

Non-Aqueous Routes to Metal Oxide Thin Films by Atomic Layer Deposition**

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The controlled deposition and growth of high-purity metal oxide thin films on various supports has tremendous implications not only in fundamental fields, such as surface science, but also in applied fields. In microelectronics, for example, new processes, methods, and approaches towards the production of ultrathin metal oxides are sought after. The main aim is to replace, in the near future, the ubiquitous gate oxides in field-effect transistors. Reduction of the equivalent gate-oxide thickness (EOT) has emerged as the most difficult challenge associated with future device scaling.^[1,2] To meet the strict leakage-current requirements in low-power applications, the introduction of higher-dielectric-constant materials, in which the tunneling current can be suppressed while maintaining the drain current, will be necessary. Therefore, improving the deposition processes to control the silicon/metal interface is indispensable.^[3]

A noble and economic process for the formation of oxide thin films is atomic layer deposition (ALD). ALD is a form of chemical vapor deposition (CVD) in which the reaction between precursor materials is separated into successive surface reactions. In this manner, the precursor materials remain separated until the adsorbed species react at the

surface in a self-limiting process,^[4,5] that is, without the presence of a gas-phase reaction. As a consequence, ALD offers excellent surface conformity. Inherent to the process is the possibility to accurately control the thickness of the deposited film at an almost atomic level by simply counting the number of deposition cycles.

Usually, the deposition of oxide thin films by means of ALD is achieved via hydrolytic reactions in which a transition-metal precursor (for example, a halide, an amide or an alkoxide) is reacted with water. Upon hydrolysis and condensation, a metal oxide network is built. General limitations of the traditional approach mainly reside in the presence of undesired impurities, which range from unreacted carbon species to halides. Therefore, a follow-up postsynthetic heat treatment is required to improve the quality of the film.

Even though recent studies have demonstrated that H-terminated Si(001) surfaces are stable against oxidation by water at temperatures up to 300 °C,^[6,7] metal oxide thin films grown by means of ALD on Si(001) substrates usually present an oxidized interfacial layer (silica or silicates), except in particular cases.^[8] Similar problems occur in other common ALD processes that employ stronger oxidizing agents, such as ozone.

To date, only a few alternative routes based on nonoxidizing agents have been proposed to ALD. Amongst these, the most successful depositions were reported for the reaction of metal alkoxides with metal halides,^[9] in which the metal oxide is formed via an alkyl halide elimination. The formation of silica and silicates based on metal alkylamide and alkoxysilanol species has also been reported.^[10,11]

Taking a closer look at the chemistry, it is noticed that the evolution of ALD follows a development which is similar to that of sol-gel chemistry. In both cases, approaches were pursued to improve the metal oxide formation, either by modifying the precursor^[12,13] or by using alternative non-hydrolytic reactions.^[9,14–17]

Inspired by non-aqueous sol-gel routes for the formation of metal oxides in solution, we introduce herein a new approach for the ALD of metal oxide films. This approach is based on the reaction between a metal alkoxide and a carboxylic acid on a substrate at temperatures between 50 and 350 °C. The main advantages of this procedure are: 1) the low oxidative character of carboxylic acids, 2) a large deposition-temperature range, and 3) the high-quality and purity of the films. Moreover, the low-temperature process avoids decomposition of the precursor and enables a self-limiting growth. It should be noted that this has not been achieved so far for the ALD of hafnia from alkoxides and water.^[18,19] In fact, the depositions of hafnia and titania according to the present

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approach with acetic acid as the oxygen source show typical ALD windows between 175–250 and 150–200 °C, respectively (see Figure 1). In these temperature ranges, the growth-per-cycle (GPC) values are constant (namely, 0.5 and

