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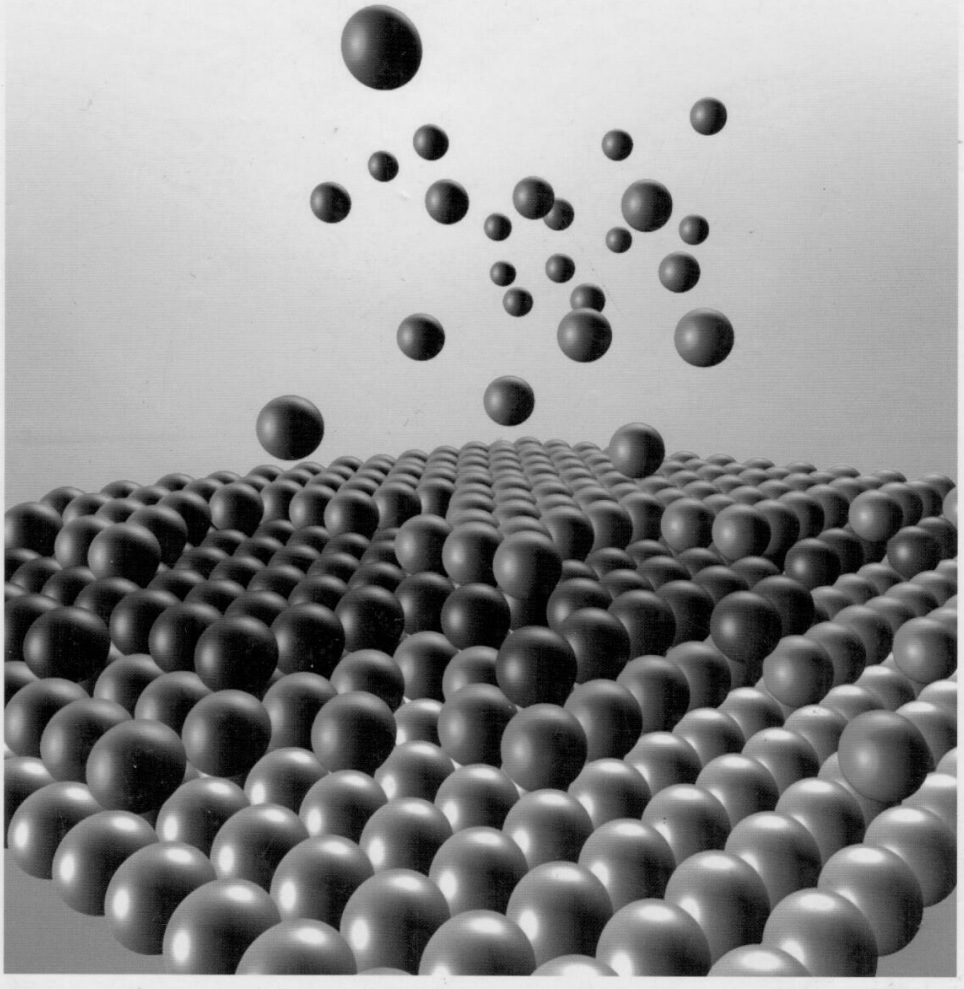
Atomic Layer Deposition of Nanostructured Materials



The Editors

Prof. Dr. Nicola Pinna
Department of Chemistry and CICECO
University of Aveiro
Campus Universitario de Santiago
3810-193 Aveiro
Portugal

and

School of Chemical and Biological Engineering
College of Engineering
Seoul National University (SNU)
151-744 Seoul
Korea

Dr. Mato Knez
MPI für Mikrostrukturphysik
Experimental Dept. II
Weinberg 2
06120 Halle
Germany

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Matti Putkonen

3.1
Introduction

Since atomic layer deposition (ALD) is a chemical gas-phase thin film deposition method based on sequential, self-saturating surface reactions, the selection of the suitable reactants, that is, precursors, is extremely critical. Typically, two or more chemical precursors are needed, each containing different elements of the materials being deposited. Precursors are adsorbed onto the substrate surface separately. Each precursor saturates the surface forming a monolayer of material and purging between reactants excludes gas-phase reactions. Process temperatures range from room temperature to over 500 °C. The largest selection of ALD processes operates around 300 °C. ALD processes have been developed for oxides, nitrides, carbides, fluorides, certain metals, II–VI and III–V compounds, and recently also for the organic materials [1].

