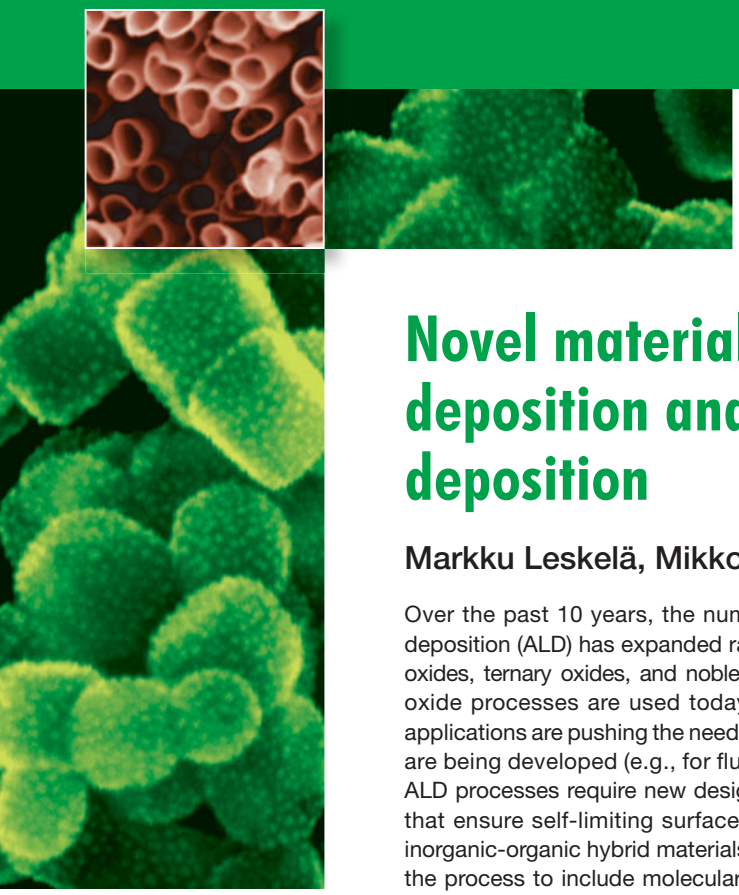


Novel materials by atomic layer deposition and molecular layer deposition

Markku Leskelä, Mikko Ritala, and Ola Nilsen

Over the past 10 years, the number of materials that can be processed by atomic layer deposition (ALD) has expanded rapidly. Significant progress has been seen in ALD of high-κ oxides, ternary oxides, and noble metals, which have been studied quite extensively. High-κ oxide processes are used today in various industrial applications. However, many new applications are pushing the need for less common compounds, and therefore new processes are being developed (e.g., for fluorides, Li containing compounds, and phosphates). New ALD processes require new designs for volatile precursors to deliver elements with ligands that ensure self-limiting surface reactions. In addition to inorganics, new polymeric and inorganic-organic hybrid materials are opening new frontiers for ALD, including expansion of the process to include molecular layer deposition. A combination of inorganic and organic parts in the deposited layers offers expanding opportunities for tailoring materials properties.

Introduction

Atomic layer deposition (ALD) has experienced rapid growth in the past decade in both scientific research and industrial applications. The number of publications in this field has increased almost exponentially, as has the number of application areas. From the materials point of view, the largest part of the research has been devoted to high dielectric constant (high-κ) oxides aimed at applications in microelectronics. By replacing SiO_2 ($\kappa = 3.9$) with HfO_2 or ZrO_2, κ-values of 20–40 can be reached. New ALD thin-film materials have been introduced among metals, especially noble metals, ternary oxides, metal fluorides, and hybrid materials. Materials fabricated by ALD range from single material types to the more recent lithium-containing compounds, tellurides, and selenides.

Puurunen has reviewed all of the ALD processes published before 2005.[1] The list of ALD materials and processes that are currently available is lengthy but still far from comprehensive. There are many elements and a large number of different types of compounds that have never been deposited using ALD, probably because there has not yet been a need to develop ALD processes for these materials. ALD processes are needed, in general, when the films have to be conformal. Very thin films, nanolaminates, and deposition on nanomaterials are other reasons to employ ALD.[2]

In the present review, the focus is on new ALD processes developed during the last 10 years. The focus is specifically on thermal ALD processes, while keeping in mind that plasma-ALD has significantly increased in importance over the past few years. Kessels and Putkonen discuss advances in plasma ALD and related methods in this issue of *MRS Bulletin*.

High-κ oxides

High permittivity oxide thin films are needed in both complementary metal oxide semiconductor (CMOS) transistors and dynamic random-access memory (DRAM) capacitors to replace silicon oxide. The shrinking of device sizes requires increasing capacitance density without extensively increasing leakage. This can be done using high-κ oxides that can be applied as thicker films than silicon oxide, giving the same capacitance density and low enough leakage current.

The replacement of silicon oxide by hafnium oxide-based high-κ material in CMOS devices in 2008 was a revolutionary development.[3] Researchers were able to continue shrinking device dimensions in accordance with Moore's law. Also in the case of DRAMs, the development has been rapid. The architecture of DRAMs changed in the 1990s from two-dimensional to three-dimensional stacked or trench capacitor structures, and when high-κ oxides came into the picture, ALD was needed in

Markku Leskelä, University of Helsinki, Finland; markku.leskela@helsinki.fi
Mikko Ritala, University of Helsinki, Finland; Mikko.Ritala@helsinki.fi
Ola Nilsen, University of Oslo, Norway; ola.nilsen@kjemi.uio.no
DOI: 10.1557/mrs.2011.240

© 2011 Materials Research Society

https://doi.org/10.1557/mrs.2011.240 Published online by Cambridge University Press

film deposition. Currently, the capacitance equivalent thickness (CET) requirement in DRAMs for the oxide film is below 1 nm and will decrease to 0.5 nm in the near future, while keeping the leakage current density below 10^{-7} A/cm^2 at 1 V.[4] At the moment, the most widely used dielectric material in DRAMs is an ALD-formed ZrO_2-Al_2O_3-ZrO_2 nanolaminate.[5]

The transition of ALD high-κ oxides to the product level required extensive research and development, including the analysis of a wide range of precursor materials and processes. Most of the attention has been devoted to hafnium and zirconium oxides, but rare-earth metal oxides and other doping systems have also been studied. In DRAM studies, zirconium and hafnium oxides have been the most popular materials, but titanium dioxide has also received attention.

TiO_2 is an interesting high-κ material because of its high dielectric constant, which varies from 40 to 160 depending on the phase. Several ALD processes have been developed for TiO_2 films,[6] but the problem is the high leakage currents in these films. Researchers have tried to improve the situation by doping or using nanolaminates where the TiO_2 layer is sandwiched between oxides that leak less, for example Al_2O_3 and HfO_2. TiO_2 films grown at low temperatures (<300°C) from different precursors (chlorides, alkoxides, alkylamides) crystallize in the anatase structure.[6] However, the high dielectric constant rutile structure is the more desired polymorph. The formation of the rutile phase can be enhanced by an underlayer, and recent reports have shown that a rutile structured RuO_2 electrode promotes the rutile phase of TiO_2.[7] High-κ values (155) and low CET values (<0.5 nm) have been reported for RuO_2/TiO_2 devices. The leakage problem still exists, but Kim et al. solved that through aluminum doping.[8] When 8% Al is homogeneously doped into rutile TiO_2, the leakage currents can be lowered by several orders of magnitude (**Figure 1**).

The ALD high-κ oxide studies were first focused on HfO_2 films and hafnium oxide-based materials, and these materials were subsequently employed in Intel's transistors.[3] Hafnium was preferred over zirconium since it is more stable with polysilicon, which was used as the gate electrode material in transistors. This requirement is no longer relevant because metal gates have replaced polysilicon as the material of choice. In addition, the fabrication of a phase pure material was easier with HfO_2 than ZrO_2, both of which have several different crystal structures. Especially in DRAM applications, ZrO_2 has become more important than HfO_2 since the cubic and tetragonal phases of ZrO_2 show higher κ values (40) than the corresponding HfO_2 phases (30). The monoclinic phases of both oxides have κ values around 20.

