Stepwise mechanism and H$_2$O-assisted hydrolysis in atomic layer deposition of SiO$_2$ without a catalyst

Guo-Yong Fang$^{1,2,*}$, Li-Na Xu$^2$, Lai-Guo Wang$^1$, Yan-Qiang Cao$^1$, Di Wu$^1$ and Ai-Dong Li$^1*$

**Abstract**

Atomic layer deposition (ALD) is a powerful deposition technique for constructing uniform, conformal, and ultrathin films in microelectronics, photovoltaics, catalysis, energy storage, and conversion. The possible pathways for silicon dioxide (SiO$_2$) ALD using silicon tetrachloride (SiCl$_4$) and water (H$_2$O) without a catalyst have been investigated by means of density functional theory calculations. The results show that the SiCl$_4$ half-reaction is a rate-determining step of SiO$_2$ ALD. It may proceed through a stepwise pathway, first forming a Si-O bond and then breaking Si-Cl/O-H bonds and forming a H-Cl bond. The H$_2$O half-reaction may undergo hydrolysis and condensation processes, which are similar to conventional SiO$_2$ chemical vapor deposition (CVD). In the H$_2$O half-reaction, there are massive H$_2$O molecules adsorbed on the surface, which can result in H$_2$O-assisted hydrolysis of the Cl-terminated surface and accelerate the H$_2$O half-reaction. These findings may be used to improve methods for the preparation of SiO$_2$ ALD and H$_2$O-based ALD of other oxides, such as Al$_2$O$_3$, TiO$_2$, ZrO$_2$, and HfO$_2$.

**Keywords:** Silicon dioxide; Atomic layer deposition; H$_2$O-assisted hydrolysis

**Background**

Atomic layer deposition (ALD) is a powerful deposition technique for constructing uniform, conformal, and ultrathin films in microelectronics, photovoltaics, catalysis, energy storage, and conversion [1,2]. Compared to other fabrication techniques, such as physical vapor deposition (PVD) and chemical vapor deposition (CVD), ALD is capable of accurately controlling the thickness of thin films at the atomic scale [1]. Essentially, the principle of ALD is similar to that of CVD, except that ALD breaks the CVD reaction into two half-reactions and retains two precursors separately during the reaction [2]. Taking silicon dioxide (SiO$_2$) as an example, SiO$_2$ CVD using silicon tetrachloride (SiCl$_4$) and water (H$_2$O) can be divided into two half-reactions, A and B, of SiO$_2$ ALD [3-6]:

- **CVD:** SiCl$_4$ + 2H$_2$O $\rightarrow$ SiO$_2$ + 4HCl
- **ALD:** (A) Si-OH$^+$ + SiCl$_4$ $\rightarrow$ Si-O-SiCl$_3^+$ + HCl,
  (B) Si-O-SiCl$_3^+$ + H$_2$O $\rightarrow$ Si-O-Si-OH$^+$ + HCl,

where an asterisk designates the surface species.

* Correspondence: fanggy@wzu.edu.cn; adli@nju.edu.cn
1 National Laboratory of Solid State Microstructures, College of Engineering and Applied Sciences, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China
2 Zhejiang Provincial Key Laboratory of Carbon Materials, College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 320035, China

In order to get more insight into the reaction mechanism of SiO$_2$ ALD, theoretical calculation has been performed that illustrates the reaction pathways [7]. It was proposed that on the Si(001) surface, the substituted half-reaction of SiCl$_4$ with surface hydroxyl group (–OH) proceeds through a concerted pathway via a four-membered ring (4MR) transition state (TS), forming Si-O and H-Cl bonds while simultaneously breaking Si-Cl and O-H bonds [7]. Unlike the Lewis acids, such as AlCl$_3$, TiCl$_4$, ZrCl$_4$, and HfCl$_4$, however, SiCl$_4$ seems to have no strong nucleophilicity [8-10]. Furthermore, it was found experimentally that the rate-determining step (RDS) of the full cycle of SiO$_2$ ALD is the SiCl$_4$ half-reaction, not the H$_2$O half-reaction [3-6]. To date, the reaction mechanism of the full SiO$_2$ ALD process on the actual SiO$_2$ surface has remained unclear. In this work, we have performed detailed density functional theory (DFT) calculations to investigate the reaction mechanism of the full cycle of SiO$_2$ ALD, involving the SiCl$_4$ half-reaction (A1 and A2) and H$_2$O half-reaction (B1 to B10), as shown in Figure 1. It is demonstrated that the SiCl$_4$ half-reaction may undergo a stepwise pathway and H$_2$O can accelerate the H$_2$O half-reaction. The insights gained into the reaction mechanism of SiO$_2$ ALD may be used to improve methods for SiO$_2$.
ALD and H₂O-based ALD of other oxides, such as Al₂O₃, TiO₂, ZrO₂, and HfO₂.

