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Feature Article

Advanced electronic and optoelectronic materials by Atomic Layer Deposition: An overview with special emphasis on recent progress in processing of high-*k* dielectrics and other oxide materials

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The principle and practice of Atomic Layer Deposition (ALD) are described with special emphasis on the advantages of the method for processing of thin films for advanced applications in electronics, catalysis and sensor technology. The examples of ALD-processed materials include ZrO_2 and other high-*k* dielectrics especially the rare earth oxides, SnO_2 for gas sensors and ZnO for optoelectronics. The various precursor chemistries leading to these materials are discussed.

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1 Introduction

Atomic Layer Deposition (ALD), originally called atomic layer epitaxy (ALE), was developed in the 1970s by Suntola and Antson [1] to meet the needs of producing high-quality, large-area flat panel displays based on thin film electroluminescence (TFEL). The core of a TFEL device consists of a large band-gap, doped semiconducting layer (e.g. ZnS:Mn) surrounded from both sides by insulating oxide layers (aluminum titanium oxide, ATO) which all could be fabricated by ALD.

The ALD processes and their applications in thin film technology have been frequently reviewed [2], most recently in a comprehensive manner by Ritala and Leskelä [3, 4]. The development of TFEL devices marked the beginning of not only oxide ALD but also the industrial applications of ALD [5]. Current worldwide interest in ALD, however, stems mainly from the drive by semiconductor industry in integrated circuit manufacturing to decrease feature sizes while increasing aspect ratio and complexity. This requires the deposition of very thin, conformal, and highly-insulating oxide layers in the nanometer range. The so-called high-*k* oxides are refractive materials not easily processed in a controlled manner by thin film deposition techniques other than ALD. Another major application area in microelectronics is the transition-metal nitride and metal ALD. Current status of these applications has been recently reviewed [6]. Also it should be mentioned that thin film head reader devices for data storage exploiting ALD-grown alumina films have recently been announced to be in industrial production [7].

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2 Principle of ALD

An ideal ALD growth proceeds by exposing the substrate surface alternatively to the different precursors. It differs from chemical vapor deposition (CVD) by keeping the precursors strictly separated from each other in the gas phase.

An ALD-growth cycle can be divided into four steps (Fig. 1):

1. exposure of the substrate surface to pulse of the first gaseous precursor and chemisorption of the first precursor onto the substrate
2. inert gas purge to remove the excess of unreacted precursor
3. introduction of the second precursor followed by surface reaction to produce the desired thin film material
4. inert gas purge to expel gaseous reaction by-products.

It should be noted that only in an ideal case a monolayer (ML) is formed. In practice, due to steric hindrances, one reaction cycle usually produces only a distinct fraction of a monolayer, e.g. up to 1/2 ML.

A useful concept, first introduced by Suntola et al. [8], is the so-called 'ALD-window' indicating the temperature range where thin film growth proceeds by surface control in an ALD-mode (Fig. 2). Outside the ALD-window, the growth is limited by precursor condensation, decomposition, and desorption or by insufficient reactivity. The surface-controlled ALD mechanism is corroborated by the fact that the precursor pulse length (dose) has no effect on the growth rate provided that the surface is saturated, i.e. all available surface sites are occupied by adsorbed precursor molecules (steps 2 and 4 in Fig. 1). However, many recently studied organometallic precursors for oxide films do not exhibit a distinct ALD window and thus the deposition rate in these processes is dependent on the temperature, but nevertheless they can still be used for self-limiting ALD processes. This has been explained by their high reactivity towards reactive surface sites, typically -OH groups, whose amount is dependent on the deposition temperature [9].

