Electronic Supplementary Information

Reactivity of Different Surface Sites with Silicon Chlorides during Atomic Layer Deposition of Silicon Nitride

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This supporting information explains in detail the procedure of calculation to obtain lowest adsorption energy values, and also shows in detail the structures of adsorption, transition state, and reaction of silicon precursors on different silicon nitride surfaces.

We considered two orientations and four positions of $SiCl_4$ and Si_2Cl_6 above the silicon nitride surface. For $SiCl_4$, we construct two extreme orientation, as shown in Fig. S1. First one is that three chlorine atoms of tetrahedral $SiCl_4$ is facing toward the silicon nitride surface, and second one is that only one chlorine atom is facing towards the surface. Also, four different positions were considered on the surface: (1) N_T atom, (2) the center of the big six-member ring, (3) N_C atom, and (4) the center of the small six-member ring. The energies of adsorption of $SiCl_4$ calculated for each orientation and position were summarized in Table S1. For Si_2Cl_6, we considered the same four surface positions, as shown in Fig. S2. Regarding the orientation, however, we considered orientations differently from the $SiCl_4$ case due to the different symmetry of the molecule. The Si–Si bond of the precursor was either horizontal or vertical to the surface. The energies of adsorption of Si_2Cl_6 calculated for each orientation and position were summarized in Table S1.

Figures S3– S8 shows the plan views and the cross-sectional views of the optimized structures for the adsorption, the transition state, and reaction of the silicon precursors on three types of silicon nitride surfaces. We only include the cross-sectional views in the main text due to the limitation of the page length. A surface reconstruction was obviously observed on the β-Si_3N_4 surfaces due to the precursors on the

NH*/SiNH$_2$* surface sites. The hydrogen atoms below the precursor position on the surface of the NH*/SiNH$_2$* was slightly shifted. There was no obvious surface reconstruction in NH*/SiH* and in under-coordinated bare >Si=N– surfaces. The changed in NH*/SiNH$_2$* surface sites probably due to the "not packed" position of N-H* sites in the upper surface, makes the surface easily affected by precursors. Meanwhile in NH*/SiH* surface the "full packed" surface with hydrogen atoms would form strong bonds with either N or Si on the surface, preventing precursors from giving a significant influence to the surface. We also observed the repulsive force between nearest hydrogen atoms on the NH*/SiH* surface also plays important role in this part.

