

## Review

# Formation of Metal Oxide Particles in Atomic Layer Deposition During the Chemisorption of Metal Chlorides: A Review

By Riikka L. Puurunen\*

As has been known for a decade, metal oxide particles can form in a single reaction of gaseous metal chlorides with solid oxides. This is an undesirable effect in the fabrication of thin films by atomic layer deposition (ALD). This work reviews the experimental results related to the metal oxide particle formation and the mechanisms suggested to account for it. The suggested mechanisms cannot explain the observations, but systematic analysis of the possible reaction paths delivers one reaction mechanism candidate, based on a reaction between surface chlorine groups and the hydroxyl groups of gaseous metal hydroxychloride intermediates. The consequences of the proposed mechanism are discussed.

Keywords: Atomic layer deposition, Growth per cycle, Hydroxychloride, Metal chloride, Particle formation

## 1. Introduction

Atomic layer deposition (ALD) is a materials growth technique suitable for manufacturing inorganic material layers, with thickness down to a fraction of a monolayer.<sup>[1–3]</sup> ALD permits the coating of extremely complex shapes with a conformal material layer of high quality, which is unique amongst thin film deposition techniques.<sup>[1–5]</sup> Consequently, materials produced using ALD have a wide range of present and future applications, from catalysts to electroluminescent displays to microelectronics and beyond.<sup>[1–4]</sup>

ALD is based on sequentially applied, self-terminating gas–solid reactions.<sup>[1–5]</sup> Self-terminating gas–solid reactions

refer to irreversible saturating chemisorption, where multilayer adsorption should, by definition, be excluded. Most metal reactants used in ALD fulfill the criteria of self-termination and adsorption in a monolayer. In the reaction of metal chloride reactants ( $MCl_n$ ) with solid oxide materials, however,  $MO_{n/2}$  particles can form in a single saturating reaction of  $MCl_n$ ,<sup>[6–12]</sup> and so multilayer formation occurs.

The first report of  $MO_{n/2}$  particle formation in  $MCl_n$  chemisorption seems to date from 1992, when Kooyman et al.<sup>[6]</sup> observed  $TiO_2$  particles after the reaction of  $TiCl_4$  with silica crystals. The particles were 0.2–3  $\mu m$  in size and were chemically anchored to the silica substrate.<sup>[6]</sup> In ALD investigations,  $MO_{n/2}$  particle formation was first reported in 1993 by Haukka et al.,<sup>[7]</sup> who discovered  $TiO_2$  particles, or “ $TiO_2$  agglomerates” as they called them, after the chemisorption of  $TiCl_4$  on porous high surface area silica.<sup>[7]</sup> Haukka et al.<sup>[8]</sup> examined the particle formation in more detail, and found the  $TiO_2$  particles to be thin and plate-like, with maximum dimensions of about 2  $\mu m$ , which findings were in accord with the report by Kooyman et al.<sup>[6]</sup> Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the  $TiO_2$  particles measured by Haukka et al.<sup>[8]</sup> are shown in Figures 1 and 2. These authors concluded that the  $TiO_2$  formation is saturating and limited by the number of hydroxyl groups on the silica substrate; confirmed that the  $TiO_2$  particles are bonded to the silica substrate; and found that the process conditions, such as reaction temperature and silica heat treatment temperature, affect the size and crystallinity of the particles. The authors suggested that the  $TiO_2$  particles

[\*] Dr. R. L. Puurunen<sup>[+]</sup>  
Interuniversity Microelectronics Center (IMEC vzw)  
Kapeldreef 75, B-3001 Leuven, (Belgium)  
E-mail: riikka.puurunen@iki.fi

Dr. R. L. Puurunen<sup>[+]</sup>  
University of Leuven (K.U. Leuven), INSYS  
Kasteelpark Arenberg, B-3001 Leuven, (Belgium)

[+] Present Address: VTT Technical Research Center of Finland,  
P.O. Box 1208, FI-02044 VTT, Finland.

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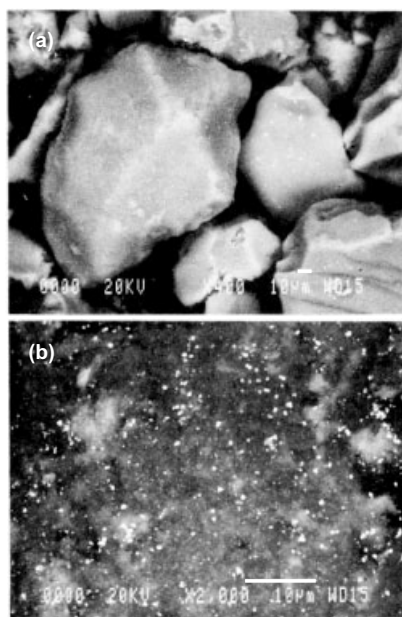


Fig. 1 Backscattered electron micrographs of the external surface of high surface area silica particles, heat-treated at 450 °C, after the saturating reaction of  $\text{TiCl}_4$  at 450 °C.  $\text{TiO}_2$  particles are seen as white spots inside the silica particles. Panel (b) is an enlargement of the surface of the largest silica particle shown in panel (a). A more detailed image of  $\text{TiO}_2$  particles is shown in Figure 2. (Reprinted with permission from Haukka et al. [8]. Copyright 1993 American Chemical Society.)

originated from the formation and decomposition of volatile hydroxychloride intermediates  $\text{Ti}(\text{OH})_m\text{Cl}_{4-m}$  ( $m = 1-3$ ).

In 1993, Ritala et al.<sup>[13,14]</sup> also reported unexpected observations when they investigated the growth of  $\text{TiO}_2$  on flat oxide substrates by the  $\text{TiCl}_4/\text{H}_2\text{O}$  ALD process. They reported surface roughening in the beginning of the ALD growth and interplay between two substrates of different chemical composition, which were simultaneously present in the ALD reactor. To explain the interplay between the substrates, some gas-phase migration processes needed to be assumed.<sup>[13,14]</sup> Recently, Elam et al. and Graugnard et al. again observed  $\text{TiO}_2$  particles to form in the  $\text{TiCl}_4/\text{H}_2\text{O}$  process.<sup>[15,16]</sup> In 1996, Kytöki et al.<sup>[9]</sup> reported the existence of  $\text{ZrO}_2$  particles when they investigated the  $\text{ZrCl}_4$  chemi-

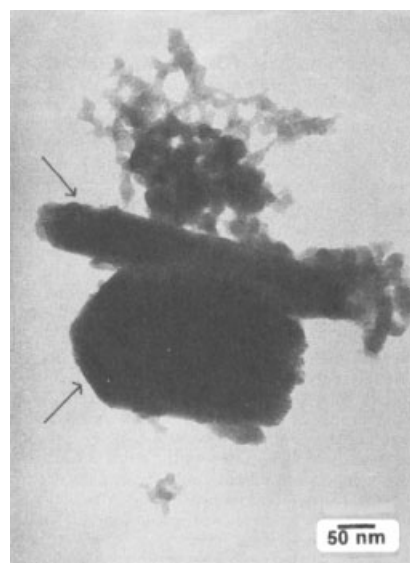


Fig. 2. Bright field transmission electron micrograph of ground high surface area silica particles that support  $\text{TiO}_2$  particles. The  $\text{TiO}_2$  particles are indicated by arrows. (Reprinted with permission from Haukka et al. [8]. Copyright 1993 American Chemical Society.)

sorption on porous high surface area silica and alumina. Compared to the  $\text{TiO}_2$  particles observed on high surface area substrates, the  $\text{ZrO}_2$  particles were considerably smaller, with dimensions in the order of 10 nm.<sup>[10]</sup> Kytöki et al.<sup>[9]</sup> suggested that the  $\text{ZrO}_2$  particles could originate from the formation and decomposition of hydroxychloride  $\text{Zr}(\text{OH})_m\text{Cl}_{4-m}$  or oxychloride  $\text{ZrOCl}_2$  intermediates. Kytöki and Haukka<sup>[11]</sup> showed, by infrared measurements, that the  $\text{TiO}_2$  and  $\text{ZrO}_2$  particles are bonded to the silica substrate through Si–O–Ti and Si–O–Zr bonds, respectively. The fact that Si–O–Ti bonds form is supported by the infrared measurements of Lebeda et al.<sup>[17]</sup>

