

Theoretical Understanding of the Reaction Mechanism of SiO₂ Atomic Layer Deposition

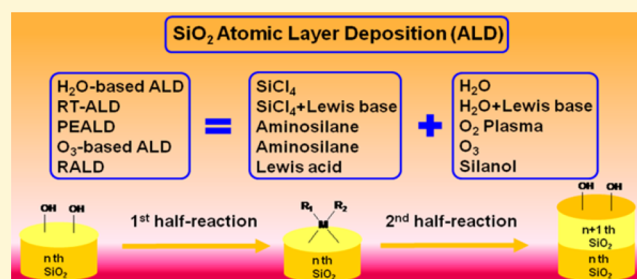
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ABSTRACT: Atomic layer deposition (ALD) is a powerful nanofabrication technique for the preparation of uniform, conformal, and ultrathin films and allows accurate control of the composition and thickness of thin films at the atomic level. To date, ALD has been used for the growth of various materials, including oxides, nitrides, sulfides, metals, elements, compound semiconductors, and organic and organic–inorganic hybrid materials. As one of the most important inorganic materials, silicon dioxide (SiO₂) has been used in the fields of microelectronics, catalysis, and energy storage and conversion. Various SiO₂ ALD methods have been developed, which have expanded the research and applications of ALD chemistry and technology. Recent advances concerning the reaction mechanisms of SiO₂ ALD have further deepened our understanding of the surface chemistry and related catalysis in the ALD of SiO₂ and other oxides. Thin films of SiO₂ can be obtained by means of thermal ALD and energy-enhanced ALD. Thermal ALD of SiO₂ includes H₂O-based ALD without a catalyst, room-temperature ALD (RT-ALD) catalyzed by a Lewis base, and rapid ALD (RALD) catalyzed by a Lewis acid. Energy-enhanced ALD of SiO₂ encompasses plasma-enhanced ALD and O₃-based ALD using aminosilane. In this review, we highlight the significance and advantages of ALD and introduce many methods of SiO₂ ALD. Subsequently, theoretical advances concerning reaction mechanisms of SiO₂ ALD are summarized. The related catalysis phenomena are highlighted, and their possible applications are speculated upon. Finally, a conclusion and perspective on the catalysis in the ALD growth of SiO₂ is provided. It is expected that theoretical research on SiO₂ ALD will enhance our comprehension of the chemistry and catalysis pertaining to ALD, provide a guide for the design of more effective Si precursors for SiO₂ ALD, and lead to further improvement in the ALD preparation of other oxides and their nanolaminates.



1. INTRODUCTION

As a nanotechnology, atomic layer deposition (ALD), formerly named atomic layer epitaxy (ALE), is a valuable technique that can be used to fabricate uniform, conformal, and ultrathin films. It has been used in the fields of microelectronics, optoelectronics, photonics, display technology, energy production, catalysis, and coatings.^{1–14} ALD is based on sequential and self-limiting gas–solid reactions on the surface. Essentially, ALD is a variant of chemical vapor deposition (CVD), namely, atomic layer CVD (ALCVD), but the CVD reaction is divided into two half-reactions and the precursors are separately introduced into the reaction chamber. By repeating ALD reaction cycles, films with the desired thickness can be obtained. The precursor can also be substituted to obtain a film with the desired composition. Therefore, ALD can be used to accurately control the thickness and composition of thin films at the atomic scale and has been used for the growth of various materials, including oxides, nitrides, sulfides, metals,

elements, compound semiconductors, and organic and organic–inorganic hybrid materials.^{1–3}

As one of the most important inorganic materials, thin films of silicon dioxide (SiO₂) have excellent physical, chemical, and surface properties and have been widely applied in many fields, including microelectronics, catalysis, and energy storage and conversion.^{15,16} In general, thin films of SiO₂ can be obtained by means of thermal ALD and energy-enhanced ALD. Thermal ALD of SiO₂ includes H₂O-based ALD using SiCl₄ and H₂O, room-temperature ALD (RT-ALD) catalyzed by a Lewis base, and rapid ALD (RALD) using silanol and a Lewis acid catalyst. Energy-enhanced ALD of SiO₂ encompasses plasma-enhanced ALD (PEALD) and O₃-based ALD using aminosilane at low temperature, namely, low-temperature ALD (LT-ALD).

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In this paper, we review theoretical advances concerning the reaction mechanism of SiO₂ ALD and provide reference and instruction for the design of highly efficient Si precursors and the ALD preparation of other oxides. Table 1 summarizes

Table 1. Overview of Theoretical Studies of SiO₂ ALD

| precursor | substrate | model | method | ref |
|--|------------------|---------|--------|-----|
| H₂O-based ALD without catalyst | | | | |
| SiCl ₄ + H ₂ O | Si(100) | cluster | B3LYP | 17 |
| SiCl ₄ + H ₂ O | SiO ₂ | cluster | M06-2X | 18 |
| RT-ALD with Lewis base | | | | |
| SiCl ₄ + H ₂ O + NH ₃ | Si(100) | cluster | MP2 | 19 |
| SiCl ₄ + H ₂ O + NH ₃ or NC ₅ H ₅ | SiO ₂ | cluster | B3LYP | 20 |
| SiCl ₄ + H ₂ O + NH ₃ or NC ₅ H ₅ | SiO ₂ | cluster | M06-2X | 21 |
| PEALD with aminosilane | | | | |
| BDMAS ^a + O ₂ plasma | SiO ₂ | cluster | M06-2X | 22 |
| O₃-based ALD with aminosilane | | | | |
| BTBAS ^a + O ₃ | SiO ₂ | slab | PW91 | 23 |
| DSBAS ^a + O ₃ | SiO ₂ | slab | PW91 | 24 |
| self-catalysis of aminosilane | | | | |
| BDEAS ^a | Si(100) | slab | PBE | 25 |
| DMAS, BDMA, TDMAS, TKDMS ^a | Si(100) | slab | PBE | 26 |
| TDMAS | SiO ₂ | slab | PW91 | 27 |
| BDMAS, BDEAS, BEMAS, BTBAS ^a | SiO ₂ | slab | BP86 | 28 |
| RALD with Lewis acid | | | | |
| TMA + BMMTS ^a | SiO ₂ | Slab | PW91 | 29 |
| TMA + TBS ^a | SiO ₂ | Cluster | M06-2X | 30 |

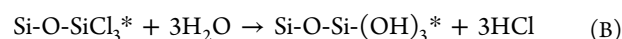
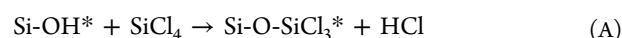
^aAnnotations: BDMA = bis-dimethylaminosilane (SiH₂[N(CH₃)₂]₂); BTBAS = bis-*tert*-butylaminosilane (SiH₂[NHC(CH₃)₃]₂); DSBAS = di-*sec*-butylaminosilane (SiH₃N(CH₂CH₂C₂H₅)₂); BDEAS = bis-diethylaminosilane (SiH₂[N(C₂H₅)₂]₂); DMAS = dimethylaminosilane (SiH₃N(CH₃)₂); TDMAS = tris-dimethylaminosilane (SiH[N(CH₃)₂]₃); TKDMS = tetrakis-dimethylaminosilane (Si[N(CH₃)₂]₄); BEMAS = bis-ethylmethylaminosilane (SiH₂[N(C₂H₅)(CH₃)]₂); TMA = trimethylaluminum (Al(CH₃)₃); BMMTS = bis-methoxyl-monobutoxysilanol (HO-Si(OCH₃)₂OC(CH₃)₃); TBS = tris-*tert*-butoxy-silanol (HO-Si(OC(CH₃)₃)₃).

theoretical advances in H₂O-based ALD, RT-ALD, PEALD, O₃-based ALD, and RALD of SiO₂ with different precursors, substrates, computational models, and methods.^{17–30} Three kinds of Si precursors, SiCl₄, aminosilane, and silanol, and three

kinds of oxygen sources, H₂O, O₃, and plasma O₂, have been investigated. The catalysts have included Lewis bases, ammonia (NH₃), and pyridine (NC₅H₅), and a Lewis acid, trimethylaluminum (TMA). The substrates with cluster and slab models have been based on Si(100) and SiO₂ surfaces. The computational methods have been mostly conducted in the framework of density functional theory (DFT) with B3LYP, M062X, PW91, PBE, and BP86 functionals. Some new phenomena and concepts in SiO₂ ALD have been found and discussed, such as H₂O-assisted catalysis, self-catalysis, and noncovalent catalysis, which can facilitate surface reactions of ALD growth and catalytic reactions on the surface. In the rest of the paper, we describe all of this theoretical work of SiO₂ ALD including H₂O-based ALD, RT-ALD, PEALD, O₃-based ALD, and RALD.