The list of calculation results for both with vdW and without vdW calculation results are showed in Fig. S9 and Table S3. Under-coordinated >Si=N- surface showed the most reactive surface compared with the other surfaces, NH*/SiH* and NH*/SiNH$_2$* as we can see in the graphics of energy diagrams in Fig. S9. The initial state at under-coordinated surface using vdW interaction can't be obtained due to high reactivity of the surface, which means both SiCl$_4$ and Si$_2$Cl$_6$ easily react with the surface to form final structure. As for the local structure and bonds, we showed a case study of initial structure of SiCl$_4$ on NH*/SiNH$_2$* surface in Table S3. The local structures with or without vdW interaction are very similar although the distance between SiCl$_4$ and the surface was slightly reduced from 3.14 to 2.82 Å by considering vdW interaction and that the lengths and angles of bonds are almost the same for both cases.
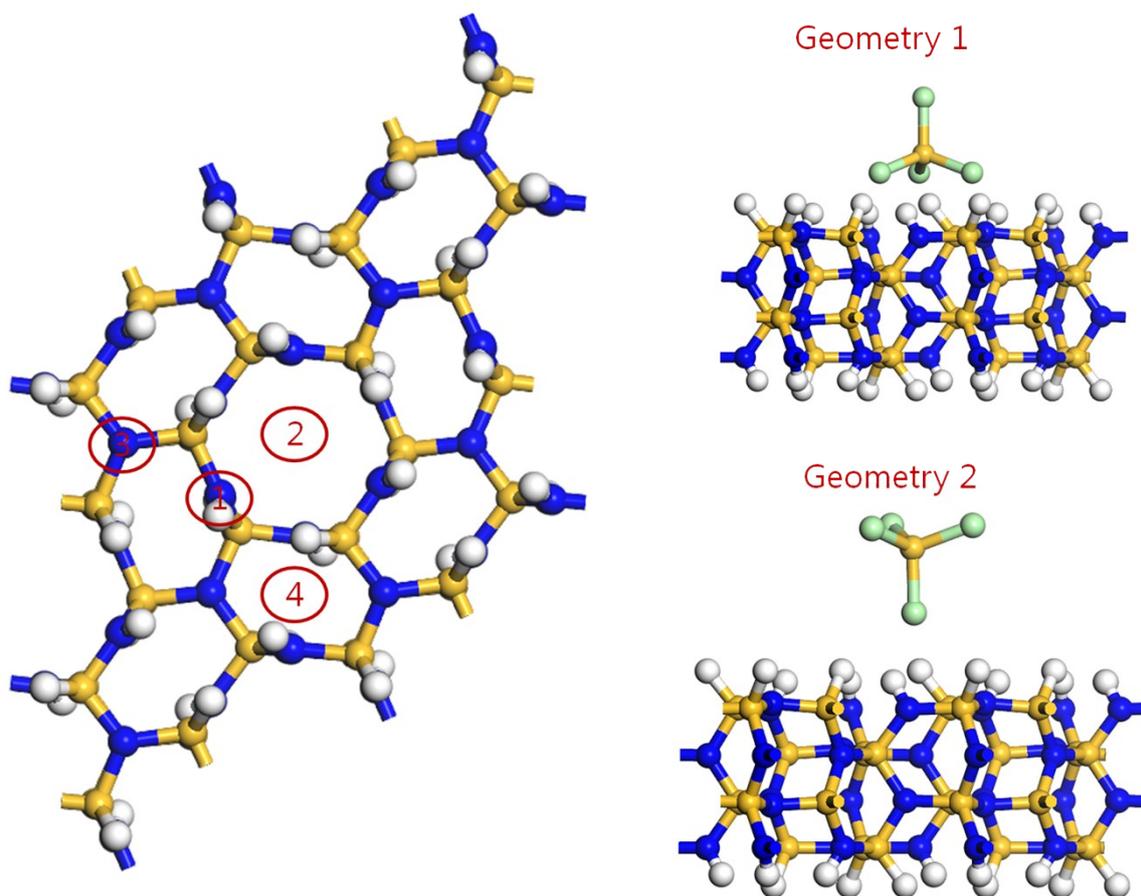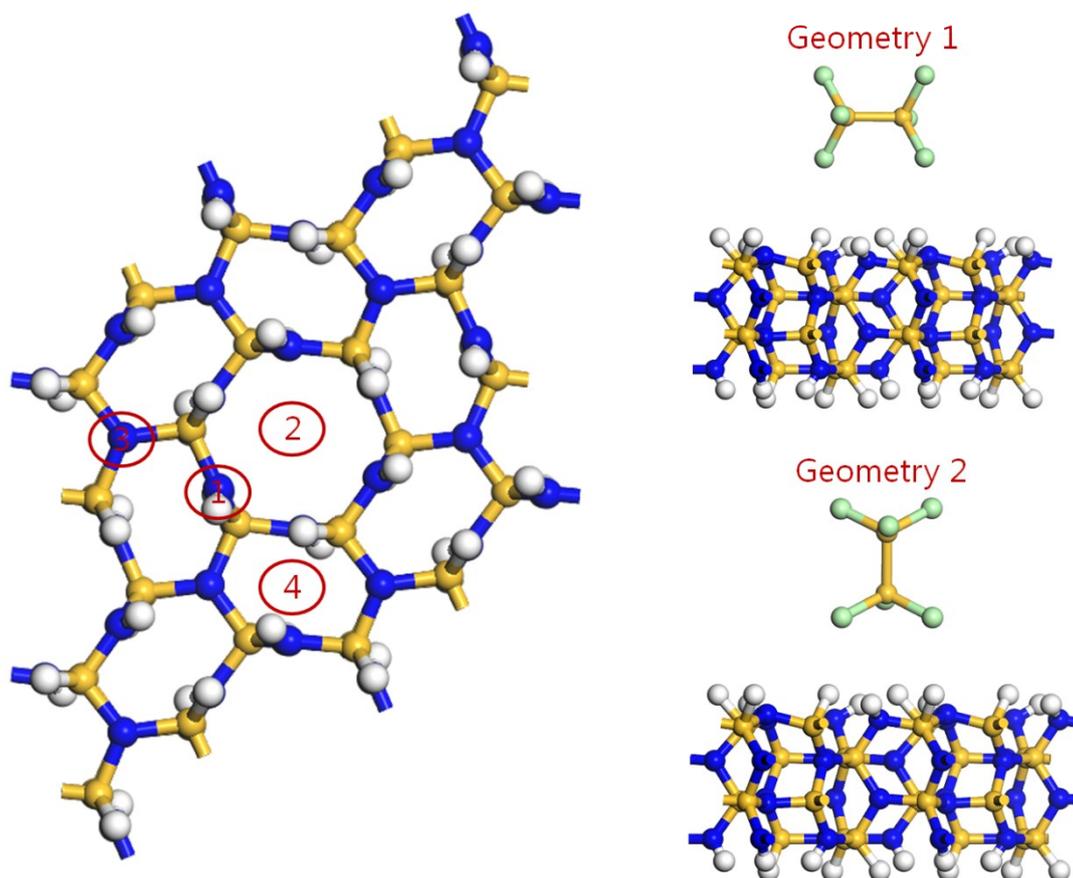
Figure S1. Two orientations and four positions of $SiCl_4$ on NH*/SiH*-terminated β-Si_3N_4 surface.

Table S1. The energies of adsorption of $SiCl_4$ calculated for each orientation and position.

