

Design of Efficient Mono-Aminosilane Precursors for Atomic Layer Deposition of SiO₂ Thin Films

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Electronic Supplementary Information (ESI)

S1. The equations for calculating adsorption energy (ΔE_{AD}), reaction energy barrier (ΔE_a), reaction energy (ΔE) and desorption energy (ΔE_{DE})

(1) The adsorption energy (ΔE_{AD}) was calculated using

$$\Delta E_{AD} = E_{Surf} + E_{Pr} - E_{AD}$$

where E_{AD} and E_{Surf} are the energies of the precursor-adsorbed and clean hydroxylated SiO₂(001) surfaces, respectively, and E_{Pr} is the energy of the Si precursor.

(2) The reaction energy barrier (ΔE_a) was calculated using

$$\Delta E_a = E_{TS} - E_{AD}$$

where E_{TS} is the energy at the transition state.

(3) The reaction energy (ΔE), which is the energy difference between the adsorbed and reacted configurations, was calculated using

$$\Delta E = E_{RE} - E_{AD}$$

where E_{RE} is the energy of the reacted configuration with the by-product nearby. By definition of reaction energy (ΔE), an exothermic reaction has a negative value and an endothermic reaction has a positive value.

(4) The desorption energy (ΔE_{DE}) of by-product was calculated using

$$\Delta E_{DE} = E_{Surf+SiH_3} + E_{BP} - E_{RE}$$

where $E_{Surf+SiH_3}$ is the energy of the reacted hydroxylated SiO_2 (001) surfaces with SiH_3 group nearby, and E_{BP} is the energy of by-product.

S2. The bond dissociation energy(BDE) of Si–N bond in precursors.

The Si precursors were optimized in a $20 \times 20 \times 20 \text{ \AA}^3$ vacuum box with a $1 \times 1 \times 1$ Monkhorst-Pack grid k-point mesh in order to obtain the most favorable structures.

To calculate the bond dissociation energy (BDE) between the Si atom and N atom in the precursors, the precursors were divided into two ligands by breaking the Si–N bond while maintaining the molecular structures of the two ligands.

Obviously, bond dissociation energies of Si–N bond were larger than the adsorption energy of precursors, indicating that the precursors will not decompose in the gas phase between the estimated ALD window.

Table S1. The calculated adsorption energy (ΔE_{AD}), reaction energy barrier (ΔE_a), desorption energy (ΔE_{DE}) and bond dissociation energy (BDE) of Si–N bond

Precursor	Energies (kcal/mol)			
	ΔE_{AD}	ΔE_a	ΔE_{DE}	BDE (Si–N)
DMAS	18.9	12.5	5.1	106.8
DEAS	19.5	13.7	7.5	105.4
DPAS	17.8	9.4	8.3	107.2
DIPAS	18.8	10.9	8.1	100.1
DSBAS	17.7	12.0	8.9	99.2
DTBAS	16.2	13.5	8.7	95.6

S3.Kinetic analysis for the dissociation of precursors on hydroxylated SiO_2 (001) surfaces.

The reaction rate constants (k) for precursor's dissociation on hydroxylated SiO_2 (001) surfaces at different temperatures (350- 800 K) were calculated using harmonic Transition State Theory (TST):

$$k = \frac{k_B T}{h} \frac{q_{TS}}{q_R} \exp(-E_a/k_B T) \quad (R1)$$

where k_B is the Boltzmann constant, h is the Planck constant, T is the absolute temperature, E_a is the zero-point-corrected energy difference between the transition state and the initial reactant.

For partition functions, q , we only consider vibrational degrees of freedom for surface reactions, and they are calculated in the harmonic model, where ν is the vibrational frequency.

$$q = \frac{1}{\prod_{i=1}^{Vibrations} (1 - \exp(-h\nu_i/k_B T))}$$

Table S2. The reaction rate constants ($\ln k$) for precursor's dissociation on hydroxylated SiO₂ (001) surfaces at different temperatures (350- 800 K)