Because of the self-limiting and sequential operating mode of ALD, its practical advantages include:

- accurate and simple thickness control (growth per cycle)
- no need to control the reactant flux homogeneity (surface saturation), possibility for *in situ*-generation of precursors

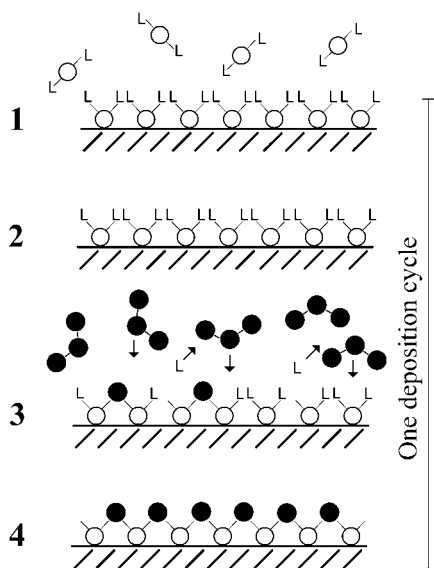


Fig. 1 Schematic illustration of an ALD-growth cycle (1–4) leading to the formation of an imaginary binary oxide film of metal (○) and oxygen (●). L refers to the precursor ligand.

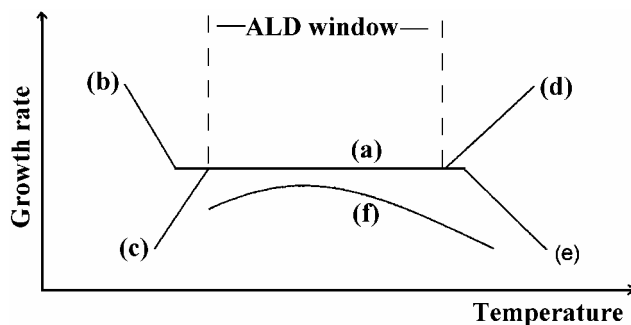


Fig. 2 Scheme of (a) an ALD processing window limited by (b) precursor condensation, (c) insufficient reactivity, (d) precursor decomposition and (e) precursor desorption. If the deposition rate is dependent on the number of available reactive sites as in (f), actual ALD window cannot be observed.

- large area uniformity, straightforward scale-up
- excellent conformality (step coverage, coating of porous materials)
- dense and pinhole free films
- facile doping and interface modification
- low processing temperature by suitable selection of precursor chemistry
- elimination of gas-phase reactions.

There are some limiting factors in the application of ALD to thin film processing, however, which include:

- generally rather low deposition rates
- some difficult elements, e.g. Ba (for YBCO) and Si (for SiO₂)
- processing of ternary and more complicated compounds requires the constituent precursors to volatilize and then react at a common temperature ('ALD window') because during the growth process the reactor temperature cannot be changed
- in some cases low crystallinity due to the low deposition temperature.

3 Precursor chemistry – Key to a successful ALD process

There are some general requirements for a good ALD precursor which include the following:

- sufficient volatility at the deposition temperature
- no self-decomposition allowed at the deposition temperature
- precursors must adsorb or react with the surface sites
- sufficient reactivity towards the other precursor, e.g. H₂O
- no etching of the substrate or the growing film
- availability at a reasonable price
- safe handling and preferably non-toxicity

One of the major advantages in ALD precursor chemistry compared with CVD, for instance, is the fact that because ALD is based on surface saturation exact precursor dosage is not needed. The only requirement is that there are enough precursor molecules to cover the adsorption sites on the surface; the excess will be blown away by the inert gas purge. This makes it possible to use *in situ*-generation of the precursors and thus have a fresh supply of otherwise instable precursor molecules onto the substrate surface [10].

The volatile metal-containing precursors which satisfy the ALD criteria fall into four main categories: (i) halides, (ii) β -diketonate-complexes, (iii) alkoxides and (iv) true organometallics, viz. metal alkyls and cyclopentadienyl-type compounds. Also amido complexes have recently gained attention. Occasionally, other compounds have been used, for instance, metal nitrates. At the early stages of ALD technology [11], the halides and β -diketonates were the most frequently used precursors but more recently the emphasis has moved towards the true organometallics. Figure 3 shows examples of the various precursor types used. Besides volatility and reactivity, there are additional issues, however, which need to be taken into account when choosing the precursor chemistry, one of them being the impurities left into the film.

The most commonly used non-metal precursors, other than oxygen sources discussed in chapter 4, include NH₃, amines and hydrazine for nitride films and hydrides such as H₂S, H₂Te, PH₃ and AsH₃.

4 Oxide materials by ALD

In general, metal oxides offer a variety of interesting properties for technical applications. The oxides may be insulating, semiconducting, conducting or even superconducting. They can also be used as catalysts, light-emitting phosphors, or gas sensors. By doping, the properties can be changed or enhanced.