The first and still used HfO_2 ALD process is based on hafnium chloride and water. During the last 10 years, several new precursors and processes have been developed. The precursors include alkylamides, amidinates, alkoxides, cyclopentadienyls, and heteroleptic, mixed ligand complexes of these four precursors.[9] In most cases, water or ozone can be used as the oxygen source. Except for cyclopentadienyl compounds, limited

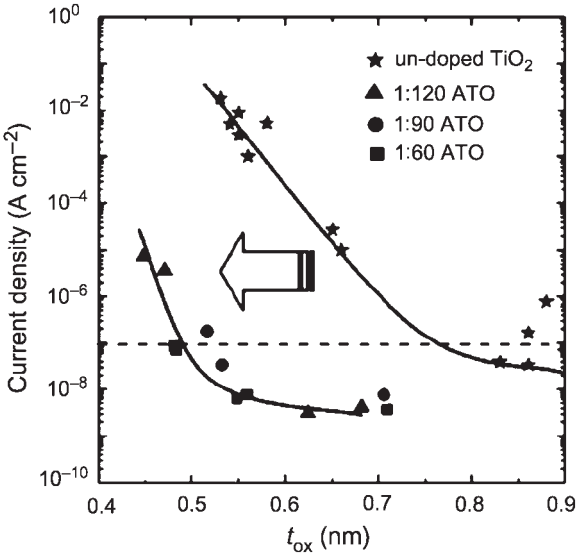


Figure 1. Leak current density at 0.8 V versus capacitance equivalent thickness (t_{ox}) for TiO_2 and TiO_2:Al films with different cycle ratios (1:60, 1:90, 1:120). The dashed line shows the acceptable leakage current level (10^{-7} A/cm^2).[8] ATO, aluminum-doped TiO_2. Reprinted with permission. © 2008, Wiley.

thermal stability is typical for the complexes containing organic ligands, which sets the maximum deposition temperature to 300°C. Higher deposition temperatures are often beneficial for achieving purer films and the desired crystalline phase. The alkylamides are very reactive toward water and ozone, resulting in low impurity oxide films with high κ-value, but, on the other hand, they suffer from thermal instability at 300°C. The process using $Zr(NEtMe)_4$ (Et = ethyl, Me = methyl) and ozone at 275°C has yielded, on TiN electrodes, a κ value close to 40 and a CET value of 0.8 nm.[10] In the presence of the high-κ phase, similar CET values and low leakage currents have been reported for mixed ligand $CpZr(NMe_2)_3$ (Cp = cyclopentadienyl).[11] Cyclopentadienyl compounds are versatile precursors enabling tailoring of the properties by substitutions in the five-membered ring. The Cp precursors show good thermal stability and moderate growth rates but result in mixed crystallographic phases of HfO_2 and ZrO_2. Recent results on $(CpR)M(NMe_2)_3$ (R = alkyl group, M = Zr, Hf) mixed ligand compounds show the beneficial properties of both corresponding homoleptic compounds (one type of ligand is bound to the metal ion): good thermal stability, reactivity and growth rate, enhanced formation of high-κ phases, and good conformability of the films (**Figure 2**).[11]

The concern with ZrO_2 was the formation of the monoclinic phase and stabilization of the high-κ phases. It seems that it is possible to affect the structure by precursor selection. The other well-known method is doping. Yttrium-stabilized zirconia and hafnia have the cubic/tetragonal structure.[12] Theoretical predictions indicate that ions with a smaller ionic radius than Zr or Hf favor the stabilization of the tetragonal phase, and ions with larger ionic radius favor the cubic form.[13] It has been experimentally verified that doping of ALD ZrO_2 and HfO_2 with

https://doi.org/10.1557/mrs.2011.240 Published online by Cambridge University Press

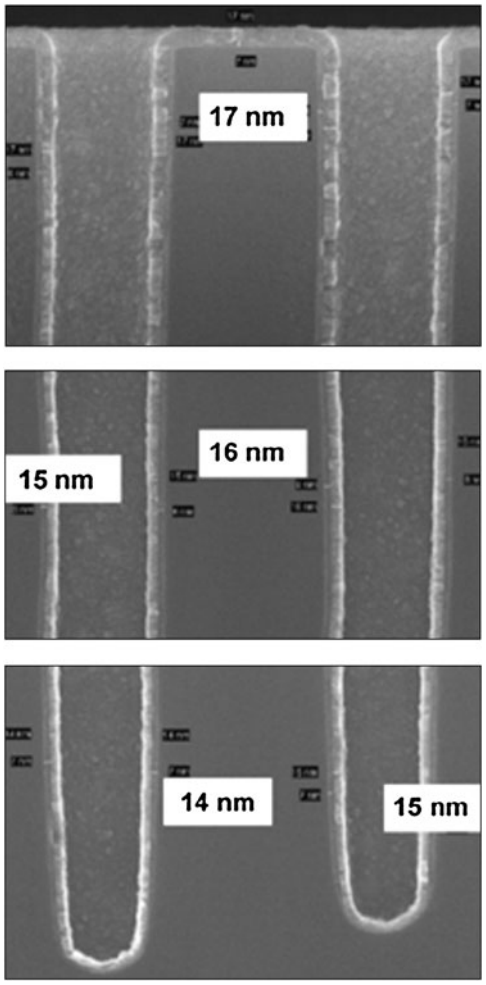


Figure 2. Cross-sectional scanning election microscopy images of a ZrO_2 film grown by the $CpZr(NMe_2)_3/O_3$ process at 275°C into 60:1 aspect ratio trenches. The upper image shows the top part of the trench, and those below are the middle and bottom parts. The trench opening is 115 nm wide with a depth of 6.75 mm. Labels denote the ZrO_2 film thicknesses.[11] Cp = cyclopentadienyl; Me = methyl. Reprinted with permission. © 2008, Royal Chemical Society.

5–8 cation-% rare earth ions results in films with the cubic/tetragonal phase.[9]

Ternary oxides

The number of ternary and quaternary oxides studied within ALD is limited but increasing. Interest in the multicomponent oxides stems from their favorable electrical, ferroelectric, or magnetic properties. There are several ways ternary compounds can be processed: (1) mixing of binary oxide deposition cycles, (2) use of bimetallic precursors, and (3) use of precursors that introduce two of the three elements into the film. The mixing of binary oxide processes to get the right stoichiometry is quite straightforward, but the optimum process temperatures may be different in the binary processes, making the temperature window for the ternary processes narrow.[14] The growth rate can also be different on the binary oxide itself rather than on the other oxide. This effect can even be beneficial, as has been seen in the case of $SrTiO_3$ and $BaTiO_3$, where the growth of the reactive binaries SrO and BaO is challenging, but the growth of the ternaries is easier.

The use of bimetallic single-source precursors is common in chemical vapor deposition (CVD) but has been very rarely investigated for ALD. The most well-known case is the deposition of $SrTa_2O_6$ from $SrTa_2(OEt)_{10}dmae_2$ (dmae = dimethylaminoethoxide) and water.[15] The reason for the limited use of bimetallic precursors is the lack of volatile, thermally stable, and reactive compounds. The third way to deposit ternary compounds is the use of a reactant that supplies two of the three elements into the film, for example, in the case of silicates, where reactions between metal chlorides and silicon alkoxides produce metal silicates.[16]

The number of quaternary oxide films made by ALD is very small. In the deposition of ferroelectric $SrBi_2Ta_2O_9$, the bimetallic $SrTa_2(OEt)_{10}dmae_2$ has been used together with a bismuth precursor.[17] Three metal precursors and a separate oxygen precursor have been successfully used in the case of Bi-Ti-Si-O films.[18] Maintaining the right stoichiometry in deep trenches is a challenge. With quaternary compounds, the temperature window can be even narrower than with ternary compounds. Liquid injection ALD, where the precursor solution is injected in a vaporization chamber and further into the reactor, can then be useful, and introduction of quaternary precursor mixtures has been successfully employed in oxide depositions.[19]

The first ALD ternary oxides were deposited in the 1990s, targeting magnetic oxides. These transition metals containing compounds ($LaCoO_3$, $LaNiO_3$) were made using thd-chelates (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) and ozone as precursors.[20] The other common feature in ALD of ternary oxides is the amorphous structures in the as-deposited state. Annealing is needed to get crystalline films with the desired magnetic and electric properties.