Orientation	Position	E ads (Ha)	E ads (eV)
1	1	-0.000554	-0.02
1	2	-0.001245	-0.03
1	3	-0.001318	-0.04
1	4	-0.001532	-0.04
2	1	-0.000680	-0.02
2	2	-0.001088	-0.03
2	3	-0.001389	-0.04
2	**4**	**-0.001565**	**-0.04**

Figure S2. Two orientations and four positions of Si_2Cl_6 on NH*/SiH*-terminated β-Si_3N_4 surface

Table S2. The energies of adsorption of Si_2Cl_6 calculated for each orientation and position.

| Geometry	Position	E ads (Ha)	E ads (eV)
1	1	-0.000700	-0.02
1	2	-0.000343	-0.01
1	3	-0.000499	-0.01
1	4	-0.000404	-0.01
2	1	0.000577	0.02
2	2	-0.000150	-0.00
2	3	0.000097	0.00
2	**4**	**-0.001664**	**-0.04**
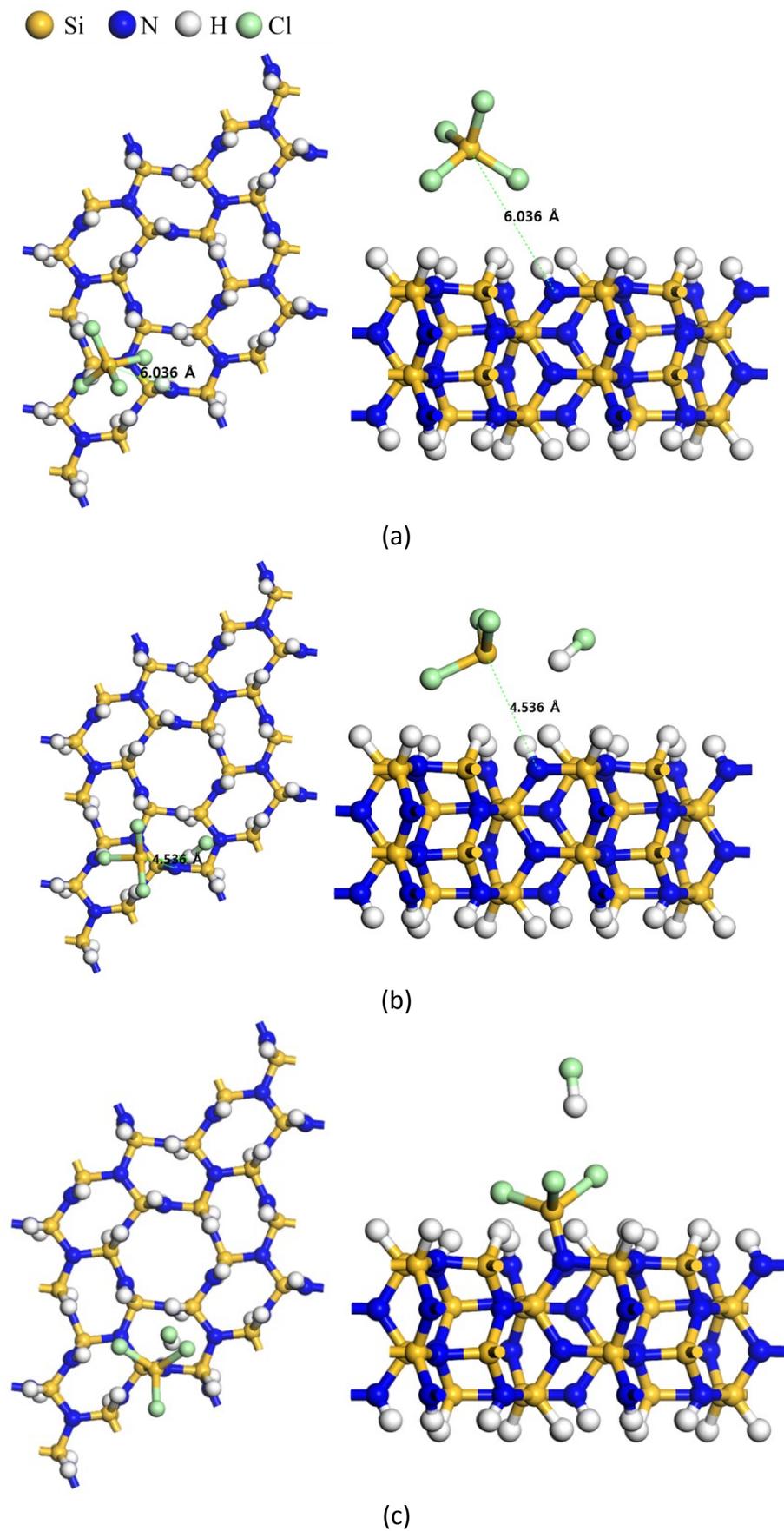
Figure S3. The optimized structures for (a) adsorption, (b) transition state and (c) reaction of a SiCl$_4$ molecule on the NH*/SiH*-terminated β-Si$_3$N$_4$ surface.
