

# Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/ water process

Cite as: J. Appl. Phys. **97**, 121301 (2005); <https://doi.org/10.1063/1.1940727>

Submitted: 20 September 2004 . Accepted: 08 April 2005 . Published Online: 30 June 2005

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**APPLIED PHYSICS REVIEWS****Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process**Riikka L. Puurunen<sup>a)</sup>

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(Received 20 September 2004; accepted 8 April 2005; published online 30 June 2005)

Atomic layer deposition (ALD), a chemical vapor deposition technique based on sequential self-terminating gas–solid reactions, has for about four decades been applied for manufacturing conformal inorganic material layers with thickness down to the nanometer range. Despite the numerous successful applications of material growth by ALD, many physicochemical processes that control ALD growth are not yet sufficiently understood. To increase understanding of ALD processes, overviews are needed not only of the existing ALD processes and their applications, but also of the knowledge of the surface chemistry of specific ALD processes. This work aims to start the overviews on specific ALD processes by reviewing the experimental information available on the surface chemistry of the trimethylaluminum/water process. This process is generally known as a rather ideal ALD process, and plenty of information is available on its surface chemistry. This in-depth summary of the surface chemistry of one representative ALD process aims also to provide a view on the current status of understanding the surface chemistry of ALD, in general. The review starts by describing the basic characteristics of ALD, discussing the history of ALD—including the question who made the first ALD experiments—and giving an overview of the two-reactant ALD processes investigated to date. Second, the basic concepts related to the surface chemistry of ALD are described from a generic viewpoint applicable to all ALD processes based on compound reactants. This description includes physicochemical requirements for self-terminating reactions, reaction kinetics, typical chemisorption mechanisms, factors causing saturation, reasons for growth of less than a monolayer per cycle, effect of the temperature and number of cycles on the growth per cycle (GPC), and the growth mode. A comparison is made of three models available for estimating the sterically allowed value of GPC in ALD. Third, the experimental information on the surface chemistry in the trimethylaluminum/water ALD process are reviewed using the concepts developed in the second part of this review. The results are reviewed critically, with an aim to combine the information obtained in different types of investigations, such as growth experiments on flat substrates and reaction chemistry investigation on high-surface-area materials. Although the surface chemistry of the trimethylaluminum/water ALD process is rather well understood, systematic investigations of the reaction kinetics and the growth mode on different substrates are still missing. The last part of the review is devoted to discussing issues which may hamper surface chemistry investigations of ALD, such as problematic historical assumptions, nonstandard terminology, and the effect of experimental conditions on the surface chemistry of ALD. I hope that this review can help the newcomer get acquainted with the exciting and challenging field of surface chemistry of ALD and can serve as a useful guide for the specialist towards the fifth decade of ALD research.

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## I. INTRODUCTION

Atomic layer deposition (ALD) is a chemical vapor deposition (CVD) technique suitable for manufacturing inorganic material layers with thickness down to a fraction of a monolayer.<sup>1,2</sup> ALD has the capability to coat extremely complex shapes with a conformal material layer of high quality, a capability unique among thin-film deposition techniques.<sup>1-3</sup> Consequently, ALD-grown materials have a wide range of applications, from catalysts to electroluminescent displays to microelectronics and beyond.<sup>1-3</sup>

ALD can be defined as a film deposition technique that is based on the sequential use of self-terminating gas-solid reactions. It has its roots in experiments made in the 1960s and the 1970s.<sup>1,2</sup> Interest in ALD has increased in steps in the beginning of the 1990s and 2000s, as indicated by the evolution, yearly, of the number of scientific publications on ALD, shown in Fig. 1. A major driving force for the recent interest is the prospectives seen for ALD in scaling down microelectronic devices.<sup>5</sup>

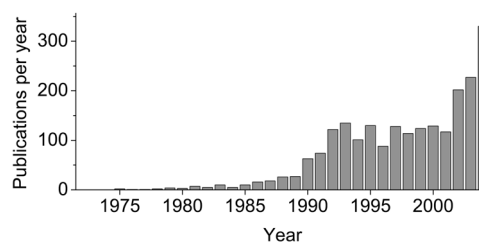


FIG. 1. Number of ALD publications per year between 1972 and 2004. Search made with ISI Web of Science (see Ref. 4).

Despite the numerous successful practical applications of ALD, many physicochemical processes that control ALD growth are not yet sufficiently understood. A better understanding of these physicochemical processes should lead to improved control of the properties of the ALD-grown materials, perhaps even enabling new applications. To increase the understanding of ALD processes, overviews are needed not only of the existing ALD processes and their applications, but also of the knowledge of the surface chemistry of specific ALD processes. So far, the latter types of overviews have scarcely been made, although there are numerous more general reviews on ALD.<sup>3,6-66</sup>

The goal of this work is to start the detailed reviews on the surface chemistry of specific ALD processes. Since, to my knowledge, comparable reviews do not yet exist, this work also aims to provide an overview of the current status of understanding the surface chemistry of ALD in general, with the hope that an in-depth review of one representative process has broader implications. The trimethylaluminum/water ( $\text{AlMe}_3/\text{H}_2\text{O}$ ) process was chosen as an example because it can be considered a rather typical and "ideal" ALD process, because it has been studied at various experimental conditions, and also because I am familiar with it. This review covers literature approximately until the end of 2004. The previous review on the surface chemistry of ALD was published in 1996 by George *et al.*<sup>40</sup> For other aspects of ALD than its surface chemistry, the reader is referred to the recent review by Ritala and Leskelä.<sup>3</sup> Furthermore, for different views on the development of ALD over the years, I would recommend the reviews by Aleskovskii,<sup>6</sup> Goodman and Pessa,<sup>8</sup> Suntola,<sup>11</sup> George *et al.*,<sup>40</sup> Malygin *et al.*,<sup>42</sup> Niinistö *et al.*,<sup>39</sup> Haukka *et al.*,<sup>50</sup> Leskelä and Ritala,<sup>51</sup> and Ritala and Leskelä.<sup>3</sup>

This review is organized as follows: Section II introduces the basic characteristics of ALD processing, discusses the history of ALD, and presents an overview of the two-reactant ALD processes investigated to date. In Sec. III, basic concepts related to the surface chemistry of ALD are formulated and discussed from a theoretical viewpoint. The discussion is generic for compound-reactant-based ALD processes, where the reactions are truly self-terminating and undesired side reactions are absent. Phenomena specifically related to ALD processes based on element reactants are not discussed. In Sec. IV, the experimental results for the  $\text{AlMe}_3/\text{H}_2\text{O}$  process are reviewed, especially looking for conclusions reached and quantitative information obtained on the surface chemistry. Because of differences in the experimental conditions (e.g., type of substrate, pressure, time, and temperature), in-

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terpreting the results of different kinds of investigations together may not always be straightforward, however.<sup>67</sup> The ALD literature contains also problematic historical assumptions and terminology, which may further cause confusion. The historical assumptions, terminology, and effect of experimental conditions on the surface chemistry of ALD are discussed in Sec. V.

## II. GENERAL BACKGROUND

This section describes the basics of ALD processing, discusses the history of ALD, and presents an overview of the investigated ALD processes based on two reactants.

### A. Basic characteristics of ALD

ALD can be defined as a film deposition technique that is based on the sequential use of self-terminating gas–solid reactions.<sup>68–70</sup> The growth of material layers by ALD consists of repeating the following characteristic four steps:

- (1) A self-terminating reaction of the first reactant (Reactant A).
- (2) A purge or evacuation to remove the nonreacted reactants and the gaseous reaction by-products.
- (3) A self-terminating reaction of the second reactant (Reactant B)—or another treatment to activate the surface again for the reaction of the first reactant.<sup>71</sup>
- (4) A purge or evacuation.

Steps 1–4 constitute a *reaction cycle*. Steps 1 and 3 are sometimes referred to as *half reactions* of an ALD reaction cycle.<sup>40,72</sup>

One ALD reaction cycle is illustrated schematically in Fig. 2. Each reaction cycle adds a given amount of material to the surface, referred to as the *growth per cycle* (GPC). To grow a material layer, reaction cycles are repeated until the desired amount of material has been deposited.<sup>73</sup> Before starting the ALD process, the surface is stabilized to a known, controlled state, for example, by a heat treatment. The use of self-terminating reactions leads to the conclusion that ALD is a surface-controlled process, where process parameters other than the reactants, substrate, and temperature have little or no influence. Because of the surface control, ALD-grown films are extremely conformal and uniform in thickness.

### B. Early experiments on ALD

The starting point of ALD is somewhat controversial: depending on the source, the credit of first realizing the principles of ALD is given to different groups.

According to the more commonly acknowledged origin, ALD was developed under the name “atomic layer epitaxy (ALE)” in Finland by Suntola and co-workers. The beginning of ALD is then traced back to a patent published in the 1970s,<sup>2</sup> for which the first experiments were made in 1974.<sup>74,75</sup> In this patent,<sup>2</sup> ALD growth is demonstrated for processes based on element reactants: the Zn/S process to grow ZnS, the Sn/O<sub>2</sub> process to grow SnO<sub>2</sub>, and the Ga/P process to grow GaP.<sup>2</sup> In later patents,<sup>76,77</sup> Suntola and co-

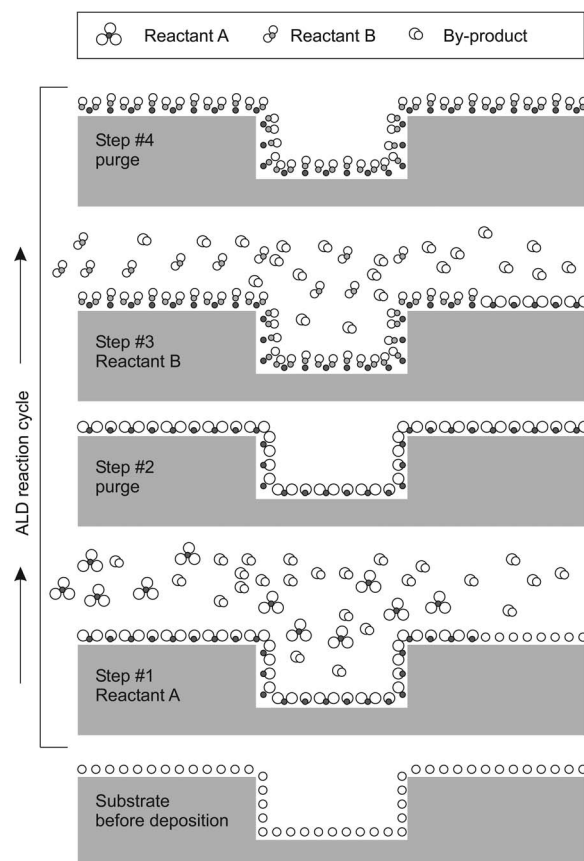


FIG. 2. Schematic illustration of one ALD reaction cycle.

workers demonstrated ALD also for processes based on compound reactants: the TaCl<sub>5</sub>/H<sub>2</sub>O process to grow Ta<sub>2</sub>O<sub>5</sub>, the Zn(Mn)Cl<sub>2</sub>/H<sub>2</sub>S process to grow Zn(Mn)S, and the AlCl<sub>3</sub>/H<sub>2</sub>O process to grow Al<sub>2</sub>O<sub>3</sub>. The research originated by Suntola and co-workers has led to commercial applications of ALD for making thin-film electroluminescent displays already in the 1980s. An overview of the development of ALD was recently given by Suntola.<sup>74</sup>

The less commonly acknowledged origin of ALD dates back to the work made in the Soviet Union in the 1960s by the group of Professor Aleskovskii. In the proceedings of a conference organized in 1965 and published in 1967, Shevjakov *et al.*<sup>1</sup> describe the TiCl<sub>4</sub>/H<sub>2</sub>O process to grow TiO<sub>2</sub> and the GeCl<sub>4</sub>/H<sub>2</sub>O process to grow GeO<sub>2</sub>. The first experiments in the group of Aleskovskii were made on high-surface-area silica substrates, but soon dielectric layers were grown on single-crystal substrates, too.<sup>78</sup> Already in the 1960s, a publication series on the “molecular layering reactions” was started by Kol’tsov and co-workers (e.g., Refs. 79–85).

Of the numerous review articles written on ALD over the years,<sup>3,6–66</sup> only the ones authored by Russians<sup>6,20,42,43,48,56</sup> describe the Soviet origin of ALD. In the beginning, the two groups have apparently not been aware of each other’s work. Connection between the groups has been established already in the late 1980s,<sup>20,86</sup> however, and scientists of the two groups have even met.<sup>74</sup> To help the interested reader to explore the Soviet–Russian branch of ALD, and as an attempt to correct the historical mistake of



disregarding this work,<sup>87</sup> an overview of the Soviet–Russian ALD investigations is given in Table I. Most of the publications referred to in Table I have been published in Soviet–Russian journals, which have been translated into English. The overview of Table I is meant to be introductory, and it can by no means be expected to be complete. A more detailed description of the Soviet–Russian ALD work was recently provided by Malygin.<sup>56</sup>

Partly because of its history, the ALD technique is referred to with many names. The Soviet–Russian researchers call the technique “молекулярное наплавление (MH),”<sup>152</sup> which has been translated into English in many ways, “molecular layering (ML)” being perhaps the most common.<sup>3</sup> In addition to the Finnish and Soviet researchers, Japanese researchers, lead by Nishizawa, have carried out ALD research systematically under a different name, “molecular layer epitaxy (MLE).”<sup>153</sup> The name “atomic layer deposition (ALD),” used in this work, dates back to the early 1990s.<sup>19</sup> Some names commonly used to refer to the ALD technique are listed in Table II.

## C. ALD processes

### 1. Materials investigated

ALD processes have been developed for manufacturing many types of solid inorganic materials. Figure 3 visualizes in the form of the Periodic Table, the elements of which some materials have been grown by ALD: oxides, nitrides, sulphides, selenides, tellurides, pure elements, and other. Table III provides references to the experimental investigations of ALD processes based on the use of two reactants, and Table IV lists the computational chemistry investigations of the surface chemistry of ALD processes. Tables III and IV provide only references that are easily accessible; most references to conference proceedings and patents have been left out intentionally. Inclusion in Table III does not mean that the processes would obey the requirements of ALD fully. Deviation from pure ALD may have occurred, for example, through partial decomposition of the reactants. These two tables are aimed to be comprehensive and contain all relevant references reporting on the particular ALD system, but some references have undoubtedly been accidentally overlooked, for which I already apologize. To help the reader, Fig. 4 further summarizes the types of ligands that have been used in the metal reactants in ALD. Although for most groups of elements, some materials have been grown by ALD (Fig. 3), for alkali metals (group 1) and actinoids there are no reports yet. The future will show if there will be interest and success in their deposition.

From the different types of inorganic materials grown by ALD, oxides have been the type most often investigated, as evident from Fig. 3. Oxides have been grown for alkaline-earth metals, transition metals including lanthanoids, and group 13–15 elements. As evident from Table III, the oxygen source in oxide deposition has most typically been water  $H_2O$  or, somewhat less often, diatomic oxygen  $O_2$ , ozone  $O_3$ , alcohols  $ROH$ , or atomic oxygen created through oxygen plasma. Table III also reveals the use of some more uncommon oxygen sources ( $H_2O$ +catalyst,  $H_2O_2$ ,  $N_2O$ ,  $NO_2$ ,

$N_2O_4$ , and metal alkoxide reactants). Nitrides have analogously most often been manufactured from the metal compound and ammonia  $NH_3$  or  $N_2/NH_3$  plasma (or, less often,  $N_2$ ,  $NH_3$ +catalyst,  $RNH_2$ ,  $N_2H_4$ ,  $R_2NNH_2$ , or an alkylamide reactant); sulphides from hydrogen sulphide  $H_2S$  (or, less often,  $S$  or  $Et_2S_2$ ); selenides from hydrogen selenide  $H_2Se$  (or, less often,  $Se$ ,  $Et_2Se$ , or  $Et_2Se_2$ ); and tellurides from  $Te$  or  $MeAyTe$  (or, less often,  $R_2Te$ ). Several other nonmetal reactants have also occasionally been used (see Table III).

While ALD is most suited for growing compound materials, some successes have recently been booked in the deposition of pure elements also. Tungsten can be deposited by reacting the fluoride reactants with disilane,  $Si_2H_6$ ,<sup>1066,1076–1078</sup> and preliminary surface science experiments suggest that a similar process could work also for tantalum.<sup>1063</sup> For most other elements, in contrast, reduction by diatomic hydrogen,<sup>483,546,561,570–572,575,873,875</sup> hydrogen plasma,<sup>331,332,515,516,1062</sup> or, in some cases, alcohols<sup>577</sup> has been required to deposit the pure element. However, for some metals (e.g.,  $Ru$ ,  $Pd$ ,  $Ir$ ,  $Pt$ ), the tendency of the metal to reduce dominates the deposition process, and the pure elements are obtained even when oxygen is used as the ligand-removal agent.<sup>564,866–869,872,874,1081,1082</sup>

### 2. Classes of metal reactants used

General requirements of reactants used in ALD are that they must be volatile (either at room temperature or at elevated temperatures), the reactants may not decompose thermally at the ALD processing temperatures, and the gas–solid reactions of the reactants have to fulfill the criterion of self-termination. Other properties of the different types of reactants may differ, however. The reactants used in ALD can be divided into two main groups: inorganic and metalorganic. Metalorganic reactants can further be classified in those containing a direct metal–carbon bond, that is, organometallic reactants,<sup>1126</sup> and those containing no direct metal–carbon bond. Typically, of inorganic reactants, elements and halides have been used; of organometallic reactants, alkyls and cyclopentadienyls have been used; and of other metalorganic reactants, alkoxides,  $\beta$ -diketonates, amides, and amidinates have been used in ALD experiments. Figure 5 summarizes which types of reactants have been used for which elements, and the following paragraphs summarize the typical features of the different reactant groups.

Elements are the most simple type of reactants used in ALD and have been used in ALD investigations since the 1970s.<sup>2,154,171,534,887</sup> Elements are versatile: they react both with elemental nonmetal reactants and with compounds of hydrogen, and they have been used to deposit many types of materials (oxides, nitrides, sulphides, etc), as summarized in Table V. A benefit of element reactants is also that since the elements do not carry extra ligands, the ligands cannot stay as impurities in the grown film. The lack of ligands means also the lack of steric hindrance effects caused by the ligands.<sup>1127,1128</sup> Nevertheless, less than a monolayer growth may be observed because of surface reconstructions.<sup>36</sup> Although popular in the 1970s and 1980s, the interest in element reactants has decreased. This decrease is partly explained by the fact that few elements have sufficiently high

TABLE I. Some Soviet–Russian ALD investigations.

$Z^a$	Material	Reactant $A$	Reactant $B$	Substrate <sup>b</sup>	Refs.
5 Boron	$B_2O_3$	$BBr_3$	$H_2O$	$SiO_2$ gel	85
	$B_xP_yO_z$	$B(OMe)_3$	$POCl_3$	$SiO_2$ gel	88 and 89
13 Aluminum	$Al_2O_3$	$AlCl_3$	$H_2O$	$SiO_2$ gel	83, 90, and 91
		$AlCl_3$	$H_2O$	$Al_2O_3$ gel	90
		$AlCl_3$	$H_2O$	Si, Al	91
		$AlBr_3$	$H_2O$	Si	92
		$AlMe_3$	$NO_2$	Si	93
	$Al_xSi_yO_z$	$AlCl_3$	$Si(OEt)_4$	$SiO_2$ gel	94
	$Al_xCr_yO_z$	$AlMe_3$	$CrO_2Cl_2$	Si	93
14 Silicon	$SiO_2$	$SiCl_4$	$H_2O$	Si	78
		$SiCl_4$	$H_2O$	Ge	95
		$SiCl_4$	$H_2O$	$SiO_2$ gel	90
		$SiCl_4$	$H_2O$	$Al_2O_3$ gel	90
		$SiCl_4$	$H_2O$	SiC	96
		$SiCl_3H$	$H_2O$	$SiO_2$ gel	97–99
	$Si_xAl_yO_z$	$Si(OEt)_4$	$AlCl_3$	$SiO_2$ gel	94
	$Si_xTi_yO_z$	$Si(OEt)_4$	$TiCl_4$	$SiO_2$ gel	88
15 Phosphorus	$PO_x$	$PCl_3$	$H_2O$	$SiO_2$ gel	82 and 100–102
		$PCl_3$	<sup>c</sup>	polymer	103
		$POCl_3$	<sup>c</sup>	$SiO_2$ gel	104 and 105
		$POCl_3$	$H_2O$	SiC	96
	$P_xB_yO_z$	$POCl_3$	$B(OMe)_3$	$SiO_2$ gel	88 and 89
22 Titanium	$TiO_2$	$TiCl_4$	$H_2O$	$SiO_2$ gel	1, 79, 80, 100, 101, and 106–113
		$TiCl_4$	$H_2O$	Si	81, 114, and 115
		$TiCl_4$	$H_2O$	Ge	116 and 117
		$TiCl_4$	$H_2O$	SiC	96 and 116
		$TiCl_4$	$H_2O$	glass	118–122
		$TiCl_4$	$H_2O$	C	123–125
		$TiCl_4$	$H_2O$	GaAs	126
		$TiCl_4$	$H_2O$	Al	127
		$TiCl_4$	$H_2O$	$Al_2O_3$	128–132
		$TiCl_4$	$H_2O$	MgO	133
	$Ti_xSi_yO_z$	$Ti(OBu)_4$	$H_2O$	glass	134
		$TiCl_4$	$H_2O$	$SiO_2$ gel	88
23 Vanadium	$VO_x$	$VOCl_3$	$H_2O$	$SiO_2$ gel	135–137
		$VOCl_3$	$H_2O$	Ge	117
		$VOCl_3$	$H_2O$	glass	121
		$VOCl_3$	$H_2O$	SiC	96
		$VOCl_3$	<sup>c</sup>	polymer	103
24 Chromium	$CrO_x$	$CrO_2Cl_2$	<sup>c</sup>	$SiO_2$ gel	105 and 138–140
		$CrO_2Cl_2$	<sup>c</sup>	Si	84
		$CrO_2Cl_2$	<sup>c</sup>	Ge	84 and 117
		$CrO_2Cl_2$	<sup>c</sup>	Ni	141
		$CrO_2Cl_2$	<sup>c</sup>	Ti	141
		$CrO_2Cl_2$	$H_2O$	glass	121
		$CrO_2Cl_2$	$H_2O$	SiC	96
		$CrO_2Cl_2$	MeOH	Si	93
		$CrO_2Cl_2$	<sup>c</sup>	polymer	103
	$Cr_xAl_yO_z$	$CrO_2Cl_2$	$H_2$	$SiO_2$ gel	142
		$CrO_2Cl_2$	$AlMe_3$	Si	93

TABLE I. (Continued.)

$Z^a$	Material	Reactant A	Reactant B	Substrate <sup>b</sup>	Refs.
26 Iron	$\text{FeO}_x$	$\text{FeCl}_3$	<sup>c</sup>	$\text{SiO}_2$ gel	143
30 Zinc	ZnO	$\text{ZnCl}_2$	$\text{H}_2\text{O}$	$\text{SiO}_2$ gel	144
	ZnS	$\text{ZnCl}_2$	$\text{H}_2\text{S}$	$\text{SiO}_2$ gel	86
		$\text{ZnEt}_2$	$\text{H}_2\text{S}$	$\text{SiO}_2$	145
32 Germanium	$\text{GeO}_2$	$\text{GeCl}_4$	$\text{H}_2\text{O}$	$\text{SiO}_2$ gel	1 and 146
38 Cadmium	CdS	Cd	S	GaAs	147
		$\text{CdMe}_2$	$\text{H}_2\text{S}$	$\text{SiO}_2$	145
	CdSe	Cd	Se	GaAs	147 and 148
		$\text{CdMe}_2$	$\text{H}_2\text{Se}$	$\text{SiO}_2$	145
		$\text{CdMe}_2$	$\text{H}_2\text{Se}$	glass, GaAs	149
	CdTe	Cd	Te	GaAs	147
		Cd	Te	Si	148
50 Tin	$\text{SnO}_2$	$\text{SnCl}_4$	$\text{H}_2\text{O}$	$\text{SiO}_2$ gel	111 and 150
		$\text{SnMe}_4$	$\text{N}_2\text{O}_4$	Si	151
		$\text{SnEt}_4$	$\text{N}_2\text{O}_4$	Si	151
73 Tantalum	$\text{Ta}_2\text{O}_5$	$\text{TaCl}_5$	$\text{H}_2\text{O}$	Si, Al	91

<sup>a</sup> $Z$ =atomic number.<sup>b</sup>"Glass" substrate refers to various mixed oxides, "polymer" to various organic polymer substrates.<sup>c</sup>Only one half reaction of an ALD reaction cycle was carried out.

vapor pressure to be evaporated as such [Fig. 5(a)]. In addition, the adsorption of elements is likely to be a reversible process, and the limited self-terminating characteristics of the reactions potentially limit their usability.

Halides are the oldest class of ALD reactants, with the first experiments made already in the 1960s.<sup>1,77,78,83,97,100,106,135,138,150,614</sup> Recently they have been extensively investigated, for example, for the deposition of high-dielectric-constant oxides.<sup>1129–1131</sup> A benefit of halide reactants is the availability of volatile halides for many metals, as shown in Fig. 5(b). Halides are also generally regarded highly reactive and thermally stable. The high reactivity of halides is reflected in the variety of materials grown from them: oxides, nitrides, sulphides, etc. (Table VI). To

give an example of the thermal stability, the  $\text{HfCl}_4/\text{H}_2\text{O}$  ALD process has been used even at and above 800 °C.<sup>980,981,1013</sup> In addition to the high reactivity, the small size of the halide ligands can be regarded advantageous, since the steric hindrance effects related to ligands<sup>1127,1128</sup> are then minimized. Despite the small ligand size, the GPC obtained from halides is typically a small fraction of a monolayer of the material to be grown. For example, for the  $\text{HfCl}_4/\text{H}_2\text{O}$  process at 300 °C, the GPC is about 0.05 nm, corresponding to 15% of a monolayer.<sup>982,984,985,992,998,1127,1132–1134</sup> The low GPC has led to a suggestion that it may be the number of reactive surface groups and not steric hindrance that controls the amount deposited in halide-based processes.<sup>992</sup> Despite the many favorable sides of halide reactants for ALD, there are also several drawbacks. Many halides are solids, and vaporizing solid reactants is a challenge, since particles are easily transported into the films. The gaseous reaction by-products with hydrogen-containing nonmetal reactants ( $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , etc.) are HF, HCl, HBr, and HI. These gases are corrosive and can etch the film constituents or the reactor material.<sup>864,1036,1042</sup> The gaseous reaction products may also readsorb on the surface after their formation, blocking reactive sites and causing undesired thickness gradients.<sup>432,433</sup> Part of the halide ligands may remain as impurities in the films after the growth, which can be problematic for some applications. For example,  $\text{HfO}_2$  films grown from  $\text{HfCl}_4$  and  $\text{H}_2\text{O}$  at 300 °C have been reported to contain about 0.3-

TABLE II. Different names of ALD.

