Electronic Supplementary Information (ESI)

Self-Catalysis by Aminosilanes and Strong Surface Oxidation by O$_2$ Plasma in Plasma-Enhanced Atomic Layer Deposition of High-Quality SiO$_2$

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Experimental details and product characterization

SiO$_2$ films were deposited in a commercial plasma-enhanced atomic layer deposition (PE-ALD) system (Picosun SUNALE™ R-200). Tris(dimethylamino)silane (TDMAS) and O$_2$ plasma were used as Si precursor and oxidant for SiO$_2$ deposition, respectively. TDMAS was kept at room temperature. The O$_2$ plasma was of the remote type, and its power and O$_2$ gas flow rate were 2500 W and 160 sccm, respectively. Pure N$_2$ (99.999%) was used as carrier gas and purge gas. SiO$_2$ films were deposited on GaAs substrates at room temperature or 250 ºC for 100

(or 200) cycles, where one cycle consisted of 1 s Si source injection, 10 s N_2 purging, 13.5 s O_2 plasma injection, and 4 s N_2 purging.

The chemical behavior of the films was investigated by *ex situ* X-ray photoelectron spectroscopy (XPS, Thermo Fisher K-Alpha) with a standard Al K_α (1486.7 eV) X-ray source for excitation of photoelectrons at a take-off angle of 90º. The binding energy scale was calibrated using the energy position of the C 1*s* peak at 284.6 eV. **Figure S1** shows the Si 2*p* XPS spectra of SiO_2 films deposited on GaAs at room temperature and 250 ºC. Both samples showed the Si 2*p* peak at 103.5 eV, corresponding to the Si-O bond. The results demonstrate that SiO_2 films can be deposited at both room temperature and 250 ºC using TDMAS and O_2 plasma.
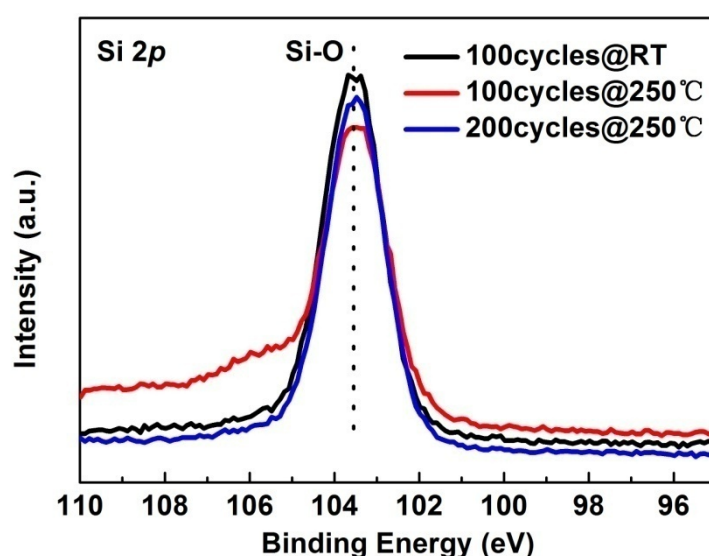

Figure S1. Si 2*p* XPS spectra of the SiO_2 films deposited on GaAs at room temperature (RT) and 250 ºC.

Computational details

In order to model the two half-reactions of SiO_2 PE-ALD, we have adopted two kinds of cluster models, **I** and **II**, $Si_{16}O_{26}H_{26}$-$Si_7(OH)_{14}$ and $Si_{13}O_{22}H_{22}$-SiH_2,

respectively, as shown in **Figure S2**, both of which are based on the hydroxylated α-SiO$_2$ (0001) surface. Due to the large molecular size of bis(dimethylamino)silane (BDMAS), the large cluster model **I** was used for the aminosilane half-reaction and the small cluster model **II** was used for the O$_2$ plasma half-reaction. The cluster model **I** consists of -Si$_7$(OH)$_{14}$ that reacts with the aminosilane, two layers of SiO$_2$ (Si$_{16}$O$_{26}$), and 26 hydrogen atoms that serve to saturate the dangling bonds. The cluster model **II** includes the –SiH$_2$ group that reacts with O$_2$ plasma species, three layers of SiO$_2$ (Si$_{13}$O$_{22}$), and 22 hydrogen atoms. To simulate a surface, the lower two layers of SiO$_2$ atoms in the two models were fixed in the geometry optimizations.