Development of new ALD precursors and processes has been very active over the past 35 years at several universities, R&D centers, and companies. ALD was first demonstrated for the TFEL application by ZnS deposition using elemental zinc and sulfur in mid 1970s, followed by the use of $ZnCl_2$ and H_2S [1]. After the initial period, several other precursor types have emerged. During the second half of 1980s, metal-organic precursors were also adapted for ALD [2, 3]. This opened plenty of possibilities for new ALD chemistry and processes. A large number of ALD processes have been demonstrated and published up to date, and the list is growing all the time.

In this chapter, different precursors used in ALD are discussed in detail. Generally, ALD processes can be divided according to ligand types used in the volatile precursors. The volatile metal-containing precursors typically fall into the following categories: elemental precursors, inorganic precursors, and organometallic ALD precursors. These classes are discussed in detail and some examples of chemical surface reactions are provided.

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3.2
General Requirements for ALD Precursors

Although ALD resembles chemical vapor deposition (CVD) quite closely, the requirements for ALD precursors differ from other chemical gas-phase methods since all gas-phase reactions should be excluded and reactions should occur only at the surface. In the early history of ALD, CVD reactants were also used, but nowadays specific tailor-made precursors often provide better results [4, 5]. For example, the use of different exchange reactions at the surface makes it possible to create novel ways to produce challenging thin film materials other than traditional oxides and nitrides. ALD growth mode allows the use of significantly more reactive precursors than CVD. In CVD methods, a constant flow of the precursor vapor is needed to obtain a controlled process, but because ALD relies on self-limiting reactions, only a limited amount of the precursor is required during one pulse to cover the adsorption sites on the surface; the excess amount is removed during the inert gas purge or pumpdown. This makes it possible to use, in some cases, *in situ* generation of the metal precursors and thus have a fresh supply of otherwise instable precursor molecules onto the substrate surface [6, 7]. This technique has been successfully applied to produce β-diketonate compounds of alkaline earth metals (Sr, Ba) by pulsing ligand vapor over heated metal or metal hydroxide [8].

In order to avoid uncontrolled reactions, sufficient thermal stability of the precursors is needed in the gas phase as well as on the substrate surface within the deposition temperature range, which is typically 150–450 °C. Because ALD is a gas-phase process, solid and liquid precursors must be volatile under the operating temperature and pressure, and if heating is required to obtain sufficient vapor pressure, thermal stability of the precursor over a prolonged time is necessary. Stability is the key issue especially when coating porous materials or nanostructures requiring long precursor diffusion times.