2. SiO₂ H₂O-ALD WITHOUT CATALYST

SiO₂ ALD without a catalyst can be achieved using SiCl₄ and H₂O as silicon and oxygen sources, respectively. The ALD growth of SiO₂ requires high deposition temperatures (>600 K) and large precursor fluxes.^{31–33} SiO₂ ALD involves two separate half-reactions, A and B



where the asterisk designates the surface species.

The initial growth mechanism of SiO₂ ALD on the bare Si(100)-2×1 surface was investigated by density functional theory (DFT) calculations.¹⁷ First, the bare Si(100)-2×1 surface was hydroxylated to produce surface hydroxyl (Si-OH) and silane (Si-H) groups through the dissociative adsorption of H₂O, which has a low energy barrier and is strongly exothermic. Subsequently, another H₂O molecule can further oxidize a surface silane (Si-H) group through H₂ desorption with a relatively low barrier, which is different from the previous mechanism involving an epoxidized surface intermediate and a very high energy barrier. Next, SiCl₄ can react with surface -OH to form a Si-O bond and a Si-O-SiCl₃* product accompanied by the release of HCl. The product Si-O-SiCl₃* can further react with neighboring surface -OH on the same dimer or an adjacent dimer to generate a Cl-terminated siloxane bridge (-O-SiCl₂*-O-). Finally, the Cl-

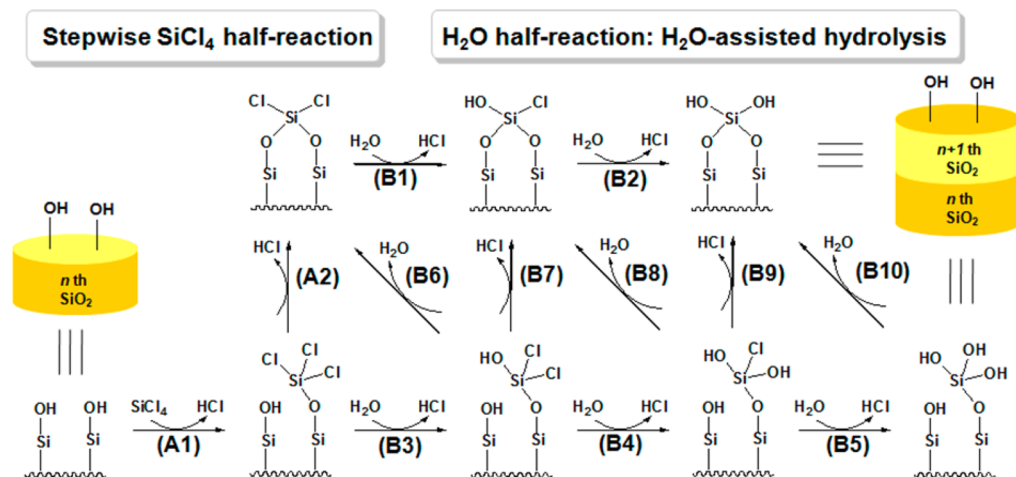


Figure 1. Full cycle of SiO₂ ALD using SiCl₄ and H₂O. Reprinted with permission from ref 18. Copyright 2015 Springer.

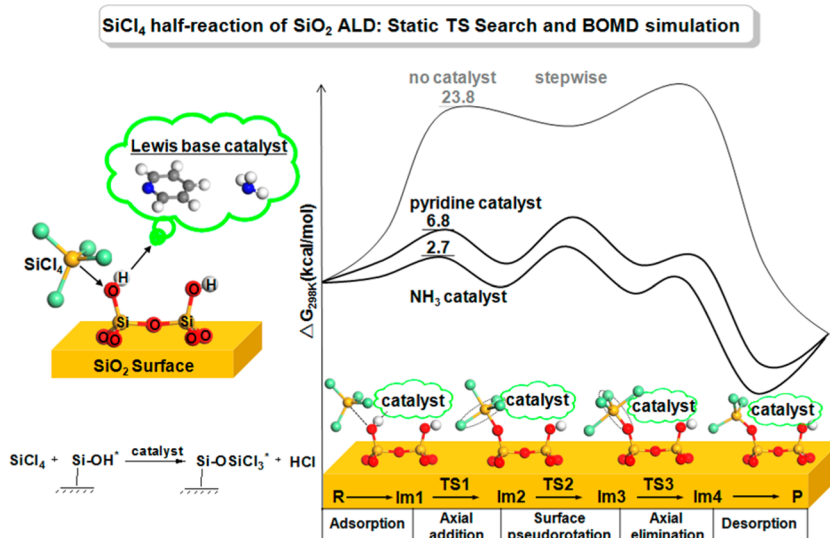


Figure 2. SiCl₄ half-reaction of SiO₂ ALD catalyzed by Lewis bases. Reprinted with permission from ref 21. Copyright 2012 American Chemical Society.

terminated surface group can be transformed to a siloxane bridge ($-\text{O}-\text{Si}(\text{OH})_2^*-\text{O}-$) through hydrolysis and release of HCl in the H₂O half-reaction.

Recently, the reaction mechanism of the full SiO₂ ALD on a SiO₂ surface was studied in detail by means of DFT calculations, involving the SiCl₄ half-reaction and H₂O half-reaction (Figure 1).¹⁸ Similar to the situation on a hydroxylated Si(100) surface, the SiCl₄ half-reaction on a SiO₂ surface can form two products, Si-O-SiCl₃* and Si-O-SiCl₂*-O-Si, respectively. In contrast to the previous concerted mechanistic interpretation,¹⁷ Si-O formation in both Si-O-SiCl₃* and Si-O-SiCl₂*-O-Si proceeds through a stepwise pathway with initial formation of a Si-O bond and a pentacoordinated intermediate with a trigonal-bipyramidal (TBP) geometry through a rotated transition state, followed by breaking of the Si-Cl and O-H bonds and formation of a H-Cl bond through a four-centered transition state. The SiCl₄ half-reaction has a large activation free energy of 44.5 kcal/mol and is also the rate-determining step (RDS) of the overall cycle of SiO₂ ALD.¹⁸

In the H₂O half-reaction of ALD, the hydrolysis and condensation processes can lead to the formation of SiO₂, which is similar to conventional SiO₂ CVD. First, bulk H₂O can hydrolyze the Cl-terminated surface by exchange of the Cl ligands and the hydroxyl ($-\text{OH}$) groups of adsorbed H₂O on the surface, thereby converting surface Cl-containing species ($-\text{Si}-\text{Cl}^*$) into surface hydroxyl species ($-\text{Si}-\text{OH}^*$). At the same time, condensations involving H₂O or HCl elimination can further result in the formation of a siloxane bridge ($-\text{O}-\text{Si}-\text{O}-$), the elementary unit of SiO₂, thereby ensuring the ALD growth of SiO₂. As a special catalyst, further H₂O can also participate in hydrolysis reactions of all the Cl-terminated surface species, that is, $-\text{O}_2\text{Si}-\text{Cl}_2^*$, $-\text{O}_2\text{SiOH}-\text{Cl}^*$, $-\text{OSi}-\text{Cl}_3^*$, $-\text{OSiOH}-\text{Cl}_2^*$, and $-\text{OSi}(\text{OH})_2-\text{Cl}^*$, and accelerate the H₂O half-reaction. This phenomenon can be termed H₂O-assisted hydrolysis or H₂O-assisted catalysis and has also been found in the H₂O-based ALD of other oxides, such as Al₂O₃ and HfO₂,^{18,34,35} and other chemical reactions, such as hydrolysis, tautomerization, and decomposition.^{36–38}