The presence of  $\text{MO}_{n/2}$  particles after  $\text{MCl}_n$  chemisorption indicates that multilayers have formed and deviation from ideal ALD has occurred. While formation of metal oxide particles during the reaction of metal chlorides with oxide substrates may be useful for some applications, the particle formation can ruin the atomic scale conformality and thickness uniformity of films produced by ALD. Dis-



*Riikka Puurunen was born in Pori, Finland, in 1974. She received her degree of Master of Science in Technology in 1998 and that of Doctor of Science in Technology in 2002 from Helsinki University of Technology, Finland. Her doctoral research, carried out in collaboration with Professor Krause and Fortum Oil and Gas Oy, dealt with the preparation of catalysts by atomic layer deposition (ALD). During 2003–2004, she was a post-doctoral fellow at the Interuniversity Microelectronics Center (IMEC), Leuven, Belgium, modeling ALD especially for high- $\kappa$  gate dielectric applications. In October 2004, she joined the MEMS technology group at the VTT Technical Research Centre of Finland. Her general scientific interest is in understanding the physicochemical processes that control the growth of materials in ALD. She is the first author of fifteen experimental and theoretical articles on ALD.*

continuities in these films may follow, adversely affecting the performance of the films in microelectronic devices. Understanding how the metal oxide particles form is, therefore, of the utmost importance in order that, in time, their formation may be prevented.

This work reviews the experimental results and the mechanisms suggested to result in metal oxide particle formation. For background, the more conventional reactions that occur during metal chloride chemisorption are summarized. None of the mechanisms suggested so far can account for the experimental observations of metal oxide particle formation. A mechanism that could account for the experimental observations is systematically sought. One suitable mechanism, based on the ligand exchange reaction typical for ALD with hydroxyl and chlorine groups as reactive sites, is found. The consequences of the newly proposed mechanism are discussed.

## 2. Reactions of Metal Chlorides with Oxide Substrates

In this section, the reactions of metal chlorides with oxide substrates are reviewed. The conventional reactions are discussed in Section 2.1., after which the most important experimental observations relating to metal oxide particle formation are summarized in Section 2.2. Finally, the mechanisms proposed to explain metal oxide particle formation are reviewed in Section 2.3. The  $\text{TiCl}_4$  reaction will be used as a representative example of the reactions of metal chlorides, both related to conventional chemisorption reactions, as well as to metal oxide particle formation, because the chemisorption of  $\text{TiCl}_4$  on oxides has been extensively investigated on both high surface area substrates,<sup>[2,7,8,11,17–39]</sup> and flat substrates.<sup>[13,14, 40–50]</sup>

### 2.1. Summary of the More Conventional Reactions

Ligand exchange, dissociation, association, and secondary reactions of HCl can be considered as the more conventional chemisorption mechanisms.<sup>[5]</sup> These reactions are summarized schematically in Figure 3 and their characteristics are discussed in the following subsections.

#### 2.1.1. Ligand Exchange

The so-called ligand exchange reaction of  $\text{TiCl}_4$  with surface  $\text{—OH}$  groups (Figure 3, scheme Ia–c) is generally accepted to occur. In this reaction, the O–H bond is broken. The hydrogen atom of a  $\text{—OH}$  group combines with a chlorine of the  $\text{TiCl}_4$  molecule, releasing HCl, while the remaining parts of the  $\text{TiCl}_4$  molecule are bonded to the surface, forming a  $\text{—O—TiCl}_3$  species. Ligand exchange reaction has been proposed to occur with one,<sup>[7,17,20,34,35]</sup> two,<sup>[7,17,20,34,35]</sup> or maybe even three<sup>[2,17–19,34]</sup>  $\text{—OH}$  groups at the same

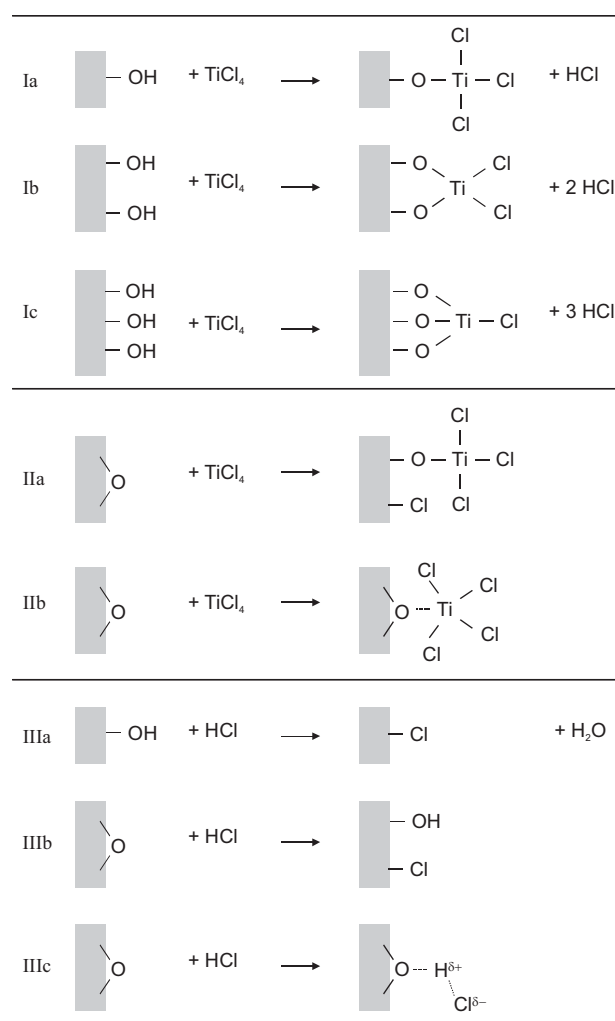


Fig. 3. Summary of the different reactions that may be involved during the chemisorption of  $\text{TiCl}_4$  on oxide substrates: (I) ligand exchange of  $\text{TiCl}_4$  with one (Ia), two (Ib), or three (Ic) OH groups; (IIa) dissociation of  $\text{TiCl}_4$  in oxygen bridges; (IIb) association of  $\text{TiCl}_4$  on surface oxygen sites (oxygen in siloxane bridges (as shown) or in hydroxyl groups); (III) secondary reactions of HCl through ligand exchange with OH groups (IIIa), dissociation in oxygen bridges (IIIb), or association in surface oxygen sites (IIIc). The structures are simplified for clarity; in reality,  $\text{Ti}^{4+}$  is likely to have a coordination number larger than four [22].

time. At room temperature, ligand exchange reaction already occurs although not all  $\text{—OH}$  groups are consumed through ligand exchange at this temperature.

#### 2.1.2. Dissociation

Dissociation of  $\text{TiCl}_4$  in oxygen bridges on silica (Figure 3, scheme IIa) has been a matter of debate. Hair and Hertl,<sup>[51]</sup> and Kinney and Staley,<sup>[26]</sup> proposed that dissociation could occur. Ellestad and Blindheim,<sup>[27]</sup> questioned the earlier conclusion, and Haukka et al.<sup>[7]</sup> excluded the occurrence of dissociation, while Schrijnemakers et al.<sup>[35,39]</sup> recently argued in its favor.

Kinney and Staley<sup>[26]</sup> investigated the reaction using infrared measurements. On the basis that significant amounts

of  $\text{TiCl}_4$  reacted before any change in the intensity of O–H stretch was observed, they proposed that the reaction initially takes place with siloxane bridges. Ellestad and Blindheim<sup>[27]</sup> however, questioned the validity of these interpretations. On the basis of a review of earlier literature, Ellestad and Blindheim concluded that, at that time, there was no evidence to favor dissociation in siloxane bridges.<sup>[27]</sup>

Hair and Hertl,<sup>[51]</sup> Haukka et al.,<sup>[7]</sup> and Schrijnemakers et al.<sup>[35]</sup> investigated the  $\text{TiCl}_4$  chemisorption on silica by chemical analysis, through measuring the Cl/Ti ratio after the reaction and comparing the amount of titanium adsorbed to the amount of  $\text{–OH}$  groups present on silica before the reaction. The results of various investigations are shown together in Table 1. Hair and Hertl<sup>[51]</sup> concluded that most of the  $\text{TiCl}_4$  reacts with one  $\text{–OH}$  group through

Table 1. Summary of the quantitative results obtained by Hair and Hertl<sup>[51]</sup>, Haukka et al.<sup>[7]</sup>, and Schrijnemakers et al.<sup>[35]</sup> for the  $\text{TiCl}_4$  chemisorption on silica.  $T_r$  indicates the reaction temperature,  $T_s$  the silica heat-treatment temperature.

