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

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(Dated: 18th March 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. As no recent general review exists on the surface chemistry of ALD, 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 is 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 investigations 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, non-standard terminology, and the effect of experimental conditions on the surface chemistry of ALD. I hope that this review can help the newcomer to get acquainted with the exciting and challenging field of surface chemistry of ALD and that it can serve as a useful guide for the specialist towards the fifth decade of ALD research.

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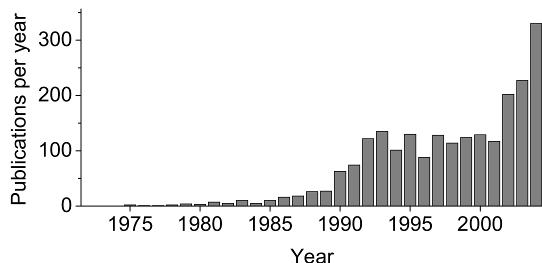


Figure 1: Number of ALD publications per year between 1972 and 2004. Search made with ISI Web of Science.[5]

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.[1,2] ALD has the capability to coat extremely complex shapes with a conformal material layer of high quality, a capability unique amongst thin film deposition techniques.[1–3] Consequently, ALD-grown materials have a wide range of applications, from catalysts to electroluminescent displays to microelectronics and beyond.[1–3]

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.[1,2] Interest in ALD has increased in steps in the beginning of the 1990s and 2000s, as indicated by the evolution of the yearly number of scientific publications on ALD, shown in Figure 1. A major driving force for the recent interest is the prospectives seen for ALD in scaling down microelectronic devices.[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 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.[3,6–66]

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 ($AlMe_3/H_2O$) 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 have experience 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.[40] For other aspects of ALD than its surface chemistry, the reader is referred to the recent review by Ritala and Leskelä.[3] Furthermore, for different views on the development of ALD over the years, I would recommend the reviews by Aleskovskii,[6] Goodman and Pessa,[8] Suntola,[11] George et al.,[40] Malygin et al.,[42] Niinistö et al.,[39] Haukka et al.,[50] Leskelä and Ritala,[51] and Ritala and Leskelä.[3]

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 Section 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 Section IV, the experimental results for the $AlMe_3/H_2O$ 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), interpreting the results of different kinds of investigations together may not always be straightforward, however.[67] 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 Section V.

II. GENERAL BACKGROUND

This section describes the basics of ALD processing, discusses the history of ALD, and overviews 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.[68–70] The growth of material layers by ALD consists of repeating the following characteristic four steps:

Step #1: a self-terminating reaction of the first reactant (Reactant A),

Step #2: a purge or evacuation—to remove the non-reacted reactants and the gaseous reaction by-products,

Step #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,[71]

Step #4: a purge or evacuation.

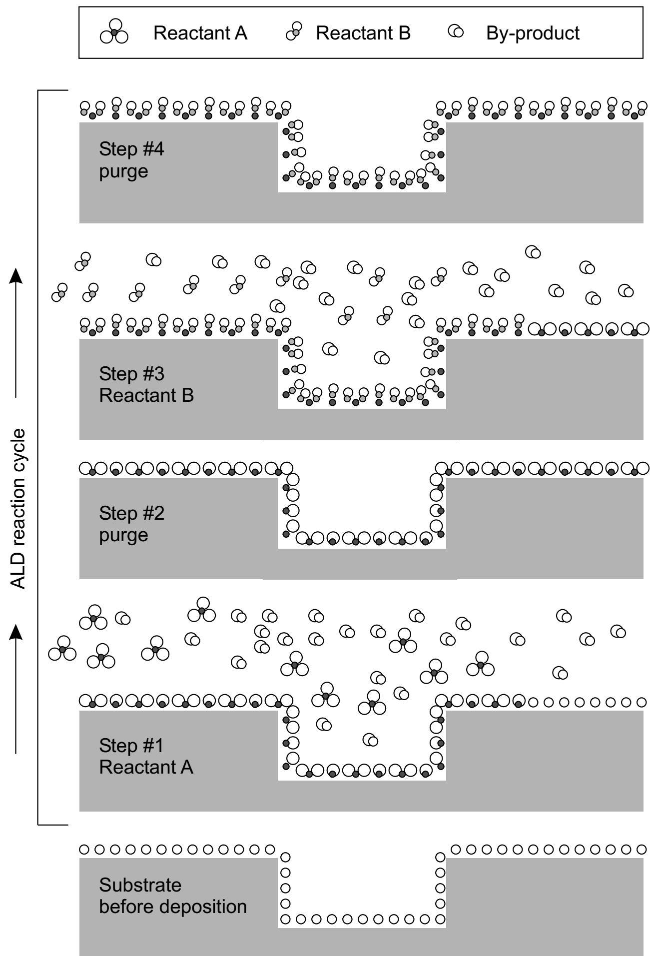


Figure 2: Schematic illustration of one ALD reaction cycle.

Steps #1 to #4 constitute a *reaction cycle*. Steps #1 and #3 are sometimes referred to as *half-reactions* of an ALD reaction cycle.[40,72]

One ALD reaction cycle is illustrated schematically in Figure 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.[73] 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 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 Dr. Suntola and co-workers. The beginning of ALD is then traced back to a patent published in the 1970s,[2] for which the first experiments were made in 1974.[74,75] In this patent,[2] ALD growth is demonstrated for processes based on element reactants: the Zn/S process to grow ZnS, the Sn/O_2 process to grow SnO_2, and the Ga/P process to grow GaP.[2] In later patents,[76,77] Suntola and co-workers demonstrated ALD also for processes based on compound reactants: the $TaCl_5$/H_2O process to grow Ta_2O_5, the Zn(Mn)Cl_2/H_2S process to grow Zn(Mn)S, and the $AlCl_3$/H_2O process to grow Al_2O_3. 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.[74]

The less commonly acknowledged origin of ALD dates back to work made in the Soviet Union in the 1960s, in the group of Prof. Aleskovskii. In the proceedings of a conference organized in 1965 and published in 1967, Shevyakov et al.[1] describe the $TiCl_4$/H_2O process to grow TiO_2 and the $GeCl_4$/H_2O process to grow GeO_2. 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.[78] 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,[3,7–65] only the ones authored by Russians[6,20,42,43,48,56] 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,[20,86] however, and scientists of the two groups have even met.[74] 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,[87] 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.[56]

Table I: Some Soviet–Russian ALD investigations

Z^a Material	Reactant A	Reactant B	Substrate ^{b}	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	88,89
13 aluminum				
Al_2O_3	$AlCl_3$	H_2O	SiO_2 gel	83,90,91
	$AlCl_3$	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

Table I: (*Continued*)

Z [a]	Material	Reactant A	Reactant B	Substrate [b]	Refs.
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	82,100–102
		PCl_3	— [c]	polymer	103
		$POCl_3$	— [c]	SiO_2 gel	104,105
		$POCl_3$	H_2O	SiC	96
	$P_xB_yO_z$	$POCl_3$	$B(OMe)_3$	SiO_2 gel	88,89
22 titanium					
	TiO_2	$TiCl_4$	H_2O	SiO_2 gel	1,79,80,100, 101,106–113
		$TiCl_4$	H_2O	Si	81,114,115
		$TiCl_4$	H_2O	Ge	116,117
		$TiCl_4$	H_2O	SiC	96,116
		$TiCl_4$	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
		$Ti(OBu)_4$	H_2O	glass	134
	$Ti_xSi_yO_z$	$TiCl_4$	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
		$VOCl_3$	— [c]	polymer	103
24 chromium					
	CrO_x	CrO_2Cl_2	— [c]	SiO_2 gel	105,138–140
		CrO_2Cl_2	— [c]	Si	84
		CrO_2Cl_2	— [c]	Ge	84,117
		CrO_2Cl_2	— [c]	Ni	141
		CrO_2Cl_2	— [c]	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	— [c]	polymer	103
		CrO_2Cl_2	H_2	SiO_2 gel	142
	$Cr_xAl_yO_z$	CrO_2Cl_2	$AlMe_3$	Si	93
26 iron					
	FeO_x	$FeCl_3$	— [c]	SiO_2 gel	143
30 zinc					
	ZnO	$ZnCl_2$	H_2O	SiO_2 gel	144
	ZnS	$ZnCl_2$	H_2S	SiO_2 gel	86
		$ZnEt_2$	H_2S	SiO_2	145
32 germanium					
	GeO_2	$GeCl_4$	H_2O	SiO_2 gel	1,146
38 cadmium					
	CdS	Cd	S	GaAs	147
		$CdMe_2$	H_2S	SiO_2	145
	CdSe	Cd	Se	GaAs	147,148
		$CdMe_2$	H_2Se	SiO_2	145
		$CdMe_2$	H_2Se	glass, GaAs	149
	CdTe	Cd	Te	GaAs	147
		Cd	Te	Si	148
50 tin					
	SnO_2	$SnCl_4$	H_2O	SiO_2 gel	111,150
		$SnMe_4$	N_2O_4	Si	151
		$SnEt_4$	N_2O_4	Si	151
73 tantalum					
	Ta_2O_5	$TaCl_5$	H_2O	Si, Al	91

[a] Z = atomic number.
[b] ”Glass” substrate refers to various mixed oxides, ”polymer” to various organic polymer substrates.
[c] Only one half-reaction of an ALD reaction cycle was carried out.

Table II: Different names of ALD

Name	Abbreviation	Ref., e.g.
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

Partly because of its history, the ALD technique is referred to with many names. The Soviet–Russian researchers call the technique ”молекулярное наслаивание (МН),”[152] which has been translated into English in many ways, ”molecular layering (ML)” being perhaps the most common.[3] 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).”[153] The name ”atomic layer deposition (ALD),” used in this work, dates back to the early 1990s.[19] 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 for which elements 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, Figure 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 (Figure 3), for alkali metals (group 1) and actinoids there are no reports yet. Future will show if there will be interest and success in their deposition.

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

Z	Material	Reactant A [a]	Reactant B	Refs.
5 boron				
	B_2O_3	BBr_3	H_2O	85
	BN	BCl_3	NH_3	158
		BBr_3	NH_3	159
	$B_xP_yO_z$	$B(OMe)_3$	$POCl_3$	88,89
6 carbon				
	C [b]	CF_x	H [c]	160
		CCl_3	H [c]	161
12 magnesium				
	MgO	$MgCp_2$	H_2O	162–166
		$Mg(thd)_2$	H_2O_2	167
		$Mg(thd)_2$	O_3	168
	MgTe	Mg	Te	169,170
13 aluminum				
	Al_2O_3	$AlCl_3$	H_2O	76,77,83,90, 91,91,171–184
		$AlCl_3$	O_2	185,186
		$AlCl_3$	ROH [d]	173,181,187
		$AlCl_3$	$Al(OEt)_3$	188
		$AlCl_3$	$Al(O^iPr)_3$	188,189
		$AlBr_3$	H_2O	92
		$AlMe_3$	H_2O	166,179,190–262
		$AlMe_3$	H_2O_2	263–269

Table III: (*Continued*)

Z	Material	Reactant A [a]	Reactant B	Refs.
		$AlMe_3$	O_3	236,244,245, 270–273
		$AlMe_3$	O_2 [e]	274–276
		$AlMe_3$	N_2O	266
		$AlMe_3$	NO_2	194
		$AlMe_3$	N_2O_4	151
		$AlMe_3$	^iPrOH	277
		$AlMe_3$	$Al(O^iPr)_3$	188
		$AlMe_2Cl$	H_2O	278
		$AlMe_2O^iPr$	H_2O	279,280
		$AlEt_3$	H_2O	163
		$Al(OEt)_3$	H_2O	173
		$Al(OEt)_3$	O_2	173
		$Al(O^nPr)_3$	H_2O	173,181
		$Al(O^nPr)_3$	O_2	173
		$Al(mmp)_3$	H_2O	281
	AlN	$AlCl_3$	NH_3	282,283
		$AlCl_3$	$NH_3 + H_2$ [e]	284,285
		$AlMe_3$	NH_3	209,216,283, 286–292
		$AlEt_3$	NH_3	293,294
		$Me_3N{:}AlH_3$	NH_3	295
		$Me_2EtN{:}AlH_3$	NH_3	296–298
	AlP	$AlMe_2H$	PH_3	299–301
		$Me_2EtN{:}AlH_3$	PH_3	302
	AlAs	$AlCl_3$	AsH_3	303,304
		$AlMe_3$	AsH_3	305–315
		$AlMe_2H$	AsH_3	316–320
		$AlEt_3$	AsH_3	309,311
		Al^iBu_3	AsH_3	321
		$Me_3N{:}AlH_3$	AsH_3	322
		$Me_3N{:}AlH_3$	$As(NMe_2)_3$	323,324
		$Me_2EtN{:}AlH_3$	AsH_3	320,325–330
	Al	$AlMe_3$	H_2 [e]	331,332
	$Al_xSi_yO_z$	$AlCl_3$	$Si(OEt)_4$	94
	Al_2O_3/ SiO_2 [f]	$AlMe_3$	$(^tBuO)_3SiOH$	157
	$Al_xTi_yO_z$	$AlCl_3$	$Ti(OEt)_4$	188
		$AlCl_3$	$Ti(O^iPr)_4$	188
		$AlMe_3$	$Ti(O^iPr)_4$	188
	$Al_xCr_yO_z$	$AlMe_3$	CrO_2Cl_2	93
	$Al_xZr_yO_z$	$Al(OEt)_3$	$ZrCl_4$	188
	$Al_xHf_yO_z$	$Al(OEt)_3$	$HfCl_4$	188
14 silicon				
	SiO_2	$SiCl_4$	H_2O	78,90,95,96, 195,214,333–337
		$SiCl_4$	H_2O + cat. [g]	335,338–341
		$SiCl_3H$	H_2O	97–99
		$SiCl_2H_2$	O_3	342
		$Si(OEt)_4$	H_2O + cat.	343
		HMDS [h]	O_2	344
		$Si(NCO)_4$	H_2O	345
		$Si(NCO)_4$	NEt_3	346
		$MeOSi(NCO)_3$	H_2O_2	347,348
	Si_3N_4	$SiCl_4$	NH_3	349–352
		$SiCl_2H_2$	NH3	352
		$SiCl_2H_2$	NH_3 [e]	353
		$SiCl_2H_2$	NH_3 + cat.	354,355
		Si_2Cl_6	N_2H_4	356

Figure 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/, dated 1 November 2004).