**Methods**

In order to model the two half-reactions of SiO₂ ALD, we adopt the cluster model Si₂₃O₄₀H₄₀, as shown in Figure 2, which is based on a hydroxylated α-SiO₂(0001) surface. The cluster model consists of three layers of SiO₂ (Si₂₃O₄₀), and 40 hydrogen atoms which are used to saturate the dangling bonds. To stimulate the surface, the lower two layers of the SiO₂ atoms of the two models were fixed in optimized geometries.

All the species in ALD SiO₂ reactions were optimized using the M06-2X functional within the framework of DFT [11,12]. In order to gain 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. For each stationary point on the potential energy surface, a frequency calculation was carried out to determine if it is a minimum or a TS. All the transition states were verified by intrinsic reaction coordinates (IRC) calculations. Gibbs free energies of all species were estimated from the partition functions, and the enthalpy and entropy terms at 600 K. The energies reported here include zero-point energy (ZPE) corrections. We note that the solid surface lacks translational and rotational freedom, and the entropy of the surface only has a vibrational contribution. In other words, after being adsorbed onto the surface, the gas molecules lose translational and rotational momenta and produce new vibrational modes. All calculations in this work were performed with Gaussian 09 program [13].
Results and discussion
SiCl\textsubscript{4} half-reaction: stepwise mechanism

The reaction pathway for the SiCl\textsubscript{4} half-reaction between SiCl\textsubscript{4} precursor and the surface hydroxyl (-OH) is shown in Figure 3. Due to high levels of hydroxyls on the SiO\textsubscript{2} surface after H\textsubscript{2}O half-reaction, SiCl\textsubscript{4} and hydroxyl may exchange ligands twice in the SiCl\textsubscript{4} half-reaction. Firstly, reaction A1 between SiCl\textsubscript{4} and -OH goes through a rotation transition state, TS\textsubscript{1A1}, with a Gibbs free energy barrier (G\textsubscript{a}) of 34.5 kcal mol\textsuperscript{−1} and forms a pentacoordinated intermediate, Im\textsubscript{2A1}. Subsequently, the unstable intermediate undergoes the second transition state, TS\textsubscript{2A1}, forming the product -OSiCl\textsubscript{3}\textsuperscript{+}, P\textsuperscript{A1} and accompanied by the release of HCl. Secondly, -OSiCl\textsubscript{3}\textsuperscript{+} can further react with another adjacent hydroxyl (-OH) on the surface to form the bridged product -OSiCl\textsubscript{2}, P\textsuperscript{A2}. Similar to reaction A1, reaction A2 between -OSiCl\textsubscript{3}\textsuperscript{+} and -OH also undergoes two transition states, TS\textsubscript{1A2} and TS\textsubscript{2A2}, and a pentacoordinated intermediate, Im\textsubscript{1A2}. The overall SiCl\textsubscript{4} half-reaction is exergonic by 24.0 kcal mol\textsuperscript{−1}. The highest activation free energy of the SiCl\textsubscript{4} half-reaction is 44.5 kcal mol\textsuperscript{−1} (TS\textsubscript{2A1}), indicating that the SiCl\textsubscript{4} half-reaction is very difficult. This difficulty can be overcome by the introduction of Lewis base catalysts, such as ammonia, pyridine, and aminosilane [14-22].