All of the species involved in the first half-reaction (**A**) of SiH$_4$ and BDMAS of PE-ALD SiO$_2$ were optimized using the M06-2X functional in the framework of density functional theory (DFT).[S1,S2] The spin-unrestricted method DFT/UM06-2X was used for all species of the O$_2$ plasma half-reaction (**B**). To achieve a compromise between accuracy and computational cost, the 6-31G basis set was used for the fixed atoms of the substrate and the 6-31G(d,p) basis set was employed for other atoms on the surface and all atoms of gas molecules, including the two reactants SiH$_4$ and BDMAS, by-products, H$_2$, and dimethylamine (DMA), and all species of the O$_2$ plasma. For each stationary point on the potential energy surface, a frequency calculation was carried out to determine whether it was a minimum or a transition state (TS). All of the transition states were verified by intrinsic reaction coordinate (IRC) calculations. Gibbs free energies of all species were estimated from the partition functions and the enthalpy and entropy terms at 298 K. The energies reported here include zero-point energy (ZPE) corrections. All calculations in this work were performed with the Gaussian 09 program.[S3] To represent the stationary points along the pathways in a concise way, we simply use denotations of intermediates **Im1**, **Im2**,

and **Im3**, transition states **TS1** and **TS2**, and products **P1** and **P2**, with the superscripts **A** (or **SiH₄**) and **B** (**Figures 1** and **2** in the paper) representing the two respective half-reactions. Partial bond distances at the reactive center were listed in **Tables S1** and **S2**. The molecular models of all species in two half-reactions were shown in **Figures S3** and **S4**, respectively.
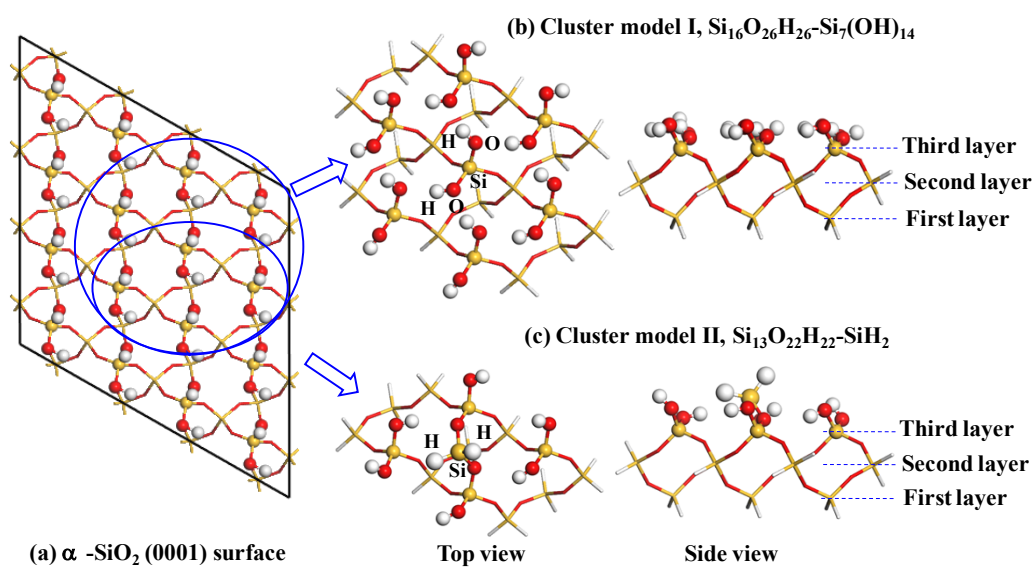

Figure S2. α-SiO$_2$ (0001) surface (a) and cluster models **I** and **II**: (b) Si$_{16}$O$_{26}$H$_{26}$-Si$_7$(OH)$_{14}$ and (c) Si$_{13}$O$_{22}$H$_{22}$-SiH$_2$.