Further interest in ternary oxides came from applications to DRAMs, where a shift away from SiO_2 to binary high-κ oxides or more preferably to very high-κ materials such as titanates started early in the 2000s. $SrTiO_3$ has attracted consistent interest as a possible material for DRAM capacitors. The limited Sr precursor chemistry has slowed the industrial use of ALD of $SrTiO_3$. The oldest and still most commonly used chemistry is based on Sr cyclopentadienyls.[21] Mixed rare-earth oxides form a third type of ternary oxides receiving attention as possible candidates for high-κ materials in microelectronics. The combination of large rare-earth ions with small ones can produce separate ternary compounds with a perovskite structure, such as $LaLuO_3$ and $GdScO_3$.

Yet another ternary oxide material type is formed by ferroelectrics. The earlier mentioned quaternary compound $SrBi_2Ta_2O_9$ is an interesting ferroelectric material. From ternaries, $BaTiO_3$ is a well-known ferroelectric material, and it was made by ALD over a decade ago.[21] Bismuth titanates, $Bi_4Ti_3O_{12}$, form another group of ferroelectric materials ALD.

https://doi.org/10.1557/mrs.2011.240 Published online by Cambridge University Press

In this case, the precursor chemistry of bismuth has played a critical role, and so far the most versatile precursor has been $Bi(OCMe_2{}^iPr)_3$ (i = iso).[22] Lead-containing ternary compounds are interesting due to their applications in sensors and as lead zirconate titanate ferroelectrics. $PbZrO_3$ films have been grown using Ph_4Pb, $Zr(thd)_4$ and ozone at around 300°C.[23]

Ternary oxide films are usually deposited at low temperatures because of the low thermal stability of the precursors. Crystalline films are obtained after high temperature annealing. In many cases, it would be beneficial to get crystalline films directly in the as-deposited state, as has been done, for example, by selecting a strontium precursor that is stable at higher temperatures, allowing crystalline $SrTiO_3$ films to be deposited at 370°C.[24]

Metals

Tungsten and molybdenum were two of the first metals deposited by ALD. Their process follows the ALD principle of exchange reaction type. The reaction involves reduction of WF_6 (MoF_6) by silanes and boranes.[25] The reaction mechanism explains the high growth rate (2.5 Å/cycle) through alternating W-SiH_yF_z and W-WF_x surfaces. This fluorosilane elimination reaction is thermodynamically favorable and results in high and complete reactivity.

Copper has been one of the most desired ALD metals, but its deposition is very challenging. As reviewed by Kim in 2003,[26] no process was available for application at that time. Processes where metals are fabricated via an oxide route (i.e., first an oxide is made with water or ozone, and then the oxide is reduced to metal with H_2) have been reported for copper and nickel.[27] The discovery of amidinate precursors (an amidinate salt has the general structure $M^+[RNRCNR]^-$ where R is an alkyl group) was also a significant step forward in ALD copper chemistry.[28] The direct reduction of Cu precursors with hydrogen has not been possible, but amidinates perform better in this sense. However, the ALD Cu problem is not completely solved, and new processes are being studied, such as those reducing Cu dimethylamino-propoxide with diethyl zinc at 100–120°C[29] and catalyzing the hydrogen reduction of $Cu(hfac)_2$ (hfac = hexafluoroacetylacetonate) by pyridine at room temperature.[30]

Noble metal ALD, first reported in 2003, has been a success story. With thermal ALD, all platinum group noble metals (Ru, Rh, Pd, Os, Ir, Pt) have been deposited using O_2 as the other precursor, together with metal-organic and organometallic compounds.[31] With platinum-group noble metals, this oxidative process is possible because of their strong tendency to form metal films instead of oxides. Oxygen, as the other reactant, reinforces this preference for forming metal, and the main mechanism in the process is combustion of the hydrocarbons of the ligands by oxygen, though some exchange reactions may take place too. Metals themselves activate the otherwise quite inert O_2 molecule by dissociating it to atomic oxygen. Noble metal processes have been studied *in situ* using quartz crystal microbalance and quadrupole mass spectroscopy measurements (the quartz crystal microbalance measures the weight gain on the substrate after each ALD cycle, and the quadrupole mass spectrometry records the gaseous reaction products released from the growth process), and the reaction mechanisms are rather well understood (**Figure 3**).[32] This kind of process has been developed for Ru, Rh, Pd, Ir, Os, and Pt. When ozone is used instead of oxygen, noble metal oxides can be deposited at low temperatures (< 200°C), but at higher temperatures, this process also produces metal films.[33] The processes with a pulsing sequence of ML_n–O_3–H_2 (ML = metal-ligand) produce metal films already below 200°C.[34] The nucleation of noble metal films on oxide surfaces is a problem, since a long incubation time is usually needed. Relatively thick films (5 nm) are needed to obtain continuous, well conducting layers. The incubation time depends on both substrate surface and the ruthenium precursor. Even the structure of the substrate may have an effect, as seen in the case of TiO_2, where Ru films showed a slightly shorter incubation time on anatase than on rutile or amorphous surfaces.[35] The use of noble metal oxide as the growth initiator layer and reduction of the oxide to metal could improve the situation, as shown with Pt and Ir films.[33,34]

Only a few processes have been developed for the first row transition metals (Fe, Co, Ni, Cu). Those based on amidinate precursors rely on H_2 reduction chemistry.[28] The growth rates in these processes vary, indicating that the surface chemistry is not favorable in all cases. The electropositive metals (Al, Ti, Ta) are of interest not only because they are conductive, but also because they can be used as adhesion layers and barrier layers in Cu interconnects. Thermal ALD of these electropositive metals would require conditions that are not possible with the existing reactors. Therefore it was necessary to use hydrogen plasma in their deposition.[26] The extreme oxygen

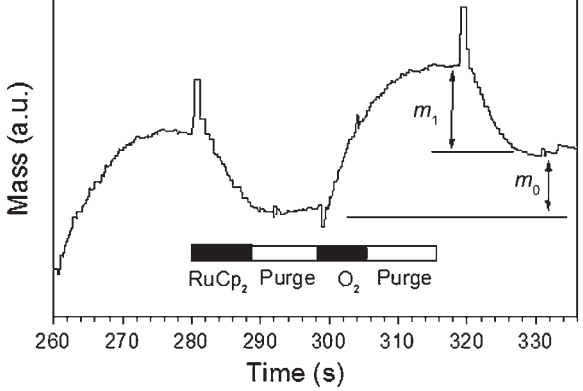


Figure 3. Quartz crystal microbalance data measured during the reaction cycles for $RuCp_2$ and O_2. m_0 denotes the total mass change during one complete reaction cycle, and m_1 denotes the mass change during the $RuCp_2$ pulse. Note that the mass increases during the O_2 pulse and decreases during $RuCp_2$ pulse, indicating adsorption of excess oxygen onto the surface.[32] Reprinted with permission. © 2005, Electrochemical Society.

https://doi.org/10.1557/mrs.2011.240 Published online by Cambridge University Press

sensitivity of these metals makes their ALD very challenging, however.