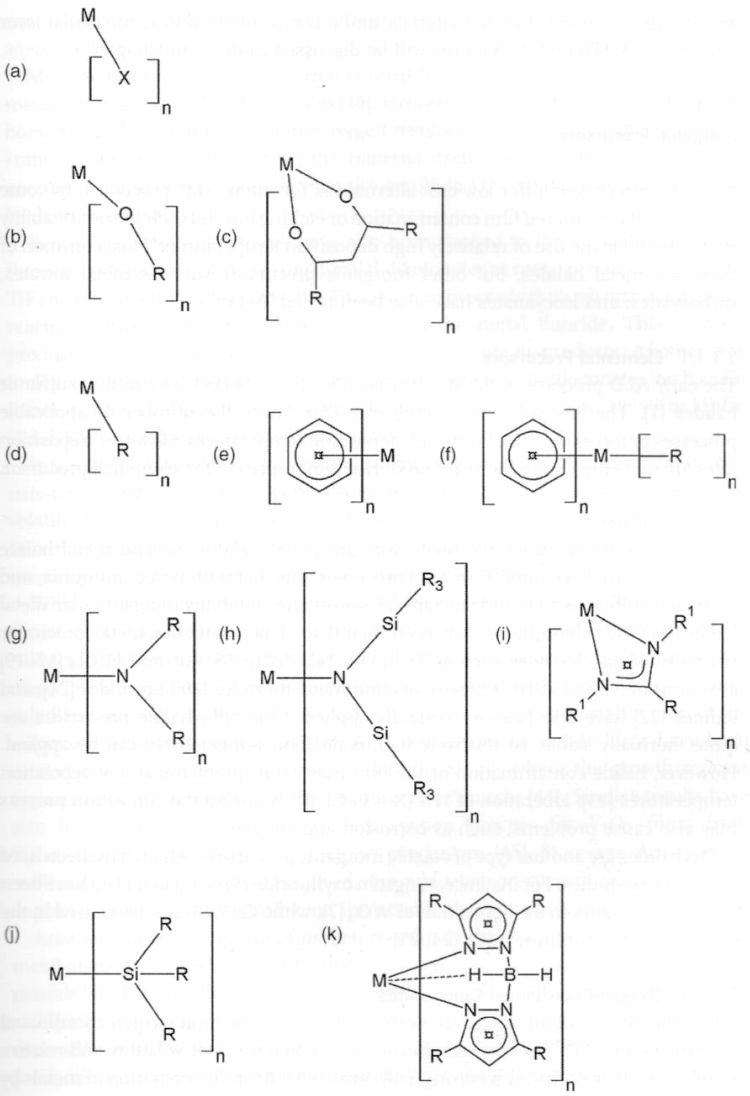
There are some general requirements for ALD precursors:

- sufficient volatility at the deposition temperature;
- no self-decomposition or reaction on itself at the deposition temperature;
- precursors must adsorb or react with the surface sites;
- sufficient reactivity toward the other precursors;
- no etching of the substrate or the growing film;
- availability at a reasonable price;
- safe handling and preferably nontoxicity.

Quite often, the ALD precursors do not fulfill all of these requirements. Moreover, sensitive substrates may give additional limitations to precursor selection.

3.3
Metallic Precursors for ALD

In the ALD of inorganic materials, at least one metal-containing precursor is needed (Scheme 3.1). Recently, the ALD process has also been applied to organic materials



Scheme 3.1 Examples of precursors for ALD depositions. Volatile halides (a), alkoxides (b), and β-diketonates (c) are traditionally used as ALD precursors. Organometallic precursors such as metal alkyls (d) and homo- and heteroleptic cyclopentadienyl-type compounds (e and f) have often favorable properties. Nitrogen-coordinated compounds such as metal amides (g), silylamides (h), amidinates (i), and guanidinates (i, if R = NR_2) have also been successfully applied to ALD. More recently, alkylsilyl compounds (j) and pyrazolyl borate-type ligands (k) have been used for the demanding ALD processes.

and inorganic/organic hybrid materials, and it is now referred to as molecular layer deposition (MLD) and its features will be discussed in detail in Chapter 5.

3.3.1 Inorganic Precursors

Inorganic precursors offer low-cost alternatives for many ALD processes. In some cases, they have suffered film contamination or etching but still their thermal stability makes possible the use of relatively high deposition temperatures. Most common of these are metal halides, but other inorganic precursors such as metal nitrates, carboxylates, and isocyanates have also been tested [9–11].

3.3.1.1 Elemental Precursors

The early ALD processes utilized either volatile elements such as zinc and sulfur or halides [1]. The low volatility of pure elements limits the number of applicable processes or forces the use of very high deposition temperatures. However, deposition rates are quite high since there are no sterical hindrances in the elemental precursor.

3.3.1.2 Halides

The most common inorganic precursors are metal halides. Several metal halide precursors have been applied in ALD processes, together with water, ammonia, and hydrogen sulfide as a second reactant. However, the suitability of a particular metal halide for ALD depositions has been found to depend on the metal precursor reactivity. Metal chlorides such as $TiCl_4$ [12–14], $ZrCl_4$ [15, 16], and $HfCl_4$ [17–19] are commonly used as ALD precursors, but metal fluorides [20], bromides [21], and iodides [22] have also been successfully applied. Generally, halide precursors are quite thermally stable, so relatively high deposition temperatures can be applied. However, halide contamination of the film may cause problems at low deposition temperatures [23]. Liberation of HX (X = F, Cl, Br, I) during the deposition process may also cause problems, such as corrosion and etching.

