Electronic Supplementary Information

Dissociation Reaction of B2H6 on TiN Surfaces during Atomic Layer Deposition: First-Principles Study

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This supporting information explains the detailed structures of adsorption, transition, and reaction state of B_2H_6 on three different TiN surfaces. The adsorption energy (E_{ads}) was calculated using

$$E_{ads} = E_{tot,ads} - (E_{surf} + E_{pre})$$

where $E_{tot,ads}$, E_{surf}, and E_{pre} are the total energy of the system after adsorption, and the energy of the surface only and the energy of the precursor only, respectively. The activation energy (E_a) was calculated using

$$E_a = E_{tot,tran} - E_{tot,b.tr}$$

where $E_{tot,tran}$ and $E_{tot,ads}$ are the total energy of the transition state and the total energy before transition, respectively. The reaction energy (E_{rxn}) was calculated using

$$E_{rxn} = E_{tot,a.tr} - E_{tot,b.tr}$$

where $E_{tot,a.tr}$, and $E_{tot,b.tr}$ are the total energies of the system after transition and after transition, respectively.

We considered three orientations and three positions of B_2H_6 above the TiN (001), Ti-terminated TiN (111), and N-terminated (111) TiN surfaces as shown in Figures S1-S3. As for the three orientations, first one is that the B-B bond of the precursor was vertical to the surface. Second one is that the B-B bond of one was horizontal to the surface with two hydrogen atoms facing towards the surface, and third one is that the B-B bond of one was horizontal to the surface with only one hydrogen is facing towards the surface. Also, three different positions were considered on the surface:

For TiN (001) surface, (1) Ti site, (2) Hollow site, (3) N site

For Ti-terminated TiN (111) surface, (1) Ti site (2) N site, (3) Hollow site

For N-terminated TiN (111) surface, (1) N site (2) Ti site, (3) Hollow site

The adsorption energies of B_2H_6 precursor calculated on three different TiN surfaces for each orientation and position were summarized in Table S1-S3.

Figures S4-S6 show the optimized structures at specific reaction states, such as initial, transition, and final step, for B_2H_6 decomposition on the different TiN surfaces according to the reaction steps. Both initial and final state were calculated at the position of remaining B, H, and BH_x species on the most stable site of those surfaces. Since diffusion barrier energies of H atom on the (001) TiN, Ti-terminated (111) TiN, and N-terminated (111) TiN are somewhat low, 0.43, 0.33, and 0.39 eV, respectively, we assume that the adsorbed H atom diffuses far away from the adsorbed BH_x species on the three different TiN surfaces under W ALD process. Therefore, we didn't put the diffused H atom in the next reaction steps because we assume that the H atom is diffused away. Table S4-S6 indicate the activation energies and reaction energies for the overall

reactions of B_2H_6 decomposition on three different TiN surfaces. These tables provide information on whether the B_2H_6 reaction is energetically stable or unstable for certain TiN surfaces.