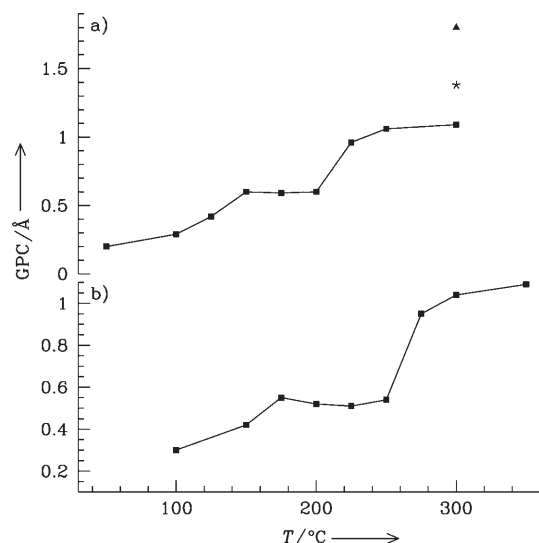


Figure 1. Growth per cycle (GPC) of a) titania deposited on a silicon substrate (using acetic acid) as a function of the temperature. At 300 °C, the GPC is modulated by the opening time of the alkoxide valve (■: 1 s, *: 1.5 s, ▲: 2 s). b) Analogous results for hafnia.

0.6 Å cycle⁻¹, respectively) and are in agreement with the values usually observed for these oxides.^[20–23] However, at temperatures above 250 °C (for hafnia) and 200 °C (for titania), the decomposition of the metal alkoxide species begins, thus leading to an increase in the GPC. At such high temperatures, the ALD regime is no longer sustained and the GPC depends on the amount of alkoxide introduced (see Figure 1a, experimental points at 300 °C). In the ALD window, the trend of the GPC as a function of the opening time further proves the self-limiting behavior. In fact, at 200 °C, the GPC achieves a steady regime at an opening time of 0.4 s (see Figure 2) and does not increase further. Similar results were obtained by replacing acetic acid with formic acid (see Table 1 in the Supporting Information). However, because of the higher reactivity and lower temperature stability of formic acid, the ALD window is narrower and shifted towards lower temperatures.

To demonstrate the versatility of the process, a wide range of materials have been coated; these materials include carbon nanotubes (CNTs); wool and cellulose fibers; and Si and monocrystalline oxide substrates (that is, LaAlO₃, SrTiO₃). Scanning electron microscopy (SEM) images of the CNTs after ALD of titania are shown in Figure 3A. At a medium resolution, the tubes reveal a smooth surface, whereas at a higher resolution, a texturing can be observed. The inset in Figure 3A shows a region of a single tube with defects in the coating, thereby exposing the carbon underneath.^[24] CNTs were also coated with HfO₂. Again, a tube with a partly defective coating was selected to demonstrate that they are indeed coated (see Figure 3B). The tubes are also coated

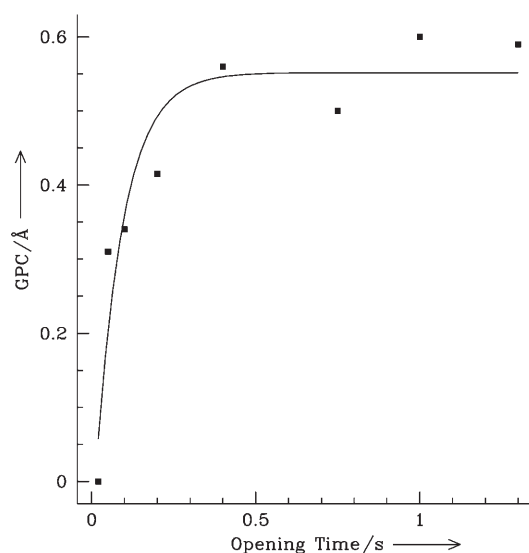


Figure 2. GPC of titania as a function of the opening time of the alkoxide valve (at 200 °C).

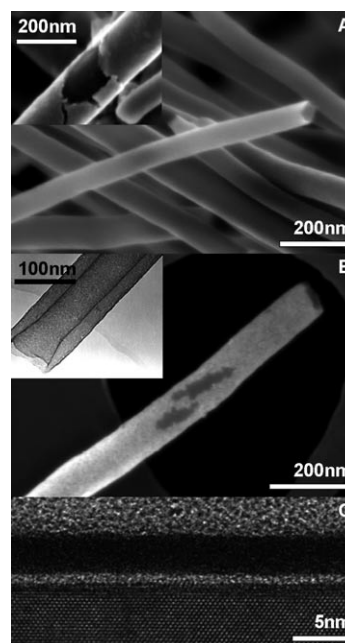


Figure 3. SEM image of carbon nanotubes coated with A) titania and B) hafnia, both deposited at 200 °C. The insets show high-resolution SEM and TEM images, respectively. C) HRTEM image of a 3.5-nm thick hafnia film on Si(001) (deposited at 225 °C).