Silver and gold are important metals, not only because of their low resistivity but also due to their catalytic and optical properties. The surface plasmon properties of silver have recently received much attention. Only two reports have been published on silver ALD, and both of them are based on the hydrogen radical-enhanced reduction of (2,2-dimethylpropionato)silver(I)triphenylphosphine[36] or Ag(fod)(PEt_3) (fod = 2,2,-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato).[37]

Fluorides

ALD of halide films has focused on fluorides, since fluorides are stable and non-hygroscopic and have interesting optical properties, with only one paper on chlorides. The chloride work focused on the growth of CuCl nanoparticles from [bis(trimethylsilyl)acetylene]-(hexafluoroacetylacetonato) copper(I) and hydrogen chloride.[38] The first fluoride process developed was based on HF, which was obtained by the thermal decomposition of NH_4F. The more recent studies exploit volatile metal fluorides (TiF_4, TaF_5) as fluorine precursors. They react with β-diketonato complexes of alkaline earth and rare earth metals to form stable solid fluorides (CaF_2, MgF_2, LaF_3, and YF_3).[39,40] These exchange reactions produce pure fluoride films with only about 1% Ti or Ta impurities (**Figure 4**). The quality of the films is high enough for optic applications, but better transmittance in the UV region would be desirable. The use of organic or fluorine-containing ligands is one way to obtain fluoride films, as exemplified by the work of Putkonen with CaF_2.[41]

Li compounds

Alkali metals containing thin films have been studied very little in ALD because they have not been needed for ALD applications. Lithium compounds are, at the moment, the most interesting due to their need in Li-ion batteries. The designs of all solid-state 3D structure batteries show features that make the use of ALD relevant. In 3D structures, all the components—electrodes, barrier layers, and electrolyte—need to be conformal thin films. In all solid-state structures, the electrolyte is also solid and probably should be made by ALD. Therefore increased research activities are ongoing to develop processes for Li-containing materials usable in batteries.

Li precursors have been synthesized and studied in ALD reactions. The Li(thd) and ozone process produces lithium carbonate,[42] whereas the films obtained from lithium tert-butoxide (Li^tOBu) and water were either oxide or hydroxide. Experiments for pure lithium oxide have not been successful, but the previously mentioned lithium precursors can be used for ternary or quaternary compounds, as shown with lithium lantanate and lithium lanthanum titanate.[43] Recently, lithium phosphate and silicate films also have been deposited.[44] The precursors were trimethylphosphate (TMP) and either $Li(N(SiMe_3))_2$ or LiO^tBu for the phosphate, and lithium bis(trimethylsilyl)amide ($LiN(SiMe_3)_2$) and ozone for the silicate.

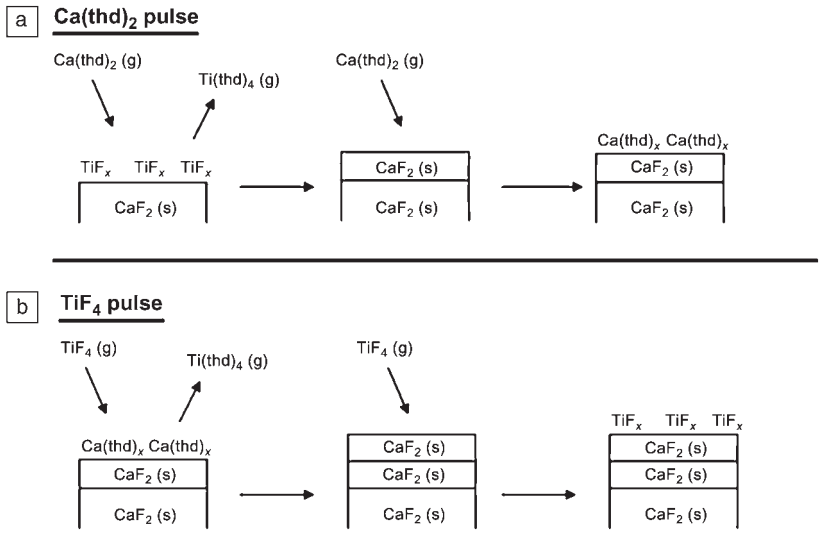


Figure 4. Suggested reaction schemes for CaF_2 atomic layer deposition (ALD) during the (a) $Ca(thd)_2$ pulse and (b) TiF_4 pulse.[39] Note: thd, = 2,2,6,6-tetramethyl-3,5-heptanedione. The incoming $Ca(thd)_2$ reacts with the TiF_x terminated surface forming CaF_2 on the substrate and $Ti(thd)_4$ vapor. When the $Ca(thd)_2$ dose is high enough, it forms a $Ca(thd)_x$ terminated surface. In the next step, the incoming TiF_4 reacts with the $Ca(thd)_x$ terminated surface and also forms solid CaF_2 and $Ti(thd)_4$ vapor. A high TiF_4 dose saturates the surface, leaving TiF_x surface groups, and the cycle can start again. Reprinted with permission. © 2007, American Chemical Society.

Selenides/tellurides and antimonides

Telluride films have been grown by ALD since the 1980s using an element as the precursor. The metal precursors used were elemental as well, which is possible with group 12 metals (Zn, Cd, Hg). The interest toward these telluride films came from their use in thin-film solar cells. For other metal chalcogenides, H_2Se and H_2Te are possible precursors, but their toxicity is of significant concern, and they cannot be used in a normal laboratory environment.

Recently, ALD of tellurides and selenides using alkylsilyls of tellurium and selenium and various metal halides as precursors has been reported.[45] This chemistry was found to work at very low temperatures (i.e., below 100ºC), and this was explained in terms of the favorable formation of alkylsilyl halides as volatile by-products. The motivation for the telluride films was fabrication of germanium antimony tellurides for phase change memory (PCM), where information is not stored as electrons but as different resistive states. PCM uses the reversible phase change between the conductive crystalline state and less-conductive amorphous

https://doi.org/10.1557/mrs.2011.240 Published online by Cambridge University Press

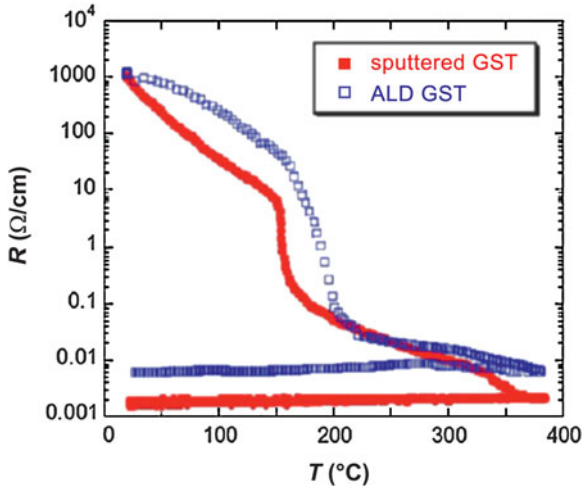


Figure 5. Resistivity (*R*) versus temperature (*T*) data for Ge-Sb-Te (GST) films made by atomic layer deposition (ALD) (open boxes) and sputtering (closed boxes) showing very similar behavior.[46] Reprinted with permission. © 2009, Elsevier.

phase (**Figure 5**).[46] The ternary $Ge_2Sb_2Te_5$ has been the most interesting PCM material, but the binary tellurides $SbTe_x$ and GeTe have also gained attention as phase change materials.[47]

The reaction between alkylsilyl compounds and chlorides also can be exploited for elemental antimony that was deposited by the dehalosilylation reaction between $(Et_3Si)_3Sb$ and $SbC1_3$.[48] For the first time, an element other than a metal was deposited by ALD (**Figure 6**). Pure and conformal thin films of elemental antimony were prepared by thermal ALD. *In situ* reaction mechanism studies showed that the dehalosilylation reactions are very efficient in eliminating the ligands from the growing surface. Various antimony compounds, such as GeSb, Sb_2Te, GaSb, and AlSb, can also be deposited by reacting $(Et_3Si)_3Sb$ with other metal halides or mixing Sb growth cycles with other ALD processes.

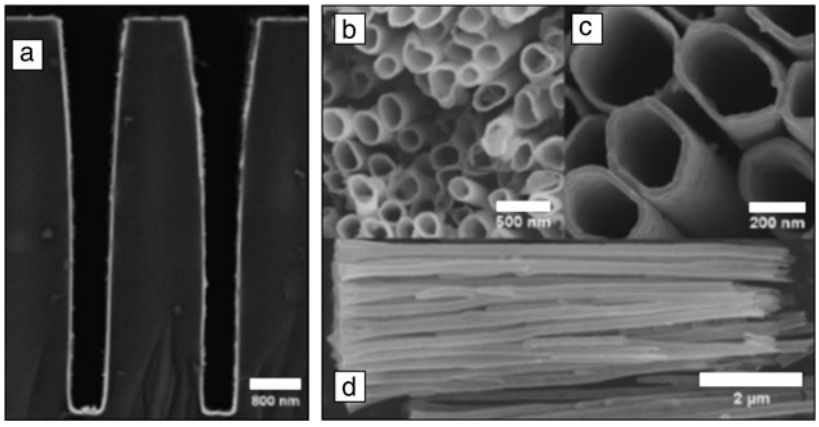


Figure 6. Conformability of the $SbCl_3$-$(Et_3Si)_3Sb$ atomic layer deposition (ALD) process. (a) Cross-section field-emission scanning electron microscope (FESEM) image of a Sb film deposited on a high-aspect-ratio trench structure. (b)–(d) FESEM images of Sb nanotubes prepared using a porous alumina membrane as a template. The deposition temperature was 100°C, and the number of ALD cycles was 1000. Pulse/purge times were 2/10 s for $SbCl_3$ and 4/10 s for $(Et_3Si)_3Sb$.[47] Et = ethyl. Reprinted with permission. © 2011, American Chemical Society.