In Figure 3, TS\textsubscript{1A1} and TS\textsubscript{1A2}, with imaginary frequencies of 42\textit{i} and 57\textit{i} cm\textsuperscript{−1}, respectively, represent the formation of a Si-O bond accompanied by the rotation of SiCl\textsubscript{4} and -SiCl\textsubscript{3}. The pentacoordinated intermediates, Im\textsubscript{2A1} and Im\textsubscript{1A2}, have a trigonal bipyramidal (TBP) geometry with five ligands of four Cl atoms and one O atom or three Cl atoms and two O atoms. The TS\textsubscript{2A1} and TS\textsubscript{2A2}, with imaginary frequencies of 129\textit{i} and 458\textit{i} cm\textsuperscript{−1}, respectively, represent cleavages of the Si-Cl and O-H bonds and the formation of a H-Cl bond. As listed in Table 1, the Si...O and H...Cl distances in reaction A1 gradually decrease from 2.01 and 2.62 Å to 1.62 and 1.29 Å, respectively, indicating the formation of new Si-O and H-Cl bonds. Simultaneously, the O-H and Si-Cl distances increase from 1.03 and 2.11 Å to 4.86 and 4.88 Å, respectively, indicating cleavage of old O-H and Si-Cl bonds. Similar to reaction A1, the Si...O and H...Cl distances in reaction A2 gradually decrease from 2.95 and 3.81 Å to 1.62 and 1.29 Å, respectively, indicating the formation of new Si-O and H-Cl bonds. Simultaneously, the O-H and Si-Cl distances increase from 0.97 and 2.05 Å to 3.44 and 4.02 Å, respectively, indicating the cleavage of these bonds.

H\textsubscript{2}O half-reaction: H\textsubscript{2}O-assisted hydrolysis

In conventional SiO\textsubscript{2} CVD, SiCl\textsubscript{4} and H\textsubscript{2}O are introduced into the reaction chamber simultaneously. Subsequent hydrolysis and condensation lead to the formation of SiO\textsubscript{2}. Although two reactants are separately introduced into the chamber, hydrolysis and condensation also occur in SiO\textsubscript{2} ALD. In fact, the half-reaction between water and the Cl-terminated surface exchanges Cl

Table 1 Selected bond distances (in Å) of all species for SiCl\textsubscript{4} half-reaction

| Species | Si-O | O-H | Si-Cl | H-Cl |
|---------|------|-----|-------|------|
| Im\textsuperscript{A1} | 2.01 | 1.03 | 2.24 | 2.62 |
| TS\textsuperscript{1A1} | 1.83 | 1.08 | 2.24 | 2.83 |
| Im\textsuperscript{2A1} | 1.79 | 1.13 | 2.24 | 3.21 |
| TS\textsuperscript{2A1} | 1.77 | 1.02 | 2.94 | 2.01 |
| Im\textsuperscript{A2} | 1.62 | 4.86 | 4.88 | 1.29 |
| P\textsuperscript{A1} | 2.95 | 0.97 | 2.05 | 3.81 |
| TS\textsuperscript{1A2} | 2.10 | 1.00 | 2.11 | 2.95 |
| Im\textsuperscript{A2} | 1.83 | 1.02 | 2.27 | 2.76 |
| TS\textsuperscript{2A2} | 1.79 | 1.14 | 2.50 | 1.65 |
| Im\textsuperscript{2A2} | 1.62 | 3.44 | 4.02 | 1.29 |
and -OH ligands and changes Si-Cl* species into Si-OH* species. Due to this the possible reactions of the H₂O half-
reaction (B) may include the formation of silanol (-Si-OH) via the exchange of ligands between Cl and -OH (reactions B1, B2, B3, B4, and B5) and the formation of -O-Si-O- bridge bonds by removing H₂O (reactions B6, B8, and B9) and HCl (reactions B7 and B10) similar to the hydrolysis (-Si-OH) and condensation (-O-Si-O-) processes of SiO₂ CVD.