Reference	Cl/Ti	Ti [nm <sup>-2</sup> ]	OH [nm <sup>-2</sup> ]	$T_r$ [°C]	$T_s$ [°C]
51	3.4	1.52	1.7	r.t. [a]	800
7	2.4	2.0	6.5	175	200
7	2.7	1.4	3.4	175	450
7	2.9	1.1	2.2	175	560
7	3.1	0.7	1.1	175	750
7	3.1	0.7	1.1	175	820
35	2.51	2.87	4.7	20	200
35	2.68	2.72	4.1	20	300
35	2.85	2.40	3.2	20	400
35	2.90	1.93	2.3	20	500
35	2.96	1.66	1.55	20	600
35	3.04	1.2	1.1	20	700

[a] r.t. = room temperature

ligand exchange (Fig. 3, scheme Ia). In addition, to account for the high chlorine content, the probable participation of chlorination (Reactions 1 and 2 below) and/or dissociation of  $\text{TiCl}_4$  was proposed. Haukka et al.<sup>[7]</sup> investigated the reaction in more detail and at higher temperatures. With increasing heat treatment of silica, and thus decreasing  $\text{–OH}$  group content, the Cl/Ti ratio increased, but did not go beyond three.<sup>[7]</sup> Using  $^1\text{H}$  NMR, Haukka et al. also measured the difference between the number of  $\text{–OH}$  groups before and after the reaction and found this to be, within analytical accuracy, the same as the amount of titanium bonded to the surface in the  $\text{TiCl}_4$  reaction. Both the Cl/Ti ratio and the  $^1\text{H}$  NMR results therefore indicated that  $\text{TiCl}_4$  needs one  $\text{–OH}$  group to react to the surface, and that dissociation of  $\text{TiCl}_4$  in siloxane bridges does not take place. Schrijnemakers et al.<sup>[35]</sup> reported similar results, as can be seen in Table 1, but their interpretation was somewhat different as they saw a Cl/Ti ratio of slightly above three and Ti contents slightly higher than the OH content of the silica as supporting the indication that dissociation did take place.<sup>[35,39]</sup> Keeping in mind that each measurement (OH, Ti, and surface area determination) has some analytical error ( $\sim 5\%$ ), the results

of Schrijnemakers et al.<sup>[35]</sup> can be interpreted to show the same trends as those of Haukka et al.,<sup>[7]</sup> however: a Cl/Ti ratio of maximum three and a Ti content no higher than the  $\text{–OH}$  group content of the substrate.

In summary, according to the experimental evidence currently available, dissociation of  $\text{TiCl}_4$  in siloxane bridges does not take place. Although  $\text{TiCl}_4$  does not dissociate on silica, dissociation might occur on other substrates. After the  $\text{TiCl}_4$  reaction with ALD-grown  $\text{TiO}_2$ , for example, Cl/Ti ratios up to four have been measured, and dissociation has been suggested.<sup>[50]</sup>

### 2.1.3. Association

Association of  $\text{TiCl}_4$  on surface oxygen sites (Fig. 3, scheme IIb) has generally not been considered as a possible reaction path for  $\text{TiCl}_4$  chemisorption on silica. Moreover, its occurrence can be excluded on the basis of the same considerations through which dissociation of  $\text{TiCl}_4$  on silica was excluded.

Association has been proposed to occur on substrates other than silica, for example in the  $\text{TiCl}_4$  chemisorption on  $\text{TiO}_2$ .<sup>[50]</sup> On alumina, association of  $\text{TiCl}_4$  has been excluded, however.<sup>[28]</sup> Quantum chemical calculations indicate that associated complexes can be energetically favorable for  $\text{ZrCl}_4$ <sup>[52,53]</sup> and  $\text{HfCl}_4$ ,<sup>[54]</sup> at least when the surface oxygen is in a hydroxyl group.<sup>[52–54]</sup>

### 2.1.4. Secondary Reactions of HCl

Secondary reactions of HCl, released in ligand exchange (Fig. 3, scheme I), may occur simultaneously with the  $\text{TiCl}_4$  reaction. HCl could compete to react with the same sites as  $\text{TiCl}_4$ , with surface  $\text{–OH}$  groups and oxygen bridges (Fig. 3, schemes IIIa–c). Secondary reactions of HCl are not ideal in ALD since they can cause concentration or thickness gradients in ALD-grown thin materials.<sup>[33,45,46,55,56]</sup> Moreover, secondary reactions of HCl increase the Cl/Ti ratio on the surface and therefore complicate the analysis of reaction mechanisms (ligand exchange vs. dissociation or association) from the Cl/Ti ratio.

Haukka et al.<sup>[7]</sup> investigated the reaction of HCl on pure silica to evaluate its importance as a secondary reaction during  $\text{TiCl}_4$  chemisorption. Below 350 °C, the effect of HCl adsorption was found to be negligible.<sup>[7]</sup> Its importance increased with increasing temperature (at temperatures up to 350 °C, the chlorine content after a HCl reaction with silica remained below 0.1 nm<sup>-2</sup>; at 450 °C it was about 0.5 nm<sup>-2</sup>; and at 550 °C it was about 1.0 nm<sup>-2</sup>).<sup>[7]</sup> According to  $^1\text{H}$  NMR, HCl reacted at 450 °C only with  $\text{–OH}$  groups; no dissociation or association on oxygen sites occurred.<sup>[7]</sup>

Secondary reactions of HCl may be more pronounced on substrates other than silica. On alumina, HCl already adsorbs at 200 °C and continues to do so up to at least 600 °C.<sup>[57]</sup> HCl may also adsorb on  $\text{TiO}_2$  during ALD growth.<sup>[45,46]</sup>



## 2.2. Key Observations Related to $\text{MO}_{n/2}$ Particle Formation

Key experimental observations related to the formation of  $\text{TiO}_2$  and  $\text{ZrO}_2$  particles during a single saturating  $\text{TiCl}_4$  or  $\text{ZrCl}_4$  reaction with oxide substrates, corresponding to one ALD half reaction, are summarized below.