Table III: (*Continued*)

Z	Material	Reactant A [a]	Reactant B	Refs.
	SiC	$SiCl_2H_2$	C_2H_4	357,358
		$SiEt_2H_2$	— [i]	359
		Si_2H_6	C_2H_4	360
		Si_2H_6	C_2H_2	361–364
	Si	$SiCl_4$	Si_2H_6	365
		$SiCl_2H_2$	H_2	366,367
		$SiCl_2H_2$	H [c]	368–375
		$SiCl_2H_2$	— [j]	376–378
		$SiEt_2H_2$	— [k]	379
		SiH_4	— [k]	380–382
		Si_2Cl_6	Si_2H_6	371,372,383, 384
		Si_2Cl_6	H [c]	385
		Si_2H_6	— [k]	386–394
		Si_2H_6	— [j]	395–399
		Si_2H_6	— [k]	394,400
		Si_2H_6	— [l]	401
		Si_3H_8	— [k]	370,402
	$Si_xAl_yO_z$	$Si(OEt)_4$	$AlCl_3$	94
	SiO_2/ Al_2O_3 [f]	$(^tBuO)_3SiOH$	$AlMe_3$	157
	$Si_xTi_yO_z$	$Si(OEt)_4$	$TiCl_4$	88
	$Si_xZr_yO_z$	$SiCl_4$	$Zr(O^tBu)_4$	403
		$Si(OEt)_4$	$ZrCl_4$	188
		$Si(O^nBu)_4$	$ZrCl_4$	188,404
		$Si(O^nBu)_4$	$Zr(NEt_2)_4$	405
	$Si_xHf_yO_z$	$Si(OEt)_4$	$HfCl_4$	406
		$Si(OEt)_4$	HfI_4	406

Table III: (*Continued*)

Z	Material	Reactant A [a]	Reactant B	Refs.
		$(^tBuO)_3SiOH$	$Hf(NMe_2)_4$	407
15 phosphorus				
	PO_x	PCl_3	H_2O	82,100–103
		$POCl_3$	H_2O	96,104,105
	$P_xB_yO_z$	$POCl_3$	$B(OMe)_3$	88,89
20 calcium				
	CaO ($CaCO_3$)	$Ca(thd)_2$	H_2O	408
		$Ca(thd)_2$	O_3	409
	CaS	$Ca(thd)_2$	H_2S	408,410–414
	CaF_2	$Ca(thd)_2$	HF	415
21 scandium				
	Sc_2O_3	$ScCp_3$	H_2O	416
		$Sc(thd)_3$	O_3	416
		$Sc(thd)_3$	$O_3 + H_2O_2$	416
22 titanium				
	TiO_2	$TiCl_4$	H_2O	1,79–81,96, 100,101,106–133,207,212, 237,260,336, 417–453
		$TiCl_4$	H_2O_2	267,269,454
		TiI_4	H_2O	455
		TiI_4	H_2O_2	456–458
		TiI_4	O_2	459,460
		$Ti(OMe)_4$	H_2O	461

Table III: (*Continued*)

Z	Material	Reactant A [a]	Reactant B	Refs.
		$Ti(OEt)_4$	H_2O	206,212,462–466
		$Ti(O^iPr)_4$	H_2O	212,467–474
		$Ti(O^iPr)_4$	O_2	434,475
		$Ti(O^iPr)_4$	O_2 [e]	476
		$Ti(O^iPr)_4$	O_3	477
		$Ti(O^iPr)_2(dmae)_2$	H_2O	478
		$Ti(OBu)_4$	H_2O	134
		$Ti(NMe_2)_4$	O_2 [e]	479
	TiN	$TiCl_4$	NH_3	480–494
		$TiCl_4$	NH_3 + cat.	205,481–483
		$TiCl_4$	N_2,H_2 [e]	274
		$TiCl_4$	Me_2NNH_2	495
		$TiCl_4$	$^tBuNH_2$	496
		$TiCl_4$	$AyNH_2$	496
		TiI_4	NH_3	483,497
		TiI_4	$^tBuNH_2$	496
		TiI_4	$AyNH_2$	496
		$Ti(NMe_2)_4$	NH_3	498–507
		$Ti(NMe_2)_4$	NH_3 [e]	508,509
		$Ti(NMe_2)_4$	N_2 [e]	509–512
		$Ti(NMe_2)_4$	H_2 [e]	509,511,512
		$Ti(NEt_2)_4$	NH_3	506
		$Ti(NEtMe)_4$	NH_3	513,514
	Ti	$TiCl_4$	H_2 [e]	515,516
	$Ti_xAl_yO_z$	$Ti(OEt)_4$	$AlCl_3$	188
		$Ti(O^iPr)_4$	$AlCl_3$	188
		$Ti(O^iPr)_4$	$AlMe_3$	188
	$Ti_xSi_yO_z$	$TiCl_4$	$Si(OEt)_4$	88
	$Ti_xZr_yO_z$	$Ti(O^iPr)_4$	$ZrCl_4$	188,517,518
	$Ti_xHf_yO_z$	$Ti(O^iPr)_4$	$HfCl_4$	188
23 vanadium				
	VO_x	$VOCl_3$	H_2O	96,103,117,121,135–137
		$VO(O^iPr)_3$	H_2O	519,520
		$VO(O^iPr)_3$	O_2	521–523
		$VO(acac)_2$	O_2	524,525
24 chromium				
	CrO_x	CrO_2Cl_2	H_2O	84,96,103,105,117,121,138–142
		CrO_2Cl_2	MeOH	93
		$Cr(acac)_3$	O_2	434,526–530
	$Cr_xAl_yO_z$	CrO_2Cl_2	$AlMe_3$	93
25 manganese				
	MnO_x	$Mn(thd)_3$	O_3	531–533
	MnS	$MnCl_2$	H_2S	76,77
	MnTe	Mn	Te	170,534–543
26 iron				
	FeO_x	$Fe(acac)_3$	O_2	544
		$Fe(thd)_3$	O_3	545
		$Fe(^tBuAMD)_2$	H_2O	546
	Fe	$Fe(^tBuAMD)_2$	H_2	546
27 cobalt				
	CoO_x	$Co(acac)_2$	O_2	547,548
		$Co(acac)_3$	O_2	547–554
		$Co(thd)_2$	O_3	555

Table III: (*Continued*)

Z	Material	Reactant A [a]	Reactant B	Refs.
		$Co(^iPrAMD)_2$	H_2O	546
	Co	$Co(^iPrAMD)_2$	H_2	546
28 nickel				
	NiO	$NiCp_2$	H_2O	556
		$Ni(acac)_2$	O_2	557–559
		$Ni(acac)_2$	O_3	560,561
		$Ni(thd)_2$	O_3	562
		$Ni(apo)_2$	O_3	560
		$Ni(dmg)_2$	O_3	560
	Ni	$Ni(acac)_2$	H_2	561
		$Ni(^iPrAMD)_2$	H_2	546
29 copper				
	CuO	$Cu(acac)_2$	O_2	563
		$Cu(thd)_2$	O_2	46,50,564
		$Cu(hfac)_2$	H_2O	565
	Cu_xS	$Cu(thd)_2$	H_2S	566–569
	Cu	CuCl	H_2	570,571
		CuCl	$H_2 + H_2O$	571,572
		CuCl	Zn	573
		$Cu(acac)_2$	H_2	561
		$Cu(acac)_2$	H_2 [e]	574
		$Cu(thd)_2$	H_2	575,576
		$Cu(hfac)_2$	ROH [d]	577
		$Cu(hfac)_2$	HCHO [m]	577
		$Cu(^iPrAMD)$	H_2	546
30 zinc				
	ZnO	Zn	O_2	578
		Zn	H_2O	579
		$ZnCl_2$	H_2O	144
		$ZnCl_2$	O_2	580–582
		$ZnMe_2$	H_2O	583,584
		$ZnEt_2$	H_2O	201,229,231,584–607
		$ZnEt_2$	H_2O [n]	598
		$ZnEt_2$	O_2	605
		$Zn(OAc)_2$	H_2O	608–610
	ZnS	Zn	S	2,171,611,612
		Zn	H_2S	613
		$ZnCl_2$	H_2S	76,77,86,177,614–626
		$ZnMe_2$	H_2S	583,627–635
		$ZnEt_2$	H_2S	145,596,636,637
		$ZnEt_2$	Et_2S_2	638
		$Zn(OAc)_2$	H_2S	415,608,615,616,618–620,639
	ZnSe	Zn	Se	578,611,640–655
		Zn	H_2Se	656
		Zn	Et_2Se	657
		$ZnCl_2$	H_2Se	658–660
		$ZnMe_2$	H_2Se	633–635,661–671
		$ZnEt_2$	H_2Se	672
		$ZnEt_2$	Et_2Se_2	638
		$Zn[N(SiMe_3)_2]_2$	H_2Se	672

Table III: (*Continued*)

Z	Material	Reactant A [a]	Reactant B	Refs.
	ZnTe	Zn	Te	154,536, 640,643–645,647,673–679
		$ZnMe_2$	Et_2Te	680
		$ZnMe_2$	MeAyTe	680
	ZnF	$Zn(OAc)_2$	HF	415
31 gallium				
	Ga_2O_3	$Ga(acac)_3$	O_3	681,682
		$Ga(acac)_3$	H_2O	681
	GaN	Ga	N_2	683,684
		GaCl	NH_3	685,686
		$GaCl_3$	NH_3	687
		$GaMe_3$	NH_3	290,688–692
		$GaEt_3$	NH_3	294,693,694
		$GaEt_3$	NH_3 [o]	695
	GaP	Ga	P	2
		GaCl	PH_3	696
		$GaMe_3$	PH_3	299,313,697–701
		$GaEt_3$	PH_3 [n]	702
	GaAs	GaCl	AsH_3	696,703–716
		$GaCl_3$	AsH_3	303,304,717–721
		$GaCl_3$	As	720
		GaBr	AsH_3	722
		GaI	AsH_3	722
		$GaMe_3$	AsH_3	153,305–308,311,313, 315,318,321, 698,701,723–771
		$GaMe_3$	$EtAsH_2$	772
		$GaMe_3$	$^tBuAsH_2$	773–780
		$GaEt_3$	AsH_3	26,309,311, 698,729,738, 743,781–788
		$GaEt_3$	$^tBuAsH_2$	779,789
		$GaEt_3$	$(Me_2N)_3As$	324,790,791
		$GaEt_2Cl$	As	792
		$GaEt_2Cl$	AsH_3	755,793
		$GaEt_2Me$	AsH_3	698
		Ga^iBu_3	AsH_3	26
		$GaNp_3$	$^tBuAsH_2$	779,794
32 germanium				
	GeO_2	$GeCl_4$	H_2O	1,146
	Ge	$GeCl_4$	H [c]	795,796
		$GeMe_2H_2$	H [c]	797–799
		$GeEt_2H_2$	— [k]	800,801
		GeH_4	— [k]	382,802
		Ge_2H_6	— [k]	803,804
38 strontium				
	SrO ($SrCO_3$)	$Sr(Cp^iPr_3)_2$	H_2O	805,806
		$Sr(thd)_2$	O_3	807
		$Sr(methd)_2$	O_2 [e]	476
	SrS	$Sr(CpMe_5)_2$	H_2S	808
		$Sr(Cp^iPr_3)_2$	H_2S	808,809

Table III: (*Continued*)

Z	Material	Reactant A [a]	Reactant B	Refs.
		$Sr(thd)_2$	H_2S	410,412,810–812
	SrF_2	$Sr(thd)_2$	HF	415
39 yttrium				
	Y_2O_3	YCp_3	H_2O	813
		$Y(CpMe)_3$	H_2O	813
		$Y(thd)_3$	O_2	814
		$Y(thd)_3$	O_3	219,237,814, 815
	Y_2O_2S	$Y(thd)_3$	H_2S	816
40 zirconium				
	ZrO_2	$ZrCl_4$	H_2O	212,219,222, 230,246,434, 817–834
		$ZrCl_4$	H_2O_2	825,826
		$ZrCl_4$	O_2	835,836
		ZrI_4	H_2O	837
		ZrI_4	H_2O_2	838–841
		$ZrCp_2Cl_2$	O_3	842,843
		$ZrCp_2Me_2$	H_2O	844
		$ZrCp_2Me_2$	O_3	842,845
		$Zr(O^iPr)_2(dmae)_2$	H_2O	846
		$Zr(O^tBu)_4$	H_2O	471,473,474, 847–851
		$Zr(O^tBu)_4$	O_2	851
		$Zr(O^tBu)_4$	O_2 [e]	852–855
		$Zr(O^tBu)_4$	N_2O	851
		$Zr(O^tBu)_4$	Ar [e]	855
		$Zr(O^tBu)_2(dmae)_2$	H_2O	846,856
		$Zr(dmae)_4$	H_2O	846
		$Zr(thd)_4$	O_3 [e]	842
		$Zr(NMe_2)_4$	H_2O	857,858
		$Zr(NEt_2)_4$	H_2O	857
		$Zr(NEt_2)_4$	O_2 [e]	853
		$Zr(NEtMe)_4$	H_2O	857
		$Zr[N(SiMe_3)_2]_2Cl_2$	H_2O	859
	Zr_3N_4	$Zr(NMe_2)_4$	NH_3	860
		$Zr(NEtMe)_4$	NH_3	860
		$Zr(NEt_2)_4$	NH_3	860
	$Zr_xAl_yO_z$	$ZrCl_4$	$Al(OEt)_3$	188
	$Zr_xSi_yO_z$	$ZrCl_4$	$Si(OEt)_4$	188,861
		$ZrCl_4$	$Si(O^nBu)_4$	188,404
		$Zr(O^tBu)_4$	$SiCl_4$	403
		$Zr(NEt_2)_4$	$Si(O^nBu)_4$	405
	$Zr_xTi_yO_z$	$ZrCl_4$	$Ti(O^iPr)_4$	188,517,518
41 niobium				
	Nb_2O_5	$Nb(OEt)_5$	H_2O	184,206,465, 820,862,863
	NbN	$NbCl_5$	NH_3	480,482,864
		$NbCl_5$	NH_3 + cat.	482,864
		$NbCl_5$	Me_2NNH_2	495
42 molybdenum				
	Mo_xN	$MoCl_5$	NH_3	480
		$MoCl_5$	Me_2NNH_2	495
	Mo	$MoCl_5$	Zn	865
44 ruthenium				
	RuO	$Ru(CpEt)_2$	O_2	866

Table III: (*Continued*)

Z	Material	Reactant A [a]	Reactant B	Refs.
	Ru	$RuCp_2$	O_2	867–869
		$Ru(CpEt)_2$	O_2	866
		$Ru(CpEt)_2$	NH_3 [e]	870,871
		$Ru(od)_3$	O_2	872
		$Ru(thd)_3$	H_2	873
		$Ru(thd)_3$	O_2	869,874
46 palladium				
	Pd	$Pd(thd)_2$	H_2	873
		$Pd(thd)_2$	O_2	564
		$Pd(hfac)_2$	H_2	875
		$Pd(hfac)_2$	HCOCOOH	875
48 cadmium				
	CdS	Cd	S	147,876
		$CdCl_2$	H_2S	623
		$CdMe_2$	H_2S	145,877–881
	CdSe	Cd	Se	147–149,611,882–886
		$CdMe_2$	H_2Se	145,662
	CdTe	Cd	Te	147,148, 170,534–539,541–543,655,675, 679,886–911
		$CdMe_2$	Et_2Te	680
		$CdMe_2$	MeAyTe	680,912–914
		$CdMe_2$	$^iPr_2Te$	915,916
49 indium				
	In_2O_3	$InCl_3$	H_2O	212,917–921
		$InCl_3$	H_2O_2	921
		$InMe_3$	H_2O	922
	In_2S_3	$InCl_3$	H_2S	923
		$In(acac)_3$	H_2S	596,597,924–927
	InN	In	N_2	928
		$InEtMe_2$	NH_3	290,689,690
	InP	InCl	PH_3	696
		InCl	$^tBuPH_2$	712
		$InMe_3$	PH_3	741,754,929–937
		$InMe_3$	$^tBuPH_2$	938–940
		$InEt_3$	PH_3	697,699
		$InEt_3$	$^tBuPH_2$	941
	InAs	InCl	AsH_3	704,705,717
		$InMe_3$	AsH_3	733,942,943
		$InMe_3$	$^tBuAsH_2$	780,931,933, 944,945
		$InClMe_2$	AsH_3	946
		$InEt_3$	AsH_3	726,947,948
	InSb	In	Sb	949,950
50 tin				
	SnO_2	Sn	O_2	2
		$SnCl_4$	H_2O	111,150,212, 445,682,951–960
		$SnCl_4$	H_2O_2	959,961,962
		SnI_4	H_2O_2	959
		SnI_4	O_2	959,961–964

Table III: (*Continued*)

Z	Material	Reactant A [a]	Reactant B	Refs.
		$SnMe_4$	N_2O_4	151
		$SnEt_4$	N_2O_4	151
51 antimony				
	Sb_2O_5	$SbCl_5$	H_2O	952
56 barium				
	BaS	$Ba(CpMe_5)_2$	H_2S	808,809
		$Ba(thd)_2$	H_2S	410,965
57 lanthanum				
	La_2O_3	$La(thd)_3$	O_2	46,50
		$La(thd)_3$	O_3	555,562,966, 967
		$La[N(SiMe_3)_2]_3$	H_2O	407,968,969
		$La(^iPrAMD)_3$	H_2O	546
	La_2S_3	$La(thd)_3$	H_2S	970
	$La_xSi_yO_x$	$La[N(SiMe_3)_2]_3$	$(^tBuO)_3Si$	407
58 cerium				
	CeO_2	$Ce(thd)_4$	O_2	46,50
		$Ce(thd)_4$	O_3	971
		$Ce(thd)_3phen$	O_3	971
59 praseodymium				
	PrO_x	$Pr[N(SiMe_3)_2]_3$	H_2O	972
60 neodymium				
	Nd_2O_3	$Nd(thd)_3$	O_3	973
62 samarium				
	Sm_2O_3	$Sm(thd)_3$	O_3	973
63 europium				
	Eu_2O_3	$Eu(thd)_3$	O_3	973
64 gadolinium				
	Gd_2O_3	$Gd(thd)_3$	O_3	973
66 dysprosium				
	Dy_2O_3	$Dy(thd)_3$	O_3	973
67 holmium				
	Ho_2O_3	$Ho(thd)_3$	O_3	973
68 erbium				
	Er_2O_3	$Er(thd)_3$	O_3	973,974
69 thulium				
	Tm_2O_3	$Tm(thd)_3$	O_3	973
71 lutetium				
	Lu_2O_3	$Lu[Cp(SiMe_3)]_2Cl$	H_2O	975
72 hafnium				
	HfO_2	$HfCl_4$	H_2O	219,238,244, 252,253,255–257,259,439, 822,832,837, 969,976–1008
		$HfCl_4$	O_2	1009,1010
		$HfCl_4$	O_3	990
		$HfCl_2[N(SiMe_3)_2]_2$	H_2O	1011
		HfI_4	H_2O	837,989,994, 1012

