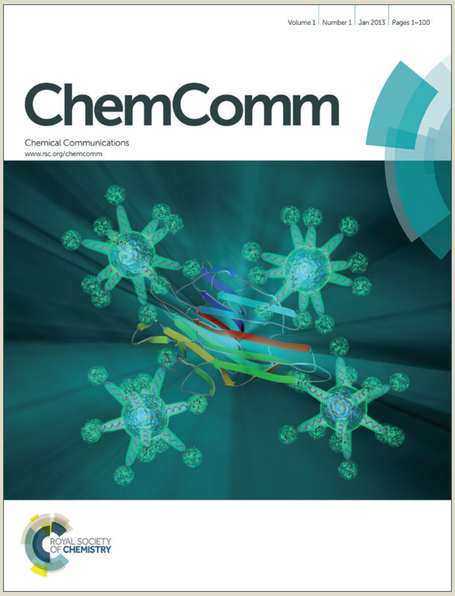

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Self-Catalysis by Aminosilanes and Strong Surface Oxidation by O_2 Plasma in Plasma-Enhanced Atomic Layer Deposition of High-Quality SiO_2

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Plasma-enhanced atomic layer deposition (PE-ALD) has been applied to prepare high-quality ultrathin films for microelectronics, catalysis, and energy applications. The possible pathways for SiO_2 PE-ALD using aminosilanes and O_2 plasma have been investigated by density functional theory calculations. The silane half-reaction between SiH_4 and surface -OH is very difficult and requires a high activation free energy of 57.8 kcal mol^{-1}. The introduction of an aminosilane, such as BDMAS, can reduce the activation free energy to 11.0 kcal mol^{-1} and the aminosilane plays a role of self-catalysis in Si-O formation through the relevant half-reaction. Among the various species generated in O_2 plasma, $^3O_2$ is inactive towards surface silane groups, similar to ordinary oxygen gas. The other three species, $^1O_2$, ^1O, and ^3O, can strongly oxidize surface silane groups through one-step or stepwise pathways. In the ^3O pathway, the triplet must be converted to the singlet and follow the ^1O pathway. Meanwhile, ^1O and ^3O can both decay to $^1O_2$ and enter into the relevant oxidation pathway. The concept of self-catalysis of aminosilanes may be invoked to design and prepare more effective Si precursors for SiO_2 ALD. At the same time, the mechanism of strong surface oxidation by O_2 plasma may be exploited in the PE-ALD preparation of other oxides, such as Al_2O_3, HfO_2, ZrO_2, and TiO_2.

In the past few decades, silicon dioxide (SiO_2) has played a very important role in the microelectronics industry.[1-3] High-quality SiO_2 is usually obtained by chemical vapor deposition (CVD), physical vapor deposition (PVD), or thermal oxidation.[1] However, due to the continuous miniaturization of devices, these techniques cannot meet the requirements for ultrathin SiO_2 films. As a nanofabrication technique, atomic layer deposition (ALD) allows accurate control of the thickness of thin films at the atomic scale.[4-7] In general, SiO_2 ALD without a catalyst requires high temperatures and a large precursor flux.[8,9] Room-temperature ALD (RT-ALD) of SiO_2 can be achieved by introducing a Lewis-base catalyst, such as pyridine or ammonia.[10-18] Another mechanism of rapid atomic layer deposition (RALD) of SiO_2 employing a Lewis-acid catalyst, such as $Al(CH_3)_3$, has also been reported.[19-21]

Recently, as an energy-enhanced ALD technique, plasma-enhanced atomic layer deposition (PE-ALD) has been developed to prepare high-quality SiO_2 thin films at low temperatures.[22] SiO_2 PE-ALD usually employs a Si precursor bearing an amino ligand and an O_2 plasma as the oxidant. Because it requires no catalyst and generates no corrosive by-product, SiO_2 PE-ALD has shown promising results and wide application.[23-26] The role of the amino group, the mechanism of oxidation by O_2 plasma, and the formation process of SiO_2 have hitherto remained unclear. In this work, we have performed detailed density functional theory (DFT) calculations to investigate the mechanism of the reaction involving aminosilanes and O_2 plasma in SiO_2 PE-ALD (see the computational details in the ESI). It is demonstrated that the amino ligand can catalyze reaction of the aminosilane with surface hydroxyl groups (-OH). Such catalysis involving the amino group may be termed self-catalysis. The surface oxidation mechanism by the O_2 plasma is also addressed in detail. The insights gained into the reaction mechanism of SiO_2 PE-ALD may be helpful to devise improved methods for preparing SiO_2 and other oxides, such as Al_2O_3, HfO_2, ZrO_2, and TiO_2.