3. SiO₂ RT-ALD WITH LEWIS BASE AND SURFACE PSEUDOROTATION

SiO₂ ALD using SiCl₄ and H₂O usually requires large precursor fluxes and high temperatures.^{31–33} By the introduction of a Lewis base catalyst, such as NH₃ or NC₅H₅, the precursor fluxes of SiO₂ RT-ALD can be decreased by about 5 orders of magnitude and the growth temperature can be dramatically reduced to ambient.^{4,39–45}

The initial mechanism and catalytic behavior of SiO₂ RT-ALD were also examined by means of second-order Møller–Plesset perturbation theory (MP2) calculations.¹⁹ First, on the basis of the Cl-terminated Si(001) surface cluster model, H₁₂Si₉Cl₂, one H₂O molecule can exchange the Cl ligand and two H₂O molecules can completely hydroxylate the Cl-terminated Si(001) surface to form Si-O bonds, affording a hydroxylated Si(001) surface. SiCl₄ can then react with a hydroxyl ($-\text{OH}$) group on the hydroxylated Si(001) surface, forming a Si-O bond and the product $-\text{O}-\text{SiCl}_3$. By using NH₃ as a model catalyst of NC₅H₅, the activation energies of the H₂O and SiCl₄ half-reactions decrease to 7.0 and 5.6 kcal/mol, respectively, and are thus smaller than the experimental value for catalyzed SiO₂ ALD.⁴ It may be that previous computational models underestimated the interaction between the Lewis base catalyst, surface, and precursors.

The influences of the alkalinity and steric hindrance of Lewis base catalysts on the ALD of SiO₂ and the possible catalytic mechanisms have also been discussed.²⁰ On the basis of the minimal SiO₂ cluster model, (H₃SiO)₃SiOH, a Lewis base catalyst can effectively catalyze both half-reactions in the ALD growth of SiO₂ through strong hydrogen-bonding interaction with reaction substrates. Considering the alkalinity and steric hindrance, a Lewis base catalyst with strong alkalinity and low steric hindrance may effectively catalyze the growth of SiO₂ ALD.²⁰

Recently, NC₅H₅- and NH₃-catalyzed mechanisms of SiO₂ RT-ALD were explored in detail by combining a static transition-state search and Born–Oppenheimer molecular dynamics (BOMD) simulation.²¹ Herein, the computational model needs to be explained. Because of the locality of the chemical reactions, the cluster and slab models can give similar

reaction pathways and the difference is often the height of the reaction energy.^{35,46} On the basis of different computational models and density functionals, it is impractical to obtain absolutely accurate reaction energies. The first goal of theoretical study on a reaction mechanism is usually to obtain the reasonable reaction pathway. As shown in Figure 2, with both NC_5H_5 and NH_3 , the catalytic RT-ALD of SiO_2 may proceed through the same multistep pathway: adsorption of the precursor, axial addition, surface pseudorotation (SPR), axial elimination, and desorption of the byproduct.²¹ Furthermore, due to a lower Gibbs free energy of activation, NH_3 has a higher catalytic activity than NC_5H_5 in the RT-ALD of SiO_2 , which is in agreement with the experimental results.^{4,39–45}

First, the Lewis base (NH_3 or NC_5H_5) and SiCl_4 can coadsorb on the hydroxylated SiO_2 surface through hydrogen bonding between the surface hydroxyl ($-\text{OH}$) groups and the N atom of the Lewis base and form a surface complex intermediate. The coadsorbed complex can then be converted into a pentacoordinated silicon intermediate with TBP geometry through axial addition, which involves a concerted transition state and leads to $\text{Si}-\text{O}$ formation and $\text{O}-\text{H}$ cleavage. Because of the TBP geometry, the surface pentacoordinated silicon intermediate can be converted into another pentacoordinated intermediate through SPR, which exchanges the axial and equatorial ligands and involves three possible transition states with low energy barriers. Subsequently, the transformed pentacoordinated intermediate may dissociate the axial Cl ligand through axial elimination, whereby the Cl anion and the protonated Lewis base cation (NH_4^+ or HNC_5H_5^+) can form the chloride or the complex between the Lewis base and HCl . Finally, the chloride or complex can desorb from the SiO_2 surface.²¹

As mentioned above, a special pseudorotation phenomenon on the surface is termed surface pseudorotation (SPR), which is similar to Berry pseudorotation (BPR) of pentacoordinated compounds with TBP geometry (Figure 3).^{21,47–53} Both SPR and BPR are associated with low energy barriers. In the pseudorotation process, the original TBP geometry goes through a transition state with square-pyramidal (SP) geometry and changes to another TBP geometry.²¹ The difference between SPR and BPR lies in the motion state of the pivot ligand. In BPR, the pivot atom is usually free from confinement. On the contrary, in SPR, one ligand pivot is linked to the surface and the other four ligands can interchange. Hence, BPR may be periodic behavior and result in the rapid stereomutation of TBP molecules. SPR can be reactive behavior and result in surface reactions with other molecules, which are accompanied by the cleavage of old chemical bonds and the formation of new chemical bonds. SPR can readily occur in surface reactions and catalytic reactions involving pentacoordinated main-group element and transition-metal compounds with TBP geometry, such as catalysts containing Si, P, Fe, and Ru.^{21,47–53}

4. SiO_2 PEALD WITH AMINOSILANE

In recent years, SiO_2 ALD has also been performed by employing an aminosilane as a Si source and O_2 plasma, O_3 , or H_2O_2 as a strong oxidant.^{54–57} The deposition temperature can be reduced to ambient levels (under 300°C), namely, LT-ALD.

Recently, the reaction mechanism of SiO_2 PEALD was investigated by means of DFT calculations.²² It was demonstrated that aminosilane can self-catalyze the aminosilane half-reaction with hydroxyl groups ($-\text{OH}$) on the surface and that three active species of O_2 plasma can strongly oxidize the

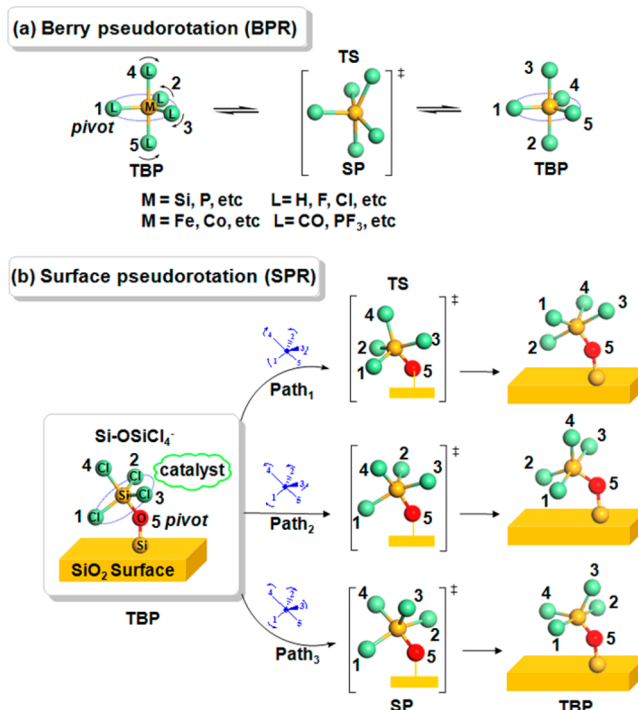


Figure 3. Schematic illustrations of (a) Berry pseudorotation and (b) surface pseudorotation. Reprinted with permission from ref 21. Copyright 2012 American Chemical Society.

surface silane groups to silanol groups. The concept of self-catalysis by aminosilanes and strong surface oxidation by O_2 plasma may be applied to the design of high-performance precursors for SiO_2 ALD and the PEALD preparation of other oxides, such as Al_2O_3 , HfO_2 , ZrO_2 , and TiO_2 .²²

In order to explore the catalytic role of the aminosilane, bis(dimethylamino)silane (BDMAS) and silane (SiH_4) were selected for a comparative study (Figure 4).²² Without an amino ligand, the SiH_4 half-reaction has a very high activation free energy for $\text{Si}-\text{O}$ formation and requires a high temperature. In the presence of an aminosilane, such as BDMAS, the activation free energy for $\text{Si}-\text{O}$ formation dramatically decreases to about 10.0 kcal/mol and the aminosilane half-reaction can occur at low temperature, even under ambient conditions. This is because the amino ligand of the aminosilane can interact with a surface hydroxyl ($-\text{OH}$) group by hydrogen bonding and facilitate attack of the Si atom of the aminosilane on the O atom of the hydroxyl group via a pentacoordinated transition state. This catalytic behavior of the aminosilane is termed self-catalysis. The self-catalysis by the aminosilane originates from the amino ligand and is similar to the catalytic role of a Lewis base catalyst in the RT-ALD of SiO_2 .²¹