Temperature	Rate constants ($\ln k$)						
	DMAS	DEAS	DPAS	DIPAS	DSBAS	DIBAS	DTBAS
350 K	12.63	12.24	16.26	14.92	7.24	6.40	6.88
375 K	13.81	13.63	17.14	15.97	8.28	7.77	8.06
400 K	14.84	14.84	17.90	16.88	9.18	8.96	9.08
425 K	15.75	15.91	18.56	17.68	9.95	10.01	9.96
450 K	16.55	16.86	19.14	18.39	10.63	10.94	10.74
475 K	17.26	17.71	19.66	19.02	11.23	11.76	11.42
500 K	17.90	18.47	20.12	19.57	11.76	12.49	12.03
525 K	18.47	19.16	20.53	20.07	12.23	13.15	12.57
550 K	18.98	19.78	20.89	20.52	12.64	13.75	13.05
575 K	19.45	20.35	21.22	20.93	13.01	14.27	13.49
600 K	19.88	20.87	21.52	21.30	13.35	14.77	13.88
625 K	20.27	21.34	21.79	21.63	13.65	15.22	14.23
650 K	20.63	21.78	22.04	21.94	13.92	15.63	14.55
675 K	20.95	22.18	22.26	22.22	14.16	16.00	14.84
700 K	21.26	22.55	22.47	22.471	14.38	16.35	15.11
725 K	21.53	22.90	22.65	22.71	14.58	16.66	15.35
750 K	21.79	23.22	22.82	22.93	14.76	16.96	15.57
775 K	22.03	23.52	22.98	23.12	14.93	17.23	15.78
800 K	22.25	23.79	23.13	23.31	15.08	17.48	15.96
825 K	22.46	24.05	23.26	23.48	15.22	17.71	16.14
850 K	22.65	24.29	23.38	23.64	15.34	17.93	16.29

S3.The optimized structures of DMAS, DEAS, DPAS, DIPAS, DSBAS, and DTBAS.

