Reactivity of Different Nitriding Agents with Chlorine-terminated Surface During Atomic Layer Deposition of Silicon Nitride

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This supporting information includes the simulation of the reaction of NH_3 and N_2H_4 on the $NSiCl_2$*/SiCl*-terminated silicon nitride surface with the second reaction pathways shown in equations 10 and 12 of the main text, respectively. Calculations for the recombination of radicals in the NH_3 plasma were also included.

Figures S1 and S2 show the energy diagrams and the optimized geometries of the second reaction pathway of the surface reactions with NH_3 and N_2H_4, respectively. The abstraction of the chlorine atom from the silicon nitride surface by NH_3 or N_2H_4 was endothermic with reaction energies of 2.02 eV and 2.12 eV, respectively, indicating unfavored reactions.

Figure S3 shows the energy diagrams and the optimized geometries of the surface reaction and recombination of two NH· radicals on the $NSiCl_2$*/SiCl*-terminated silicon nitride surface. The surface reaction shows the chemisorption of two NH· radicals to form Si–NHCl and Si–NH bridge surface groups with the reaction energy of -8.55 eV, which is more favorable than the recombination reaction with the reaction energy of -5.81 eV.

Figure S4 shows the energy diagrams and the optimized geometries of the surface reaction and recombination of two H· radicals on the $NSiCl_2$*/SiCl*-terminated silicon nitride surface. The surface reaction shows the abstraction of two chlorine atoms from the surface to form two HCl molecules with the reaction energy of -4.77 eV, which is more favorable than the recombination reaction to form H_2 with reaction energy of -4.56 eV.

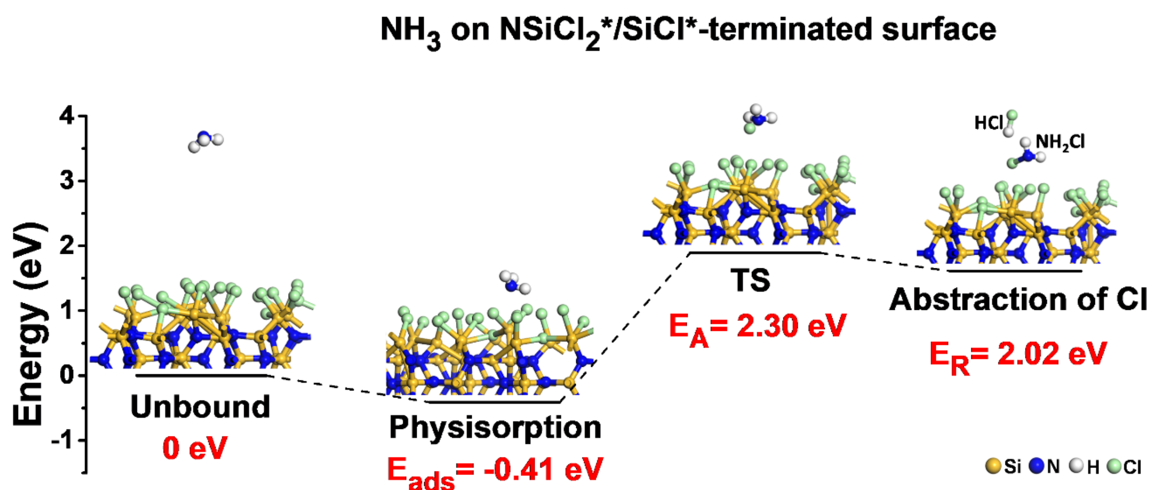

Figure S1. Energy diagram for the second pathway surface reaction of an NH_3 molecule on the $NSiCl_2$*/SiCl*-terminated silicon nitride surface.