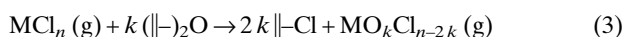
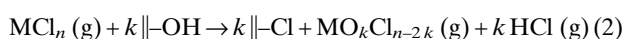
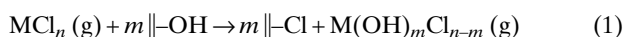
- #1. Whether  $\text{TiO}_2$  particles form in the  $\text{TiCl}_4$  reaction with high surface area silica depends strongly on the reaction temperature. The tendency for  $\text{TiO}_2$  particle formation increases sharply at about  $300^\circ\text{C}$ ; below about  $300^\circ\text{C}$ , no  $\text{TiO}_2$  particles are observed.<sup>[7,8]</sup> The  $\text{ZrO}_2$  formation in the  $\text{ZrCl}_4$  chemisorption on high surface area substrates has a similar temperature dependency.<sup>[9]</sup>
- #2. The  $\text{TiO}_2$  particles formed in the  $\text{TiCl}_4$  reaction with high surface area silica are crystalline and have either anatase or rutile structure,<sup>[8,33]</sup> which phase is formed depending on both reaction temperature and on substrate heat-treatment temperature. Typically, anatase forms below  $350^\circ\text{C}$ , and the fraction of rutile increases with temperature.<sup>[8,33]</sup> In contrast, on high surface area alumina, rutile is observed at low temperatures and anatase at high temperatures.<sup>[33]</sup> In investigations where  $\text{TiO}_2$  has been grown on flat substrates from  $\text{TiCl}_4$  and  $\text{H}_2\text{O}$ , the phase of  $\text{TiO}_2$  has also been highly sensitive to the process parameters (e.g., type of substrate, reaction temperature, partial pressures of the reactants).<sup>[42,43,48]</sup>
- #3. The  $\text{TiO}_2$  particles formed in the  $\text{TiCl}_4$  reaction on high surface area silica have been reported to be thin and plate-like.<sup>[8]</sup>
- #4. The  $\text{TiO}_2$  particles formed in the  $\text{TiCl}_4$  reaction on porous high surface area silica are of various sizes, as demonstrated by SEM and TEM measurements.<sup>[8]</sup> It is proposed that the largest particles form in the largest pores of the silica substrate, and the smallest particles in the smallest pores.<sup>[8]</sup>
- #5. The reaction of  $\text{TiCl}_4$  with oxide substrates is saturating, at least within the range  $150\text{--}550^\circ\text{C}$ , as shown by element determinations for high surface area substrates,<sup>[7,8]</sup> and in-situ quartz crystal microbalance (QCM) measurements for flat substrates.<sup>[42,49]</sup> Therefore, the  $\text{TiCl}_4$  reaction is also saturating in the range where  $\text{TiO}_2$  particles form ( $\geq 300^\circ\text{C}$ ).
- #6. Practically all  $\text{||-OH}$  groups on high surface area silica substrates react with  $\text{TiCl}_4$  at  $450^\circ\text{C}$ ,<sup>[7,31]</sup> where  $\text{TiO}_2$  particle formation is the dominant reaction mechanism.
- #7.  $\text{HCl}$  is released during the reaction of  $\text{TiCl}_4$  with titanium dioxide at all processing temperatures ( $150\text{--}400^\circ\text{C}$ ), as seen by mass spectrometry (MS) measurements on flat substrates.<sup>[50]</sup> Other gaseous reaction products have not been detected. The hydroxychlorides or oxychlorides presumably formed in the  $\text{TiCl}_4$  reaction are therefore true short-lived reaction intermediates.
- #8. The  $\text{Cl/Ti}$  ratio measured after  $\text{TiCl}_4$  chemisorption on high surface area silica depends mainly on the reaction temperature, but also to some degree on the substrate heat-treatment temperature. At low reaction tempera-

tures ( $\sim 200^\circ\text{C}$ ), the  $\text{Cl/Ti}$  ratio is close to three.<sup>[7,8,35]</sup> With increasing reaction temperature the  $\text{Cl/Ti}$  ratio decreases until it stabilizes at two, at about  $300^\circ\text{C}$ .<sup>[7,8,35]</sup> When the reaction temperature is increased beyond  $450^\circ\text{C}$ , the  $\text{Cl/Ti}$  ratio increases above two,<sup>[8]</sup> most likely because of secondary reactions of  $\text{HCl}$ .<sup>[7]</sup> Therefore, when  $\text{TiO}_2$  particle formation is the main chemisorption mode and the  $\text{HCl}$  released has not yet re-adsorbed on the surface ( $\sim 300\text{--}400^\circ\text{C}$ ), the  $\text{Cl/Ti}$  ratio is exactly two.

- #9. The number of titanium atoms attached to the surface settles exactly to half of the amount of  $\text{||-OH}$  groups present on the surface of high surface area silica, at temperatures where  $\text{TiO}_2$  formation is the main chemisorption mode on silica ( $\geq 300^\circ\text{C}$ ).<sup>[7]</sup> The ratio of  $\text{||-OH}$  consumed to  $\text{Ti}$  attached is therefore exactly two, and the amount of  $\text{Ti}$  bonded is limited by the number of  $\text{||-OH}$  groups on the silica surface. The number of  $\text{||-OH}$  groups also limits the  $\text{ZrO}_2$  formation in the  $\text{ZrCl}_4$  reaction on high surface area silica.<sup>[9]</sup>
- #10. The  $\text{TiO}_2$  and  $\text{ZrO}_2$  particles formed in the chemisorption of  $\text{TiCl}_4$  and  $\text{ZrCl}_4$  on high surface area silica are bonded to the silica substrate through  $\text{Si-O-Ti}$  and  $\text{Si-O-Zr}$  bonds.<sup>[11]</sup>
- #11. When compared to the number of  $\text{M}$  atoms ( $\text{M} = \text{Ti}, \text{Zr}$ ) in the  $\text{MO}_2$  crystals on high surface area substrates, the number of  $\text{OH}$  groups on the  $\text{MO}_2$  crystals is low (below detection limit) after hydrolysis of the chlorine bonds.<sup>[7,9]</sup> Most likely then, the number of  $\text{Cl}$  groups on the  $\text{MO}_2$  crystals before hydrolysis is also low.
- #12. Mass balance is valid in the  $\text{TiCl}_4$  reaction on high surface area silica, indicating that no intermediate hydroxychloride or oxychloride species are formed from  $\text{TiCl}_4$  that would escape from porous high surface area silica.<sup>[8]</sup>

## 2.3. Reaction Mechanisms Proposed for $\text{MO}_{n/2}$ Particle Formation

For metal oxide particles,  $\text{MO}_{n/2}$ , to form in the reaction of  $\text{MCl}_n$ , oxygen must somehow be transported from the oxide substrate to the  $\text{MO}_{n/2}$  particles. Intermediate volatile hydroxychlorides,  $\text{M}(\text{OH})_m\text{Cl}_{n-m}$ ,<sup>[4,7-10,12,14,36,42,49,50,58]</sup> or oxychlorides,  $\text{MO}_k\text{Cl}_{n-2k}$ ,<sup>[4,7,9,10,12,46,49,50]</sup> have been suggested as the means of this transport. Hydroxychlorides and oxychlorides have been proposed to form in so-called chlorination reactions, where chloride ligands of  $\text{MCl}_n$  are exchanged with surface  $\text{||-OH}$  groups,<sup>[7-12,14,42,49-51,59]</sup> or with surface oxygen bridges,  $(\text{||-})_2\text{O}$ ,<sup>[4,12]</sup> as in Reactions 1–3.



Symbol  $\text{||}$  denotes the surface, (g) refers to gas phase species, and (s) refers to a solid phase. In the chlorination

Reactions 1 and 2, at least one bond between oxygen and the surface is broken. Although chlorination Reaction 1 can be considered as one type of ligand exchange reaction, it must not be confused with the conventional ligand exchange reaction that typically occurs between  $\text{MCl}_n$  and  $\text{||-OH}$  groups (reactions 1a–c in Fig. 3).  $\text{Ti}(\text{OH})_2\text{Cl}_2$  can be released in the reaction of HCl with  $\text{TiO}_2$ ,<sup>[60,61]</sup> and  $\text{COCl}_2$  forms in the reaction of  $\text{CCl}_4$  with silica.<sup>[51]</sup> Both hydroxychloride and oxychloride molecules (or even hydroxyoxychlorides) could be reasonable intermediates in the formation of metal oxide particles.

Kooyman et al.<sup>[6]</sup> did not propose any mechanism for particle formation. Haukka et al.<sup>[8,32]</sup> suggested that  $\text{TiO}_2$  particles form in the decomposition of the intermediate hydroxychloride species in the vicinity of siloxane bridges. This suggestion originates from considering two types of surface sites, hydroxyl groups and oxygen bridges, as possible bonding sites.<sup>[8]</sup> All hydroxyl groups were concluded to have been consumed, either by chlorination or ligand exchange with  $\text{TiCl}_4$ .<sup>[8]</sup> This left oxygen bridges as the only possible bonding site.<sup>[8]</sup> The scheme proposed by Haukka et al.<sup>[8,32,62]</sup> is summarized in Figure 4.