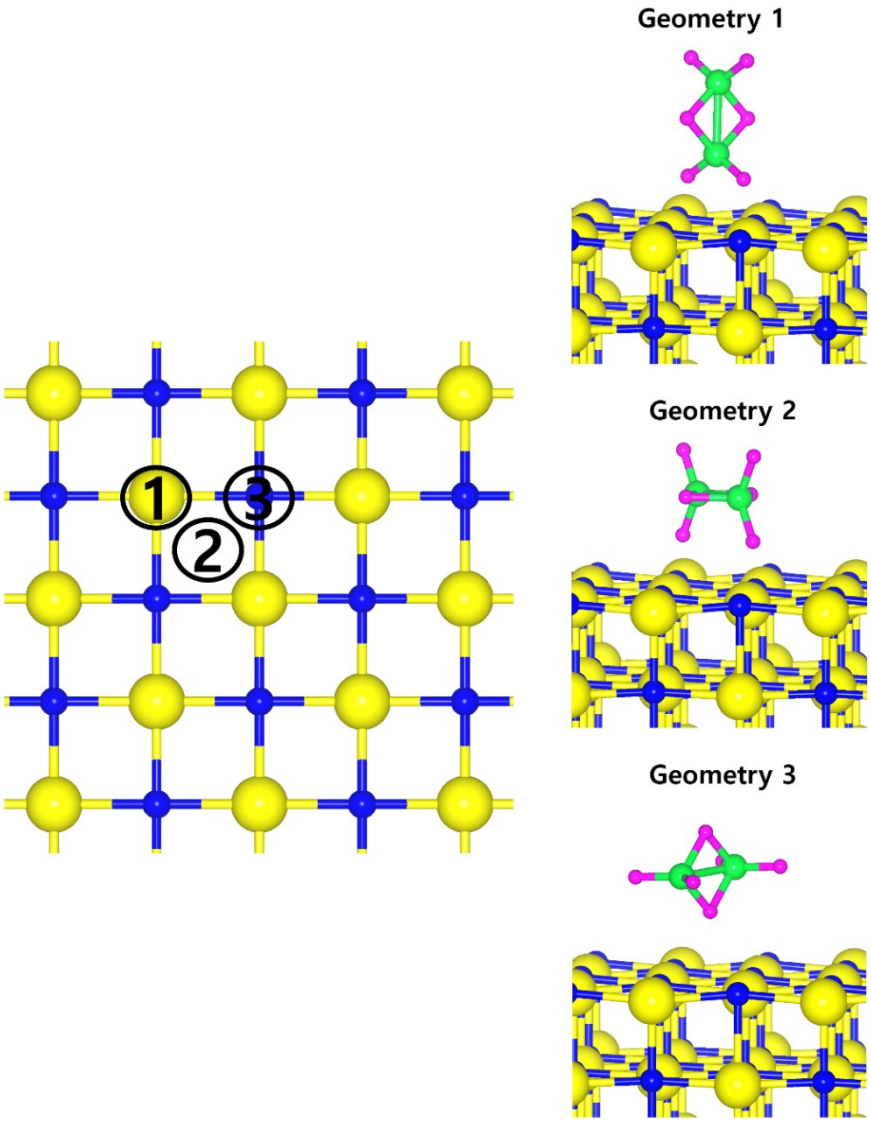

Figure S1. Three orientations and three positions of B_2H_6 on the TiN (001) surface.

Table S1. The adsorption energies of B_2H_6 calculated on the TiN (001) surface for each orientation and position.

Geometry	Position	E ads (eV)
1	1	-0.0261
1	2	0.0554
1	3	0.0477
2	1	-0.0573
2	2	-0.0098
2	3	0.0449
3	1	-0.0057
3	2	-0.0077
3	**3**	**-0.0624**

