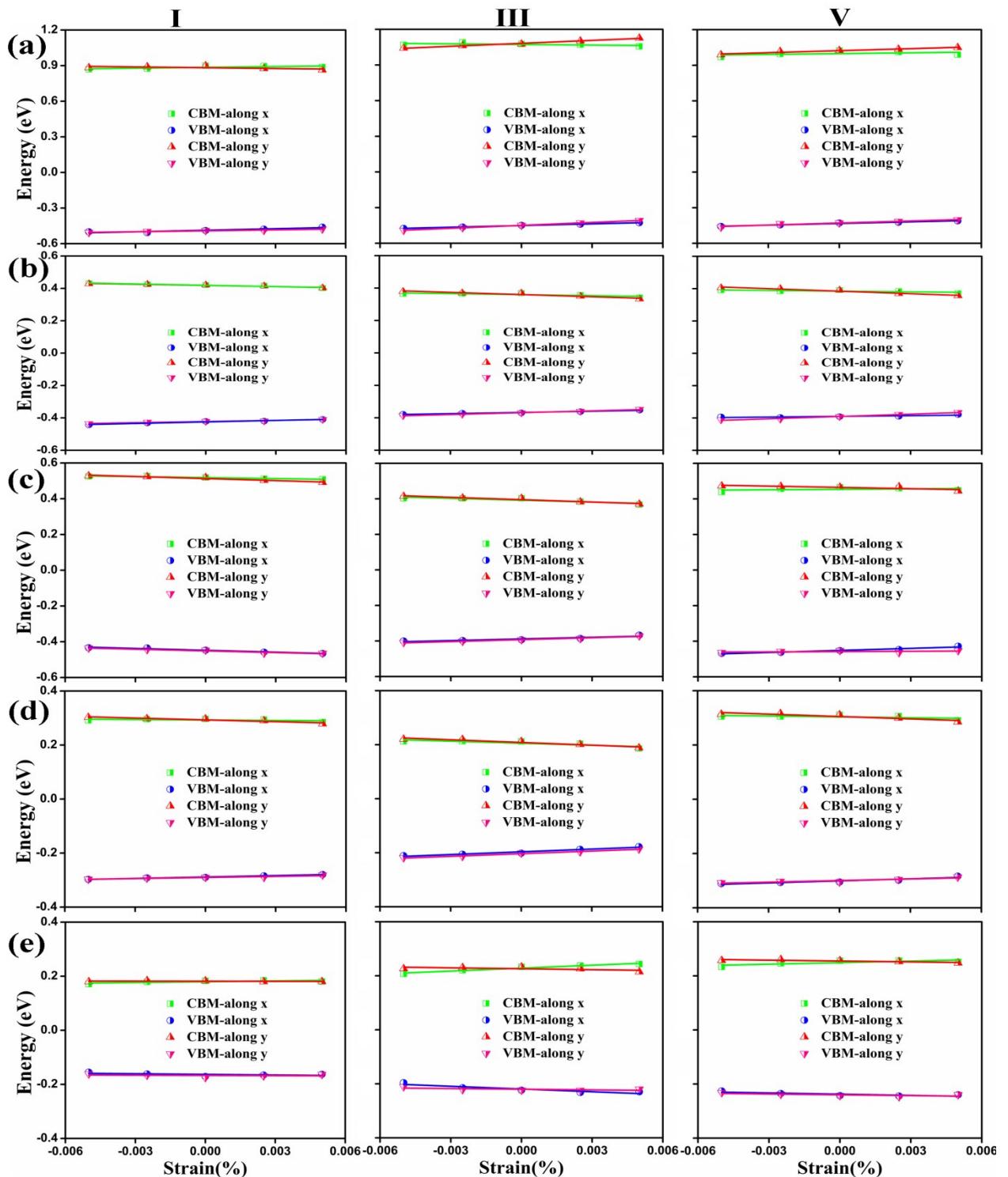
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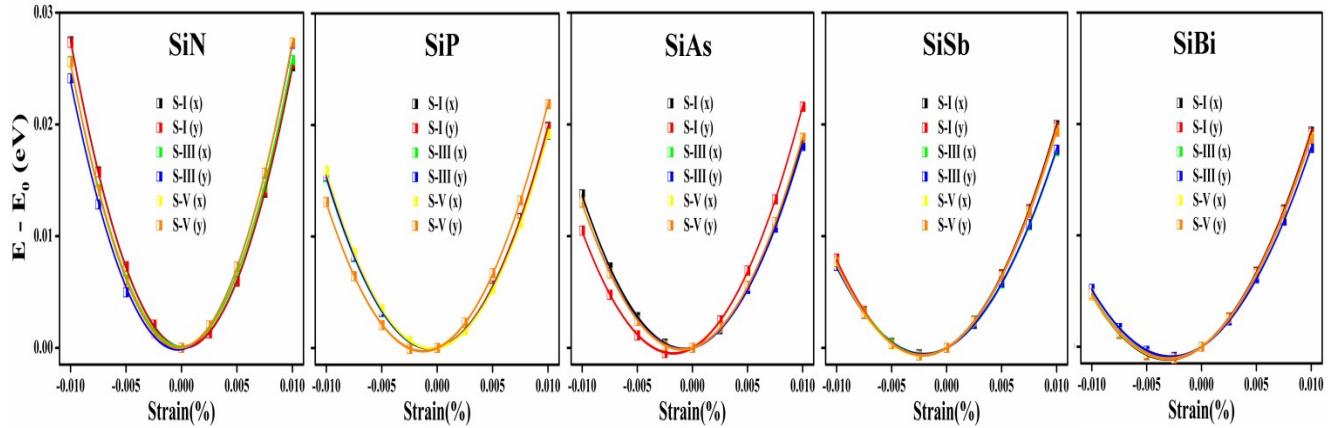
Fig. S6