Table III: (*Continued*)

Z	Material	Reactant A [a]	Reactant B	Refs.
		HfI_4	H_2O_2	1012
		HfI_4	O_2	994,1013–1016
		$Hf(O^tBu)_4$	O_3	1017,1018
		$Hf(O^tBu)_4$	O_2 [e]	854
		$Hf(O^tBu)_2(mmp)_2$	H_2O	1019
		$Hf(mmp)_4$	H_2O	1020
		$Hf(ONEt_2)_4$	H_2O	1021
		$Hf(NMe_2)_4$	H_2O	407,857,858,1022,1023
		$Hf(NMe_2)_4$	O_3	1023
		$Hf(NEt_2)_4$	H_2O	857,1024,1025
		$Hf(NEt_2)_4$	O_2	1026
		$Hf(NEt_2)_4$	O_2 [e]	1026
		$Hf(NEtMe)_4$	H_2O	244,857,1005,1027–1029
		$Hf(NEtMe)_4$	O_3	1018
		$Hf[N(SiMe_3)_2]_2Cl_2$	H_2O	1030
		$Hf(NO_3)_4$	H_2O	1031–1033
	Hf_3N_4	$Hf(NMe_2)_4$	NH_3	860
		$Hf(NEt_2)_4$	NH_3	860
		$Hf(NEtMe)_4$	NH_3	860
	$Hf_xAl_yO_z$	$HfCl_4$	$Al(OEt)_3$	188
	$Hf_xSi_yO_z$	$HfCl_4$	$Si(OEt)_4$	406
		$HfCl_4$	$Si(O^nBu)_4$	1034,1035
		HfI_4	$Si(OEt)_4$	406
		$Hf(NMe_2)_4$	$(^tBuO)_3SiOH$	407
	$Hf_xTi_yO_z$	$HfCl_4$	$Ti(O^iPr)_4$	188
73 tantalum				
	Ta_2O_5	$TaCl_5$	H_2O	76,77,91,174,183,212,614,822,863,976,1036–1040
		$TaCl_5$	$Ta(OEt)_5$	188,1041
		TaI_5	H_2O_2	1042
		TaI_5	O_2	1043
		$Ta(OEt)_5$	H_2O	178,184,206,207,212,465,820,863,978,1044–1047
		$Ta(OEt)_5$	O_2 [e]	1048
		$Ta(OEt)_5$	O_2 [n]	1049
		$Ta(NMe_2)_5$	H_2O	466
		$Ta(NEt_2)_5$	H_2O	1050
		$Ta(NEt)(NEt_2)_3$	H_2O	1050
	TaN_x	$TaCl_5$	NH_3	480,1051
		$TaCl_5$	NH_3 + cat.	1051
		$TaCl_5$	Me_2NNH_2	495
		$TaCl_5$	$^tBuNH_2$	1052
		$TaCl_5$	$AyNH_2$	1052
		$TaCl_5$	N_2 [e]	1053–1055
		$TaBr_5$	$^tBuNH_2$	1052
		$Ta(NMe_2)_5$	NH_3	1056,1057
		$Ta(N^tBu)(NEt_2)_3$	NH_3	1058
		$Ta(N^tBu)(NEt_2)_3$	H_2 [e]	1059,1060
		$Ta(N^tBu)(NEtMe)_3$	NH_3	1061
		$Ta(N^tBu)(NEtMe)_3$	NH_3 [e]	1061
	Ta	$TaCl_5$	H_2 [e]	515,1062

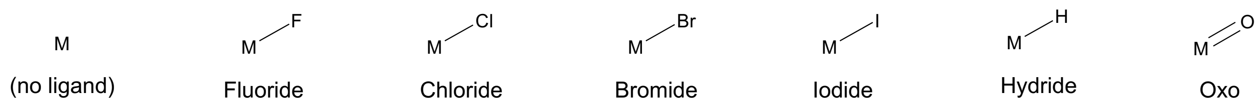
Table III: (*Continued*)

Z	Material	Reactant A [a]	Reactant B	Refs.
		TaF_5	Si_2H_6 [p]	1063
74 tungsten				
	WO_3	WF_6	H_2O	1064
		WF_xO_y	H_2O	1064
		$WOCl_4$	— [q]	1065
	W_xN	WF_6	NH_3	490,491,1066,1067
		WF_6	NH_3 [e]	1068–1070
		$W(N^tBu)_2(NMe_2)_2$	NH_3	1071–1073
	WS_2	WF_6	H_2S	1074
	W_xC	$W(N^tBu)_2(NMe_2)_2$	H_2, N_2 [e]	1075
	W	WF_6	Si_2H_6	249,602,1066,1076–1080
77 iridium				
	Ir	$Ir(acac)_3$	O_2	1081
78 platinum				
	Pt	$Pt(CpMe)Me_3$	O_2	867,869,1082
		$Pt(acac)_2$	H_2	561
80 mercury				
	HgTe	$HgMe_2$	MeAyTe	912,914
82 lead				
	PbS	$PbBr_2$	H_2S	1083
		PbI_2	H_2S	1083
		$Pb(OAc)_2$	H_2S	1083
		$Pb(O^tBu)_2$	H_2S	1084
		$Pb_4O(O^tBu)_6$	H_2S	1084
		$Pb(thd)_2$	H_2S	1083,1084
		$Pb(dedtc)_2$	H_2S	1083,1084
83 bismuth				
	BiO_x	$Bi[N(SiMe_3)_2]_3$	H_2O	1085

[a] The metal thd complexes may have been slightly oligomerized and contain a neutral adduct molecule.
[b] Diamond.
[c] Atomic hydrogen.
[d] R refers to alkyl chains of various lengths.
[e] Plasma.
[f] This process is atypical for ALD: it deposits nanolaminates of Al_2O_3 and SiO_2, where the growth-per-cycle is many nanometers, through a catalytic mechanism.[157]
[g] Cat. = catalyst.
[h] HMDS = hexamethyldisilazane, $(Me_3Si)_2NH$.
[i] Controlled desorption.
[j] Irradiation.
[k] Temperature treatment, such as flash heating or temperature modulation.
[l] He plasma treatment.
[m] Reactant B was formaline, containing ∼ 37% of formaldehyde HCHO and some ethanol in water.
[n] Photo-assisted.
[o] Decomposed.
[p] Preliminary surface science investigation.
[q] Only one half-reaction of an ALD reaction cycle was carried out.

From the different types of inorganic materials grown by

Inorganic



Metalorganic

Organometallic

Methyl (Me)
Ethyl (Et)
Isopropyl (^{i}Pr)
Allyl (Ay)
n-Butyl (^{n}Bu)
Isobutyl (^{i}Bu)
Tert-butyl (^{t}Bu)
Neopentyl (Np)

Cyclopentadienyl (Cp)
Methylcyclopentadienyl (CpMe)
Pentamethylcyclopentadienyl ($CpMe_5$)
Ethylcyclopentadienyl (CpEt)
Tri-isopropylcyclopentadienyl (Cp^iPr_3)
Trimethylsilylcyclopentadienyl [$Cp(SiMe_3)$]

Methoxy (OMe)
Ethoxy (OEt)
Isopropoxy (O^iPr)
Isobutoxy (O^iBu)
Tert-butoxy (O^tBu)
1-Methoxy-2-methyl-2-propoxy (mmp)
Dimethylaminoethoxy (dmae)

Acetylacetonato (acac)
2,2,6,6-Tetramethyl-3,5-heptanedionato (thd)
1,1,1,5,5,5-Hexafluoroacetylacetonato (hfac)
Octane-2,4-dionato (od)
1-(2-Methoxyethoxy)-2,2,6,6-tetramethyl-3,5-heptanedionato (methd)
2-Amino-pent-2-en-4-onato (apo)

Acetoxy (OAc)
Dimethylamido (NMe_2)
Ethylmethylamido (NEtMe)
Diethylamido (NEt_2)
Bis(trimethylsilyl)amido [$N(SiMe_3)_2$]
Tert-butylimido (N^tBu)

N,N'-diisopropylacetamidinato (^{i}PrAMD)
N,N'-ditertbutylacetamidinato (^{t}BuAMD)
1,10-phenanthroline (phen)
Dimethylglyoximato (dmg)
Diethyldithiocarbamato (dedtc)

Figure 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[1086] 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, ^{i}Pr, Ay, ^{n}Bu, ^{i}Bu, ^{t}Bu, and Np], cyclopentadienyls [Cp, CpMe, $CpMe_5$, CpEt, Cp^iPr_3, and $Cp(SiMe_3)$], alkoxides [OMe, OEt, O^iPr, O^iBu, O^tBu, mmp, and dmae], β-diketonates [acac, thd, hfac, od, and methd], alkylamides and silylamides [NMe_2, NEtMe, NEt_2, and $N(SiMe_3)_2$], and amidinates [^{i}PrAMD and ^{t}BuAMD].

Table IV: Computational chemistry investigations on ALD processes

Z	Material	Reactant A	Reactant B	Refs.
5 boron				
	BPO_4	$B(OMe)_3$	$POCl_3$	89
6 carbon				
	C [a]	CF_3	—	1087
13 aluminum				
	Al_2O_3	$AlCl_3$	H_2O	1088
		$AlMe_3$	H_2O	1089–1098
14 silicon				
	SiO_2	$SiCl_4$	H_2O	1099
		$SiCl_4$	H_2O + cat. [b]	1100
	Si_3N_4	SiH_4	NH_3	1101
	Si	$SiCl_3H$	H_2	1102
20 calcium				
	CaS	$Ca(thd)_2$	—	1103
22 titanium				
	TiO_2	$TiCl_4$	H_2O	1104,1105
	TiN	$TiCl_4$	NH_3	1106
28 copper				
	Cu	CuCl	H_2	1107–1109
30 zinc				
	ZnS	$ZnCl_2$	H_2S	1110–1112
	ZnSe	$ZnCl_2$	H_2Se	1112
	ZnTe	$ZnCl_2$	H_2Te	1112
31 gallium				
	GaAs	GaCl	AsH_3	711,1113–1115
40 zirconium				
	ZrO_2	$ZrCl_4$	H_2O	1092,1116–1122
72 hafnium				
	HfO_2	$HfCl_4$	H_2O	1092,1120,1123,1124
		$HfCl_4$	$Hf(OEt)_4$	1125
		$Hf(OEt)_4$	H_2O	1125
73 tantalum				
	Ta_2O_5	$TaCl_5$	H_2O	1126

[a]Diamond.
[b]Cat. = catalyst.

ALD, oxides have been the types most often investigated, as evident from Figure 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, Et_2Se_2); and tellurides from Te or MeAyTe (or, less often, R_2Te). Several other non-metal 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,[1066,1076–1078] and preliminary surface science experiments suggest that a similar process could work also for tantalum.[1063] For most other elements, in contrast, reduction by diatomic hydrogen,[483,546,561,570–572,575,873,875] hydrogen plasma,[331,332,515,516,1062] or in some cases alcohols[577] 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.[564,866–869,872,874,1081,1082]

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 in two main groups: inorganic and metalorganic. Metalorganic reactants can further be classified in those containing a direct metal–carbon bond, that is, organometallic reactants,[1086] 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, β-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.[2,154,171,534,887] Elements are versatile: they react both

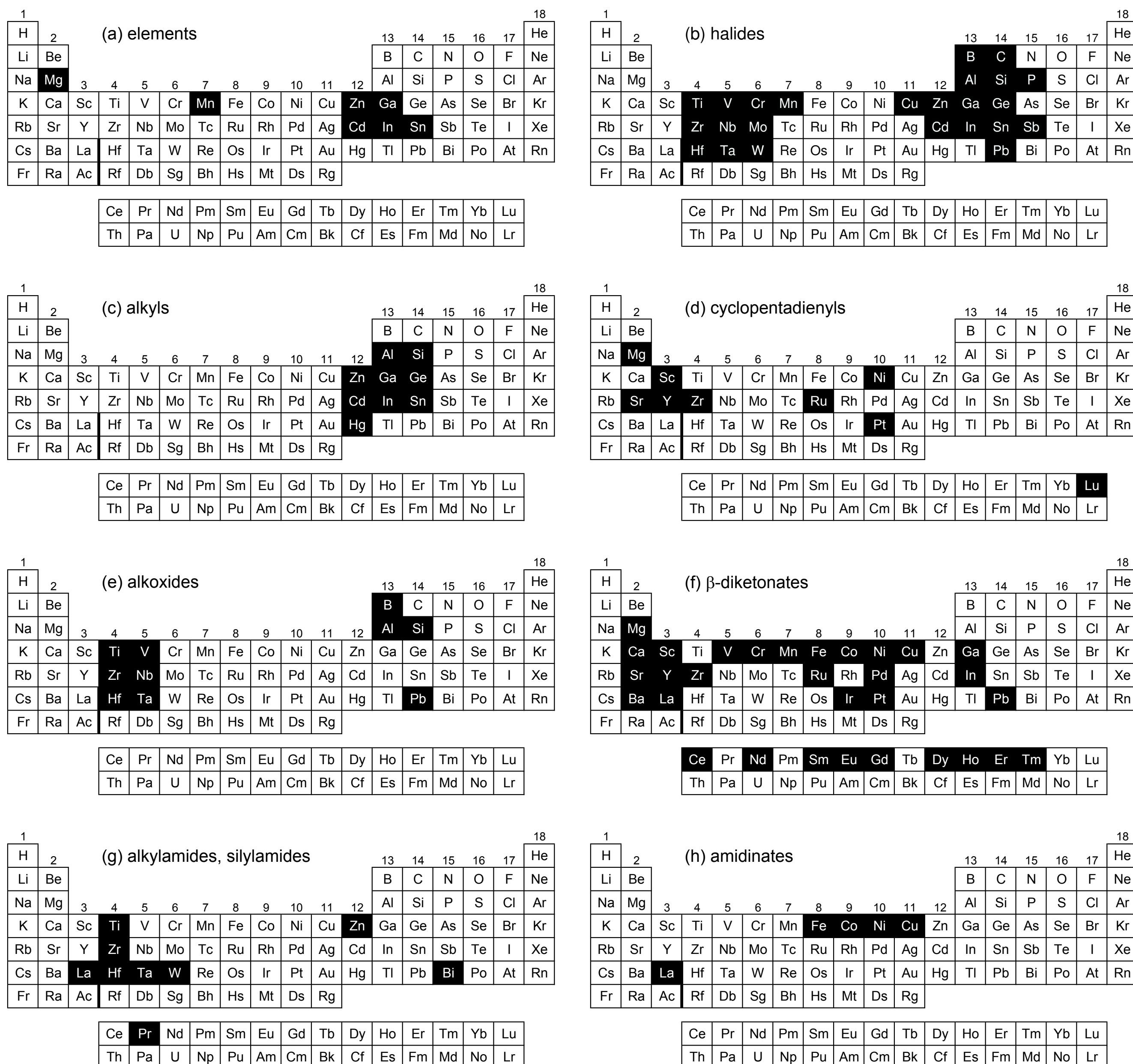


Figure 5: Overview of the different types of metal reactants used in ALD (based on the list of Reactants A in Table III). Dark background indicates that metal reactants containing the particular type of ligand have been used for ALD: (a) elements [no ligands], (b) halides [F, Cl, Br, and I], (c) alkyls [Me, Et, ^{i}Pr, Ay, ^{n}Bu, ^{i}Bu, ^{t}Bu, and Np], (d) cyclopentadienyls [Cp, CpMe, $CpMe_5$, CpEt, $Cp^{i}Pr_3$, and $Cp(SiMe_3)$], (e) alkoxides [OMe, OEt, O^{i}Pr, O^{i}Bu, O^{t}Bu, mmp, and dmae], (f) β-diketonates [acac, thd, hfac, od, and methd], (g) alkylamides and silylamides [NMe_2, NEtMe, NEt_2, and $N(SiMe_3)_2$], and (h) amidinates [^{i}PrAMD and ^{i}BuAMD].

with elemental non-metal 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 lack of steric hindrance effects caused by the ligands.[1127,1128] Nevertheless, less than monolayer growth may be observed because of surface reconstructions.[36] 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 vapor pressure to be evaporated as such [Figure 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 limits their usability.