Oxyhalides are another type of volatile inorganic precursors, which have been used in only a few studies. For instance, tungsten oxyfluoride (WO_xF_y) and H_2O have been used as precursors in the deposition of WO_3 [7], while CrO_2Cl_2 has been used in the deposition of chromium oxide [24, 25].

3.3.1.3 Oxygen-Coordinated Compounds

β-Diketonate-type compounds are perhaps the most common oxygen-coordinated precursors for ALD. These metal chelates are known for their volatility and relative stability and therefore they were originally synthesized for the separation of metals by fractional sublimation [26] and gas chromatography [27]. In the 1970s, they were utilized for the first time in CVD depositions [28]. β-Diketonates in ALD processes were first utilized in the 1980s as dopant precursors (e.g., for Tb, Ce, Eu, and Th) for ZnS [29] and other sulfide thin films [30] since halides for these dopants suffered low vapor pressures. Somewhat later, they were applied in metal oxide depositions [31], but quite high deposition temperatures are required to obtain favorable reaction with

water, hydrogen peroxide, or oxygen. Another approach is to use a strong oxidizing agent, such as ozone.

Metal β-diketonates have also been studied for the deposition of metals [32–34], metal nitrides [35], and metal sulfides [36]. However, since they have metal to oxygen bond present, there might be some oxygen residues present in the deposited films. Impurity levels depend a lot on the material itself; for example, $Y(thd)_3 + H_2S$ precursor combination leads to yttrium oxysulfide [37], whereas $In(acac)_3 + H_2S$ leads to In_2S_3 [38].

Recently, metal β-diketonates have also been applied to the deposition of metal fluorides (MgF_2, CaF_2, LaF_3) using metal β-diketonates as metal precursors and solid TiF_4 or TaF_5 as a fluoride source [39]. This reaction proceeds through ligand exchange reaction between the metal β-diketonate and the metal fluoride. This reaction produces titanium or tantalum β-diketonates as volatile by-products. Another way to deposit fluoride thin films is by using fluorinated metal β-diketonates such as $Ca(hfac)_2$ or metal β-diketonates with separate fluorine source such as HF [40] or Hhfac (1,1,1,5,5,5-haxafluoroacetylacetonate) [41].

It has been observed in CVD and ALD that coordinatively unsaturated β-diketonate-type compounds may oligomerize or react with the moisture and become less volatile [6, 8]. This is observed especially with large and basic metal centers such as strontium and barium. β-Diketonate-type chelates can be protected against oligomerization and hydrolysis by adducting them with a neutral molecule [42].

With adducted precursors, volatilization behavior during heating depends on the choice of metal, ligand, and adduct and on the bond strengths between them. Adducted precursors may sublime in a single-step process, or alternatively they may dissociate during heating, releasing the neutral adduct, which leads to a two-stage volatilization process where the second step corresponds to the sublimation of the original unadducted compound [43]. ALD depositions of sulfide films have been carried out using $Ca(thd)_2$(tetraen) or $Ce(thd)_3$(phen), where the growth process appears to be similar to that of the unadducted precursor [44]. Similar results have also been obtained in the case of deposition process for Y_2O_3 films from $Y(thd)_3$(phen), $Y(thd)_3$(bipy), and O_3 as precursors [45]. It seems that, even if sublimation at one stage is observed, the adducted precursors dissociate at the deposition temperatures, producing the unadducted precursor [44].

Another interesting group of oxygen-coordinated metal precursors includes the metal alkoxides. They are usually more thermally unstable than β-diketonate compounds [46, 47], but offer lower evaporation temperatures. Titanium precursors such as $Ti(OCH_3)_4$ [48], $Ti(OCH_3CH_4)_4$ [49], and $Ti\text{-}(O^iPr)_4$ [50, 51] have been shown to be especially useful when depositing ternary strontium-containing materials to suppress the formation of strontium chloride impurities originating from the $TiCl_4$ precursor [52, 53].