ALD is generally well-suited for the deposition of oxide thin films and overlayers for various applications [12]. As an oxygen source, to react with the volatile metal source, water is most frequently em-

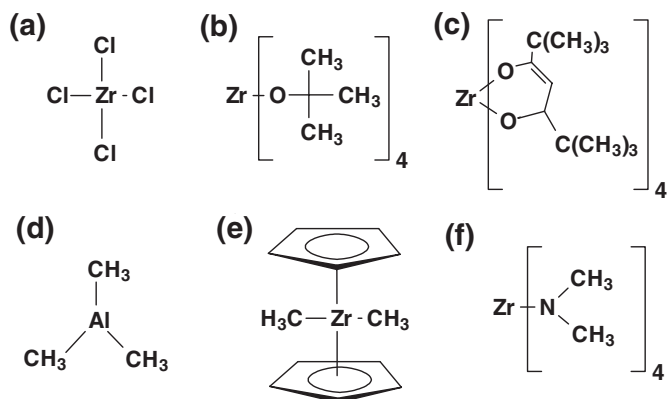


Fig. 3 Examples of ALD precursors for thin films: (a) halides, (b) alkoxides, (c) β-diketonates, (d) organometallics, (e) organometallic cyclopentadienyl-type compounds and (f) amido complexes.

ployed. For instance, water readily reacts with $\text{Al}(\text{CH}_3)_3$ to form amorphous alumina layer on native oxide-free silicon substrate without an interfacial layer [13]. In contrast, the often studied $\text{ZrCl}_4/\text{H}_2\text{O}$ process on HF-etched Si creates inhomogeneous microstructure and interfacial layer formation [14]. Other oxygen sources used include H_2O_2 , O_2 , O_3 as well as oxygen plasma. Ozone is a strong oxidizer producing dense films and furthermore for some weakly reactive precursors, such as the β-diketonates, ozone (or H_2O_2) remains the only alternative to obtain the metal oxides and at the same time reduce the impurities to a reasonable level. Still, the interfacial oxide formation increases the equivalent oxide thickness (EOT) value, and therefore O_3 has not been considered well-suited for high- k oxide depositions. For instance, in the case of Y_2O_3 films grown by the $\text{Y}(\text{thd})_3/\text{O}_3$ ALD process (thd = 2, 2, 6, 6-tetramethyl-3, 5-heptanedione), 1.1–1.4 nm thick interfacial SiO_x layer was formed [15]. However, quite recently Park et al. [16] have shown that most electrical properties were in fact improved by O_3 as compared to H_2O when depositing HfO_2 from HfCl_4 . Also in the case of alumina by ALD, the dielectric properties were improved by the use of ozone [17].

An interesting example of smart precursor chemistry is the catalytic process of silica nanolaminates described by Hausmann et al. [18]. In this study the growth rate obtained for $\text{SiO}_2/\text{Al}_2\text{O}_3$ was extremely high (12 nm/cycle or 32 ML/cycle). The ALD-like process was based on catalytic mechanism yielding SiO_2 films of high conformality. This kind of new innovation can lead to completely new application areas and contradict the common belief of ALD being inherently too slow a technique.

Besides the binary oxides, also multicomponent oxides, such as SrTa_2O_6 [19] or ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ [20] have been deposited by plasma enhanced ALD (PEALD). In this review, however, we concentrate on the binary high- k gate oxides, including rare earth oxides. In addition, two relevant examples of other ALD-grown binary oxides, namely ZnO and SnO_2 , are presented here.

4.1 Zinc oxide

Zinc oxide is an attractive optoelectronic material. It has a wide band gap (3.3 eV) which is tunable within 2.8–4 eV by alloying. Er-doping of ZnO leads to the 1.54 μm emission. ZnO is used also as buffer layers in solar cells or, when doped, as transparent conductor. Devices exploiting the properties of ZnO include piezoelectric transducers and varistors [21]. Another application of ZnO is its use as antireflection coating. Due to small lattice mismatch ZnO is also considered as the most promising substrate material for GaN [22]. Quite recently, it was discovered that Mn-doped ZnO exhibits ferromagnetism above room temperature [23].