In general, O_2 plasma is a high-energy state with numerous component species and can be used as a strong oxidant. Among these plasma species, $^3\text{O}_2$, $^1\text{O}_2$, ^3O , and ^1O are the most abundant, which together constitute over 99.99% of the total.^{58–60} $^3\text{O}_2$ is the most stable and hence is inactive toward surface silane groups. The other three species, $^1\text{O}_2$, ^3O , and ^1O , are active and can oxidize surface silane groups to silanol groups through one-step or stepwise oxidation pathways (Figure 5). All of these oxidation reactions are strongly exergonic.²²

$^1\text{O}_2$ can frontally attack two H atoms of the silane to produce two $-\text{OH}$ groups and the product through a one-step oxidation

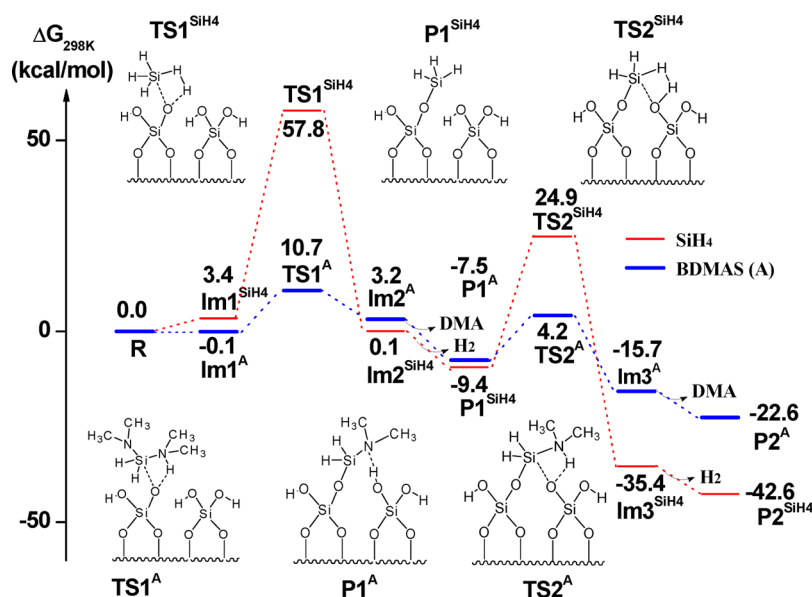


Figure 4. Self-catalysis of aminosilane in SiO₂ PEALD. Reprinted with permission from ref 22. Copyright 2015 Royal Society of Chemistry.

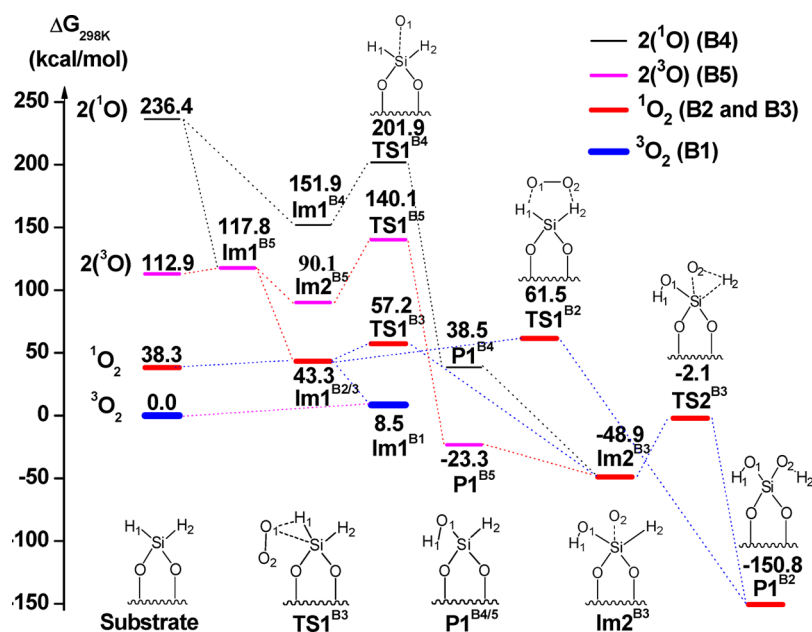


Figure 5. Strong surface oxidation of O₂ plasma in SiO₂ PEALD. Reprinted with permission from ref 22. Copyright 2015 Royal Society of Chemistry.

transition state. Meanwhile, ¹O₂ can also attack one H atom of the silane from the side to generate a single –OH intermediate and then oxidize another Si–H bond of the silane to Si–OH. ¹O can gradually oxidize Si–H bonds on the surface in a stepwise manner, which is similar to the second section of the stepwise oxidation pathway of ¹O₂. In ³O oxidation, the triplet state can first be converted to a singlet and then follow the ¹O oxidation pathway. Because of interaction between the active species and the surface or the reactor in ALD, all of the aforementioned active species, ¹O₂, ³O, and ¹O, can decay and lose their activity.²²

5. SiO₂ O₃-BASED ALD WITH AMINOSILANE

When SiO₂ LT-ALD is performed with an aminosilane as the Si source, the second half-reaction also utilizes O₃ as a strong oxidant at low temperature (under 300 °C).^{56,57}

The reaction mechanism of O₃-based ALD of SiO₂ has also been investigated by means of DFT calculations (Figure 6).^{23,24} In the first half-reaction, dissociative chemisorptions of two aminosilanes, DSBAS and BTBAS, on the hydroxylated SiO₂ surface are associated with low activation energies and are both thermodynamically and kinetically favorable,^{23,24} which is consistent with the self-catalysis of aminosilanes in SiO₂ PEALD discussed above.²² In the second half-reaction, O₃, as a strong oxidant, can oxidize surface silane groups (–SiH₂ or –SiH₃) to silanol groups (–Si(OH)₂ or –Si(OH)₃) in a stepwise manner.

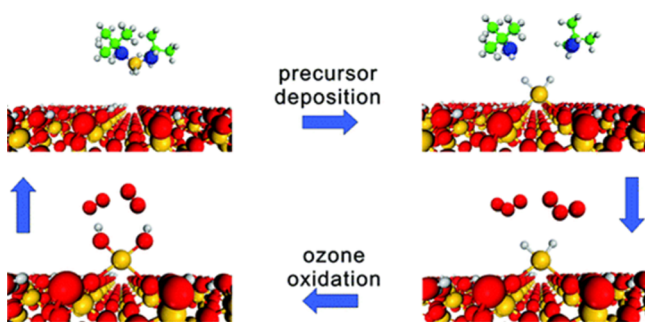


Figure 6. O_3 -based ALD of SiO_2 with aminosilane. Reprinted with permission from ref 23. Copyright 2012 American Chemical Society.

