



Cite this: *Chem. Commun.*, 2015, 51, 1341

Received 9th October 2014,
Accepted 1st December 2014

DOI: 10.1039/c4cc08004a

www.rsc.org/chemcomm

Self-catalysis by aminosilanes and strong surface oxidation by O₂ plasma in plasma-enhanced atomic layer deposition of high-quality SiO₂†

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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 SiO₂ PE-ALD using aminosilanes and O₂ plasma have been investigated by density functional theory calculations. The silane half-reaction between SiH₄ 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 the role of a self-catalyst in Si–O formation through the relevant half-reaction. Among the various species generated in O₂ plasma, ³O₂ is inactive towards surface silane groups, similar to ordinary oxygen gas. The other three species, ¹O₂, ¹O, and ³O, can strongly oxidize surface silane groups through one-step or stepwise pathways. In the ³O pathway, the triplet must be converted into the singlet and follow the ¹O pathway. Meanwhile, both ¹O and ³O can decay to ¹O₂ 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 SiO₂ ALD. At the same time, the mechanism of strong surface oxidation by O₂ plasma may be exploited in the PE-ALD preparation of other oxides, such as Al₂O₃, HfO₂, ZrO₂, and TiO₂.

In the past few decades, silicon dioxide (SiO₂) has played a very important role in the microelectronics industry.^{1–3} High-quality SiO₂ 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 SiO₂ 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, SiO₂ ALD without a catalyst requires high temperatures and a large precursor flux.^{8,9} Room-temperature ALD (RT-ALD) of SiO₂ 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 SiO₂ employing a Lewis-acid catalyst, such as Al(CH₃)₃, has also been reported.^{19–21}

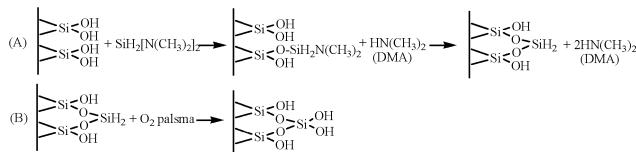
Recently, as an energy-enhanced ALD technique, plasma-enhanced atomic layer deposition (PE-ALD) has been developed to prepare high-quality SiO₂ thin films at low temperatures.²² SiO₂ PE-ALD usually employs a Si precursor bearing an amino ligand and O₂ plasma as the oxidant. Because it requires no catalyst and generates no corrosive by-product, SiO₂ PE-ALD has shown promising results and a wide range of applications.^{23–26} The role of the amino group, the mechanism of oxidation by O₂ plasma, and the formation process of SiO₂ 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 O₂ plasma in SiO₂ PE-ALD (see the computational details in the ESI†). It is demonstrated that the amino ligand can catalyze the 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 O₂ plasma is also addressed in detail. The insights gained into the reaction mechanism of SiO₂ PE-ALD may be helpful to devise improved methods for preparing SiO₂ and other oxides, such as Al₂O₃, HfO₂, ZrO₂, and TiO₂.

Similar to thermal ALD, SiO₂ PE-ALD comprises two half-reactions, involving aminosilane (A) and O₂ 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 the

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4cc08004a

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

aminosilane, silane (SiH_4) and BDMAS ($\text{SiH}_2[\text{N}(\text{CH}_3)_2]_2$) half-reactions (A) were selected for a comparative study, as shown in Scheme 1. Ideally, after the first half-reaction of BDMAS with two $-\text{OH}$ groups on the surface catalyzed by two amino groups, a silane ($-\text{SiH}_2$) group should remain on the surface, which can be further oxidized to a silanol ($-\text{Si}(\text{OH})_2$) group by O_2 plasma. The second half-reaction (B), without by-product formation, allows us to elucidate the oxidation mechanism by O_2 plasma through a quantum mechanical approach.