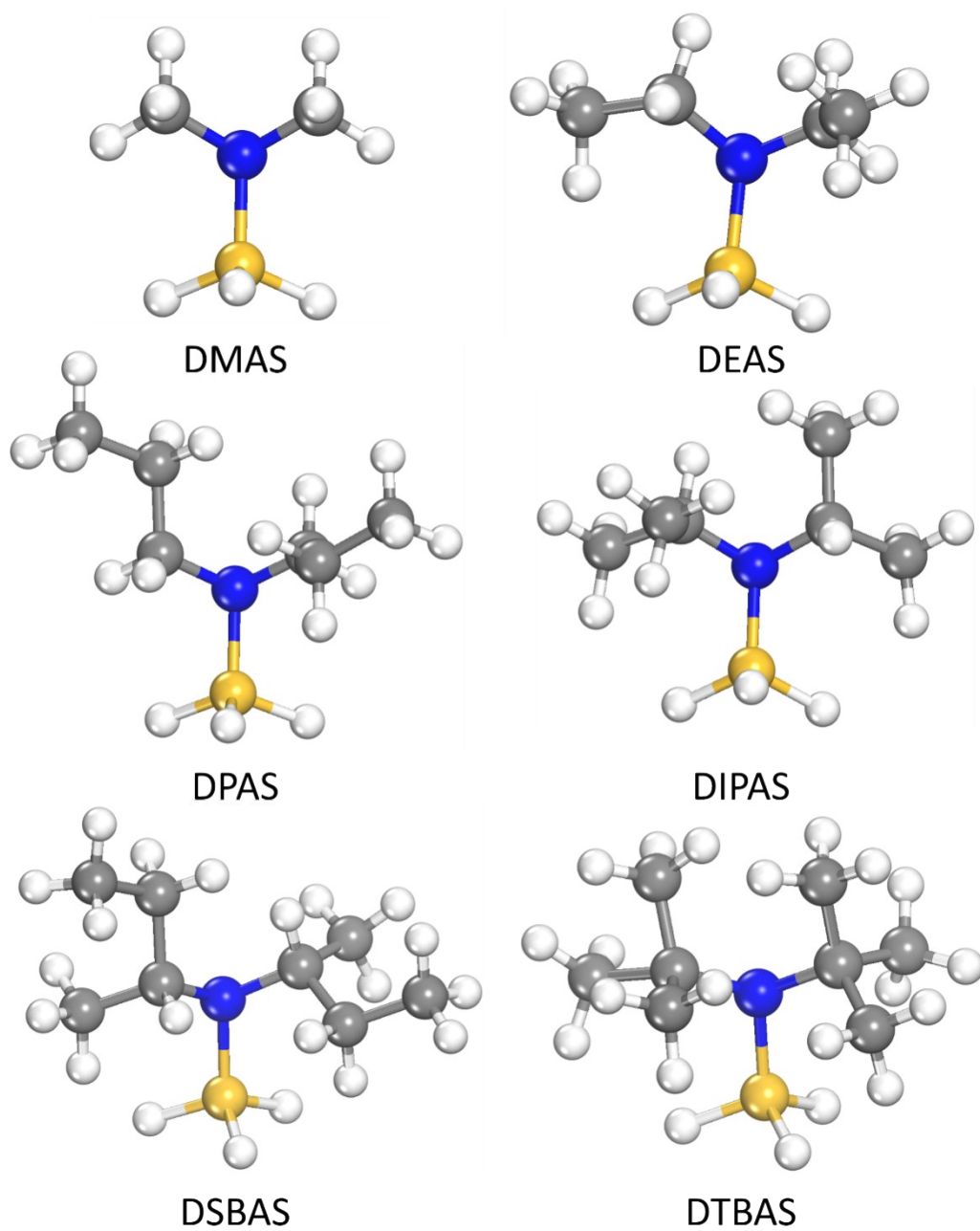


Fig S1.The optimized structures of DMAS, DEAS, DPAS, DIPAS, DSBAS, and DTBAS.

S4. The optimized structures, main structural parameters and energy variation for the dissociative reaction of precursors on hydroxylated SiO₂ (001) surfaces.

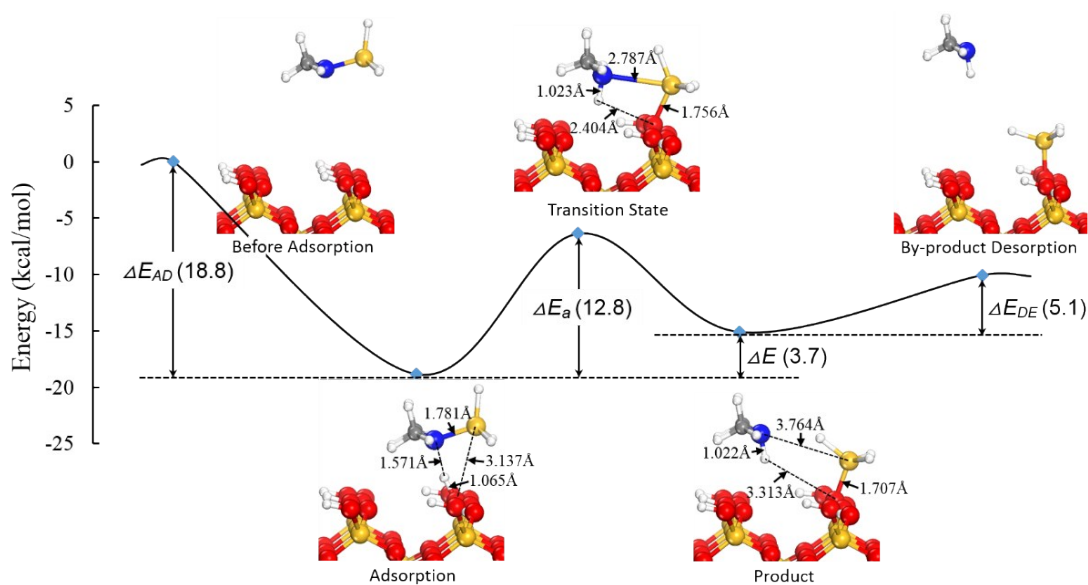


Fig S2. Energy variation for DMAS reaction with the hydroxylated SiO₂ (001) surface.