After the SiCl₄ half-reaction, the hydroxylated surface is terminated by Cl atoms and changes to -O₂SiCl₂* and -OSiCl₃* surfaces, which are both hydrolyzed in subsequent H₂O half-reaction. Firstly, H₂O and the bridged surface (-O₂SiCl₂) can exchange the ligands via reactions B1 and B2, shown in Figure 4. The first Cl exchange of the hydrolysis of -O₂SiCl₂ requires a high activation free energy of 37.6 kcal mol⁻¹ and goes through a transition state, TS₁B₁, to form -Si-OH* species and release HCl from the surface. Subsequently, the second Cl atom of -O₂SiCl₂ can also be exchanged by -OH via a transition state, TS₁B₂, with an activation free energy of 31.7 kcal mol⁻¹. If H₂O-assisted role is considered, the activation free energy of the hydrolysis of -O₂SiCl₂ decreases to approximately 21.2 kcal mol⁻¹, indicating that H₂O can accelerate -Si-OH formation and Cl elimination. The reason for this is mainly that H₂O can form hydrogen bonding interactions through H₂O...H₂O bonds and lower the activation energy of Si-O bond formation and Cl elimination via a six-member ring (6MR) transition state, H₂O-assisted-TS₁(B₁), shown in Figure 4. The accelerated

![Figure 4 Gibbs free energy profiles of the hydrolysis reactions of -O₂SiCl₂, B1 and B2, in H₂O half-reaction. The inset shows the structures of three transition states, TS₁B₁, TS₁B₂, and H₂O-assisted-TS₁(B₁), and two products, P₁B₁ and P₂B₁.](image1)

![Figure 5 Gibbs free energy profiles of the hydrolysis reactions of -OSiCl₃, B3, B4, and B5, in H₂O half-reaction. The inset shows the structures of seven transition states, TS₁B₃, TS₂B₃, TS₁B₄, TS₂B₄, TS₁B₅, TS₂B₅, and H₂O-assisted-TS₂B₅, a pentacoordinated intermediate, H₂O-assisted-Im₂B₃, and three products, P₃B₃, P₄B₃, and P₅B₃.](image2)
half-reaction via the hydrogen bonding interaction of H₂O...H₂O may be termed as H₂O-assisted hydrolysis, which is similar to Lewis-base catalysis in SiO₂ ALD through the OH...N hydrogen bond [14,23,24]. As a matter of fact, there are H₂O-assisted reactions in nature, such as hydrolysis or solvolysis [25-28], tautomerization or proton transfer [29-34], decomposition [35-37], and catalysis [38,39]. H₂O-assisted hydrolysis and solvolysis facilitate the exchange and dissociation of Cl ligand in HfO₂ ALD using HfCl₄ and H₂O [40].

Secondly, another Cl-terminated surface (-OSiCl₃*) can also hydrolyze step-by-step and go through pathways, B3, B4, and B5, shown in Figure 5. Three ligand exchange reactions undergo two transition states, TS₁B³ and TS₂B³, TS₁B⁴ and TS₂B⁴, and TS₁B⁵ and TS₂B⁵. Similar to the SiCl₄ half-reaction, the first represents the formation of Si-O bonds and the second represents the cleavages of Si-Cl and O-H bonds and the formation of H-Cl bond. It is found that the activation free energies of -OSiCl₃* hydrolysis are lower than that of -O₂SiCl₂ hydrolysis. Unlike the rigid -O₂SiCl₂ group, the -OSiCl₃ group is more flexible. As shown in TS₁B³ of Figure 5, the hydroxyl (-OH) on the surface can interact with H₂O through hydrogen bonding, HOH...OH, and cause the rotation of the -OSiCl₃ group, which can accelerate the hydrolysis of -OSiCl₃ and H₂O exchange with the Cl ligand. The first hydrolysis of -OSiCl₃* requires a low activation free energy of 23.3 kcal mol⁻¹; however, the hydroylation of -OSiOH-Cl₂* and -OSi(OH)₂-Cl require slightly higher activation free energies. The reason for this may be that the direction of the hydrolyzed Cl atom of -OSiCl₃ is more downward than that of -OSiOH-Cl₂ or -OSi(OH)₂-Cl, which results in a hydrogen bonding interaction between -OH and H₂O. In the H₂O half-reaction, there are massive H₂O molecules adsorbed on the surface, which result in H₂O-assisted hydrolysis.

Owing to the strong hydrogen bonding interaction of H₂O...H₂O, a pentacoordinated intermediate including silanol (Si-OH) ligand can be directly formed, as shown in H₂O-assisted Im²B³ in Figure 5. The hydrolysis of -OSiCl₃* and the elimination of Cl ligand occur easily and the activation free energy can decrease from 23.3 to 15.0 kcal mol⁻¹. Similarly, H₂O can also accelerate the hydrolysis of -OSiOH-Cl₂* and -OSi(OH)₂-Cl*.