As shown in Fig. 1, in the silane half-reaction, the precursor SiH_4 firstly reacts with a surface $-\text{OH}$ group to generate $-\text{SiH}_3$ through a four-membered ring (4MR) transition state, $\text{TS1}^{\text{SiH}_4}$, breaking the Si-H and O-H bonds and simultaneously forming Si-O and H-H bonds. The surface $-\text{SiH}_3$ then further reacts with the adjacent $-\text{OH}$ to generate $-\text{SiH}_2$ via a similar transition state, $\text{TS2}^{\text{SiH}_4}$. The activation free energies of the two Si-O formation processes amount to 57.8 and 34.3 kcal mol^{-1} , respectively, indicating that the silane half-reaction between the SiH_4 and surface $-\text{OH}$ groups without a catalyst at low temperature is very difficult.

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 at room temperature.^{23–26} Firstly, an intermediate, Im1^{A} , is formed by hydrogen bonding between an amino ligand of BDMAS and a surface $-\text{OH}$ group. The strongly hydrogen-bonded intermediate

Im1^{A} with an $\text{H} \cdots \text{N}$ distance of 1.40 Å is transformed into a penta-coordinated intermediate, Im2^{A} , through a 4MR transition state, TS1^{A} . The unstable Im2^{A} readily releases dimethylamine (DMA; $\text{HN}(\text{CH}_3)_2$) and produces the product, P1^{A} ($-\text{SiH}_2-\text{N}(\text{CH}_3)_2$). In the product $-\text{SiH}_2-\text{N}(\text{CH}_3)_2$, the remaining amino ligand is also strongly H-bonded with an adjacent $-\text{OH}$ on the surface with an $\text{H} \cdots \text{N}$ distance of 1.64 Å. Subsequently, proceeding through a similar 4MR transition state, TS2^{A} , and pentacoordinated intermediate, Im3^{A} , P1^{A} is converted into the product $-\text{SiH}_2$, P2^{A} .

By 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 the 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 ($-\text{OH}$) groups on the surface through strong $\text{N} \cdots \text{H}$ hydrogen bonding.^{10–18} The formation of one Si-O bond requires one amino group and one $-\text{OH}$ 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 $-\text{OH}$ has a low activation energy of about 10.0 kcal mol^{-1} , and this bis-aminosilane also showed similar catalytic behavior.²⁷ A mono-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 $-\text{SiH}_3$. 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 the self-catalysis by 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 ($-\text{N}(\text{CH}_3)_2$) of TDMAS still remains on the surface and is subsequently oxidized by 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 $-\text{OH}$ 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 an 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, $^3\text{O}_2$; singlet oxygen molecules, $^1\text{O}_2$ 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 $^3\text{O}_2$, $^1\text{O}_2$, ^3O , and ^1O , which together constitute over 99.99% of the total.^{22,30–32} As shown in Fig. 2, the ground state of the oxygen molecule, $^3\text{O}_2$, is the most stable. The energy of the excited state of the oxygen molecule, $^1\text{O}_2$, is 38.3 kcal mol^{-1} higher than that