With both DSBAS and BTBAS, the oxidation process of surface silane groups by O_3 is strongly exothermic and has a moderate activation energy barrier. One of the terminal O atoms of an O_3 molecule can attack the Si atom of a surface silane ($-\text{SiH}$) group, leading to the formation of a surface silanol ($-\text{SiOH}$) group and an O_2 molecule. Furthermore, Si-H bonds in different directions may be oxidized, which results in either crystalline or disordered growth of the SiO_2 film.²⁴ In the case of DSBAS, surface silane groups ($-\text{SiH}_3$) can also condense with surface hydroxyl ($-\text{OH}$) groups through H_2 elimination and then be oxidized by O_3 . However, the preferred pathway involves initial surface silane ($-\text{SiH}_3$) oxidation to silanol ($-\text{Si}(\text{OH})_3$), followed by condensation with adjacent surface hydroxyl ($-\text{OH}$) groups through H_2O elimination to form a siloxane bridge ($-\text{O-Si-O}-$), which also occurs in the H_2O half-reaction of SiO_2 ALD without a catalyst.^{18,24}

6. SELF-CATALYSIS OF AMINOSILANE

In both PEALD and O_3 -based ALD, aminosilane usually serves as the Si precursor. Plasma O_2 and O_3 cannot themselves enhance the aminosilane half-reaction, which can still be classified as thermal ALD and can be catalyzed by the amino group, namely, via the self-catalysis of aminosilane.²²

Recently, different aminosilane precursors, $\text{SiH}_n[\text{NR}_1\text{R}_2]_{4-n}$, where R is a hydrogen atom or an alkyl group and n is 0, 1, 2, or 3, respectively, have been designed and applied to the ALD growth of high-quality SiO_2 .^{54–57} These aminosilanes include mono-, bis-, tris-, and tetrakis-aminosilanes. The adsorption behaviors of aminosilanes on a SiO_2 surface have been investigated by means of DFT calculations. BDEAS can be

easily absorbed on an OH-terminated $\text{Si}(001)$ surface, and the dissociation has two pathways through the cleavage of Si-H and Si-N bonds. However, the energy barrier associated with Si-H bond breaking is higher than that for Si-N bond breaking (Figure 7).²⁵ Therefore, Si-N bond breaking prevails during the surface reaction of BDEAS, which is in good agreement with theoretical results concerning BDMAS reaction with the hydroxylated SiO_2 surface.²² Aminosilanes with different numbers of dimethylamino ($\text{N}(\text{CH}_3)_2$) substituents, such as DMAS, BDMAS, TDMAS, and TKDMAS, also show similar behavior of initial dissociation on a hydroxylated $\text{Si}(001)$ surface.²⁶ As for BDMAS, the second dissociation of TDMAS can only occur with a dimethylamino ligand anchored on the surface. The third dissociation of TDMAS is essentially energetically forbidden.²⁷ On the basis of a hydrolysis model, the reactivities of a series of aminosilanes, namely, BDMAS, BDEAS, BEMAS, and BTBAS, were also investigated.²⁸ According to the results of theoretical calculations, mono- and bis-aminosilanes have very low reaction energy barriers and can be recommended as suitable Si precursors for SiO_2 ALD.^{22–28} These homoleptic and heteroleptic aminosilanes have different chemical reactivities and give distinct ALD growth rates of SiO_2 .⁵⁷ When a tris-aminosilane, such as TDMAS, is used, carbon impurities in the SiO_2 film are intrinsically inevitable.^{23,27} Because of severe steric hindrance, a tetrakis-aminosilane is not suitable for the ALD growth of SiO_2 .⁵⁵

In fact, the self-catalysis of N-coordinated silicon precursors was also examined in early research. For example, SiO_2 ALD can be accomplished using TICS ($\text{Si}(\text{NCO})_4$) and H_2O as precursors at room temperature.⁶¹ Subsequently, a series of isocyanate compounds, $\text{X}_n\text{Si}[\text{NCO}]_{4-n}$, where X is a hydrogen atom, halogen atom, alkyl group, or alkoxy group, and n is 0, 1, 2, or 3, respectively, was proposed for the growth of SiO_2 by ALD.⁶²

7. SiO_2 RALD WITH LEWIS ACID

In SiO_2 ALD discussed above, the growth rate of ALD is very slow, amounting to <0.2 nm per cycle. A rapid deposition method using a Lewis acid catalyst has also been developed, namely, RALD. For example, RALD of a SiO_2 thin film can be achieved using TMA as catalyst and a silanol as a SiO_2 source, such as TBS or TPS.^{6,63–65} Similar to conventional ALD reactions, RALD also has complementary and self-limiting

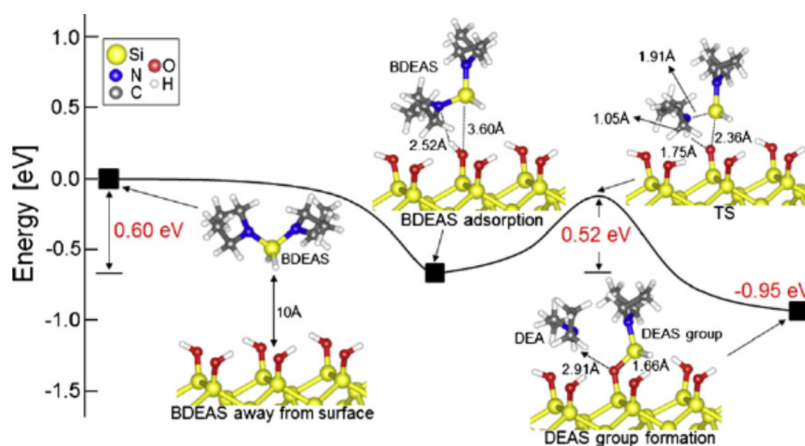


Figure 7. Dissociation reaction of BDEAS on OH-terminated $\text{Si}(001)$ surface. Reprinted with permission from ref 25. Copyright 2012 Elsevier.

characteristics. In contrast to conventional ALD, RALD can grow tens of atoms per cycle. In fact, this RALD produces a nanolaminate structure with monolayer Al_2O_3 and multilayered SiO_2 . By optimizing the Al catalyst layer density and growth temperature, the RALD growth rate of silica nanolaminate can be increased to 35 nm per cycle.^{64,65} This is because the Lewis acid catalyst can catalyze the silanol half-reaction and accelerate the propagation and growth of SiO_2 .

Recently, using BMMS as a model of TBS, the catalytic role of TMA in SiO_2 RALD was also investigated by means of DFT calculations.²⁹ In the first half-reaction, TMA can react with surface hydroxyl ($-\text{OH}$) groups with concomitant release of CH_4 , which results in anchoring of an Al atom on the substrate and the formation of a catalytic center ($\text{Al}-\text{CH}_3$) for silanol insertions. The second half-reaction is complex and includes BMMS insertion, chain growth, and cross-linking. First, BMMS can insert into the catalytic center ($\text{Al}-\text{CH}_3$) formed in the TMA half-reaction to produce $\text{Al}-\text{O}-\text{Si}$ species. Subsequently, the new catalytic center ($\text{Al}-\text{O}-\text{Si}$) can be continuously attacked by BMMS to grow the siloxane chain. Simultaneously, the siloxane chain can cross-link and its growth can be terminated for the next RALD cycle. In the growth of SiO_2 , the orbital hybridization of the central Al atom at the catalytic site can change from sp^2 to sp^3 and to sp^2 again (Figure 8).

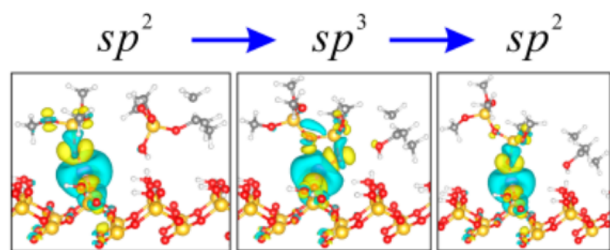


Figure 8. Hybridization forms of an Al catalytic site of $\text{Al}_2\text{O}_3/\text{SiO}_2$ nanolaminate RALD. Reprinted with permission from ref 29. Copyright 2013 Royal Society of Chemistry.