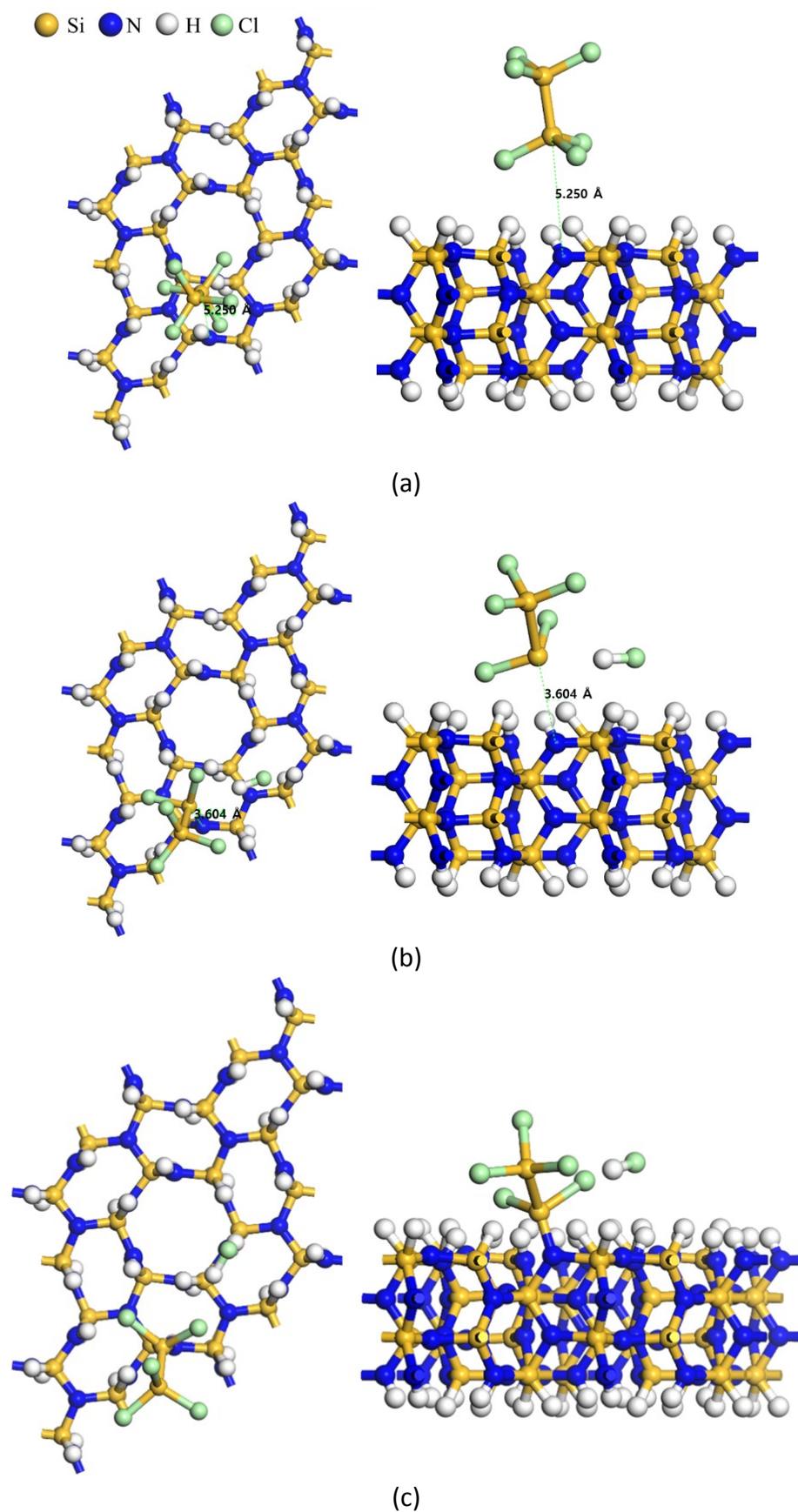
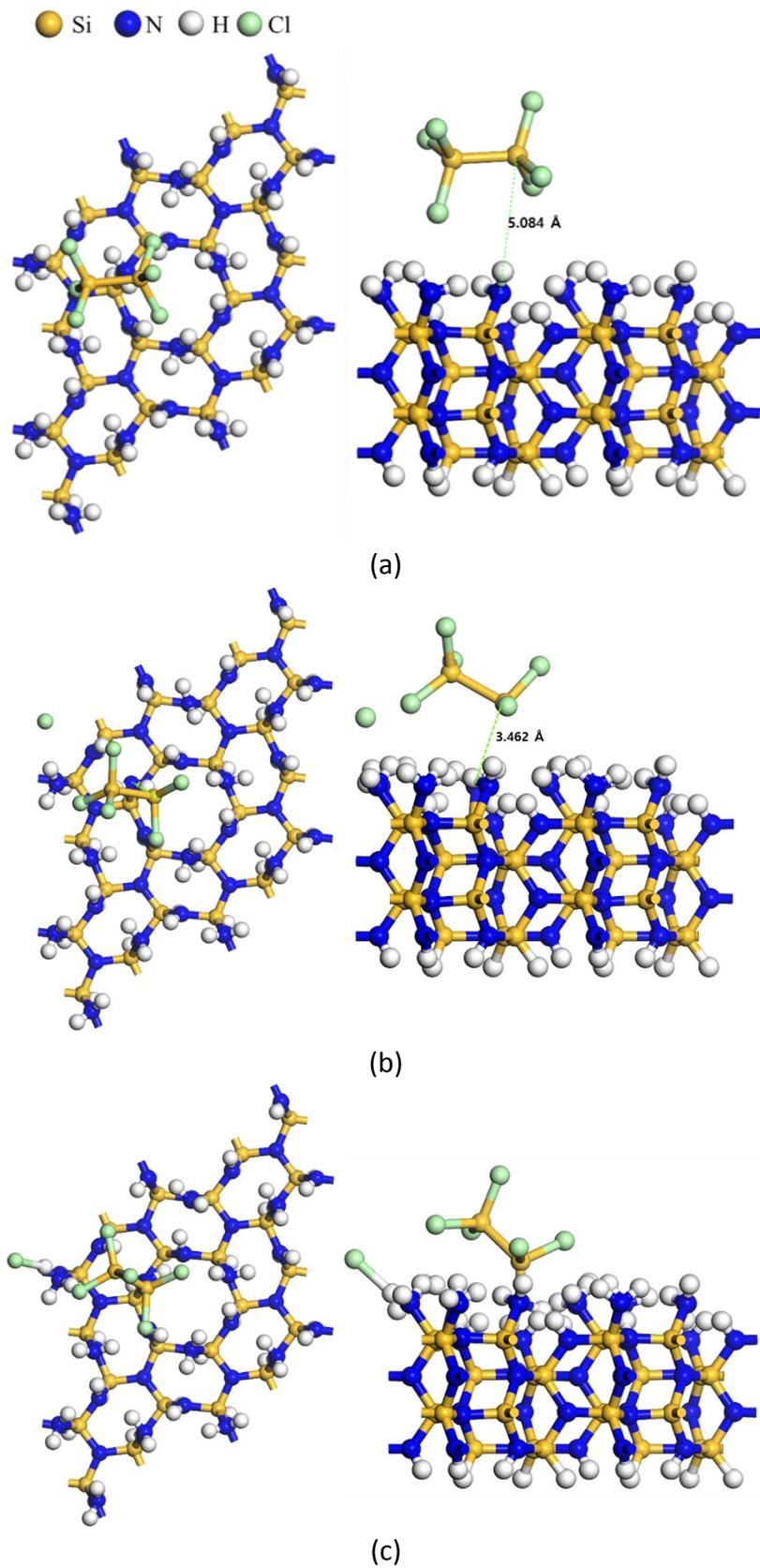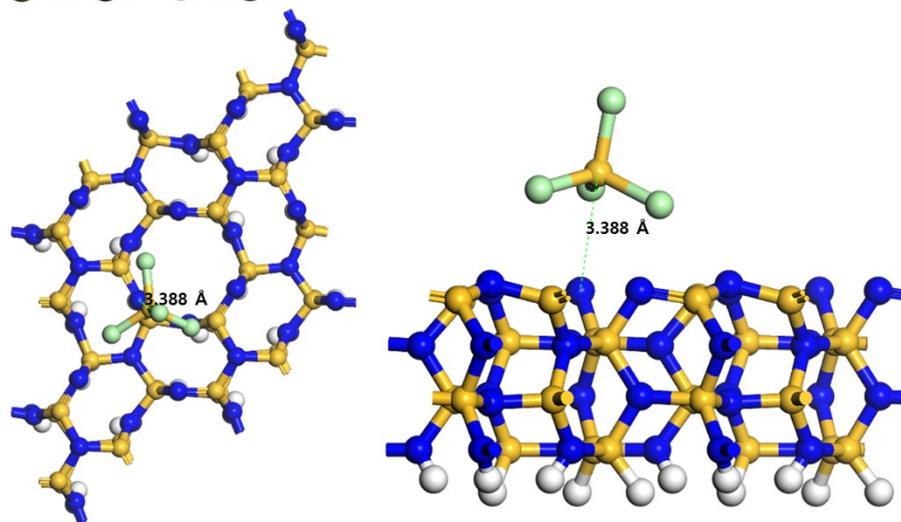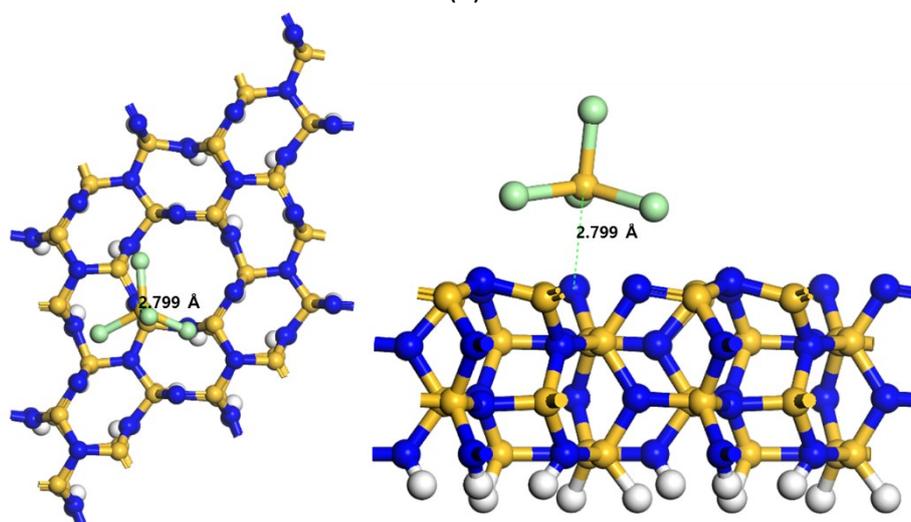**Figure S4.** The optimized structures for (a) adsorption, (b) transition state and (c) reaction of a Si_2Cl_6 molecule on the NH*/SiH*-terminated β-Si_3N_4 surface.
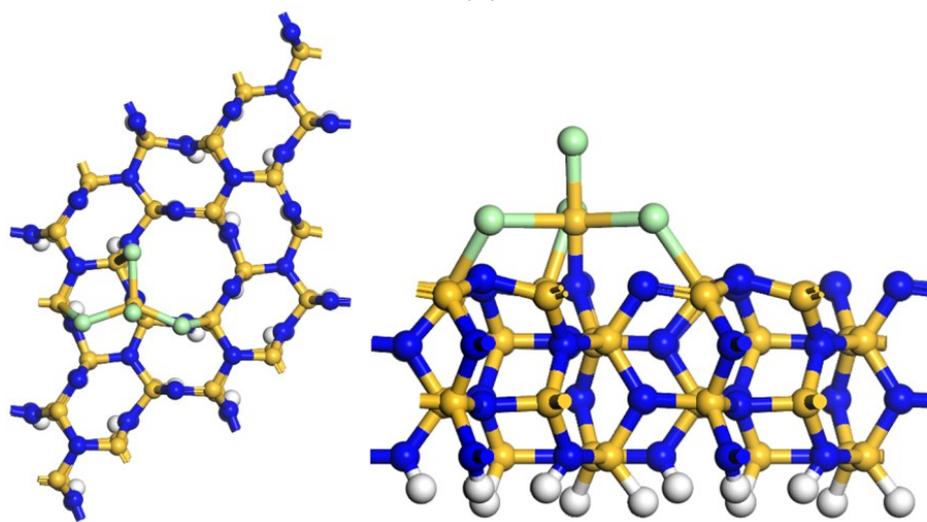
Si   N   H   Cl