Name	Abbreviation	Refs.
Atomic layer deposition	ALD	19
Atomic layer epitaxy	ALE	2
Atomic layer evaporation	ALE	154
Atomic layer growth	ALG	155
Chemical assembly		126
Molecular deposition		117
Molecular lamination		156
Molecular layer epitaxy	MLE	153
Molecular layering	ML	1
Molecular stratification		105

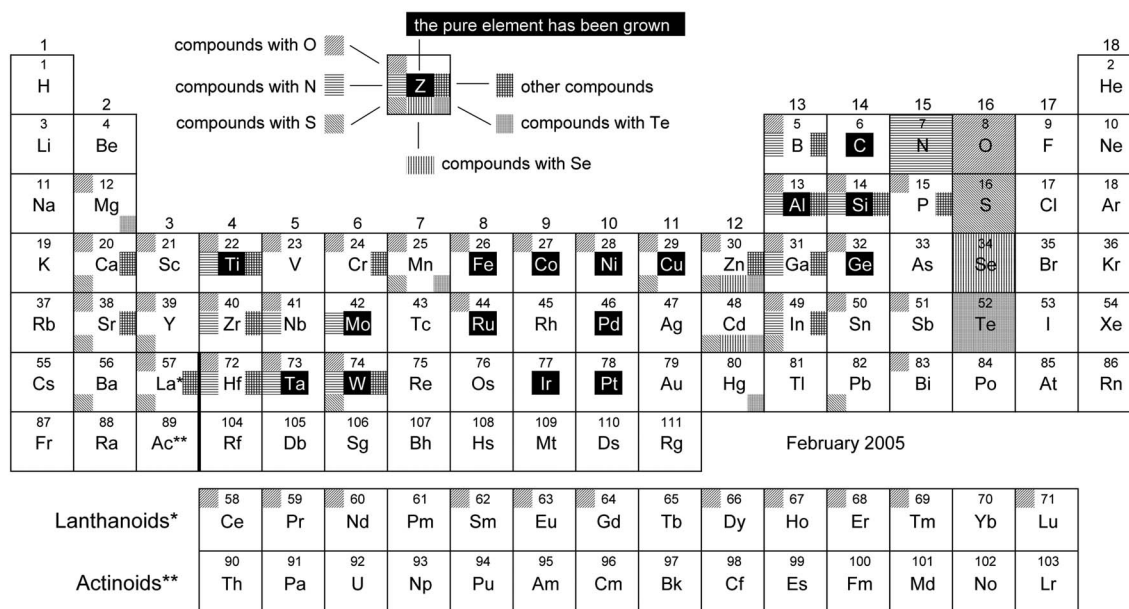


FIG. 3. Overview of the materials grown by ALD. Classification according to Reactant A, with details of the investigations in Table III. Growth of pure elements as well as compounds with oxygen, nitrogen, sulphur, selenium, tellurium, and other compounds grouped together are indicated through shadings of different types at different positions. The elements are named according to the recommendations of The International Union of Pure and Applied Chemistry (IUPAC, [http://www.iupac.org/reports/periodic\\_table/](http://www.iupac.org/reports/periodic_table/), dated 1 November 2004).

at. % chlorine and 1.6-at. % hydrogen (and, surprisingly, 0.2-at. % carbon).<sup>999</sup> Some halides, at least  $\text{TiCl}_4$ , may also react in a manner unideal for ALD, depositing particles through a so-called agglomeration process above a certain threshold temperature.<sup>419,421,1135–1137</sup> Details on how the agglomeration occurs have not yet been clarified.<sup>1135</sup>

Alkyls were introduced as ALD reactants in the mid-1980s.<sup>153,190,305,627,723,724,726,729,733,781,929</sup> Nowadays, alkyls are often used as reactants especially for aluminum and zinc. Alkyls are true organometallic compounds, which make them very reactive. Consequently, a variety of materials have been grown from alkyls (Table VII): oxides, nitrides, sulphides, etc. The alkyl ligands are also rather small, minimizing the steric hindrance effects,<sup>1127,1128</sup> and the GPC in alkyl-reactant-based processes is often rather high. For example, the GPC in the  $\text{AlMe}_3/\text{H}_2\text{O}$  process at 300 °C is about 0.09 nm,<sup>166,199,212,222,228,229,246</sup> corresponding to about 30% of a monolayer of  $\text{Al}_2\text{O}_3$ . The gaseous reaction by-products with hydrogen-containing nonmetal reactants ( $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , etc.) are typically saturated hydrocarbons, which are generally inert and do not cause problems with readsorption or corrosion. Drawbacks of alkyls are that they have been used for a rather small selection of elements (groups 12–14) [Fig. 5(c)] and that they decompose at moderate temperatures. For example,  $\text{AlMe}_3$  decomposes above 300 °C.<sup>216</sup> There is also the possibility of carbon and hydrogen residues in the grown films, although the concentrations are often low. For example,  $\text{Al}_2\text{O}_3$  films grown from  $\text{AlMe}_3$  and  $\text{H}_2\text{O}$  at 300 °C were reported to contain about 0.2-at. % carbon and 0.7-at. % hydrogen.<sup>258</sup>

Cyclopentadienyls were introduced as ALD reactants in the early 1990s<sup>162–164</sup> and have gained popularity in the 2000s. An advantage of the cyclopentadienyl reactants is the fact that they can be synthesized also for alkaline-earth met-

als, for which other compounds have been scarce [Fig. 5(d)]. Similarly as alkyls, cyclopentadienyls are organometallic, containing a direct metal–carbon bond. This makes them reactive, and, for example, oxides can be grown through reaction with  $\text{H}_2\text{O}$ . However, the material selection grown from cyclopentadienyls is still small and comprises only oxides, sulphides, and elements, as shown in Table VIII. The future will show whether or not the growth by ALD of other inorganic materials will also be successful from cyclopentadienyls. The cyclopentadienyl ligands are medium-sized, and the GPC from these reactants is often higher than for bulkier ligands such as the  $\beta$ -diketonates. For example,  $\text{Y}_2\text{O}_3$  grows through the  $\text{YCpMe}_3/\text{H}_2\text{O}$  and  $\text{Y}(\text{thd})_3/\text{O}_3$  processes at 300 °C with GPC values of 0.13 nm (Ref. 813) and 0.023 nm (Ref. 815), respectively. The gaseous by-products from reactions with the typical nonmetal reactants  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{S}$  are presumably hydrocarbons, which do not readsorb on the surface, although studies of the gaseous reaction products have been rare. One study indicated the gaseous reaction product to be the hydrogenated ligands.<sup>806</sup> Similarly as alkyls, the cyclopentadienyls decompose at moderate temperatures, and there may be carbon and hydrogen residues in the films. For example,  $\text{ZrCp}_2\text{Me}_2$  decomposes at least at 500 °C,<sup>844</sup> and perhaps even at lower temperatures. When grown at 350 °C,  $\text{ZrO}_2$  films grown from  $\text{ZrCp}_2\text{Me}_2$  and  $\text{H}_2\text{O}$  are rather pure and contain less than 0.1-at. % carbon and hydrogen, but the impurity concentrations increase if the deposition temperature is decreased or increased.<sup>844</sup>

Alkoxides were introduced as ALD reactants in the early 1990s.<sup>89,134,173,462,467,1044,1084</sup> Alkoxides have been used for rather few elements [groups 4, 5, 13, and 14, see Fig. 5(e)], and they have been used to deposit almost only oxides (Table IX). Nitrides have not been grown from alkoxides, which



TABLE III. Overview of ALD processes based on two reactants (Source: ISI Web of Science, status in February 2005). Description of the ligands in Fig. 4.

Z	Material	Reactant A <sup>a</sup>	Reactant B	Refs.
5 Boron	B <sub>2</sub> O <sub>3</sub>	BBr <sub>3</sub>	H <sub>2</sub> O	85
	BN	BCl <sub>3</sub>	NH <sub>3</sub>	158
		BBr <sub>3</sub>	NH <sub>3</sub>	159
	B <sub>x</sub> P <sub>y</sub> O <sub>z</sub>	B(OMe) <sub>3</sub>	POCl <sub>3</sub>	88 and 89
6 Carbon	C <sup>b</sup>	CF <sub>x</sub>	H <sup>c</sup>	160
		CCl <sub>3</sub>	H <sup>c</sup>	161
12 Magnesium	MgO	MgCp <sub>2</sub>	H <sub>2</sub> O	162–166
		Mg(thd) <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	167
		Mg(thd) <sub>2</sub>	O <sub>3</sub>	168
	MgTe	Mg	Te	169 and 170
13 Aluminum	Al <sub>2</sub> O <sub>3</sub>	AlCl <sub>3</sub>	H <sub>2</sub> O	76, 77, 83, 90, 91, 91, and 171–184
		AlCl <sub>3</sub>	O <sub>2</sub>	185 and 186
		AlCl <sub>3</sub>	ROH <sup>d</sup>	173, 181, and 187
		AlCl <sub>3</sub>	Al(OEt) <sub>3</sub>	188
		AlCl <sub>3</sub>	Al(O <sup>i</sup> Pr) <sub>3</sub>	188 and 189
		AlBr <sub>3</sub>	H <sub>2</sub> O	92
		AlMe <sub>3</sub>	H <sub>2</sub> O	166, 179, and 190–262
		AlMe <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	263–269
		AlMe <sub>3</sub>	O <sub>3</sub>	236, 244, 245, and 270–273
		AlMe <sub>3</sub>	O <sub>2</sub> <sup>e</sup>	274–276
		AlMe <sub>3</sub>	N <sub>2</sub> O	266
		AlMe <sub>3</sub>	NO <sub>2</sub>	194
		AlMe <sub>3</sub>	N <sub>2</sub> O <sub>4</sub>	151
		AlMe <sub>3</sub>	<sup>i</sup> PrOH	277
		AlMe <sub>3</sub>	Al(O <sup>i</sup> Pr) <sub>3</sub>	188
		AlMe <sub>2</sub> Cl	H <sub>2</sub> O	278
		AlMe <sub>2</sub> O <sup>i</sup> Pr	H <sub>2</sub> O	279 and 280
		AlEt <sub>3</sub>	H <sub>2</sub> O	163
		Al(OEt) <sub>3</sub>	H <sub>2</sub> O	173
		Al(OEt) <sub>3</sub>	O <sub>2</sub>	173
	AlN	Al(O <sup>n</sup> Pr) <sub>3</sub>	H <sub>2</sub> O	173 and 181
		Al(O <sup>n</sup> Pr) <sub>3</sub>	O <sub>2</sub>	281
		AlCl <sub>3</sub>	NH <sub>3</sub>	282 and 283
		AlCl <sub>3</sub>	NH <sub>3</sub> + H <sub>2</sub> <sup>e</sup>	284 and 285
		AlMe <sub>3</sub>	NH <sub>3</sub>	209, 216, 283, and 286–292
		AlEt <sub>3</sub>	NH <sub>3</sub>	293 and 294
		Me <sub>3</sub> N : AlH <sub>3</sub>	NH <sub>3</sub>	295
		Me <sub>2</sub> EtN : AlH <sub>3</sub>	NH <sub>3</sub>	296–298
	AlP	AlMe <sub>2</sub> H	PH <sub>3</sub>	299–301
		Me <sub>2</sub> EtN : AlH <sub>3</sub>	PH <sub>3</sub>	302
	AlAs	AlCl <sub>3</sub>	AsH <sub>3</sub>	303 and 304
		AlMe <sub>3</sub>	AsH <sub>3</sub>	305–315
		AlMe <sub>2</sub> H	AsH <sub>3</sub>	316–320
		AlEt <sub>3</sub>	AsH <sub>3</sub>	309 and 311
		Al <sup>i</sup> Bu <sub>3</sub>	AsH <sub>3</sub>	321
		Me <sub>3</sub> N : AlH <sub>3</sub>	AsH <sub>3</sub>	322
		Me <sub>3</sub> N : AlH <sub>3</sub>	As(NMe <sub>2</sub> ) <sub>3</sub>	323 and 324
		Me <sub>2</sub> EtN : AlH <sub>3</sub>	AsH <sub>3</sub>	320 and 325–330
	Al	AlMe <sub>3</sub>	H <sub>2</sub> <sup>e</sup>	331 and 332
	Al <sub>x</sub> Si <sub>y</sub> O <sub>z</sub>	AlCl <sub>3</sub>	Si(OEt) <sub>4</sub>	94
	Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> <sup>f</sup>	AlMe <sub>3</sub>	( <sup>t</sup> BuO) <sub>3</sub> SiOH	157
	Al <sub>x</sub> Ti <sub>y</sub> O <sub>z</sub>	AlCl <sub>3</sub>	Ti(OEt) <sub>4</sub>	188
		AlCl <sub>3</sub>	Ti(O <sup>i</sup> Pr) <sub>4</sub>	188
		AlMe <sub>3</sub>	Ti(O <sup>i</sup> Pr) <sub>4</sub>	188

TABLE III. (Continued.)

Z	Material	Reactant A <sup>a</sup>	Reactant B	Refs.
	Al <sub>x</sub> Cr <sub>y</sub> O <sub>z</sub>	AlMe <sub>3</sub>	CrO <sub>2</sub> Cl <sub>2</sub>	93
	Al <sub>x</sub> Zr <sub>y</sub> O <sub>z</sub>	Al(OEt) <sub>3</sub>	ZrCl <sub>4</sub>	188
	Al <sub>x</sub> Hf <sub>y</sub> O <sub>z</sub>	Al(OEt) <sub>3</sub>	HfCl <sub>4</sub>	188
14 Silicon				
	SiO <sub>2</sub>	SiCl <sub>4</sub>	H <sub>2</sub> O	78, 90, 95, 96, 195, 214, and 333–337
		SiCl <sub>4</sub>	H <sub>2</sub> O + cat. <sup>g</sup>	335 and 338–341
		SiCl <sub>3</sub> H	H <sub>2</sub> O	97–99
		SiCl <sub>2</sub> H <sub>2</sub>	O <sub>3</sub>	342
		Si(OEt) <sub>4</sub>	H <sub>2</sub> O + cat.	343
		HMDS <sup>h</sup>	O <sub>2</sub>	344
		Si(NCO) <sub>4</sub>	H <sub>2</sub> O	345
		Si(NCO) <sub>4</sub>	NEt <sub>3</sub>	346
		MeOSi(NCO) <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	347 and 348
	Si <sub>3</sub> N <sub>4</sub>	SiCl <sub>4</sub>	NH <sub>3</sub>	349–352
		SiCl <sub>2</sub> H <sub>2</sub>	NH <sub>3</sub>	352
		SiCl <sub>2</sub> H <sub>2</sub>	NH <sub>3</sub> <sup>e</sup>	353
		SiCl <sub>2</sub> H <sub>2</sub>	NH <sub>3</sub> + cat.	354 and 355
		Si <sub>2</sub> Cl <sub>6</sub>	N <sub>2</sub> H <sub>4</sub>	356
	SiC	SiCl <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	357 and 358
		SiEt <sub>2</sub> H <sub>2</sub>	<sup>i</sup>	359
		Si <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	360
		Si <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>2</sub>	361–364
	Si	SiCl <sub>4</sub>	Si <sub>2</sub> H <sub>6</sub>	365
		SiCl <sub>2</sub> H <sub>2</sub>	H <sub>2</sub>	366 and 367
		SiCl <sub>2</sub> H <sub>2</sub>	H <sup>c</sup>	368–375
		SiCl <sub>2</sub> H <sub>2</sub>	<sup>j</sup>	376–378
		SiEt <sub>2</sub> H <sub>2</sub>	<sup>k</sup>	379
		SiH <sub>4</sub>	<sup>k</sup>	380–382
		Si <sub>2</sub> Cl <sub>6</sub>	Si <sub>2</sub> H <sub>6</sub>	371, 372, 383, and 384
		Si <sub>2</sub> Cl <sub>6</sub>	H <sup>c</sup>	385
		Si <sub>2</sub> H <sub>6</sub>	<sup>k</sup>	386–394
		Si <sub>2</sub> H <sub>6</sub>	<sup>j</sup>	395–399
		Si <sub>2</sub> H <sub>6</sub>	<sup>k</sup>	394 and 400
		Si <sub>2</sub> H <sub>6</sub>	<sup>l</sup>	401
		Si <sub>3</sub> H <sub>8</sub>	<sup>k</sup>	370 and 402
	Si <sub>x</sub> Al <sub>y</sub> O <sub>z</sub>	Si(OEt) <sub>4</sub>	AlCl <sub>3</sub>	94
	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> <sup>f</sup>	( <sup>t</sup> BuO) <sub>3</sub> SiOH	AlMe <sub>3</sub>	157
	Si <sub>x</sub> Ti <sub>y</sub> O <sub>z</sub>	Si(OEt) <sub>4</sub>	TiCl <sub>4</sub>	88
	Si <sub>x</sub> Zr <sub>y</sub> O <sub>z</sub>	SiCl <sub>4</sub>	Zr(O <sup>t</sup> Bu) <sub>4</sub>	403
		Si(OEt) <sub>4</sub>	ZrCl <sub>4</sub>	188
		Si(O <sup>t</sup> Bu) <sub>4</sub>	ZrCl <sub>4</sub>	188 and 404
		Si(O <sup>t</sup> Bu) <sub>4</sub>	Zr(NEt <sub>2</sub> ) <sub>4</sub>	405
	Si <sub>x</sub> Hf <sub>y</sub> O <sub>z</sub>	Si(OEt) <sub>4</sub>	HfCl <sub>4</sub>	406
		Si(OEt) <sub>4</sub>	HfI <sub>4</sub>	406
		( <sup>t</sup> BuO) <sub>3</sub> SiOH	Hf(NMe <sub>2</sub> ) <sub>4</sub>	407
15 Phosphorus				
	PO <sub>x</sub>	PCl <sub>3</sub>	H <sub>2</sub> O	82 and 100–103
		POCl <sub>3</sub>	H <sub>2</sub> O	96, 104, and 105
	P <sub>x</sub> B <sub>y</sub> O <sub>z</sub>	POCl <sub>3</sub>	B(OMe) <sub>3</sub>	88 and 89
20 Calcium				
	CaO (CaCO <sub>3</sub> )	Ca(thd) <sub>2</sub>	H <sub>2</sub> O	408
		Ca(thd) <sub>2</sub>	O <sub>3</sub>	409
	CaS	Ca(thd) <sub>2</sub>	H <sub>2</sub> S	408 and 410–414
	CaF <sub>2</sub>	Ca(thd) <sub>2</sub>	HF	415
21 Scandium				
	Sc <sub>2</sub> O <sub>3</sub>	ScCp <sub>3</sub>	H <sub>2</sub> O	416
		Sc(thd) <sub>3</sub>	O <sub>3</sub>	416
		Sc(thd) <sub>3</sub>	O <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>	416

TABLE III. (Continued.)

Z	Material	Reactant A <sup>a</sup>	Reactant B	Refs.
22 Titanium	TiO <sub>2</sub>	TiCl <sub>4</sub>	H <sub>2</sub> O	1, 79–81, 96, 100, 101, 106–133, 207, 212, 237, 260, 336, and 417–453
		TiCl <sub>4</sub>	H <sub>2</sub> O <sub>2</sub>	267, 269, and 454
		TiI <sub>4</sub>	H <sub>2</sub> O	455
		TiI <sub>4</sub>	H <sub>2</sub> O <sub>2</sub>	456–458
		TiI <sub>4</sub>	O <sub>2</sub>	459 and 460
		Ti(OMe) <sub>4</sub>	H <sub>2</sub> O	461
		Ti(OEt) <sub>4</sub>	H <sub>2</sub> O	206, 212, and 462–466
		Ti(O <sup>i</sup> Pr) <sub>4</sub>	H <sub>2</sub> O	212 and 467–474
		Ti(O <sup>i</sup> Pr) <sub>4</sub>	O <sub>2</sub>	434 and 475
		Ti(O <sup>i</sup> Pr) <sub>4</sub>	O <sub>2</sub> <sup>c</sup>	476
		Ti(O <sup>i</sup> Pr) <sub>4</sub>	O <sub>3</sub>	477
		Ti(O <sup>i</sup> Pr) <sub>2</sub> (dmae) <sub>2</sub>	H <sub>2</sub> O	478
		Ti(Obu) <sub>4</sub>	H <sub>2</sub> O	134
		Ti(NMe <sub>2</sub> ) <sub>4</sub>	O <sub>2</sub> <sup>c</sup>	479
	TiN	TiCl <sub>4</sub>	NH <sub>3</sub>	480–494
		TiCl <sub>4</sub>	NH <sub>3</sub> + cat.	205 and 481–483
		TiCl <sub>4</sub>	N <sub>2</sub> , H <sub>2</sub> <sup>c</sup>	274
		TiCl <sub>4</sub>	Me <sub>2</sub> NNH <sub>2</sub>	495
		TiCl <sub>4</sub>	<sup>t</sup> BuNH <sub>2</sub>	496
		TiCl <sub>4</sub>	AyNH <sub>2</sub>	496
		TiI <sub>4</sub>	NH <sub>3</sub>	483 and 497
		TiI <sub>4</sub>	<sup>t</sup> BuNH <sub>2</sub>	496
		TiI <sub>4</sub>	AyNH <sub>2</sub>	496
		Ti(NMe <sub>2</sub> ) <sub>4</sub>	NH <sub>3</sub>	498–507
		Ti(NMe <sub>2</sub> ) <sub>4</sub>	NH <sub>3</sub> <sup>c</sup>	508 and 509
		Ti(NMe <sub>2</sub> ) <sub>4</sub>	N <sub>2</sub> <sup>c</sup>	509–512
		Ti(NMe <sub>2</sub> ) <sub>4</sub>	H <sub>2</sub> <sup>c</sup>	509, 511, and 512
		Ti(NEt <sub>2</sub> ) <sub>4</sub>	NH <sub>3</sub>	506
		Ti(NEtMe) <sub>4</sub>	NH <sub>3</sub>	513 and 514
		TiCl <sub>4</sub>	H <sub>2</sub> <sup>c</sup>	515 and 516
	Ti <sub>x</sub> Al <sub>y</sub> O <sub>z</sub>	Ti(OEt) <sub>4</sub>	AlCl <sub>3</sub>	188
		Ti(O <sup>i</sup> Pr) <sub>4</sub>	AlCl <sub>3</sub>	188
		Ti(O <sup>i</sup> Pr) <sub>4</sub>	AlMe <sub>3</sub>	188
		TiCl <sub>4</sub>	Si(OEt) <sub>4</sub>	88
	Ti <sub>x</sub> Si <sub>y</sub> O <sub>z</sub>	Ti(O <sup>i</sup> Pr) <sub>4</sub>	ZrCl <sub>4</sub>	188, 517, and 518
	Ti <sub>x</sub> Zr <sub>y</sub> O <sub>z</sub>	Ti(O <sup>i</sup> Pr) <sub>4</sub>	HfCl <sub>4</sub>	188
	Ti <sub>x</sub> Hf <sub>y</sub> O <sub>z</sub>			
23 Vanadium	VO <sub>x</sub>	VOCl <sub>3</sub>	H <sub>2</sub> O	96, 103, 117, 121, and 135–137
		VO(O <sup>i</sup> Pr) <sub>3</sub>	H <sub>2</sub> O	519 and 520
		VO(O <sup>i</sup> Pr) <sub>3</sub>	O <sub>2</sub>	521–523
		VO(acac) <sub>2</sub>	O <sub>2</sub>	524 and 525
24 Chromium	CrO <sub>x</sub>	CrO <sub>2</sub> Cl <sub>2</sub>	H <sub>2</sub> O	84, 96, 103, 105, 117, 121, and 138–142
		CrO <sub>2</sub> Cl <sub>2</sub>	MeOH	93
		Cr(acac) <sub>3</sub>	O <sub>2</sub>	434 and 526–530
		CrO <sub>2</sub> Cl <sub>2</sub>	AlMe <sub>3</sub>	93
	Cr <sub>x</sub> Al <sub>y</sub> O <sub>z</sub>			
25 Manganese	MnO <sub>x</sub>	Mn(thd) <sub>3</sub>	O <sub>3</sub>	531–533
	MnS	MnCl <sub>2</sub>	H <sub>2</sub> S	76 and 77
	MnTe	Mn	Te	170 and 534–543
26 Iron	FeO <sub>x</sub>	Fe(acac) <sub>3</sub>	O <sub>2</sub>	544
		Fe(thd) <sub>3</sub>	O <sub>3</sub>	545
		Fe( <sup>t</sup> BuAMD) <sub>2</sub>	H <sub>2</sub> O	546
		Fe( <sup>t</sup> BuAMD) <sub>2</sub>	H <sub>2</sub>	546
	Fe			
27 Cobalt				

TABLE III. (Continued.)

Z	Material	Reactant A <sup>a</sup>	Reactant B	Refs.
	CoO <sub>x</sub>	Co(acac) <sub>2</sub>	O <sub>2</sub>	547 and 548
		Co(acac) <sub>3</sub>	O <sub>2</sub>	547–554
		Co(thd) <sub>2</sub>	O <sub>3</sub>	555
		Co( <sup>i</sup> PrAMD) <sub>2</sub>	H <sub>2</sub> O	546
	Co	Co( <sup>i</sup> PrAMD) <sub>2</sub>	H <sub>2</sub>	546
28 Nickel	NiO	NiCp <sub>2</sub>	H <sub>2</sub> O	556
		Ni(acac) <sub>2</sub>	O <sub>2</sub>	557–559
		Ni(acac) <sub>2</sub>	O <sub>3</sub>	560 and 561
		Ni(thd) <sub>2</sub>	O <sub>3</sub>	562
		Ni(apo) <sub>2</sub>	O <sub>3</sub>	560
		Ni(dmgl) <sub>2</sub>	O <sub>3</sub>	560
	Ni	Ni(acac) <sub>2</sub>	H <sub>2</sub>	561
		Ni( <sup>i</sup> PrAMD) <sub>2</sub>	H <sub>2</sub>	546
29 Copper	CuO	Cu(acac) <sub>2</sub>	O <sub>2</sub>	563
		Cu(thd) <sub>2</sub>	O <sub>2</sub>	46, 50, and 564
		Cu(hfac) <sub>2</sub>	H <sub>2</sub> O	565
	Cu <sub>x</sub> S	Cu(thd) <sub>2</sub>	H <sub>2</sub> S	566–569
	Cu	CuCl	H <sub>2</sub>	570 and 571
		CuCl	H <sub>2</sub> +H <sub>2</sub> O	571 and 572
		CuCl	Zn	573
		Cu(acac) <sub>2</sub>	H <sub>2</sub>	561
		Cu(acac) <sub>2</sub>	H <sub>2</sub> <sup>c</sup>	574
		Cu(thd) <sub>2</sub>	H <sub>2</sub>	575 and 576
		Cu(hfac) <sub>2</sub>	ROH <sup>d</sup>	577
		Cu(hfac) <sub>2</sub>	HCHO <sup>m</sup>	577
		Cu( <sup>i</sup> PrAMD)	H <sub>2</sub>	546
30 Zinc	ZnO	Zn	O <sub>2</sub>	578
		Zn	H <sub>2</sub> O	579
		ZnCl <sub>2</sub>	H <sub>2</sub> O	144
		ZnCl <sub>2</sub>	O <sub>2</sub>	580–582
		ZnMe <sub>2</sub>	H <sub>2</sub> O	583 and 584
		ZnEt <sub>2</sub>	H <sub>2</sub> O	201, 229, 231, and 584–607
		ZnEt <sub>2</sub>	H <sub>2</sub> O <sup>n</sup>	598
		ZnEt <sub>2</sub>	O <sub>2</sub>	605
		Zn(OAc) <sub>2</sub>	H <sub>2</sub> O	608–610
	ZnS	Zn	S	2, 171, 611, and 612
		Zn	H <sub>2</sub> S	613
		ZnCl <sub>2</sub>	H <sub>2</sub> S	76, 77, 86, 177, and 614–626
		ZnMe <sub>2</sub>	H <sub>2</sub> S	583 and 627–635
		ZnEt <sub>2</sub>	H <sub>2</sub> S	145, 596, 636, and 637
		ZnEt <sub>2</sub>	Et <sub>2</sub> S <sub>2</sub>	638
		Zn(OAc) <sub>2</sub>	H <sub>2</sub> S	415, 608, 615, 616, 618–620, and 639
	ZnSe	Zn	Se	578, 611, and 640–655
		Zn	H <sub>2</sub> Se	656
		Zn	Et <sub>2</sub> Se	657
		ZnCl <sub>2</sub>	H <sub>2</sub> Se	658–660
		ZnMe <sub>2</sub>	H <sub>2</sub> Se	633–635 and 661–671
		ZnEt <sub>2</sub>	H <sub>2</sub> Se	672
		ZnEt <sub>2</sub>	Et <sub>2</sub> Se <sub>2</sub>	638
		Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	H <sub>2</sub> Se	672
	ZnTe	Zn	Te	154, 536, 640, 643–645, 647, and 673–679
		ZnMe <sub>2</sub>	Et <sub>2</sub> Te	680
	ZnF	ZnMe <sub>2</sub>	MeAyTe	680
		Zn(OAc) <sub>2</sub>	HF	415



TABLE III. (Continued.)