Meanwhile, the possible reaction pathways for RALD of the $\text{Al}_2\text{O}_3/\text{SiO}_2$ nanolaminate using TMA as catalyst and TBS as SiO_2 source were investigated in detail by means of DFT calculations (Figure 9).³⁰ The overall RALD reaction of the $\text{Al}_2\text{O}_3/\text{SiO}_2$ nanolaminate is complex and may include four steps: (A) TMA reaction, (B) silanol reaction, (C) propagation

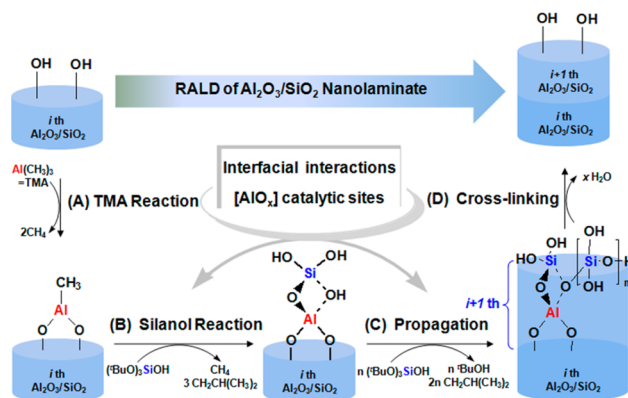


Figure 9. RALD of $\text{Al}_2\text{O}_3/\text{SiO}_2$ nanolaminate. Reprinted with permission from ref 30. Copyright 2013 Royal Society of Chemistry.

reaction, and (D) cross-linking reaction.^{30,63} The introduction of a Lewis acid catalyst, TMA, can lead to the formation of a Lewis acid catalytic site $[\text{AlO}_3]$, which further results in insertions of a large number of silanol molecules and accelerates the propagation of the siloxane polymer chain. Meanwhile, as the rate-determining step of the overall RALD, the elimination of isobutene from the *tert*-butoxy group of TBS can be catalyzed by the Brønsted acid site of $[\text{AlO}_4]$ and interfacial interactions, such as hydrogen-bonding interactions between *tert*-butoxy groups and the surface. In the propagation of the siloxane polymer, TBS insertion at $[\text{AlO}_x]$ occurs prior to insertion at $[\text{SiO}_x]$ due to strong $\text{Al}-\text{O}$ interactions. Simultaneously, the Lewis acid site $[\text{AlO}_3]$ and Brønsted acid site $[\text{AlO}_4]$ can rapidly interconvert into each other. Weak, nonbonding interactions, such as hydrogen-bonding interactions between the *tert*-butoxy groups of TBS and the surface, may play a catalytic role, namely, noncovalent catalysis. In the propagation of the SiO_2 chain, the Lewis acid site and Brønsted acid site can interconvert, whereby the orbital hybridization at the central Al atom can change from sp^2 to sp^3 and to sp^2 again, as mentioned above. In brief, the synergistic catalysis of Lewis/Brønsted acid sites $[\text{AlO}_x]$ and interfacial interactions can result in the rapid growth of $\text{Al}_2\text{O}_3/\text{SiO}_2$ nanolaminate and can also be used in the design and preparation of other silica nanolaminates, such as $\text{HfO}_2/\text{SiO}_2$, $\text{ZrO}_2/\text{SiO}_2$, and $\text{TiO}_2/\text{SiO}_2$.³⁰

8. CONCLUSION AND PERSPECTIVE

In this review, we have presented an overview of theoretical investigations on the reaction mechanisms of SiO_2 ALD, including H_2O -based ALD, RT-ALD, PEALD, O_3 -based ALD, and RALD. At the same time, the catalytic behaviors related to the ALD growth of SiO_2 have also been presented. In H_2O -based ALD, H_2O can catalyze the hydrolysis of the Cl-terminated surface. In RT-ALD, the Lewis base catalyst can lower the activation energy and decrease the deposition temperature to ambient by facilitating a new phenomenon on the surface, termed surface pseudorotation. In PEALD and O_3 -based ALD, aminosilanes play a self-catalytic role in $\text{Si}-\text{O}$ formation. In RALD, Lewis/Brønsted acid sites and interfacial interactions can synergistically catalyze the growth of silica nanolaminates. These observations indicate that surface reactions of SiO_2 ALD are very complicated and relevant to the catalysis, which, in turn, can facilitate surface reactions of ALD growth and further catalytic reactions on the surface.

Despite the theoretical progress made so far, the surface chemistry of ALD is very complex. Besides static calculations, the real reaction and growth mechanisms of ALD will be explored by considering the time and space scales. First-principles molecular dynamics (FPMD) or ab initio molecular dynamics (AIMD) simulations, such as Car–Parrinello molecular dynamics (CPMD) and Born–Oppenheimer molecular dynamics (BOMD), can be used to obtain the reasonable potential energy surfaces of surface reactions and the evolutions of geometric parameters during the reaction time.^{21,35,66,67} Although classical molecular dynamics (CMD) cannot be used to simulate the formation and cleavage of chemical bonds, the recently developed reactive molecular dynamics (RMD) may be one modeling technique suitable for ALD reactions.^{68–70} Another approach is lattice or off-lattice kinetic Monte Carlo (KMC) simulations to imitate ALD growth on the space scale.^{71–73} Through FPMD, RMD, and