4.382 Å

(a)

3.158 Å

(b)

(c)
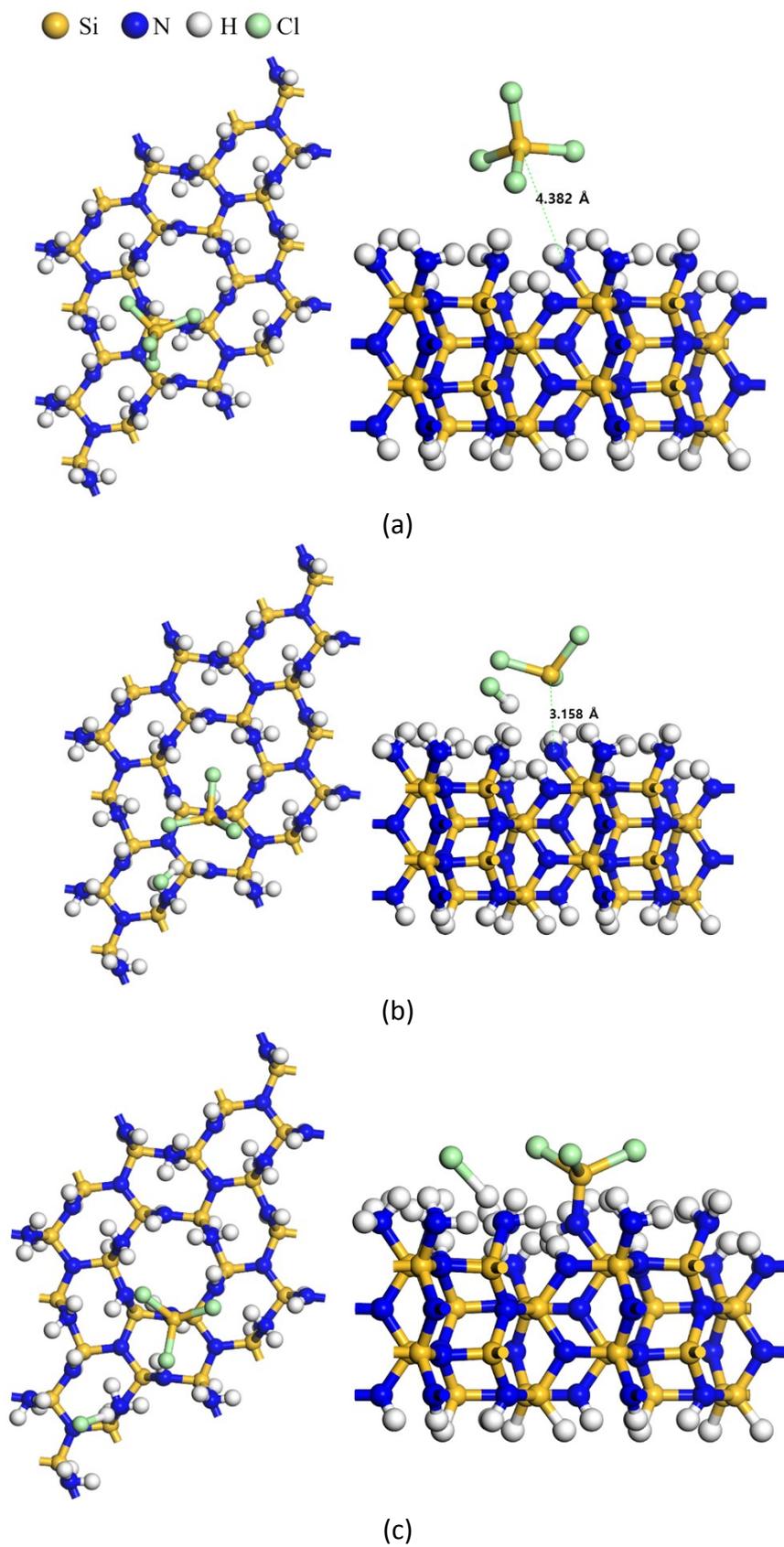
Figure S5. The optimized structures for (a) adsorption, (b) transition state and (c) reaction of a $SiCl_4$ molecule on the NH*/SiNH$_2$*-terminated β-Si$_3$N$_4$ surface.