As show in Figure 6, the formation of the O-Si-O bridge bond can result from H₂O condensation reactions, B6, B8, and B10, similar to the condensation (O-Si-O) process of SiO₂ CVD. These condensation reactions occur after the hydrolysis of -OSiCl₃*, -OSiOH-Cl₂* and -OSi(OH)₂-Cl* and include two transition states. The first transition states, TS₁B⁶, TS₁B⁸, and TS₁B¹⁰, represent O-Si-O bond formation with the activation free energies of 22.9, 21.6, 22.4, and 21.6 kcal mol⁻¹ with respect to Figures 6 and 7.
and 18.1 kcal mol\(^{-1}\), respectively. The second transition states, TS\(_{2^{86}}\), TS\(_{2^{88}}\), and TS\(_{2^{110}}\), represent H\(_2\)O removal with the activation free energies of 21.9, 18.6, and 19.8 kcal mol\(^{-1}\), respectively.

Similar to H\(_2\)O condensation, HCl condensation reactions, B7 and B9, can also result in the formation of the O-Si-O bridge bond with low activation free energies of 22.4 and 21.6 kcal mol\(^{-1}\), respectively, as shown in Figure 7. The corresponding activation free energies of HCl removal are 18.6 and 12.6 kcal mol\(^{-1}\), respectively. During H\(_2\)O or HCl removal, the two condensations both lead to the formation of the O-Si-O bridge bond, which is the elementary unit of SiO\(_2\) and ensures its ALD growth.

When reviewing the full SiO\(_2\) ALD cycle, including reactions A1 to A2 and B1 to B10, we find that the free energy barrier for the H\(_2\)O half-reaction is lower than that for SiCl\(_4\) half-reaction. The principal reason is that there are massive H\(_2\)O molecules adsorbed on the surface, which result in H\(_2\)O-assisted hydrolysis of -O\(_2\)Si-Cl\(_2\), -O\(_2\)SiOH-Cl\(_{si}\), -OSi-Cl\(_{si}\), -OSiOH-Cl\(_{si}\), and -OSi(OH)\(_2\)-Cl\(_{si}\) and accelerate the H\(_2\)O half-reaction. Therefore, the SiCl\(_4\) half-reaction is the RDS of the full ALD cycle of SiO\(_2\) and controls the ALD growth of SiO\(_2\).

Conclusions

Through detailed DFT calculations, the possible reaction pathways of (A) SiCl\(_4\) half-reaction and (B) H\(_2\)O half-reaction in SiO\(_2\) ALD without a catalyst have been investigated. The SiCl\(_4\) half-reaction is the RDS of SiO\(_2\) ALD. It may proceed through a stepwise pathway, first forming a Si-O bond and then breaking Si-Cl and O-H bonds and forming a H-Cl bond. The H\(_2\)O half-reaction is a complicated process, including hydrolysis and condensation. In the H\(_2\)O half-reaction, there are massive H\(_2\)O molecules adsorbed on the surface, which can result in H\(_2\)O-assisted hydrolysis of the Cl-terminated surface and accelerate the H\(_2\)O half-reaction. These findings may be used in SiO\(_2\) ALD and H\(_2\)O-based ALD of other oxides, such as Al\(_2\)O\(_3\), TiO\(_2\), ZrO\(_2\), and HfO\(_2\).

Competing interests

The authors declare that they have no competing interests.

Authors’ contributions

GYF and ADL proposed an idea to elucidate the mechanism of SiO\(_2\) ALD. LNX, LGW, YQC, and DW participated in the calculations and helped in the data analysis. GYF and LNX wrote the paper. All authors read and approved the final manuscript.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51202107), the State Key Program for Basic Research of China (2015CB921203 and 2011CB922104), the China Postdoctoral Science Foundation (2014 M55156), Open Project of National Laboratory of Solid State Microstructures (M27009), and Zhejiang Provincial Natural Science Foundation of China (LY130803005). ADL is also grateful for the support of the Doctoral Fund of the Ministry of Education of China (2012091110049) and the Priority Academic Program Development (PAPD) in Jiangsu Province. We thank the High Performance Computing Center of Nanjing University for providing the computing resources.