Although simple alkoxide ligands can be used for some elements, metal alkoxides also offer rather straightforward possibility to modify the ligands in order to tailor the ALD process behavior and film properties [54]. For example, bulkier ligands such as *t*-butoxide [55, 56], 1-methoxy-2-methylpropan-2-ol [57], 1-dimethylamino-2-methyl-2-propanolate [58], and dimethylaminoethoxide [59] have been successfully applied

for ALD deposition of metal oxides. Even SiO_2 can be deposited by using $H_2N(CH_2)_3Si(OEt)_3$ or $Si(OCH_2CH_3)_4$ as a silicon precursor [60, 61]. Recently, copper bis(dimethylamino)-2-propoxide has been applied for deposition of metallic copper films [62]. This reaction is based on the exchange reactions with diethylzinc leading to volatile $Zn(dmap)_2$ by-product and copper films.

3.3.1.4 Nitrogen-Coordinated Precursors

Another quite interesting class of ALD precursors includes nitrogen-coordinated compounds such as metal alkylamides and metal amidinates. They have been applied to ALD only recently and there are still emerging possibilities for these precursors. The biggest drawback for some of these compounds is the limited thermal stability.

The most common metal alkylamides are the ones developed for zirconium and hafnium. $M(NMe_2)_4$, $M(NMeEt)_4$, and $M(NEt_2)_4$ (M = Zr, Hf) can be used for the deposition of corresponding oxide and nitride films [63, 64]. Corresponding tantalum alkylamides show stability comparable to zirconium and hafnium, but titanium alkylamides seem to be too unstable to be used in ALD [65, 66]. Other alkylamides studied in ALD include dimethylamides of aluminum, gallium, germanium, antimony [67], and tungsten and alkylimidoalkylamides of tungsten and molybdenum [68, 69], for example. Recently, different aminosilanes have been studied for the deposition of silicon oxides and nitrides, such as bis(dimethylamino)silane [70], tris(dimethylamino)silane [71], and tetraethylsilaneamine [72].

Metal silylamides provide new opportunities for the selection of ALD materials but they are usually more thermally unstable compared to the corresponding metal alkylamides. $Ce[N(SiMe_3)_2]_3$ was applied for the first time in ALD for growing electroluminescent SrS:Ce thin films [73]. More recently, $M[N(SiMe_3)_2]_3$ complexes have been utilized in the ALD of LaO_x, PrO_x, and GdO_x as well as bismuth-containing films [74, 75]. In addition, $ZrCl_2[N(SiMe_3)_2]_2$ has been used for ZrO_2 thin films at relatively low temperatures [76]. In addition, the biggest drawback is that one possible decomposition pathway can lead to silicon impurities in the films.

Metal amidinates have been studied for the deposition of several metals and metal oxides [77]. Amidinates are structurally analogous to the carboxylates, except that the ligand is coordinating through nitrogen, making these compounds more reactive than the corresponding chelates coordinating through oxygen. For example, recently bis(*N*,*N*′-di-*tert*-butylacetamidinato)ruthenium [78], lanthanum tris(*N*,*N*′-diisopropylacetamidinate) [65], and tris(*N*,*N*-diisopropylformamidinato)lanthanum [66] have been used as ALD precursors. A special group of η^2-coordinated compounds includes guanidinates. For example, Gd_2O_3 films have been deposited by using $Gd(^iPrN)_2CNMe_2)_3$ as metal precursor [79]. In addition, heteroleptic guanidinate-based precursors such as $Hf(NEtMe)_2(EtMeNC(N^iPr)_2)_2$ have been used in ALD [80].

3.3.1.5 Precursors Coordinated through Other Inorganic Elements

Although most of the inorganic ALD precursors are halides and N- or O-coordinated compounds, other precursor classes are also emerging. For example, boron-coordinated precursors such as bis(tris(3,5-diethylpyrazolyl)borate)barium have been used for growing barium borate thin films [81].

Recently introduced silicon-coordinated compounds offer interesting route for complex materials. Alkylsilyl tellurium and selenium precursors make it possible to deposit $Ge_2Sb_2Te_5$ and $CuInSe_2$ [82].