Z	Material	Reactant A <sup>a</sup>	Reactant B	Refs.
	Ga <sub>2</sub> O <sub>3</sub>	Ga(acac) <sub>3</sub>	O <sub>3</sub>	681 and 682
		Ga(acac) <sub>3</sub>	H <sub>2</sub> O	681
	GaN	Ga	N <sub>2</sub>	683 and 684
		GaCl	NH <sub>3</sub>	685 and 686
		GaCl <sub>3</sub>	NH <sub>3</sub>	687
		GaMe <sub>3</sub>	NH <sub>3</sub>	290 and 688–692
		GaEt <sub>3</sub>	NH <sub>3</sub>	294, 693, and 694
		GaEt <sub>3</sub>	NH <sub>3</sub> <sup>o</sup>	695
	GaP	Ga	P	2
		GaCl	PH <sub>3</sub>	696
		GaMe <sub>3</sub>	PH <sub>3</sub>	299, 313, and 697–701
		GaEt <sub>3</sub>	PH <sub>3</sub> <sup>n</sup>	702
	GaAs	GaCl	AsH <sub>3</sub>	696 and 703–716
		GaCl <sub>3</sub>	AsH <sub>3</sub>	303, 304, and 717–721
		GaCl <sub>3</sub>	As	720
		GaBr	AsH <sub>3</sub>	722
		GaI	AsH <sub>3</sub>	722
		GaMe <sub>3</sub>	AsH <sub>3</sub>	153, 305–308, 311, 313, 315, 318, 321, 698, 701, and 723–771
		GaMe <sub>3</sub>	EtAsH <sub>2</sub>	772
		GaMe <sub>3</sub>	<sup>t</sup> BuAsH <sub>2</sub>	773–780
		GaEt <sub>3</sub>	AsH <sub>3</sub>	26, 309, 311, 698, 729, 738, 743, and 781–788
		GaEt <sub>3</sub>	<sup>t</sup> BuAsH <sub>2</sub>	779 and 789
		GaEt <sub>3</sub>	(Me <sub>2</sub> N) <sub>3</sub> As	324, 790, and 791
		GaEt <sub>2</sub> Cl	As	792
		GaEt <sub>2</sub> Cl	AsH <sub>3</sub>	755 and 793
		GaEt <sub>2</sub> Me	AsH <sub>3</sub>	698
		Ga <sup>i</sup> Bu <sub>3</sub>	AsH <sub>3</sub>	26
		GaNp <sub>3</sub>	<sup>t</sup> BuAsH <sub>2</sub>	779 and 794
32 Germanium	GeO <sub>2</sub>	GeCl <sub>4</sub>	H <sub>2</sub> O	1 and 146
	Ge	GeCl <sub>4</sub>	H <sup>c</sup>	795 and 796
		GeMe <sub>2</sub> H <sub>2</sub>	H <sup>c</sup>	797–799
		GeEt <sub>2</sub> H <sub>2</sub>	<sub>k</sub>	800 and 801
		GeH <sub>4</sub>	<sub>k</sub>	382 and 802
		Ge <sub>2</sub> H <sub>6</sub>	<sub>k</sub>	803 and 804
38 Strontium	SrO (SrCO <sub>3</sub> )	Sr(Cp <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub>	H <sub>2</sub> O	805 and 806
		Sr(thd) <sub>2</sub>	O <sub>3</sub>	807
		Sr(methd) <sub>2</sub>	O <sub>2</sub> <sup>c</sup>	476
	SrS	Sr(CpMe <sub>5</sub> ) <sub>2</sub>	H <sub>2</sub> S	808
		Sr(Cp <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub>	H <sub>2</sub> S	808 and 809
		Sr(thd) <sub>2</sub>	H <sub>2</sub> S	410, 412, and 810–812
	SrF <sub>2</sub>	Sr(thd) <sub>2</sub>	HF	415
39 Yttrium	Y <sub>2</sub> O <sub>3</sub>	YCp <sub>3</sub>	H <sub>2</sub> O	813
		Y(CpMe) <sub>3</sub>	H <sub>2</sub> O	813
		Y(thd) <sub>3</sub>	O <sub>2</sub>	814
		Y(thd) <sub>3</sub>	O <sub>3</sub>	219, 237, 814, and 815
		Y(thd) <sub>3</sub>	H <sub>2</sub> S	816
	Y <sub>2</sub> O <sub>2</sub> S	Y(thd) <sub>3</sub>	H <sub>2</sub> S	816
40 Zirconium	ZrO <sub>2</sub>	ZrCl <sub>4</sub>	H <sub>2</sub> O	212, 219, 222, 230, 246, 434, and 817–834
		ZrCl <sub>4</sub>	H <sub>2</sub> O <sub>2</sub>	825 and 826
		ZrCl <sub>4</sub>	O <sub>2</sub>	835 and 836
		ZrI <sub>4</sub>	H <sub>2</sub> O	837
		ZrI <sub>4</sub>	H <sub>2</sub> O <sub>2</sub>	838–841
		ZrCp <sub>2</sub> Cl <sub>2</sub>	O <sub>3</sub>	842 and 843
		ZrCp <sub>2</sub> Me <sub>2</sub>	H <sub>2</sub> O	844

TABLE III. (Continued.)

Z	Material	Reactant A <sup>a</sup>	Reactant B	Refs.
		ZrCp <sub>2</sub> Me <sub>2</sub>	O <sub>3</sub>	842 and 845
		Zr(O <sup>i</sup> Pr) <sub>2</sub> (dmae) <sub>2</sub>	H <sub>2</sub> O	846
		Zr(O <sup>i</sup> Bu) <sub>4</sub>	H <sub>2</sub> O	471, 473, 474, and 847–851
		Zr(O <sup>i</sup> Bu) <sub>4</sub>	O <sub>2</sub>	851
		Zr(O <sup>i</sup> Bu) <sub>4</sub>	O <sub>2</sub> <sup>c</sup>	852–855
		Zr(O <sup>i</sup> Bu) <sub>4</sub>	N <sub>2</sub> O	851
		Zr(O <sup>i</sup> Bu) <sub>4</sub>	Ar <sup>c</sup>	855
		Zr(O <sup>i</sup> Bu) <sub>2</sub> (dmae) <sub>2</sub>	H <sub>2</sub> O	846 and 856
		Zr(dmae) <sub>4</sub>	H <sub>2</sub> O	846
		Zr(thd) <sub>4</sub>	O <sub>3</sub> <sup>c</sup>	842
		Zr(NMe <sub>2</sub> ) <sub>4</sub>	H <sub>2</sub> O	857 and 858
		Zr(NEt <sub>2</sub> ) <sub>4</sub>	H <sub>2</sub> O	857
		Zr(NEt <sub>2</sub> ) <sub>4</sub>	O <sub>2</sub> <sup>c</sup>	853
		Zr(NEtMe) <sub>4</sub>	H <sub>2</sub> O	857
		Zr[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> Cl <sub>2</sub>	H <sub>2</sub> O	859
		Zr(NMe <sub>2</sub> ) <sub>4</sub>	NH <sub>3</sub>	860
		Zr(NEtMe) <sub>4</sub>	NH <sub>3</sub>	860
		Zr(NEt <sub>2</sub> ) <sub>4</sub>	NH <sub>3</sub>	860
	Zr <sub>3</sub> N <sub>4</sub>	ZrCl <sub>4</sub>	Al(OEt) <sub>3</sub>	188
	Zr <sub>x</sub> Al <sub>y</sub> O <sub>z</sub>	ZrCl <sub>4</sub>	Si(OEt) <sub>4</sub>	188 and 861
	Zr <sub>x</sub> Si <sub>y</sub> O <sub>z</sub>	ZrCl <sub>4</sub>	Si(O <sup>n</sup> Bu) <sub>4</sub>	188 and 404
		Zr(O <sup>i</sup> Bu) <sub>4</sub>	SiCl <sub>4</sub>	403
		Zr(NEt <sub>2</sub> ) <sub>4</sub>	Si(O <sup>n</sup> Bu) <sub>4</sub>	405
	Zr <sub>x</sub> Ti <sub>y</sub> O <sub>z</sub>	ZrCl <sub>4</sub>	Ti(O <sup>i</sup> Pr) <sub>4</sub>	188, 517, and 518
41 Niobium	Nb <sub>2</sub> O <sub>5</sub> NbN	Nb(OEt) <sub>5</sub>	H <sub>2</sub> O	184, 206, 465, 820, 862, and 863
		NbCl <sub>5</sub>	NH <sub>3</sub>	480, 482, and 864
		NbCl <sub>5</sub>	NH <sub>3</sub> + cat.	482 and 864
		NbCl <sub>5</sub>	Me <sub>2</sub> NNH <sub>2</sub>	495
42 Molybdenum	Mo <sub>x</sub> N	MoCl <sub>5</sub>	NH <sub>3</sub>	480
		MoCl <sub>5</sub>	Me <sub>2</sub> NNH <sub>2</sub>	495
	Mo	MoCl <sub>5</sub>	Zn	865
44 Ruthenium	RuO Ru	Ru(CpEt) <sub>2</sub>	O <sub>2</sub>	866
		RuCp <sub>2</sub>	O <sub>2</sub>	867–869
		Ru(CpEt) <sub>2</sub>	O <sub>2</sub>	866
		Ru(CpEt) <sub>2</sub>	NH <sub>3</sub> <sup>c</sup>	870 and 871
		Ru(od) <sub>3</sub>	O <sub>2</sub>	872
		Ru(thd) <sub>3</sub>	H <sub>2</sub>	873
		Ru(thd) <sub>3</sub>	O <sub>2</sub>	869 and 874
46 Palladium	Pd	Pd(thd) <sub>2</sub>	H <sub>2</sub>	873
		Pd(thd) <sub>2</sub>	O <sub>2</sub>	564
		Pd(hfac) <sub>2</sub>	H <sub>2</sub>	875
		Pd(hfac) <sub>2</sub>	HCOCOOH	875
48 Cadmium	CdS	Cd	S	147 and 876
		CdCl <sub>2</sub>	H <sub>2</sub> S	623
		CdMe <sub>2</sub>	H <sub>2</sub> S	145 and 877–881
	CdSe	Cd	Se	147–149, 611, and 882–886
		CdMe <sub>2</sub>	H <sub>2</sub> Se	145 and 662
	CdTe	Cd	Te	147, 148, 170, 534–539, 541–543, 655, 675, 679, and 886–911
		CdMe <sub>2</sub>	Et <sub>2</sub> Te	680
		CdMe <sub>2</sub>	MeAyTe	680 and 912–914
		CdMe <sub>2</sub>	<sup>i</sup> Pr <sub>2</sub> Te	915 and 916

TABLE III. (Continued.)

Z	Material	Reactant A <sup>a</sup>	Reactant B	Refs.
49 Indium	In <sub>2</sub> O <sub>3</sub>	InCl <sub>3</sub>	H <sub>2</sub> O	212 and 917–921
		InCl <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	921
		InMe <sub>3</sub>	H <sub>2</sub> O	922
	In <sub>2</sub> S <sub>3</sub>	InCl <sub>3</sub>	H <sub>2</sub> S	923
		In(acac) <sub>3</sub>	H <sub>2</sub> S	596, 597, and 924–927
	InN	In	N <sub>2</sub>	928
	InP	InEtMe <sub>2</sub>	NH <sub>3</sub>	290, 689, and 690
		InCl	PH <sub>3</sub>	696
		InCl	<sup>t</sup> BuPH <sub>2</sub>	712
		InMe <sub>3</sub>	PH <sub>3</sub>	741, 754, and 929–937
		InMe <sub>3</sub>	<sup>t</sup> BuPH <sub>2</sub>	938–940
		InEt <sub>3</sub>	PH <sub>3</sub>	697 and 699
		InEt <sub>3</sub>	<sup>t</sup> BuPH <sub>2</sub>	941
	InAs	InCl	AsH <sub>3</sub>	704, 705, and 717
		InMe <sub>3</sub>	AsH <sub>3</sub>	733, 942, and 943
		InMe <sub>3</sub>	<sup>t</sup> BuAsH <sub>2</sub>	780, 931, 933, 944, and 945
		InClMe <sub>2</sub>	AsH <sub>3</sub>	946
	InSb	InEt <sub>3</sub>	AsH <sub>3</sub>	726, 947, and 948
		In	Sb	949 and 950
50 Tin	SnO <sub>2</sub>	Sn	O <sub>2</sub>	2
		SnCl <sub>4</sub>	H <sub>2</sub> O	111, 150, 212, 445, 682, and 951–960
		SnCl <sub>4</sub>	H <sub>2</sub> O <sub>2</sub>	959, 961, and 962
		SnI <sub>4</sub>	H <sub>2</sub> O <sub>2</sub>	959
		SnI <sub>4</sub>	O <sub>2</sub>	959 and 961–964
		SnMe <sub>4</sub>	N <sub>2</sub> O <sub>4</sub>	151
		SnEt <sub>4</sub>	N <sub>2</sub> O <sub>4</sub>	151
51 Antimony	Sb <sub>2</sub> O <sub>5</sub>	SbCl <sub>5</sub>	H <sub>2</sub> O	952
56 Barium	BaS	Ba(CpMe <sub>5</sub> ) <sub>2</sub>	H <sub>2</sub> S	808 and 809
		Ba(thd) <sub>2</sub>	H <sub>2</sub> S	410 and 965
57 Lanthanum	La <sub>2</sub> O <sub>3</sub>	La(thd) <sub>3</sub>	O <sub>2</sub>	46 and 50
		La(thd) <sub>3</sub>	O <sub>3</sub>	555, 562, 966, and 967
		La[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub>	H <sub>2</sub> O	407, 968, and 969
		La( <sup>t</sup> PrAMD) <sub>3</sub>	H <sub>2</sub> O	546
	La <sub>2</sub> S <sub>3</sub>	La(thd) <sub>3</sub>	H <sub>2</sub> S	970
	La <sub>x</sub> Si <sub>y</sub> O <sub>x</sub>	La[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub>	( <sup>t</sup> BuO) <sub>3</sub> SiOH	407
58 Cerium	CeO <sub>2</sub>	Ce(thd) <sub>4</sub>	O <sub>2</sub>	46 and 50
		Ce(thd) <sub>4</sub>	O <sub>3</sub>	971
		Ce(thd) <sub>3</sub> phen	O <sub>3</sub>	971
59 Praseodymium	PrO <sub>x</sub>	Pr[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub>	H <sub>2</sub> O	972
60 Neodymium	Nd <sub>2</sub> O <sub>3</sub>	Nd(thd) <sub>3</sub>	O <sub>3</sub>	973
62 Samarium	Sm <sub>2</sub> O <sub>3</sub>	Sm(thd) <sub>3</sub>	O <sub>3</sub>	973
63 Europium	Eu <sub>2</sub> O <sub>3</sub>	Eu(thd) <sub>3</sub>	O <sub>3</sub>	973
64 Gadolinium	Gd <sub>2</sub> O <sub>3</sub>	Gd(thd) <sub>3</sub>	O <sub>3</sub>	973

TABLE III. (Continued.)

Z	Material	Reactant A <sup>a</sup>	Reactant B	Refs.
66 Dysprosium				
	Dy <sub>2</sub> O <sub>3</sub>	Dy(thd) <sub>3</sub>	O <sub>3</sub>	973
67 Holmium				
	Ho <sub>2</sub> O <sub>3</sub>	Ho(thd) <sub>3</sub>	O <sub>3</sub>	973
68 Erbium				
	Er <sub>2</sub> O <sub>3</sub>	Er(thd) <sub>3</sub>	O <sub>3</sub>	973 and 974
69 Thulium				
	Tm <sub>2</sub> O <sub>3</sub>	Tm(thd) <sub>3</sub>	O <sub>3</sub>	973
71 Lutetium				
	Lu <sub>2</sub> O <sub>3</sub>	Lu[Cp(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> Cl	H <sub>2</sub> O	975
72 Hafnium				
	HfO <sub>2</sub>	HfCl <sub>4</sub>	H <sub>2</sub> O	219, 238, 244, 252, 253, 255–257, 259, 439, 822, 832, 837, 969, and 976–1008
		HfCl <sub>4</sub>	O <sub>2</sub>	1009 and 1010
		HfCl <sub>4</sub>	O <sub>3</sub>	990
		HfCl <sub>2</sub> [N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	H <sub>2</sub> O	1011
		HfI <sub>4</sub>	H <sub>2</sub> O	837, 989, 994, and 1012
		HfI <sub>4</sub>	H <sub>2</sub> O <sub>2</sub>	1012
		HfI <sub>4</sub>	O <sub>2</sub>	994 and 1013–1016
		Hf(O <sup>i</sup> Bu) <sub>4</sub>	O <sub>3</sub>	1017 and 1018
		Hf(O <sup>i</sup> Bu) <sub>4</sub>	O <sub>2</sub> <sup>c</sup>	854
		Hf(O <sup>i</sup> Bu) <sub>2</sub> (mmp) <sub>2</sub>	H <sub>2</sub> O	1019
		Hf(mmp) <sub>4</sub>	H <sub>2</sub> O	1020
		Hf(ONeEt) <sub>4</sub>	H <sub>2</sub> O	1021
		Hf(NMe <sub>2</sub> ) <sub>4</sub>	H <sub>2</sub> O	407, 857, 858, 1022, and 1023
		Hf(NMe <sub>2</sub> ) <sub>4</sub>	O <sub>3</sub>	1023
		Hf(NEt <sub>2</sub> ) <sub>4</sub>	H <sub>2</sub> O	857, 1024, and 1025
		Hf(NEt <sub>2</sub> ) <sub>4</sub>	O <sub>2</sub>	1026
		Hf(NEt <sub>2</sub> ) <sub>4</sub>	O <sub>2</sub> <sup>c</sup>	1026
		Hf(NEtMe) <sub>4</sub>	H <sub>2</sub> O	244, 857, 1005, and 1027–1029
		Hf(NEtMe) <sub>4</sub>	O <sub>3</sub>	1018
		Hf[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> Cl <sub>2</sub>	H <sub>2</sub> O	1030
		Hf(NO <sub>3</sub> ) <sub>4</sub>	H <sub>2</sub> O	1031–1033
	Hf <sub>3</sub> N <sub>4</sub>	Hf(NMe <sub>2</sub> ) <sub>4</sub>	NH <sub>3</sub>	860
		Hf(NEt <sub>2</sub> ) <sub>4</sub>	NH <sub>3</sub>	860
		Hf(NEtMe) <sub>4</sub>	NH <sub>3</sub>	860
	Hf <sub>x</sub> Al <sub>y</sub> O <sub>z</sub>	HfCl <sub>4</sub>	Al(OEt) <sub>3</sub>	188
	Hf <sub>x</sub> Si <sub>y</sub> O <sub>z</sub>	HfCl <sub>4</sub>	Si(OEt) <sub>4</sub>	406
		HfCl <sub>4</sub>	Si(O <sup>i</sup> Bu) <sub>4</sub>	1034 and 1035
		HfI <sub>4</sub>	Si(OEt) <sub>4</sub>	406
		Hf(NMe <sub>2</sub> ) <sub>4</sub>	( <sup>i</sup> BuO) <sub>3</sub> SiOH	407
	Hf <sub>x</sub> Ti <sub>y</sub> O <sub>z</sub>	HfCl <sub>4</sub>	Ti(O <sup>i</sup> Pr) <sub>4</sub>	188
73 Tantalum				
	Ta <sub>2</sub> O <sub>5</sub>	TaCl <sub>5</sub>	H <sub>2</sub> O	76, 77, 91, 174, 183, 212, 614, 822, 863, 976, and 1036–1040
		TaCl <sub>5</sub>	Ta(OEt) <sub>5</sub>	188 and 1041
		TaI <sub>5</sub>	H <sub>2</sub> O <sub>2</sub>	1042
		TaI <sub>5</sub>	O <sub>2</sub>	1043
		Ta(OEt) <sub>5</sub>	H <sub>2</sub> O	178, 184, 206, 207, 212, 465, 820, 863, 978, and 1044–1047
		Ta(OEt) <sub>5</sub>	O <sub>2</sub> <sup>c</sup>	1048
		Ta(OEt) <sub>5</sub>	O <sub>2</sub> <sup>n</sup>	1049
		Ta(NMe <sub>2</sub> ) <sub>5</sub>	H <sub>2</sub> O	466
		Ta(NEt <sub>2</sub> ) <sub>5</sub>	H <sub>2</sub> O	1050
		Ta(NEt)(NEt <sub>2</sub> ) <sub>3</sub>	H <sub>2</sub> O	1050
	TaN <sub>x</sub>	TaCl <sub>5</sub>	NH <sub>3</sub>	480 and 1051
		TaCl <sub>5</sub>	NH <sub>3</sub> + cat.	1051



TABLE III. (Continued.)

Z	Material	Reactant A <sup>a</sup>	Reactant B	Refs.
	Ta	TaCl <sub>5</sub>	Me <sub>2</sub> NNH <sub>2</sub>	495
		TaCl <sub>5</sub>	<sup>t</sup> BuNH <sub>2</sub>	1052
		TaCl <sub>5</sub>	AyNH <sub>2</sub>	1052
		TaCl <sub>5</sub>	N <sub>2</sub> <sup>c</sup>	1053–1055
		TaBr <sub>5</sub>	<sup>t</sup> BuNH <sub>2</sub>	1052
		Ta(NMe <sub>2</sub> ) <sub>5</sub>	NH <sub>3</sub>	1056 and 1057
		Ta(N <sup>t</sup> Bu)(NEt <sub>2</sub> ) <sub>3</sub>	NH <sub>3</sub>	1058
		Ta(N <sup>t</sup> Bu)(NEt <sub>2</sub> ) <sub>3</sub>	H <sub>2</sub> <sup>c</sup>	1059 and 1060
		Ta(N <sup>t</sup> Bu)(NEtMe) <sub>3</sub>	NH <sub>3</sub>	1061
		Ta(N <sup>t</sup> Bu)(NEtMe) <sub>3</sub>	NH <sub>3</sub> <sup>c</sup>	1061
		TaCl <sub>5</sub>	H <sub>2</sub> <sup>c</sup>	515 and 1062
		TaF <sub>5</sub>	Si <sub>2</sub> H <sub>6</sub> <sup>p</sup>	1063
74 Tungsten	WO <sub>3</sub>	WF <sub>6</sub>	H <sub>2</sub> O	1064
		WF <sub>x</sub> O <sub>y</sub>	H <sub>2</sub> O	1064
		WOCl <sub>4</sub>	<sup>q</sup>	1065
	W <sub>x</sub> N	WF <sub>6</sub>	NH <sub>3</sub>	490, 491, 1066, and 1067
		WF <sub>6</sub>	NH <sub>3</sub> <sup>c</sup>	1068–1070
		W(N <sup>t</sup> Bu) <sub>2</sub> (NMe <sub>2</sub> ) <sub>2</sub>	NH <sub>3</sub>	1071–1073
	WS <sub>2</sub>	WF <sub>6</sub>	H <sub>2</sub> S	1074
	W <sub>x</sub> C	W(N <sup>t</sup> Bu) <sub>2</sub> (NMe <sub>2</sub> ) <sub>2</sub>	H <sub>2</sub> , N <sub>2</sub> <sup>c</sup>	1075
	W	WF <sub>6</sub>	Si <sub>2</sub> H <sub>6</sub>	249, 602, 1066, and 1076–1080
77 Iridium	Ir	Ir(acac) <sub>3</sub>	O <sub>2</sub>	1081
78 Platinum	Pt	Pt(CpMe)Me <sub>3</sub>	O <sub>2</sub>	867, 869, and 1082
		Pt(acac) <sub>2</sub>	H <sub>2</sub>	561
80 Mercury	HgTe	HgMe <sub>2</sub>	MeAyTe	912 and 914
82 Lead	PbS	PbBr <sub>2</sub>	H <sub>2</sub> S	1083
		PbI <sub>2</sub>	H <sub>2</sub> S	1083
		Pb(OAc) <sub>2</sub>	H <sub>2</sub> S	1083
		Pb(O <sup>t</sup> Bu) <sub>2</sub>	H <sub>2</sub> S	1084
		Pb <sub>4</sub> O(O <sup>t</sup> Bu) <sub>6</sub>	H <sub>2</sub> S	1084
		Pb(thd) <sub>2</sub>	H <sub>2</sub> S	1083 and 1084
		Pb(dedtc) <sub>2</sub>	H <sub>2</sub> S	1083 and 1084
83 Bismuth	BiO <sub>x</sub>	Bi[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub>	H <sub>2</sub> O	1085

<sup>a</sup>The metal thd complexes may have been slightly oligomerized and contain a neutral adduct molecule.<sup>b</sup>Diamond.<sup>c</sup>Atomic hydrogen.<sup>d</sup>R refers to alkyl chains of various lengths.<sup>e</sup>Plasma.<sup>f</sup>This process is atypical for ALD: it deposits nanolaminates of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, where the growth per cycle is many nanometers, through a catalytic mechanism (Ref. 157).<sup>g</sup>Cat.=catalyst.<sup>h</sup>HMDS=hexamethyldisilazane, (Me<sub>3</sub>Si)<sub>2</sub>NH.<sup>i</sup>Controlled desorption.<sup>j</sup>Irradiation.<sup>k</sup>Temperature treatment, such as flash heating or temperature modulation.<sup>l</sup>He plasma treatment.<sup>m</sup>Reactant B was formaline, containing ~37% of formaldehyde HCHO and some ethanol in water.<sup>n</sup>Photoassisted.<sup>o</sup>Decomposed.<sup>p</sup>Preliminary surface science investigation.<sup>q</sup>Only one half reaction of an ALD reaction cycle was carried out.