Table S1. Bond distances (in units of Å) at the reactive center in the self-catalytic half-reaction of BDMAS.

Species	O-H	Si-O	Si-N	N-H
R^A	0.99		1.72	
Im1^A	1.11	3.50	1.82	1.40
TS1^A	1.93	3.02	1.89	1.04
Im2^A	2.21	1.92	1.97	1.02
P1^A	1.00	3.15(1.66)	1.77	1.64

TS2^A	1.58	2.49	1.88	1.06
Im3^A	2.64	1.70	2.18	1.02
P2^A		1.65		1.01

Table S2. Bond distances (in units of Å) at the reactive center in oxidation reactions with O_2 plasma.

Species	O1-O2	Si-H1	Si-O1	O1-H1	Si-H2	Si-O2	O2-H2
Im1^{B1}	1.20	1.47			1.47		
Im1$^{B2/3}$	1.20	1.47			1.47		
TS1^{B2}	1.28	1.62		1.36	1.51		1.73
P1^{B2}			1.63	0.96		1.65	0.96
TS1^{B3}	1.26	1.61		1.33	1.47		
Im2^{B3}	1.44		2.46	0.98	1.47	1.67	2.50
TS2^{B3}	1.86		1.83	0.99	1.63	1.60	1.80
Im1^{B4}/Im2^{B5}		1.47			1.47		
TS1^{B4}/TS1^{B5}		1.52	1.90	1.84	1.47		
P1^{B4}/P1^{B5}			1.64	0.96	1.47		
Im1^{B5}		1.47			1.47		
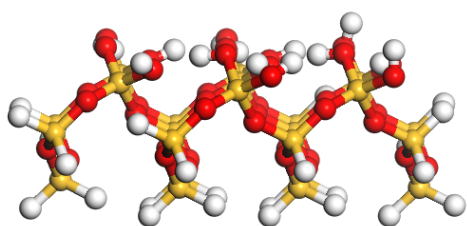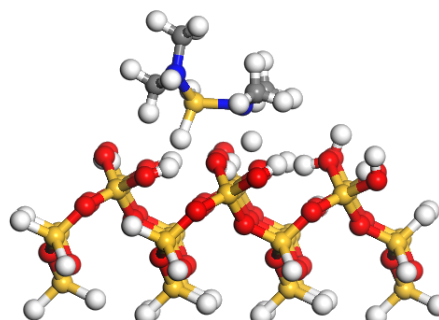
Substrate^A   **Im1^A**
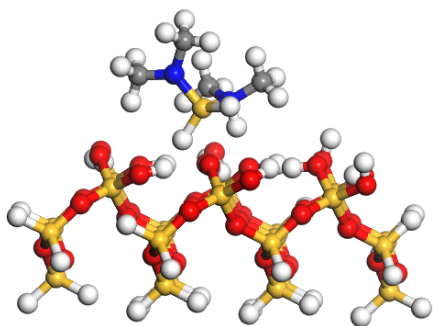
TS1^A
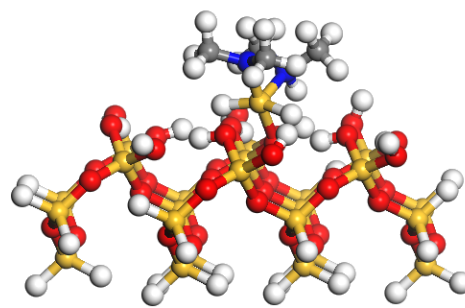
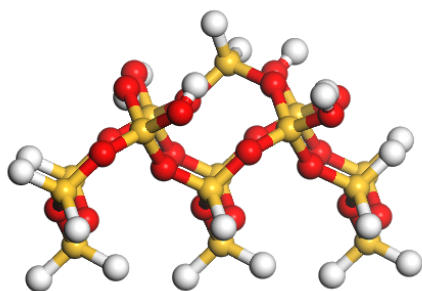**Im2^A**
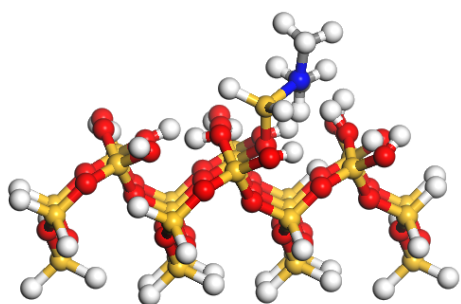
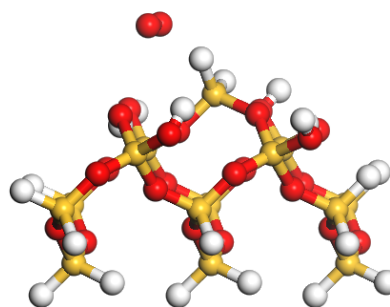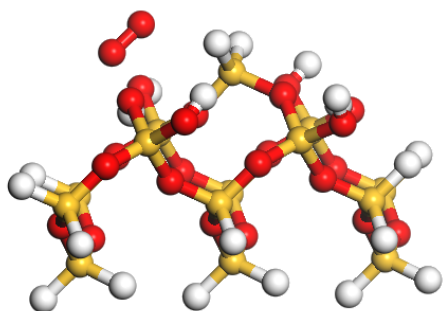**P1^A**
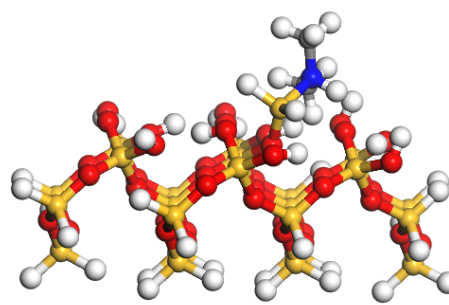
TS2^A
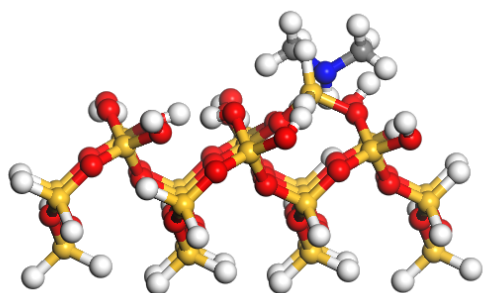
Im3^A
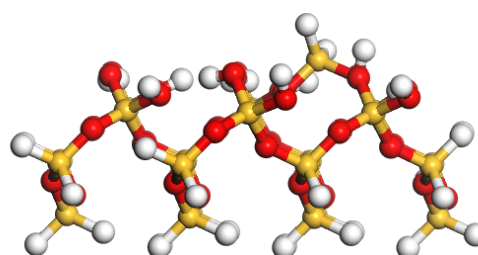
P2^A