3.3.2 Organometallic ALD Precursors

By IUPAC definition, organometallic compounds have bonding between at least one carbon atom and the metal atom. The chemistry of organometallic compounds has been studied for almost 200 years and the ALD relevant cyclopentadienyl compounds have been known from the beginning of the 1950s. During the past few years, the volatility and high reactivity of organometallics have been exploited in ALD. First, ALD processes exploiting organometallic precursors were studied using metal alkyls as precursors. Later on, various compounds containing cyclopentadienyl or other bulkier ligands have been successfully utilized.

3.3.2.1 Metal Alkyls

ALD processes based on organometallic precursors were first developed for the GaAs depositions by using either $(CH_3)_3Ga$ [83, 84] or $(CH_3CH_2)_3Ga$ [85] and AsH_3 as an arsenic source. Analogous indium alkyls, mainly $(CH_3)_3In$, have been used to deposit InAs [86], InP [87], and In_2O_3 [88] thin films.

Aluminum alkyls, for example, $(CH_3)_3Al$, $(CH_3)_2AlH$, and $(CH_3CH_2)_3Al$, have been used for the deposition of several III–V materials, such as AlAs [89], AlP [90], and AlN [91], using AsH_3, PH_3, and NH_3 as second precursors, respectively. The most common use of aluminum alkyls (e.g., $(CH_3)_3Al$, $(CH_3)_2AlCl$ [92], $(CH_3)_2AlH$ [93], or $(CH_3CH_2)_3Al$) is for the deposition of Al_2O_3 thin films. Al_2O_3 is probably the most frequently studied ALD-processed material since $(CH_3)_3Al$ has been used with H_2O [94], H_2O_2 [95], NO_2, [96] N_2O, [97], O_2 plasma [98], or O_3 [99] as an oxygen source.

Transparent conductive SnO_2 has been deposited using $(CH_3)_4Sn$ or $(CH_3CH_2)_4Sn$ as a metal precursor and N_2O_4 as an oxygen source [100]. In order to dope SnO_2 films, BF_3 pulses were added to the processes resulting in almost two orders of magnitude higher conductivity of the as-deposited material. In a similar manner, zinc alkyls, for example, $(CH_3)_4Zn$ and $(CH_3CH_2)_4Zn$, have been used as ALD precursors for ZnS [101], ZnSe [102], and ZnTe [103] thin films with H_2S, H_2Se, and H_2Te as chalcogen sources, respectively. In addition, they have been utilized for the deposition of ZnO thin films using H_2O as an oxygen source and have also been doped with boron [104], gallium [105], or aluminum [106] from B_2H_6, $(CH_3)_3Ga$, or $(CH_3)_3Al$, respectively. Furthermore, $(CH_3CH_2)_4Pb$ has been utilized as an ALD precursor for PbS thin films with H_2S as the second precursor [107].

3.3.2.2 Cyclopentadienyl-Type Compounds

Chemistry of cyclopentadienyl compounds is studied for almost every element [108]. The main application is their use as catalysts, but they are also suitable for use as precursors in MOCVD [109]. Although cyclopentadienyl compounds have attracted

considerable interest as precursors in CVD depositions, they are sometimes too reactive [110]. However, high reactivity and thermal stability make cyclopentadienyl compounds very attractive precursors for ALD, where high reactivity can be controlled by sequential pulsing of the precursors.

For group 2 (Be, Mg, Sr, Ba) elements, several different Cp precursors are utilized. For example, $(C_5H_5)_2Mg$ has been successfully used in the ALD deposition of MgO thin films [111, 112]. Because of the larger size of the heavier alkaline earth metals, simple $(C_5H_5)_2Sr$ and $(C_5H_5)_2Ba$ compounds are not suitable for ALD. Therefore, deposition of strontium- and barium-containing films has been studied by using bulkier ligands. For example, $SrTiO_3$ and $BaTiO_3$ thin films have been deposited from $(C_5{}^iPr_3H_2)_2Sr$, $(C_5Me_5)_2Ba$, and $(C_5{}^tBu_3H_2)_2Ba$ as alkaline earth metal precursors and $Ti(OCH(CH_3)_2)_4$ and H_2O as titanium and oxygen sources, respectively [113]. In addition, SrS and BaS thin films have been deposited from $(C_5{}^iPr_3H_2)_2Sr$, $(C_5Me_5)_2Sr$, and $(C_5Me_5)_2Ba$ using H_2S as the second reactant [114].