Similar to thermal ALD, SiO_2 PE-ALD comprises two half-reactions, involving the aminosilane (**A**) and the O_2 plasma (**B**), respectively. In half-reaction **A**, the aminosilane may be (dimethylamino)silane (DMAS), bis(dimethylamino)silane (BDMAS), bis(diethylamino)silane (BDEAS), bis(ethylmethylamino)silane (BEMAS), bis(*tert*-butylamino)silane (BTBAS), tris(dimethylamino)silane (TDMAS), tetrakis(dimethylamino)silane (TKDMAS), and so on. Among these Si precursors, aminosilanes with two amino ligands have been reported to be especially excellent candidates.[23-26] In order to investigate the self-catalytic role of the amino ligand of

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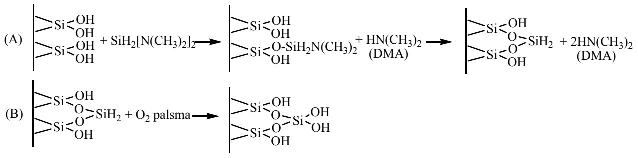
the aminosilane, silane (SiH_4) and BDMAS ($SiH_2[N(CH_3)_2]_2$) half-reactions (**A**) were selected for a comparative study, as shown in **Scheme 1**. Ideally, after the first half-reaction of BDMAS with two –OH groups on the surface catalyzed by two amino groups, a silane ($-SiH_2$) group should remain on the surface, which can be further oxidized to a silanol ($-Si(OH)_2$) group by the O_2 plasma. The second half-reaction (**B**), without by-product formation, allows us to elucidate the oxidation mechanism by the O_2 plasma through a quantum mechanical approach.



Scheme 1. Aminosilane (**A**) and O_2 plasma (**B**) half-reactions in SiO_2 PE-ALD.

As shown in **Figure 1**, in the silane half-reaction, the precursor SiH_4 firstly reacts with a surface -OH group to generate-SiH_3 through a four-membered ring (4MR) transition state, **TS1**^{SiH4}, breaking the Si-H and O-H bonds and simultaneously forming Si-O and H-H bonds. The surface -SiH_3then further reacts with the adjacent -OH to generate -SiH_2 via a similar transition state, **TS2**^{SiH4}. The activation free energies of the two Si-O formations amount to 57.8and 34.3 kcal mol^{-1}, respectively, indicating that the silane half-reaction between the SiH_4 and surface -OH groups without a catalyst at low temperature is very difficult.

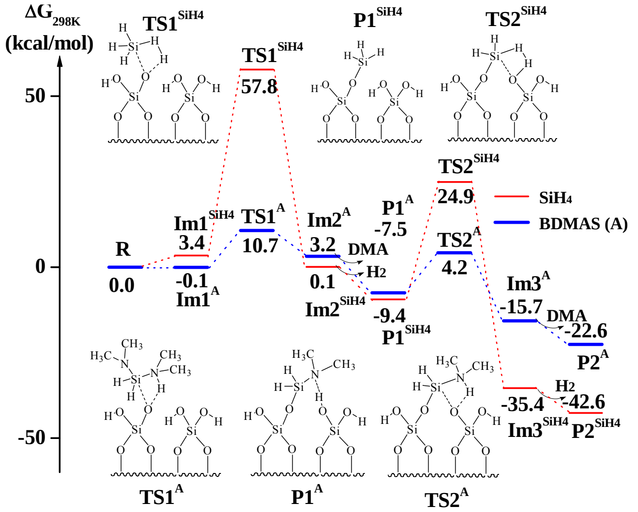
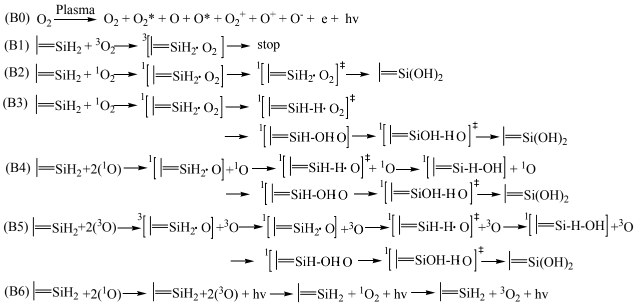