Figure S6. The optimized structures for (a) adsorption, (b) transition state and (c) reaction of a Si_2Cl_6 molecule on the $NH^*/SiNH_2^*$-terminated β-Si_3N_4 surface.

Figure S7. The optimized structures for (a) adsorption, (b) transition state and (c) reaction of a $SiCl_4$ molecule on the under-coordinated bare >Si=N– β-Si_3N_4 surface.
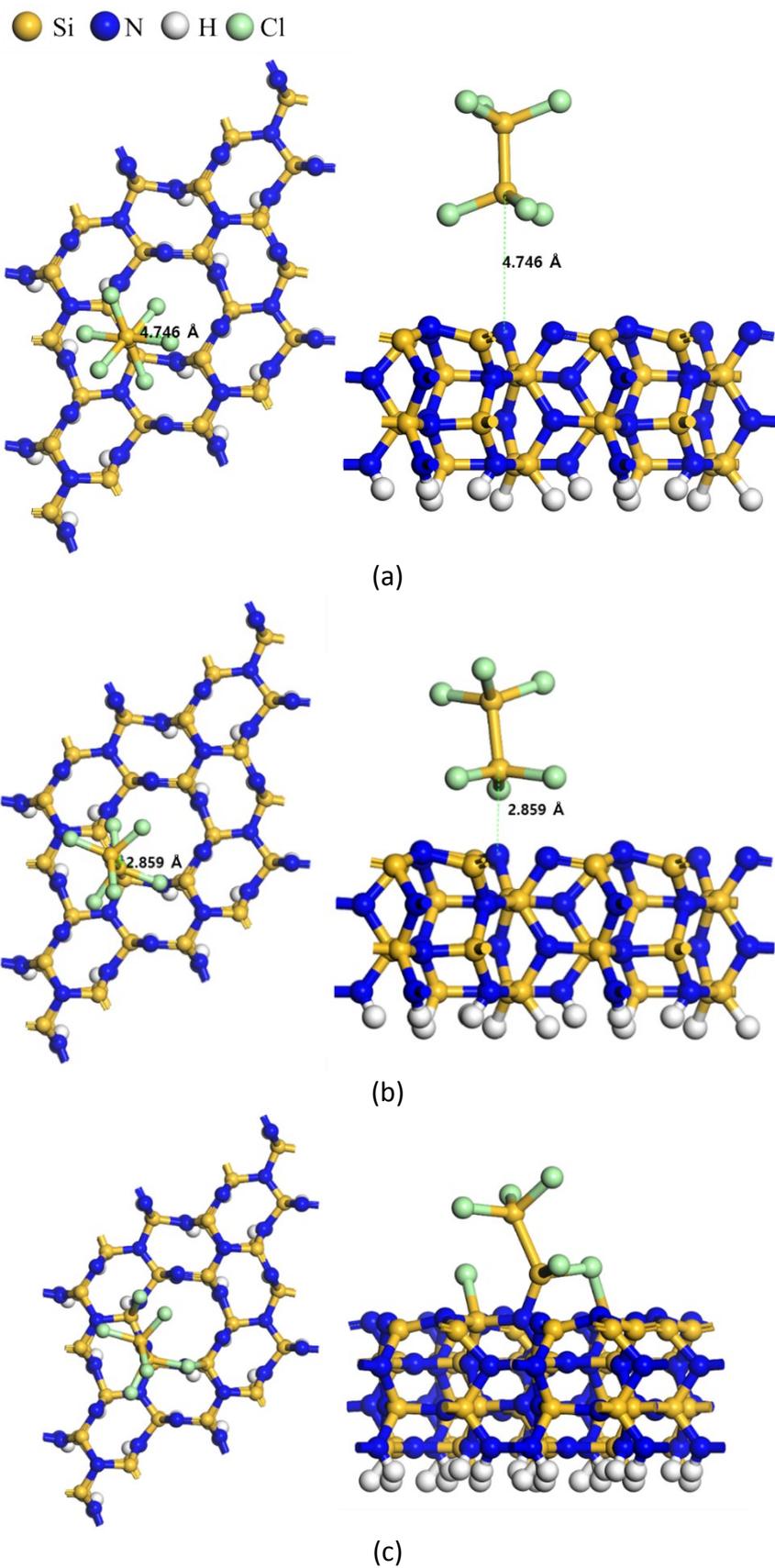
Figure S8. The optimized structures for (a) adsorption, (b) transition state and (c) reaction of a Si_2Cl_6 molecule on the under-coordinated bare >Si=N– β-Si_3N_4 surface.