inside, as is evidenced in the transmission electron microscopy (TEM) image by the high contrast at the outer and inner walls of the tube (see inset of Figure 3B and the Supporting Information). Finally, in Figure 3C, a high-resolution TEM (HRTEM) image of the cross-section of an unprocessed Si(001) wafer coated with HfO₂ is presented. The thickness of the amorphous SiO₂ film after deposition is only 0.7 nm, which roughly corresponds to the thickness of the native surface oxide layer of unprocessed Si wafers. The as-deposited

metal oxide thin films were amorphous, as demonstrated by the HRTEM results where the 3.5-nm-thick HfO_2 layer shows no evidence of crystallinity (Figure 3C). The amorphous character of the films was also evidenced by means of X-ray diffraction measurements performed on various films deposited on silicon and selected-area electron diffraction spectra recorded on coated carbon nanotubes (not shown).

The chemical composition of the metal oxide films deposited on silicon substrates was analyzed by using X-ray photoelectron spectroscopy (XPS) whereas that of the films formed on carbon nanotubes was studied by means of energy dispersive X-ray spectroscopy (EDX) and EDX mapping (see Figures 2–4 in the Supporting Information). The experiments show that metal oxides are formed and XPS, in particular, proves that they possess a low content of carbon impurities.

Electrical measurements were performed to demonstrate the quality of the films. All measurements were carried out on approximately 10-nm-thick films deposited at temperatures between 100 and 350 °C (without postgrowth treatment). With increasing deposition temperature, the global relative dielectric constant (ϵ_r) rises from 12.5 to 21.3 for hafnia and from 11.5 to 43 for titania, thus confirming the good quality of the films (see Table 1 in the Supporting Information).

We have demonstrated that the applied process leads to ALD growth of high-quality films. In the following, we will discuss the chemical mechanisms taking place during deposition.

The reaction between metal alkoxide compounds and carboxylic acids is found in organic chemistry for the production of esters^[25] and in sol–gel chemistry for modifying the reactivity of alkoxides.^[13] According to recent work on direct esterification, the reaction of equimolar amounts of carboxylic acid and alcohol compounds is achievable in the presence of hafnium alkoxides and other metal salts which act as catalysts.^[25] The Lewis acidity of the metal center is responsible for the catalytic activity in direct esterification reactions. In traditional sol–gel chemistry, the reaction of an alkoxide with a carboxylic acid immediately leads to a mixed alkoxide–carboxylate complex via a rapid and exothermic ligand exchange, which is then followed by metal-oxo-cluster formation.^[26] Indeed, an esterification reaction takes place between free carboxylic acid and the released alcohol molecules. Hence, the water produced in situ induces hydrolysis and condensation and leads to the formation of oxo bridges. A possible secondary mechanism was also proposed, namely, an intramolecular esterification that takes place in the coordination sphere of the metal and leads to a hydrolyzed precursor. However, since the products of both mechanisms are the same, the intramolecular esterification could not be experimentally verified.^[26–28]

To explore the mechanism behind the proposed ALD process, the reaction products were analyzed by means of ^{13}C and ^1H nuclear magnetic resonance (NMR) and gas-chromatography-coupled mass spectrometry (GC-MS). As expected, the unreacted precursors, the alcohol, and the corresponding ester were detected. Since the ester can also be subsequently formed on trapping of the products, the NMR and GC-MS experiments do not conclusively elucidate the reaction mechanism. However, it is evident that a surface reaction of

the metal alkoxide with the carboxylic acid is responsible for the growth of the metal oxide film.

Indeed, 1) the presence of an ALD window (Figure 1) rules out the decomposition of the metal alkoxide in that temperature range.^[12,29] 2) Reactions of carboxylic acid compounds with metal oxide surfaces were extensively studied in ultrahigh vacuum. It is generally accepted that the carboxylic acids adsorb dissociatively.^[30,31] Here, no clean oxide surfaces are directly exposed, and thus, reactions can only take place with the adsorbed species.^[32] 3) The reaction of titanium isopropoxide and acetic acid in an autoclave at temperatures up to 180 °C leads to the quantitative formation of isopropyl acetate and—at low yield—to the precipitation of nanocrystalline titania (see the Supporting Information).