TABLE IV. Computational chemistry investigations on ALD processes.

Z	Material	Reactant A	Reactant B	Refs.
5 Boron				
	BPO <sub>4</sub>	B(OMe) <sub>3</sub>	POCl <sub>3</sub>	89
6 Carbon				
	C <sup>a</sup>	CF <sub>3</sub>	...	1086
13 Aluminum				
	Al <sub>2</sub> O <sub>3</sub>	AlCl <sub>3</sub>	H <sub>2</sub> O	1087
		AlMe <sub>3</sub>	H <sub>2</sub> O	1088–1097
14 Silicon				
	SiO <sub>2</sub>	SiCl <sub>4</sub>	H <sub>2</sub> O	1098
		SiCl <sub>4</sub>	H <sub>2</sub> O + cat. <sup>b</sup>	1099
	Si <sub>3</sub> N <sub>4</sub>	SiH <sub>4</sub>	NH <sub>3</sub>	1100
	Si	SiCl <sub>3</sub> H	H <sub>2</sub>	1101
20 Calcium				
	CaS	Ca(thd) <sub>2</sub>	...	1102
22 Titanium				
	TiO <sub>2</sub>	TiCl <sub>4</sub>	H <sub>2</sub> O	1103 and 1104
	TiN	TiCl <sub>4</sub>	NH <sub>3</sub>	1105
28 Copper				
	Cu	CuCl	H <sub>2</sub>	1106–1108
30 Zinc				
	ZnS	ZnCl <sub>2</sub>	H <sub>2</sub> S	1109–1111
	ZnSe	ZnCl <sub>2</sub>	H <sub>2</sub> Se	1111
	ZnTe	ZnCl <sub>2</sub>	H <sub>2</sub> Te	1111
31 Gallium				
	GaAs	GaCl	AsH <sub>3</sub>	711 and 1112–1114
40 Zirconium				
	ZrO <sub>2</sub>	ZrCl <sub>4</sub>	H <sub>2</sub> O	1091 and 1115–1123
72 Hafnium				
	HfO <sub>2</sub>	HfCl <sub>4</sub>	H <sub>2</sub> O	1091, 1119, 1122, and 1123
		HfCl <sub>4</sub>	Hf(OEt) <sub>4</sub>	1124
		Hf(OEt) <sub>4</sub>	H <sub>2</sub> O	1124
73 Tantalum				
	Ta <sub>2</sub> O <sub>5</sub>	TaCl <sub>5</sub>	H <sub>2</sub> O	1125

<sup>a</sup>Diamond.<sup>b</sup>Cat. = catalyst.

may be related to the difficulty of cleaving the  $M-O$  bond present in the alkoxides. Decomposition at low temperatures is a typical drawback of alkoxide reactants. For example,  $Ti(O^iPr)_4$  decomposes already at 200 °C.<sup>475</sup> Although the decomposition product is the desired oxide, the decomposition inevitably leads to a decreased film conformality. A second drawback is the generation of alcohols as by-products in the gas–solid reactions. Alcohols are reactive and may read-sorb on the surface and interface with the growth.<sup>465,470</sup> A third drawback is the high concentrations of carbon and hydrogen impurities in the films. For example,  $ZrO_2$  films grown at 250 °C through the  $Zr(O^iBu)_4/H_2O$  process have been reported to contain 8-at. % hydrogen and 2-at. % carbon.<sup>847</sup> The popularity of alkoxides for growing binary oxides seems to have been decreasing in the recent years, although some new studies keep appearing. Nowadays,

alkoxides have been most often used for growing ternary oxides in combination with metal halide reactants. This reaction concept was demonstrated by Brei *et al.*,<sup>88,94</sup> and it was made more widely known by Ritala *et al.*<sup>188,1138</sup>

$\beta$ -diketonates are in use as ALD reactants since the late 1980s.<sup>408,410–412,415,814,1083,1084</sup> As evident from Fig. 5(f), there are  $\beta$ -diketonate reactants available for groups 2–14 elements (except group 12 has not been demonstrated), which make them the most broadly used class of ALD reactants. Before the recent introduction of cyclopentadienyls,  $\beta$ -diketonates were the only reactant types available for alkaline-earth metals. Although available for a broad variety of metals, only a few types of materials have been made from  $\beta$ -diketonates (Table X): mostly oxides, and some sulphides, fluorides, and metals. Similarly as for alkoxides, nitrides are missing from the types of materials made, which

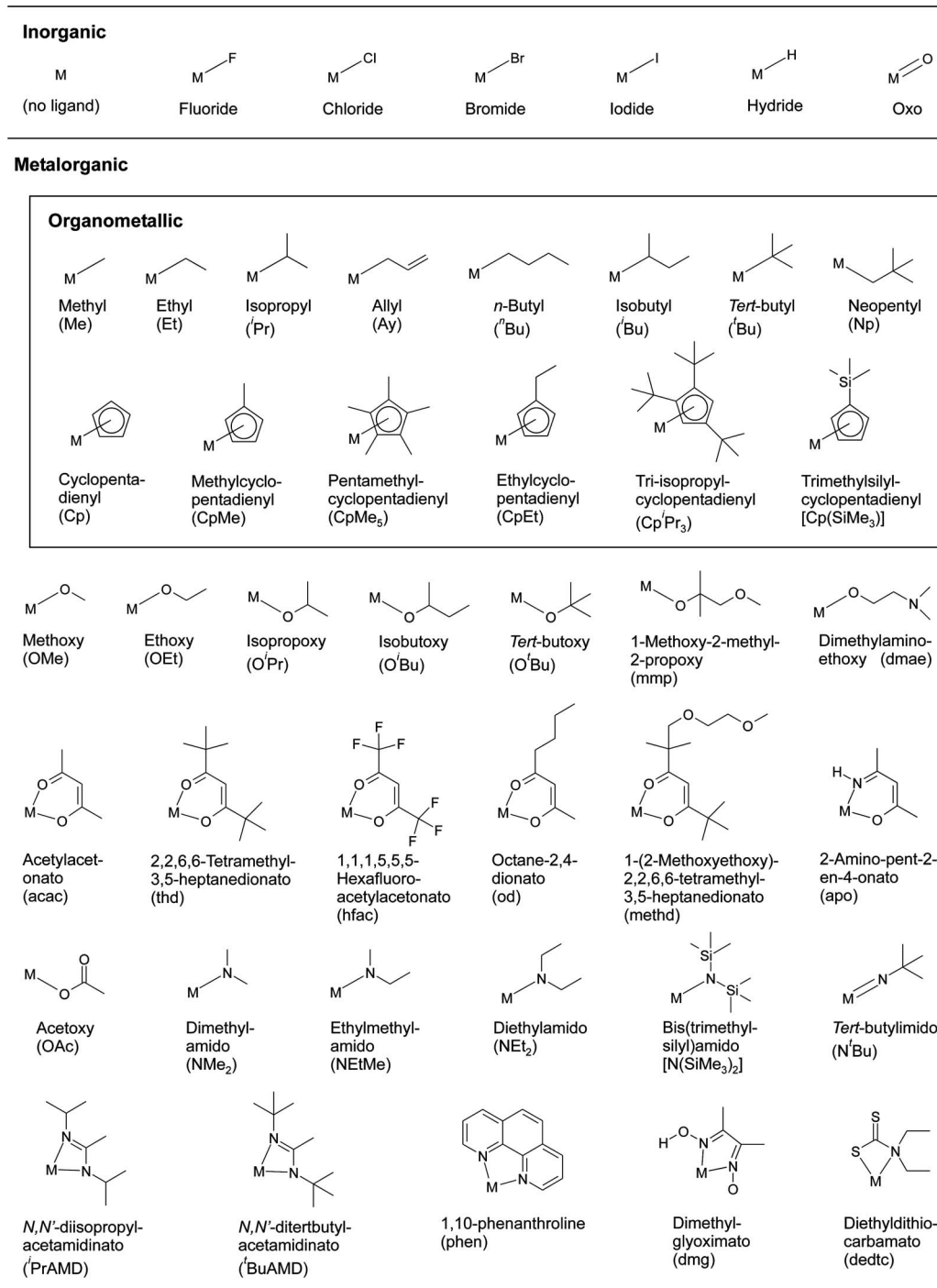


FIG. 4. Typical ligands  $L$  of the reactants  $ML_n$  used in ALD.  $M$  represents the central atom, most often a metal. The ALD reactants can be divided into two main groups, inorganic and metalorganic; organometallic reactants with a direct metal–carbon bond (Ref. 1126) form a subgroup of the latter. In this work, eight main ligand groups are further distinguished: elements [no ligands], halides [F, Cl, Br, and I], alkyls [Me, Et, <sup>i</sup>Pr, Ay, <sup>n</sup>Bu, <sup>i</sup>Bu, <sup>t</sup>Bu, and Np], cyclopentadienyls [Cp, CpMe, CpMe<sub>5</sub>, CpEt, CpPr<sub>3</sub>, and Cp(SiMe<sub>3</sub>)], alkoxides [OMe, OEt, O<sup>i</sup>Pr, O<sup>n</sup>Bu, O<sup>t</sup>Bu, mmp, and dmae],  $\beta$ -diketonates [acac, thd, hfac, od, and methd], alkylamides and silylamides [NMe<sub>2</sub>, NEtMe, NEt<sub>2</sub>, and N(SiMe<sub>3</sub>)<sub>2</sub>], and amidates [<sup>i</sup>PrAMD and <sup>t</sup>BuAMD].

may be related to the difficulty of replacing the metal–oxygen bond in the  $\beta$ -diketonate with a metal–nitrogen bond. The lower reactivity of the  $\beta$ -diketonates is also reflected in the observation that the oxygen source in the growth of oxide materials is most often not H<sub>2</sub>O, but O<sub>3</sub> (or O<sub>2</sub> may be used at higher temperatures).  $\beta$ -diketonates decompose at moderate temperatures. For example, La(thd)<sub>3</sub> decomposes at 300 °C.<sup>966</sup> A drawback in using  $\beta$ -diketonate reactants is their size. The bulky ligands cause marked steric

hindrance,<sup>1127,1128</sup> and the GPC obtained from these reactants is typically low, some percent of a monolayer.<sup>237,815</sup> The reaction mechanisms related to removing the  $\beta$ -diketonate differ from most ALD processes, since the ligands are most often oxidized with O<sub>3</sub>. Whether or not the oxidation is complete and H<sub>2</sub>O and CO<sub>2</sub> form as by-products has apparently not yet been verified. The films grown from  $\beta$ -diketonate reactants often contain considerable amounts of carbon and hydrogen impurities. For example, Y<sub>2</sub>O<sub>3</sub> deposited through

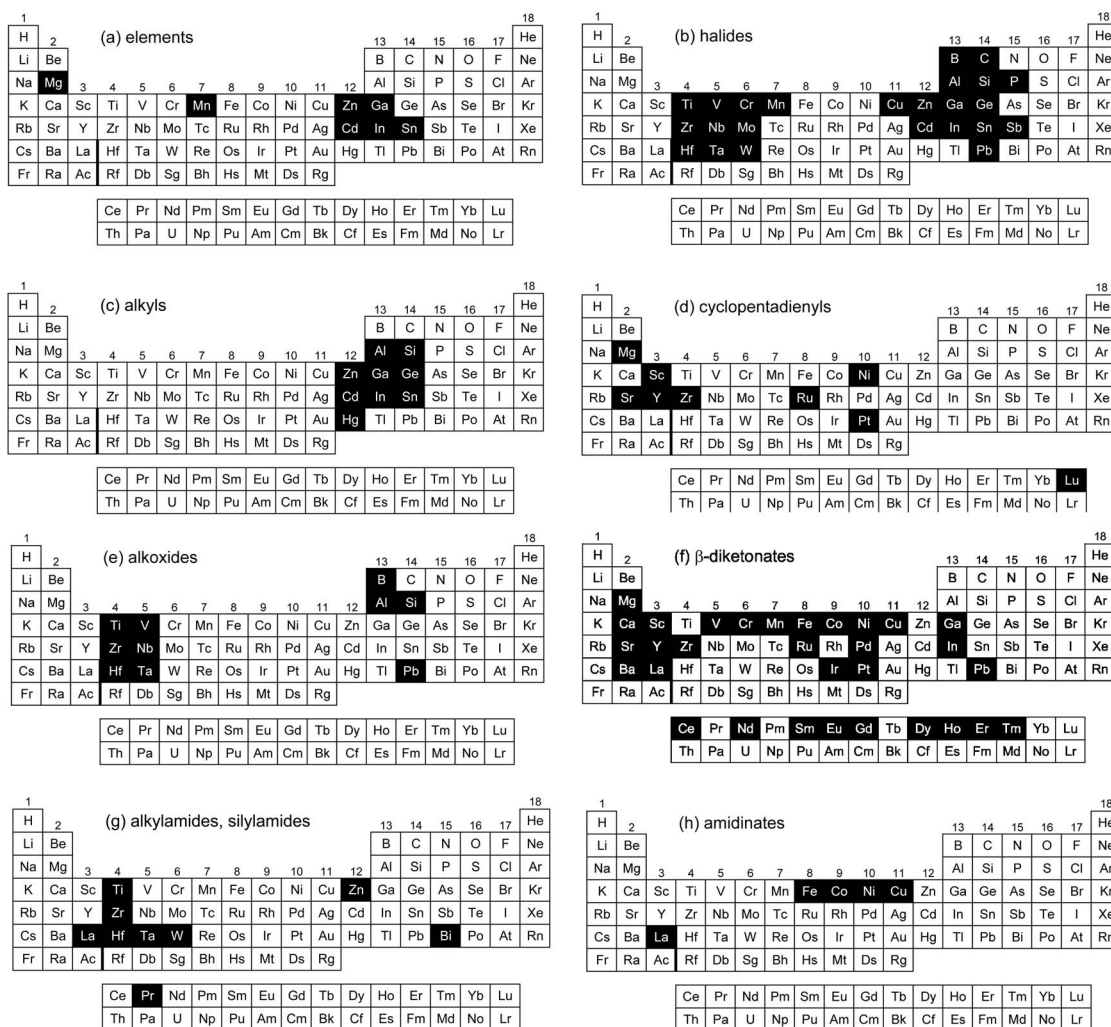


FIG. 5. Overview of the different types of metal reactants used in ALD (based on the list of Reactants A in Table III). The dark background indicates that metal reactants containing the particular type of ligand have been used for ALD: (a) elements [no ligands], (b) halides [F, Cl, Br, and I], (c) alkyls [Me, Et, <sup>i</sup>Pr, Ay, <sup>n</sup>Bu, <sup>i</sup>Bu, and Np], (d) cyclopentadienyls [Cp, CpMe, CpMe<sub>5</sub>, CpEt, Cp<sup>i</sup>Pr<sub>3</sub>, and Cp(SiMe<sub>3</sub>)<sub>3</sub>], (e) alkoxides [OMe, OEt, O<sup>i</sup>Pr, O<sup>i</sup>Bu, O<sup>n</sup>Bu, mmp, and dmae], (f) β-diketonates [acac, thd, hfac, od, and methd], (g) alkylamides and silylamides [NMe<sub>2</sub>, NEtMe, NEt<sub>2</sub>, and N(SiMe<sub>3</sub>)<sub>2</sub>], and (h) amidinates [<sup>i</sup>PrAMD and <sup>i</sup>BuAMD].

the Y(thd)<sub>3</sub>/O<sub>3</sub> process at 300 °C was reported to contain about 2 at. % of both carbon and hydrogen.<sup>815</sup> Because of the generation of CO<sub>2</sub> during the oxidation of the ligands, carbonate films may form in place of the more-often-desired oxides.<sup>409,807</sup>

TABLE V. Typical ALD processes of the type Reactant A+Reactant B →Material, reported for element reactants (references in Table III).

Reactant B	Material	Reactant A (M)
O <sub>2</sub>	MO <sub>x</sub>	Zn, Sn
H <sub>2</sub> O	MO <sub>x</sub>	Zn
N <sub>2</sub>	MN <sub>x</sub>	Ga, In
S	MS <sub>x</sub>	Zn, Cd
H <sub>2</sub> S	MS <sub>x</sub>	Zn
P	MP <sub>x</sub>	Ga
Se	MSe <sub>x</sub>	Zn, Cd
H <sub>2</sub> Se	MSe <sub>x</sub>	Zn
Te	MTe <sub>x</sub>	Mg, Mn, Zn, Cd
Sb	MSb <sub>x</sub>	In

An interesting observation was recently made regarding the reactivity of lanthanoid (Ln) β-diketonates. Päiväsaari *et al.*<sup>973</sup> studied the ALD growth of several lanthanoid oxides from Ln(thd)<sub>3</sub> and ozone at a constant temperature (300 °C). Päiväsaari *et al.*<sup>973</sup> noticed the thickness increment per ALD reaction cycle to increase systematically with increasing ionic radius of the lanthanides (the ionic radius of the lanthanoid cautions decreases with increasing atomic number, known as the “lanthanoid contraction”<sup>973,1139</sup>). A similar qualitative trend of the GPC (in thickness units) as reported by Päiväsaari *et al.*<sup>973</sup> would be created simply if the same number of lanthanoid atoms was, in all cases, deposited per unit surface area per cycle. Namely, the larger the ionic radius of the lanthanoid (Ln), the larger the volume *v* occupied by a LnO<sub>3/2</sub> unit and the larger the average thickness  $\bar{h}^{\text{ml}}$  corresponding to one monolayer of LnO<sub>3/2</sub> ( $\bar{h}^{\text{ml}} = v^{1/3}$ ).<sup>1128,1140</sup> The GPC could be expected to be constant in units of atoms per unit surface area, if the steric hindrance by the bulky thd ligands completely dominated the chemi-



TABLE VI. Typical ALD processes of the type Reactant A+Reactant B →Material, reported for metal halides that contain one type of ligand (references in Table III).

Reactant B	Material	Reactant A ( $ML_n$ : atom M–ligand L)
H <sub>2</sub> O	$MO_x$	B–Br, Al–(Cl,Br), Si–Cl, P–Cl, Ti–(Cl,I), Zn–Cl, Ge–Cl, Zr–(Cl,I), In–Cl, Sb–Cl, Hf–(Cl,I), Ta–Cl, W–F
O <sub>2</sub>	$MO_x$	Ti–I, Zn–Cl, Sn–I, Hf–(Cl,I)
O <sub>3</sub>	$MO_x$	Hf–Cl
NH <sub>3</sub>	$MN_x$	B–(Cl,Br), Al–Cl, Si–Cl, Ti–(Cl,I), Ga–Cl, Nb–Cl, Mo–Cl, Ta–Cl, W–F
H <sub>2</sub> S	$MS_x$	Mn–Cl, Zn–Cl, Cd–Cl, In–Cl, W–F, Pb–(Br,I)
PH <sub>3</sub>	$MP_x$	In–Cl
H <sub>2</sub> Se	$MSe_x$	Zn–Cl
AsH <sub>3</sub>	$MAs_x$	Ga–(Cl,Br,I), In–Cl
H <sub>2</sub>	$M$	Cu–Cl
N <sup>a</sup>	$MN_x$	Ta–Cl
H <sup>b</sup>	$M$	C–Cl, Ti–Cl, Ge–Cl, Ta–Cl
Si <sub>2</sub> H <sub>6</sub>	$M$	Ta–F, W–F

<sup>a</sup>Atomic nitrogen, for example, in plasma.<sup>b</sup>Atomic hydrogen, for example, in plasma.

sorption process.<sup>1127,1128</sup> However, the mechanical contribution of the ionic radius appears too small to explain the full quantitative trend reported by Päiväsaari *et al.*,<sup>973</sup> and the amount of lanthanoid atoms deposited per unit surface area per cycle also must increase with increasing ionic radius. The types of chemical changes occurring in the Ln(thd)<sub>3</sub> molecules with increasing ionic radius are yet to be clarified.

Alkylamides and silylamides have been investigated as ALD reactants since the late 1990s.<sup>407,498,499,513,857,1059</sup> Alkylamides and silylamides appear as a versatile group of reactants, both in terms of the elements for which they are available [Fig. 5(g)] and the types of materials made from them (Table XI): oxides, nitrides, and selenides. Decomposition at low temperatures is a problem for these amides, however.

TABLE VII. Typical ALD processes of the type Reactant A+Reactant B →Material, reported for metal alkyls that contain one type of ligand (references in Table III).

Reactant B	Material	Reactant A ( $ML_n$ : atom M–ligand L)
H <sub>2</sub> O	$MO_x$	Al–(Me,Et), Zn–(Me,Et), In–Me
O <sub>2</sub>	$MO_x$	Zn–Et
O <sub>3</sub>	$MO_x$	Al–Me
ROH <sup>a</sup>	$MO_x$	Al–Me
NH <sub>3</sub>	$MN_x$	Al–(Me,Et), Ga–(Me,Et)
H <sub>2</sub> S	$MS_x$	Zn–(Me,Et), Cd–Me
PH <sub>3</sub>	$MP_x$	Ga–Me, In–(Me,Et)
H <sub>2</sub> Se	$MSe_x$	Zn–(Me,Et), Cd–Me
AsH <sub>3</sub>	$MAs_x$	Al–(Me,Et, <sup>i</sup> Bu), Ga–(Me,Et, <sup>i</sup> Bu), In–(Me,Et)
O <sup>b</sup>	$MO_x$	Al–Me
H <sup>c</sup>	$M$	Al–Me

<sup>a</sup>Alcohols with various organic chains R.<sup>b</sup>Atomic oxygen, for example, in plasma.<sup>c</sup>Atomic hydrogen, for example, in plasma.

TABLE VIII. Typical ALD process of the type Reactant A+Reactant B →Material, reported for metal cyclopentadienyls that contain one type of ligand (references in Table III).

Reactant B	Material	Reactant A ( $ML_n$ : atom M–ligand L)
H <sub>2</sub> O	$MO_x$	Mg–Cp, Sc–Cp, Ni–Cp, Sr–Cp <sup>i</sup> Pr <sub>3</sub> , Y–(Cp,CpMe)
O <sub>2</sub>	$M$	Ru–(Cp,CpEt)
H <sub>2</sub> S	$MS_x$	Sr–(CpMe <sub>5</sub> , Cp <sup>i</sup> Pr <sub>3</sub> )

For example, the Ti(NMe<sub>2</sub>)<sub>4</sub> reactant decomposes already at 150 °C.<sup>505</sup> Rather typical also is that the GPC from amides, at least for alkylamides of titanium, exceeds a monolayer.<sup>499–501,513</sup> Although a theory has been built to explain the beyond-monolayer-growth through “readsorption,”<sup>499–501,509</sup> I suspect that decomposition remains a candidate to explain the high GPC values. Little investigations seem to have been carried out to identify the gaseous reaction by-products in alkylamide- and silylamide-based ALD processes. Impurities are often found in the films, which for alkylamide reactants may be nitrogen, carbon, and hydrogen, and for silylamide reactants additional silicon. As an example of films grown from alkylamides, TiN films grown through the Ti(NEt<sub>2</sub>)<sub>4</sub>/NH<sub>3</sub> process at 200 °C contained about 4-at. % carbon and 6-at. % hydrogen.<sup>513</sup> As an example of films grown from silylamides, PrO<sub>x</sub> films grown through the Pr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>/H<sub>2</sub>O process at 250 °C contained about 3-at. % carbon, 20-at. % hydrogen, and 6-at. % silicon.<sup>972</sup>

Amidates are the most recent class of ALD reactants, introduced only in 2003.<sup>546,1141</sup> Because of their novelty, their use in ALD has so far been investigated only for a few elements, as summarized in Fig. 5(h). The material selection (Table XII) may broaden in the future, however, because amidates should be available for most metals.<sup>1142</sup> The reactions seem self-terminating.<sup>546,1143</sup> Decomposition temperatures are typically around 300 °C.<sup>1141,1143</sup> Potentially, the films may contain residues of carbon, hydrogen, and nitrogen. The gaseous reaction by-products remain to be identified.

In addition to the eight reactant classes described above, many miscellaneous types of reactants have been tried out

TABLE IX. Typical ALD processes of the type Reactant A+Reactant B →Material, reported for metal alkoxides that contain one type of ligand (references in Table III).

Reactant B	Material	Reactant A ( $ML_n$ : atom M–ligand L)
H <sub>2</sub> O	$MO_x$	Al–(OEt, O <sup>i</sup> Pr), Si–OEt, Ti–(OMe, OEt, O <sup>i</sup> Pr, OBu), Zr–(O <sup>i</sup> Bu, dmae), Nb–OEt, Ta–OEt, Hf–mmp
O <sub>2</sub>	$MO_x$	Al–(OEt, O <sup>i</sup> Pr), Ti–O <sup>i</sup> Pr, Zr–O <sup>i</sup> Bu
O <sub>3</sub>	$MO_x$	Ti–O <sup>i</sup> Pr, Hf–O <sup>i</sup> Bu
H <sub>2</sub> S	$MS_x$	Pb–O <sup>i</sup> Bu
O <sup>a</sup>	$MO_x$	Ti–O <sup>i</sup> Pr, Zr–O <sup>i</sup> Bu, Hf–O <sup>i</sup> Bu, Ta–OEt

<sup>a</sup>Atomic oxygen, for example, in plasma.

TABLE X. Typical ALD processes of the type Reactant A + Reactant B → Material, reported for metal  $\beta$ -diketonates that contain one type of ligand (references in Table III).

Reactant B	Material	Reactant A ( $ML_n$ : atom M–ligand L)
H <sub>2</sub> O	$MO_x$	Ca–thd, <sup>a</sup> Cu–Hfac, Ga–acac
O <sub>2</sub>	$MO_x$	Cr–acac, Fe–acac, Co–acac, Ni–acac, Cu–(acac,thd), Y–thd, La–thd, Ce–thd
O <sub>2</sub>	$M$	Ru–od, Ru–thd, Pd–thd, Ir–acac
O <sub>3</sub>	$MO_x$	Mg–thd, Ca–thd, <sup>a</sup> Sc–thd, Mn–thd, Fe–thd, Co–thd, Ni–(acac,thd), Ga–acac, Sr–thd, <sup>a</sup> Y–thd, La–thd, Ce–thd, Nd–thd, Sm–thd, Eu–thd, Gd–thd, Dy–thd, Ho–thd, Er–thd, Tm–thd
ROH <sup>b</sup>	$M$	Cu–hfac
H <sub>2</sub> S	$MS_x$	Ca–thd, Cu–thd, Sr–thd, Y–thd, In–acac, Ba–thd, La–thd, Pb–thd
HF	$MF_x$	Ca–thd, Sr–thd
H <sub>2</sub>	$M$	Ni–acac, Cu–(acac,thd), Ru–thd, Pd–thd, Pd–hfac, Pt–acac

<sup>a</sup> $M(CO_3)_x$ .<sup>b</sup>R refers to alkyl chains of various lengths.<sup>c</sup> $MO_xS_y$ .

for ALD. For example, hydrides have been used for depositing especially silicon and germanium (references in Table III); acetates for zinc and lead-containing films;<sup>415,608,609,615,616,618–620,639,1083</sup> nitrate and hydroxylamide for hafnium oxide;<sup>1021,1031–1033</sup> and a carbonyl compound for cobalt.<sup>1144</sup> The specific characteristics of these processes are not discussed further in this review.