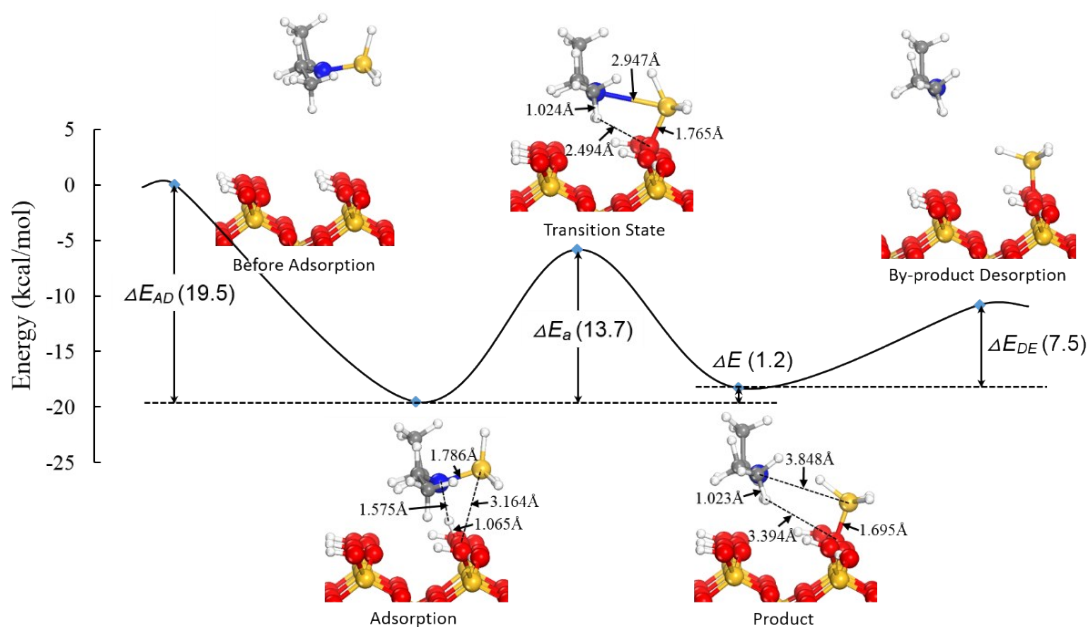


Fig S3. Energy variation for DEAS reaction with the hydroxylated SiO₂ (001) surface.

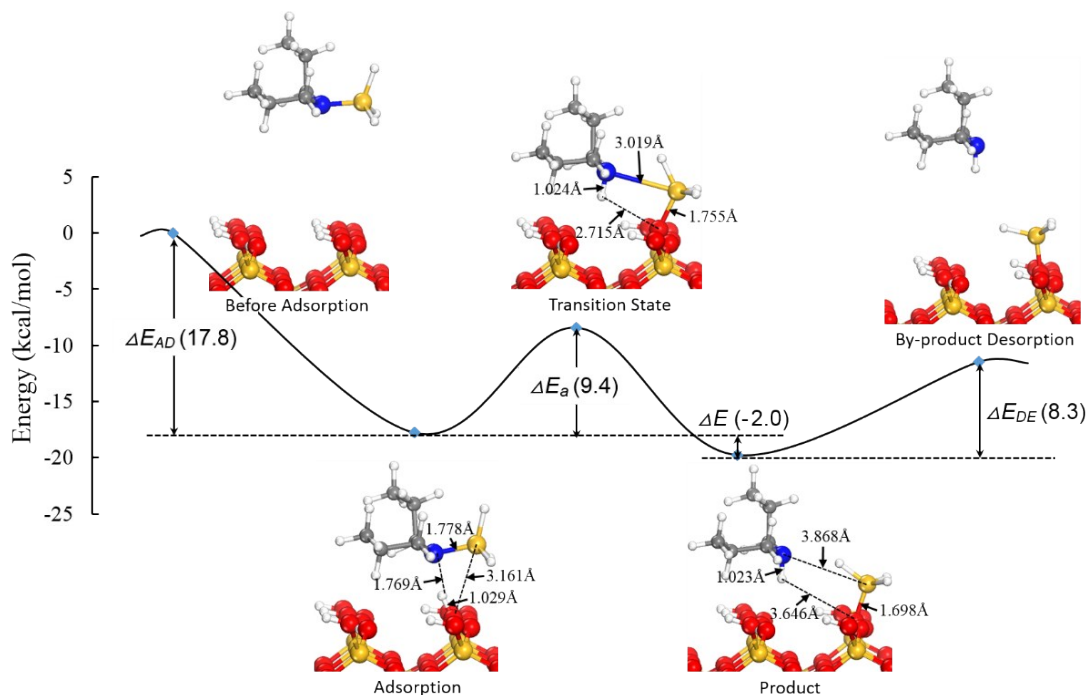


Fig S4. Energy variation for DPAS reaction with the hydroxylated SiO_2 (001) surface.