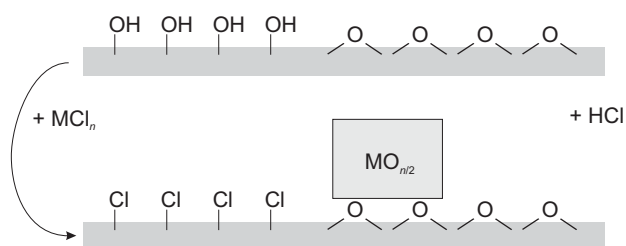
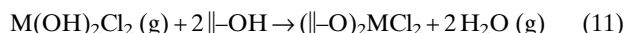
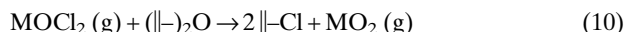
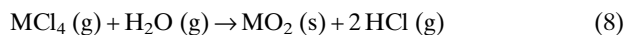
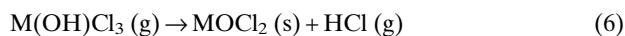
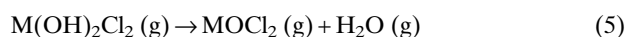
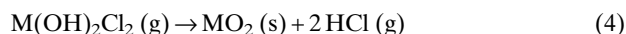


Fig. 4. Scheme for the  $\text{MO}_{n/2}$  particle formation, as reported by Haukka et al.<sup>[32]</sup>.  $\text{MO}_{n/2}$  grows on oxygen bridges.

Kytökiivi et al.<sup>[9]</sup> extended the suggestion of Haukka et al. to the formation of  $\text{ZrO}_2$  in  $\text{ZrCl}_4$  chemisorption on silica and alumina. On alumina, there are no siloxane bridges, but rather coordinatively unsaturated (c.u.s.) Al–O pairs.<sup>[63]</sup> Coincidentally, Kytökiivi et al.<sup>[9]</sup> suggested the decomposition would occur in the vicinity of the c.u.s. Al–O pairs. Moreover, in addition to hydroxychlorides, oxychlorides were proposed as reaction intermediates.<sup>[9]</sup> Somewhat later however, on the basis of the finding that the particles are bonded to the surface through Si–O–M bonds ( $\text{M} = \text{Ti}, \text{Zr}$ ),<sup>[11]</sup> Kytökiivi<sup>[12]</sup> questioned the earlier conclusion. She argued that the  $\text{MO}_{n/2}$  particles cannot originate purely from decomposition, but the formation of chemical bonds between oxygen bridges and the Ti or Zr species must be involved.<sup>[12]</sup>

Many reaction mechanisms have been proposed by various authors to be involved in the  $\text{MO}_{n/2}$  formation. These reaction mechanisms are summarized in Reactions 4–11 below, for  $n = 4$ .



It has been proposed that the hydroxychloride species decompose to metal oxide (Reaction 4)<sup>[8,12,49,50,58]</sup> or to oxychloride species (Reactions 5 and 6),<sup>[7,49,50]</sup> releasing HCl (Reactions 4 and 6) or  $\text{H}_2\text{O}$  (Reaction 5). It has been suggested that gaseous oxychloride decomposes to metal oxide and the metal chloride (Reaction 7).<sup>[12]</sup> Gas phase reaction between the metal chloride and water has also been proposed (Reaction 8),<sup>[7,8,14]</sup> either with water released in a reaction of HCl with  $\text{||-OH}$  groups<sup>[7,8,13,14]</sup> or with water released in Reaction 5.<sup>[7]</sup> Reactions have been written down where gaseous oxychloride would react with  $\text{||-OH}$  groups (Reaction 9),<sup>[12]</sup> or with oxygen bridges (Reaction 10),<sup>[12]</sup> resulting in  $\text{||-Cl}$  groups and (gaseous) metal oxide. It has been proposed that the hydroxychloride species react through its OH group with  $\text{||-OH}$  groups, resulting in  $(\text{||-O})_2\text{MCl}_2$  species and the release of water (Reaction 11).<sup>[50]</sup>

Reactions 4–11, alone or in their combinations, cannot account for the observed metal oxide particle formation, particularly because of the facts that particle formation is saturating in nature and that the particles are attached to the surface through metal–oxygen bonds. In Reactions 4, 7, and 8, solid metal oxide particles form, but they are not chemically bonded to the surface. In Reaction 11, metal species are bonded to the surface through metal–oxygen bonds, but this reaction cannot account for metal oxide particle formation, because most of the  $\text{||-OH}$  groups are inevitably consumed in competing reactions by  $\text{MCl}_n$ . An alternative explanation must exist to account for the formation of metal oxide particles in the chemisorption of metal chloride reactants.

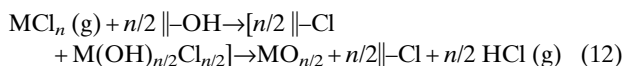
### 3. New Mechanism for $\text{MO}_{n/2}$ Particle Formation

The objective is to find and to evaluate a reaction mechanism that could account for the formation of  $\text{MO}_{n/2}$  particles in the  $\text{MCl}_n$  chemisorption, so that the experimental observations listed in Section 2.2 are fulfilled. Section 3.1 systematically lists the possible reaction mechanisms. The one candidate reaction, possibly accounting for the  $\text{MO}_{n/2}$  particle formation, is analyzed in Section 3.2. The candidate reaction is in accord with the experimental observations, as discussed in Section 3.3.

### 3.1. Possible Reaction Mechanisms

Let us start by considering the three mechanisms suggested to result in the formation of volatile hydroxychloride or oxychloride molecules and the chlorination of the surface (Reactions 1–3). In Reactions 1 and 2, the hydroxychloride and oxychloride molecules form in a reaction with surface hydroxyl groups, whereas in Reaction 3, oxychloride molecules form in a reaction with oxygen bridges. The number of hydroxyl groups is known to control the amount of metal adsorbed (#9). On that basis, the occurrence of Reaction 3 can be excluded. We can now restrict consideration to Reactions 1 and 2 as possible initial steps in  $\text{MO}_{n/2}$  particle formation.

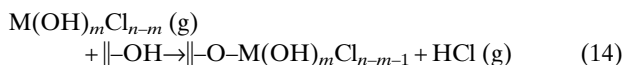
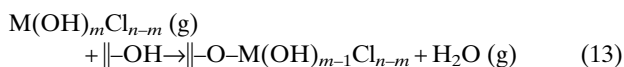
Transport of oxygen from the substrate according to Reactions 1 and 2 through intermediate hydroxychloride or oxychloride species to  $\text{MO}_{n/2}$  particles assumes the average overall stoichiometry given in Reaction 12.



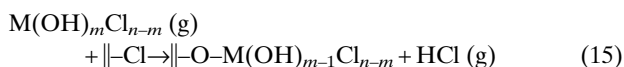
The key question is how  $\text{MO}_{n/2}$  is formed, so that the mechanism agrees with the experimental observations listed in Section 2.2.

Let us first assume that hydroxychloride molecules (from Reaction 1) act as the necessary intermediate species. Hydroxyl groups, chlorine groups, and oxygen bridges are considered as possible bonding sites, and ligand exchange, dissociation, and association are considered as possible reaction mechanisms. The possibilities are thus similar to those reviewed for the  $\text{TiCl}_4$  and  $\text{HCl}$  adsorption (Sec. 2.1). In previous investigations,<sup>[7,8,12–14,49,50,58]</sup> surface chlorine groups have not been considered as potential reactive sites.

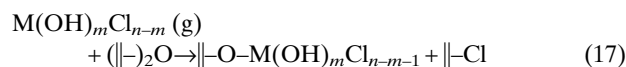
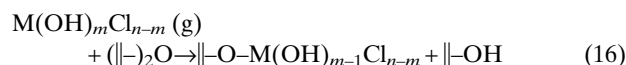
The hydroxychloride molecule can react with the bonding sites in six ways so that an oxygen–metal bond is formed. A ligand exchange reaction can occur between surface  $\text{||-OH}$  groups and the OH groups or Cl groups of the hydroxychloride molecule (Reactions 13 and 14, respectively; Reaction 13 is similar to Reaction 11).



A ligand exchange reaction also can occur between surface  $\text{||-Cl}$  groups and OH groups of the hydroxychloride molecule (Reaction 15).



Moreover, the hydroxychloride molecule can dissociate (Reactions 16 and 17) or associate (Reaction 18) on the surface.