### 3. $AlMe_3/H_2O$ versus other ALD processes

In this work, the current status of understanding the surface chemistry of ALD is reviewed using the  $AlMe_3/H_2O$  ALD process as a vehicle. All ALD processes have their individual characteristics, and no ALD process can be ex-

TABLE XI. Typical ALD process of the type Reactant A + Reactant B → Material, reported for metal amides that contain one type of ligand (references in Table III).

Reactant B	Material	Reactant A ( $ML_n$ : atom M–ligand L)
H <sub>2</sub> O	$MO_x$	Zr–(NMe <sub>2</sub> ,NEt <sub>2</sub> ), La–N(SiMe <sub>3</sub> ) <sub>2</sub> , Pr–N(SiMe <sub>3</sub> ) <sub>2</sub> , Hf–(NMe <sub>2</sub> ,NEt <sub>2</sub> ), Ta–(NMe <sub>2</sub> ,NEt <sub>2</sub> ), Bi–N(SiMe <sub>3</sub> ) <sub>2</sub>
O <sub>2</sub>	$MO_x$	Hf–NEt <sub>2</sub>
O <sub>3</sub>	$MO_x$	Hf–NMe <sub>2</sub>
NH <sub>3</sub>	$MN_x$	Ti–(NMe <sub>2</sub> ,NEt <sub>2</sub> ), Zr–(NMe <sub>2</sub> ,NEt <sub>2</sub> ), Hf–(NMe <sub>2</sub> ,NEt <sub>2</sub> ), Ta–NMe <sub>2</sub>
H <sub>2</sub> Se	$MSe_x$	Zn–N(SiMe <sub>3</sub> ) <sub>2</sub>
O <sup>a</sup>	$MO_x$	Ti–NMe <sub>2</sub> , Zr–NEt <sub>2</sub> , Hf–NEt <sub>2</sub>
N <sup>b</sup>	$MN_x$	Ti–NMe <sub>2</sub>
H <sup>c</sup>	$MN_x$	Ti–NMe <sub>2</sub>

<sup>a</sup>Atomic oxygen, for example, in plasma.<sup>b</sup>Atomic nitrogen, for example, in plasma.<sup>c</sup>Atomic hydrogen, for example, in plasma.

TABLE XII. Typical ALD processes of the type Reactant A + Reactant B → Material, reported for metal amidinates that contain one type of ligand (references in Table III).

Reactant B	Material	Reactant A ( $ML_n$ : atom M–ligand L)
H <sub>2</sub> O	$MO_x$	Fe– <sup>i</sup> BuAMD, Co– <sup>i</sup> PrAMD, La– <sup>i</sup> PrAMD
H <sub>2</sub>	$M$	Fe– <sup>i</sup> BuAMD, Co– <sup>i</sup> PrAMD, Ni– <sup>i</sup> PrAMD, Cu– <sup>i</sup> PrAMD

pected to fully represent the others. The  $AlMe_3/H_2O$  process still seems a good choice as one of the most representative processes, for at least four reasons.

First, the  $AlMe_3/H_2O$  process represents “thermal ALD.” The advantage of thermal ALD over various “energy-enhanced” ALD processes is that thermal ALD processes fulfill best the requirement of self-terminating reactions on complex three-dimensional (3D) substrates. In energy-enhanced processes, typically utilizing energetic but unstable reactants such as ozone or plasma, problems with conformality may arise through reactant decomposition, at least on 3D substrates.

Second, the  $AlMe_3/H_2O$  process deposits an oxide material and uses water to deposit it. Oxides are the inorganic materials most frequently grown by ALD, and water is the most frequently used oxygen source.

Third, the  $AlMe_3/H_2O$  process uses trimethylaluminum as the aluminum source. If a choice is made to review the growth characteristics of aluminum oxide (the growth of another metal oxide could as well have been chosen),  $AlMe_3$  is a justified choice as the aluminum source, as it is perhaps the most commonly used aluminum source in ALD. Further advantages of using  $AlMe_3$ , as a general example, is that the reactions are rather ideal: the reactions are truly self-terminating, the  $AlMe_3$  reactant is highly reactive and many types of compounds have been grown from it (oxides, nitrides, arsenides, and pure Al; see Tables III and VII), and the gaseous reaction products (methane) are rather inert. Many other reactant classes, such as elements, halides, alkoxides,  $\beta$ -diketonates, and alkyl/silylamides would have difficulties fulfilling at least some of these criteria, whereas alkyls, cyclopentadienyls, and perhaps amidinates fulfill them better. A disadvantage in using an alkyl reactant, as a general example, is the fact that alkyls are available for a limited selection of elements only [Fig. 5(c)]. Some reaction mechanisms are likely to be specific for the particular reactant or for the reactant group. A similar disadvantage of having reactant-specific or reactant-group-specific reactions would be encountered, however, for reactants from other groups as well.

Fourth, the  $AlMe_3/H_2O$  process is one of the most studied ALD processes (Table III). There is therefore material to be reviewed.

Although it will not be possible to transfer the specific conclusions regarding the  $AlMe_3/H_2O$  process directly to other ALD processes, it is likely that if a specific physicochemical phenomenon is an issue for the  $AlMe_3/H_2O$  process, it will be so also for other ALD processes. Additional

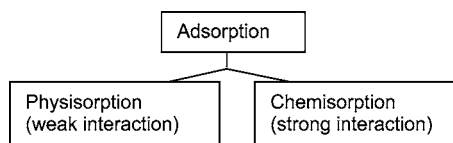


FIG. 6. Adsorption classes.

physicochemical phenomena may play a role in the surface chemistry of other ALD processes, caused, for example, by the occurrence of reactant decomposition (either purely thermally or through the use of energy-enhanced processes) or the formation of noninert gaseous reaction products. Understanding these unideal phenomena should be possible through building additional models on top of the models describing ideal ALD systems.

### III. GENERAL CHARACTERISTICS OF THE SURFACE CHEMISTRY OF ALD

To provide a framework for discussing the surface chemistry of the  $\text{AlMe}_3/\text{H}_2\text{O}$  and other ALD processes, the general concepts and characteristics of the surface chemistry of ALD are summarized here. Section III A discusses the chemical requirements for self-terminating reactions and Sec. III B the kinetic characteristics of such reactions. Section III C describes the three classes of chemisorption reactions typically involved in ALD, and Sec. III D identifies the possible factors causing the termination of the reactions. Section III E illustrates, with the aid of published models, how steric hindrance typically limits the GPC to less than a monolayer. Sections III F and III G, respectively, discuss why the GPC varies with temperature and with the number of reaction cycles. Finally, Sec. III H introduces the possible growth modes that define how the material gets arranged on the surface during the growth.

#### A. Requirements for self-terminating reactions

ALD can be defined to be based on the sequential use of *self-terminating gas–solid reactions*. In the reaction of a gaseous compound reactant with the solid surface, atoms which are to be included in the ALD-grown film are adsorbed on the surface. Simultaneously, atoms which are not to be included in the film may be removed as gaseous reaction by-products.

Adsorption can be divided into two general classes on the basis of the strength of interaction between the adsorbing molecule (“adsorptive”) and the solid surface (“adsorbent”): *physisorption* (i.e., physical adsorption) and *chemisorption* (i.e., chemical adsorption),<sup>1145</sup> as shown in Fig. 6. Physisorption originates from weak interactions, where minimal changes typically occur in the structure of the adsorbing molecule. The interactions are not specific to the molecule–surface pair, and consequently, adsorption may occur in multilayers. Chemisorption, in turn, involves the making and optionally breaking of chemical bonds. Because in chemisorption, chemical bonds are formed between the adsorbing molecule and the surface, the surface “accepts” only one layer, a *monolayer*, of the adsorbed species (“adsorbate”).<sup>1145</sup> In relation with ALD, one must realize that a monolayer of

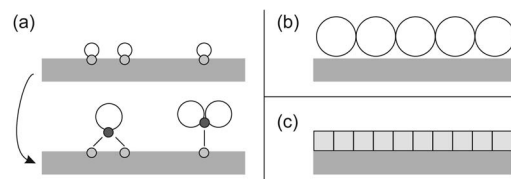


FIG. 7. Three different types of monolayers relevant to ALD: (a) a chemisorbed monolayer (the substrate before chemisorption indicated above, with reactive sites shown), (b) a physisorbed monolayer, and (c) a monolayer of the ALD-grown material.

the adsorbed species, such as  $\text{Al}(\text{Me})_2$ , differs both from a monolayer of the reactant molecule,  $\text{AlMe}_3$ , and from a monolayer of the ALD-grown material,  $\text{Al}_2\text{O}_3$  (Fig. 7):

- Monolayer (capacity) for chemisorption is defined<sup>1145</sup> as “the amount of adsorbate (adsorbed species) which is needed to occupy all adsorption sites as determined by the structure of the adsorbent (surface) and the chemical nature of the adsorptive (the reactant).”
- Monolayer (capacity) for physisorption is defined<sup>1145</sup> as “the amount needed to cover the surface with a complete monolayer of molecules in a close-packed array.”
- Monolayer for the ALD-grown material  $\text{MZ}_x$  can be defined as one plane of  $\text{MZ}_x$  units in a crystalline face of the bulk  $\text{MZ}_x$  material in the preferred orientation of growth.<sup>1146</sup>

The amount of material adsorbed in gas–solid reactions can depend on time in various ways, as schematically illustrated in Fig. 8. Both *irreversible* and *reversible* adsorption can be saturating in nature [panels (a) and (b), respectively]. For the adsorption to be self-terminating, however, the adsorbed material may not desorb from the surface during the purge or evacuation. Consequently, in ALD, the type of adsorption is limited to irreversible adsorption (irreversible in the time scale of the experiment). Because physisorption is always reversible, whereas chemisorption can be reversible or irreversible, the requirement of irreversibility restricts the type of adsorption to chemisorption. In addition to irreversible adsorption, reversible adsorption may occur, but it does not contribute to ALD growth [panel (c)]. Irreversible adsorption as such is not a sufficient requirement to achieve ALD growth, however, as irreversible adsorption can also be continuous and nonsaturating [panel (d)]. Moreover, to take advantage of the self-terminating features, the irreversible, saturating reactions must be allowed to terminate, to go to completion [panel (e)].<sup>1147</sup>

#### B. Adsorption kinetics

Chemical kinetics describes the effect of process parameters such as temperature and reactant concentrations on reaction (adsorption) rates.<sup>1148</sup> A simple example of molecular adsorption of a gaseous compound  $A$  on a surface site  $\parallel^*$  illustrates the characteristics of adsorption kinetics in ALD. In the general case, the adsorption can be considered reversible, as illustrated in reactions (1) and (2),



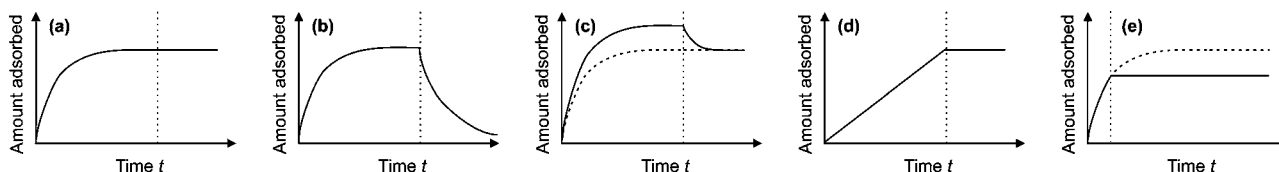


FIG. 8. Examples of how the amount of material adsorbed can vary with time: (a) irreversible saturating adsorption (i.e., self-terminating reaction), (b) reversible saturating adsorption, (c) combined irreversible and reversible saturating adsorption, (d) irreversible nonsaturating adsorption (deposition), and (e) irreversible saturating adsorption not allowed to saturate. The vertical dashed line marks the end of the reactant supply and the beginning of a purge or evacuation.



Adsorption rate  $r_a$  refers to the amount of molecules  $A$  attached to the surface per unit time and desorption rate  $r_d$  to the amount of molecules  $A$  detached from the surface per unit time.

The partial pressure of the reactant is a central parameter describing the adsorption process. For illustrating the effect of pressure, three assumptions are made that are often used in the ALD literature:<sup>192,196,1149–1154</sup> the maximum amount of adsorbed species is assumed to be a monolayer (as in chemisorption), all adsorption sites on the surface are assumed equal, and neighboring adsorbed species are assumed not to interact with each other. The coverage of adsorbed species is referred here to as *chemisorption coverage* and denoted as  $Q$ .<sup>1155</sup> The adsorption rate  $r_a$  equals the adsorption rate constant  $k_a$  times the partial pressure  $p$  of the molecule  $A$  times the fraction  $(1-Q)$  of unoccupied surface sites, and the desorption rate  $r_d$  equals the desorption rate constant  $k_d$  times the fraction  $Q$  of occupied surface sites. The rate of change of the chemisorption coverage,  $dQ/dt$ , is obtained by subtracting the desorption rate from the adsorption rate,

$$\frac{dQ}{dt} = r_a - r_d = k_a p (1 - Q) - k_d Q. \quad (3)$$

After saturation, the chemisorption coverage is constant ( $dQ/dt=0$ ), and we get from Eq. (3) the *Langmuir isotherm*, giving the equilibrium chemisorption coverage  $Q^{eq}$  as a function of reactant partial pressure,

$$Q^{eq} = \frac{k_a p}{k_a p + k_d} = \frac{1}{1 + (Kp)^{-1}}. \quad (4)$$

The right side of Eq. (4) has been obtained by recognizing that  $K=k_a/k_d$  is the *equilibrium constant* of the adsorption. In the general case of reversible adsorption ( $k_a \neq 0 \neq k_d$ ),  $Q^{eq}$  increases with  $p$ , as illustrated in Fig. 9(a). To achieve ALD conditions with self-terminating reactions, however, the adsorption must be irreversible (Sec. III A). Equations (3) and (4) describe practically irreversible reactions if the equilibrium constant  $K$  is allowed to approach infinity (or  $k_d$  to approach zero). Solving Eq. (4) with this assumption, we get

$$\lim_{K \rightarrow \infty} Q^{eq} = 1. \quad (5)$$

In irreversible chemisorption, the chemisorption coverage  $Q$  does not increase with  $p$ , but settles to unity even at negligibly low reactant partial pressures  $p$  [Fig. 9(b)].

Time is also a central parameter in the adsorption process. Solving by integrating from Eq. (3), assuming constant pressure and temperature, the chemisorption coverage  $Q$  is obtained as a function of time  $t$ ,

$$Q = Q^{eq} (1 - e^{-(k_a p + k_d)t}). \quad (6)$$

For irreversible chemisorption, Eq. (6) reduces to  $Q = 1 - e^{-k_a p t}$ . Figure 10(a) illustrates the chemisorption coverage  $Q$  as a function of time for irreversible chemisorption. During the reaction of Reactant  $A$  (Step 1), typically a compound reactant  $ML_n$ , the chemisorption coverage increases until it settles to one when the reaction has terminated. (The higher the  $p$  and  $k_a$ , the faster the reaction is completed.) During the following purge/evacuation (Step 2), the chemisorption coverage remains constant. The reaction of Reactant  $B$  (Step 3) causes the chemisorption coverage of the species adsorbed from Reactant  $A$  to decrease, ideally down to zero. Reactant  $B$  brings other types of adsorbed species on the surface, the coverage of which increases from zero to one during the reaction. During the following purge/evacuation (Step 4), the chemisorption coverages remain constant. During repeating reaction cycles of Steps 1–4, the chemisorption coverages therefore switch between zero and one [Fig. 10(a)].

Time affects the chemisorption coverage  $Q$  in a different way than it affects the total amount of material deposited  $c_M$ . As illustrated in Fig. 10(b), the amount of atoms  $M$  deposited  $c_M$  increases during Step 1 of the reaction cycles. The deposition rate  $dc_M/dt$  varies with time [Fig. 10(c)], implying that the process is in a transient state.<sup>1156</sup> For comparison, in this example, the amount of material deposited  $c_M$  increases linearly with the number of reaction cycles [Fig. 10(d)] and the GPC  $\Delta c_M$  is constant [Fig. 10(e)]. The number of reaction cycles  $n$  is clearly a discrete variable,<sup>992,1140</sup> whereas time  $t$  is continuous.

The temperature dependency of adsorption and desorp-

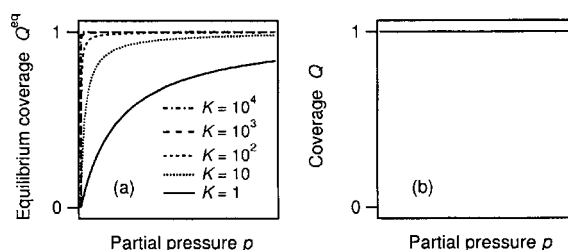


FIG. 9. Effect of the reactant partial pressure  $p$  on the amount of material chemisorbed in a gas–solid reaction: (a) the equilibrium chemisorption coverage  $Q^{eq}$  in reversible adsorption (equilibrium constants  $1 \leq K \leq 10^4$ ) and (b) the chemisorption coverage  $Q$  after saturation in irreversible adsorption.



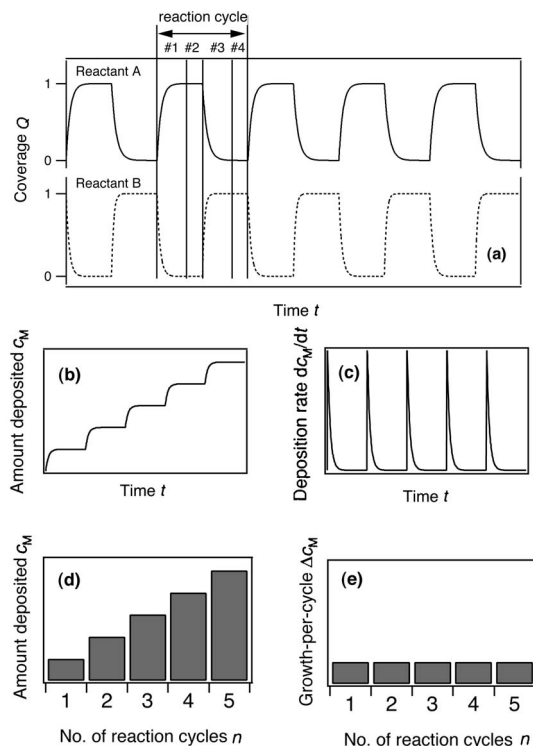


FIG. 10. Schematic representation of five reaction cycles, assuming irreversible adsorption: (a) chemisorption coverage  $Q$  as a function of time  $t$  (solid line:  $ML_z$  species adsorbed in the reaction of the Reactant A assumed to be of type  $ML_n$ , dashed line: species adsorbed in the reaction of Reactant B; the beginning and end of a reaction cycle and Steps 1–4 are indicated), (b) the amount of atoms  $M$  adsorbed  $c_M$  as a function of time  $t$ , (c) the deposition rate of  $M$  atoms  $dc_M/dt$  as a function of time  $t$  [obtained as the time derivative of the curve in panel (b)], (d) amount of material deposited  $c_M$  as a function of the number of reaction cycles  $n$ , and (e) the GPC  $\Delta c_M$  as a function of the number of reaction cycles  $n$ .

tion rate constants  $k_i$  is typically described by the *Arrhenius equation*,

$$k_i = A e^{-E_i/RT}. \quad (7)$$

In this equation,  $A$  is the pre-exponential factor,  $E_i$  is the activation energy,  $R$  is the gas constant, and  $T$  is the absolute temperature. The higher the temperature, the faster the reactions go to completion. Although reactions are faster at higher temperatures, the amount of material adsorbed at saturation is dictated by factors other than the reaction rate, as will be discussed in Sec. III F.

In addition to adsorption kinetics, mass transport kinetics affect the amount of material adsorbed at a given time. Mass-transport kinetics are reactor-specific and depend also on the shape of the substrate, and are not discussed further here. Mass transport in ALD has been discussed at least in Refs. 432, 1038, 1152–1154, and 1157–1160.

### C. Chemisorption mechanisms

Three main classes of chemisorption mechanisms have been identified for the self-terminating reactions of compound reactants in ALD.<sup>1161</sup> In *ligand exchange*, the reactant molecule ( $ML_n$ ) is split on the surface.<sup>1162</sup> The ligand ( $L$ ) combines with a surface group  $\parallel -a$  to form a volatile compound that is released as a gaseous reaction

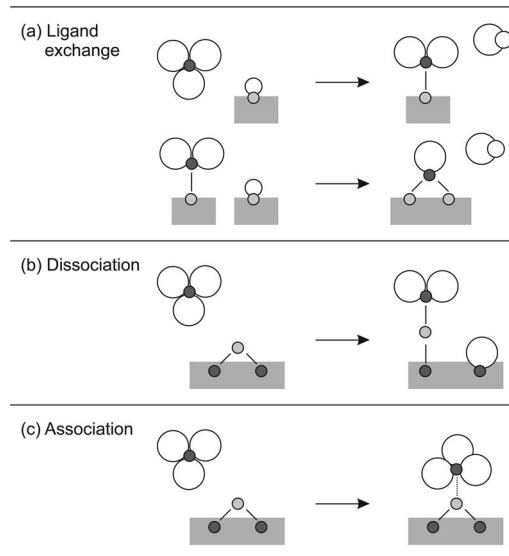
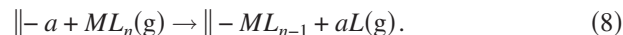
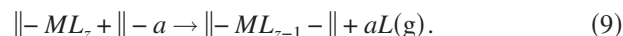


FIG. 11. Chemisorption mechanisms identified for ALD: (a) ligand exchange reaction of the  $ML_n$  reactant with surface “ $-a$ ” groups, releasing gaseous  $aL$ , (b) dissociation of the  $ML_n$  in surface  $M-Z$  sites, and (c) association of the  $ML_n$  species onto the surface. In this scheme,  $n=3$ .

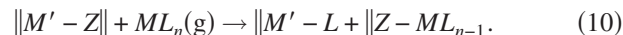
by-product,  $aL$ , and the remaining part of the molecule chemisorbs to the surface as a  $ML_{n-1}$  species [Eq. (8)],<sup>98,197,209,216,419,526,818,1163–1165</sup>



Ligand-exchange reaction can also occur for more than one ligand of the  $ML_n$  reactant or between an adsorbed  $ML_z$  species ( $1 \leq z \leq n$ ) and a surface  $\parallel -a$  group. These reactions release ligands as  $aL$  and consume additional  $\parallel -a$  groups, but do not result in bonding more metal  $M$  on the surface [Eq. (9), reaction of an adsorbed  $ML_z$  species]:



In *dissociation*, the reactant molecule is split onto reactive  $M' - Z$  sites on the surface [Eq. (10)],<sup>197,209,216,1163,1164</sup>



Similarly as ligand-exchange reaction, dissociation may proceed further on the surface, but this reaction affects neither the number of bonded  $M$  atoms nor the number of bonded ligands. In *association*, the reactant molecule forms a coordinative bond with a reactive site on the surface and is chemisorbed without a release of ligands [Eq. (11)],<sup>101,144,1110,1165–1167</sup>



The three classes of chemisorption mechanisms are schematically illustrated in Fig. 11.

When reactions (8)–(11) occur, a simple mass balance<sup>1128</sup> governs the chemisorption. The amount of ligands  $L$  chemisorbed  $\Delta c_L$  equals  $n$  times the amount of metal  $M$  chemisorbed  $\Delta c_M$ , subtracted by the number of ligands  $L$  released in the ligand-exchange reaction with surface  $\parallel -a$  groups, that is, the amount of surface  $\parallel -a$  groups reacted  $\Delta c_a$ . The mass balance is summarized in Eq. (12),

$$\Delta c_L = n \Delta c_M - \Delta c_a. \quad (12)$$

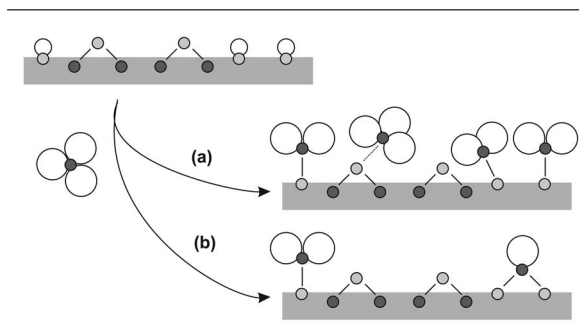


FIG. 12. Factors identified to cause saturation of irreversible chemisorption: (a) steric hindrance of the ligands and (b) number of reactive surface sites.

Sometimes, reactions other than those presented in Eqs. (8)–(11) occur. For example, the oxidation state of the elements may change during the ALD processing.<sup>63,102,1066,1168</sup> The mass balance of Eq. (12) may then not be valid. A special class of self-terminating reactions has been observed for metal chloride reactants, where metal oxide particles can form in a single reaction.<sup>419,421,818,1135,1169</sup> The so-called non-growth ligand-exchange reactions<sup>1088,1135,1170</sup> may be involved in the metal oxide particle formation, which is unideal in ALD since multilayers form in a single reaction. The details of the metal oxide particle formation process are not yet sufficiently understood, as reviewed elsewhere.<sup>1135</sup> Unexplained formation of particles, or “nanorods,” has been reported also for the  $\text{ZnEt}_2/\text{H}_2\text{O}$  ALD process.<sup>600</sup>

#### D. Factors causing saturation

Two factors have been identified to cause the saturation of the surface with adsorbed species in a self-terminating gas–solid reaction, as illustrated in Fig. 12: *steric hindrance of the ligands*<sup>209,216,237,291,292,530,548,554</sup> and *the number of reactive surface sites*.<sup>419,819</sup> Steric hindrance of the ligands can cause the ligands of the chemisorbed  $\text{ML}_z$  species to shield part of the surface from being accessible to the  $\text{ML}_n$  reactant. The surface can be considered “full.” The number of bonding sites on the surface may also be less than that required for achieving the maximum ligand coverage. In that case, although space remains available on the surface, no bonding sites are accessible. Irrespective of the factor causing saturation, the chemisorption coverage  $Q$  equals one after the self-termination of the reactions.