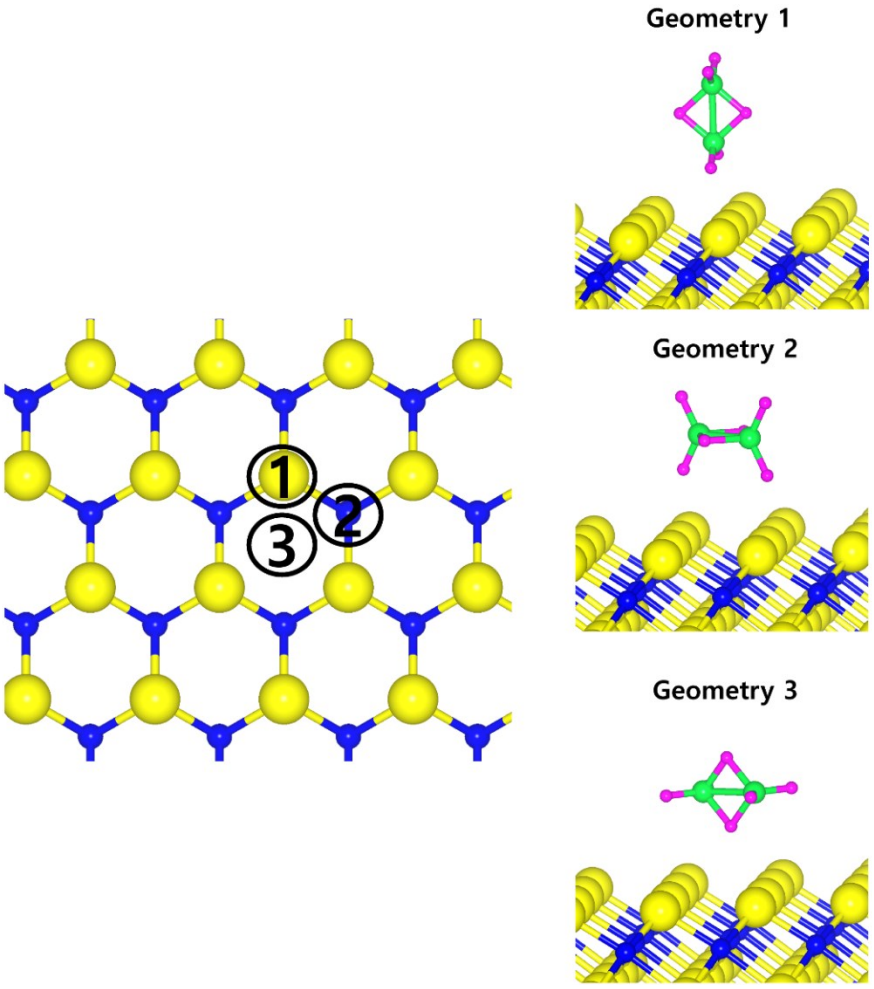

Figure S2. Three orientations and three positions of B_2H_6 on the Ti-terminated TiN (111) surface.

Table S2. The adsorption energies of B_2H_6 calculated on the Ti-terminated TiN (111) surface for each orientation and position.

Geometry	Position	E ads (eV)
1	1	-0.0112
1	2	0.0086
1	3	0.0113
2	1	-0.0366
2	2	0.0160
2	3	0.0200
3	1	0.2217
3	2	-2.3147
3	**3**	**-4.46**

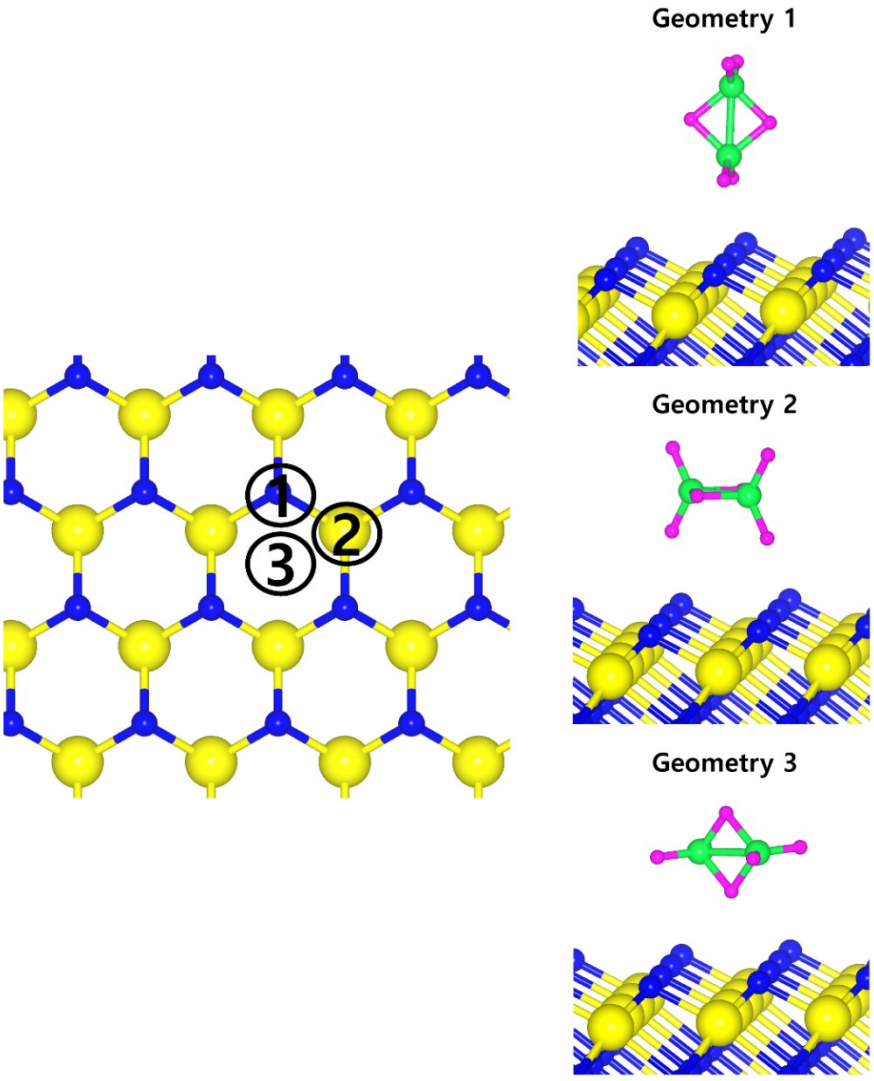

Figure S3. Three orientations and three positions of B_2H_6 on the N-terminated TiN (111) surface.