First ALD process of ZnO was based on zinc acetate and H_2O [24]. The unexpectedly high growth rate of ZnO can be related to the formation and geometry of the tetrameric, volatile oxometallate complex $\text{Zn}_4\text{O}(\text{Ac})_6$. X-ray crystallography [25] has revealed that $\text{Zn}_4\text{O}(\text{Ac})_6$ is a well-tailored molecular

model of ZnO as the Zn–O coordinations in zinc acetate and zinc oxide resemble each other [26]. The high growth rate of ZnO with $\text{Zn}_4\text{O}(\text{Ac})_6$ as precursor can be explained by the fact that one volatile $\text{Zn}_4\text{O}(\text{Ac})_6$ precursor molecule carries four Zn atoms onto the substrate.

More recently, processes based on zinc alkyls (dimethylzinc = DMZn and diethylzinc = DEZn) have been developed [27]. Because of the reactivity of the organometallics, the processes based on DMZn and DEZn and water can be operated at relatively low temperatures, *viz.* below 200 °C. The ZnO films can be easily doped by Al or B, for instance. In a comparative study [28], it has been found that ALD-processed ZnO films are highly stable compared to MOCVD films.

4.2 Tin dioxide

Due to its advantageous properties tin dioxide is a frequently applied material in optoelectronics and sensor technology, for instance. Thin films of SnO_2 can be prepared by several physical deposition methods as well as by CVD and ALD.

Tin dioxide can be deposited by ALD in a straightforward manner from simple inorganic precursors, *viz.* tin tetrachloride and water: $\text{SnCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SnO}_2 + 4\text{HCl}$ [29]. Doping by Sb, also at a sophisticated level, is possible by simply replacing one of the $\text{SnCl}_4/\text{H}_2\text{O}$ cycles by a $\text{SbCl}_5/\text{H}_2\text{O}$ cycle. Thus, δ -doping was achieved and confirmed by SIMS measurements when the Sb/Sn pulsing ratio was 1:1200 [30]. Epitaxial growth of SnO_2 is possible onto a matching substrate, *viz.* sapphire (1102) [31].

For gas sensing applications, very thin films (10 nm) are desired as they exhibit the maximum sensitivity for CO detection in air. The films are assumed to function as single grain [32]. An interesting finding is that the conductivity of SnO_2 and thus its gas sensing properties can be controlled by oxygen or hydrocarbon assisted ALD [33].

5 ALD of high-*k* oxides

Many materials are currently under consideration as potential candidates for gate dielectrics for sub 0.1 μm CMOS technology. Silicon dioxide with a dielectric constant of 3.9 will be replaced by so-called high-*k* materials. Candidates for gate dielectrics include the oxides and silicates of yttrium, lanthanum, zirconium and hafnium, which have much higher dielectric constants than SiO_2 . Hf-based high-*k* dielectrics, e.g. nitrided silicates are presently considered as most promising candidates. Current status of the high-*k* gate dielectrics has been discussed by Wilk et al. [34, 35]. ALD offers probably the best way to prepare these materials as thin and uniform layers with controlled interface layer. The three most frequently studied materials in ALD high-*k* research are ZrO_2 , HfO_2 and Al_2O_3 , but other interesting materials can also be processed by ALD, including rare earth oxides as well as mixed oxides, silicates and nanolaminates of Zr, Hf and Al. However, only the deposition of ZrO_2 is considered in detail here, while the ALD of rare earth oxides will be discussed in Chapter 6. ALD processes and precursor combinations of hafnia are very similar to those of zirconia, the $\text{HfCl}_4/\text{H}_2\text{O}$ process being the most frequently studied process [36–38]. The $\text{Al}(\text{CH}_3)_3/\text{H}_2\text{O}$ process for alumina can be considered as an excellent ALD process [9, 13, 39], but unfortunately for future gate oxide applications the dielectric constant of alumina is definitely too low.