Figure 1. Comparison of Gibbs free energy profiles for SiH_4 and BDMAS half-reactions. The inset shows the structures of **TS1**^{SiH4}, **P1**^{SiH4}, **TS2**^{SiH4}, **TS1**^{A}, **P1**^{A}, and **TS2**^{A}.

When BDMAS is introduced, the activation free energy is dramatically lowered to about 11.0 kcal mol^{-1} and the aminosilane half-reaction proceeds very easily, which is consistent with the results of experiments at low temperatures, even room temperature.[23-26] Firstly, an intermediate, **Im1**^{A}, is formed by hydrogen bonding between an amino ligand of BDMAS and a surface -OH group. The strongly hydrogen-bonded intermediate **Im1**^{A} with an H···N distance of 1.40 Å is transformed to a pentacoordinated intermediate, **Im2**^{A}, through a 4MR transition state, **TS1**^{A}. The unstable **Im2**^{A} readily releases dimethylamine (DMA; $HN(CH_3)_2$) and produces the product, **P1**^{A} ($-SiH_2-N(CH_3)_2$). In the product $-SiH_2-N(CH_3)_2$, the remaining amino ligand is also strongly H-bonded with an adjacent -OH on the surface with an H···N distance of 1.64 Å. Subsequently, proceeding through a similar 4MR transition state, **TS2**^{A}, and pentacoordinated intermediate, **Im3**^{A}, **P1**^{A} is converted to the product -SiH_2, **P2**^{A}.

From comparison of the activation free energies of the SiH_4 and BDMAS half-reactions, it was found that the amino group of the aminosilane can remarkably catalyze the Si-O formation to generate SiO_2. We refer to the catalytic aminosilane reaction involving the amino ligand as self-catalysis. This self-catalysis by an amino ligand is similar to room temperature ALD (RT-ALD) of SiO_2 using Lewis-base catalysts, such as ammonia and pyridine, whereby the N atom can interact with hydroxyl (-OH) groups on the surface through strong N···H hydrogen bonding.[10-18] The formation of one Si-O bond requires one amino group and one –OH group. Because the bis-aminosilane precursor has two amino ligands and the stoichiometric ratio with respect to SiO_2 is 1:2, BDMAS can produce highly pure and stoichiometric SiO_2 films. Recently, it was reported that the half-reaction between another bis-aminosilane precursor, BTBAS, and surface -OH has a low activation energy of about 10.0 kcal mol^{-1}, and this bis-aminosilane also showed similar catalytic behavior.[27] Amono-aminosilane precursor, DMAS, can also catalyze the growth of SiO_2. The self-catalytic process is similar to the first Si-O formation in the BDMAS half-reaction, proceeding via a 4MR TS and producing -SiH_3. Similar to BDMAS, a tris-aminosilane precursor, TDMAS, can also catalyze the formation of two Si-O bonds. Our experiments on SiO_2 PE-ALD using TDMAS at ambient and low temperatures further proved self-catalysis by the aminosilane through its amino ligand (see the experimental details and product characterization of SiO_2 PE-ALD in the ESI). However, the third amino group ($-N(CH_3)_2$) of TDMAS still remains on the surface and is subsequently oxidized by the O_2 plasma, inevitably leading to carbon and nitrogen contamination of the SiO_2 film.[28] Due to severe steric hindrance, reaction of the tetrakis-aminosilane precursor, TKDMAS, with surface-OH groups to form a SiO_2 film is hampered.[29] In order to design more effective Si precursors for SiO_2 ALD, the best approach would seem to be elaboration of those based on bis-aminosilane, such as BEMAS and BTBAS.