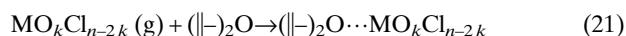
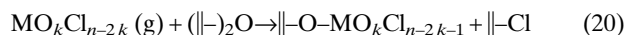
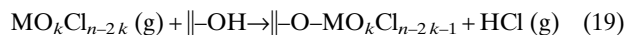
Consider the ligand exchange reaction of surface  $\text{||-OH}$  groups and the OH groups or Cl groups of the hydroxychloride (Reactions 13 and 14, respectively). The  $\text{MCl}_n$  molecules, present in the gas phase in high concentrations, also react with surface  $\text{||-OH}$  groups, through ligand exchange (Figure 3, scheme I) or chlorination (Reaction 1). That means there is inevitably competition to react with the  $\text{||-OH}$  groups (either originally present on the surface, or attached to the surface as in Reactions 13 or 14). A large portion of the  $\text{||-OH}$  groups would, in the case of competing reactions, be consumed by  $\text{MCl}_n$  rather than by  $\text{M(OH)}_m\text{Cl}_{n-m}$ . Consequently, quantitative bonding of all  $\text{M(OH)}_m\text{Cl}_{n-m}$  molecules to the surface (#12) would not be possible through Reactions 13 and 14. Moreover, because of the competing reactions, the  $\text{TiO}_2$  particles could not grow large through these reactions: a reaction of  $\text{MCl}_n$  with the surface  $\text{||-OH}$  groups would terminate the particle growth. To account for the quantitative bonding of the hydroxychloride molecules to the surface, there should exist a reaction mechanism where competitive reactions are absent.

Ligand exchange could occur between surface  $\text{||-Cl}$  groups and the OH groups of the hydroxychloride (Reaction 15). Surface  $(\text{||-O})_m\text{MCl}_{n-m}$  species, formed through the ligand exchange reaction of  $\text{MCl}_n$  (Fig. 3, scheme I) could, for example, provide the necessary surface  $\text{||-Cl}$  groups, or the  $\text{||-Cl}$  groups could come from the reverse of Reaction 1.  $\text{M(OH)}_m\text{Cl}_{n-m}$  is the only molecule present in the gas phase that can react with  $\text{||-Cl}$  groups so competing reactions are absent. Moreover, the reaction can proceed as long as  $\text{M(OH)}_m\text{Cl}_{n-m}$  molecules remain in the gas phase, as each time that surface  $\text{||-Cl}$  groups are consumed, new  $\text{||-Cl}$  groups are attached to the surface. This reaction is clearly a candidate to account for the  $\text{MO}_{n/2}$  particle formation.

Dissociation (Reactions 16, 17) or association (Reaction 18) of  $\text{M(OH)}_m\text{Cl}_{n-m}$  can also be considered. Dissociation or association are unlikely to play a role in the  $\text{MO}_{n/2}$  particle formation, however as it was concluded (Sec. 2.1) that these do not occur in the  $\text{TiCl}_4$  reaction on silica. Analogy would suggest that dissociation or association should not occur for  $\text{M(OH)}_m\text{Cl}_{n-m}$  either. Moreover, the Cl/M ratio on the surface after dissociation or association would be  $n$ , instead of the  $n/2$  observed (#8).

Let us then assume that oxychlorides (from Reaction 2) would act as the intermediate species in  $\text{MO}_{n/2}$  particle for-

mation. The double-bonded oxygen of the oxychlorides is considered to be unreactive with the bonding sites present on the substrate.<sup>[33]</sup> Therefore, oxychlorides have one type of site that can react with the surface: the Cl group. The possible reaction mechanisms are again ligand exchange (Reaction 19), dissociation (Reaction 20), and association (Reaction 21).



Ligand exchange of oxychloride intermediates with surface ||-OH groups (Reaction 19) might occur, in a manner analogous to the ligand exchange of metal chlorides (Fig. 3, schemes Ia–c) or hydroxychlorides (Reaction 14). The importance of the ligand exchange of oxychloride with ||-OH groups in the metal oxide particle formation can be excluded however, on the basis of inevitable competing reactions by  $\text{MCl}_n$ .

Dissociation or association of oxychlorides (Reactions 20 and 21, respectively) do not generally fulfill the observed Cl/M stoichiometry (#8): they give a Cl/M ratio above  $n/2$ . There is one exception that could be in accord with the observed Cl/M ratio:  $k = n/2$ . In this case however, the intermediate species would not be hydroxychlorides but gaseous metal oxide units,  $\text{MO}_{n/2}(\text{g})$ , but such species should not form at the temperatures used.

In conclusion, one two-step reaction mechanism has been found that seems to be the probable cause of the formation of metal oxide particles in the chemisorption of metal chloride reactants on oxide materials: a combination of Reactions 1 and 15.

## 3.2. Analysis of the Proposed Reaction Mechanism

The proposed mechanism to account for the growth of  $\text{MO}_{n/2}$  particles consists of two consecutive reactions, Reactions 1 and 15. The growth can be visualized as a chain reaction, where  $\text{MO}_{n/2}$  units are inserted under chlorine groups that terminate the growing particle, as illustrated schematically in Figure 5.

The proposed two-step reaction mechanism comprises two types of elementary steps, illustrated in Figure 6. The total number of required elementary steps equals the number of chlorine ligands in the metal chloride reactant ( $n$ ). In the first type of elementary step (1-\*), a chlorine ligand bonded to M is exchanged with an OH group bonded to the cation of the substrate oxide. Hydroxychloride molecules are created. In the case of  $\text{TiCl}_4$  chemisorption on silica, for example, a chlorine is transferred from titanium to silicon at the same time as a hydroxyl group is transferred

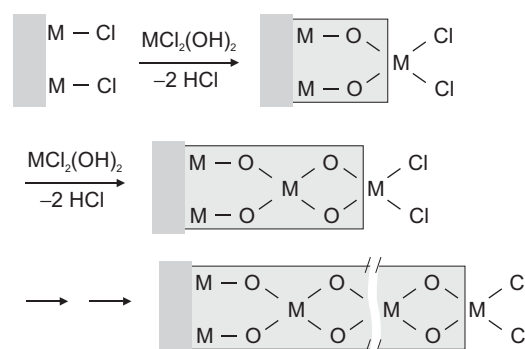


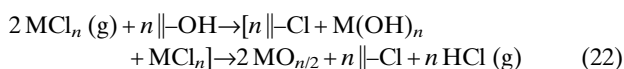
Fig. 5. Schematic summary of the mechanism proposed to result in growth of  $\text{MO}_{n/2}$  crystals in a single saturating reaction of  $\text{MCl}_n$  with oxide substrates. In this scheme,  $n = 4$  and  $m = 2$ .

from silicon to titanium. In the second type of elementary step (2-\*), a hydrogen atom of a hydroxyl group of the hydroxychloride molecule reacts with a surface chlorine group, attaching the M to the surface through an oxygen bridge. In this process, a HCl molecule is released.

The first type of elementary step (1-\*) is neither typical nor ideal in ALD. It is a gas–solid reaction where no metal complex is adsorbed onto the surface. This reaction seems necessary, however, in order to account for  $\text{MO}_{n/2}$  particle formation. The possibility of this type of a “non-growth exchange reaction” has recently been indicated by quantum chemical calculations.<sup>[64,65]</sup>

The second type of elementary step (2-\*) is a ligand exchange reaction, typical in ALD. There is one difference between the proposed reaction and the “normal” ligand exchange reaction, however: the locations of the hydroxyl group and chlorine are switched. In the current case, the hydroxyl group comes from the gas phase while the chlorine group is on the surface, whereas in the normal ligand exchange, the chlorine group comes from the gas phase while the hydroxyl group is on the surface. The type of ligand exchange proposed in this work is analogous to the ligand removal step in  $\text{MCl}_n/\text{H}_2\text{O}$  ALD processes however; OH groups from the gas phase release the surface ||-Cl group as HCl, attaching the rest of the molecule ( $-\text{OH}$  vs.  $-\text{OM}(\text{OH})_{m-1}\text{Cl}_{n-m}$ ) to the surface.

The  $\text{MO}_{n/2}$  formation process has an average stoichiometry where  $m = n/2$  in the intermediate hydroxychloride molecules (Reaction 12). If  $m < n/2$ , growth of large  $\text{MO}_{n/2}$  particles cannot occur. If  $m > n/2$ ,  $\text{MO}_{n/2}$  particles can grow since the hydroxychloride molecules bring an excess of ||-OH groups, with which the  $\text{MCl}_n$  molecules can react, to the surface. Alternatively, the ||-OH groups can dehydroxylate and release water which can react with ||-Cl groups and release HCl. The average overall stoichiometry of the process (Reaction 12) is retained, as shown in Reaction 22 for  $m = n$ .