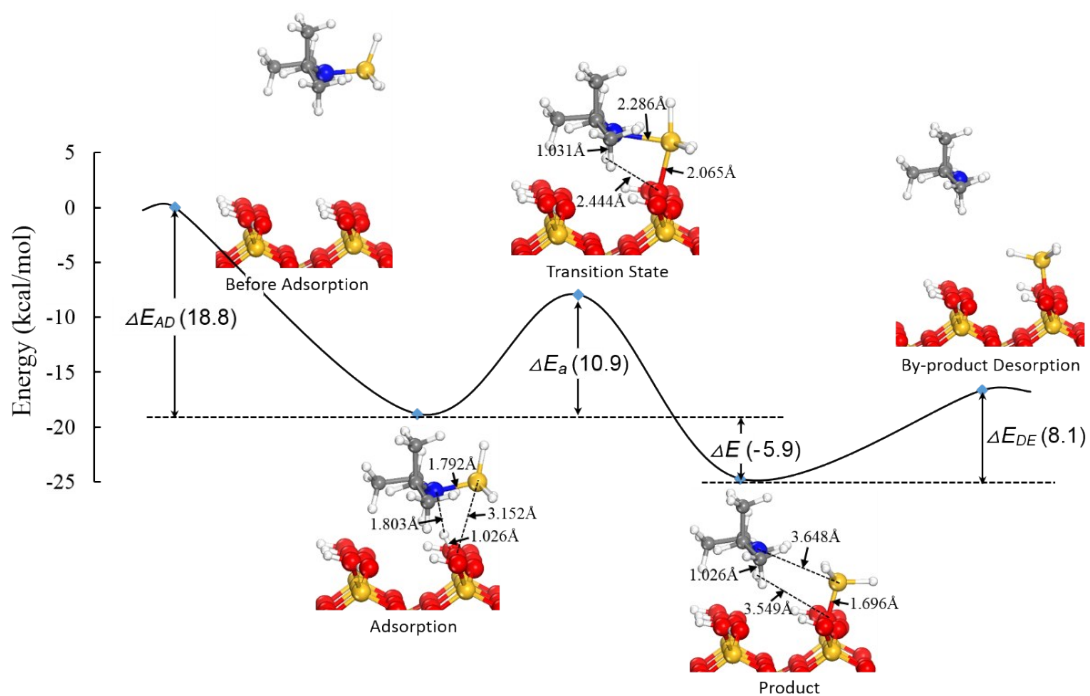


Fig S5. Energy variation for DIPAS reaction with the hydroxylated SiO_2 (001) surface.