Halides are the oldest class of ALD reactants, with the first experiments made already in the 1960s.[1,77,78,83,97,100,106,135,138,150,614] Recently they have been extensively investigated for example for the deposition

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_2	MO_x	Zn, Sn
H_2O	MO_x	Zn
N_2	MN_x	Ga, In
S	MS_x	Zn, Cd
H_2S	MS_x	Zn
P	MP_x	Ga
Se	MSe_x	Zn, Cd
H_2Se	MSe_x	Zn
Te	MTe_x	Mg, Mn, Zn, Cd
Sb	MSb_x	In

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_2O	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_2	MO_x	Ti–I, Zn–Cl, Sn–I, Hf–(Cl,I)
O_3	MO_x	Hf–Cl
NH_3	MN_x	B–(Cl,Br), Al–Cl, Si–Cl, Ti–(Cl,I), Ga–Cl, Nb–Cl, Mo–Cl, Ta–Cl, W–F
H_2S	MS_x	Mn–Cl, Zn–Cl, Cd–Cl, In–Cl, W–F, Pb–(Br,I)
PH_3	MP_x	In–Cl
H_2Se	MSe_x	Zn–Cl
AsH_3	MAs_x	Ga–(Cl,Br,I), In–Cl
H_2	M	Cu–Cl
N [a]	MN_x	Ta–Cl
H [b]	M	C–Cl, Ti–Cl, Ge–Cl, Ta–Cl
Si_2H_6	M	Ta–F, W–F

[a] Atomic nitrogen, for example in plasma.
[b] Atomic hydrogen, for example in plasma.

of high-dielectric-constant oxides.[1129–1131] A benefit of halide reactants is the availability of volatile halides for many metals, as shown in Figure 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 $HfCl_4/H_2O$ ALD process has been used even at and above 800 °C.[980,981,1013] 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[1127,1128] 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 $HfCl_4/H_2O$ process at 300 °C, the GPC is about 0.05 nm, corresponding to 15% of a monolayer.[982,984,985,992,998,1127,1132–1134] The low GPC has lead 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.[992] 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 non-metal reactants (H_2O, NH_3, H_2S, etc.) are HF, HCl, HBr, and HI. These gases are corrosive and can etch the film constituents or the reactor material.[864,1036,1042] The gaseous reaction products may also re-adsorb on the surface after their formation, blocking reactive sites and causing undesired thickness gradients.[432,433] Part of the halide ligands may remain as impurities in the films after the growth, which can be problematic for some applications. For example, HfO_2 films grown from $HfCl_4$ and H_2O at 300 °C have been reported to contain about 0.3 at-% chlorine and 1.6 at-% hydrogen (and, surprisingly, 0.2 at-% carbon).[999] Some halides, at least $TiCl_4$, may also react in a manner unideal for ALD, depositing particles through a so-called ”agglomeration” process above a certain threshold temperature.[419,421,1135–1137] Details how the agglomeration occurs have not yet been clarified.[1135]

Alkyls were introduced as ALD reactants in the mid-1980s.[153,190,305,627,723,724,726,729,733,781,929] Nowadays, alkyls are often used as reactants especially for aluminum and zinc. Alkyls are true organometallic compounds, which makes 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,[1127,1128] and the GPC in alkyl-reactant-based processes is often rather high. For example, the GPC in the $AlMe_3/H_2O$ process at 300 °C is about 0.09 nm,[166,199,212,222,228,229,246] corresponding to about 30% of a monolayer of Al_2O_3. The gaseous reaction by-products with hydrogen-containing non-metal reactants (H_2O, H_2S, NH_3, etc.) are typically saturated hydrocarbons, which are generally inert and do not cause problems with re-adsorption or corrosion. Drawbacks of alkyls are that they have been used for a rather small selection of elements (groups 12–14) [Figure 5(c)], and that they decompose at moderate temperatures. For example, $AlMe_3$ decomposes above 300 °C.[216] There is also the possibility of carbon and hydrogen residues in the grown films, although the concentrations are often low. For example, Al_2O_3 films grown from $AlMe_3$ and H_2O at 300 °C were reported to contain about 0.2 at-% carbon and 0.7 at-% hydrogen.[258]

Cyclopentadienyls were introduced as ALD reactants in the early 1990s[162–164] 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 metals, for which other compounds have been scarce [Figure 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 H_2O. However, the material selection grown from cyclopenta-

Table VII: Typical ALD processes of the type Reactant A + Reactant B $\rightarrow$ 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_2O	MO_x	Al–(Me,Et), Zn–(Me,Et), In–Me
O_2	MO_x	Zn–Et
O_3	MO_x	Al–Me
ROH ^{a}	MO_x	Al–Me
NH_3	MN_x	Al–(Me,Et), Ga–(Me,Et)
H_2S	MS_x	Zn–(Me,Et), Cd–Me
PH_3	MP_x	Ga–Me, In–(Me,Et)
H_2Se	MSe_x	Zn–(Me,Et), Cd–Me
AsH_3	MAs_x	Al–(Me,Et,^{i}Bu), Ga–(Me,Et,^{i}Bu), In–(Me,Et)
O ^{b}	MO_x	Al–Me
H ^{c}	M	Al–Me

^{a}Alcohols with various organic chains R.
^{b}Atomic oxygen, for example in plasma.
^{c}Atomic hydrogen, for example in plasma.

Table VIII: Typical ALD processes of the type Reactant A + Reactant B $\rightarrow$ 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_2O	MO_x	Mg–Cp, Sc–Cp, Ni–Cp, Sr–Cp^{i}Pr$_3$, Y–(Cp,CpMe)
O_2	M	Ru–(Cp,CpEt)
H_2S	MS_x	Sr–(CpMe$_5$,Cp^{i}Pr$_3$)

dienyls is still small and comprises only oxides, sulphides, and elements, as shown in Table VIII. Future will show, whether 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 β-diketonates. For example, Y_2O_3 grows through the $YCpMe_3/H_2O$ and $Y(thd)_3/O_3$ 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 non-metal reactants H_2O, NH_3, H_2S are presumably hydrocarbons, which do not re-adsorb 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.[806] Similarly as alkyls, the cyclopentadienyls decompose at moderate temperatures, and there may be carbon and hydrogen residues in the films. For example, $ZrCp_2Me_2$ decomposes at least at 500 °C,[844] and perhaps even at lower temperatures. When grown at 350 °C, ZrO_2 films grown from $ZrCp_2Me_2$ and H_2O 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.[844]

Alkoxides were introduced as ALD reactants in the early 1990s.[89,134,173,462,467,1044,1084] Alkoxides have been used for

Table IX: Typical ALD processes of the type Reactant A + Reactant B $\rightarrow$ 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_2O	MO_x	Al–(OEt,O^{n}Pr), Si–OEt, Ti–(OMe,OEt,O^{i}Pr,OBu), Zr–(O^{t}Bu,dmae), Nb–OEt, Ta–OEt, Hf–mmp
O_2	MO_x	Al–(OEt,O^{n}Pr), Ti–O^{i}Pr, Zr–O^{t}Bu
O_3	MO_x	Ti–O^{i}Pr, Hf–O^{t}Bu
H_2S	MS_x	Pb–O^{t}Bu
O ^{a}	MO_x	Ti–O^{i}Pr, Zr–O^{t}Bu, Hf–O^{t}Bu, Ta–OEt

^{a}Atomic oxygen, for example in plasma.

rather few elements [groups 4, 5, 13, and 14, see Figure 5(e)], and they have been used to deposit almost only oxides (Table IX). Nitrides have not been grown from alkoxides, which 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^{i}Pr)$_4$ decomposes already at 200 °C.[475] Although the decomposition product is the desired oxide, the decomposition inevitably leads to decreased film conformality. A second drawback is the generation of alcohols as by-products in the gas–solid reactions. Alcohols are reactive and may re-adsorb on the surface and interfere with the growth.[465,470] 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^{t}Bu)$_4$/H_2O process have been reported to contain 8 at-% hydrogen and 2 at-% carbon.[847] 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.,[88,94] and it was made more widely known by Ritala et al.[188,1138]

β-Diketonates are in use as ALD reactants since the late 1980s.[408,410–412,415,814,1083,1084] As evident from Figure 5(f), there are β-diketonate reactants available for group 2–14 elements (except group 12 has not been demonstrated), which makes them the most broadly used class of ALD reactants. Before the recent introduction of cyclopentadienyls, β-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 β-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 may be related to the difficulty of replacing the metal–oxygen bond in the β-diketonate with a metal–nitrogen bond. The lower reactivity of the β-diketonates is also reflected in the observation that the oxygen source in the growth of oxide materials is most often not H_2O but O_3 (or O_2 may be used at higher temperatures). β-Diketonates decompose at moderate temperatures. For example, La(thd)$_3$ decomposes at 300 °C.[966] A drawback

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

Reactant B	Material	Reactant A (ML_n: atom M–ligand L)
H_2O	MO_x	Ca–thd,[a] Cu–Hfac, Ga–acac
O_2	MO_x	Cr–acac, Fe–acac, Co–acac, Ni–acac, Cu–(acac,thd), Y–thd, La–thd, Ce–thd
O_2	M	Ru–od, Ru–thd, Pd–thd, Ir–acac
O_3	MO_x	Mg–thd, Ca–thd,[a] Sc–thd, Mn–thd, Fe–thd, Co–thd, Ni–(acac,thd), Ga–acac, Sr–thd,[a] Y–thd, La–thd, Ce–thd, Nd–thd, Sm–thd, Eu–thd, Gd–thd, Dy–thd, Ho–thd, Er–thd, Tm–thd
ROH [b]	M	Cu–hfac
H_2S	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_2	M	Ni–acac, Cu–(acac,thd), Ru–thd, Pd–thd, Pd–hfac, Pt–acac

[a] $M(CO_3)_x$
[b] R refers to alkyl chains of various lengths
[c] MO_xS_y

Table XI: Typical ALD processes 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_2O	MO_x	Zr–(NMe_2,NEt_2), La–N($SiMe_3$)$_2$, Pr–N($SiMe_3$)$_2$, Hf–(NMe_2,NEt_2), Ta–(NMe_2,NEt_2), Bi–N($SiMe_3$)$_2$
O_2	MO_x	Hf–NEt_2
O_3	MO_x	Hf–NMe_2
NH_3	MN_x	Ti–(NMe_2,NEt_2), Zr–(NMe_2,NEt_2), Hf–(NMe_2,NEt_2), Ta–NMe_2
H_2Se	MSe_x	Zn–N($SiMe_3$)$_2$
O [a]	MO_x	Ti–NMe_2, Zr–NEt_2, Hf–NEt_2
N [b]	MN_x	Ti–NMe_2
H [c]	MN_x	Ti–NMe_2

[a] Atomic oxygen, for example in plasma.
[b] Atomic nitrogen, for example in plasma.
[c] Atomic hydrogen, for example in plasma.

in using β-diketonate reactants is their size. The bulky ligands cause marked steric hindrance,[1127,1128] and the GPC obtained from these reactants is typically low, some percents of a monolayer.[237,815] The reaction mechanisms related to removing the β-diketonate differ from most ALD processes, since the ligands are most often oxidized with O_3. Whether the oxidation is complete and H_2O and CO_2 form as by-products, has apparently not yet been verified. The films grown from β-diketonate reactants contain often considerable amounts of carbon and hydrogen impurities. For example, Y_2O_3 deposited through the Y(thd)$_3$/O_3 process at 300 °C was reported to contain about 2 at-% of both carbon and hydrogen.[815] Because of the generation of CO_2 during oxidation of the ligands, carbonate films may form in place of the more-often-desired oxides.[409,807]

An interesting observation was recently made regarding the reactivity of lanthanoid (Ln) β-diketonates. Päiväsaari et al.[973] studied the ALD growth of several lanthanoid oxides from Ln(thd)$_3$ and ozone at a constant temperature (300°C). Päiväsaari et al.[973] noticed the thickness increment per ALD reaction cycle to increase systematically with increasing ionic radius of the lanthanides (the ionic radius of the lanthanoid cations decreases with increasing atomic number, known as the "lanthanoid contraction"[973,1139]). A similar qualitative trend of the GPC (in thickness units) as reported by Päiväsaari et al.[973] 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 $LnO_{3/2}$ unit, and the larger the average thickness $\bar{h}^{\rm ml}$ corresponding to one monolayer of $LnO_{3/2}$ $\left(\bar{h}^{\rm ml} = v^{1/3}\right)$.[1128,1140] 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 chemisorption process.[1127,1128] However, the mechanical contribution of the ionic radius appears too small to explain the full quantitative trend reported by Päiväsaari et al.,[973] 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)$_3$ molecules with increasing ionic radius are yet to be clarified.

Alkylamides and silylamides have been investigated as ALD reactants since the late 1990s.[407,498,499,513,857,1059] Alkylamides and silylamides appear a versatile group of reactants, both in terms of the elements for which they are available [Figure 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. For example, the Ti(NMe_2)$_4$ reactant decomposes already at 150 °C.[505] Rather typical is also that the GPC from amides, at least for alkylamides of titanium, exceeds a monolayer.[499–501,513] Although a theory has been built to explain the beyond-monolayer-growth through "readsorption,"[499–501,509] 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 additionally silicon. As an example of films grown from alkylamides, TiN films grown through the Ti(NEt_2)$_4$/NH_3 process at 200 °C contained about 4 at-% carbon and 6 at-% hydrogen.[513] As an example of films grown from silylamides, PrO_x films grown through the Pr[N($SiMe_3$)$_2$]$_3$/H_2O process at 250 °C contained about 3 at-% carbon, 20 at-% hydrogen, and 6 at-% silicon.[972]

Amidinates are the most recent class of ALD reactants, introduced only in 2003.[546,1141] Because of their novelty, their use in ALD has so far been investigated only for a few el-

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_2O	MO_x	Fe–^{t}BuAMD, Co–^{i}PrAMD, La–^{i}PrAMD
H_2	M	Fe–^{t}BuAMD, Co–^{i}PrAMD, Ni–^{i}PrAMD, Cu–^{i}PrAMD

ements, as summarized in Figure 5(h). The material selection (Table XII) may broaden in the future, however, because amidinates should be available for most metals.[1142] The reactions seem self-terminating.[546,1143] Decomposition temperatures are typically around 300 °C.[1141,1143] 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 for ALD. For example, hydrides have been used for depositing especially silicon and germanium (refs. in Table III); acetates for zinc and lead-containing films;[415,608,609,615,616,618–620,639,1083] nitrate and hydroxylamide for hafnium oxide;[1021,1031–1033] and a carbonyl compound for cobalt.[1144] The specific characteristics of these processes are not discussed further in this review.

3. *$AlMe_3/H_2O$ vs. 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 expected 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." Advantage of "thermal ALD" over various "energy-enhanced" ALD processes is that thermal ALD processes fulfill the 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, β-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 [Figure 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 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 non-inert 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 $AlMe_3/H_2O$ 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 Section III B the kinetic characteristics of such reactions. Section III C describes the three classes of chemisorption reactions typically involved in ALD, and Section III D identifies the possible factors causing 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, Section III H introduces the possible growth modes that define how the material gets arranged on the surface during the growth.

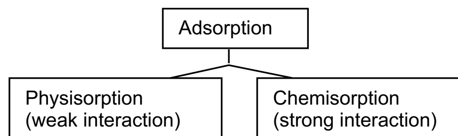


Figure 6: Adsorption classes.

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, elements 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 in 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),[1145] as shown in Figure 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”).[1145] In relation with ALD, one must realise that a monolayer of the adsorbed species, such as $||Al(Me)_2$, differs both from a monolayer of the reactant molecule, $AlMe_3$, and from a monolayer of the ALD-grown material, Al_2O_3 (Figure 7):

- *Monolayer (capacity)* for chemisorption is defined[1145] 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 by the chemical nature of the adsorptive <the reactant>.”