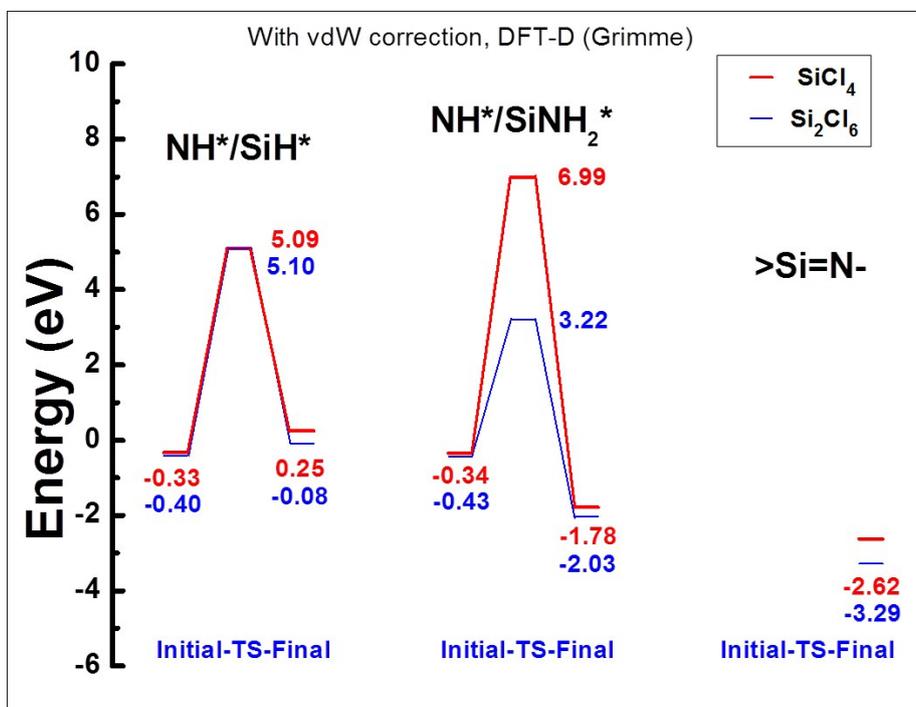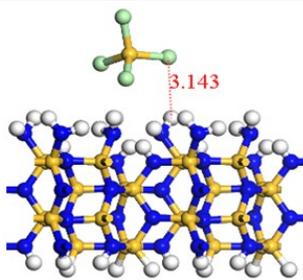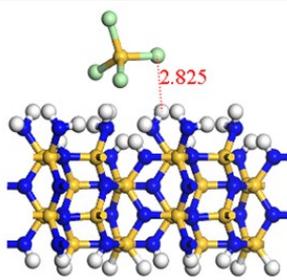
Figure S9. Energy diagram of SiCl$_4$ and Si$_2$Cl$_6$ on the NH*/SiH*-terminated, the NH*/SiNH$_2$*-terminated, and the under-coordinated bare >Si=N– β-Si$_3$N$_4$ surfaces with considering vdW interaction.

Table S3. The comparison of local structure and distance of initial structure of SiCl$_4$ on NH*/SiNH$_2$* surface with and without using van der Waals approach as a case study.

Structure		
	Without vdW	With vdW
Distance (Å)	3.143	2.825
N – H bond (Å)	1.022	1.021
Si – Cl bond (Å)	2.044	2.047
H – N – H Bond angle (°)	108.96	109.96