Table S3. The adsorption energies of B_2H_6 calculated on the N-terminated TiN (111) surface for each orientation and position.

Geometry	Position	E ads (eV)
1	1	0.0108
1	2	-0.0162
1	3	-0.0146
2	1	-0.0202
2	2	-0.0193
2	3	-0.0176
3	1	-0.0080
3	2	-0.0113
3	**3**	**-0.0259**

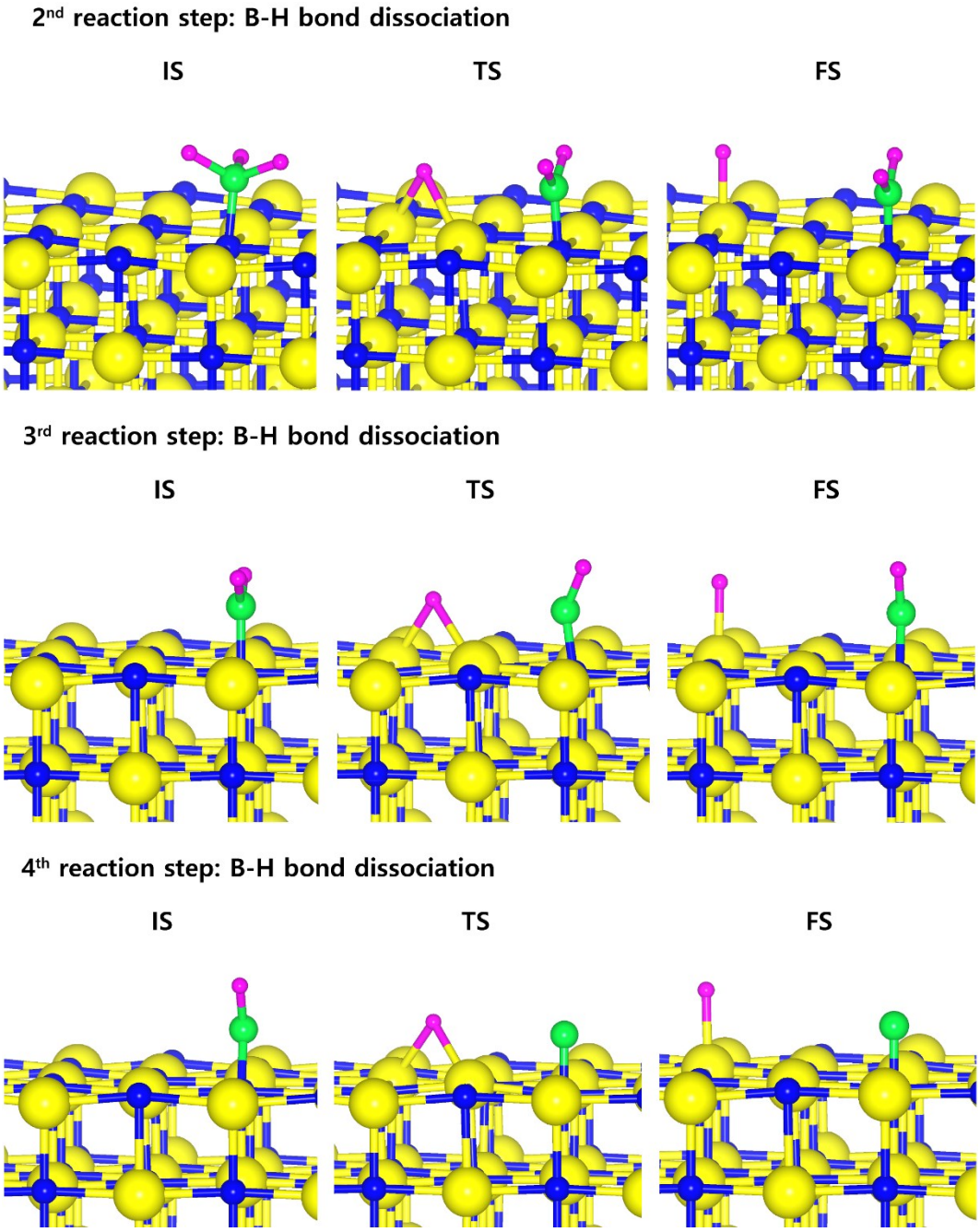

Figure S4. Initial (IS), transition (TS), and final (FS) states of intermediate reactions from the 2nd reaction step to the 4th reaction step for the TiN (001) surface.