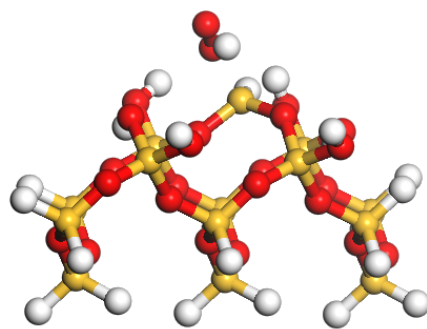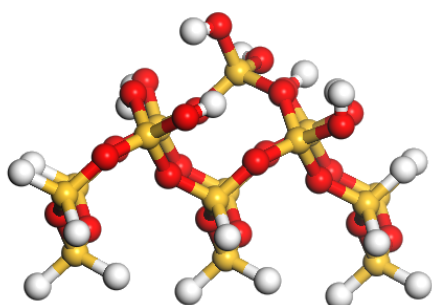**Figure S3.** Molecular models of all species in half-reaction **A**.
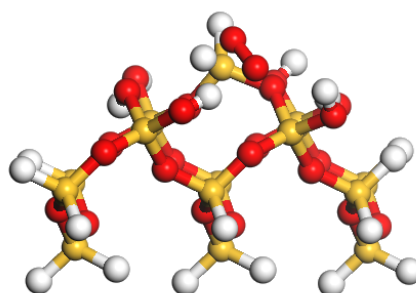
Substrate^B