KMC simulations, surface reactions and growth in ALD and related phenomena may be explored.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Pinna, N.; Knez, M. *Atomic Layer Deposition of Nanostructured Materials*; Wiley-VCH: New York, 2012.
- (2) Kääriäinen, T.; Cameron, D.; Kääriäinen, M.-L.; Sherman, A. *Atomic Layer Deposition: Principles, Characteristics, and Nanotechnology Applications*, 2nd ed.; Wiley-VCH: New York, 2013.
- (3) Hwang, C. S.; Yoo, C. Y. *Atomic Layer Deposition for Semiconductors*; Springer: New York, 2014.
- (4) Klaus, J. W.; Sneh, O.; George, S. M. Growth of SiO₂ at Room Temperature with the Use of Catalyzed Sequential Half-Reactions. *Science* **1997**, *278*, 1934–1936.
- (5) Ritala, M.; Kukli, K.; Rahtu, A.; Räsänen, P. I.; Leskelä, M.; Sajavaara, T.; Keinonen, J. Atomic Layer Deposition of Oxide Thin Films with Metal Alkoxides as Oxygen Sources. *Science* **2000**, *288*, 319–321.
- (6) Hausmann, D.; Becker, J.; Wang, S.; Gordon, R. G. Rapid Vapor Deposition of Highly Conformal Silica Nanolaminates. *Science* **2002**, *298*, 402–406.
- (7) Lim, B. S.; Rahtu, A.; Gordon, R. G. Atomic Layer Deposition of Transition Metals. *Nat. Mater.* **2003**, *2*, 749–754.
- (8) Costescu, R. M.; Cahill, D. G.; Fabreguette, F. H.; Sechrist, Z. A.; George, S. M. Ultra-Low Thermal Conductivity in W/Al₂O₃ Nanolaminates. *Science* **2004**, *303*, 989–990.
- (9) Chen, Y. W.; Prange, J. D.; Dühnen, S.; Park, Y.; Gunji, M.; Chidsey, C. E. D.; McIntyre, P. C. Atomic Layer-Deposited Tunnel Oxide Stabilizes Silicon Photoanodes for Water Oxidation. *Nat. Mater.* **2011**, *10*, 539–544.
- (10) Lu, J.; Fu, B.; Kung, M. C.; Xiao, G.; Elam, J. W.; Kung, H. H.; Stair, P. C. Coking- and Sintering-Resistant Palladium Catalysts Achieved Through Atomic Layer Deposition. *Science* **2012**, *335*, 1205–1208.
- (11) Liu, Y.; Gokcen, D.; Bertocci, U.; Moffat, T. P. Self-Terminating Growth of Platinum Films by Electrochemical Deposition. *Science* **2012**, *338*, 1327–1330.
- (12) Switzer, J. A. Atomic Layer Electrodeposition. *Science* **2012**, *338*, 1300–1301.
- (13) Lu, J.; Low, K.-B.; Lei, Y.; Libera, J. A.; Nicholls, A.; Stair, P. C.; Elam, J. W. Toward Atomically-Precise Synthesis of Supported Bimetallic Nanoparticles Using Atomic Layer Deposition. *Nat. Commun.* **2014**, *5*, 3264.
- (14) Kim, K.; Lee, H.-B.-R.; Johnson, R. W.; Tanskanen, J. T.; Liu, N.; Kim, M.-G.; Pang, C.; Ahn, C.; Bent, S. F.; Bao, Z. Selective Metal Deposition at Graphene Line Defects by Atomic Layer Deposition. *Nat. Commun.* **2014**, *5*, 4781.
- (15) Seshan, K. *Handbook of Thin Film Deposition*, 3rd ed.; William Andrew: New York, 2012.
- (16) Doering, R.; Nishi, Y. *Handbook of Semiconductor Manufacturing Technology*, 2nd ed.; CRC Press: Boca Raton, FL, 2007.
- (17) Kang, J. K.; Musgrave, C. B. Mechanism of Atomic Layer Deposition of SiO₂ on the Silicon (100)-2 × 1 Surface Using SiCl₄ and H₂O as Precursors. *J. Appl. Phys.* **2002**, *91*, 3408–3414.
- (18) Fang, G.-Y.; Xu, L.-N.; Wang, L.-G.; Cao, Y.-Q.; Wu, D.; Li, A.-D. Stepwise Mechanism and H₂O-Assisted Hydrolysis in Atomic Layer Deposition of SiO₂ without a Catalyst. *Nanoscale Res. Lett.* **2015**, *10*, 68.
- (19) Okamoto, Y. Initial Stage of the Catalyzed Growth of SiO₂ Films on Si(001): An Ab Initio Study. *J. Phys. Chem. B* **1999**, *103*, 11074–11077.
- (20) Chen, S.; Fang, G.; Qian, X.; Li, A.; Ma, J. Influence of Alkalinity and Steric Hindrance of Lewis-Base Catalysts on Atomic Layer Deposition of SiO₂. *J. Phys. Chem. C* **2011**, *115*, 23363–23373.
- (21) Fang, G.; Chen, S.; Li, A.; Ma, J. Surface Pseudorotation in Lewis-Base-Catalyzed Atomic Layer Deposition of SiO₂: Static Transition State Search and Born-Oppenheimer Molecular Dynamics Simulation. *J. Phys. Chem. C* **2012**, *116*, 26436–26448.
- (22) Fang, G. Y.; Xu, L. N.; Cao, Y. Q.; Wang, L. G.; Wu, D.; Li, A. D. Self-Catalysis by Aminosilanes and Strong Surface Oxidation by O₂ Plasma in Plasma-Enhanced Atomic Layer Deposition of High-Quality SiO₂. *Chem. Commun.* **2015**, *51*, 1341–1344.
- (23) Han, B.; Zhang, Q.; Wu, J.; Han, B.; Karwacki, E. J.; Dereskei, A.; Xiao, M.; Lei, X.; O'Neill, M. L.; Cheng, H. On the Mechanisms of SiO₂ Thin-Film Growth by the Full Atomic Layer Deposition Process Using Bis(*t*-butylamino)silane on the Hydroxylated SiO₂(001) Surface. *J. Phys. Chem. C* **2012**, *116*, 947–952.
- (24) Huang, L.; Han, B.; Han, B.; Dereskei-Kovacs, A.; Xiao, M.; Lei, X.; O'Neill, M. L.; Pearlstein, R. M.; Chandra, H.; Cheng, H. First-Principles Study of a Full Cycle of Atomic Layer Deposition of SiO₂ Thin Films with Di(*sec*-butylamino)silane and Ozone. *J. Phys. Chem. C* **2013**, *117*, 19454–19463.
- (25) Baek, S.-B.; Kim, D.-H.; Kim, Y.-C. Adsorption and Surface Reaction of Bis-diethylaminosilane as a Si Precursor on an OH-Terminated Si (001) Surface. *Appl. Surf. Sci.* **2012**, *258*, 6341–6344.
- (26) Jeong, Y.-C.; Baek, S.-B.; Kim, D.-H.; Kim, J.-S.; Kim, Y.-C. Initial Reaction of Silicon Precursors with a Varying Number of Dimethylamino Ligands on a Hydroxyl-Terminated Silicon (001) Surface. *Appl. Surf. Sci.* **2013**, *280*, 207–211.
- (27) Li, J.; Wu, J.; Zhou, C.; Han, B.; Karwacki, E. J.; Xiao, M.; Lei, X.; Cheng, H. On the Dissociative Chemisorption of Tris-(dimethylamino)silane on Hydroxylated SiO₂ (001) Surface. *J. Phys. Chem. C* **2009**, *113*, 9731–9736.
- (28) Murray, C. A.; Elliott, S. D.; Hausmann, D.; Henri, J.; LaVoie, A. Effect of Reaction Mechanism on Precursor Exposure Time in Atomic Layer Deposition of Silicon Oxide and Silicon Nitride. *ACS Appl. Mater. Interfaces* **2014**, *6*, 10534–10541.
- (29) Ni, G.; Han, B.; Cheng, H. Effect of Al Electronic Configuration on the SiO₂ Thin Film Growth via Catalytic Self-Assembling Deposition. *J. Phys. Chem. C* **2013**, *117*, 22705–22713.
- (30) Fang, G.; Ma, J. Rapid Atomic Layer Deposition of Silica Nanolaminates: Synergistic Catalysis of Lewis/Bronsted Acid Sites and Interfacial Interactions. *Nanoscale* **2013**, *5*, 11856–11869.
- (31) George, S. M.; Sneh, O.; Dillon, A. C.; Wise, M. L.; Ott, A. W.; Okada, L. A.; Way, J. D. Atomic Layer Controlled Deposition of SiO₂ and Al₂O₃ Using ABAB... Binary Reaction Sequence Chemistry. *Appl. Surf. Sci.* **1994**, *82–83*, 460–467.
- (32) Sneh, O.; Wise, M. L.; Ott, A. W.; Okada, L. A.; George, S. M. Atomic Layer Growth of SiO₂ on Si(100) Using SiCl₄ and H₂O in a Binary Reaction Sequence. *Surf. Sci.* **1995**, *334*, 135–152.
- (33) Klaus, J. W.; Ott, A. W.; Johnson, J. M.; George, S. M. Atomic Layer Controlled Growth of SiO₂ Films Using Binary Reaction Sequence Chemistry. *Appl. Phys. Lett.* **1997**, *70*, 1092–1094.
- (34) Weckman, T.; Laasonen, K. First Principles Study of the Atomic Layer Deposition of Alumina by TMA-H₂O-Process. *Phys. Chem. Chem. Phys.* **2015**, *17*, 17322–17334.
- (35) Mukhopadhyay, A. B.; Musgrave, C. B.; Sanz, J. F. Atomic Layer Deposition of Hafnium Oxide from Hafnium Chloride and Water. *J. Am. Chem. Soc.* **2008**, *130*, 11996–12006.