Table S4. Activation energies (E_a, eV) and reaction energies (E_{rxn}, eV) of B_2H_6 dissociation on the TiN (001) surface.

Reaction step	Bond dissociation	E_a (eV)	E_{rxn} (eV)
step 1	B-B	1.11	-1.89
step 2	B-H	1.65	1.29
step 3	B-H	1.75	1.45
step 4	B-H	1.83	1.51

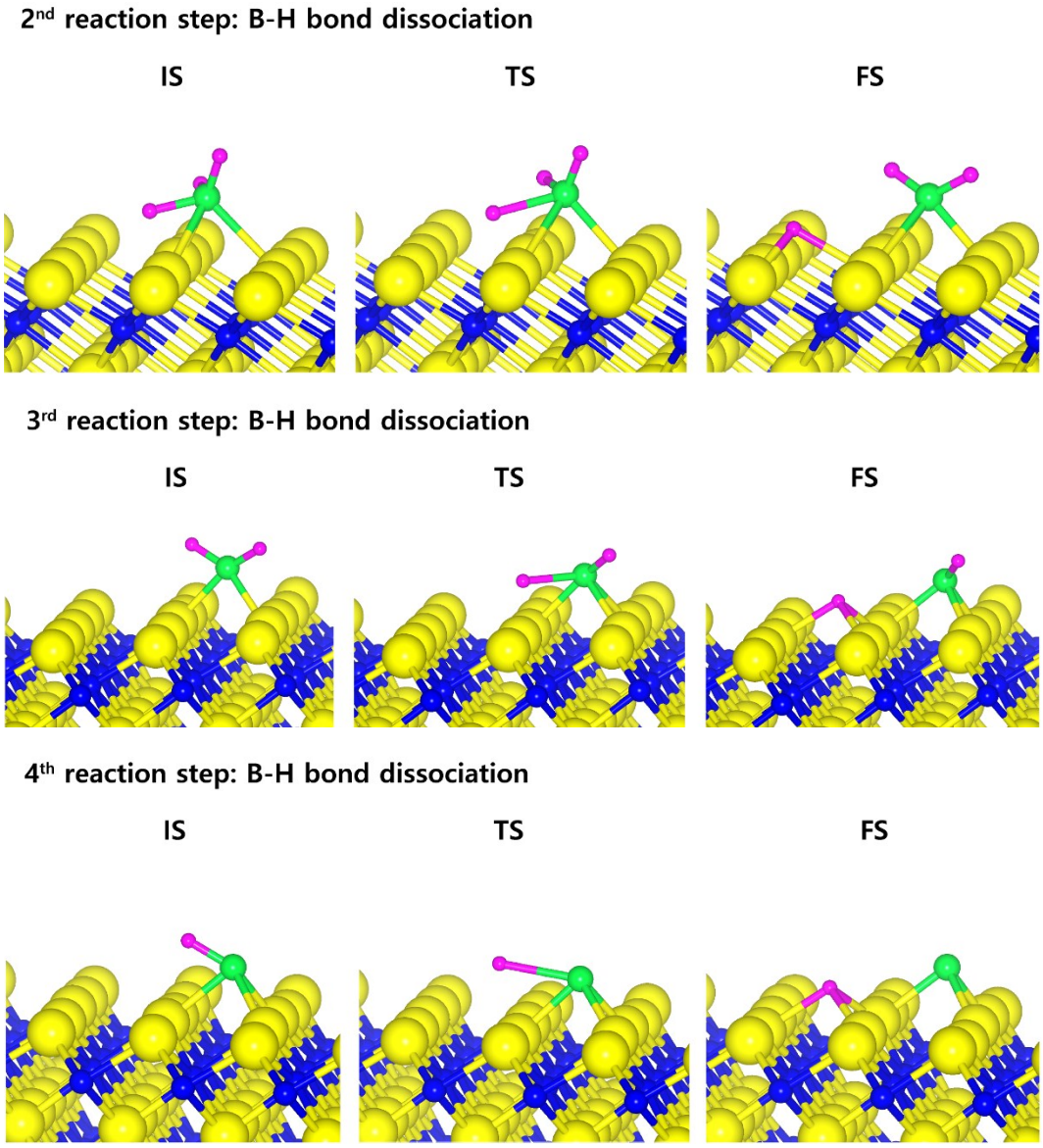

Figure S5. Initial (IS), transition (TS), and final (FS) states of intermediate reactions from the 2nd reaction step to the 4th reaction step for the Ti-terminated TiN (111) surface.