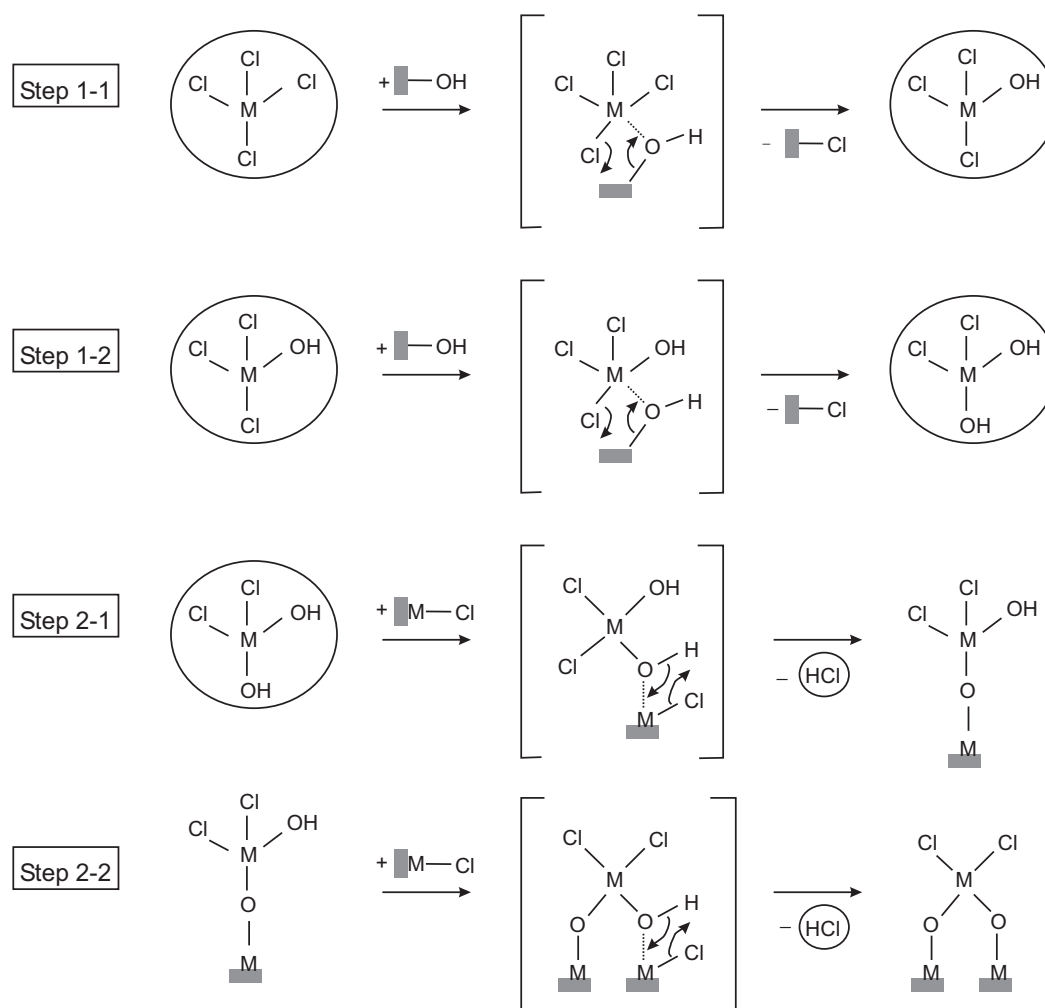


Fig. 6. Proposed elementary steps in the growth of  $\text{MO}_{n/2}$  in the reaction of  $\text{MCl}_n$  with an oxide substrate. Steps 1-\* represent chlorination reactions (Reaction 1) and steps 2-\* ligand exchange reactions (Reaction 15). The illustration is given for the case  $n = 4$  and  $m = 2$ . Depending on the M atom, additional coordination bonds may form.

In conclusion, the growth of large  $\text{MO}_{n/2}$  particles can occur when the average stoichiometry in the intermediate hydroxychloride molecules is  $n/2 \leq m \leq n$ .

### 3.3. Comparison with Experimental Results

All observations related to the stoichiometry of the  $\text{MO}_{n/2}$  particle formation process are fulfilled by the proposed mechanism (Sec. 2.2.). The  $\text{MO}_{n/2}$  formation is saturating in nature and limited by the number of  $\text{OH}$  groups on the surface (#5). All  $\text{OH}$  groups can be consumed (#6).  $\text{HCl}$  is released (#7). The average Cl/M ratio on the surface equals  $n/2$  (#8). The number of metal atoms attached is the content of the surface  $\text{OH}$  groups divided by  $n/2$  (#9). Once the intermediate hydroxychloride molecules have formed, competing reactions are absent, so the hydroxychloride molecules can quantitatively bond to the surface so that the mass balance is valid (#12).

The bonding of the particles to the surface is in accord with experimental findings. The  $\text{MO}_{n/2}$  particles are bonded to the surface through metal–oxygen bonds (#10).

The observations related to the types of sites left in the  $\text{MO}_{n/2}$  particles are also fulfilled. No hydroxyl groups are left in the  $\text{MO}_{n/2}$  particles according to the proposed mechanism, and the number of Cl groups is low (#11). To estimate the Cl/M ratio in the  $\text{TiO}_2$  particles, we assume a typical average particle size of about  $500 \text{ nm} \times 500 \text{ nm} \times 1.5 \text{ nm}$ ,<sup>[8]</sup> and that the particle grows from two of the narrow faces. A density of  $3.84 \text{ g cm}^{-3}$  and molar mass of  $80 \text{ g mol}^{-1}$  gives the number of titanium atoms in the  $\text{TiO}_2$  particles as about  $10^7$ . The surface area of the growing faces would be about  $1500 \text{ nm}^2$  ( $2 \times 1.5 \text{ nm} \times 500 \text{ nm}$ ). Assuming the growing area would contain about one Cl per  $\text{nm}^2$ , the particle would contain a total of  $1.5 \times 10^3$  Cl atoms. The Cl/M ratio in the particle would thus be about 0.004. This number is low, and is in accord with experimental observations.

The morphology of the particles is reasonable. In the production of  $\text{MO}_{n/2}$  particles, the mechanism shows no bias towards either the amorphous or the crystalline phase (#2). The bulk faces of the  $\text{MO}_{n/2}$  particles do not contain Cl groups or OH groups, so particle growth may occur in width rather than in thickness, in accord with the thin, plate-like form of the particles (#3). Larger  $\text{MO}_{n/2}$  particles can form in larger pores (#4). This can be seen by considering the areas inside the pores. If the  $\text{||-OH}$  group content per unit surface area is constant, large pores contain more  $\text{||-OH}$  groups than small pores. Let us consider further that chlorination (Reaction 1) dominates over ligand exchange (Fig. 3, scheme I), and that reaction occurs to  $\text{M-Cl}$  bonds rather than to  $\text{||-Cl}$  bonds. In an extreme case, all hydroxychloride species would migrate to bond to the same  $\text{MO}_{n/2}$  particle. Larger pores with a larger total  $\text{||-OH}$  group content enable the formation of larger  $\text{MO}_{n/2}$  particles.

The proposed mechanism is also in line with the fact that the particle formation is strongly temperature-dependent (#1). The ligand exchange (Fig. 3, scheme I) and chlorination (Reaction 1) must be competing reactions: the reacting species are the same, but the products differ. In ligand exchange, an oxygen–hydrogen bond is broken, whereas in chlorination, a metal–oxygen bond is broken. The energetics of these competing reactions are expected to differ. Increase of the reaction temperature over a certain threshold can, consequently, cause a sudden change in the dominating reaction mechanism.

In conclusion, the proposed reaction mechanism (Reactions 1 and 15) is in agreement with the experimental observations listed in Section 2.2.

