

## Supplementary Material

# Atomic Layer Deposition of Silicon Oxide Films Using Bis(dimethylaminomethylsilyl)trimethylsilylamine and Ozone: First-principle and Experimental Study

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Figure S1–S3 shows the atomistic structures of the reactant, transition, and product states of the pathways not shown in Fig. 5. Figure S1 shows that all three ligands of DTDN-2H2 face the substrate surface in  $\mathbf{R}_a$ . Next, in  $\mathbf{TS}_{ab}$  of Fig. S1(a), the H atom of surface  $-\text{OH}^*$  migrates to the central N atom of  $(\text{Me}_3\text{Si})\underline{\text{N}}(\text{SiHMeNMe}_2)_2$ , leaving  $-\text{O}^*$ . Unlike Fig. 5(a), no bond is formed between the Si atom of the  $\text{Me}_3\text{Si}$  group and the surface  $-\text{O}^*$  yet, resulting in slightly higher activation energy than  $\mathbf{TS}_{aa}$ . Finally, in  $\mathbf{P}_b$ , the Si–N bond is broken, causing the  $\text{SiHMeNMe}_2$  ligand to bond with the surface  $-\text{O}^*$  to form  $\text{OSiHMeNMe}_2^*$ .

On the other hand, in  $\mathbf{TS}_{ac}$  of Fig. S1(b), the H atom of surface  $-\text{OH}^*$  migrates to the N atom in the  $\text{SiHMeNMe}_2$  ligand, releasing  $\text{HNMe}_2$ , which is different from  $\mathbf{TS}_{aa}$  of Fig. 5(a) or  $\mathbf{TS}_{ab}$  of Fig. S1(a). The high activation energy of 3.68 eV in Fig. 4 is due to the cleavage of the Si–N and O–H bonds and over-coordination of the central N atom despite the formation of N–H and the transition of Si–N to Si=N. Finally, in  $\mathbf{P}_c$ , the Si=N bond is transformed to Si–N to form Si–O bond, forming  $-\text{OSiH}(\text{Me})\text{N}(\text{SiMe}_3)(\text{SiHMeNMe}_2)^*$ .