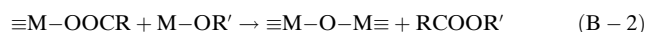
Based on the above observations, the most plausible mechanism involves an esterification reaction.^[33]

There are two possible mechanisms by which the carboxylic acid can react with the metal precursor in an ALD process. When the carboxylic acid is introduced, it can react either by A) a one-step esterification reaction between the alkoxide ligands on the surface and the acid, thereby producing hydroxy groups [see reaction (A-1)], or B) the replacement of the alkoxy ligands by carboxylate groups under the elimination of an alcohol [see reaction (B-1)].



Here, \equiv stands for any kind of ligand (for example, OR' , OH , OOR , OM) coordinated to the metal M , R stands for H or CH_3 , and R' is an alkyl group.

In the next step, when the metal precursor is introduced, it can react with the hydroxylated surface species (mechanism A), thus leading to the formation of metal–oxygen–metal bonds under the elimination of an alcohol [reaction (A-2)]. Alternatively, in the case of mechanism B, a reaction with the carboxylate surface species takes place under the elimination of an ester [reaction (B-2)]:



Additional secondary condensation reactions can occur during a complete ALD cycle, for example, 1) the condensation of two adjacent surface $\text{M}-\text{OH}$ groups, thereby forming an $\text{M}-\text{O}-\text{M}$ bond under the elimination of water, 2) the condensation of adjacent surface $\text{M}-\text{OH}$ and alkoxy groups ($\text{M}-\text{OR}'$) under the elimination of alcohol [$\text{R}'\text{OH}$, similar to reaction (A-2)], and 3) the condensation of two adjacent surface alkoxy groups under the elimination of ether. The secondary reactions (1) and (2) require the previous formation of hydroxy species and can therefore only take place in the case of the first mechanism (A-1). Regarding the side reaction (3), it was recently shown that ether elimination is responsible for the formation of hafnia nanoparticles from an alkoxide precursor in benzyl alcohol.^[34] To rule out ether elimination, we conducted an ALD control experiment using

only metal alkoxide as the precursor. No film growth was observed under these conditions. This result confirms that ether elimination according to secondary reaction (3) is unlikely and that a carboxylic acid is definitively required for thin-film formation. Furthermore, no ether was detected by means of NMR and GC-MS studies.

To determine whether the process followed mechanism A or B, we gained additional insights into the kinetics of film formation by monitoring the film GPC as a function of the valve opening time and the residence time of the precursors inside the chamber. In the case of acetic acid, it was observed that the pause between the acid pulse and the purging did not influence the GPC. On the other hand, for the metal alkoxide precursor introduced in the second step, a pause of several seconds was required to complete the reaction and reach the nominal GPC value (namely, 0.5–0.6 Å per cycle).

This behavior supports a reaction according to mechanism B. The modification of an alkoxide by a carboxylic acid [such as in reaction (B-1)] is fast and does not require a thermal activation.^[26] In contrast, the ester elimination process [reaction (B-2)] that takes place between the carboxylate ligands at the surface of the film and the metal alkoxide is much slower, which is in agreement with the experimental observations. If the reaction would follow the path proposed in mechanism A, the opposite behavior would be expected because the hydroxy groups are very reactive towards alkoxide species.^[35] In that case, the required residence time for the alkoxide precursor in the second step would be shorter. Based on the above reasoning, we conclude that a surface esterification reaction consistent with mechanism B is responsible for the growth of the metal oxide films.

In conclusion, the only condition required to deposit oxide thin films by using the present method appears to be the reaction of a carboxylic acid with a metal alkoxide. Hence, the process might be extended to a large variety of metal oxides. The non-aqueous chemistry involved allows the growth of high-quality metal oxide films—even at very low temperatures—without the need of oxidizing agents. Moreover, these findings do not only bring new insights into the fields of thin films, but they also contribute to the understanding of sol–gel chemistry and ester synthesis (an industrially relevant area). This ALD process can be regarded as a model system for the mechanistic study of the Lewis acid catalysis in the esterification reaction by metal salts. The elucidation of these reaction mechanisms will probably allow the development of new catalysts based on a more fundamental understanding.

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