## 4. Discussion

In this section is a discussion of some of the consequences of the  $\text{MO}_{n/2}$  particle formation for ALD growth. Section 4.1. shows that the current proposal changes the view of where the  $\text{MO}_{n/2}$  particles can be expected on the surface. Section 4.2. contains a discussion of how the probability of  $\text{MO}_{n/2}$  particle formation depends on the particular  $\text{MCl}_n$  reactant. Section 4.3. contains an analysis of the effect the  $\text{MO}_{n/2}$  particle formation should have on the temperature dependency of the growth per cycle in ALD.

### 4.1. Location of the $\text{MO}_{n/2}$ Particles on the Surface

The view of how  $\text{MO}_{n/2}$  particles are attached to the surface changes on the basis of the proposed mechanism. Earlier, oxygen bridges were suggested as the sites where  $\text{MO}_{n/2}$  particle growth is initiated.<sup>[8,32,62]</sup> According to the proposed reaction mechanism, oxygen bridges do not participate in  $\text{MO}_{n/2}$  particle formation, rather the growth begins at surface hydroxyl groups. The revised schematic

view of metal oxide particle formation is presented in Figure 7.

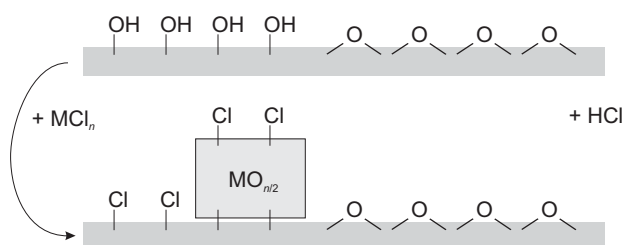


Fig. 7. Revised scheme for  $\text{MO}_{n/2}$  particle formation.  $\text{MO}_{n/2}$  grows on hydroxyl groups.

### 4.2. Effect of $\text{MCl}_n$ Reactant on $\text{MO}_{n/2}$ Particle Formation

The extent to which  $\text{MO}_{n/2}$  particle formation occurs depends on the metal chloride compound in question, reaction temperature, and substrate material.<sup>[7–9]</sup> The differences may originate at least from the probability that intermediate hydroxychloride molecules are formed in the reaction of  $\text{MCl}_n$  molecule with  $\text{||-OH}$  groups, and from the stoichiometry and/or the stability of the intermediate species.

For the same probability of hydroxychloride molecule formation and a suitable stoichiometry of the hydroxychloride molecules ( $n/2 \leq m \leq n$ ), the lifetime of the hydroxychloride molecules can probably be related to the size of the  $\text{MO}_{n/2}$  particles. It may be that, in practice, extremely unstable intermediates do not form at all. Rather unstable intermediates probably react quickly after their formation with sites nearby, producing small  $\text{MO}_{n/2}$  particles. Relatively stable intermediates may migrate longer on the surface before finding a suitable bonding site, producing larger  $\text{MO}_{n/2}$  crystals. Stable hydroxychlorides or oxychlorides molecules, in turn, may be transported out of the system unreacted, without contributing to particle growth.

$\text{Zr(OH)}_m\text{Cl}_{4-m}$  probably represents rather unstable intermediates, as small  $\text{ZrO}_2$  crystals are formed.<sup>[9,10]</sup>  $\text{Ti(OH)}_m\text{Cl}_{4-m}$  is likely to represent relatively stable intermediates, as large  $\text{TiO}_2$  crystals form in the saturating reaction of  $\text{TiCl}_4$  with porous silica.<sup>[8]</sup> As examples of stable oxychlorides,  $\text{TaOCl}_3$  and  $\text{NbOCl}_3$  can be mentioned; these are transported, unreacted, out of the reactor during ALD processing.<sup>[66,67]</sup>

### 4.3. Effect of $\text{MO}_{n/2}$ Formation on the Growth per Cycle in ALD

The amount of metal bonded in the saturating reaction of metal chlorides with oxide substrates decreases with increasing reaction temperature. This effect has been seen in pure form in experiments made on high surface area substrates, where the  $\text{||-OH}$  group content has been stabilized

to a constant value before the reaction,<sup>[7–11,31,33]</sup> and, together with the effect of decreasing  $\text{||-OH}$  group content, in experiments made on flat substrates.<sup>[48–50,68]</sup> A decrease in the amount of bonded metal with increasing reaction temperature is somewhat unusual for reactants used in ALD. For organometallic reactants, the amount bonded typically stays constant (e.g.,  $\text{AlMe}_3$ <sup>[69]</sup>) and for metal  $\beta$ -diketonates, it typically increases (e.g.,  $\text{La}(\text{thd})_3$ <sup>[70]</sup>).

The proposed mechanism for  $\text{MO}_{n/2}$  particle formation offers an explanation for the observed decrease in the amount of metal bonded. At low reaction temperatures, ligand exchange (Fig. 3, scheme I) is the predominant reaction mechanism. In the ligand exchange reaction, a minimum of one  $\text{||-OH}$  group is required to chemisorb one  $\text{MCl}_n$  molecule. The tendency for  $\text{MO}_{n/2}$  particle formation, a competing reaction path, increases with increasing reaction temperature. In  $\text{MO}_{n/2}$  particle formation, the number of  $\text{||-OH}$  groups needed to chemisorb one  $\text{MCl}_n$  molecule is  $n/2$ . A shift from ligand exchange to  $\text{MO}_{n/2}$  particle formation with increasing reaction temperature is thus expected to result in a lower amount of bonded metal, which is in accord with the experimental findings.

Finally, it should be noted that the metal oxide particle formation discussed in this work is a separate physicochemical phenomenon from island growth in ALD on poorly reactive substrates.<sup>[71–75]</sup> Island growth typically goes together with “substrate-inhibited ALD of type 2”,<sup>[76]</sup> where the growth per cycle is low in the beginning, increases, goes through a maximum, and finally decreases to a constant value. Island growth results in islands that are visible after several ALD reaction cycles.<sup>[71,72,74,77]</sup> The phenomenon of metal oxide particle formation discussed in this work is not related to substrate-inhibited ALD. Moreover, metal oxide particles form in just one ALD half-reaction, that is, before an ALD reaction cycle is completed (Figs. 1 and 2).

## 5. Summary and Outlook

Experimental results, and mechanisms suggested to result in the formation of  $\text{MO}_{n/2}$  particles in a single saturating reaction of  $\text{MCl}_n$  reactants with oxide surfaces, were reviewed. None of the suggested mechanisms can account for the experimental observations related to the metal oxide particle formation, particularly the facts that particle formation is saturating in nature, and that the particles are attached to the surface through metal–oxygen bonds.

A new mechanism to account for the experimental observations was systematically sought. One suitable mechanism was found. The proposed mechanism consists of two types of steps, and it is based on the ligand exchange reaction typical for ALD, and hydroxyl and chlorine groups as reactive sites. To arrive at the proposed mechanism, one had to realize that not only surface hydroxyl groups and oxygen bridges, but also surface chlorine groups, act as reactive sites. In the first proposed step,  $\text{MCl}_n$  chlorinates the sur-

face hydroxyl groups, forming an intermediate hydroxychloride molecule. In the second proposed step, the hydroxychloride reacts, through its hydroxyl groups, with surface chlorine groups. According to this mechanism,  $\text{MO}_{n/2}$  particle growth begins at surface hydroxyl groups, not at oxygen bridges, as suggested earlier.

The new reaction mechanism hypothesis fits with the experimental observations, but this does not exclude the possibility that the metal oxide particle formation process may be more complex than the proposed mechanism suggests. Theoretical calculations should be made to further investigate the proposed mechanism, and to identify possible additional reaction paths. More experimental work is also needed. Merely indirect experimental evidence is available regarding the formation of surface-bonded Cl groups in the chemisorption of  $\text{MCl}_n$ , which is assumed to be an essential step in  $\text{MO}_{n/2}$  particle formation.

Many fundamental questions are to be further investigated. Could the strong temperature dependence of the  $\text{MO}_{n/2}$  formation process be related to the relative stability of Si–O and O–H bonds? Is the varying tendency for  $\text{MO}_{n/2}$  particle formation ( $\text{M} = \text{Ti}, \text{Zr}$ , etc.) related to the stoichiometry or to the stability of the intermediate hydroxychloride molecules? Can particle formation also occur in the chemisorption of  $\text{MCl}_n$  compounds on substrate materials other than oxides, for example, on nitride substrates?

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