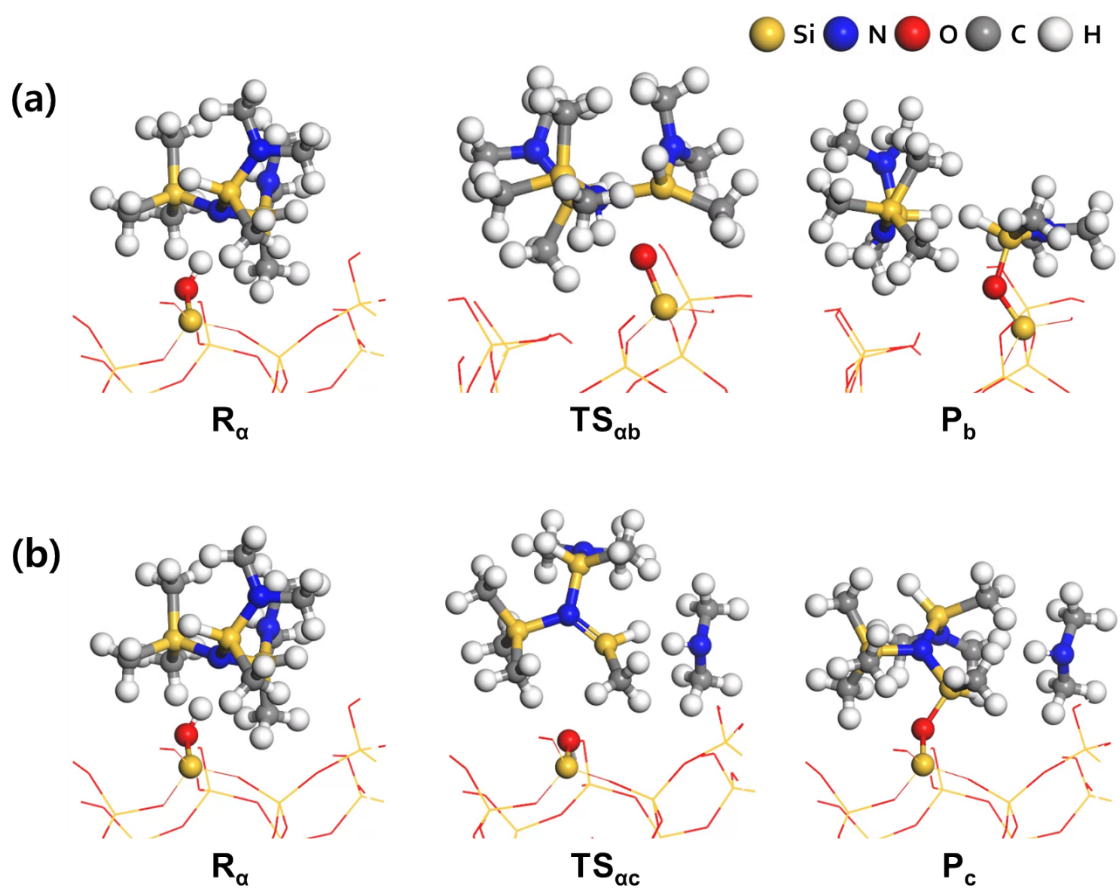


Fig. S1. The atomistic structures of the chemisorption pathway for  $R_\alpha$  in which all three ligands of DTDN-2H2 face the substrate surface. The orientation of each figure was adjusted to show atoms clearly.

Figure S2 shows that only the SiMe<sub>3</sub> ligand of DTDN-2H2 faces the substrate in **R<sub>β</sub>**. Next, in **TS<sub>βa</sub>** of Fig. S2(a), the Si–N bond between SiMe<sub>3</sub> and the central N atom is broken, and SiMe<sub>3</sub> is inserted between the O and H atoms of a surface hydroxyl group. The high activation energy of 5.02 eV in Fig. 4 is due to the cleavage of Si–N and O–H bonds, the under-coordination of the central N atom, and the over-coordination of the Si atom of –OSiHMe<sub>3</sub>\* despite the formation of Si–O and Si–H bonds. Finally, in **P<sub>a</sub>**, the H atom of –OSiMe<sub>3</sub>H\* migrates to the under-coordinated N atom to form HN(SiHMeNMe<sub>2</sub>)<sub>2</sub>, leaving –OSiMe<sub>3</sub>\* on the surface.

On the other hand, in **TS<sub>βc</sub>** of Fig. S2(b), the H atom of the SiHMeNMe<sub>2</sub> ligand migrates to the N atom in the same ligand, releasing HNMe<sub>2</sub>. The relatively high activation energy of 2.38 eV is due to the cleavage of the Si–H bond and undercoordination of the Si atom despite the formation of N–H and the transition of Si–N to Si=N. Finally, in **P<sub>c</sub>**, the Si=N bond is transformed to Si–N, and the O–H bond of a surface hydroxyl group is broken to form Si–O bond, forming –OSiH(Me)N(SiMe<sub>3</sub>)(SiHMeNMe<sub>2</sub>)\*.