The $\text{ZrCl}_4/\text{H}_2\text{O}$ process of zirconia has previously been studied in a detailed way [14, 40–43]. However, the ZrCl_4 process has some drawbacks, which include halide contamination and interfacial layer formation increasing the overall EOT value and leading to retarded growth on H-terminated Si. Suppressing the EOT value below 1 nm is extremely difficult and careful interface engineering is needed. To achieve such low EOT values an ideal case would be to have a sharp interface between the oxide and H-terminated Si. On the other hand, it is commonly considered that ultrathin, preferably a ~0.5 nm thick SiO_x or SiO_xN_y interfacial layer is beneficial in order to achieve low EOT value with good electrical properties. For these reasons it is important to study other precursor combinations and techniques, such as plasma enhanced ALD (PEALD).

The ZrO_2 thin films have also been deposited using ZrI_4 as metal precursor and a mixture of H_2O and H_2O_2 as oxygen source [44]. The use of iodide precursor for Zr leads to a somewhat different surface

chemistry, and therefore to a different phase composition. A comparative study between $\text{HfCl}_4/\text{H}_2\text{O}$ and $\text{HfI}_4/\text{H}_2\text{O}$ processes showed that HfO_2 thin films deposited from iodide precursor had slightly better electrical properties, however [37]. Unfortunately, the $\text{ZrI}_4/\text{H}_2\text{O}$ process is not an entirely self-limiting process, probably due to the partial decomposition of thermally labile ZrI_4 [44].

Besides halides also the alkoxides of zirconium have been considered in detail as ALD precursors, zirconium tert-butoxide, $\text{Zr}[\text{OC}(\text{CH}_3)_3]_4$, being the most carefully studied volatile compound [45–48]. In this case, both water and oxygen can be used as the oxidizer, but the oxygen process requires the use of higher deposition temperatures. ALD processes based on zirconium tert-butoxide can be applied to deposit conformal and uniform ZrO_2 thin films, but it seems, that zirconium tert-butoxide decomposes and therefore the process is not self-limiting [47]. Carbon and hydrogen contents are reported to be rather high, approximately 2–6 at% and 8–23 at%, respectively, depending on the deposition temperature and precursor combination [45, 48]. Replacing two butoxide groups in $\text{Zr}[\text{OC}(\text{CH}_3)_3]_4$ by dimethylaminoethoxide, $\text{OCH}_2\text{CH}_2\text{NMe}_2$, enhances the thermal stability of the complex, but does not significantly affect the properties of the resulting ALD-grown ZrO_2 films [49]. Alkyl amides is another precursor group, which is currently of interest in zirconia ALD studies. Metal amides are also considered as promising precursors because of their volatility and reactivity. So far, ZrO_2 films have been prepared by ALD using $\text{Zr}(\text{NMe}_2)_4$, $\text{Zr}(\text{NEtMe})_4$ or $\text{Zr}(\text{NEt}_2)_4$ as the metal precursors, while water or oxygen have been used as the oxygen source [48, 50]. Very low deposition temperatures, even 50 °C, can be employed in the amide/water ALD processes to produce conformal ZrO_2 films [50]. Alkyl amides and alkoxides have also been used as Zr-precursors in plasma enhanced ALD. In the PEALD studies of zirconia, oxygen plasma was applied to activate Zr-precursors and thereupon widening the processing window and reducing impurity content [48, 51].

The true organometallics, such as cyclopentadienyl (Cp , $-\text{C}_5\text{H}_5$) compounds, offer an interesting alternative because of their reactivity and volatility. The deposition of ZrO_2 thin films has been studied using chlorine-free $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ as Zr-precursor and ozone or water as oxygen source [52, 53]. ALD-type growth was observed at the optimized ZrO_2 deposition temperature of 350 °C. Ozone as oxygen source yielded a slightly higher growth rate ($0.55 \text{ \AA cycle}^{-1}$) than water ($0.43 \text{ \AA cycle}^{-1}$). In both cases, the films were stoichiometric and uniform. Carbon and hydrogen impurities were extremely low, i.e. approximately 0.1 at%. Transmission electron microscopy and electrical measurements of the very thin (2–20 nm) ZrO_2 films grown on H-terminated Si(100) showed that the use of water leads to strong inhibition of growth and interfacial layer formation. Similar problems have been reported for the $\text{ZrCl}_4/\text{H}_2\text{O}$ ALD process [14, 40]. With ozone as an oxygen source some of the electrical properties were improved but the problematic interfacial oxide formation remained. Thus, despite the described attempts a significantly better process than that based on ZrCl_4 has not yet been developed.