- *Monolayer (capacity)* for physisorption is defined[1145] 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 MZ_x can be defined as one plane of MZ_x units in a crystalline face of the bulk MZ_x material in the preferred orientation of growth.[1146]

The amount of material adsorbed in gas–solid reactions can depend on time in various ways, as schematically illustrated in Figure 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

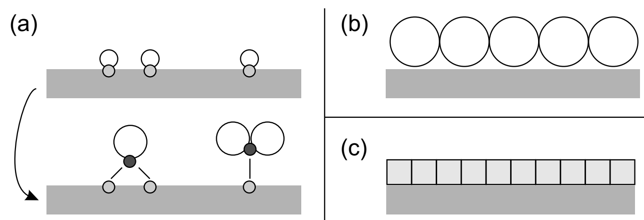


Figure 7: Three different types of monolayers relevant to ALD: (a) a chemisorbed monolayer (the substrate before chemisorption indicated above, with reactive sites shown), (b) a physisorbed monolayer, and (c) a monolayer of the ALD-grown material.

the 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, non-saturating (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).[1147]

B. Adsorption kinetics

Chemical kinetics describes the effect of process parameters such as temperature and reactant concentrations on reaction (adsorption) rates.[1148] A simple example of molecular adsorption of a gaseous compound A on a surface site $||*$ 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.

$$||* + \mathrm{A(g)} \overset{r_a}{\rightarrow} ||*\mathrm{A} \quad (1)$$

$$||*\mathrm{A} \overset{r_d}{\rightarrow} ||* + \mathrm{A(g)} \quad (2)$$

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:[192,196,1149–1154] 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 Q.[1155] 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

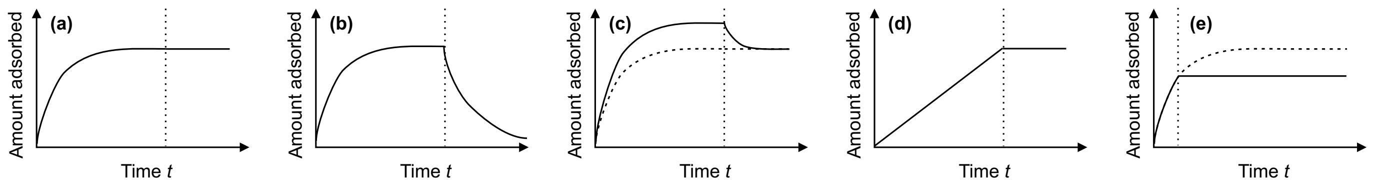


Figure 8: Examples of how the amount of material adsorbed can vary with time: (a) irreversible saturating adsorption (i.e., self-terminating reaction), (b) reversible saturating adsorption, (c) combined irreversible and reversible saturating adsorption, (d) irreversible non-saturating adsorption (deposition), 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.

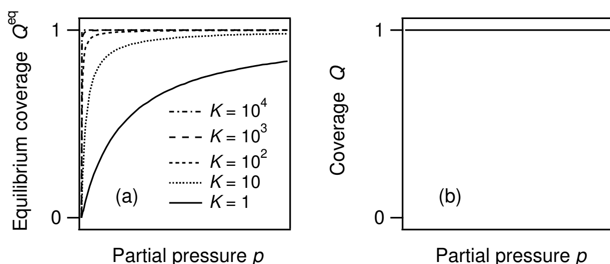


Figure 9: Effect of the reactant partial pressure p on the amount of material chemisorbed in a gas–solid reaction: (a) the equilibrium chemisorption coverage Q^{eq} in reversible adsorption (equilibrium constants $1 \leq K \leq 10^4$) and (b) the chemisorption coverage Q after saturation in irreversible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

the chemisorption coverage, $\mathrm{d}Q/\mathrm{d}t$, is obtained by subtracting the desorption rate from the adsorption rate:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = r_\mathrm{a} - r_\mathrm{d} = k_\mathrm{a}\, p\,(1-Q) - k_\mathrm{d}\, Q. \tag{3}$$

After saturation, the chemisorption coverage is constant ($\mathrm{d}Q/\mathrm{d}t = 0$), and we get from Equation 3 to the *Langmuir isotherm*, giving the equilibrium chemisorption coverage Q^{eq} as a function of reactant partial pressure:

$$Q^{eq} = \frac{k_\mathrm{a}\, p}{k_\mathrm{a}\, p + k_\mathrm{d}} = \frac{1}{1+(Kp)^{-1}}. \tag{4}$$

The right side of Equation 4 has been obtained by recognizing that $K = k_\mathrm{a}/k_\mathrm{d}$ is the *equilibrium constant* of the adsorption. In the general case of reversible adsorption ($k_\mathrm{a} \neq 0 \neq k_\mathrm{d}$), Q^{eq} increases with p, as illustrated in Figure 9(a). To achieve ALD conditions with self-terminating reactions, however, the adsorption must be irreversible (Section 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 Equation 4 with this assumption, we get

$$\lim_{K\to\infty} Q^{eq} = 1. \tag{5}$$

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

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

$$Q = Q^{eq}\left(1 - e^{-(k_\mathrm{a}p+k_\mathrm{d})\,t}\right). \tag{6}$$

For irreversible chemisorption, Equation 6 reduces to $Q = 1 - e^{-k_\mathrm{a}\, p\, t}$. 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, whose coverage 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 [Figure 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 Figure 10(b), the amount of atoms M deposited c_M increases during Steps #1 of the reaction cycles. The deposition rate $\mathrm{d}c_\mathrm{M}/\mathrm{d}t$ varies with time [Figure 10(c)], implying that the process is in a transient state.[1156] For comparison, in this example, the amount of material deposited c_M increases linearly with the number of reaction cycles [Figure 10(d)] and the GPC Δc_M is constant [Figure 10(e)]. The number of reaction cycles n is clearly a discrete variable,[992,1140] whereas time t is continuous.

The temperature dependency of adsorption and desorption rate constants k_i is typically described by the *Arrhenius equation*:

$$k_i = A\, e^{-E_i/RT}. \tag{7}$$

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 other factors than the reaction rate, as will be discussed in Section III F.

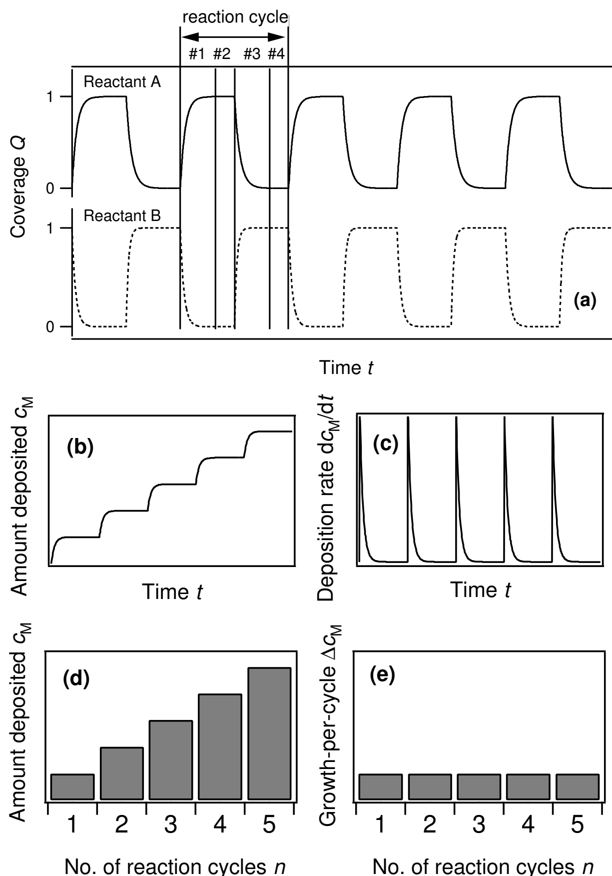


Figure 10: Schematic representation of five reaction cycles, assuming irreversible adsorption: (a) chemisorption coverage Q as a function of time t (solid line: ML_z species adsorbed in the reaction of the Reactant A assumed to be of type ML_n, dashed line: species adsorbed in the reaction of Reactant B; the beginning and end of a reaction cycle and Steps #1 to #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 Δc_M as a function of the number of reaction cycles n.

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. 432,1038,1152–1154,1157–1160.

C. Chemisorption mechanisms

Three main classes of chemisorption mechanisms have been identified for the self-terminating reactions of compound reactants in ALD.[1161] In *ligand exchange*, the reactant molecule (ML_n) is split on the surface.[1162] Ligand (L) combines with a surface group ||–a to form a volatile compound that is released as a gaseous reaction by-product, aL, and the remaining part of the molecule chemisorbs to the surface as a ML_{n-1}

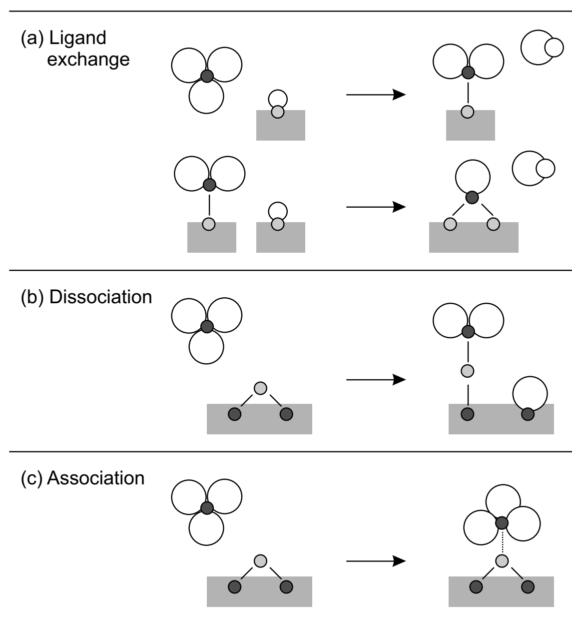
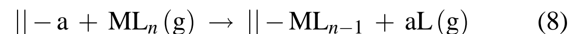


Figure 11: Chemisorption mechanisms identified for ALD: (a) ligand exchange reaction of the ML_n reactant with surface "–a" groups, releasing gaseous aL, (b) dissociation of the ML_n in surface M–Z sites, and (c) association of the ML_n species onto the surface. In this scheme, $n = 3$.

species (Equation 8).[98,197,209,216,419,526,818,1163–1165]



$$||-\mathrm{a} + \mathrm{ML}_n\,(\mathrm{g}) \rightarrow ||-\mathrm{ML}_{n-1} + \mathrm{aL}\,(\mathrm{g}) \qquad (8)$$

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 ||–a group. These reactions release ligands as aL and consume additional ||–a groups but do not result in bonding more metal M on the surface (Equation 9, reaction of an adsorbed ML_z species).

$$||-\mathrm{ML}_z + ||-\mathrm{a} \rightarrow ||-\mathrm{ML}_{z-1}-|| + \mathrm{aL}\,(\mathrm{g}) \qquad (9)$$

In *dissociation*, the reactant molecule is split onto reactive M′–Z sites on the surface (Equation 10).[197,209,216,1163,1164]

$$||\mathrm{M}'-\mathrm{Z}|| + \mathrm{ML}_n\,(\mathrm{g}) \rightarrow ||\mathrm{M}'-\mathrm{L} + ||\mathrm{Z}-\mathrm{ML}_{n-1} \qquad (10)$$

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 (Equation 11).[101,144,1111,1165–1167]

$$|| + \mathrm{ML}_n\,(\mathrm{g}) \rightarrow ||\cdots\mathrm{ML}_n \qquad (11)$$

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

When reactions 8–11 occur, a simple mass balance[1128] governs the chemisorption. The amount of ligands L chemisorbed Δc_L equals n times the amount of metal M chemisorbed Δc_M,

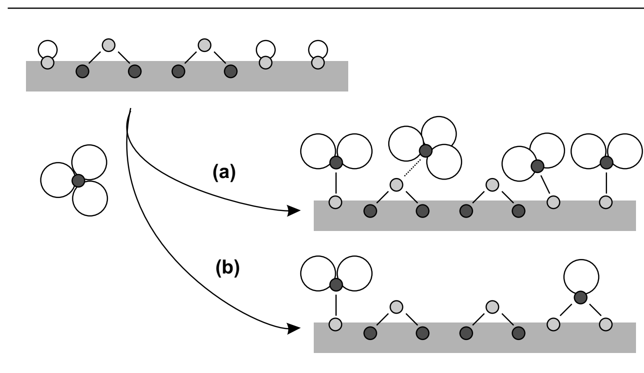


Figure 12: Factors identified to cause saturation of irreversible chemisorption: (a) steric hindrance of the ligands and (b) number of reactive surface sites.

subtracted by the number of ligands L released in ligand exchange reaction with surface ||–a groups, that is, the amount of surface ||–a groups reacted Δc_a. The mass balance is summarized in Equation 12:

$$\Delta c_L = n\Delta c_M - \Delta c_a. \tag{12}$$

Sometimes, reactions other than those presented in Equations 8–11 occur. For example, the oxidation state of the elements may change during the ALD processing.[63,102,1066,1168] The mass balance of Equation 12 may then not be valid. A special class of self-terminating reactions has been observed for metal chlorides reactants, where metal oxide particles can form in a single reaction.[419,421,818,1135,1169] So-called non-growth ligand exchange reactions[1088,1135,1170] 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.[1135] Unexplained formation of particles, or ”nanorods,” has been reported also for the $ZnEt_2/H_2O$ ALD process.[600]

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 Figure 12: *steric hindrance of the ligands*[209,216,237,291,292,530,548,554] and *the number of reactive surface sites*.[419,819] Steric hindrance of the ligands can cause the ligands of the chemisorbed ML_z species to shield part of the surface from being accessible to the ML_n reactant. The surface can be considered ”full.” The number of bonding sites on the surface may also be less than 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.

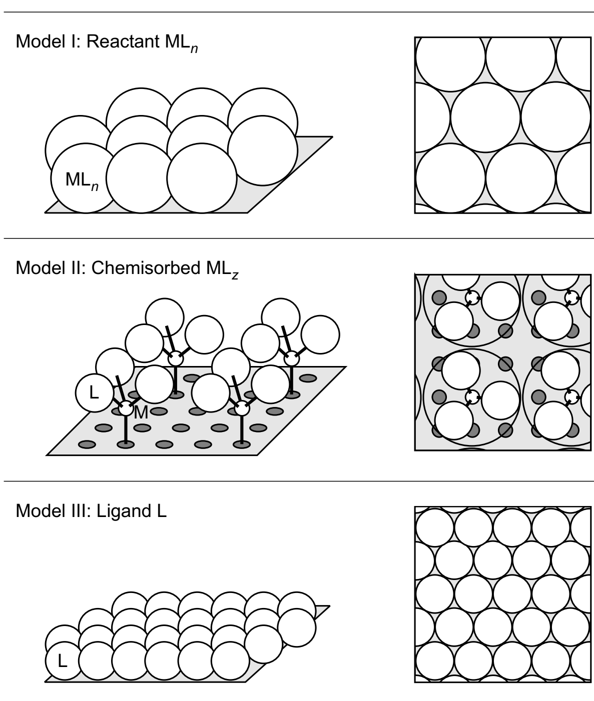


Figure 13: Schematic illustration for analyzing sterically hindered chemisorption on the basis of the size of the ML_n reactant (Model I by Ritala et al.[462,468] and Morozov et al.[133]), the size and geometry of the chemisorbed ML_z species (Model II by Ylilammi[1127]), and the size and number of ligands L (Model III by Siimon and Aarik[432] and Puurunen[1128]). Left: side view, right: top view.

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 reacts through ligand exchange, releasing thereby the maximum number of ligands into the gas phase, and reaction continues until steric hindrance terminates it.[1128]

Irrespective of the factor causing saturation and the absolute amount of material adsorbed, a monolayer of the chemisorbed ML_z species has formed by definition when the chemisorption has saturated (Section IV B). It is of interest to analyze to which GPC, in monolayers of the ALD-grown MZ_x material, the monolayer of adsorbed 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.[1171] Three models have been developed for analyzing the GPC when steric hindrance causes saturation, as summarized in Figure 13.

Ritala et al.[462,468] and Morozov et al.[133] developed a model, referred to as *Model I*, to estimate the maximum GPC from the size of the ML_n reactant [Figure 13(a)]. The size of the 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 ML_n. Model I, in fact, corresponds to a

physisorbed monolayer of the ML_n molecules (Section III A). Because the chemisorbed ML_z species differs from the ML_n reactant, Model I gives at best a rough estimate of the achievable GPC.