Im1^{B1}

Im1$^{B2/3}$

TS1^{B2}

P1^{B2}

TS1^{B3}
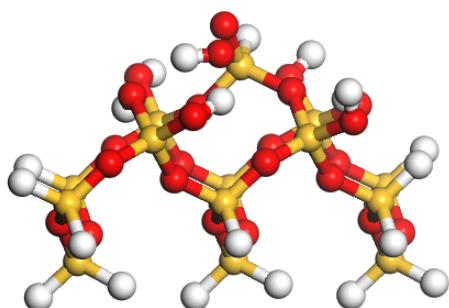
Im2^{B3}
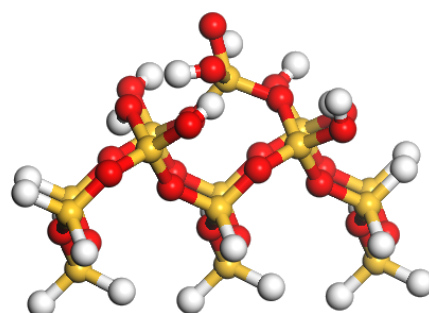
TS2^{B3}
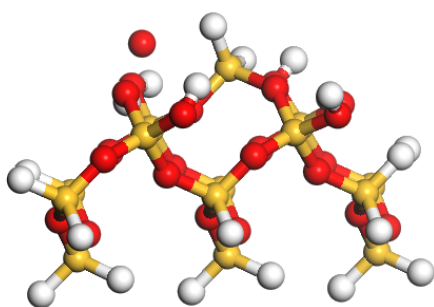
Im1^{B4}/Im2^{B5}
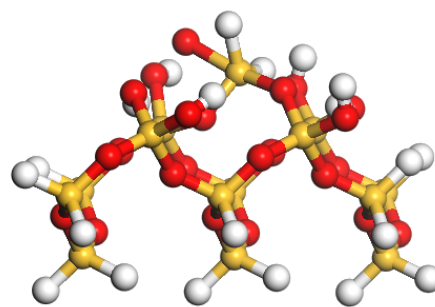
TS1^{B4}/TS1^{B5}

P1^{B4}/P1^{B5}   **Im1^{B5}**
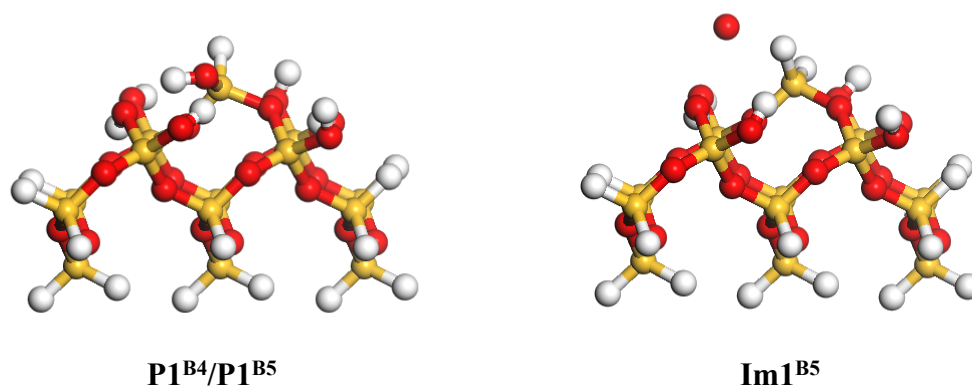
Figure S4. Molecular models of all species in half-reaction **B**.

References

S1 Y.Zhao and D. G. Truhlar, *Acc. Chem. Res.*, 2008, **41**, 157.

S2 Y.Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.

S3 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowskiand D. J. Fox, *Gaussian 09*, Revision B.02, Gaussian, Inc., Wallingford CT, 2009.