Received: 12 November 2014 Accepted: 23 December 2014 Published online: 18 February 2015

References

1. Doering R, Nishi Y. Handbook of semiconductor manufacturing technology. 3rd ed. Boca Raton: CRC; 2007.
2. Pinna N, Knez M. Atomic layer deposition of nanostuctured materials. New York: Wiley-VCH; 2011.
3. George SM, Sneh O, Dillon AC, Wise ML, Ott AW, Okada LA, et al. Atomic layer controlled deposition of SiO\(_2\) and Al\(_2\)O\(_3\) using ABAAB… binary reaction sequence chemistry. Appl Surf Sci. 1994;82–83:460–7.
4. Sneh O, Wise ML, Ott AW, Okada LA, George SM. Atomic layer growth of SiO\(_2\) on Si(100) using SiCl\(_4\) and H\(_2\)O in a binary reaction sequence. Surf Sci. 1995;334:135–52.
5. George SM, Ott AW, Klaus JW. Surface chemistry for atomic layer growth. J Phys Chem. 1996;100:13121–31.
6. Klaus JW, Ott AW, Johnson JW, George SM. Atomic layer controlled growth of SiO\(_2\) films using binary reaction sequence chemistry. Appl Phys Lett. 1997;70:1092–4.
7. Kang JK, Musgrave CB. Mechanism of atomic layer deposition of SiO\(_2\) on the silicon (100)-2 \times 1 surface using SiCl\(_4\) and H\(_2\)O as precursors. J Appl Phys. 2002;91:3408–14.
8. Ritala M, Kuikka K, Rahtu A, Riihinen PJ, Leskilä M, Sajavaara T, et al. Atomic layer deposition of oxide thin films with metal alkoxides as oxygen sources. Science. 2000;288:319–21.
9. Haissmann D, Becker J, Wang S, Gordon RG. Rapid vapor deposition of highly conformal silica nanolaminates. Science. 2002;298:402–6.
10. Fang G, Ma J. Rapid atomic layer deposition of silica nanolaminates: synergistic catalysis of Lewis/Brønsted acid sites and interfacial interactions. Nanoscale. 2013;5:1856–69.
11. Zhao Y, Truhlar DG. Density functionals with broad applicability in chemistry. Acc Chem Res. 2008;41:157–67.
12. Zhao Y, Truhlar DG. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functional. Theor Chem Acc. 2008;120:215–41.
13. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09. Revision B.02. Wallingford CT: Gaussian, Inc; 2009.
14. Klaus JW, Sneh O, George SM. Growth of SiO\(_2\) at room temperature with the use of catalyzed sequential half reaction. Science. 1997;278:1934–6.
15. Klaus JW, Sneh O, Ott AW, George SM. Atomic layer deposition of SiO\(_2\) using catalyzed and uncatalyzed self-limiting surface reactions. Surf Rev Lett. 1999;6:435–48.
16. Klaus JW, George SM. Atomic layer deposition of SiO\(_2\) at room temperature using NH\(_3\)-catalyzed sequential surface reactions. Surf Sci. 2000;447:81–90.
17. Klaus JW, George SM. SiO\(_2\) chemical vapor deposition at room temperature using SiCl\(_4\) and H\(_2\)O with an NH\(_3\) catalyst. J Electrochem Soc. 2000;147:2658–64.
18. Ferguson JD, Smith ER, Weimer AW, George SM. ALD of SiO\(_2\) at room temperature using TEOS and H\(_2\)O with NH\(_3\) as the catalyst. J Electrochem Soc. 2004;151:G528–35.
19. Du Y, Du X, George SM. SiO\(_2\) film growth at low temperatures by catalyzed atomic layer deposition in a viscous flow reactor. Thin Sol Film. 2005;491:43–53.
20. Du Y, Du X, George SM. Mechanism of pyridine-catalyzed SiO\(_2\) atomic layer deposition studied by Fourier transform infrared spectroscopy. J Phys Chem C. 2007;111:219–26.
21. Hatton B, Kitaev V, Porecic D, Ozin G, Alzenberg J. Low-temperature synthesis of nanoscale silica multilayers - atomic layer deposition in a test tube. J Mater Chem. 2010;20:6609–13.