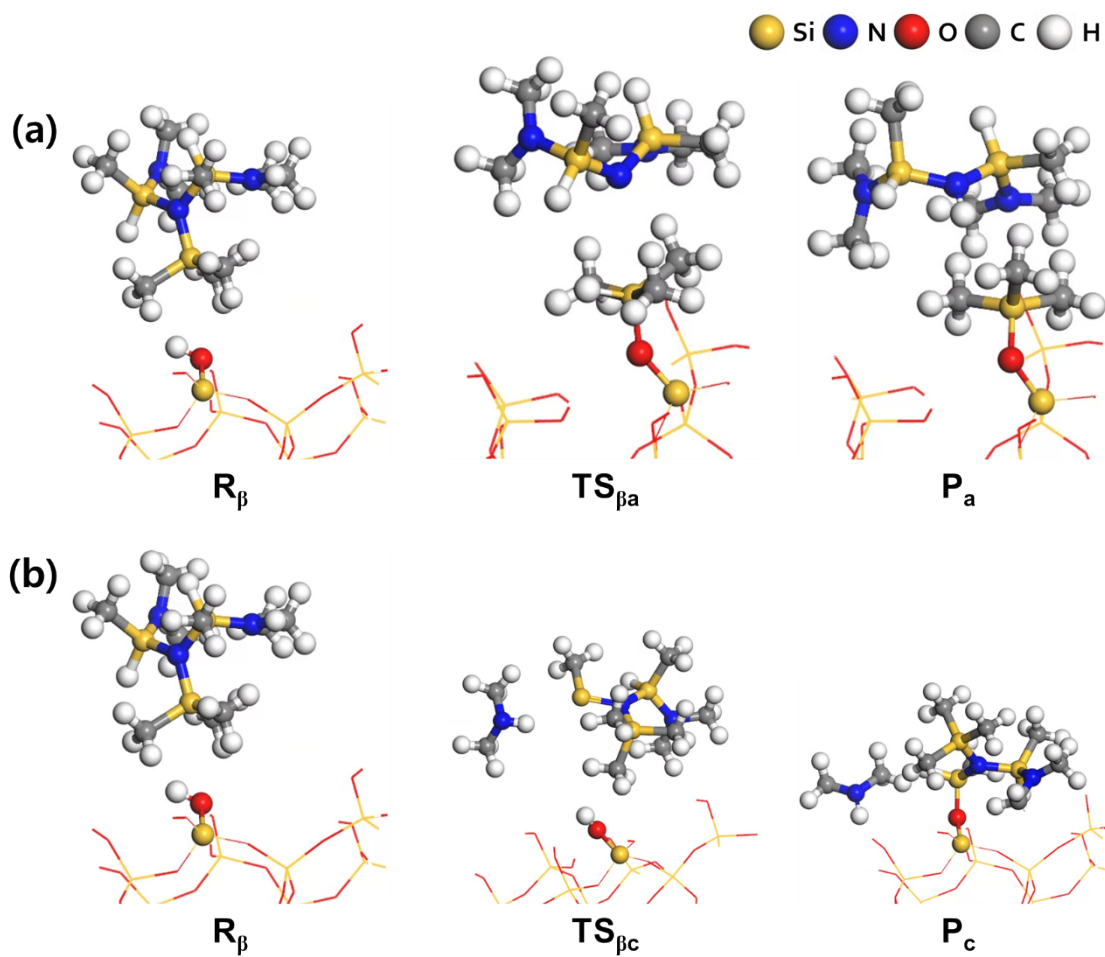


Fig. S2. The atomistic structures of the chemisorption pathway for  $R_{\beta}$  in which only  $SiMe_3$  ligand of DTDN-2H2 faces the substrate. The orientation of each figure was adjusted to show atoms clearly.

Figure S3 shows that only one SiHMeNMe<sub>2</sub> ligand of DTDN-2H2 faces the substrate in **R<sub>γ</sub>**. Next, in **TS<sub>γa</sub>** of Fig. S3(a), the H atom of surface –OH\* migrates to the central N atom of (Me<sub>3</sub>Si)N(SiHMeNMe<sub>2</sub>)<sub>2</sub>, leaving –O\*, while the SiMe<sub>3</sub> group migrates to the N atom of SiHMeNMe<sub>2</sub> ligand, resulting in an over-coordination of the N atom. The relatively high activation energy of 2.01 eV in Fig. 4 is due to the cleavage of O–H and Si–N bonds and the over-coordination of the N atom, despite the formation of N–H and Si–N bonds. Finally, in **Pa**, the SiMe<sub>3</sub> group migrates to the surface –O\*, forming –OSiMe<sub>3</sub>\* on the surface.