- (36) Antonczak, S.; Ruiz-Lopez, M. F.; Rivail, J. L. Ab Initio Analysis of Water-Assisted Reaction Mechanisms in Amide Hydrolysis. *J. Am. Chem. Soc.* **1994**, *116*, 3912–3921.
- (37) Markova, N.; Enchev, V.; Timtcheva, I. Oxo-hydroxy Tautomerism of 5-Fluorouracil: Water-Assisted Proton Transfer. *J. Phys. Chem. A* **2005**, *109*, 1981–1988.
- (38) Huang, J.; Yeung, C. S.; Ma, J.; Gayner, E. R.; Phillips, D. L. A Computational Chemistry Investigation of the Mechanism of the Water-Assisted Decomposition of Trichloroethylene Oxide. *J. Phys. Chem. A* **2014**, *118*, 1557–1567.
- (39) Klaus, J. W.; Sneh, O.; Ott, A. W.; George, S. M. Atomic Layer Deposition of SiO₂ Using Catalyzed and Uncatalyzed Self-Limiting Surface Reactions. *Surf. Rev. Lett.* **1999**, *06*, 435–448.
- (40) Klaus, J. W.; George, S. M. Atomic Layer Deposition of SiO₂ at Room Temperature Using NH₃-Catalyzed Sequential Surface Reactions. *Surf. Sci.* **2000**, *447*, 81–90.
- (41) Klaus, J. W.; George, S. M. SiO₂ Chemical Vapor Deposition at Room Temperature Using SiCl₄ and H₂O with an NH₃ Catalyst. *J. Electrochem. Soc.* **2000**, *147*, 2658–2664.
- (42) Ferguson, J. D.; Smith, E. R.; Weimer, A. W.; George, S. M. ALD of SiO₂ at Room Temperature Using TEOS and H₂O with NH₃ as the Catalyst. *J. Electrochem. Soc.* **2004**, *151*, G528–G535.
- (43) Du, Y.; Du, X.; George, S. M. SiO₂ Film Growth at Low Temperatures by Catalyzed Atomic Layer Deposition in a Viscous Flow Reactor. *Thin Solid Films* **2005**, *491*, 43–53.
- (44) Du, Y.; Du, X.; George, S. M. Mechanism of Pyridine-Catalyzed SiO₂ Atomic Layer Deposition Studied by Fourier-Transform Infrared Spectroscopy. *J. Phys. Chem. C* **2007**, *111*, 219–226.
- (45) Hatton, B.; Kitaev, V.; Perovic, D.; Ozin, G.; Aizenberg, J. Low-Temperature Synthesis of Nanoscale Silica Multilayers - Atomic Layer Deposition in a Test Tube. *J. Mater. Chem.* **2010**, *20*, 6009–6013.
- (46) Tracey, D. F.; Delley, B.; McKenzie, D. R.; Warschkow, O. Molecular Adsorption on Silicon (001): A Systematic Evaluation of Size Effects in Slab and Cluster models. *AIP Adv.* **2013**, *3*, 042117.
- (47) Berry, R. S. Correlation of Rates of Intramolecular Tunneling Processes with Application to Some Group V Compounds. *J. Chem. Phys.* **1960**, *32*, 933–938.
- (48) Deiters, J. A.; Holmes, R. R. Pathways for Nucleophilic Substitution at Silicon. A Molecular Orbital Approach. *J. Am. Chem. Soc.* **1987**, *109*, 1686–1692.
- (49) Cahoon, J. F.; Sawyer, K. R.; Schlegel, J. P.; Harris, C. B. Determining Transition-State Geometries in Liquids Using 2D-IR. *Science* **2008**, *319*, 1820–1823.
- (50) Mislow, K. Role of Pseudorotation in the Stereochemistry of Nucleophilic Displacement Reactions. *Acc. Chem. Res.* **1970**, *3*, 321–331.
- (51) Holmes, R. R. The Stereochemistry of Nucleophilic Substitution of Tetracoordinate Silicon. *Chem. Rev.* **1990**, *90*, 17–31.
- (52) Holmes, R. R. Comparison of Phosphorus and Silicon: Hypervalency, Stereochemistry, and Reactivity. *Chem. Rev.* **1996**, *96*, 927–950.
- (53) Legrand, O.; Brunel, J. M.; Buono, G. Stereospecific Migration of P from N to C_{sp2}: Ring-Expansion Reaction of Chiral Diazaphospholidine Oxides. *Angew. Chem., Int. Ed.* **1999**, *38*, 1479–1483.
- (54) Kobayashi, A.; Tsuji, N.; Fukazawa, A.; Kobayashi, N. Temperature Dependence of SiO₂ Film Growth with Plasma-Enhanced Atomic Layer Deposition. *Thin Solid Films* **2012**, *520*, 3994–3998.
- (55) Burton, B. B.; Kang, S. W.; Rhee, S. W.; George, S. M. SiO₂ Atomic Layer Deposition Using Tris(dimethylamino)silane and Hydrogen Peroxide Studied by in situ Transmission FTIR Spectroscopy. *J. Phys. Chem. C* **2009**, *113*, 8249–8257.
- (56) Bachmann, J.; Zierold, R.; Chong, Y. T.; Hauert, R.; Sturm, C.; Schmidt-Grund, R.; Rheinländer, B.; Grundmann, M.; Gösele, U.; Nielsch, K. A Practical, Self-Catalytic, Atomic Layer Deposition of Silicon Dioxide. *Angew. Chem., Int. Ed.* **2008**, *47*, 6177–6179.
- (57) Mallikarjunan, A.; Chandra, H.; Xiao, M.; Lei, X.; Pearlstein, R. M.; Bowen, H. R.; O'Neill, M. L.; Dereskei-Kovacs, A.; Han, B. Designing High Performance Precursors for Atomic Layer Deposition of Silicon Oxide. *J. Vac. Sci. Technol., A* **2015**, *33*, 01A137.
- (58) Profijt, H. B.; Potts, S. E.; van de Sanden, M. C. M.; Kessels, W. M. M. Plasma-Assisted Atomic Layer Deposition: Basics, Opportunities, and Challenges. *J. Vac. Sci. Technol., A* **2011**, *29*, 050801.
- (59) Potts, S. E.; Kessels, W. M. M. Energy-Enhanced Atomic Layer Deposition for More Process and Precursor Versatility. *Coord. Chem. Rev.* **2013**, *257*, 3254–3270.
- (60) Lieberman, M. A.; Lichtenberg, A. J. *Principles of Plasma Discharges and Materials Processing*, 2nd ed.; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2005.
- (61) Gasser, W.; Uchida, Y.; Matsumura, M. Quasi-Monolayer Deposition of Silicon Dioxide. *Thin Solid Films* **1994**, *250*, 213–218.
- (62) Morishita, S.; Gasser, W.; Usami, K.; Matsumura, M. New Substances for Atomic-Layer Deposition of Silicon Dioxide. *J. Non-Cryst. Solids* **1995**, *187*, 66–69.
- (63) Burton, B. B.; Boleslawski, M. P.; Desombre, A. T.; George, S. M. Rapid SiO₂ Atomic Layer Deposition Using Tris(*tert*-pentoxy)silanol. *Chem. Mater.* **2008**, *20*, 7031–7043.
- (64) Won, S. J.; Kim, J. R.; Suh, S.; Lee, N.-I.; Hwang, C. S.; Kim, H. J. Effect of Catalyst Layer Density and Growth Temperature in Rapid Atomic Layer Deposition of Silica Using Tris(*tert*-pentoxy)silanol. *ACS Appl. Mater. Interfaces* **2011**, *3*, 1633–1639.
- (65) Choi, D.-W.; Chung, K.-B.; Park, J.-S. Rapid Vapor Deposition SiO₂ Thin Film Deposited at a Low Temperature Using Tris(*tert*-pentoxy)silanol and Trimethylaluminum. *Mater. Chem. Phys.* **2013**, *142*, 614–618.
- (66) Machado, E.; Kaczmariski, M.; Ordejón, P.; Garg, D.; Norman, J.; Cheng, H. First-Principles Analyses and Predictions on the Reactivity of Barrier Layers of Ta and TaN toward Organometallic Precursors for Deposition of Copper Films. *Langmuir* **2005**, *21*, 7608–7614.
- (67) Machado, E.; Kaczmariski, M.; Braidia, B.; Ordejón, P.; Garg, D.; Norman, J.; Cheng, H. Interaction of Copper Organometallic Precursors with Barrier Layers of Ti, Ta and W and Their Nitrides: A First-Principles Molecular Dynamics Study. *J. Mol. Model.* **2007**, *13*, 861–864.
- (68) van Duin, A. C. T.; Strachan, A.; Stewman, S.; Zhang, Q.; Xu, X.; Goddard, W. A., III ReaxFFSiO Reactive Force Field for Silicon and Silicon Oxide Systems. *J. Phys. Chem. A* **2003**, *107*, 3803–3811.
- (69) Cheng, T.; Jaramillo-Botero, A.; Goddard, W. A., III; Sun, H. Adaptive Accelerated ReaxFF Reactive Dynamics with Validation from Simulating Hydrogen Combustion. *J. Am. Chem. Soc.* **2014**, *136*, 9434–9442.
- (70) Hu, X.; Schuster, J.; Schulz, S. E.; Gessner, T. Surface Chemistry of Copper Metal and Copper Oxide Atomic Layer Deposition From Copper(II) Acetylacetonate: a Combined First-Principles and Reactive Molecular Dynamics Study. *Phys. Chem. Chem. Phys.* **2015**, *17*, 26892–26902.
- (71) Dkhissi, A.; Estève, A.; Mastail, C.; Olivier, S.; Mazaleyra, G.; Jeloica, L.; Djafari Rouhani, M. Multiscale Modeling of the Atomic Layer Deposition of HfO₂ Thin Film Grown on Silicon: How to Deal with a Kinetic Monte Carlo Procedure. *J. Chem. Theory Comput.* **2008**, *4*, 1915–1927.
- (72) Shirazi, M.; Elliott, S. D. Atomistic Kinetic Monte Carlo Study of Atomic Layer Deposition Derived from Density Functional Theory. *J. Comput. Chem.* **2014**, *35*, 244–259.
- (73) Elliott, S. D.; Dey, G.; Maimaiti, Y.; Ablat, H.; Filatova, E. A.; Fomengia, G. N. Modeling Mechanism and Growth Reactions for New Nanofabrication Processes by Atomic Layer Deposition. *Adv. Mater.* **2015**, DOI: 10.1002/adma.201504043.