22. Bachmann J, Zierold R, Chong YT, Hauert R, Sturm C, Schmidt-Grund R, et al. A practical, self-catalytic, atomic layer deposition of silicon dioxide. Angew Chem Int Ed. 2008;47:1677–9.
23. Fang G, Chen S, Li A, Ma J. Surface pseudorotation in Lewis-base-catalyzed atomic layer deposition of SiO\(_2\); static transition state search and Born–Oppenheimer molecular dynamics simulation. J Phys Chem C. 2012;116:26436–48.
24. Fang GY, Xu LN, Cao YQ, Wang LG, Wu D, Li DL. Self-catalysis by aminosilanes and strong surface oxidation by O₂ plasma in plasma-enhanced atomic layer deposition of high-quality SiO₂. Chem Commun. 2015;51:1341–4.
25. Antonczak S, Ruiz-López MF, Rivali JL. Ab initio analysis of water-assisted reaction mechanisms in amide hydrolysis. J Am Chem Soc. 1994;116:3912–21.
26. Schmeer G, Stumm P. A quantum chemical approach to the water assisted neutral hydrolysis of ethyl acetate and its derivatives. Phys Chem Chem Phys. 1999;1:1025–30.
27. Tsuchida N, Satou H, Yamabe S. Reaction paths of the water-assisted solvolysis of N,N-dimethylformamide. J Phys Chem A. 2007;111:6296–303.
28. Gao JY, Zeng Y, Zhang CH, Xue Y. Theoretical studies on the water-assisted hydrolysis of N,N-dimethyl-N’-(2,3'-dideoxy-3’-thiacytidine) formamidine with three water molecules. J Phys Chem A. 2009;113:325–31.
29. Bell RL, Truong TN. Primary and solvent kinetic isotope effects in the water-assisted tautomerization of formamidine: an ab initio direct dynamics study. J Phys Chem A. 1997;101:7802–8.
30. Gu J, Leszczynski J. A DFT study of the water-assisted intramolecular proton transfer in the tautomers of adenine. J Phys Chem A. 1999;103:2744–50.
31. Liu GX, Li ZS, Ding YH, Fu Q, Huang XR, Sun CC, et al. Water-assisted isomerization from linear propargylium (H₂CCCH⁺) to cyclopropenylium(C₃H₃⁺). J Phys Chem A. 2002;106:10415–22.
32. Balta B, Aviyente V. Solvent effects on glycine II. Water-assisted tautomerization. J Comput Chem. 2004;25:690–703.
33. Markova N, Enchev V, Timtcheva I. Oxo-hydroxy tautomerism of 5-fluorouracil: water-assisted proton transfer. J Phys Chem A. 2005;109:1981–8.
34. Michalkova A, Kosenkov D, Gorb L, Leszczynski J. Thermodynamics and kinetics of intramolecular water assisted proton transfer in Na⁺-1-methylcytosine water complexes. J Phys Chem B. 2008;112:8624–33.
35. Aplincourt P, Anglada JM. Theoretical studies of the isoprene ozonolysis under tropospheric conditions. 2. Unimolecular and water-assisted decomposition of the r-hydroxy hydroperoxides. J Phys Chem A. 2003;107:5812–20.
36. Jacobs G, Patterson PM, Graham UM, Crawford AC, Dozier A, Davis BH. Catalytic links among the water–gas shift, water-assisted formic acid decomposition, and methanol steam reforming reactions over Pt-promoted thoria. J Cat. 2005;235:79–91.
37. Huang J, Yeung CS, Ma J, Gayner ER, Phillips DL. A computational chemistry investigation of the mechanism of the water-assisted decomposition of trichloroethylene oxide. J Phys Chem A. 2014;118:1557–67.
38. Ouchi M, Yoda H, Terashima T, Sawamoto M. Aqueous metal-catalyzed living radical polymerization: highly active water-assisted catalysis. Polym J. 2012;44:51–8.
39. Thorat PB, Goswami SV, Jadhav VN, Bhusare SR. Water-assisted organocatalysis: an enantioselective green protocol for the henry reaction. Aust J Chem. 2013;66:661–6.
40. Mukhopadhyay AB, Musgrave CB, Sanz JF. Atomic layer deposition of hafnium oxide from hafnium chloride and water. J Am Chem Soc. 2008;130:11996–2006.