#### E. Growth of less than a monolayer per cycle

How much material is adsorbed in irreversible, saturating chemisorption is defined by the reaction mechanisms and the factor causing saturation. The highest obtainable GPC values correspond to a chemistry where the maximum number of surface sites react through ligand exchange, releasing thereby the maximum number of ligands into the gas phase, and reaction continues until steric hindrance terminates it.<sup>1128</sup>

Irrespective of the factor causing saturation and the absolute amount of material adsorbed, a monolayer of the chemisorbed  $\text{ML}_z$  species has formed by definition when the chemisorption has saturated (Sec. IV B). It is of interest to analyze to which GPC, in monolayers of the ALD-grown

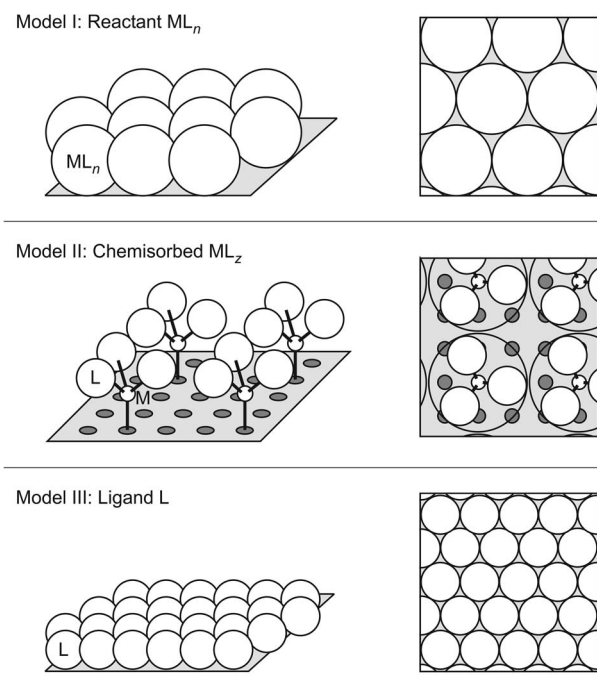


FIG. 13. Schematic illustration for analyzing sterically hindered chemisorption on the basis of the size of the  $\text{ML}_n$  reactant [Model I by Ritala *et al.* (Refs. 462 and 468) and Morozov *et al.* (Ref. 133)], the size and geometry of the chemisorbed  $\text{ML}_z$  species [Model II by Ylilammi (Ref. 1127)], and the size and number of ligands  $L$  [Model III by Siimon and Aarik (Ref. 432) and Puurunen (Ref. 1128)]. Left: side view, right: top view.

$\text{ML}_z$  material, the monolayer of adsorbed  $\text{ML}_z$  species converts. Often, it has been assumed that a monolayer of the ALD-grown material should form per cycle, but this assumption is obviously incorrect.<sup>1171</sup> Three models have been developed for analyzing the GPC when steric hindrance causes saturation, as summarized in Fig. 13.

Ritala *et al.*<sup>462,468</sup> and Morozov *et al.*<sup>133</sup> developed a model, referred to as *Model I*, to estimate the maximum GPC from the size of the  $\text{ML}_n$  reactant [Fig. 13(a)]. The size of the  $\text{ML}_n$  reactant is calculated from the density of the liquid reactant and the area covered by the reactant, assuming a close-packed monolayer of  $\text{ML}_n$ . Model I, in fact, corresponds to a physisorbed monolayer of the  $\text{ML}_n$  molecules (Sec. III A). Because the chemisorbed  $\text{ML}_z$  species differs from the  $\text{ML}_n$  reactant, Model I gives at best a rough estimate of the achievable GPC.

Ylilammi<sup>1127</sup> developed a model, *Model II*, for calculating the maximum GPC from the size and geometry of the adsorbed  $\text{ML}_z$  species [Fig. 13(b)]. The sizes of the ligand  $L$  and the metal  $M$  must be known. Also the bond lengths and angles must be known or assumed for the adsorbed species. In Model II, the GPC increases in steps with decreasing size of the adsorbate  $\text{ML}_z$ .<sup>1127</sup>

Siimon and Aarik<sup>432</sup> and Puurunen<sup>237,1128</sup> developed, independently of each other, basically the same model, *Model III*, for calculating the maximum GPC from the size and number of the adsorbed ligands  $L$  [Fig. 13(c)]. A theoretical maximum amount of ligands adsorbed is calculated assuming a close-packed monolayer of the ligands. This theoretical

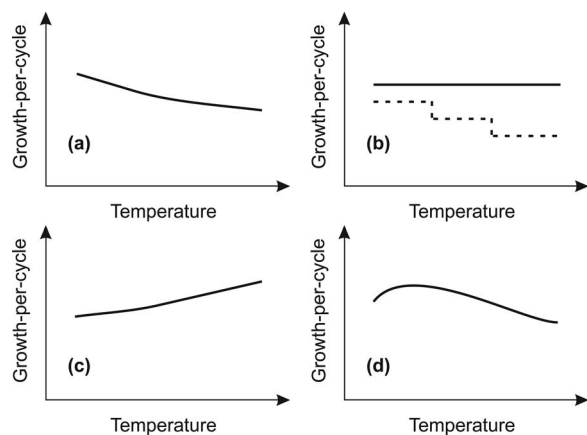


FIG. 14. Variation of the GPC with the ALD processing temperature in the ALD window: (a) the GPC decreases with temperature, (b) the GPC is constant with temperature (possible with different values at different temperature ranges, as shown by the dashed line), (c) the GPC increases with temperature, and (d) the GPC first increases and then decreases with temperature.

arrangement corresponds to a “physisorbed monolayer” of the ligands.<sup>1172</sup> A theoretical maximum is calculated for the amount of metal  $M$  adsorbed by dividing the amount of ligands adsorbed by the  $L/M$  ratio in the  $ML_z$  adsorbate. As should be expected, the GPC increases with decreasing size of the adsorbate.<sup>1128</sup>

Because of steric hindrance, the GPC in ALD from compound reactants should be considerably less than a monolayer of the ALD-grown material, as indicated by all three models. For example, for the  $TiCl_4$  reaction with one surface  $||-OH$  group to give a surface  $||-TiCl_3$  species, the maximum GPC predicted with the models, in monolayers of  $TiO_2$ , is about 28% (Model I,<sup>133,468</sup> calculated for the  $TiCl_4$  molecule), 19% [Model II (Ref. 1127)], and 33% [Model III (Ref. 237)].<sup>1173</sup> Experimental GPC values vary within about 15%–30% of a monolayer, depending on the growth temperature.<sup>237</sup>

## F. Effect of temperature on the GPC

The GPC in ALD typically varies with temperature. The temperature dependency of the GPC can come at least from the effect of temperature on the number and type of reactive sites present on the surface before and after the chemisorption, and from the effect of temperature on the preferred reaction mechanisms.<sup>1174</sup>

Four characteristic ways the GPC may depend on temperature in the ALD window—the temperature range where an ALD process fulfills the requirement of self-terminating reactions<sup>1175</sup>—are illustrated in Fig. 14. (i) The GPC may decrease with temperature [panel (a)]. This occurs typically if the number of reactive surface sites affects the amount and/or the type of chemisorbed species and if increasing the temperature decreases the number of reactive surface sites.<sup>130,216,548,554</sup> Increasing the reaction temperature may also change the inherent reaction mechanisms, for example, so that the  $L/M$  ratio in the chemisorbed  $ML_z$  species changes.<sup>418,419,421,818</sup> (ii) The GPC may stay constant with temperature [panel (b)]. This can occur, for example, if steric

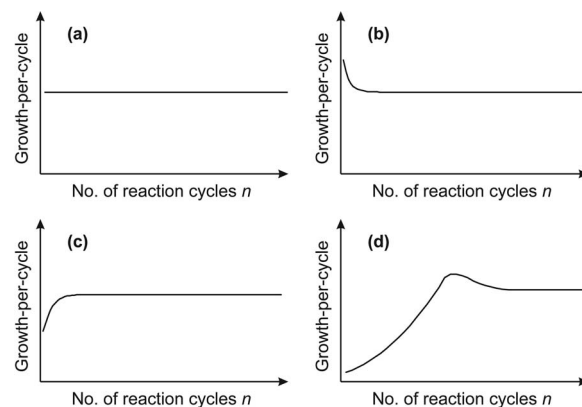


FIG. 15. Dependency of the GPC on the number of reaction cycles in different types of ALD processes (Ref. 247): (a) linear growth, (b) substrate-enhanced growth, (c) substrate-inhibited growth of Type 1, and (d) substrate-inhibited growth of Type 2.

hindrance causes saturation and the number of reactive sites does not affect the amount of adsorbed species.<sup>237,530,815</sup>

Sometimes, the GPC settles to different constant values at different temperatures.<sup>898</sup> (iii) The GPC can also increase with increasing temperature [panel (c)]. At higher temperatures, some energy barriers may be overcome and reactions occur, which do not occur at lower temperatures.<sup>481,1071</sup> (iv) The GPC can also increase first and then decrease with temperature [panel (d)]; first, some reactions are activated with increasing temperature, after which the decreasing number of reactive sites starts decreasing the GPC.<sup>199,243</sup> However, this can also be an artifact caused by incomplete reactions: the GPC has been measured for a constant reactant exposure as a function of temperature, and at lower temperatures with lower reaction rates [Eq. (7)] and slower mass transport, the reactions have not been completed [see, e.g., Fig. 8(e)].<sup>422</sup>

## G. Effect of the number of cycles on the GPC

The ALD process modifies the chemical composition of the surface through material deposition. The first ALD reaction cycle occurs on the surface of the original substrate material, the following cycles are usually on a surface with both the original substrate and the ALD-grown material exposed, and, after several ALD reaction cycles—the exact number depending on the GPC and the growth mode<sup>246,247,1140</sup>—finally, on a surface with only the ALD-grown material exposed. If the chemical composition of the surface changes, the GPC should be expected to vary with the number of cycles.

ALD processes can be classified into four groups on the basis of how the GPC varies with the number of ALD reaction cycles,<sup>247</sup> as shown in Fig. 15. In all four cases, the GPC is expected to settle to a constant value after a sufficient number of ALD reaction cycles. In *linear growth*, the GPC is constant over the cycles, from the first cycle on. The growth is always in the *steady regime*. Linear growth<sup>527,528,530</sup> can occur, for example, if the number of reactive sites on the surface does not change with the cycle number or if the  $L/M$  ratio in the adsorbed  $ML_z$  species is constant and steric hindrance of the ligands of the adsorbed species causes saturation. In *substrate-enhanced growth*, the GPC is higher in the



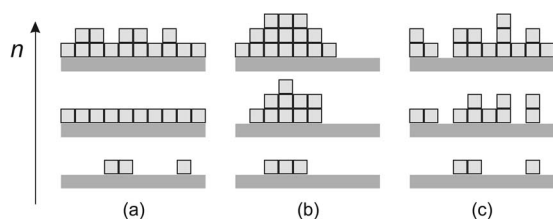


FIG. 16. Schematic illustration with increasing number of reaction cycles  $n$  of selected growth modes possible in ALD: (a) two-dimensional growth, (b) island growth and, (c) random deposition.

beginning of the growth than at the steady regime. The initial, nonconstant growth is referred to as being in a *transient regime*. Substrate-enhanced growth<sup>110,118,132,516,548,1008</sup> can occur, for example, if the number of reactive sites on the substrate is higher than on the ALD-grown material. In *substrate-inhibited growth of Type 1* and *Type 2*,<sup>247</sup> the GPC is lower in the beginning of the growth than at the steady regime. In *Type 2* substrate-inhibited growth, the GPC additionally goes through a maximum before settling to the constant value. Substrate-inhibited growth is caused by a lower number of reactive sites on the substrate than on the ALD-grown material.<sup>123,223,224,231,292,488,984,992,1176,1177</sup> In substrate-inhibited growth of *Type 2*,<sup>488,499–501,984,992,1151,1178</sup> island growth further seems to occur.<sup>488,992,1179</sup>

## H. Growth mode

The way the material gets arranged on the surface during ALD growth is defined by the *growth mode*. For the growth of a full monolayer per cycle, two-dimensional growth may be expected because multilayer adsorption should be excluded by definition in ALD. For the growth of less than a monolayer per cycle, in turn, other growth modes can prevail.

Several growth modes are possible in ALD. In *two-dimensional growth* (layer-by-layer growth, Frank–van der Merwe growth), the deposited material settles always in the lowest unfilled material layer and one monolayer of the ALD-grown material covers the substrate completely.<sup>246,1180</sup> While sometimes achieved,<sup>1077,1181</sup> this growth mode is not universally valid. In *island growth* (Volmer–Weber growth), the new material units are preferentially deposited on the ALD-grown material.<sup>246,247,1180</sup> Island growth has been concluded for several ALD processes.<sup>132,134,154,214,246,247,488,771,1182</sup> A model has recently been derived to describe island growth in ALD.<sup>247</sup> *Random deposition* is a statistical growth mode, where the new material units are deposited with an equal probability on all surface sites.<sup>1140</sup> Because of the self-terminating reactions, random deposition results in smoother layers in ALD than in continuous deposition processes (“shower model” versus “rain model” of random deposition).<sup>992,1140</sup> Random deposition has been concluded at least for two ALD processes.<sup>292,544</sup> Figure 16 compares schematically two-dimensional growth, island growth, and random deposition.

The growth mode may also change during growth. For example, the growth mode may be two-dimensional for the deposition of the first monolayer and island growth or ran-

dom deposition thereafter (Stranski–Krastanov growth).<sup>1180</sup> Vice versa, the growth mode may be first island growth, and when the islands have coalesced to form a continuous layer, two-dimensional growth may occur.<sup>1077</sup>

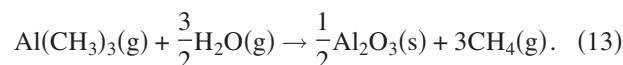
Assigning a relation between the way the GPC varies with the number of cycles and the growth mode would be attractive. The experimental investigations published so far do not support the existence of such a relation, however, except for the substrate-inhibited growth of *Type 2*, which seems to correspond to an island growth mode.<sup>246,247,488,1177</sup> Linear growth has corresponded to two-dimensional growth mode<sup>527</sup> as well as random deposition.<sup>544</sup> Substrate-enhanced growth of *Type 1* has corresponded to island growth mode<sup>558</sup> and random deposition.<sup>292</sup>

## IV. SURFACE CHEMISTRY OF THE $\text{AlMe}_3/\text{H}_2\text{O}$ PROCESS

This section reviews the current status of understanding the surface chemistry of the  $\text{AlMe}_3/\text{H}_2\text{O}$  process. This process is considered ideal for ALD: the reactants are highly reactive, but at the same time thermally stable, and the gaseous reaction product, methane, does not interfere with the growth. The process gives smooth, conformal films on highly complex structures. Section IV A introduces the general characteristics of the process. Self-termination of the reactions is verified in Sec. IV B. The chemisorption mechanisms identified to occur during the  $\text{AlMe}_3$  and  $\text{H}_2\text{O}$  reactions are summarized in Sec. IV C. Section IV D discusses the decreasing effect of increasing growth temperature on the GPC and Sec. IV E discusses steric hindrance as the factor causing saturation. The effect of the surface OH group concentration on the GPC is explored in Sec. IV F. Section IV G summarizes the (little) experimental information available on the kinetics of the reactions, and Secs. IV H and IV I summarize the way the GPC varies with the number of reaction cycles and the growth mode, respectively. Finally, Sec. IV J summarizes the findings.

### A. General characteristics

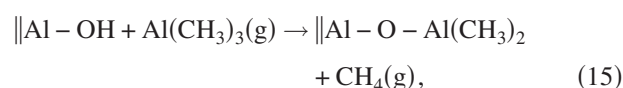
The  $\text{AlMe}_3/\text{H}_2\text{O}$  process follows the overall stoichiometry presented in Eq. (13) ( $\text{Me}=\text{CH}_3=\text{methyl}$ ),



The aluminum and oxygen retain their oxidation states, and the mass balance of Eq. (12) is valid. For the  $\text{AlMe}_3$  reaction, the mass balance converts to Eq. (14),

$$\Delta c_{\text{Me}} = 3\Delta c_{\text{Al}} - \Delta c_{(\text{O})\text{H}}. \quad (14)$$

The chemistry of the  $\text{AlMe}_3/\text{H}_2\text{O}$  process is often described by the two successive “half reactions” presented in the Eqs. (15) and (16),<sup>192,196</sup>



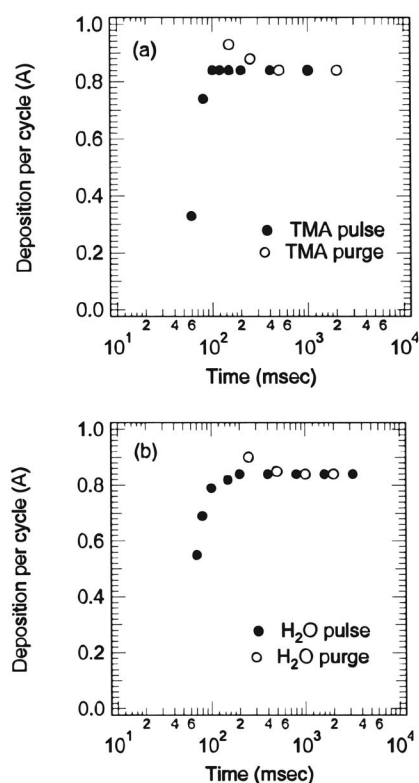
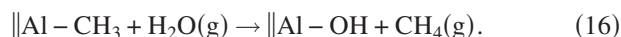


FIG. 17. Self-termination in the  $\text{AlMe}_3/\text{H}_2\text{O}$  process ( $\text{TMA}=\text{AlMe}_3$ ) at  $300^\circ\text{C}$  in the steady-growth regime: effect on the measured GPC (labeled “deposition per cycle”) of (a) the  $\text{AlMe}_3$  pulse and the following purge times (Steps 1 and 2) and (b) the  $\text{H}_2\text{O}$  pulse and the following purge times (Steps 3 and 4). (Reprinted from Sneh *et al.* (Ref. 222) with permission. Copyright 2002, Elsevier.)



That the surface switches from methyl-terminated to hydroxyl-terminated and vice versa is well known and illustrated, for example, by infrared measurements.<sup>196</sup> The  $\text{AlMe}_3/\text{H}_2\text{O}$  process is more complex than revealed by Eqs. (15) and (16), however, as discussed in the following sections.

## B. Verification of self-termination

The  $\text{AlMe}_3/\text{H}_2\text{O}$  process is self-terminating with respect to time. For sufficiently long reactant pulses and purges, lengthening the  $\text{AlMe}_3$  and  $\text{H}_2\text{O}$  pulses and the purges in between (Steps 1–4) does not affect the amount of species adsorbed,<sup>222,227</sup> as illustrated in Fig. 17. When the  $\text{AlMe}_3$  and  $\text{H}_2\text{O}$  exposures (Steps 1 and 3) are sufficiently long, the reactions go to completion and the GPC does not increase with increasing exposure time. The purges between the  $\text{AlMe}_3$  and  $\text{H}_2\text{O}$  reactions (Steps 2 and 4) must also be sufficiently long. If the purges are too short, the GPC increases because  $\text{AlMe}_3$  and  $\text{H}_2\text{O}$  are simultaneously present in the gas phase, enabling continuous CVD-type deposition.<sup>222,227</sup>

The  $\text{AlMe}_3/\text{H}_2\text{O}$  process seems self-terminating also with respect to the  $\text{AlMe}_3$  pressure. In the experiments of Kumagai *et al.*<sup>267</sup> for the  $\text{AlMe}_3/\text{H}_2\text{O}_2$  ALD process (oxygen source is  $\text{H}_2\text{O}_2$  instead of  $\text{H}_2\text{O}$ ), the GPC was independent of the reactant pressures, as shown in Fig. 18. The indepen-

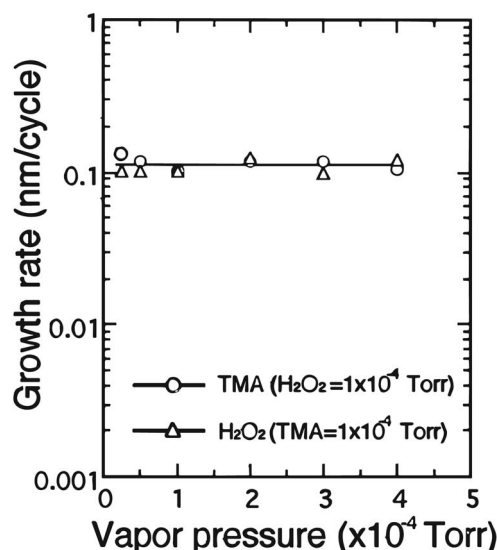


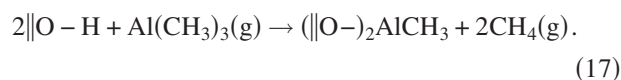
FIG. 18. Self-terminating reactions in the  $\text{AlMe}_3/\text{H}_2\text{O}_2$  ALD process ( $\text{TMA}=\text{AlMe}_3$ ) in the steady-growth regime: effect of reactant pressures to the GPC (labeled “growth rate”) at  $340^\circ\text{C}$  (Ref. 267). [Reprinted from Kumagai *et al.* (Ref. 267) with permission. Copyright 1994, Institute of Pure and Applied Physics.]

dence of the GPC from the  $\text{AlMe}_3$  pressure is consistent with irreversible, saturating reaction of  $\text{AlMe}_3$  on aluminum oxide.

Whether or not the  $\text{H}_2\text{O}$  pressure affects the amount of  $\text{H}_2\text{O}$  chemisorbed on aluminum oxide is not entirely clear. In some investigations,<sup>211,212,234</sup> the effect of reactant dose (exposure time multiplied with reactant partial pressure) on the  $\text{AlMe}_3/\text{H}_2\text{O}$  process has been suggested. A systematic study of the effect of  $\text{H}_2\text{O}$  exposure time and pressure is missing, however.

## C. Identified chemisorption mechanisms

Several reactions have both been experimentally and theoretically identified to occur when gaseous  $\text{AlMe}_3$  interacts with oxide supports.  $\text{AlMe}_3$  reacts through ligand exchange with the hydrogen atoms in surface OH groups, producing O–Al bonds and releasing methane [Eq. (15)].<sup>190,192,193,196,1088,1163,1164,1183–1186</sup> Other gaseous reaction products, in addition to methane, have not been found.<sup>211,217,227,243,443</sup> The  $\text{AlMe}_3$  molecule can also react through ligand exchange simultaneously with two OH groups, in the reaction described by Eq. (17),<sup>196,209,216,217</sup>



Practically all OH groups on silica and alumina react with  $\text{AlMe}_3$  through ligand exchange, at least at temperatures between  $80$  and  $300^\circ\text{C}$ .<sup>209,216</sup> In addition to the ligand exchange reaction [Eqs. (15) and (17)],  $\text{AlMe}_3$  reacts dissociatively with the oxygen bridges of silica [Eq. (18)],<sup>197,209,1163,1164,1183,1187,1188</sup>

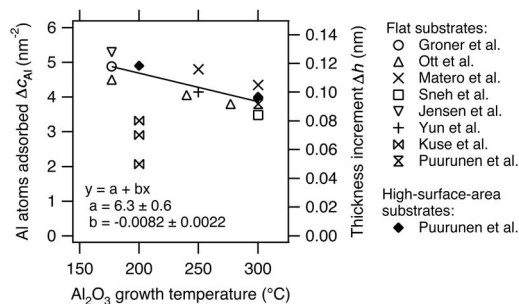
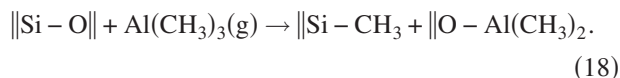
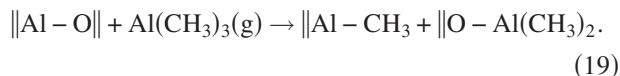


FIG. 19. GPC in the  $\text{AlMe}_3/\text{H}_2\text{O}$  process to grow amorphous aluminum oxide on flat substrates in the steady-growth regime (Refs. 228, 199, 212, 222, 229, 179, 234, and 246). The GPC is expressed as the amount of aluminum atoms attached per cycle per square nanometer of surface  $\Delta c_{\text{Al}}$  ( $\text{nm}^{-2}$ ), which converts to the thickness increment per cycle  $\Delta h$  (nm) through  $\Delta c_{\text{Al}} = \rho N_A M^{-1} \Delta h$  ( $\rho = 3.5 \text{ g cm}^{-3}$ ) (Refs. 237 and 1128). A line was fitted to the data on flat substrates, except the points of Kuse *et al.*, which probably represent unsaturated conditions. Confidence limit of one standard deviation is shown. Data points obtained on high-surface-area alumina substrates are shown for reference (Ref. 216). The results (Ref. 216) were calculated through the mass balance [Eq. (23) for  $\text{AlMe}_3$  reaction at  $150^\circ\text{C}$  with alumina heat treated at the temperature indicated in the  $x$  axis. The results for  $\text{AlMe}_3$  reaction at  $150^\circ\text{C}$  can be used for the comparison, because increasing the temperature to  $300^\circ\text{C}$  does not affect the amount of adsorbed species (Fig. 20).



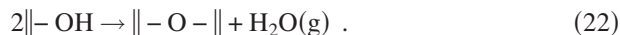
Dissociation to several oxygen bridges bonded to the same silicon atom leads also to surface species of type  $\|\text{Si}(\text{Me})_2$  and  $\|\text{Si}(\text{Me})_3$ .<sup>197,209</sup>  $\text{AlMe}_3$  seems also to react dissociatively with coordinatively unsaturated (c.u.s.) Al–O pairs of alumina [Eq. (19)],<sup>196,216,1096</sup>



Similarly as for  $\text{AlMe}_3$  reaction on aluminum oxide, ligand-exchange reaction and dissociation has been concluded to occur in the  $\text{H}_2\text{O}$  reaction with  $\text{AlMe}_3$ -modified aluminum oxide [Eqs. (20) and (21)],<sup>192,211,215,217,220</sup>



The reversed reaction of dissociation, dehydroxylation, also occurs, through which the surface OH concentration decreases with increasing temperatures [Eq. (22)],<sup>211,215,217,220</sup>



## D. Effect of temperature on the GPC

The GPC in the steady regime of the  $\text{AlMe}_3/\text{H}_2\text{O}$  process decreases with increasing processing temperature, as shown in Fig. 19 that summarizes the results by several groups.<sup>179,199,212,216,222,228,229,234</sup> This figure does not include results beyond  $300^\circ\text{C}$ , the temperature at which  $\text{AlMe}_3$  starts to decompose thermally.<sup>216,1189</sup> The different investigations share the decreasing trend and agree quantitatively within an experimental error of about 10%. One investigations,<sup>234</sup> however, shows a significantly lower GPC.

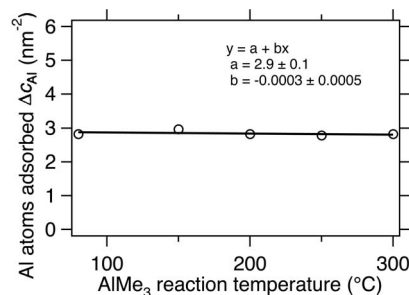


FIG. 20. Effect of the  $\text{AlMe}_3$  reaction temperature on the amount of aluminum atoms adsorbed in the  $\text{AlMe}_3$  reaction  $\Delta c_{\text{Al}}$  ( $\text{nm}^{-2}$ ) on alumina heat treated at  $560^\circ\text{C}$ , according to Puurunen *et al.* (Ref. 216). The confidence limits represent one standard deviation.

It did not confirm the saturation of the surface reactions through sufficiently long pulse and purge times, however, and the process probably operated at unsaturated conditions.