Table 1 Reported ALD processes for the ZrO_2 thin films and the studied deposition temperature range.

metal precursor		oxygen source	dep. temp./°C	ref.
halides	$\text{Zr}(\text{Cl})_4$	H_2O	180–500	[14, 40–43]
	ZrI_4	$\text{H}_2\text{O}-\text{H}_2\text{O}_2$	250–500	[44]
alkoxides	$\text{Zr}(\text{O}^t\text{Bu})_4$	H_2O	150–300	[45, 46]
	$\text{Zr}(\text{O}^t\text{Bu})_4$	O_2	250–400	[47, 48]
	$\text{Zr}(\text{O}^t\text{Bu})_4$	O_2 plasma	250	[48, 51]
	$[\text{Zr}(\text{O}^t\text{Bu})_2(\text{dmae})_2]_2$	H_2O	190–340	[49]
	$\text{Zr}(\text{thd})_4$	O_3	275–500	[54]
β -diketonates	$(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$	O_3	200–500	[54]
	$(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)_2$	O_3	250–500	[53, 54]
	$(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)_2$	H_2O	200–500	[52, 53]
alkyl amides	$\text{Zr}(\text{NMe}_2)_4$	H_2O	50–500	[50]
	$\text{Zr}(\text{NEtMe})_4$	H_2O	50–500	[50]
	$\text{Zr}(\text{NEt}_2)_4$	H_2O	50–500	[50]
	$\text{Zr}(\text{NEt}_2)_4$	O_2	250	[48]
	$\text{Zr}(\text{NEt}_2)_4$	O_2 plasma	250	[48]

6 ALD of rare earth oxides

Rare earth (RE) oxides are a versatile group of materials with high application potential in various fields of technology. They are thermodynamically very stable refractory materials, therefore being of interest as protective and corrosion resistive coatings. High refractive indices (1.91–1.98 for the C-type structure) of RE oxides make them applicable in optics, e.g. as antireflection coatings [55]. In addition, RE oxides are considered as potential candidates for high- k oxides [56], because of their high relative permittivity ($\epsilon_r = 12.4$ –14.8 [57]) and stability. Because Gd_2O_3 has been reported to effectively passivate the GaAs surface [58], RE oxide films are expected to find applications in the passivation of III–V compound semiconductors as well.

ALD has been successfully applied to the preparation of various binary and ternary RE oxides, as summarized in Table 2. In the majority of ALD processes reported, volatile β -diketonate complexes have been used as the rare earth metal sources and ozone as an oxygen precursor. In a comparative study on Ln_2O_3 thin films, the growth rates of lanthanide oxides were found to be rather linearly dependent on the ionic radii of the elements. In the same study, the electrical properties of Ln_2O_3 films were studied as well, and permittivity values of around 10 were reported for all Ln_2O_3 samples [59]. So far, the only reported lanthanide oxide ALD process not based on β -diketonates was reported by Lim et al., who used the volatile $\text{N,N}'$ -di-isopropylacetamidinato metal complex, $\text{La}^{\text{I}}\text{PrNC}(\text{CH}_3)\text{N}^{\text{I}}\text{Pr}_3$, as lanthanum source [60].

Table 2 RE oxides deposited by ALD. The growth rate presented in the Table is the value obtained at optimal deposition temperature(s). phen = 1,10-phenantroline, bipy = bipyridine, iPr = isopropyl and acac = acetylacetonate.