Organics and hybrid organic-inorganics

Deposition of organic polymers was demonstrated in 1991 by the formation of a polyimide based on sequential reactions between the bifunctional acetic anhydride, pyromellitic dianhydride, PMDA (1,2,3,5-benzenetetracarboxylic anhydride) and the diamines 2,4-diaminonitrobenzene or 4,4'diaminodiphenyl.[49] This work also coined the terminology MLD (molecular layer deposition) as a subgroup of ALD, emphasizing that the film is built using molecular entities for each growth step.

This demonstration was later expanded to include combinations of other types of functional groups used in polymerization processes, such as reactions between amines and anhydrides for the formation of imides,[49–52] acyl chlorides for the formation of amides,[53,54] aldehydes for the formation of imines,[55] isocyanates for the formation of urea,[56,57] and isothiocyanates for the formation of thiourea.[58] These processes have also been performed with heterofunctional molecules forming more complex copolymers.[59] The mentioned reactions rely on the formation of bonds between polar functional groups. A novel alternative reaction mechanism has also been suggested for the formation of covalent non-polar linkages by utilizing UV-induced thiolene reactions.[60]

One challenge with the deposition of polymer materials is the low vapor pressure of most organic compounds and also their limited thermal stability. When this is combined with a limited reactivity, rather long pulsing times may be necessary for obtaining saturated growth. However, when compared to the growth of inorganic compounds, the absolute growth rate is relatively high due to the size of the molecules being included into the film for each step.

The scientific field of polymer material deposition by MLD is still mainly focused on the demonstration of the chemistry involved in the deposition of the different polymers. However, various applications have been investigated, such as polyimides for resistive switching,[52] multilayered structures combining polymers and inorganic materials for significant reduction in leakage current,[50] and new novel types of deposition of photoresist material for deep UV lithography.[57] These studies also prove the strong benefit of using ALD/MLD for deposition of thin films of polymers due to its impressive uniformity, which is not obtainable in an efficient manner by alternative techniques.[52,57]

The reaction scheme described for production of polymers can be extended by using metals as connections between organic linkers in formation of compounds resembling metal organic frameworks (MOF), here termed as organic-inorganic hybrid materials. The layout for such reactions was described in 2006,[61] with examples from growth utilizing reactive

https://doi.org/10.1557/mrs.2011.240 Published online by Cambridge University Press

inorganic precursors such as TMA (trimethylaluminum), DEZ (di-ethyl zinc), $ZrCl_4$, and $TiCl_4$, and organic molecules containing functional groups as alcohols, carboxylic acids, amines, and thiols, among others. See also the review in Reference 62. By utilizing such highly reactive inorganic precursors as connections, a wide range of functional groups on organic compounds can be used with a reactivity enabling fast and efficient processes.

Alcohols are commonly used as functional groups forming metal cones thought to have alkoxide structures resembling those in silicone. In this manner, it is alucone materials when reacted with TMA[63,64] and similar zincone materials when reacted with DEZ.[65,66] The alucones are susceptible to reactions with moisture in ambient air, most probably due to limited saturation of the coordination sphere of the metal.

The alucones have been used for deactivation of photocatalytically active TiO_2[67] and formation of porous surfaces.[68] The alucones have also been demonstrated as successful sacrificial layers in the formation of air gaps in nanoelectromechanical systems.[69] The film is barely removed in dry-etch processes but is easily removed in acidic wet etches.

The stability in air of the organic-inorganic films is greatly enhanced when the alcohols are replaced with carboxylic acids, probably due to a more complete saturation of the coordination sphere of the metal by the carboxylic acids,[70,71] providing relatively hydrophobic surfaces.

Amines can also be used as functional groups with great success, especially when reacted with titanium, such as $TiCl_4$. This has, among others, been demonstrated in Reference 72 with the formation of a stable material when combined with 4,4'diaminodiphenyl.

A possible inhibiting step in the formation of such hybrid materials is multiple reactions with the surface by the bifunctional organic linkers. This is especially the case for homofunctional organic linkers with flexible structure such as alkanes. Such effects may be overcome using precursors with protected groups or which must be activated on the surface before subsequent reactions, or simply by exploiting different reactivities in heterofunctional organic linkers. Multiple suggestions are given in Reference 62, and a three-step (ABC) growth process using a sequence of TMA, ethanolamine, and maleic anhydride has been demonstrated in Reference 73 (see also **Figure 7**).

Similar surface-activated growth preventing multiple reactions with the surface has been demonstrated in References 74–76 using self-assembled monolayers based on 7-octenyltrichlorosilane. The monolayer is terminated by an alkene group that is converted into the more reactive carboxylic acid by reaction with ozone. This process has been combined with layers of ZnO material to form an *n*-type semiconductor[74] and thin-film transistor,[75] and combined with layers of TiO_2 to form a long-term stable resistive switching material.[76]

Subsequent polymerization of the organic linker has also been demonstrated for functionalizing the material.[65] A film based on DEZ and hexadiyne diol was formed containing alkyne bonds in close proximity. These were subsequently polymerized by UV irradiation to form a zinc oxide cross-linked polymer showing *n*-type semiconductivity with enhanced carrier mobility.

The possibilities within hybrid structures are plentiful, and prospects for scale-up are good given the enhanced growth rates of these materials. So far for as-deposited films, it has not been possible to reproduce the porosity or crystallinity of the MOF structures, which most closely resemble bulk materials. However, the amorphous films represent a new class of material where the properties are yet barely revealed.

Conclusions

There is a constant need for thin and conformal films of new materials in various applications, and this gives motivation for atomic layer deposition (ALD) research. Developments

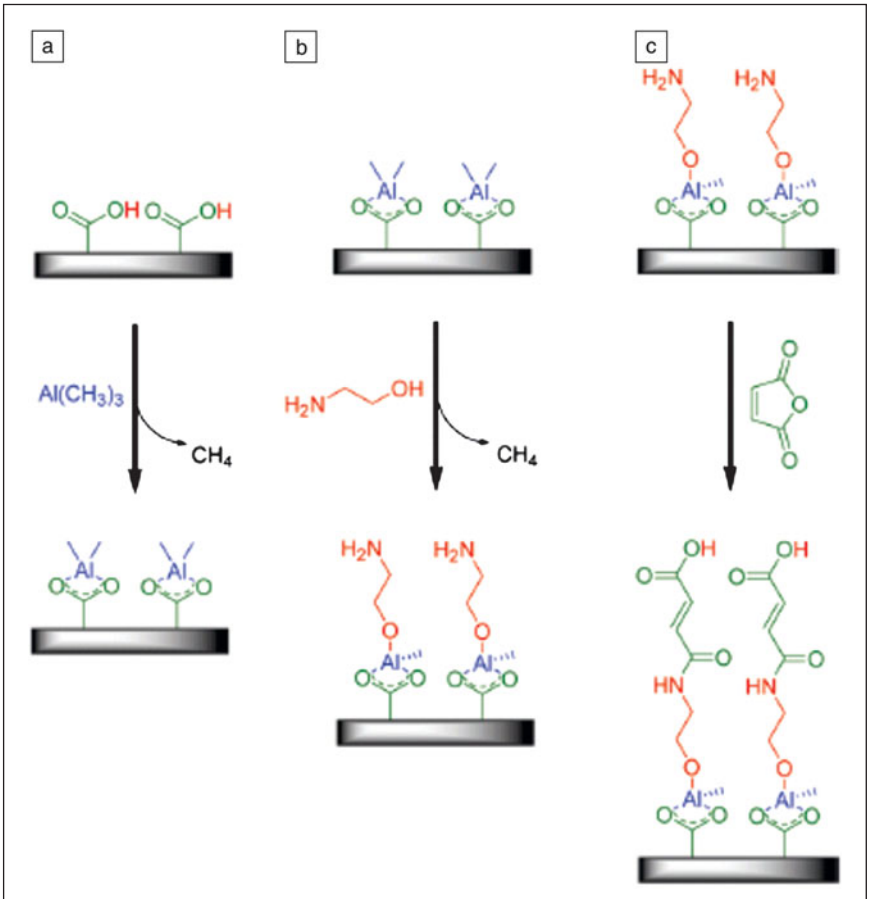


Figure 7. Schematic of a three-step (ABC) growth process for the deposition of an organic-inorganic hybrid material using a sequence of (a) trimethylaluminum, (b) ethanolamine, and (c) maleic anhydride, where an imide bond also forms.[73] Reprinted with permission. © 2009, American Chemical Society.