Ylilammi[1127] developed a model, *Model II*, for calculating the maximum GPC from the size and geometry of the adsorbed ML_z species [Figure 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 ML_z.[1127]

Siimon and Aarik[432] and Puurunen[237,1128] 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 [Figure 13(c)]. A theoretical maximum amount of ligands adsorbed is calculated assuming a close packed monolayer of the ligands. This theoretical arrangement corresponds to a "physisorbed monolayer" of the ligands.[1172] 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.[1128]

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,[133,468] calculated for the $TiCl_4$ molecule), 19% (Model II[1127]) and 33% (Model III[237]).[1173] Experimental GPC values vary within about 15–30% of a monolayer, depending on the growth temperature.[237]

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.[1174]

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[1175]—are illustrated in Figure 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 increasing temperature decreases the number of reactive surface sites.[130,216,548,554] Increasing the reaction temperature may also change the inherent reaction mechanisms, for example, so that the L/M ratio z in the chemisorbed ML_z species changes.[418,419,421,818] (ii) The GPC may stay constant with temperature (panel b). This can occur, for example, if steric hindrance causes saturation and the number of reactive sites does not affect the amount of adsorbed species.[237,530,815] Sometimes, the GPC settles to different constant values at different temperatures.[898] (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.[481,1071] (iv) The GPC can also first increase and then decrease with temperature (panel d). This can occur through that, first, some reactions are activated with increasing temperature, after which the decreasing number of reactive sites starts decreasing the GPC.[199,243] However, this can also be an artefact 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 (Equation 7) and slower mass transport, the reactions have not been completed [see, e.g., Fig. 8(e)].[422]

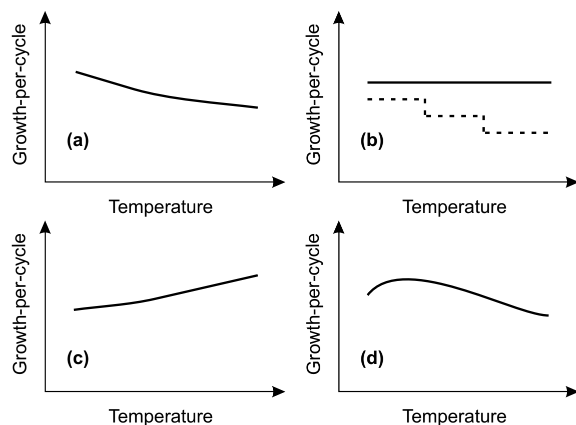


Figure 14: Variation of the GPC with the ALD processing temperature in the *ALD window*: (a) the GPC decreases with temperature, (b) the GPC is constant with temperature (possible with different values at different temperature ranges, as shown by the dashed line), (c) the GPC increases with temperature,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

G. Effect of the number of cycles on the GPC

The ALD process modifies the chemical composition of the surface through depositing material. The first ALD reaction cycle occurs on the surface of the original substrate material, the following cycles 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[246,247,1140]—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 in four groups on the basis how the GPC varies with the number of ALD reaction cycles,[247] as shown in Figure 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 cycles from the first cycle on. The growth is always in the *steady regime*. Linear growth[527,528,530] can occur, for example, if the number of reactive sites on the sur-

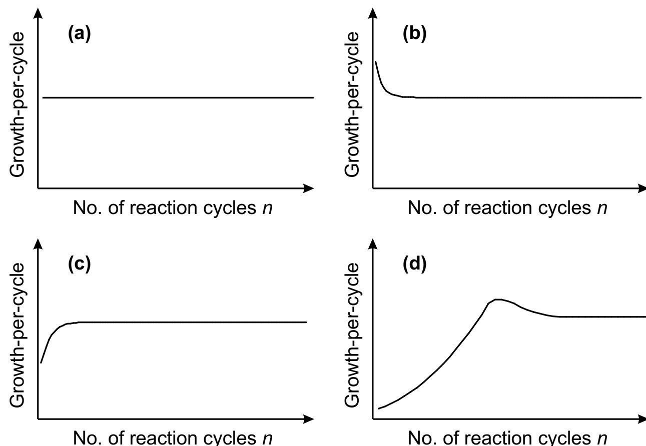


Figure 15: Dependency of the GPC on the number of reaction cycles in different types of ALD processes:[247] (a) linear growth, (b) substrate-enhanced growth, (c) substrate-inhibited growth of Type 1, and (d) substrate-inhibited growth of Type 2.

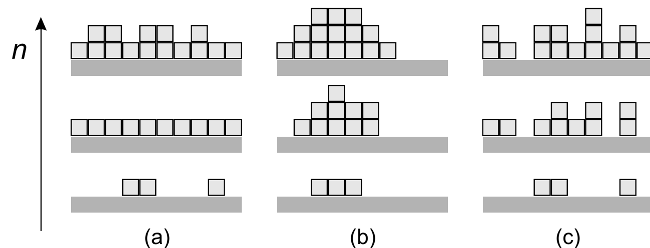


Figure 16: Schematic illustration with increasing number of reaction cycles n of selected growth modes possible in ALD: (a) two-dimensional growth, (b) island growth and, (c) random deposition.

face 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 beginning of the growth than at the steady regime. The initial, non-constant growth is referred to as being in a *transient regime*. Substrate-enhanced growth[110,118,132,516,548,1008] 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*,[247] 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.[123,223,224,231,292,488,984,992,1176,1177] In substrate-inhibited growth of Type 2,[488,499–501,984,992,1151,1178] island growth further seems to occur.[488,992,1179]

H. Growth mode

The way the material gets arranged on the surface during ALD growth is defined by the *growth mode*. For growth of a full monolayer per cycle, two-dimensional growth may be expected because multilayer adsorption should be excluded by definition in ALD. For 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.[246,1180] While sometimes achieved,[1077,1181] 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.[246,247,1180] Island growth has been concluded for several ALD processes.[132,134,154,214,246,247,488,771,1182] A model has recently been derived to describe island growth in ALD.[247] *Random deposition* is a statistical growth mode, where the new material units are deposited with an equal probability on all surface sites.[1140] Because of the self-terminating reactions, random deposition results in smoother layers in ALD than in continuous deposition processes (”shower model” vs. ”rain model” of random deposition).[992,1140] Random deposition has been concluded at least for two ALD processes.[292,544] 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 random deposition thereafter (Stranski–Krastanov growth).[1180] 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.[1077]

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 substrate-inhibited growth of Type 2 which seems to correspond to an island growth mode.[246,247,488,1177] Linear growth has corresponded to two-dimensional growth mode[527] as well as random deposition.[544] Substrate-enhanced growth of Type 1 has corresponded to island growth mode[558] and random deposition.[292]

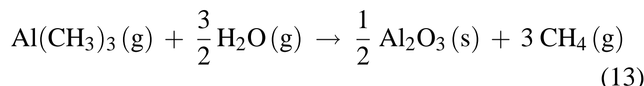
IV. SURFACE CHEMISTRY OF THE ALME$_3$/H$_2$O PROCESS

This section reviews the current status of understanding the surface chemistry of the $AlMe_3/H_2O$ 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 Section IV B. The chemisorption mechanisms identified to occur during the $AlMe_3$ and H_2O reactions are summarized in Section IV C. Section IV D discusses the decreasing effect of

increasing growth temperature on the GPC and Section IV E steric hindrance as the factor causing saturation. The effect of the surface OH group concentration on the GPC is explored in Section IV F. Section IV G summarizes the (little) experimental information available on the kinetics of the reactions, and Sections IV H and IV I the way the GPC varies with the number of reaction cycles and the growth mode, respectively. Finally, Section IV J summarizes the findings.

A. General characteristics

The $AlMe_3/H_2O$ process follows the overall stoichiometry presented in Equation 13 (Me = CH_3 = methyl).

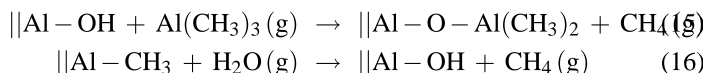


$$Al(CH_3)_3\,(g) + \frac{3}{2}H_2O\,(g) \rightarrow \frac{1}{2}Al_2O_3\,(s) + 3\,CH_4\,(g) \tag{13}$$

The aluminum and oxygen retain their oxidation states, and the mass balance of Equation 12 is valid. For the $AlMe_3$ reaction, the mass balance converts to Equation 14.

$$\Delta c_{Me} = 3\,\Delta c_{Al} - \Delta c_{(O)H} \tag{14}$$

The chemistry of the $AlMe_3/H_2O$ process is often described by the two successive "half-reactions," presented in the Equations 15 and 16.[192,196]



$$||Al-OH + Al(CH_3)_3\,(g) \rightarrow ||Al-O-Al(CH_3)_2 + CH_4\,(g) \tag{15}$$
$$||Al-CH_3 + H_2O\,(g) \rightarrow ||Al-OH + CH_4\,(g) \tag{16}$$

That the surface switches from methyl-terminated to hydroxyl-terminated and vice versa is well known and illustrated, for example, by infrared measurements.[196] The $AlMe_3/H_2O$ process is more complex than revealed by Equations 15 and 16, however, as discussed in the following sections.

B. Verification of self-termination

The $AlMe_3/H_2O$ process is self-terminating with respect to time. For sufficiently long reactant pulses and purges, lengthening the $AlMe_3$ and H_2O pulses and the purges in between (Steps #1–4) does not affect the amount of species adsorbed,[222,227] as illustrated in Figure 17. When the $AlMe_3$ and H_2O 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 $AlMe_3$ and H_2O reactions (Steps #2 and #4) must also be sufficiently long. If the purges are too short, the GPC increases because of $AlMe_3$ and H_2O are simultaneously present in the gas phase, enabling continuous CVD-type deposition.[222,227]

The $AlMe_3/H_2O$ process seems self-terminating also with respect to the $AlMe_3$ pressure. In the experiments of Kumagai et al.[267] for the $AlMe_3/H_2O_2$ ALD process (oxygen source H_2O_2 instead of H_2O), the GPC was independent of the reactant pressures, as shown in Figure 18. The independence of the GPC from the $AlMe_3$ pressure is consistent with irreversible, saturating reaction of $AlMe_3$ on aluminum oxide.

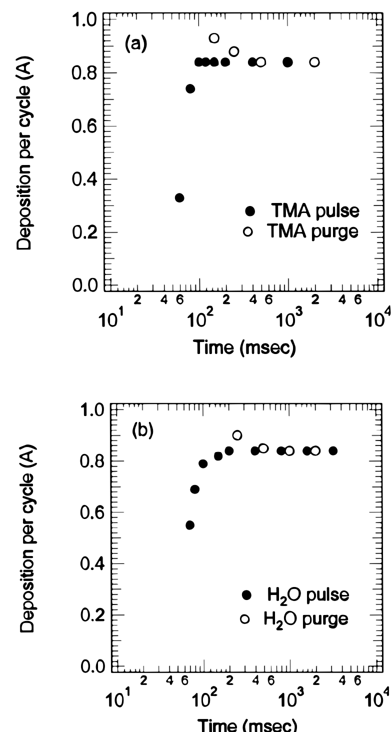


Figure 17: Self-termination in the $AlMe_3/H_2O$ process (TMA = $AlMe_3$) at 300 °C in the steady growth regime: effect on the measured GPC (labeled "deposition per cycle") of (a) the $AlMe_3$ pulse and the following purge times (Steps #1 and #2) and (b) the H_2O pulse and the following purge times (Steps #1 and #2). (Reprinted from Sneh et al.[222] with permission. Copyright 2002, Elsevier.)

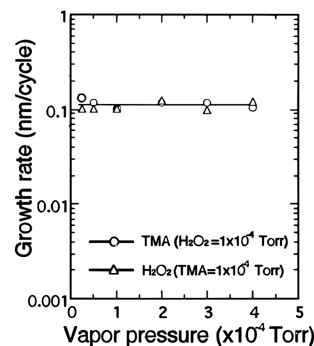
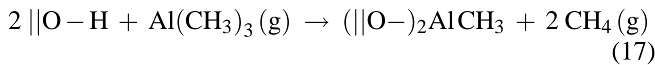


Figure 18: Self-terminating reactions in the $AlMe_3/H_2O_2$ ALD process (TMA = $AlMe_3$) in the steady growth regime: effect of reactant pressures to the GPC (labelled "growth rate") at 340 °C.[267] (Reprinted from Kumagai et al.[267] with permission. Copyright 1994, Institute of Pure and Applied Physics.)

Whether the H_2O pressure affects the amount of H_2O chemisorbed on aluminum oxide, is not entirely clear. In some investigations,[211,212,234] effect of reactant dose (exposure time multiplied with reactant partial pressure) on the $AlMe_3/H_2O$ process has been suggested. A systematic study of the effect of H_2O exposure time and pressure is missing, however.

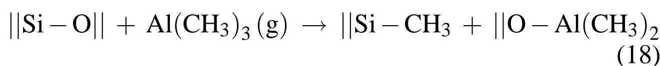
C. Identified chemisorption mechanisms

Several reactions have both experimentally and theoretically been identified to occur when gaseous $AlMe_3$ interacts with oxide supports. $AlMe_3$ reacts through ligand exchange with the hydrogen atoms in surface OH groups, producing O–Al bonds and releasing methane (Equation 15).[190,192,193,196,1089,1163,1164,1183–1186] Other gaseous reaction products in addition to methane have not been found.[211,217,227,243,443] The $AlMe_3$ molecule can also react through ligand exchange simultaneously with two OH groups, in reaction described in Equation 17.[196,209,216,217]



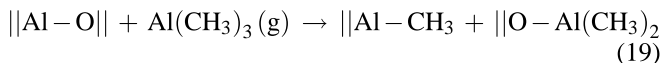
$$2\,||\mathrm{O-H} + \mathrm{Al(CH_3)_3\,(g)} \rightarrow (||\mathrm{O-})_2\mathrm{AlCH_3} + 2\,\mathrm{CH_4\,(g)} \quad (17)$$

Practically all OH groups on silica and alumina react with $AlMe_3$ through ligand exchange, at least at temperatures between 80 and 300 °C.[209,216] In addition to the ligand exchange reaction (Equations 15 and 17), $AlMe_3$ reacts dissociatively with oxygen bridges of silica (Equation 18).[197,209,1163,1164,1183,1187,1188]



$$||\mathrm{Si-O}|| + \mathrm{Al(CH_3)_3\,(g)} \rightarrow ||\mathrm{Si-CH_3} + ||\mathrm{O-Al(CH_3)_2} \quad (18)$$

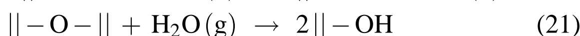
Dissociation to several oxygen bridges bonded to the same silicon atom leads also to surface species of type $||Si(Me)_2$ and $||Si(Me)_3$.[197,209] $AlMe_3$ seems also to react dissociatively with coordinatively unsaturated (c.u.s.) Al–O pairs of alumina (Equation 19).[196,216,1097]



$$||\mathrm{Al-O}|| + \mathrm{Al(CH_3)_3\,(g)} \rightarrow ||\mathrm{Al-CH_3} + ||\mathrm{O-Al(CH_3)_2} \quad (19)$$

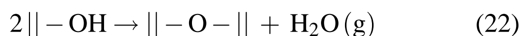
Similarly as for $AlMe_3$ reaction on aluminum oxide, ligand exchange reaction and dissociation has been concluded to occur in the H_2O reaction with $AlMe_3$-modified aluminum oxide (Equations 20 and 21).[192,211,215,217,220]

$$||\mathrm{-CH_3} + \mathrm{H_2O\,(g)} \rightarrow ||\mathrm{-OH} + \mathrm{CH_4\,(g)} \quad (20)$$



$$||\mathrm{-O-}|| + \mathrm{H_2O\,(g)} \rightarrow 2\,||\mathrm{-OH} \quad (21)$$

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



$$2\,||\mathrm{-OH} \rightarrow ||\mathrm{-O-}|| + \mathrm{H_2O\,(g)} \quad (22)$$

D. Effect of temperature on the GPC

The GPC in the steady regime of the $AlMe_3/H_2O$ process decreases with increasing processing temperature, as shown in Figure 19 that summarizes the results by several groups.[179,199,212,216,222,228,229,234] This figure does not include results beyond 300 °C, the temperature at which $AlMe_3$ starts to decompose thermally.[216,1189] The different investigations share the decreasing trend and agree quantitatively within an experimental error of about 10%. One investigation,[234] however, shows a significantly lower GPC. It did not confirm the saturation of the surface reactions through sufficiently long

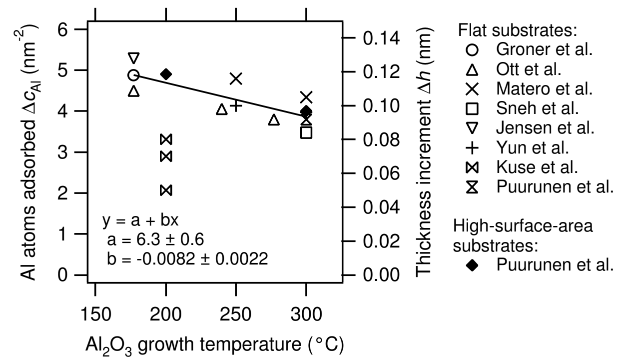


Figure 19: GPC in the $AlMe_3/H_2O$ process to grow amorphous aluminum oxide on flat substrates in the steady growth regime (Groner et al.,[228] Ott et al.,[199] Matero et al.,[212] Sneh et al.,[222] Jensen et al.,[229] Yun et al.,[179] Kuse et al.,[234] Puurunen et al.[246]). The GPC is expressed as the amount of aluminum atoms attached per cycle per square nanometer of surface Δc_{Al} (nm^{-2}), which converts to the thickness increment per cycle Δh (nm) through $\Delta c_{Al} = \rho N_A M^{-1} \Delta h$ (ρ = 3.5 g cm^{-3}).[237,1128] 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 (Puurunen et al.[216]). The results[216] were calculated through the mass balance (Equation 23) for $AlMe_3$ reaction at 150 °C with alumina heat-treated at the temperature indicated in the x-axis. The results for $AlMe_3$ reaction at 150 °C can be used for the comparison, because increasing the temperature to 300 °C does not affect the amount of adsorbed species (Figure 20).

pulse and purge times, however, and the process probably operated at unsaturated conditions.