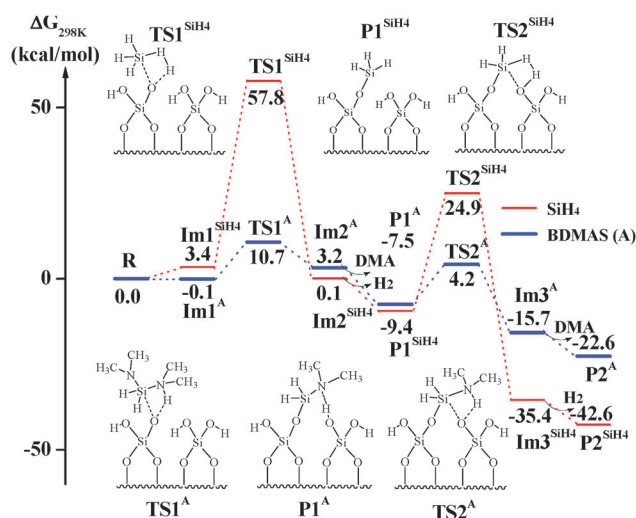
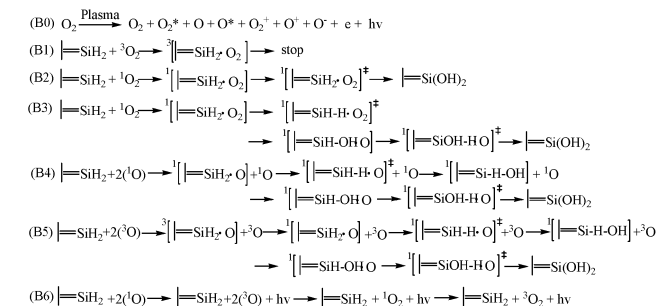
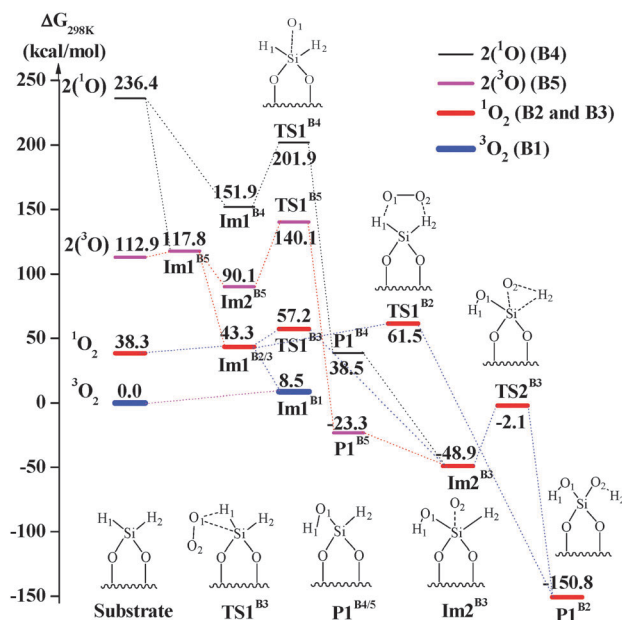


Fig. 1 Comparison of Gibbs free energy profiles for SiH_4 and BDMAS half-reactions. The inset shows the structures of $\text{TS1}^{\text{SiH}_4}$, P1^{SiH_4} , $\text{TS2}^{\text{SiH}_4}$, TS1^{A} , P1^{A} , and TS2^{A} .

Scheme 2 Possible processes (B0–B6) in the O_2 plasma half-reaction.Fig. 2 Gibbs free energy profiles for the O_2 plasma half-reaction.

of the ground state. The energy of two oxygen radicals, $2({}^3\text{O})$, is $74.6 \text{ kcal mol}^{-1}$ higher than that of ${}^1\text{O}_2$. The energy of the excited states of two oxygen radicals, $2({}^1\text{O})$, amounts to $236.4 \text{ kcal mol}^{-1}$.

The ground state of the oxygen molecule, ${}^3\text{O}_2$, 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, ${}^1\text{O}_2$, ${}^3\text{O}$, and ${}^1\text{O}$, can oxidize the surface silane and these oxidation reactions (B2–B5) are strongly exergonic.

The excited state of the oxygen molecule, ${}^1\text{O}_2$, 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 $23.2 \text{ kcal mol}^{-1}$. The overall oxidation reaction is strongly exergonic by $150.8 \text{ kcal mol}^{-1}$. From Im1^{B2} , ${}^1\text{O}_2$ frontally attacks two H atoms of the silane to simultaneously produce two –OH groups and the product, P1^{B2} . As shown in Fig. 2, TS1^{B2} has an H_2O_2 -like structure with two strong hydrogen bonds, $\text{O1}\cdots\text{H1}$ and $\text{O2}\cdots\text{H2}$.