https://doi.org/10.1557/mrs.2011.240 Published online by Cambridge University Press

in ALD have been rapid during the last 10 years. ALD applications expand in two ways: introducing existing ALD processes into new areas and developing new processes for existing and new areas. During the last decade, new processes have been developed for metals, fluorides, chalcogenides, and polymers, and many new elements have been introduced in ALD films. A new class of organic-inorganic hybrid materials has been realized by the ALD technique, opening up unexplored areas.

ALD applications have expanded from microelectronics to protective coatings, and it can be predicted that areas such as optics, solar cells, and microelectromechanical systems will be important in the near future. However, new materials and processes are still needed in microelectronics, as can be seen in the International Technology Roadmap for Semiconductors.[4] While this article has focused primarily on thermal ALD and molecular layer deposition processes, there is a strong need to develop plasma-enhanced ALD and other related processes, as described in other articles in this issue.

References

1. R.L. Puurunen, *J. Appl. Phys.* **97**, 121301 (2005).
2. M. Leskelä, M. Ritala, *Angew. Chem. Int. Ed.* **42**, 5548 (2003).
3. www.intel.com/technology/45nm/index.htm.
4. International Technology Roadmap for Semiconductors, Front End Processes, (2007); http//public.itrs.net.
5. K.H. Kuesters, M.F. Beug, U. Schroeder, N. Nagel, U. Bewersdorff, G. Dallmann, S. Jakschik, R. Knoefler, S. Kudelka, C. Ludwig, D. Manger, W. Mueller, A. Tilke, *Adv. Eng. Mater.* **11**, 241 (2009).
6. R.I. Puurunen, T. Sajavaara, E. Santala, V. Miikkulainen, M. Laitinen, M. Leskelä, *J. Nanosci. Nanotechnol.* **11** (2011), in press.
7. K. Fröhlich, M. Tapajna, A. Rosova, E. Dobrocka, K. Husekova, J. Aarik, A. Aidla, *Electrochem. Solid State Lett.* **11**, G19 (2008).
8. S.K. Kim, G.-J. Choi, S.Y. Lee, M. Seo, S.W. Lee, J.H. Han, H.-S. Ahn, S. Han, C.S. Hwang, *Adv. Mater.* **20**, 1429 (2008).
9. J. Niinistö, K. Kukli, M.J. Heikkilä, M. Ritala, M. Leskelä, *Adv. Eng. Mater.* **11**, 222 (2009).
10. S.K. Kim, C.S. Hwang, *Electrochem. Solid State Lett.* **11**, G9 (2008).
11. J. Niinistö, K. Kukli, M. Kariniemi, M. Ritala, M. Leskelä, N. Blasco, A. Pinchart, C. Lachaud, N. Laaroussi, Z. Wang, C. Dussarrat, *J. Mater. Chem.* **18**, 5243 (2008).
12. J. Niinistö, M. Mäntymäki, K. Kukli, L. Costelle, E. Puukilainen, M. Ritala, M. Leskelä, *J. Cryst. Growth* **312**, 245 (2010).
13. C.-K. Lee, E. Cho, H.-S. Lee, C.S. Hwang, S. Han, *Phys. Rev. B* **78**, 012102 (2008).
14. M. Vehkamäki, T. Hatanpää, M. Ritala, M. Leskelä, *J. Mater. Chem.* **14**, 3191 (2004).
15. M. Vehkamäki, M. Ritala, M. Leskelä, A.C. Jones, H.O. Davies, T. Sajavaara, E. Rauhala, *J. Electrochem. Soc.* **151**, F69 (2004).
16. M. Ritala, K. Kukli, A. Rahtu, P.I. Räisänen, M. Leskelä, T. Sajavaara, J. Keinonen, *Science* **288**, 319 (2000).
17. M. Vehkamäki, T. Hatanpää, M. Kemell, M. Ritala, M. Leskelä, *Chem. Mater.* **18**, 3883 (2006).
18. G.W. Hwang, W.D. Kim, C.S. Hwang, Y.-S. Min, Y.J. Cho, *J. Electrochem. Soc.* **154**, H915 (2007).
19. Y.-S. Min, Y.J. Cho, I.P. Aslanov, J.H. Han, W.D. Kim, C.S. Hwang, *Chem. Vap. Deposition* **11**, 38 (2005).
20. H. Seim, H. Mölsä, M. Nieminen, H. Fjellvåg, L. Niinistö, *J. Mater. Chem.* **7**, 449 (1997).
21. M. Vehkamäki, T. Hatanpää, T. Hänninen, M. Ritala, M. Leskelä, *Electrochem. Solid State Lett.* **2**, 504 (1999).
22. T. Hatanpää, Vehkamäki, M. Ritala, M. Leskelä, *Dalton Trans.* **39**, 3219 (2010).
23. J. Harjunoja, S. Väyrynen, M. Putkonen, L. Niinistö, E. Rauhala, *Thin Solid Films* **253**, 5228 (2007).
24. S.W. Lee, O.S. Kwon, J.H. Han, C.S. Hwang, *Appl. Phys. Lett.* **92**, 22903 (2008).
25. J.W. Klaus, S.J. Ferro, S.M. George, *Thin Solid Films* **360**, 145 (2000).
26. H. Kim, *J. Vac. Sci. Technol., B* **21**, 2231 (2003).
27. P.J. Soininen, K.-E. Elers, V. Saanila, S. Kaipio, T. Sajavaara, S. Haukka, *J. Electrochem. Soc.* **152**, G122 (2005).
28. B.S. Lim, A. Rahtu, R.G. Gordon, *Nat. Mater.* **2**, 749 (2003).
29. B.H. Lee, J.K. Hwang, J.M. Nam, S.U. Lee, J.T. Kim, S.-M. Koo, A. Baunemann, R.A. Fischer, M.M. Sung, *Angew. Chem. Int. Ed.* **48**, 4536 (2009).
30. S.-W. Kang, J.-Y. Yun, Y.H. Chang, *Chem. Mater.* **22**, 1607 (2010).
31. T. Aaltonen, P. Alén, M. Ritala, M. Leskelä, *Chem. Vap. Deposition* **9**, 45 (2003).
32. T. Aaltonen, K. Arstila, M. Ritala, M. Leskelä, *Electrochem. Solid State Lett.* **8**, C99 (2005).