Plasma is a high-energy aggregation state of matter, which includes a large number of electrons, ions, excited states of atoms, molecules, and free radicals. Taking O_2 plasma as an example, the plasma process (**B0**) can produce triplet oxygen molecules, $^3O_2$;singlet oxygen molecules, $^1O_2$ or O_2*; triplet oxygen atoms, ^3O;singlet oxygen atoms, ^1O or O*; oxygen molecule cations, O^{2+}; oxygen cations, O^+; oxygen anions, O^-; and electrons (e), as well as accompanying radiation, as shown in **Scheme 2**. The most abundant species in O_2 plasma are $^3O_2$, $^1O_2$, ^3O, and ^1O, which together constitute over 99.99% of the total.[22, 30-32] As shown in **Figure 2**, the ground state of the oxygen molecule, $^3O_2$, is the most stable. The energy of the excited state of the oxygen molecule, $^1O_2$, is 38.3 kcal mol^{-1}higher than that of the ground state. The energy of two oxygen radicals, 2(^{3}O), is 74.6 kcal mol^{-1} higher than that of $^1O_2$. The energy of the excited states of two oxygen radicals, 2(^{1}O), amounts to 236.4 kcal mol^{-1}.



Scheme 2. Possible processes (**B0-B6**) in the O_2 plasma half-reaction.

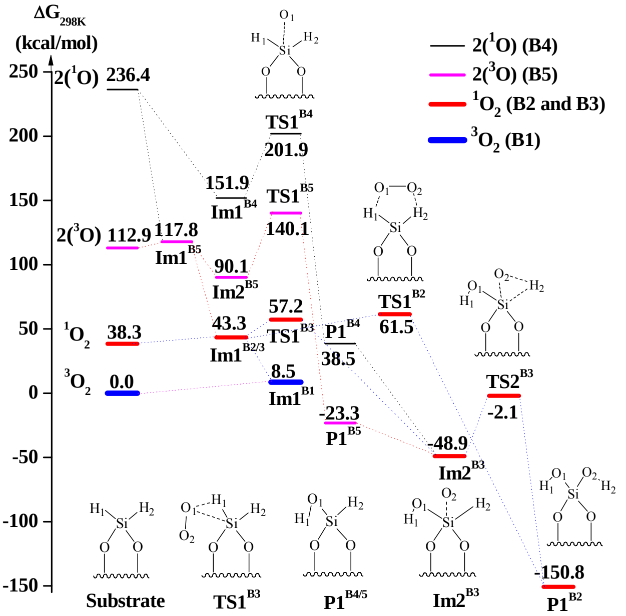


Figure 2. Gibbs free energy profiles for the O_2 plasma half-reaction.

The ground state of the oxygen molecule, $^3O_2$, can interact with the surface silane to generate a triplet intermediate, **Im1^{B1}**. The complex in process **B1** is inactive unless it is excited to the singlet state. However, the other three active species, $^1O_2$, ^{3}O, and ^{1}O, can oxidize the surface silane and these oxidation reactions (**B2-B5**) are strongly exergonic.

The excited state of the oxygen molecule, $^1O_2$, and the surface silane can form a singlet intermediate, **Im1^{B2}**. There are two pathways (**B2** and **B3**) for oxidation of the silane. The first pathway is one-step oxidation (**B2**) via a singlet transition state, **TS1^{B2}**, with an activation free energy of 23.2 kcal mol^{-1}. The overall oxidation reaction is strongly exergonic by 150.8 kcal mol^{-1}. From **Im1^{B2}**, $^1O_2$ frontally attacks two H atoms of the silane to simultaneously produce two -OH groups and the product, **P1^{B2}**. As shown in **Figure 2**, **TS1^{B2}** has an H_2O_2-like structure with two strong hydrogen bonds, O1···H1 and O2···H2.

The second oxidation pathway with $^1O_2$ is stepwise oxidation (**B3**) via two singlet transition states, **TS1^{B3}** and **TS2^{B3}**, and one singlet intermediate, **Im2^{B3}**. From **Im1^{B3}**, $^1O_2$ firstly attacks one H atom of the silane from the side via **TS1^{B3}** with an activation free energy of 18.9 kcal mol^{-1} to generate the single –OH intermediate, **Im2^{B3}**. Subsequently, another Si-H bond of **Im2^{B3}** is oxidized to the product, **P1^{B2}**, via **TS2^{B3}** with an activation free energy of 51.0 kcal mol^{-1}. As shown in **Figure 2**, after insertion of the O1 atom into the Si-H1 bond, another O atom, O2, strongly interacts with the Si atom in **Im2^{B3}**.