Change in the inherent reaction mechanisms [Eqs. (15) and (17)–(19)] with temperature might account for the decreasing GPC. To investigate this possibility, one needs to separate the effect of temperature on the reaction mechanisms from its effect on the number of reactive sites. Figure 20 shows the results obtained for the  $\text{AlMe}_3$  reaction on high-surface-area alumina, which had been stabilized by a preceding heat treatment at  $560^\circ\text{C}$  to have a surface OH group concentration  $c_{(\text{O})\text{H}}$  of  $2.0 \text{ nm}^{-2}$ .<sup>216,262</sup> The amount of aluminum atoms adsorbed  $\Delta c_{\text{Al}}$  ( $\text{nm}^{-2}$ ) could be calculated through the mass balance, Eq. (23) [rearranged from Eq. (14)],<sup>216,262</sup> because the amount of methyl groups adsorbed  $\Delta c_{\text{Me}}$  ( $\text{nm}^{-2}$ ) was measured and the amount of OH groups reacted  $\Delta c_{(\text{O})\text{H}}$  ( $\text{nm}^{-2}$ ) could be approximated with the surface OH group concentration before the reaction  $c_{(\text{O})\text{H}}$  ( $\text{nm}^{-2}$ ).<sup>209,216</sup>

$$\Delta c_{\text{Al}} = \frac{1}{3}(\Delta c_{\text{Me}} + c_{(\text{O})\text{H}}). \quad (23)$$

As seen from Fig. 20, the reaction temperature has no effect on the amount of aluminum atoms adsorbed in the  $\text{AlMe}_3$  reaction with alumina. An effect of the reaction temperature on the preferred reaction mechanisms therefore cannot explain the decreasing GPC.

The change in the number of reactive surface groups with temperature is another option to account for the decreasing GPC. Increasing the substrate heat-treatment temperature indeed decreases the amount of aluminum  $\Delta c_{\text{Al}}$  chemisorbed in the  $\text{AlMe}_3$  reaction on alumina<sup>216,262</sup> and silica,<sup>209,210,262</sup> as shown in Fig. 21. Increasing the heat-treatment temperature concurrently decreases the surface OH group concentration,<sup>209,216,1190</sup> as also indicated in the figure. Moreover, the quantitative values and temperature dependency of the amount of aluminum  $\Delta c_{\text{Al}}$  chemisorbed on alumina [Fig. 21(a)] and the GPC  $\Delta c_{\text{Al}}$  in the  $\text{AlMe}_3/\text{H}_2\text{O}$  process (Fig. 19) agree.<sup>1191</sup> The  $\text{AlMe}_3$  reaction on alumina subjected to a controlled heat-treatment therefore seems to represent the  $\text{AlMe}_3$  reaction in the steady regime of the  $\text{AlMe}_3/\text{H}_2\text{O}$  process. This representativeness is as expected, because in both cases  $\text{AlMe}_3$  reacts with an  $\text{Al}_2\text{O}_3$  surface.



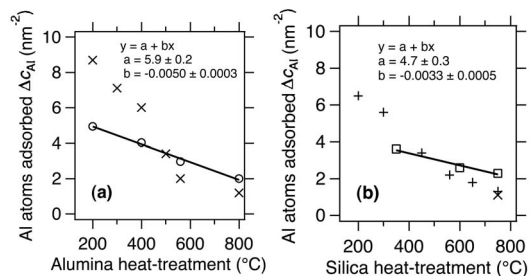


FIG. 21. Effect of the substrate heat-treatment temperature on the amount of aluminum adsorbed  $\Delta c_{Al}$  (nm<sup>-2</sup>) in the  $AlMe_3$  reaction (a) on alumina at 150 °C (○ Ref. 216) and (b) on silica at 150 or 250 °C (□ Refs. 209 and 210). The OH surface concentrations (nm<sup>-2</sup>) are shown as crosses for reference (alumina: × Ref. 216, silica: × Ref. 209, and + Ref. 1190). The confidence limits represent one standard deviation.

Consequently, a decrease in the surface OH group concentration with increasing temperature seems to explain the decreasing GPC.

### E. Factor causing saturation

Steric hindrance by methyl groups appears to cause the termination of the  $AlMe_3$  reaction by the saturation of the surface with adsorbed species.<sup>209,216,221,237,291,292,1096</sup> This conclusion originates from the fact that the methyl group content settles to approximately a constant value after saturation has been attained,<sup>209,210,216,291,292,1192</sup> as illustrated in Fig. 22(b), where the methyl group content after the  $AlMe_3$  reaction with high-surface-area alumina and silica is plotted as a function of the surface OH group concentration. Although the surface OH group concentration varies markedly (1–9 nm<sup>-2</sup>), the amount of methyl groups adsorbed is approximately constant (5–6 nm<sup>-2</sup>).

Of the three models developed for analyzing steric hindrance in self-terminating reactions in ALD (Sec. III E), only Model III has been applied for the  $AlMe_3$  reaction.<sup>237</sup> Model I has never been applied and Model II seems not to be applicable.<sup>1193</sup> The maximum theoretical amount of methyl groups adsorbed according to Model III is 7.2 nm<sup>-2</sup>,<sup>209,237,1128</sup> calculated from the van der Waals radius of methyl groups of 0.20 nm.<sup>1194</sup> The observed amount of methyl groups adsorbed is about 70%–80% of this theoretical maximum, corresponding to a ligand coverage  $\theta$  of 0.7–0.8. This ligand coverage is consistent with the conclusion that the saturation of the  $AlMe_3$  reaction is caused by the steric hindrance of methyl groups: the chemisorption of  $AlMe_3$  proceeds as long as sufficiently large areas not shielded by the methyl ligands remain on the surface.<sup>209,237,1128</sup>

### F. Effect of the surface OH group concentration

The surface concentration of OH groups affects the number and type of species adsorbed in the  $AlMe_3$  reaction. The amount of aluminum atoms  $\Delta c_{Al}$  adsorbed in the  $AlMe_3$  reaction increases, the amount of methyl groups adsorbed  $\Delta c_{Me}$  stays about constant, and the average Me/Al ratio ( $\Delta c_{Me}/\Delta c_{Al}$ ) in the adsorbed surface species decreases with increasing surface OH group concentration  $c_{(OH)}$ , as shown

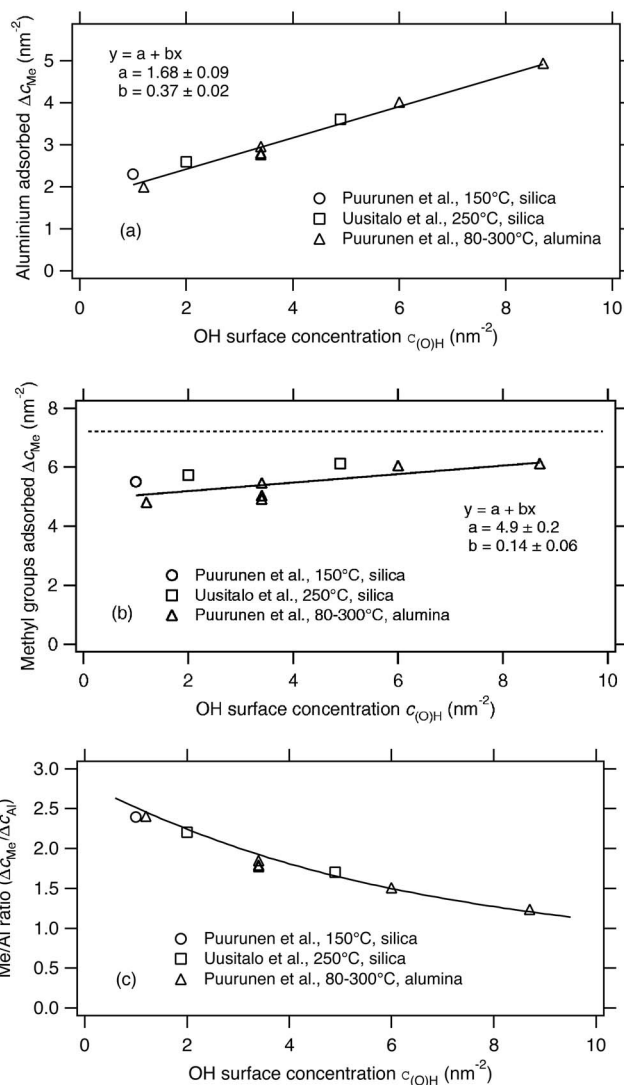


FIG. 22. Effect of the surface OH group concentration  $c_{(OH)}$  on the amount of material chemisorbed in the  $AlMe_3$  reaction on alumina and silica substrates (Ref. 262): (a) amount of aluminum atoms adsorbed in the reaction  $\Delta c_{Al}$  (nm<sup>-2</sup>), (b) methyl group concentration after the reaction  $\Delta c_{Me}$  (nm<sup>-2</sup>), and (c) the average methyl/aluminum (Me/Al) ratio in the adsorbed species ( $\Delta c_{Me}/\Delta c_{Al}$ ). Data from Ref. 216 for alumina and Refs. 209 and 210 for silica, for  $AlMe_3$  reaction at the indicated temperatures. The OH surface concentrations are from Ref. 216 for alumina and Refs. 209 and 1190 for silica. In panels (a) and (b), the lines have been fitted to the data. The confidence limits represent one standard deviation. In panel (b), the dashed line indicates the maximum theoretical methyl group concentration of 7.2 nm<sup>-2</sup> according to Model III (Refs. 237 and 1128).

in Fig. 22.<sup>262</sup> The amount of aluminum adsorbed  $\Delta c_{Al}$  (nm<sup>-2</sup>) on oxide substrates (alumina, silica) increases linearly with the OH surface concentration  $c_{(OH)}$  (nm<sup>-2</sup>),

$$\Delta c_{Al} = a + bc_{(OH)} \approx 1.68 + 0.37c_{(OH)}. \quad (24)$$

Even in the absence of OH groups, aluminum is deposited ( $a > 0$ ), a fact consistent with dissociative (or associative) reactions of  $AlMe_3$  (Sec. IV C). In dissociation or association, the Me/Al ratio is three, and the  $a$  (nm<sup>-2</sup>) in Eq. (24) expectedly corresponds to one third of the number of methyl groups adsorbed at low surface OH group concentrations [Fig. 22(b)]. In contrast to what would be expected on the

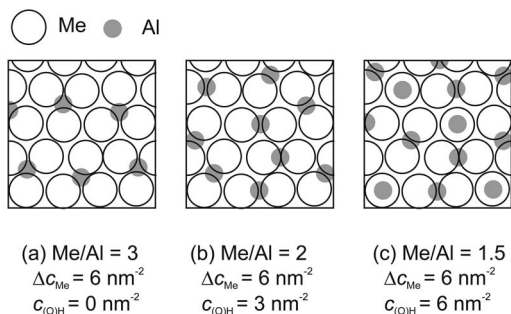


FIG. 23. Illustration of the physical situation corresponding to Eq. (24): number of aluminum atoms  $\Delta c_{\text{Al}}$  and methyl groups  $\Delta c_{\text{Me}}$  adsorbed in the self-terminating  $\text{AlMe}_3$  reaction on surfaces with different OH group concentrations  $c_{(\text{OH})}$ , resulting in average Me/Al ratios of (a) 3, (b) 2, and (c) 1.5. The squares represent an area of  $3 \text{ nm}^2$ ; the methyl groups are drawn in scale ( $r_{\text{Me}} = 0.2 \text{ nm}^2$ ). The small dependency that the number of adsorbed methyl groups has on the surface OH group concentration [Fig. 22(b)] has been neglected for simplicity.

basis of Eq. (15), there is no one-to-one correspondence between  $\Delta c_{\text{Al}}$  and  $c_{(\text{OH})}$  ( $b \neq 1$ ). Instead, almost three ( $b^{-1}$ ) OH groups are needed for attaching one additional aluminum atom. This number is consistent with the fact that steric hindrance causes the amount of adsorbed methyl groups  $\Delta c_{\text{Me}}$  to be about constant (Sec. IV E): three OH groups are needed to release the three methyl groups of one  $\text{AlMe}_3$  molecule as methane, and thereby to attach one additional aluminum atom to the surface.

The values of the parameters  $a$  and  $b$  in Eq. (24) are consistent with the reaction scheme<sup>192,195,196,209,216,237,1088,1164</sup> that  $\text{AlMe}_3$  reacts through ligand exchange with practically all OH groups, releasing methane, and additionally through dissociation or association, until steric hindrance by adsorbed methyl groups causes the reaction to terminate. The physical significance of Eq. (24) is further illustrated in Fig. 23 for the situations after the completion of the self-terminating  $\text{AlMe}_3$  reaction with oxide substrates with different surface OH group concentrations. The more OH groups there are on the substrate, the more aluminum atoms adsorb, whereas the number of adsorbed methyl groups stays about constant. As shown in Fig. 24, the GPC calculated with Eq. (24) [assuming that  $c_{(\text{OH})}$  decreases linearly with temperature from  $9 \text{ nm}^{-2}$  at  $200^\circ\text{C}$  to  $7 \text{ nm}^{-2}$  at  $300^\circ\text{C}$  (Ref. 1195)] agrees with the experimental values.

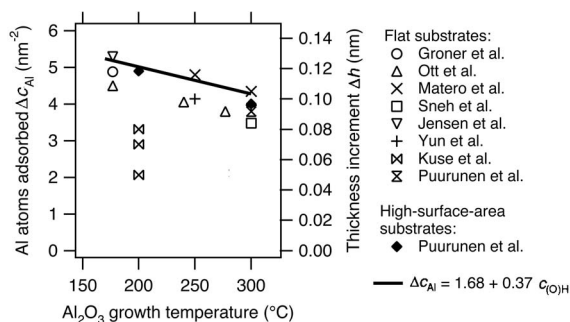


FIG. 24. The correlation of Eq. (24), marked as a solid line, is in line with the GPC in the  $\text{AlMe}_3/\text{H}_2\text{O}$  process (data points as in Fig. 19). The GPC values for the correlation were calculated assuming that  $c_{(\text{OH})}$  decreases linearly with temperature from  $9 \text{ nm}^{-2}$  at  $200^\circ\text{C}$  to  $7 \text{ nm}^{-2}$  at  $300^\circ\text{C}$  (Ref. 1195).

## G. Kinetics of the reactions

The kinetics of the  $\text{AlMe}_3$  and  $\text{H}_2\text{O}$  reactions during the  $\text{AlMe}_3/\text{H}_2\text{O}$  process have not been thoroughly investigated. Some qualitative and quantitative information on the kinetics exist or can be obtained by critically investigating published results.

Recent *in situ* mass spectrometry (MS) and quartz crystal microbalance (QCM) investigations<sup>211,217</sup> contain qualitative kinetic information of the  $\text{AlMe}_3/\text{H}_2\text{O}$  process. These investigations were carried out (mostly) under conditions where the methane-producing ligand-exchange reactions of  $\text{AlMe}_3$  and  $\text{H}_2\text{O}$  reactions have been completed.<sup>211,215,217,220</sup> However, as described below, the reactions have not yet completely self-terminated. The main results obtained in these investigations by the MS technique have been collected in Figs. 25 and 26. Results only up to a processing temperature of  $300^\circ\text{C}$  are shown because of the decomposition of  $\text{AlMe}_3$  at higher temperatures.<sup>216,1189</sup> Reinterpreting these results, to follow, indicates that the ligand-exchange reactions are completed faster than the dissociation in the self-terminating reactions of both  $\text{AlMe}_3$  and  $\text{H}_2\text{O}$  during  $\text{AlMe}_3/\text{H}_2\text{O}$  ALD.

Extracting qualitative kinetic information from the results of the  $\text{H}_2\text{O}$  reaction needs some reinterpretation. It is possible to investigate the  $\text{H}_2\text{O}$  reaction in  $\text{AlMe}_3/\text{H}_2\text{O}$  ALD under conditions where the ligand-exchange reaction of water has terminated, but other reactions have not. In Ref. 211, Juppo *et al.* investigated the  $\text{AlMe}_3/\text{H}_2\text{O}$  process under such conditions. Although in Ref. 211 they did not conclude the water reaction to be incomplete, later it was concluded to have been the case.<sup>215,217,220</sup> The fact that the amount of hydroxyl groups increased with increasing water dose [Fig. 25(b)] reveals the incomplete  $\text{H}_2\text{O}$  reaction. Because at the same time the methane production had stopped,<sup>211</sup> qualitative kinetic information exist for the water reaction: the reaction has been investigated under conditions where the methane-producing ligand-exchange reaction of water [Eq. (20)] has been completed, but the dissociation of water [Eq. (21)], or perhaps association, has not. The ligand-exchange reaction of water is evidently completed faster than the other reactions.

Extracting qualitative kinetic information from the results of the  $\text{AlMe}_3$  reaction needs additional reinterpretation. It seems to be possible to investigate the  $\text{AlMe}_3/\text{H}_2\text{O}$  process also under conditions where the ligand-exchange reaction of  $\text{AlMe}_3$  has terminated, but other reactions have not. With increasing temperature, the GPC *increased* in the experiments of Juppo *et al.* [Fig. 25(a)],<sup>211</sup> whereas in most investigations the GPC has *decreased* (Fig. 19). The increase in GPC<sup>211</sup> came mostly from the fact that more material was deposited during the  $\text{AlMe}_3$  reaction, and the amount of methyl groups present on the surface after the  $\text{AlMe}_3$  reaction increased with increasing processing temperature [Fig. 25(c)]. At saturation, however, the methyl group concentration should be approximately constant (Sec. IV E). For unsaturated reactions, increasing the reaction temperature increases the amount of material adsorbed, because reactions [Eq. (7)] as well as mass transport get faster. Saturation was

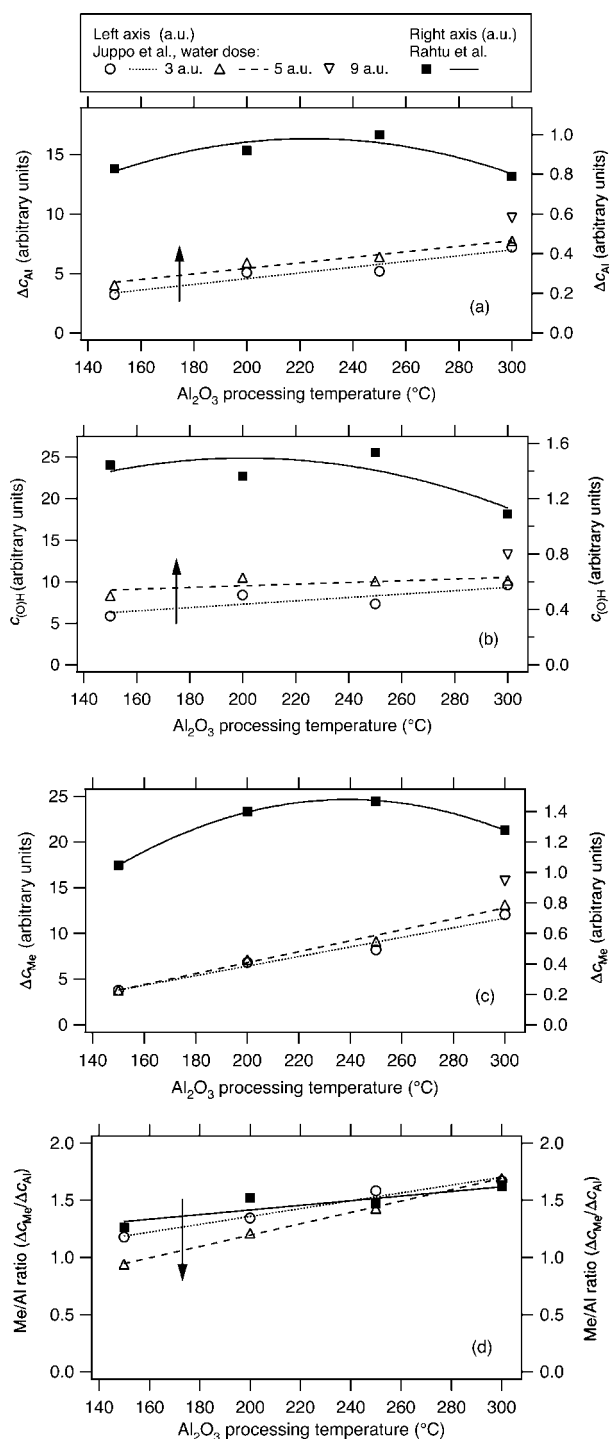


FIG. 25. Summary of the *in situ* MS results for the AlMe<sub>3</sub>/H<sub>2</sub>O process of Juppó *et al.* (Ref. 211) (open symbols, left axis) and Rahtu *et al.* (Ref. 217) (black squares, right axis): (a) total amount of methane produced during a reaction cycle divided by three, proportional to the GPC  $\Delta c_{Al}$ , (b) the amount of methane produced during the AlMe<sub>3</sub> reaction, proportional to the surface OH group concentration before the AlMe<sub>3</sub> reaction  $c_{OH}$ , (c) the amount of methane produced during the H<sub>2</sub>O reaction, proportional to the methyl group concentration after the AlMe<sub>3</sub> reaction  $\Delta c_{Me}$ , and (d) Me/Al ratio on the surface after the AlMe<sub>3</sub> reaction, obtained by dividing  $\Delta c_{Me}$  [panel (c)] with  $\Delta c_{Al}$  [panel (a)]. The results of Juppó *et al.* obtained for the shortest water pulses are not shown, because in them, the methane-producing reactions had not saturated (Ref. 211). All results are in arbitrary units (a.u.). Although the exact dependency is not known, for plotting the results in the same graphs, 25 (unnormalized) units of Juppó *et al.* (left axis) were assumed to correspond to 1.5 (normalized) units of Rahtu *et al.* (right axis).

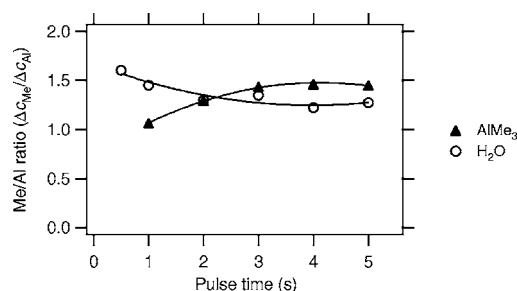


FIG. 26. Effect of AlMe<sub>3</sub> and H<sub>2</sub>O pulse times to the average Me/Al ratio after AlMe<sub>3</sub> reaction with alumina, as reported by Rahtu *et al.* (Ref. 217). The AlMe<sub>3</sub> and H<sub>2</sub>O reactions were saturated after a pulse time of about 3 s.

not confirmed in the experiments of Ref. 211, except that the methane production from ligand-exchange reactions had been completed,<sup>211</sup> and it seems that the AlMe<sub>3</sub> reaction had not fully saturated. Consequently, qualitative kinetic information exist also for the AlMe<sub>3</sub> reaction: the reaction has been investigated under conditions where the ligand-exchange reaction of AlMe<sub>3</sub> [Eqs. (15) and (17)] has been completed, but the dissociation [Eq. (19)] has not. The ligand-exchange reaction of AlMe<sub>3</sub> is therefore evidently completed faster than dissociation.

The investigations of Rahtu *et al.*,<sup>217</sup> George and co-workers,<sup>195,196</sup> and Elam *et al.*<sup>227</sup> support the interpretation made here that the ligand-exchange reaction of AlMe<sub>3</sub> is completed faster than dissociation. According to the results of Rahtu *et al.*,<sup>217</sup> for unsaturated reaction, the average Me/Al ratio of the adsorbed species is lower than when the AlMe<sub>3</sub> reaction is allowed to go to completion (Fig. 26). Therefore, ligand-exchange reactions, which give a lower Me/Al ratio, seem to occur earlier than dissociation. George and co-workers<sup>195,196</sup> showed by infrared analysis that, in the beginning of the AlMe<sub>3</sub> reaction, the O-H features decrease immediately in intensity, whereas the C-H features increase only after a delay, which is also in line with the current interpretation. Elam *et al.*<sup>227</sup> also found qualitative evidence by *in situ* MS analysis for two kinetic regimes in the AlMe<sub>3</sub> reaction, although they did not comment on the types of reactions occurring.

Quantitative kinetic information exist for the AlMe<sub>3</sub>/H<sub>2</sub>O process for narrow temperature and pressure ranges. Soto and Tysöe<sup>192</sup> investigated the process on flat substrates in ultrahigh vacuum (UHV) at room temperature. They modeled the AlMe<sub>3</sub>/H<sub>2</sub>O process with three reactions:<sup>192</sup> (i) the ligand-exchange reaction of AlMe<sub>3</sub> in the first half reaction with one surface OH group to release one methane molecule [reaction (15)], (ii) the ligand-exchange reaction of water in the second half reaction with one methyl group of a surface  $\parallel\text{AlMe}_2$  species, and (iii) the ligand-exchange reaction of water in the second half reaction with the second methyl group, now in a  $\parallel\text{Al}(\text{Me})\text{OH}$  species. The kinetics were described similarly as in Sec. III B assuming irreversible reactions. According to Soto and Tysöe,<sup>192</sup> the probability that the reactions (i), (ii), or (iii) occur when AlMe<sub>3</sub> or H<sub>2</sub>O molecules hit the surface at room temperature are 0.01, 0.25, and 0.009, respectively. Dillon *et al.*<sup>196</sup> investigated the AlMe<sub>3</sub>/H<sub>2</sub>O process on high-surface-area substrates at 227 °C and 0.01 Torr. They modeled the



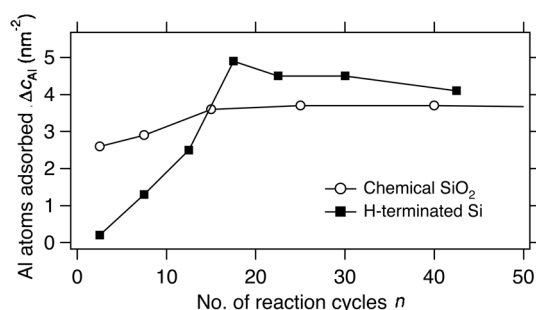


FIG. 27. GPC in the  $\text{AlMe}_3/\text{H}_2\text{O}$  process at  $300^\circ\text{C}$  as a function of the number of ALD reaction cycles when a chemical  $\text{SiO}_2$  rich in OH groups and a hydrogen-terminated silicon are used as substrates. Data from Zhao *et al.* (Ref. 1176).

$\text{AlMe}_3/\text{H}_2\text{O}$  process with reactions (15) and (16), assuming irreversible adsorption as in Sec. III B. Dillon *et al.*<sup>196</sup> extracted rate constants  $k_a$  for  $\text{AlMe}_3$  reaction of  $0.0076\text{ s}^{-1}$  and  $\text{H}_2\text{O}$  reaction of  $0.029\text{ s}^{-1}$ , where the constants are given for  $227^\circ\text{C}$  and  $0.01\text{ Torr}$ .

## H. Effect of the number of cycles on the GPC

The GPC in the  $\text{AlMe}_3/\text{H}_2\text{O}$  process depends on the number of ALD reaction cycles carried out and on the substrate used. Figure 27 shows how the GPC depends on the number of cycles.<sup>246,1176</sup> On silicon dioxide as substrate, the GPC increases with the number of cycles, and the process seems to follow Type 1 substrate-inhibited growth [Fig. 15(c)]. On hydrogen-terminated silicon as substrate, the GPC is low in the beginning of the growth, increases, goes through a maximum, and then decreases to a constant value.<sup>1176</sup> Thus, the process follows Type 2 substrate-inhibited growth [Fig. 15(d)].