Change in the inherent reaction mechanisms (Equations 15, 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 results obtained for the $AlMe_3$ reaction on high-surface-area alumina, which had been stabilized by a preceding heat treatment at 560 °C to have a surface OH group concentration $c_{(O)H}$ of 2.0 nm^{-2}.[216,262] The amount of aluminum atoms adsorbed Δc_{Al} (nm^{-2}) could be calculated through the mass balance, Equation 23 (rearranged from Equation 14),[216,262] because the amount of methyl groups adsorbed Δc_{Me} (nm^{-2}) was measured and the amount of OH groups reacted $\Delta c_{(O)H}$ (nm^{-2}) could be approximated with the surface OH group concentration before the reaction $c_{(O)H}$ (nm^{-2}).[209,216]

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

As seen from Figure 20, the reaction temperature has no effect on the amount of aluminum atoms adsorbed in the $AlMe_3$ reaction with alumina. An effect of the reaction temperature on the preferred reaction mechanisms therefore cannot explain the decreasing GPC.

Change in the number of reactive surface groups with temperature is another option to account for the decreasing GPC. Increasing substrate heat-treatment temperature in-

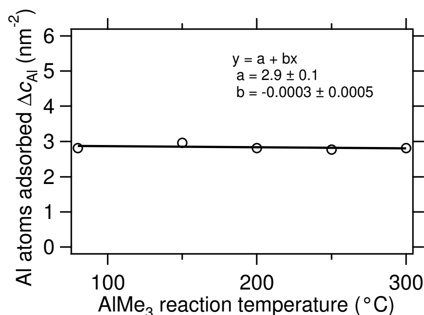


Figure 20: Effect of the $AlMe_3$ reaction temperature on the amount of aluminum adsorbed in the $AlMe_3$ reaction Δc_{Al} (nm^{-2}) on alumina heat-treated at 560 °C, according to Puurunen et al.[216] The confidence limits represent one standard deviation.

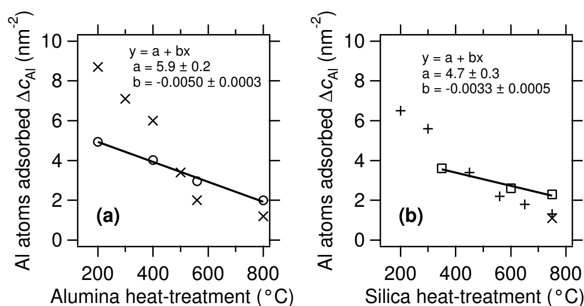


Figure 21: Effect of the substrate heat-treatment temperature on the amount of aluminum adsorbed Δc_{Al} (nm^{-2}) in the $AlMe_3$ reaction (a) on alumina at 150 °C (○ Puurunen et al.[216]) and (b) on silica at 150 °C (□ Puurunen et al.[209]) or 250 °C (◇ Uusitalo et al.[210]). The OH surface concentrations (nm^{-2}) are shown as crosses for reference (alumina: × Puurunen et al.;[216] silica: × Puurunen et al.[209] and + Haukka et al.[1190]). The confidence limits represent one standard deviation.

deed decreases the amount of aluminum Δc_{Al} chemisorbed in the $AlMe_3$ reaction on alumina[216,262] and silica,[209,210,262] as shown in Figure 21. Increasing the heat-treatment temperature concurrently decreases the surface OH group concentration,[209,216,1190] as also indicated on the figure. Moreover, the quantitative values and temperature dependency of the amount of aluminum Δc_{Al} chemisorbed on alumina (Figure 21a) and the GPC Δc_{Al} in the $AlMe_3/H_2O$ process (Figure 19) agree.[1191] The $AlMe_3$ reaction on alumina subjected to a controlled heat-treatment therefore seems to represent the $AlMe_3$ reaction in the steady regime of the $AlMe_3/H_2O$ process. This representativeness is as expected, because in both cases $AlMe_3$ reacts with an Al_2O_3 surface. 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.[209,216,221,237,291,292,1097] This conclusion originates from the fact that the methyl group content settles to approximately a constant value after saturation has been attained,[209,210,216,291,292,1192] as illustrated in Figure 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^{-2}), the amount of methyl groups adsorbed is approximately constant (5–6 nm^{-2}).

Of the three models developed for analyzing steric hindrance in self-terminating reactions in ALD (Section III E), only Model III has been applied for the $AlMe_3$ reaction:[237] Model I has never been applied and Model II seems not to be applicable.[1193] The maximum theoretical amount of methyl groups adsorbed according to Model III is 7.2 nm^{-2},[209,237,1128] calculated from the van der Waals radius of methyl groups of 0.20 nm.[1194] The observed amount of methyl groups adsorbed is about 70–80% of this theoretical maximum, corresponding to a ligand coverage θ of 0.7–0.8. This ligand coverage is consistent with the conclusion that saturation of the $AlMe_3$ reaction is caused by 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.[209,237,1128]

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 Δc_{Al} adsorbed in the $AlMe_3$ reaction increases, the amount of methyl groups adsorbed Δc_{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 $c_{(O)H}$, as shown in Figure 22.[262] The amount of aluminum adsorbed Δc_{Al} (nm^{-2}) on oxide substrates (alumina, silica) increases linearly with the OH surface concentration $c_{(O)H}$ (nm^{-2}):

$$\Delta c_{Al} = a + b c_{(O)H} \approx 1.68 + 0.37 c_{(O)H}. \qquad (24)$$

Even in the absence of OH groups, aluminum is deposited ($a > 0$), a fact consistent with dissociative (or associative) reactions of $AlMe_3$ (Section IV C). In dissociation or association, the Me/Al ratio is three, and the a (nm^{-2}) in Equation 24 expectedly corresponds to one third of the number of methyl groups adsorbed at low surface OH group concentrations (Figure 22b). In contrast to what would be expected on the basis of Equation 15, there is no one-to-one correspondence between Δc_{Al} and $c_{(O)H}$ ($b \neq 1$). 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 Δc_{Me} to be about constant (Section IV E): three OH groups are needed to release the three methyl groups of one $AlMe_3$ molecule as methane, and thereby to attach one additional aluminum atom to the surface.

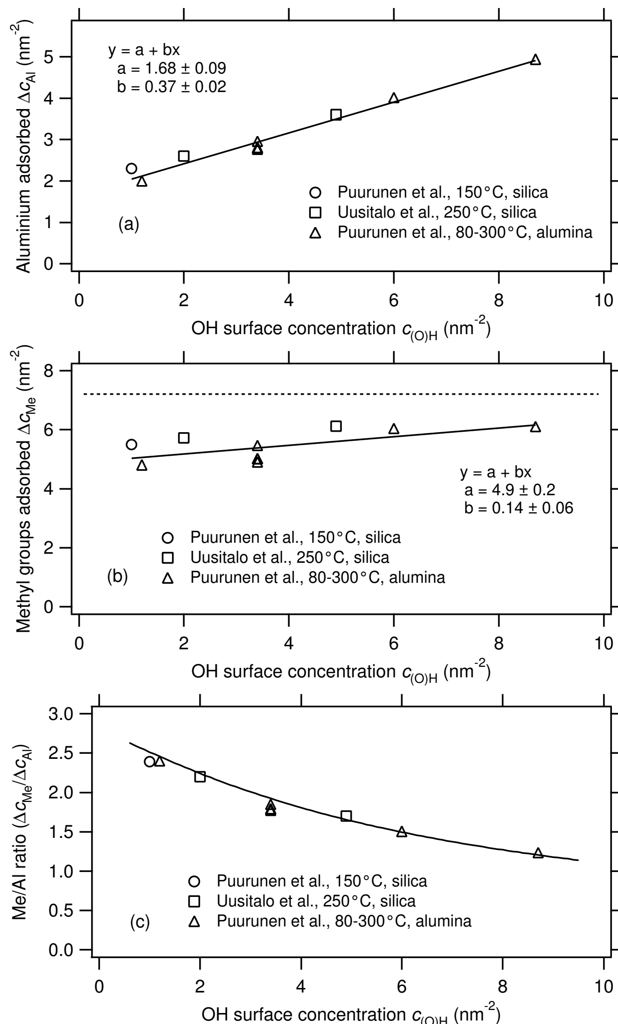


Figure 22: Effect of the surface OH group concentration $c_{(O)H}$ on the amount of material chemisorbed in the $AlMe_3$ reaction on alumina and silica substrates:[262] (a) amount of aluminum atoms adsorbed in the reaction Δc_{Al} (nm^{-2}), (b) methyl group concentration after the reaction Δc_{Me} (nm^{-2}), and (c) the average methyl/aluminum (Me/Al) ratio in the adsorbed species ($\Delta c_{Me}/\Delta c_{Al}$). Data from Puurunen et al.[216] for alumina and Puurunen et al.[209] and Uusitalo et al.[210] for silica, for $AlMe_3$ reaction at the indicated temperatures. The OH surface concentrations are from Puurunen et al.[216] for alumina and Puurunen et al.[209] and Haukka et al.[1190] for silica. In panels a and b, 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^{-2} according to Model III.[237,1128]

The values of the parameters a and b in Equation 24 are consistent the reaction scheme[192,195,196,209,216,237,1089,1164] that $AlMe_3$ 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 Equation 24 is further illustrated in Figure 23, for the situations after the completion of the self-terminating $AlMe_3$ reaction with oxide substrates with different surface

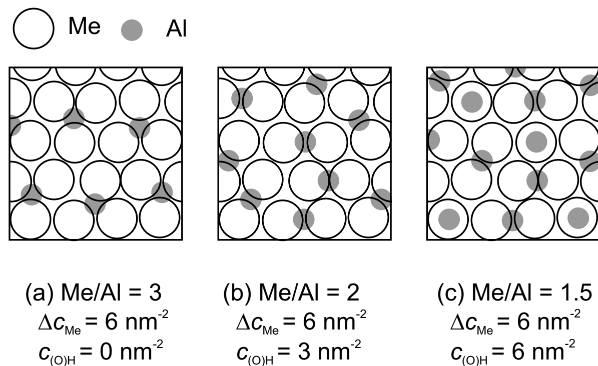


Figure 23: Illustration of the physical situation corresponding to Equation 24: number of aluminum atoms Δc_{Al} and methyl groups Δc_{Me} adsorbed in the self-terminating $AlMe_3$ reaction on surfaces with different OH group concentrations $c_{(O)H}$, resulting in average Me/Al ratios of (a) 3, (b) 2, and (c) 1.5. The squares represent an area of 3 nm^2; the methyl groups are drawn in scale ($r_{Me} = 0.2$ nm^{-2}). The small dependency the number of adsorbed methyl groups has on the surface OH group concentration [Figure 22(b)] has been neglected for simplicity.

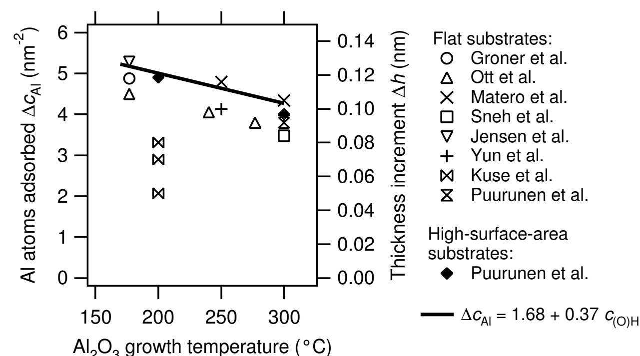


Figure 24: The correlation of Equation 24, marked as a solid line, is in line with the GPC in the $AlMe_3/H_2O$ process (data points as in Figure 19). The GPC values for the correlation were calculated assuming that $c_{(O)H}$ decreases linearly with temperature from 9 nm^{-2} at 200 °C to 7 nm^{-2} at 300 °C.[1195]

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 Figure 24, the GPC calculated with Equation 24 [assuming that $c_{(O)H}$ decreases linearly with temperature from 9 nm^{-2} at 200 °C to 7 nm^{-2} at 300 °C (Ref. 1195)] agrees with the experimental values.

G. Kinetics of the reactions

The kinetics of the $AlMe_3$ and H_2O reactions during the $AlMe_3/H_2O$ process have not been thoroughly investigated. Some qualitative and quantitative information on the kinetics exists or can be obtained by critically investigating published results.

Recent in situ mass spectrometry (MS) and quartz crystal microbalance (QCM) investigations[211,217] contain qualitative kinetic information of the $AlMe_3/H_2O$ process. These investigations were carried out (mostly) under conditions where the methane-producing ligand exchange reactions of $AlMe_3$ and H_2O reactions had been completed.[211,215,217,220] However, as described below, the reactions had not yet completely self-terminated. The main results obtained in these investigations by the MS technique have been collected in Figures 25 and 26. Results only up to a processing temperature of 300 °C are shown because of the decomposition of $AlMe_3$ at higher temperatures.[216,1189] Re-interpreting these results, to follow, indicates that the ligand exchange reactions are completed faster than dissociation in the self-terminating reactions of both $AlMe_3$ and H_2O during $AlMe_3/H_2O$ ALD.

Extracting qualitative kinetic information from the results for the H_2O reaction needs some re-interpretation. It is possible to investigate the H_2O reaction in $AlMe_3/H_2O$ 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 $AlMe_3/H_2O$ 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.[215,217,220] The fact that the amount of hydroxyl groups increased with increasing water dose [Figure 25(b)] reveals the incomplete H_2O reaction. Because at the same time the methane production had stopped,[211] qualitative kinetic information exists for the water reaction: the reaction has been investigated under conditions where the methane-producing ligand exchange reaction of water (Equation 20) has been completed, but the dissociation of water (Equation 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 for the $AlMe_3$ reaction needs additional re-interpretation. It seems to be possible to investigate the $AlMe_3/H_2O$ process also under conditions where the ligand exchange reaction of $AlMe_3$ has terminated but other reactions have not. With increasing temperature, the GPC *increased* in the experiments of Juppo et al. [Figure 25(a)],[211] whereas in most investigations the GPC has *decreased* (Figure 19). The increase in GPC[211] came mostly from that more material was deposited during the $AlMe_3$ reaction, and the amount of methyl groups present on the surface after the $AlMe_3$ reaction increased with increasing processing temperature [Figure 25(c)]. At saturation, however, the methyl group concentration should be approximately constant (Section IV E). For unsaturated reactions, increasing reaction temperature increases the amount of material adsorbed, because reactions (Equation 7) as well as mass transport get faster. Saturation was not confirmed in the experiments of Ref. 211, except that the methane production from ligand exchange reactions had been completed,[211] and it seems that the $AlMe_3$ reaction had not fully saturated. Consequently, qualitative kinetic information exists also for the $AlMe_3$ reaction: the reaction has been investigated under conditions where the ligand exchange reaction of $AlMe_3$ (Equations 15, 17) has been completed, but the dissociation (Equation 19) has not. Ligand exchange reaction of $AlMe_3$ is

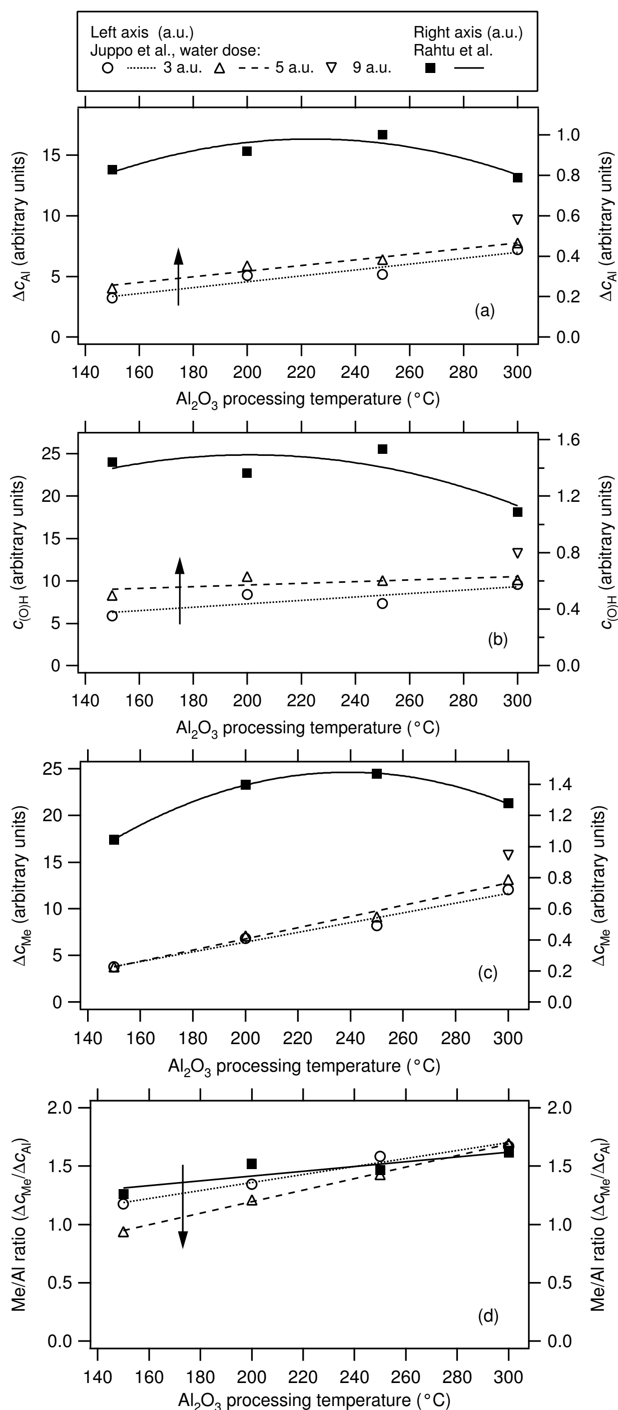


Figure 25: Summary of the in situ MS results for the $AlMe_3/H_2O$ process of Juppo et al.[211] (open symbols, left axis) and Rahtu et al.[217] (black squares, right axis): (a) total amount of methane produced during a reaction cycle divided by three, proportional to the GPC Δc_{Al}, (b) the amount of methane produced during the $AlMe_3$ reaction, proportional to the surface OH group concentration before the $AlMe_3$ reaction $c_{(O)H}$, (c) the amount of methane produced during the H_2O reaction, proportional to the methyl group concentration after the $AlMe_3$ reaction Δc_{Me}, and (d) Me/Al ratio on the surface after the $AlMe_3$ reaction, obtained by dividing Δc_{Me} [panel (c)] with Δc_{Al} [panel (a)]. The results of Juppo et al. obtained for the shortest water pulses are not shown, because in them, the methane-producing reactions had not saturated.[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 Juppo et al. (left axis) were assumed to correspond to 1.5 (normalized) units of Rahtu et al. (right axis).