OER/ORR Mechanism:

The adsorption energies consisting of oxygen intermediates for the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are calculated using;

$$\Delta E_{O^*} = E_{O^*} - E* - (E_{H_2O} - E_{H_2})$$ S(1)

$$\Delta E_{OH^*} = E_{OH^*} - E* - (E_{H_2O} - \frac{1}{2}E_{H_2})$$ S(2)

$$\Delta E_{OOH^*} = E_{OOH^*} - E* - (2E_{H_2O} - \frac{3}{2}E_{H_2})$$ S(3)

Here, * represents the active site. The total energies in free gas phase of H_2O and H_2 molecules are represented as E_{H_2O} and E_{H_2} respectively. The total energies of the active site (*) with the adsorption of O, OH, and OOH are represented as E_{O^*}, E_{OH^*}, and E_{OOH^*} respectively.

Under acidic conditions, the OER and ORR process with four-electron reaction paths is expressed as-

$$H_2O(l) + * \rightarrow OH^* + (H^+ + e^-)$$ S(4)

$$OH^* \rightarrow O^* + (H^+ + e^-)$$ S(5)

$$O^* + H_2O(l) \rightarrow OOH^* + (H^+ + e^-)$$ S(6)

$$OOH^* \rightarrow O_2(g) + * + (H^+ + e^-)$$ S(7)

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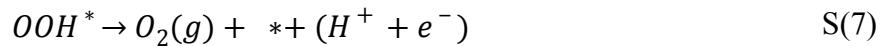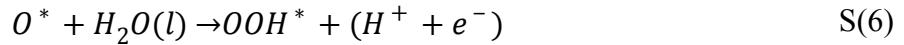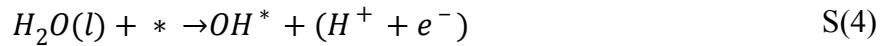
Here, the gas and liquid phases are indicated by *g* and *l* respectively; * indicates the absorption site on the catalyst surface and the absorbed intermediates are represented by O^*, OH^* and OOH^*. The opposite process of OER is the ORR reaction as listed from Equ. S(4)-S(7).

Table. S6

Homo-bilayers	position	E_{ad} (eV)		
		O*	OH*	OOH*
SiP	On-Si	2.24	1.13	1.70
	On-P	0.79	0.93	3.10
SiAs	On-Si	2.64	1.12	5.11
	On-As	2.01	1.53	4.97

Fig. S7

Fig. S8

Fig. S9