The increase in GPC with the number of cycles most likely originates from the fact that the number of reactive surface sites increases with the number of cycles. For the  $\text{AlMe}_3/\text{H}_2\text{O}$  process at  $300^\circ\text{C}$  on the silicon dioxide substrate, the surface OH group concentration  $c_{(\text{OH})}$  is expected to start from about  $3\text{--}5\text{ nm}^{-2}$  (Refs. 1190 and 1196) and to increase with deposition to the value characteristic for aluminum oxide, about  $7\text{ nm}^{-2}$ .<sup>216,1195</sup> The Si–H bonds on hydrogen-terminated silicon appear not to react with the  $\text{AlMe}_3$  and  $\text{H}_2\text{O}$  reactants.<sup>246</sup> The characteristic type of the GPC curve is explained by the fact that  $\text{AlMe}_3$  reacts initially with defect sites on the hydrogen-terminated silicon substrate, after which  $\text{Al}_2\text{O}_3$  islands begin to deposit.<sup>239,240,246,247</sup> Furthermore, the  $\text{Al}_2\text{O}_3$  islands catalyze the oxidation of hydrogen-terminated silicon surface to form reactive  $\text{SiO}_x$  species.<sup>239,240,246,247</sup>

## I. Growth mode

The growth mode in the  $\text{AlMe}_3/\text{H}_2\text{O}$  process has not been systematically investigated. The fact that smooth layers with the expected material density are obtained<sup>198,199</sup> indicates that the growth mode is generally probably close to two dimension. On hydrogen-terminated silicon as substrate, however, island growth occurs.<sup>246</sup> Islands of ALD-grown

$\text{Al}_2\text{O}_3$  are revealed both through transmission electron microscopy and through growth-mode modeling.<sup>246</sup>

## J. Summary

The  $\text{AlMe}_3/\text{H}_2\text{O}$  process can be summarized as follows:  $\text{AlMe}_3$  reacts through ligand exchange with practically all surface OH groups, releasing methane.  $\text{AlMe}_3$  reacts also through dissociation with surface oxygen bridges. The ligand-exchange reaction is completed first, after which the dissociation is completed. The  $\text{AlMe}_3$  reaction self-terminates because of steric hindrance of the methyl groups, but the surface OH group concentration affects the type and number of adsorbed species.  $\text{H}_2\text{O}$  reacts through ligand exchange with practically all surface methyl groups, releasing methane.  $\text{H}_2\text{O}$  reacts also through dissociation (and perhaps association) with surface oxygen bridges. The ligand-exchange reaction is completed first, after which the dissociation is completed. When the  $\text{H}_2\text{O}$  reaction self-terminates, the surface hydroxyl group concentration settles to a value dictated by the temperature and by the chemical nature of the surface.

Although the surface chemistry of the  $\text{AlMe}_3/\text{H}_2\text{O}$  process is qualitatively rather well understood, systematic investigations of the reaction kinetics and the growth mode on different substrates could help to further clarify the details of the process. Because the quantitative relationship between the amount of aluminum adsorbed (or the Me/Al ratio after  $\text{AlMe}_3$  chemisorption) and the surface OH group concentration is known, the  $\text{AlMe}_3$  reaction might be applicable for probing the surface OH group concentration of oxide materials.

## V. DISCUSSION

Several issues may hamper multidisciplinary surface chemistry investigations of ALD: the ALD literature contains incorrect historical assumptions and nonstandard, problematic terminology. The effect of experimental conditions on the surface chemistry is not clear,<sup>67</sup> but one needs to understand this effect to interpret together the results of investigations made at different conditions. To assist multidisciplinary surface chemistry investigations, Sec. V A discusses the problematic historical assumptions, Sec. V B discusses the problematic terminology, and Sec. V C discusses the effect of experimental conditions on the surface chemistry of ALD.

### A. Problematic historical assumptions on the surface chemistry of ALD

At least four common historical assumptions on the surface chemistry of ALD are often cited but are, in practice, seldom valid. The reasons why ALD processes do not follow these assumptions have been discussed in some research articles,<sup>237,247,432,468,488,499–501,1119,1127,1128,1140,1151,1178</sup> but only to a limited extent in existing reviews.<sup>3,6–66</sup>

#### 1. GPC of a monolayer

Perhaps the oldest of these problematic historical assumptions is GPC of a monolayer. According to this assump-

tion, ALD should lead to the growth of one monolayer of the desired material per ALD reaction cycle. This assumption was made already in the 1960s and 1970s by Soviet and Finnish scientists<sup>2,79</sup> and has been thereafter widely adopted.<sup>7-9,11,13,17,25-27,31,36,54,62,63,66,318</sup>

In real ALD processes, the GPC is typically less than a monolayer.<sup>40,62,63,246,488,984,1178,1197</sup> This is also true for the  $\text{AlMe}_3/\text{H}_2\text{O}$  process, which is otherwise known as a rather ideal ALD process (Sec. IV). Recent models<sup>1127,1128</sup> have clearly shown that in self-terminating reactions of compound reactants, “full monolayer growth” is often impossible due to steric reasons: the ligands of the adsorbed species are simply too large.

Although the reasons for assuming a GPC of a monolayer are seldom itemized in ALD publications, I believe the assumption of a GPC of a monolayer originates from a desired two-dimensional growth mode, because a full monolayer growth should in the absence of multilayer adsorption lead to two-dimensional growth. The persistence of this assumption may also be related to confusing the two definitions of a monolayer (Fig. 7): a chemisorbed monolayer and a monolayer of the ALD-grown material. Namely, a chemisorbed monolayer forms by definition in a self-terminating gas–solid reaction. However, this monolayer is unlikely to convert to a monolayer of the ALD-grown material in the second half reaction of an ALD reaction cycle.

## 2. Constant GPC over cycles

It has been often assumed,<sup>7-9,11,13,17,23,25-27,31,32,36,38,39,51,205,1198</sup> and still often is,<sup>3,55,58,59,63,64,91,1199</sup> that the amount of material deposited in an ALD reaction cycle should remain constant with the number of reaction cycles. Assuming a constant GPC over the cycles is a logical consequence of assuming a GPC of a monolayer. However, as it has been recognized that the GPC can be less than a monolayer (Secs. III E and V A 1), it should be obvious that the GPC may vary with the number of cycles when the composition of the surface changes with the number of cycles.<sup>40,63,64,246,488,984,1178</sup>

## 3. Constant GPC with temperature

Historically it has been assumed, in line with the assumed GPC of a monolayer, that the GPC in ALD should remain constant with temperature.<sup>11,30</sup> However, as the GPC may be less than a monolayer, and the GPC is a sensitive function of the reactivity of the reactant molecule and the number and type of reactive sites present on the surface, it is natural that the GPC may change with temperature. The  $\text{AlMe}_3/\text{H}_2\text{O}$  ALD process is an example of a process where the GPC decreases with temperature due to a decrease in OH surface concentration (Sec. IV F). Correspondingly, the assumption of a constant GPC with temperature seems mostly abandoned.<sup>3,36</sup>

## 4. Two-dimensional growth mode

Two-dimensional growth mode is also an old assumption in ALD,<sup>2</sup> and is interlinked with the assumed GPC of a monolayer: In the absence of multilayer deposition, a GPC

of a monolayer should result in two-dimensional growth. Historically, the assumption of two-dimensional growth has been rather widely accepted,<sup>9,13,15,19,21,23,26,318</sup> even though island growth (in the beginning of ALD growth) was reported already early.<sup>154</sup> Thereafter, island growth has been observed in many processes.<sup>246,247,292,488,544,558,1077</sup>

A special deviation from the expected growth mode is the yet unexplained particle formation in the  $\text{TiCl}_4/\text{H}_2\text{O}$  and  $\text{ZnEt}_2/\text{H}_2\text{O}$  ALD processes: multilayer growth occurs even during one ALD reaction cycle, although the reactions otherwise seem to fulfill the basic ALD requirement of self-termination.<sup>419,421,600,818,1135,1169</sup>

## B. Problematic terminology

In a multidisciplinary field, clear and correct terminology is required for fluent communication between different researchers and research groups. In the field of ALD, at least two terms have nonstandard or otherwise difficult definitions. Even the name “ALD” itself could need reconsideration.

### 1. Growth rate (amount/cycle)

The most common way to refer to the amount of material deposited per reaction cycle is the “growth rate (amount/cycle).”<sup>3,25,26,31,32,40,59,63,66,126,927,985,1178</sup> This term is nonstandard, however, as the amount of material deposited per reaction cycle is not a rate.

In general terms, “rate” refers to a change of a property per unit of time. Continuous deposition processes are typically characterized by a constant growth rate [derivative of the growth curve showing the amount of material deposited versus time, giving a growth rate (amount/time)]. Growth rate (amount/cycle) has analogously been adopted as a term for ALD, replacing the time in the unit by the number of cycles. This term is confusing not only because it is of nonstandard nature, but also because ALD processes have rates, too, which are of interest regarding the surface chemistry and the throughput of the process. The instantaneous growth rate in ALD (amount/time) is related to the kinetics of the reactions and is typically nonconstant [see Fig. 10(c); deposition rate=growth rate]. The overall growth rate (amount/time), which gives the amount of material deposited in a time unit and which depends on the specific process and on the reactor construction, in turn, is important considering the throughput of the processes. Calling the amount of material deposited per reaction cycle also a rate (amount/cycle) is confusing, as illustrated also by the problems it has given in modeling substrate-inhibited ALD of Type 2.<sup>992,1178,1200</sup>

To avoid misconceptions, using the term growth rate (amount/cycle) to describe the amount of material deposited per cycle should be discouraged. In 1986, Goodman and Pessa<sup>8</sup> suggested “growth per cycle” as a better term, which has been adopted also in this work [written as growth per cycle (GPC)].

### 2. Monolayer

Monolayer is a convenient unit for discussing ALD growth: it can be considered as a theoretical maximum for

the GPC, and the GPC when given in monolayers is useful as a statistical quantity in modeling growth modes in ALD.<sup>246,247,1140</sup> However, defining the characteristics of a monolayer is not always easy.

The first difficulty is that distinction has often not been made in the ALD literature between a chemisorbed monolayer and a monolayer of the ALD-grown material. Intermixing the two types of monolayers is confusing.

Second, it is not easy to define a monolayer for polycrystalline and amorphous materials. For crystalline materials with a well-defined direction of growth, a suitable crystalline plane of the bulk material may be chosen to represent a monolayer of the ALD-grown material, but how to choose the reference monolayer when the direction of growth is not known? A rather widely used and easy approximation is to calculate in that case the monolayer properties from the density of the bulk material.<sup>199,237,292,333,984,1127,1128,1140,1177</sup> The representativeness of such monolayer can, of course, still be questioned.

Third, in ALD, one deposits a bulk material through reactions that occur on the surface. The deposition characteristics are therefore defined by the surface. Because of the discontinuity caused by the surface, the characteristics of the uppermost material layer are likely to differ from those of the bulk material. Therefore, even for single-crystal materials defining the monolayer through the bulk structure may not be fully meaningful.

The fourth complication is related to defining a monolayer in catalysis-related ALD work. It has been a custom in the field of catalysis to define the monolayer to correspond to the loading when multilayer formation begins, as determined by experimental techniques such as x-ray diffraction or Raman spectroscopy. Defining monolayer this way does not yet require the substrate to be fully covered by the ALD-grown film, however. Consequently, when defined this way, a monolayer contains typically a few metal atoms per square nanometer,<sup>246,523,527,819</sup> which is considerably less than typically obtained, for example, by the density method.

Defining a monolayer is not easy, but discussing ALD growth in terms of monolayers is illustrative. To avoid confusions when using this term, it is important always to state how the reference monolayer has been defined.

### 3. "Atomic layer" deposition

The name "atomic layer deposition" used also in this work to refer to the technique based on sequential self-terminating gas–solid reactions is unfortunately misleading. This name gives an impression of depositing full monolayers of material on top of each other. As such, this name directly leads to the four problematic historical assumptions on ALD related to full monolayer growth, as discussed in Sec. V A. The fact that many different names have been used to refer to the same technique (Table II) testifies to the difficulty of finding a concise but, at the same time, descriptive name for the technique.

## C. Effect of experimental conditions on the surface chemistry

The effect of the experimental conditions on self-terminating gas–solid reactions must be well understood to be able to compare the results of different investigations. To help comparing different investigations and making multidisciplinary studies of ALD, this section discusses the effect of temperature, pressure, type of substrate, saturation/unsaturation of the reactions, and time on ALD reactions. Some challenges in extracting the GPC on high-surface-area substrates are also pointed out.

### 1. Reaction temperature

Temperature is one of the three parameters, together with the reactant and the surface, that determine the amount and type of species adsorbed in irreversible, saturating chemisorption. Consequently, different experiments should be expected to compare directly only if they have been carried out at the same temperature. (For the effect of substrate heat treatments, see Sec. V C 3.) Temperature-dependent experiments, such as temperature-programmed desorption (TPD), can be useful for elucidating the possible chemisorption reactions. If the results are overinterpreted, however, these experiments can also lead to misleading conclusions. For example, the amount of methyl groups chemisorbed in the  $\text{AlMe}_3$  reaction has been suggested to decrease with increasing temperature<sup>40,199</sup> on the basis of TPD experiments made after the  $\text{AlMe}_3$  reaction at room temperature.<sup>196</sup> Experiments made for the  $\text{AlMe}_3$  reaction at different temperatures have indicated, however, that temperature has almost no effect on the number of methyl groups adsorbed (Fig. 20).

### 2. Partial pressure of the reactant

For truly saturating, irreversible reactions, partial pressures are not expected to affect the amount of material adsorbed at saturation (Sec. III A). There are ALD reactions,<sup>212,1165</sup> however, where the partial pressure has been suggested to affect the amount of adsorbed species. More systematic studies on the effect of partial pressures would be needed. Sometimes, gaseous reaction products released in the ligand-exchange reaction can readsorb onto the surface. For example, the HCl released in the reaction of metal chlorides with OH groups reabsorbs on the surface and, in this case, the partial pressure of HCl affects the main adsorption process.<sup>135,139,143,432,433,1201</sup> Such readsorption is undesired in ALD.

A "pressure gap" has been hypothesized to exist between ALD growth at typical pressures ( $\sim 0.1$ – $10$  kPa) and in UHV.<sup>3,211</sup> Experimental investigations on the effect of the reactant pressure on reactions occurring in ALD are infrequent and, as of today, no report has indicated that reactions which occur during typical ALD conditions would not occur in UHV. In contrast, for the  $\text{AlMe}_3/\text{H}_2\text{O}$  process, similar reactions have been concluded to occur in UHV and at higher pressures.<sup>192</sup>



### 3. Substrate

Differences in the surface characteristics of the substrates can cause differences in ALD experiments carried out for the same reactants and reaction temperature(s). The number and type of reactive surface sites may sometimes differ inherently on two substrates, even if the general chemical composition of the substrates are the same. Moreover, differences can be induced for example by thermal or chemical treatments. The reaction chemistry investigation for the  $\text{AlMe}_3$  reaction with high-surface-area substrates, discussed in Sec. IV D, provides an example of differences induced by thermal treatments: with increasing heat-treatment temperature, the OH surface concentration on the substrate decreased. The work of Nechiporenko *et al.*,<sup>141</sup> in turn, illustrates the differences induced by chemical treatments: depending on the surface treatment of Ti and Ni substrates, different amounts of chromium chemisorbed in the saturating reaction of chromyl chloride  $\text{CrO}_2\text{Cl}_2$ . The work of Ferguson *et al.*<sup>214,337</sup> who investigated the  $\text{SiCl}_4/\text{H}_2\text{O}$  process on boron nitride particles, illustrates inherent differences. The  $\text{SiO}_2$  film deposited only patchlike on the basal planes of the boron nitride particles, whereas the edges of the particles were conformally coated.<sup>214,337</sup> Evidently, the basal planes of boron nitride contained fewer sites reactive with the  $\text{SiCl}_4$  molecule than the edges of the particles. Some substrates may mostly consist of edgeareas, whereas other substrates expose primarily well-defined basal planes, which may lead to a different amount of material deposited. The crystalline face exposed may also affect the adsorption process and the structures formed.<sup>109,318,442,703,986,1202</sup>

The ALD process modifies the chemical composition of the surface through material deposition. In reaction mechanism investigations on high-surface-area materials, the number of ALD reaction cycles has been typically below ten.<sup>209,216,291,292,344,418,419,421,434,521,526,527,530,548,552,554,557,818,819,873,1165–1167,1203</sup> The high-surface-area substrates have not yet been fully covered by the ALD-grown film; the initial substrate has still been partly exposed, influencing the growth. On flat substrates, the number of ALD reaction cycles has typically been hundreds to thousands, and the initial substrate has been covered by the ALD-grown material.<sup>211,217,422,425,426,443,487,518,827,844,867,868,1082</sup>

When investigating the surface chemistry, one must take into account the type of surface exposed at the particular experimental conditions.

### 4. Saturation/unsaturation of the reactions

Saturation of the surface with adsorbed species by allowing each reaction to go to completion is a prerequisite for material growth by the ALD technique. To compare different experiments in a meaningful way, one must know whether or not the experiments were made at saturated or unsaturated conditions. If it is not known whether or not saturation had occurred, comparing different experiments is often of little value. For example, *in situ* investigations made for the  $\text{AlMe}_3/\text{H}_2\text{O}$  process provided important qualitative information of the reaction kinetics, but only after realizing that the investigations were made for unsaturated conditions (Sec.

IV G). In other types of investigations, GPC values both higher and lower than the generally accepted trend (Fig. 19) have been reported because of insufficient purge or evacuation<sup>198</sup> and unsaturated reactions,<sup>200,234</sup> respectively.

### 5. Time

The time needed for completing the self-terminating reactions can differ in orders of magnitude between different types of experiments. For fast reactions, where mass transport dictates the time required to saturate the surface with adsorbed species,<sup>1159,1204,1205</sup> the use of high-surface-area substrates lengthens the processing times compared to flat substrates.<sup>1206</sup> The use of UHV compared to higher pressures also lengthens the processing times.

If different reactions would occur in experiments with different reactant exposure times, as has been suggested,<sup>3,211,217</sup> this fact would be expected to be reflected in the value of the GPC, since the GPC is directly related to the reaction chemistry. Quantitative agreement exists between the GPC in the  $\text{AlMe}_3/\text{H}_2\text{O}$  process on high-surface-area substrates and flat substrates (Fig. 19), suggesting the occurrence of similar reactions. The time scale of the experiment seems not to affect the number or type of species adsorbed in irreversible, saturating gas–solid reactions. Nevertheless, slow, nonsaturating reactions, such as thermal decomposition of the ALD reactants or of the adsorbed species, do often manifest themselves at lower temperatures and longer processing times.<sup>197,216,468,475,922,942,944</sup> The insensitivity of the GPC to the process parameters (time, pressure) when the reactions are truly self-terminating is in unison with the excellent upscaling capability of the ALD processes<sup>3,201,1207</sup> and the fact that close to 100% step coverage can be obtained by ALD in deep-trench structures.<sup>205,1204</sup>

### 6. GPC on high-surface-area substrates

To calculate the GPC on high-surface-area materials, the amount of material adsorbed is typically measured by conventional chemical means, giving the mass of metal  $M$  per unit mass of sample,  $w_M$  ( $\text{g}_M \text{g}_{\text{sample}}^{-1}$ ). To compare the results with those of other ALD investigations, the results are converted to the amount of metal  $M$  atoms adsorbed per unit surface area of the substrate,  $c_M$  ( $\text{nm}^{-2}$ ). Typically, the specific surface area of the substrate,  $S$  ( $\text{m}^2 \text{g}_{\text{subst}}^{-1}$ ), is measured for this conversion. However, the relative mass of the original substrate in the samples decreases with increasing amount of material deposited. In addition to the specific surface area of the substrate, the ratio of the total mass of the sample (the substrate and the adsorbed material together)  $m_{\text{sample}}$  ( $\text{g}_{\text{sample}}$ ) to the mass of the substrate  $m_{\text{subst}}$  ( $\text{g}_{\text{subst}}$ ) is needed for calculating  $c_M$ .

$$c_M = \frac{w_M N_A}{M_M S} \frac{m_{\text{sample}}}{m_{\text{subst}}} \quad (25)$$

In this equation,  $N_A$  is Avogadro's number ( $\text{mol}^{-1}$ ) and  $M_M$  is the molar mass of metal  $M$  ( $\text{g}_M \text{mol}^{-1}$ ).

If term  $m_{\text{sample}}/m_{\text{subst}}$  is ignored and the  $c_M$  is calculated from a simplified equation,

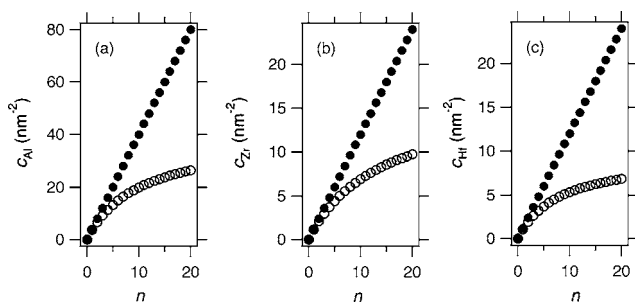


FIG. 28. Illustration of the importance of taking into account the mass of the deposited layer when calculating the GPC on high-surface-area substrates. Difference between Eqs. (25) [full symbols] and (26) [open symbols] for a substrate with a specific surface area of  $300 \text{ m}^2 \text{ g}^{-1}$ : (a)  $\text{Al}_2\text{O}_3$ , assuming a constant GPC  $\Delta c_{\text{Al}} = 4 \text{ nm}^2$ ; (b)  $\text{ZrO}_2$ , assuming  $\Delta c_{\text{Zr}} = 1.2 \text{ nm}^2$ ; and (c)  $\text{HfO}_2$ , assuming  $\Delta c_{\text{Hf}} = 1.2 \text{ nm}^2$ .  $n$  indicates the number of ALD reaction cycles.

$$c_M = \frac{w_M N_A}{M_M S}, \quad (26)$$

an error is created that increases with increasing mass of the deposited material. Although the need for this correction was noted already by Kol'tsov and co-workers,<sup>79,98</sup> in more recent work, the correction has not always been made. The error may be small for low cycle numbers and light materials, but it increases with increasing number of ALD reaction cycles and molar mass of the ALD-grown material, as illustrated in Fig. 28. The error also increases with increasing specific surface area of the substrate.

## VI. CONCLUSION

This work has given an overview of the basic characteristics of ALD, its history, existing ALD processes, and current status of understanding the surface chemistry of, in particular, the trimethylaluminum/water ALD process. I hope that this review serves its main purpose; that it helps the newcomer to get acquainted with the exciting and challenging field of surface chemistry of ALD, and that it is also a useful guide for the specialist. I also wish that it initiates discussion on the history, assumptions, and terminology of ALD now that we are about to enter the fifth decade of ALD research.

## ACKNOWLEDGMENTS

Past and present colleagues are acknowledged for numerous discussions related to ALD, which have contributed to my present-day understanding of ALD and have thereby assisted in writing this review. Thanks go especially to Dr. Suvi Haukka (ASM Microchemistry), Professor Outi Krause (Helsinki University of Technology, HUT), Dr. Marina Lindblad (Fortum), Dr. Marko Tuominen (ASM Microchemistry), and Dr. Annelies Delabie (IMEC). Dr. Jaana Kanervo (HUT) helped to formulate the description of adsorption kinetics for this work. Professor Anatoly Malygin and Mr. Vitality Dorofeev (St. Petersburg State Technological Institute) assisted me to get started exploring the Soviet–Russian branch of ALD, and the IMEC library provided invaluable help in finding many of the cited publications. Dr. Robin Ras

(K.U.Leuven, HUT) and Dr. Jörg Schuhmacher (IMEC) gave useful general comments regarding this manuscript and Dr. Jean-luc Doumont (JL Consulting) gave valuable advice on scientific writing. I gratefully acknowledge a postdoctoral fellowship by IMEC/K.U.Leuven and support from the Academy of Finland (decision 105364) and the National Technology Agency of Finland (Tekes) through the “Nanoramems” project.

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- <sup>68</sup>No universally accepted definition of ALD is currently available. The definition used in this work is built on the recognized practice of ALD and covers most of ALD processes with compounds as well as elements as reactants. Also other distinctively different definitions have been suggested, for example, that the GPC should be a monolayer or the GPC should be constant over the cycles. Most ALD processes do not fulfill these criteria, however.
- <sup>69</sup>In addition to “self-terminating” used to refer to ALD reactions in this work, ALD reactions have been referred to being saturating, self-limiting, self-extinguishing, etc.
- <sup>70</sup>In this review, ALD is defined to be based on gas–solid reactions. Analogous experiments have been made from liquid phase [e.g., S. Lindroos, T. Kanninen, and M. Leskelä, *Appl. Surf. Sci.* **75**, 70 (1994)] and electrochemically [e.g., J. L. Stickney, *Electroanal. Chem.* **21**, 75 (1999)] as well. Although in some publications such experiments may be classified as ALD, in this work they are excluded from the definition.
- <sup>71</sup>Instead of the reactant of Reactant B, Step 3 may be, for example, a thermal treatment (see Table III).
- <sup>72</sup>The term “half reaction” in ALD should not be confused with the conceptual half reactions in electrochemistry. In ALD, the half reactions are real reactions.
- <sup>73</sup>Some ALD processes consist of repeating the self-terminating reactions of more than two reactants, for example, the  $\text{WF}_6/\text{BET}_3/\text{NH}_3$  (Et = ethyl) process to grow  $\text{WC}_x\text{N}_y$  [e.g., A. Martin Hoyas, J. Schuhmacher, D. Shamiryan, J. Waeterloos, W. Besling, J. P. Celis, and K. Maex, *J. Appl. Phys.* **95**, 381 (2004)]. Each new reactant adds a reaction step and a purge/evacuation step to the reaction cycle.
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- <sup>1146</sup> For amorphous and polycrystalline materials, defining a monolayer may be more difficult, as discussed in Sec. V B 2.
- <sup>1147</sup> Sometimes the reactions used in ALD investigations do not fulfill the criterion of self-termination. Typical deviations of self-terminating adsorption are caused by (i) continuous adsorption, often caused by too low processing temperatures and unoptimized purge times, (ii) desorption of the adsorbed reactants during purge or evacuation, often caused by too high processing temperatures, (iii) nonsaturating irreversible chemisorption, caused by thermal decomposition of the gas-phase reactant or the adsorbed surface species, and (iv) unsaturation, caused by insufficient time or reactant dose for the reactions to go to completion.
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- <sup>1172</sup> In relation with Model III, it is probably, in practice, not possible to reach a ligand content equivalent to a physisorbed monolayer of the ligands, because the ligands are bounded to surface atoms and thus are not free to move in the same way as truly physisorbed molecules.
- <sup>1173</sup> Desorption of the adsorbed species during purging periods has also been suggested to account for the GPC of less than a monolayer (Refs. 1116, 1120, 1122, and 1153). This suggestion, however, contradicts the essential requirement of irreversibility for the self-terminating ALD reactions (Sec. III A).
- <sup>1174</sup> Increase in temperature may also turn an irreversible reaction into a reversible reaction. Such effect is not discussed in this work, because through it, the self-terminating characteristics of the reaction are lost.
- <sup>1175</sup> In this work, the term *ALD window* is used for referring to the temperature range where an ALD process fulfills the criterion of self-terminating reactions. The same term has been used for referring to other things also, most particularly, to a temperature range where the GPC is constant (e.g., Refs. 11 and 30).
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