On the other hand, in **TS<sub>γb</sub>** of Fig. S3(b), the Si–N bond between the central N atom and the Si atom of the SiHMeNMe<sub>2</sub> ligand is broken, and the Si–N bond in the ligand is transformed to Si=N. The high activation energy of 4.60 eV is due to the cleavage of the Si–N bond and undercoordination of the central N atom despite the transition of Si–N to Si=N. Finally, in **P<sub>b</sub>**, the Si=N bond is transformed to Si–N, and a surface hydroxyl group's O–H bond is broken to form Si–O bond, forming –OSiHMeNMe<sub>2</sub>\*. The H atom of surface –OH\* migrates to the central N atom to form (Me<sub>3</sub>Si)NH(SiHMeNMe<sub>2</sub>) as the byproduct.

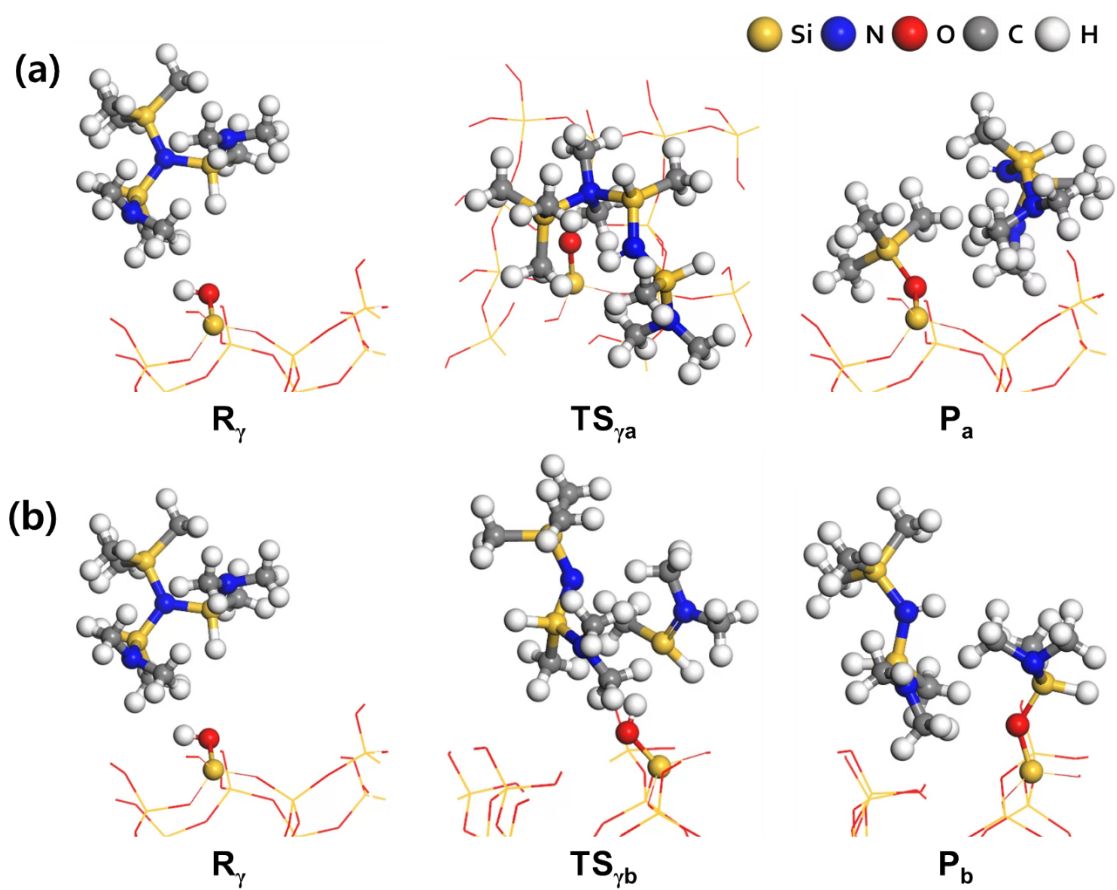


Fig. S3. The atomistic structures of the chemisorption pathway for  $R_\gamma$  in which only one  $\text{SiHMeNMe}_2$  ligand of DTDN-2H2 faces the substrate.