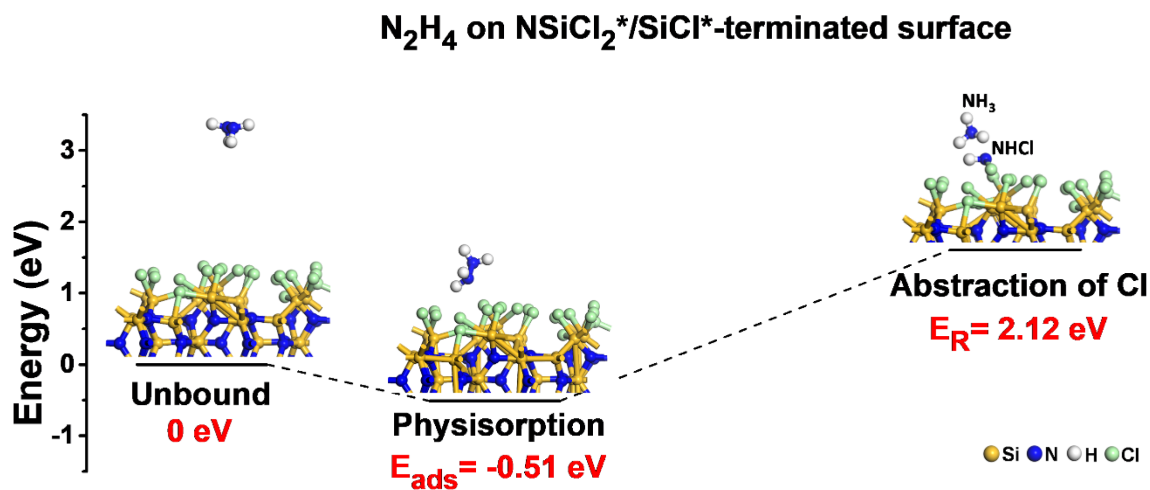

Figure S2. Energy diagram for the second pathway surface reaction of an N_2H_4 molecule on the $NSiCl_2$*/SiCl*-terminated silicon nitride surface.

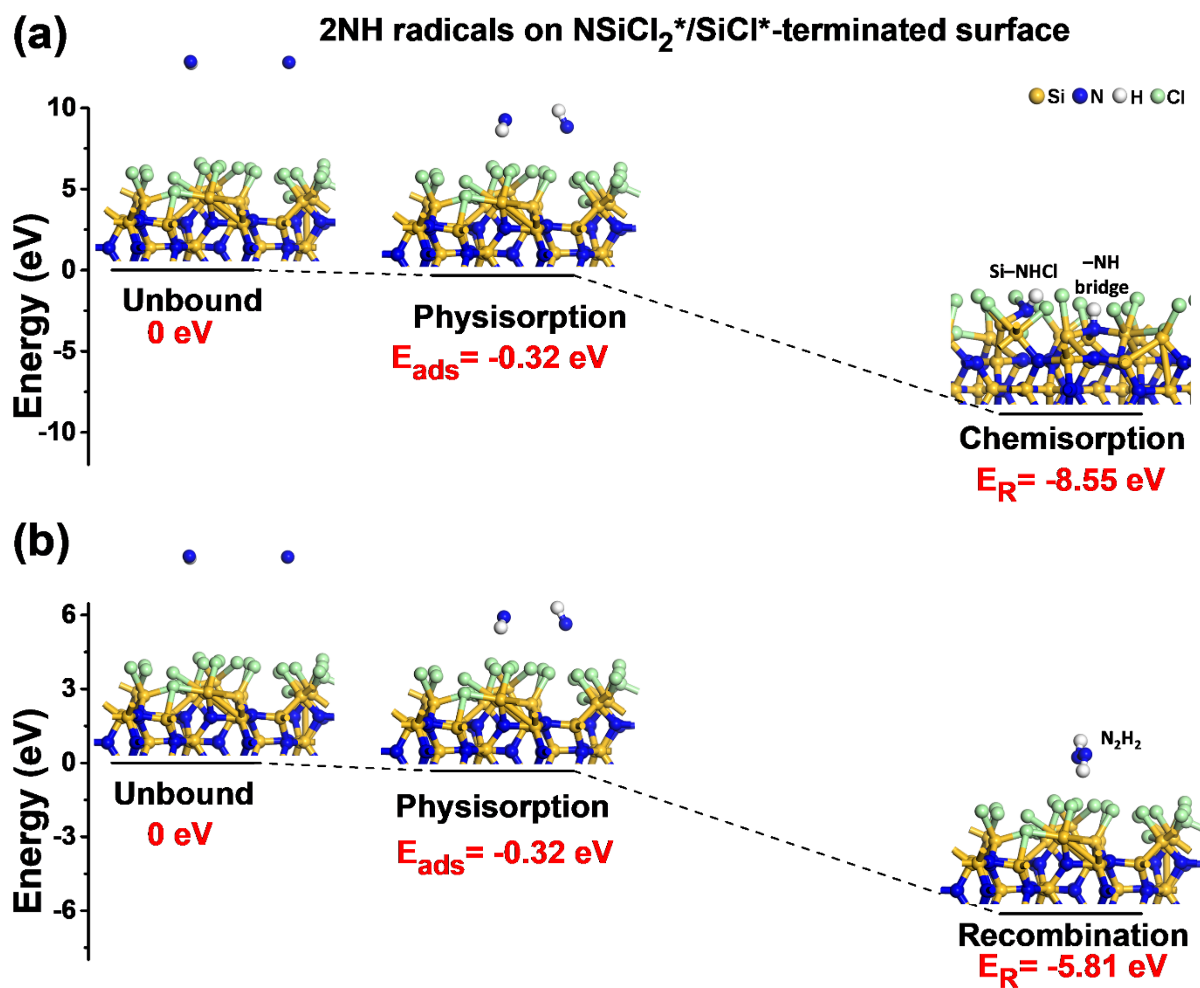

Figure S3. Energy diagram for (a) the surface reaction and (b) the recombination of two NH· radicals on the $NSiCl_2$*/SiCl*-terminated silicon nitride surface.