Singlet oxygen atoms, ^{1}O, can gradually oxidize two Si-H bonds on the surface through reaction **B4**. Firstly, one singlet oxygen atom, ^{1}O, and the silane form a singlet intermediate, **Im1^{B4}**, which proceeds through a singlet transition state, **TS1^{B4}** with an activation free energy of 50.0 kcal mol^{-1}. The first Si-H bond is further oxidized to a single -OH group and the product, **P1^{B4}**. Subsequently, **P1^{B4}** and another singlet oxygen atom, ^{1}O, form the singlet intermediate, **Im2^{B3}**, which undergoes a second stepwise oxidation pathway (**B3**) with$^1O_2$, **Im2^{B3}→TS2^{B3}→P1^{B2}**. Ultimately, both Si-H bonds are oxidized to Si-OH groups. The overall reaction of oxidation with ^{1}O is barrierless and strongly exergonic by 387.2 kcal mol^{-1}.

The triplet oxygen atom, ^{3}O, separately interacts with the surface silane to form a triplet intermediate, **Im1^{B5}**, which is converted to a singlet intermediate, **Im2^{B5}**. The subsequent pathway, going through a singlet transition state, **TS1^{B5}**, and forming product, **P1^{B5}**, is the same as the ^{1}O pathway (**B4**), **Im1^{B4}→TS1^{B4}→P1^{B4}**. The singlet product, **P1^{B5}**, and another ^{3}O also form the singlet intermediate, **Im2^{B3}**, and enter the second oxidation pathway (**B3**) with$^1O_2$, **Im2^{B3}→TS2^{B3}→P1^{B2}**. In the ^{3}O pathway (**B5**), the oxidation can only proceed if the triplet complex is converted into a singlet intermediate.

Due to strong interactions between the active species in the O_2 plasma and the surface, the unstable highly energetic ^{1}O rapidly decays to a triplet and further reacts through the ^{3}O pathway, according to reaction **B6**. Similarly, ^{3}O and ^{1}O can both produce singlet oxygen molecules, which enter the $^1O_2$ pathway. When all active oxygen species are converted to the triplet oxygen molecule, $^3O_2$, and accompanying radiation, the particles lose their activity.

When reviewing the O_2 plasma half-reaction, including reactions **B1-B6**, we find that the ground state of the oxygen molecule, $^3O_2$, is inactive towards surface silane groups, similar to ordinary oxygen gas. However, the other three species, $^1O_2$, ^{1}O, and ^{3}O, are active and can strongly oxidize surface silane groups through one-step or stepwise pathways.

Conclusions

In summary, DFT calculations have been used to investigate self-catalysis by the aminosilane and the mechanism of oxidation by the O_2 plasma in PE-ALD of SiO_2. The results show that the activation free energy of the half-reaction between SiH_4 and surface -OH is high, at up to 57.8 kcal mol^{-1}. The introduction of BDMAS can reduce the activation free energy to 11.0 kcal mol^{-1}, and the aminosilane plays a role of self-catalysis in Si-O formation through the relevant half-reaction involving its amino ligand. Among the various species in the O_2 plasma, $^{3}O_2$ is inactive. $^{1}O_2$, ^{1}O, and ^{3}O are active and can strongly oxidize the surface silane groups. Oxidation by $^{1}O_2$ proceeds by two pathways: one-step and stepwise processes. ^{1}O and ^{3}O can both gradually oxidize two Si-H bonds. In the ^{3}O pathway, the triplet must be converted to a singlet and then follow the ^{1}O pathway. Due to strong interactions between the active species and the surface, highly energetic ^{1}O can decay to ^{3}O and then follow the relevant ^{3}O pathway. ^{3}O and ^{1}O can both produce $^{1}O_2$ and enter into the oxidation pathway thereof. We anticipate that the concept of self-catalysis of aminosilanes may be invoked in the design of more effective Si precursors for SiO_2, and the mechanism of strong surface oxidation by O_2 plasma may improve PE-ALD methodologies for the preparation of other oxides, such as Al_2O_3, HfO_2, ZrO_2, and TiO_2.

Acknowledgements

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