The smallest cyclopentadienyl compounds of the series can be utilized in ALD rather straightforwardly for lanthanide elements [115], but thermal stability of the corresponding lanthanum and cerium compounds needs more precursor tailoring. Generally, bulkier ligands will protect the metal central better and decrease the tendency of thermal decomposition. Recently, $La({}^iPrCp)_3$ has been successfully utilized for La_2O_3 deposition [116]. $(C_5Me_4H)_3Ce$ has been successfully used for the doping of ALD-grown SrS thin films [117]. More recently, mixed ligand-type Cp compounds have also been applied [118].

Several volatile cyclopentadienyl-type compounds of group 4 elements have been utilized in ALD. First organometallic ALD experiments to process ZrO_2 and HfO_2 thin films were carried out using $(C_5H_5)_2MCl_2$ and $(C_5H_5)_2M(CH_3)_2$ [119, 120]. Additional heteroleptic compounds of Ti, Zr, and Hf containing alkoxy [121, 122] or N-coordinated ligands [123, 124] have been successfully used as precursors.

Only few other transition metal cyclopentadienes have been studied in ALD. For example, volatile $(C_5H_5)_2Mn$ and $(C_5MeH_4)Mn(CO)_3$ have been used as manganese sources for doping ZnS thin films to produce yellow-emitting thin film electroluminescent devices as well as for the deposition of MnO [125]. In addition, ferrocene has been utilized for the deposition of Fe_2O_3 thin films [126] and CpIn for In_2O_3 [127]. A different approach has been utilized for processing metallic nickel thin films by ALD [128]. During the first stage, NiO thin films were deposited by one ALD cycle of $(C_5H_5)_2Ni$ and H_2O. The NiO layer formed was then reduced to metallic nickel by pulsing hydrogen radicals into the reactor. Nickel and cobalt can also be deposited by three-stage deposition using an oxidizer followed by hydrogen as a reducing agent [129] or directly using a plasma-enhanced process [130].

Cyclopentadienyl precursors for noble metals have gained significant interest. Typically, oxygen or air is used as a second reactant in these processes [131]. These processes are based on the fact that O_2 does not oxidize the noble metal film, but only decomposes the organic ligand. Adsorbed oxygen atoms react with the ligands of the noble metal precursor during the metal precursor pulse [132]. For example, Ru films have been deposited from $(C_5H_5)_2Ru$ [132] or $(C_5EtH_4)_3Ru$ [133]. If longer oxidizer pulses or additional energy is used, for example, in the form of plasma, noble metal

oxides (e.g., RuO_2 and PtO_2) can also be deposited [134, 135]. Deposition of platinum metal films has been studied in a similar manner using $(C_5MeH_4)PtMe_3$ and O_2 as precursors [136], but β-diketonate-type precursors can also be used [137], as shown in Section 3.3.1.3.

3.3.2.3 Other Organometallic Precursors

In addition to metal alkyls and cyclopentadienyl compounds, other types of true organometallic precursors have also been applied to ALD. For example, $(C_6H_5)_3Bi$ [138, 139] and $(C_6H_5)_4Pb$ [139] have been used for the preparation of bismuth- and lead-containing oxide thin films. These compounds are not extremely reactive and therefore ozone is needed [138, 139]. Metallic bismuth was observed as an impurity if H_2O_2 was used as an oxygen source [138].

3.4 Nonmetal Precursors for ALD

Because reactants are separated in the ALD process, it is possible to control the reactivity and the reactions between the precursors by using different precursor combinations. In addition to traditional ALD deposition mechanism that is based on metal and nonmetal precursors, more innovative reaction mechanisms have also been developed. For example, metal alkoxides have been used as oxygen sources [140]. No separate oxygen source is needed in this type of special process because the metal alkoxide serves as both metal and oxygen sources. Other reactions such as ALD mechanism based on the catalytic precursors [61, 141], ligand exchange reactions [39], or replacement reactions at the surface [142] have also been developed.