Table S5. Activation energies (E_a, eV) and reaction energies (E_{rxn}, eV) of B_2H_6 dissociation on the Ti-terminated TiN (111) surface.

Reaction step	Bond dissociation	E_a (eV)	E_{rxn} (eV)
step 1	B-B	0.74	0.36
step 2	B-H	0.07	-0.78
step 3	B-H	0.61	-0.12
step 4	B-H	0.93	-0.34

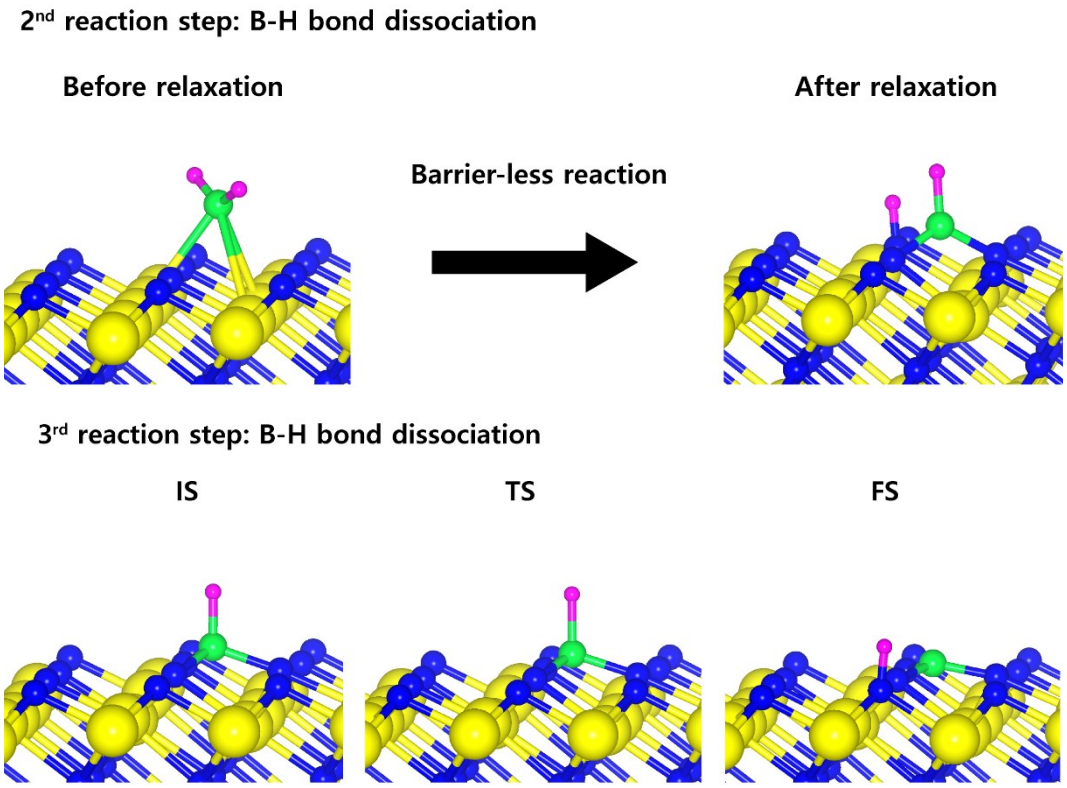

Figure S6. Before and after energy relaxation procedure for 2nd reaction step and Initial (IS), transition (TS), and final (FS) states of intermediate reactions from the 3rd reaction step for the N-terminated TiN (111) surface.

Table S6. Activation energies (E_a, eV) and reaction energies (E_{rxn}, eV) of B_2H_6 dissociation on the N-terminated TiN (111) surface.

Reaction step	Bond dissociation	E_a (eV)	E_{rxn} (eV)
step 1	B-B & B-H	0.39	-7.14
step 2	B-H	Barrier-less reaction	-9.13
step 3	B-H	0.14	-2.70

Movie S1. Represented atoms of the movie, such as Ti, N, B, and H, are grey, blue, pink, and white, respectively.