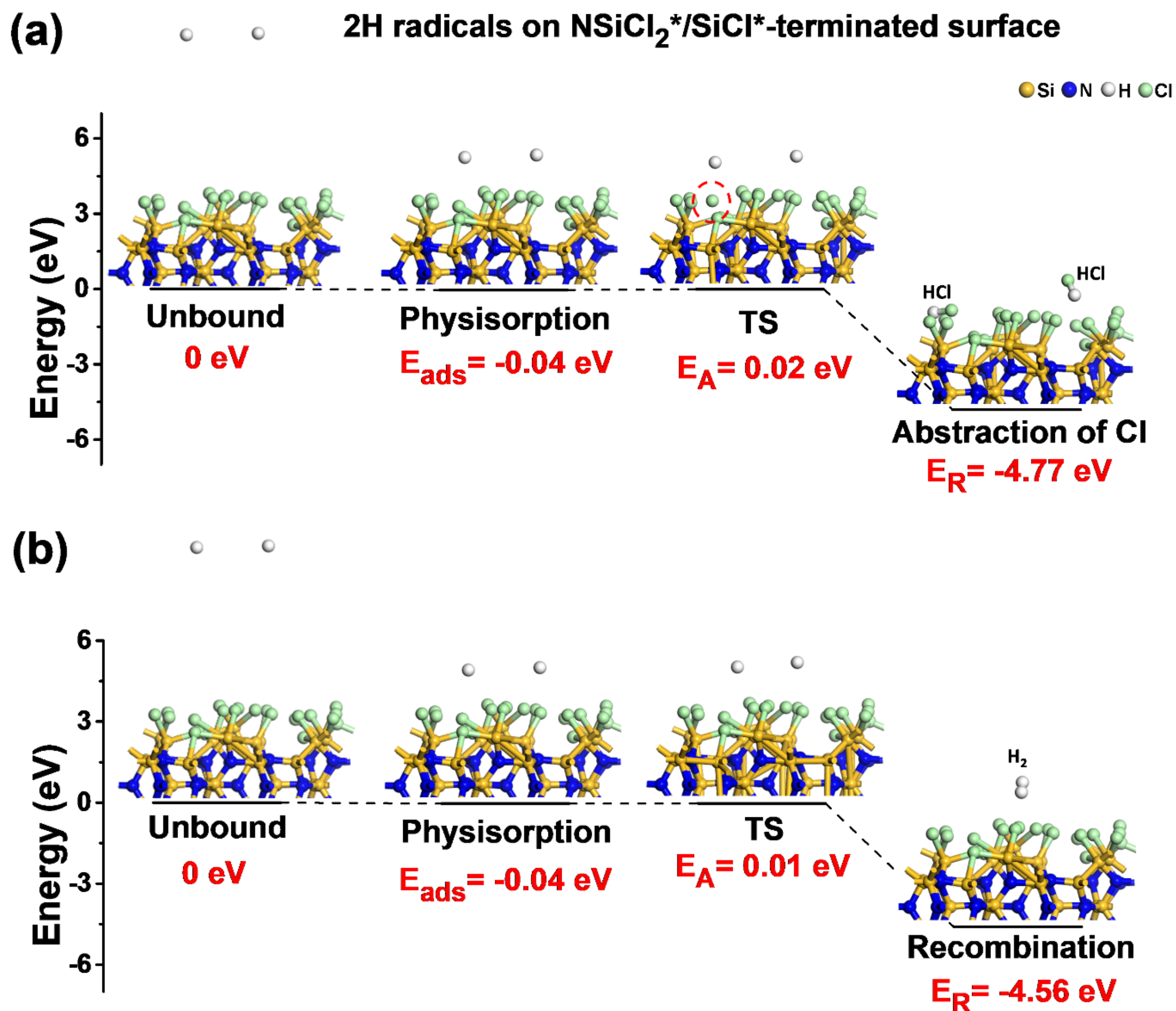

Figure S4. Energy diagram for (a) the surface reaction and (b) the recombination of two H· radicals on the $NSiCl_2$*/SiCl*-terminated silicon nitride surface.