3.4.1 Reducing Agents

Sometimes a reducing precursor is needed although in many ALD processes no redox reactions occur and the oxidation state of the metal does not change. Hydrogen is perhaps the most widely used reducing agent, but metallic zinc vapor [143], different silanes [144], TMA [145], and B_2H_6 [146] have also been successfully applied. Molecular hydrogen is quite inert toward typical metal precursors and therefore either high deposition temperatures or plasma is needed to maintain ALD reactions.

3.4.2 Oxygen Sources

Typically in the case of ALD-processed oxide films, precursors attached to the surface can be transformed to the respective oxide with H_2O, H_2O_2 [147], N_2O_4 [100], N_2O [96], O_2 [126], or O_3 [148], the choice depending on the metal precursor reactivity or desired properties. Water has frequently been used as an oxygen source and indeed it readily reacts with many metal precursors. Alcohols have also been successfully

applied as oxygen sources in processes involving inorganic precursors and alkoxides. For example, deposition of Al_2O_3 has been carried out with an $AlCl_3$ and ROH precursor combination, where R is H, CH_3, CH_2OHCH_2OH, t-C_4H_9OH, or n-C_4H_9OH [149].

The high thermal stability of the β-diketonate-type complexes or low reactivity of cyclopentadienyl-based precursors usually does not allow their use in ALD with mild oxygen sources. The use of H_2O, H_2O_2, N_2O, CH_3COOH, and O_2 has been explored for β-diketonate-type compounds [150, 151], but the reactivities are usually insufficient, producing either no film growth or films with a high impurity content. The use of a strong oxidizer, such as O_3 or oxygen plasma, guarantees that only a small amount of carbon is left in the film as residues and can also improve the film properties [152, 153].

3.4.3 Nitrogen Sources

Deposition of nitride thin films by ALD requires both a nitrogen source and a reducing agent in order to obtain clean surface reactions [154]. In many cases, one compound, for example, NH_3, serves as both a nitrogen source and a reducing agent. In addition, other nitrogen-containing compounds such as N_2H_4, $(CH_3)NNH_2$, $^tBuNH_2$, and CH_2CHCH_2NH have also been studied as nitrogen sources [155, 156]. Ammonia has been used for depositing several nitride materials such as TiN, Ta_3N_5, W_2N, NbN, and WCN thin films by ALD [157]. Quite often, plasma processes are utilized due to low reactivity of ammonia as well as need for lower resistivity films [158, 159].

3.4.4 Sulfur and Other Chalcogenide Precursors

For chalcogenide thin films, it is possible to use elemental S, Se, and Te as precursors provided that the other source is volatile and reactive enough [160]. ZnS deposition using elemental zinc and sulfur was the first ALD process developed. For other than elemental metal precursors, the reactivity of elemental chalcogens is often not sufficient. For halides, β-diketonates, and organometallics, simple hydrides such as H_2S, H_2Se, and H_2Te have been typically used as a second precursor [161, 162]. Due to the toxicity of these materials, *in situ* generation of H_2S has been studied by using thioacetamide decomposition [163]. Recently, different alkylsilylamines with lower toxicity have also been developed for Se and Te [82].

3.5 Conclusions

Since atomic layer deposition is a chemical gas-phase method, its success relies on the development of well-behaving ALD precursors. Although a number of good ALD

processes are available, there is still room for improvement. Conventional inorganic precursors have been used since the beginning of the ALD era over some 35 years ago. To replace the classical precursors, for example, volatile halides and inorganic complexes, organometallics and nitrogen-coordinated precursors are widening the ALD process selection at the moment. Recent developments of metal processes and other "difficult" materials confirm that novel processes are constantly emerging. Nevertheless, additional research is still needed to develop special precursors and further improve process and thin film quality. In the future, more precursors and processes relying on smart reaction mechanisms are expected to appear.

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