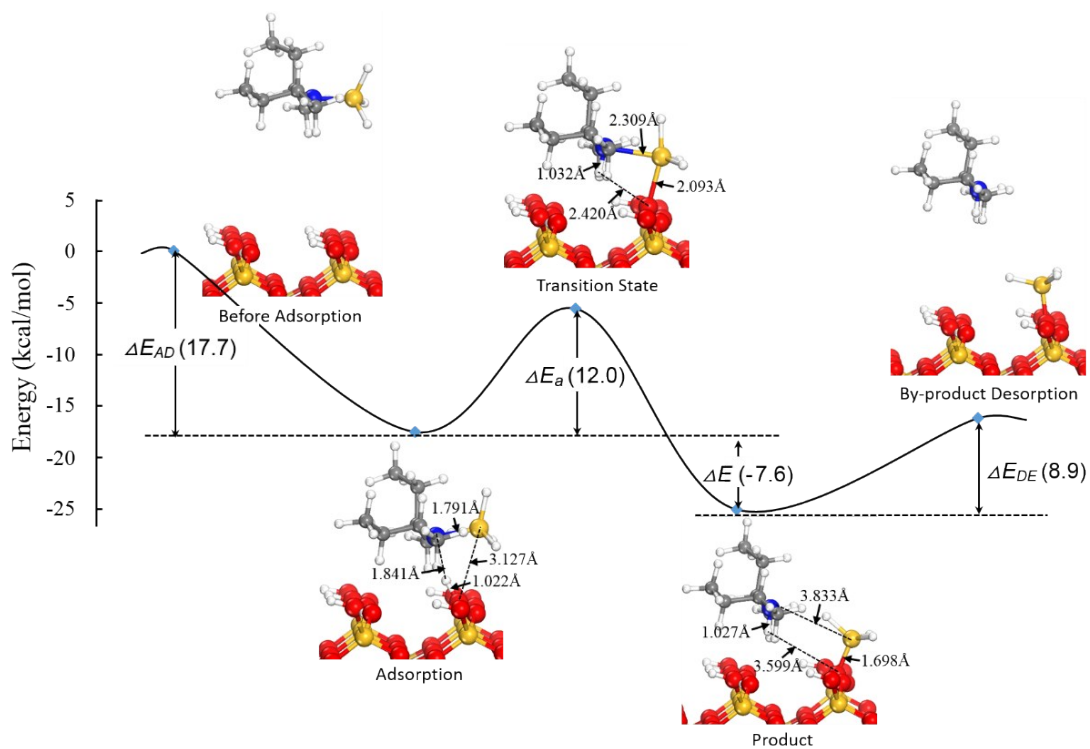


Fig S6. Energy variation for DSBAS reaction with the hydroxylated SiO₂(001) surface.

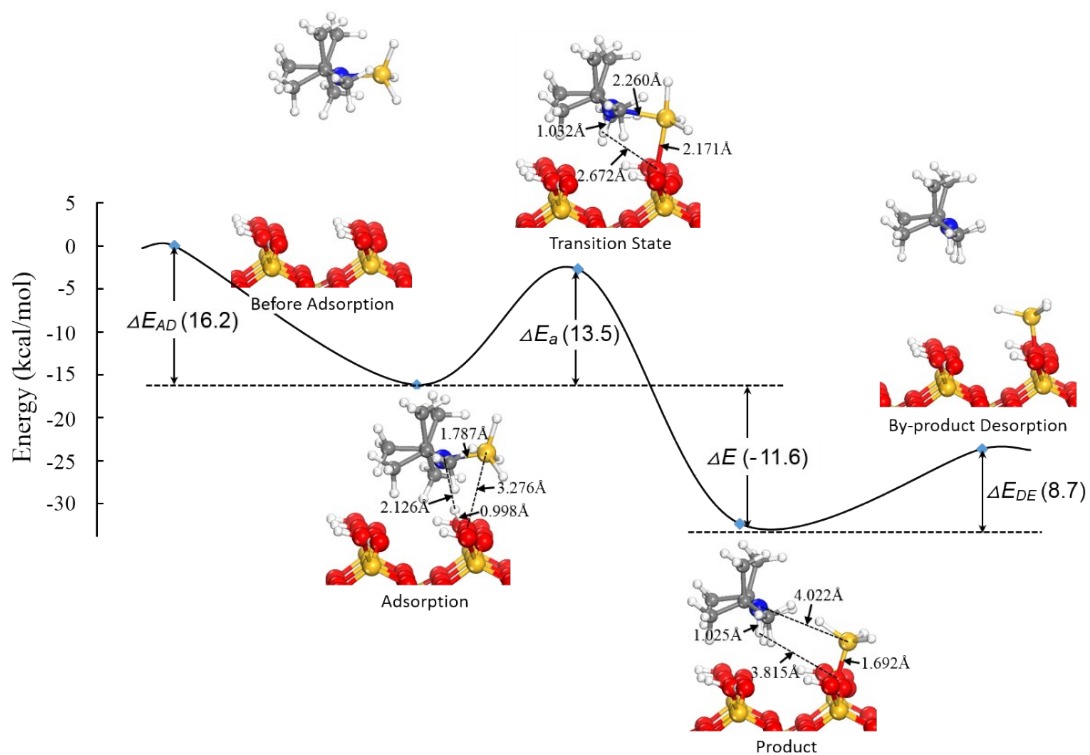


Fig S7. Energy variation for DTBAS reaction with the hydroxylated SiO₂(001) surface.