The second oxidation pathway with ${}^1\text{O}_2$ is stepwise oxidation (B3) via two singlet transition states, TS1^{B3} and TS2^{B3} , and one singlet intermediate, Im2^{B3} . From Im1^{B3} , ${}^1\text{O}_2$ first attacks one H atom of the silane from the side via TS1^{B3} with an activation free energy of $18.9 \text{ kcal mol}^{-1}$ 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 $51.0 \text{ kcal mol}^{-1}$. As shown in Fig. 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, ${}^1\text{O}$, can gradually oxidize two Si–H bonds on the surface through reaction B4. Firstly, one singlet oxygen atom, ${}^1\text{O}$, and the silane form a singlet intermediate, Im1^{B4} , which proceeds through a singlet transition state, TS1^{B4} with an activation free energy of $50.0 \text{ kcal mol}^{-1}$. 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, ${}^1\text{O}$, form the singlet intermediate, Im2^{B3} , which undergoes a second stepwise oxidation pathway (B3) with ${}^1\text{O}_2$, $\text{Im2}^{\text{B3}} \rightarrow \text{TS2}^{\text{B3}} \rightarrow \text{P1}^{\text{B2}}$. Ultimately, both Si–H bonds are oxidized to Si–OH groups. The overall reaction of oxidation with ${}^1\text{O}$ is barrierless and strongly exergonic by $387.2 \text{ kcal mol}^{-1}$.

The triplet oxygen atom, ${}^3\text{O}$, separately interacts with the surface silane to form a triplet intermediate, Im1^{B5} , which is converted into a singlet intermediate, Im2^{B5} . The subsequent pathway, going through a singlet transition state, TS1^{B5} , and forming a product, P1^{B5} , is the same as the ${}^1\text{O}$ pathway (B4), $\text{Im1}^{\text{B4}} \rightarrow \text{TS1}^{\text{B4}} \rightarrow \text{P1}^{\text{B4}}$. The singlet product, P1^{B5} , and another ${}^3\text{O}$ also form the singlet intermediate, Im2^{B3} , and enter the second oxidation pathway (B3) with ${}^1\text{O}_2$, $\text{Im2}^{\text{B3}} \rightarrow \text{TS2}^{\text{B3}} \rightarrow \text{P1}^{\text{B2}}$. In the ${}^3\text{O}$ 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 O_2 plasma and the surface, the unstable highly energetic ${}^1\text{O}$ rapidly decays to a triplet and further reacts through the ${}^3\text{O}$ pathway, according to reaction B6. Similarly, both ${}^3\text{O}$ and ${}^1\text{O}$ can produce singlet oxygen molecules, which enter the ${}^1\text{O}_2$ pathway. When all active oxygen species are converted into the triplet oxygen molecules, ${}^3\text{O}_2$, 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, ${}^3\text{O}_2$, is inactive towards surface silane groups, similar to ordinary oxygen gas. However, the other three species, ${}^1\text{O}_2$, ${}^1\text{O}$, and ${}^3\text{O}$, are active and can strongly oxidize surface silane groups through one-step or stepwise pathways.

In summary, DFT calculations have been used to investigate self-catalysis by aminosilane and the mechanism of oxidation by 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 $57.8 \text{ kcal mol}^{-1}$. The introduction of BDMAS can reduce the activation free energy to $11.0 \text{ kcal mol}^{-1}$, and aminosilane plays the role of a self-catalyst in Si–O formation through the relevant half-reaction involving its amino ligand. Among the various species in O_2 plasma, ${}^3\text{O}_2$ is inactive. ${}^1\text{O}_2$, ${}^1\text{O}$, and ${}^3\text{O}$ are active and can strongly oxidize the surface

silane groups. Oxidation by $^1\text{O}_2$ proceeds by two pathways: one-step and stepwise processes. Both ^1O and ^3O can gradually oxidize two Si-H bonds. In the ^3O pathway, the triplet must be converted into a singlet and then follow the ^1O pathway. Due to strong interactions between the active species and the surface, highly energetic ^1O can decay to ^3O and then follow the relevant ^3O pathway. Both ^3O and ^1O can produce $^1\text{O}_2$ 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 .

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 (2014M551556), Open Project of National Laboratory of Solid State Microstructures (M27009), and Zhejiang Provincial Natural Science Foundation of China (LY13B030005). We thank Professor Jing Ma of Nanjing University for discussion and the High Performance Computing Center of Nanjing University for providing the computing resources. Ai-Dong Li is also grateful for the support of the Doctoral Fund of the Ministry of Education of China (20120091110049) and the Priority Academic Program Development (PAPD) in Jiangsu Province.

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