material	metal precursor	oxygen source	deposition temp./ °C	growth rate/ Å (cycle) ^{−1}	ref.
<i>binary</i>					
Sc_2O_3	$\text{Sc}(\text{thd})_3$	O_3	335–375	0.13	[63]
	$(\text{C}_5\text{H}_5)_3\text{Sc}$	H_2O	250–350	0.75	[63]
Y_2O_3	$\text{Y}(\text{thd})_3$	O_3	250–375	0.23	[62]
	$\text{Y}(\text{thd})_3\text{phen}$	O_3	250–375	0.22	[62]
	$\text{Y}(\text{thd})_3\text{bipy}$	O_3	250–375	0.23	[62]
	$(\text{C}_5\text{H}_5)_3\text{Y}$	H_2O	200–350	1.4–1.7	[61]
	$(\text{C}_5\text{H}_4\text{CH}_3)\text{Y}$	H_2O	200–400	1.2–1.3	[61]
	$\text{La}(\text{thd})_3$	O_3	225–275	0.36	[64]
La_2O_3	$\text{La}^{\text{I}}\text{PrNC}(\text{CH}_3)\text{N}^{\text{I}}\text{Pr}_3$	H_2O	300	0.9	[60]
	$\text{Ce}(\text{thd})_4$	O_3	175–250	0.32	[65]
CeO_2	$\text{Ce}(\text{thd})_3\text{phen}$	O_3	225–275	0.42	[65]
Nd_2O_3	$\text{Nd}(\text{thd})_3$	O_3	310	0.44	[59]
Sm_2O_3	$\text{Sm}(\text{thd})_3$	O_3	300	0.36	[59]
Eu_2O_3	$\text{Eu}(\text{thd})_3$	O_3	300	0.32	[59]
Gd_2O_3	$\text{Gd}(\text{thd})_3$	O_3	300	0.31	[59]
Dy_2O_3	$\text{Dy}(\text{thd})_3$	O_3	300	0.31	[59]
Ho_2O_3	$\text{Ho}(\text{thd})_3$	O_3	300	0.25	[59]
Er_2O_3	$\text{Er}(\text{thd})_3$	O_3	250–375	0.25	[59, 66]
Tm_2O_3	$\text{Tm}(\text{thd})_3$	O_3	300	0.22	[59]
<i>ternary</i>					
LaAlO_3	$\text{La}(\text{thd})_3 + \text{Al}(\text{acac})_3$	O_3	350–375	0.39	[67]
LaGaO_3	$\text{La}(\text{thd})_3 + \text{Ga}(\text{acac})_3$	O_3	350–390	0.40	[68]
LaMnO_3	$\text{La}(\text{thd})_3 + \text{Mn}(\text{thd})_3$	O_3	250–300	0.15–0.2	[69]
LaCoO_3	$\text{La}(\text{thd})_3 + \text{Co}(\text{thd})_2$	O_3	350	0.35	[70]
LaNiO_3	$\text{La}(\text{thd})_3 + \text{Ni}(\text{thd})_2$	O_3	215–250	0.08	[71]

β -Diketonate processes have two major drawbacks, which may limit their applicability. First of all, β -diketonate complexes do not readily react with water but require the use of a stronger oxidizer such as ozone. The use of ozone can be unfavourable regarding the high- k applications because it leads to the formation of an interfacial SiO_x layer, thus increasing the EOT value. Secondly, the growth rates obtained in β -diketonate processes are rather low leading to long processing times. However, the other type of precursors applied in ALD of RE oxides, namely metalorganic cyclopentadienyl compounds, seem to be capable for overcoming these problems. The growth rates obtained are significantly higher than in the β -diketonate processes and besides water can be used as an oxygen source. For example, in the case of Y_2O_3 the growth rates reported for $(\text{CpCH}_3)_3\text{Y}/\text{H}_2\text{O}$ and $\text{Y}(\text{thd})_3/\text{O}_3$ were 1.2 and 0.23 Å (cycle)⁻¹, respectively [61, 62]. However, thermal stability of Cp-compounds is rather low compared to the β -diketonate compounds, and therefore Cp-processes have until now been developed only for Sc_2O_3 [63] and Y_2O_3 [61]. So far, all ALD-grown ternary rare earth oxides are lanthanum-based (see Table 2), and β -diketonates have been used as metal sources as in all cases.

7 Concluding remarks

ALD is now a mature technique for high-quality thin film depositions being adopted by the semiconductor industry. As shown above, ALD offers through its chemical versatility possibilities to develop new or improved materials and processes. It is especially well suited for depositing metal oxide thin films, including refractive oxides. However, new smart chemistries are needed for the precursor development.

By its inherent surface-controlled character at a molecular level, ALD represents true nanometer scale control of depositing very thin and uniform films even on complex shaped substrates.

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