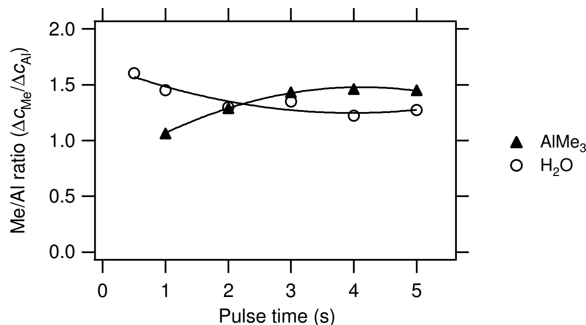


Figure 26: Effect of $AlMe_3$ and H_2O pulse times to the average Me/Al ratio after $AlMe_3$ reaction with alumina, as reported by Rahtu et al.[217] The $AlMe_3$ and H_2O reactions were saturated after a pulse time of about 3 s.

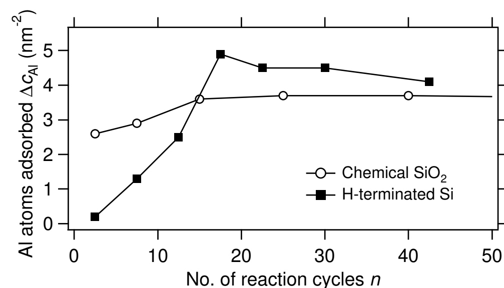


Figure 27: GPC in the $AlMe_3/H_2O$ process at 300 °C as a function of the number of ALD reaction cycles when a chemical SiO_2 rich in OH groups and a hydrogen-terminated silicon are used as substrates. Data from Zhao et al.[1176]

therefore evidently completed faster than dissociation.

The investigations of Rahtu et al.,[217] George and co-workers,[195,196] and Elam et al.[227] support the interpretation made here that ligand exchange reaction of $AlMe_3$ is completed faster than dissociation. According to the results of Rahtu et al.,[217] for unsaturated reaction, the average Me/Al ratio of the adsorbed species is lower than when the $AlMe_3$ reaction is allowed to go to completion (Figure 26). Therefore, ligand exchange reactions, which give a lower Me/Al ratio, seem to occur earlier than dissociation. George and co-workers[195,196] showed by infrared analysis that, in the beginning of the $AlMe_3$ 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.[227] also found qualitative evidence by in situ MS analysis for two kinetic regimes in the $AlMe_3$ reaction, although they did not comment on the types of reactions occurring.

Quantitative kinetic information exists for the $AlMe_3/H_2O$ process for narrow temperature and pressure ranges. Soto et al.[192] investigated the process on flat substrates in ultrahigh vacuum (UHV) at room temperature. They modelled the $AlMe_3/H_2O$ process with three reactions:[192] (i) the ligand exchange reaction of $AlMe_3$ 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 $||AlMe_2$ species, and (iii) the ligand exchange reaction of water in the second half-reaction with the second methyl group, now in a $||$Al(Me)OH species. The kinetics were described similarly as in Section III B assuming irreversible reactions. According to Soto et al.,[192] the probability that the reactions (i), (ii), or (iii) occur when $AlMe_3$ or H_2O molecules hit the surface at room temperature are 0.01, 0.25 and 0.009, respectively. Dillon et al.[196] investigated the $AlMe_3/H_2O$ process on high-surface-area substrates at 227 °C and 0.01 Torr. They modelled the $AlMe_3/H_2O$ process with reactions 15 and 16, assuming irreversible adsorption as in Section III B. Dillon et al.[196] extracted rate constants k_a for $AlMe_3$ reaction of 0.0076 s^{-1} and H_2O reaction of 0.029 s^{-1}, where the constants are given for 227 °C and 0.01 Torr.

H. Effect of the number of cycles on the GPC

The GPC in the $AlMe_3/H_2O$ 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.[246,1176] On silicon dioxide as substrate, the GPC increases with the number of cycles, and the process seems to follow Type 1 substrate-inhibited growth [Figure 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 the constant value[1176]. Thus, the process follows Type 2 substrate-inhibited growth [Figure 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 $AlMe_3/H_2O$ process at 300 °C on the silicon dioxide substrate, the surface OH group concentration $c_{(O)H}$ is expected to start from about 3–5 nm^{-2},[1190,1196] and to increase with deposition to the value characteristic for aluminum oxide, about 7 nm^{-2}.[216,1195] The Si–H bonds on hydrogen-terminated silicon appear not to react with the $AlMe_3$ and H_2O reactants.[246] The characteristic type of GPC curve is explained by that $AlMe_3$ reacts initially with defect sites on the hydrogen-terminated silicon substrate, after which Al_2O_3 islands begin to deposit.[239,240,246,247] Furthermore, the Al_3O_3 islands catalyze the oxidation of hydrogen-terminated silicon surface to form reactive SiO_x species.[239,240,246,247]

I. Growth mode

The growth mode in the $AlMe_3/H_2O$ process has not been systematically investigated. The fact that smooth layers with the expected material density are obtained[198,199] indicates that the growth mode is generally probably close to two-dimensional. On hydrogen-termination silicon as substrate, however, island growth occurs.[246] Islands of ALD-grown Al_2O_3 are revealed both through transmission electron microscopy and through growth mode modeling.[246]

J. Summary

The $AlMe_3/H_2O$ process can be summarized as follows. $AlMe_3$ reacts through ligand exchange with practically all surface OH groups, releasing methane. $AlMe_3$ reacts also through dissociation with surface oxygen bridges. The ligand exchange reaction is completed first, after which the dissociation is completed. The $AlMe_3$ 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. H_2O reacts through ligand exchange with practically all surface methyl groups, releasing methane. H_2O 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 H_2O 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 $AlMe_3/H_2O$ 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 $AlMe_3$ chemisorption) and the surface OH group concentration is known, the $AlMe_3$ 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 non-standard, problematic terminology. The effect of experimental conditions on the surface chemistry is not clear,[67] but one needs to understand this effect to interpret together the results of investigations made at different conditions. To assist multidisciplinary surface chemistry investigations, Section V A discusses the problematic historical assumptions, Section V B the problematic terminology, and Section V C 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[237,247,432,468,488,499–501,1120,1127,1128,1140,1151,1178] but only to a limited extent in existing reviews.[3,6–66]

1. *GPC of a monolayer*

Perhaps the oldest of these problematic historical assumptions is GPC of a monolayer. According to this assumption, ALD should lead to 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[2,79] and has been thereafter widely adopted.[7–9,11,13,17,25–27,31,36,54,62,63,66,318]

In real ALD processes, the GPC in ALD processes is typically less than a monolayer.[40,62,63,246,488,984,1178,1197] This is also true for the $AlMe_3/H_2O$ process, which is otherwise known as a rather ideal ALD process (Section IV). Recent models[1127,1128] 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 (Figure 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,[7–9,11,13,17,23,25–27,31,32,36,38,39,51,205,1198] and still often is,[3,55,58,59,63,64,91,1199] 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 (Sections 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.[40,63,64,246,488,984,1178]

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.[11,30] 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 $AlMe_3/H_3O$ ALD process is an example of a process where the GPC decreases with temperature due to decrease in OH surface concentration

(Section IV F). Correspondingly, the assumption of a constant GPC with temperature seems mostly abandoned.[3,36]

4. Two-dimensional growth mode

Two-dimensional growth mode is also an old assumption in ALD,[2] and 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,[9,13,15,19,21,23,26,318] even though island growth (in the beginning of ALD growth) was reported already early.[154] Thereafter, island growth has been observed in many processes.[246,247,292,488,544,558,1077]

A special deviation from the expected growth mode is the yet unexplained particle formation in the $TiCl_4/H_2O$ and $ZnEt_2/H_2O$ 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.[419,421,600,818,1135,1169]

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 non-standard 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 ”growth rate (amount/cycle).”[3,25,26,31,32,40,59,63,66,126,927,985,1178] This term is non-standard, however: the amount of material deposited per reaction cycle is no 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 vs. 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 non-standard 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 non-constant [see Figure 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.[992,1178,1200]

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[8] 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.[246,247,1140] 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.[199,237,292,333,984,1127,1128,1140,1177] 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,[246,523,527,819] 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 Section V A. The fact that many different names have been used to refer to the same technique (Table II) testifies of 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, pressures, 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 Section 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 over-interpreted, however, these experiments can also lead to misleading conclusions. For example, the amount of methyl groups chemisorbed in the $AlMe_3$ reaction has been suggested to decrease with increasing temperature[40,199] on the basis of TPD experiments made after the $AlMe_3$ reaction at room temperature.[196] Experiments made for the $AlMe_3$ reaction at different temperatures have indicated, however, that temperature has almost no effect on the number of methyl groups adsorbed (Figure 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 (Section III A). There are ALD reactions,[212,1165] 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 re-adsorb onto the surface. For example, the HCl released in the reaction of metal chlorides with OH groups re-adsorbs on the surface, and in this case the partial pressure of HCl affects the main adsorption process.[135,139,143,432,433,1201] Such re-adsorption 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.[3,211] 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 $AlMe_3/H_2O$ process, similar reactions have been concluded to occur in UHV and at higher pressures.[192]

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 is the same. Moreover, differences can be induced for example by thermal or chemical treatments. The reaction chemistry investigation for the $AlMe_3$ reaction with high-surface-area substrates, discussed in Section 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.,[141] in turn, illustrates 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 CrO_2Cl_2. The work of Ferguson et al.,[214,337] who investigated the $SiCl_4/H_2O$ process on boron nitride particles, illustrates inherent differences. The SiO_2 film deposited only patch-like on the basal planes of the boron nitride particles, whereas the edges of the particles were conformally coated.[214,337] Evidently, the basal planes of boron nitride contained fewer sites reactive with the $SiCl_4$ molecule than the edges of the particles. Some substrates may mostly consist of edges areas, 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.[109,318,442,703,986,1202]

The ALD process modifies the chemical composition of the surface through depositing material. In reaction mechanism investigations on high-surface-area materials, the number of ALD reaction cycles has been typically below ten.[209,216,291,292,344,418,419,421,434,521,526,527,530,548,552,554,557,818,819,873,1 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.[211,217,422,425,426,443,487,518,827,844,867,868,1082]

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 through allowing each reaction to go to completion is a prerequisite for materials growth by the ALD technique. To compare different experiments in a meaningful way, one must know whether the experiments were made at saturated or unsaturated conditions. If it is not known whether saturation had occurred, comparing different experiments is often of little value. For example, in situ investigations made for the $AlMe_3/H_2O$ process provided important qualitative information of the reaction kinetics, but only after realizing that the investigations were made for unsaturated conditions (Section IV G). In other types of investigations, GPC values both higher and lower than the generally accepted trend (Figure 19) have been reported because of insufficient purge or evacuation[198] and unsaturated reactions,[200,234] 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,[1159,1204,1205] the use of high-surface-area substrates lengthens the processing times compared to flat substrates.[1206] 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,[3,211,217] 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 $AlMe_3/H_2O$ process on high-surface-area substrates and flat substrates (Figure 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, non-saturating 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.[197,216,468,475,922,942,944] 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[3,201,1207] and the fact that close to 100% step coverage can be obtained by ALD in deep trench structures.[205,1204]

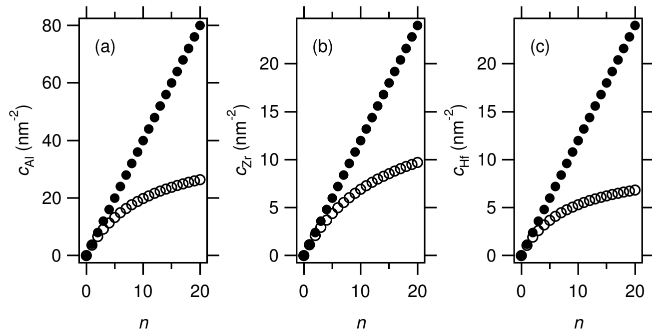


Figure 28: Illustration of the importance of taking into account the mass of the deposited layer when calculating the GPC on high-surface-area substrates. Difference between Eqs. 25 (full symbols) and 26 (open symbols) for a substrate with a specific surface area of 300 m^2 g^{-1}: (a) Al_2O_3, assuming a constant GPC $\Delta c_{Al} = 4$ nm^{-2}; (b) ZrO_2, assuming $\Delta c_{Zr} = 1.2$ nm^{-2}; and (c) HfO_2, assuming $\Delta c_{Hf} = 1.2$ nm^{-2}. n indicates the number of ALD reaction cycles.

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 ($g_M\, g_{samp}^{-1}$). To compare the results with those of other ALD investigations, the results are converted to the amount metal M atoms adsorbed per unit surface area of the substrate, c_M (nm^{-2}). Typically the specific surface area of the substrate, S (m$^2\, g_{subst}^{-1}$), 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 sample (the substrate and the adsorbed material together) m_{samp} (g_{samp}) to the mass of the substrate only m_{subst} (g_{subst}) is needed for calculating c_M:

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

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

If term m_{samp}/m_{subst} is ignored, and the c_M is calculated from a simplified equation:

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

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,[79,98] 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 Figure 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.

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[69] 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.
[70] In this review, ALD is defined to be based on gas–solid reactions. Analogous experiments have been made from liquid phase [e.g., Lindroos et al., Appl. Surf. Sci. **75**, 70 (1994)] and electrochemically [e.g., 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.
[71] Instead of the reactant of Reactant B, Step #3 may be, for example, a thermal treatment (see Table III).
[72] 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.
[73] Some ALD processes consist of repeating the self-terminating reactions of more than two reactants, for example, the $WF_6/BEt_3/NH_3$ (Et = ethyl) process to grow WC_xN_y [e.g., Martin Hoyas et al., 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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1147 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) non-saturating 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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1162 One can visualize the ligand exchange reaction in two ways: either the central metal atom of the ML_n compound (or of the ML_z species) exchanges one of its ligands L with a bond to the surface; or the surface exchanges its ligand –a with another "ligand," a MZ_z species.

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1172 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 bonded to surface atoms and thus are not free to move in the same way as truly physisorbed molecules.

1173 Desorption of the adsorbed species during purging periods has also been suggested to account for the GPC of less than a monolayer.[1117,1121,1123,1153] This suggestion, however, contradicts the essential requirement of irreversibility for the self-terminating ALD reactions (Section III A).

1174 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.

1175 In this work, 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. 11,30).

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