33. J. Hämäläinen, F. Munnik, M. Ritala, M. Leskelä, *Chem. Mater.* **20**, 3564 (2008).
34. J. Hämäläinen, E. Puukilainen, M. Kemell, L. Costelle, M. Ritala, M. Leskelä, *Chem. Mater.* **21**, 4868 (2009).
35. S.K. Kim, S. Han, J.H. Han, C.S. Hwang, *Appl. Surf. Sci.* **257**, 4302 (2011).
36. A. Niskanen, T. Hatanpää, K. Arstila, M. Leskelä, M. Ritala, *Chem. Vap. Deposition* **13**, 408 (2007).
37. M. Kariniemi, J. Niinistö, T. Hatanpää, M. Kemell, T. Sajavaara, M. Ritala, M. Leskelä, *Chem. Mater.* **23**, 2901 (2011).
38. G. Natrajan, P.S. Maydannik, D.C. Cameron, I. Akopyan, B.V. Novikov, *Appl. Phys. Lett.* **97**, 241905 (2010).
39. T. Pilvi, K. Arstila, M. Leskelä, M. Ritala, *Chem. Mater.* **19**, 3387 (2007).
40. T. Pilvi, E. Puukilainen, U. Kressig, M. Leskelä, M. Ritala, *Chem. Mater.* **20**, 5023 (2008).
41. M. Putkonen, technical program and abstracts, 9th International Conference on Atomic Layer Deposition, ALD 2009, Monterey (2009), p. 142.
42. M. Putkonen, T. Aaltonen, M. Alnes, T. Sajavaara, O. Nilsen, H. Fjellvåg, *J. Mater. Chem.* **19**, 8767 (2009).
43. T. Aaltonen, M. Alnes, O. Nilsen, L. Costelle, H. Fjellvåg, *J. Mater. Chem.* **20**, 2877 (2010).
44. J. Hämäläinen, T. Hatanpää, J. Holopainen, F. Munnik, M. Ritala, M. Leskelä, technical program and abstracts, 11th International Conference on Atomic Layer Deposition, ALD 2011, Cambridge, MA (2011), p. 153.
45. V. Pore, T. Hatanpää, M. Ritala, M. Leskelä, *J. Am. Chem. Soc.* **131**, 3478 (2009).
46. M. Ritala, V. Pore, T. Hatanpää, M. Heikkilä, M. Leskelä, K. Mizohata, A. Schrott, S. Raoux, S.M. Rossnagel, *Microelectron. Eng.* **86**, 1946 (2009).
47. M. Wuttig, N. Yamada, *Nature Mat.* **6**, 824 (2007).
48. V. Pore, K. Knapas, T. Hatanpää, T. Sarnet, M. Kemell, M. Ritala, M. Leskelä, K. Mizohata, *Chem. Mater.* **23**, 247 (2011).
49. T. Yoshimura, S. Tatsuura, W. Sotoyama, *Appl. Phys. Lett.* **59**, 482 (1991).
50. L.D. Salmi, E. Puukilainen, M. Vehkamaeki, M. Heikkilae, M. Ritala, *Chem. Vap. Deposition* **15**, 221 (2009).
51. M. Putkonen, J. Harjuoja, T. Sajavaara, L. Niinistö, *J. Mater. Chem.* **17**, 664 (2007).
52. S. Yoshida, T. Ono, M. Esashi, *Micro Nano Lett.* **5** (5), 321 (2010).
53. Y. Du, S.M. George, *J. Phys. Chem. C* **111**, 8509 (2007).
54. N.M. Adamczyk, A.A. Dameron, S.M. George, *Langmuir* **24**, 2081 (2008).
55. T. Yoshimura, K.Y. Tetsuzo, *Appl. Phys. Express* **2**, 015502 (2009).
56. P.W. Loscutoff, H. Zhou, S.B. Clendenning, S.F. Bent, *ACS Nano* **4**, 331 (2010).
57. H. Zhou, S.F. Bent, *ACS Appl. Mater. Interfaces* **3**, 505 (2011).
58. P.W. Loscutoff, H.-B.-R. Lee, F.F. Bent, *Chem. Mater.* **22**, 5563 (2010).
59. R.C. Sabapathy, R.M. Crooks, *Langmuir* **16**, 7783 (2000).
60. Y.-H. Li, D. Wang, J.M. Buriak, *Langmuir* **26**, 1232 (2010).
61. O. Nilsen, H. Fjellvåg, Patent Cooperation Treat, World Intellectual Property Organization, Publication Number WO 2006071126.
62. S.M. George, B. Yoon, A.A. Dameron, *Acc. Chem. Res.* **42**, 498 (2009).
63. A.A. Dameron, D. Seghete, B.B. Burton, S.D. Davidson, A.S. Cavanagh, J.A. Bertrand, S.M. George, *Chem. Mater.* **20**, 3315 (2008).
64. D.C. Miller, R.R. Foster, Y. Zhang, S.-H. Jen, J.A. Bertrand, Z. Lu, D. Seghete, J.L. O'Patchen, R. Yang, Y.-C. Lee, *J. Appl. Phys.* **105**, 093527 (2009).
65. S. Cho, G. Han, K. Kim, M.M. Sung, *Angew. Chem. Int. Ed.* **50**, 2741 (2011).
66. Q. Peng, B. Gong, R.M. VanGundy, G.N. Parsons, *Chem. Mater.* **21**, 820 (2009).
67. X. Liang, A.W. Weimer, *J. Nanopart. Res.* **12**, 135 (2010).
68. X. Liang, Y.M. Xinhua, M. Yu, J. Li, Y.-B. Jiang, A.W. Weimer, *Chem. Commun.* **46**, 7140 (2009).
69. D. Seghete, B.D. Davidson, R.A. Hall, Y.J. Chang, V.M. Bright, S.M. George, *Sens. Actuators, A.* **A155**, 8 (2009).
70. K.B. Klepper, O. Nilsen, P.-A. Hansen, H. Fjellvåg, *Dalton Trans.* **40**, 4636 (2011).
71. K.B. Klepper, O. Nilsen, H. Fjellvåg, *Dalton Trans.* **39**, 11628 (2010).
72. A. Sood, P. Sundberg, J. Malm, M. Karppinen, *Appl. Surf. Sci.* **257**, 6435 (2011).
73. B. Yoon, D. Seghete, A.S. Cavanagh, S.M. George, *Chem. Mater.* **21**, 5365 (2009).
74. Y. Park, K.S. Han, B.H. Lee, S. Cho, K.H. Lee, S. Im, M.M. Sung, *Org. Electron.* **12**, 348 (2011).
75. B.H. Lee, K.K. Im, K.H. Lee, S. Im, M.M. Sung, *Thin Solid Films* **517**, 4056 (2009).
76. B.H. Lee, M.K. Ryu, S.-Y. Choi, K.-H. Lee, S. Im, M.M. Sung, *J. Am. Chem. Soc.* **129**, 16034 (2007). □

https://doi.org/10.1557/mrs.2011.240 Published online by Cambridge University Press

MRS Corporate Affiliates (as of October 2011)

Materials Research Society would like to thank the following for their financial support:

1-Material
3M Company
Acree Technologies Incorporated
Advanced Diamond Technologies, Inc.
Advanced Film Services
AGD Material Co., Ltd.
Agilent Technologies
Air Liquide, Delaware Research & Tech Center
AIXTRON SE
Aldrich Materials Science
AlphaMicron, Inc.
American Chemical Society
American Elements
Anasys Instruments Corp.
Angstrom Engineering Inc.
Applied Diamond, Inc.
Applied Materials, Inc.
Argonne National Laboratory
Aspen Aerogels, Inc.
Asylum Research
Azimuth Corporation
BASF SE
Bayer Material Science LLC
Beneq Oy
Blake Industries Inc.
Bruker
Cabot Corporation
Cambridge NanoTech Inc.
Cameca Instruments, Inc.
CBMM Technology Suisse SA
CEA Saclay
Cengage Learning, Inc., Global Engineering
Covidien
CrysTec GmbH
CSM Instruments Inc.
DCA Instruments, Inc.
Digital Surf SARL
Dow Chemical Company
Electron Microscopy Sciences
Element Six
FEI Company
FEI Electron Optics International B.V.
Fischione Instruments, Inc.
Gatan, Inc.
GE Global Research
Gelest, Inc.
General Electric Company
GLOBALFOUNDRIES U.S. Inc.
Glycosan Biosystems, Inc.,
a Division of Orthocyte Corp.
Harrick Plasma, Inc.
Hewlett-Packard Labs
Hitachi High Technologies America, Inc.
Hysitron, Inc.
IBM T.J. Watson Research Center
IBM Zurich Research Laboratory
ICDD (International Centre for Diffraction Data)
ICS Convention Design, Inc.
Impact Coatings
INOSTEK Inc.
IQE, Inc.
JEOL Ltd.
JEOL USA, Inc.
Kleindiek Nanotechnik GmbH
K-TEK Nanotechnology
Kurt J. Lesker Company
Lake Shore Cryotronics, Inc.
Lambda Technologies Inc.
Lawrence Livermore National Laboratory
Leica Microsystems Inc.
LifeCell Corporation
Los Alamos National Laboratory
Mad City Labs Inc.
MANTIS Deposition Ltd.
Marlow Industries, Inc.
Materion Advanced Chemicals
Micro Photonics Inc.
Micron Technology Foundation Inc.
Millipore Corporation
MORESCO Corporation
Nanofactory Instruments AB
Nanomaterials & Nanofabrication
Laboratories (NN-Labs, LLC)
Nanomechanics, Inc.
Nanonics Imaging Ltd.
Nanovea
National Electrostatics Corporation
National Institute for Materials Science (NIMS)
National Institute of Standards
and Technology (NIST)
National Renewable Energy Laboratory (NREL)
NETZSCH Instruments N.A. LLC
Oak Ridge National Laboratory
Omicron NanoTechnology
PANalytical Inc.
PARC (Palo Alto Research Center)
Park Systems Inc.
PARU Co., Ltd.
Picosun USA
Princeton Instruments
Quantachrome Instruments
Quantum Design, Inc.
Radiant Technologies, Inc.
Research and PVD Materials Corporation
RHK Technology, Inc.
Robert Bosch LLC
Rocky Mountain Vacuum Technology
Sandia National Laboratories
Sandvik AB
Schlumberger
Seki Technotron USA
Semprus Biosciences
Siemens AG
Society for Biomaterials
Solexant Corp.
Solvay SA
SPECS Surface Nano Analysis GmbH
SPI Supplies
Springer
SPS Syntex Inc.
Strategic Analysis Inc.
Strem Chemicals, Inc.
SuperPower Inc.
Tanaka Precious Metals Co., Ltd.
TE Connectivity
Teleflex Medical
Thermal Technology LLC
Thin Film Electronics ASA
Tokyo Electron America, Inc.
Transmill Technologies Inc.
UES Inc.
United Solar Ovonic LLC
United Technologies Research Center
UOP LLC
Veeco Instruments Inc.
VSP, an Imprint of Brill
Wiley-VCH Verlag GmbH & Co.
J.A. Woollam Company, Inc.
World Gold Council
Xerox Corporation
Zurich Instruments Ltd
Zygo Corporation

For more information about the Corporate Participation Program contact:

Mary E. Kaufold
Manager, Advertising & Exhibits
Materials Research Society
Tel: 724-779-2755
Cell: 724-996-5683
kaufold@mrs.org

https://doi.org/10.1557/mrs.2011.240 Published online by Cambridge University Press

ALDRICH Materials Science

Precursors for Atomic Layer Deposition

High-Tech Solutions for Your Research Needs

MRS BOOTH 1024

Nano-layers of metals, semiconducting and dielectric materials are crucial components of modern electronic devices, high-efficiency solar panels, memory systems, computer chips and a broad variety of high-performance tools.

The technique of choice for depositing nano-films on various surfaces is Atomic Layer Deposition (ALD), which is a versatile tool for nanostructuring and uses consecutive chemical reactions on a material's surface to create nanostructures with predetermined thickness and chemical composition (**Figure 1**).[1]

Aldrich Materials Science offers high-quality precursors for ALD safely packaged in steel cylinders suitable for use with a variety of deposition systems.

We continue to expand our portfolio of ALD precursors to include new materials. For an updated list of our deposition precursors, visit **aldrich.com/aldprecursors**

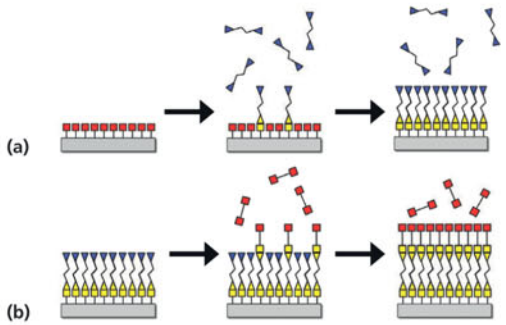


Figure 1. Schematic of the ALD method based on sequential, self-limiting surface reactions.



References:

1. Knez, M. *Material Matters* **2008**, *3*(2), 28.

Precursors Packaged for Deposition Systems

Percursors are ordered by atomic number of the metallic element.

Description	Acronym	Molecular Formula	Prod. No.
Water packaged for use in deposition systems	–	OH_2	697125
Trimethylaluminum	TMA	$Al(CH_3)_3$	663301
(3-Aminopropyl)triethoxysilane	APTS	$Si((CH_2)_3NH_2)(OC_2H_5)_3$	706493
Silicon tetrachloride	STC	$SiCl_4$	688509
Tris(*tert*-butoxy)silanol	TBS	$Si(OH)(OC(CH_3)_3)_3$	697281
Tris(*tert*-pentoxy)silanol	TPS	$Si(OH)(OC(CH_3)_2(C_2H_5))_3$	697303
Tetrakis(diethylamido)titanium(IV)	TDEAT	$Ti(N(C_2H_5)_2)_4$	725536
Tetrakis(dimethylamido)titanium(IV)	TDMAT	$Ti(N(CH_3)_2)_4$	669008
Titanium tetrachloride	TTC	$TiCl_4$	697079
Titanium(IV) isopropoxide	TTIP	$Ti[OCH(CH_3)_2]_4$	687502
Vanadium(V) oxytriisopropoxide	VTIP	$V(O)(OCH(CH_3)_2)_3$	736007
Diethylzinc	DEZ/DEZn	$Zn(C_2H_5)_2$	668729
Triethylgallium	TEG/TEGa	$Ga(C_2H_5)_3$	730726
Trimethylgallium	TMG/TMGa	$Ga(CH_3)_3$	730734
Tris[N,N-bis(trimethylsilyl)amide]yttrium	YTDTMSA	$Y(N(CH_3)_3Si)_3$	702021
Bis(methyl-η5-cyclo-pentadienyl) methoxymethylzirconium	ZRCMMM/ ZRD-CO4	$Zr(CH_3C_5H_4)_2CH_3OCH_3$	725471

Description	Acronym	Molecular Formula	Prod. No.
Tetrakis(dimethylamido) zirconium(IV)	TDMAZ	$Zr(N(CH_3)_2)_4$	669016
Tetrakis(ethylmethylamido) zirconium(IV)	TEMAZ	$Zr(N(CH_3)(C_2H_5))_4$	725528
Bis(ethylcyclopentadienyl) ruthenium(II)	Ru(EtCp)2	$Ru(C_5H_4(C_2H_5))_2$	679798
Bis(methyl-η5-cyclopentadienyl) dimethylhafnium	HFCMME/ HfD-CO2	$Hf[C_5H_4(CH_3)]_2(CH_3)_2$	725501
Bis(methyl-η5-cyclopentadienyl) methoxymethylhafnium	HfD-CO4	$HfCH_3(OCH_3)[C_5H_4(CH_3)]_2$	725498
Tetrakis(dimethylamido) hafnium(IV)	TDMAH	$Hf(N(CH_3)_2)_4$	666610
Tetrakis(ethylmethylamido)hafnium(IV)	TEMAH	$Hf(N(CH_3)(C_2H_5))_4$	725544
Tris(diethylamido)(*tert*-butylimido) tantalum(V)	TBTDET	$Ta[NC(CH_3)_3][N(C_2H_5)_2]_3$	668990
Bis(*tert*-butylimino) bis(dimethylamino) tungsten(VI)	BTBMW	$W(N(CH_3)_2)_2(NC(CH_3)_3)_2$	668885
Trimethyl(methylcyclo-pentadienyl) platinum(IV)	MeCpPtMe3	$Pt(C_5H_4CH_3)(CH_3)_3$	697540

For additional vapor deposition precursors prepacked in cylinders, please contact us by email at **matsci@sial.com**.

https://doi.org/10.1557/mrs.2011.240 Published online by Cambridge University Press