Atomic layer deposition of functional multicomponent oxides

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ABSTRACT
Advances in the fabrication of multicomponent oxide thin films are crucial to prepare specific compositions with precise structures and controlled interfaces. This will enable the investigation of novel phenomena and development of new devices and applications. Atomic layer deposition (ALD) has flourished over the last decades in fabrication of conformal thin films and nanostructures with atomic-scale control. Nonetheless, the scenario of deposition of complex oxides with desired properties has proven to be challenging. In this article, we scrutinize the basics of the precursor and process design for ALD followed by a review on the major achievements in the synthesis of doped and complex oxides identifying several relevant examples that are foreseen to have direct technological applications. Finally, current challenges and perspectives on ALD complex oxides are given.

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I. INTRODUCTION

Complex oxides are a fascinating family of materials, finding technological applications in a broad variety of fields ranging from microelectronics and nanoelectronics to catalysis and energy conversion and storage, among others. In particular, the field of oxide electronics has grown at an exponential pace over the last decades since the discovery of high-temperature superconductors and new physical phenomena at interfaces and in ultrathin films, such as a high-mobility electron gas at the heterointerface of two insulating oxides.\footnote{The properties of complex oxides, e.g., colossal magnetoresistance, and (anti)ferromagnetism, ferroelectricity and ferrielectricity, ferroelasticity, and their combinations such as multiferroicity, are extremely sensitive to chemical composition and structural arrangements. To fully exploit the richness of these complex oxides, it is paramount to control their synthesis with subnanometric scale precision.}

Molecular beam epitaxy (MBE), pulsed laser deposition (PLD), and sputtering are all well-established high-vacuum thin film deposition techniques for these materials.\footnote{However, the continuous need for device miniaturization has lead to a demand of even thinner films, uniform coatings, vertical processing, higher aspect ratios, and complex 3D structures with strict requirements for quality and functionality. Atomic layer deposition (ALD) is a low-temperature (<400 °C) and low-vacuum (10^{-2} to 10 mbar) chemical gas-phase deposition technique that uniquely relies on the alternate pulsing of precursors, separate in time, that react with the surface in a self-limiting manner. These characteristics offer atomic scale control of material thickness and composition and give access to homogeneous ultrathin coatings not only on planar substrates but especially on complex features including nanorods and nanowires, deep trenches, nanoparticles, and mesoporous and nanoporous surfaces.} ALD also enables the preparation of pinhole-free thin layers with atomically sharp interfaces for a wide variety of heterostructures offering, for example, unprecedented opportunities
to study the novel physics arising at the oxide interfaces.\textsuperscript{8} This technique is already integrated in the semiconductor industry, and it is finding crucial applications in other fields such as photovoltaics,\textsuperscript{9,10} organic electronics,\textsuperscript{11} catalysis,\textsuperscript{12} and energy storage.\textsuperscript{13,14} Being a surface-limited deposition method, the deposition area is not restricted by a line-of-sight, and therefore, also batch processes are possible, and, in principle, the size of the substrates is limited only by the volume of the deposition chamber. Noteworthy, new technologies such as spatial\textsuperscript{15} and roll to roll ALD\textsuperscript{16} have been a breakthrough in manufacturing, allowing faster deposition rates even on flexible substrates. However, the material selection for high-quality coatings with these techniques is still narrow.

While ALD is traditionally being used to grow binary oxides, it also enables the deposition of more versatile chemistries, such as, ternary, quaternary, and even quinary compounds including oxides, nitrides, sulphides, selenides, arsenides, and tellurides.\textsuperscript{17} The success in the synthesis of binary oxides has encouraged the preparation of more than 130 different ternary metal oxides using a remarkable amount of elements of the periodic table (Fig. 1).\textsuperscript{17} There is a strong motivation to expand ALD for even a wider range of materials and to explore new functionalities and applications of complex oxides. Moreover, the capability of epitaxial integration of ALD oxides onto semiconductors provides new opportunities for CMOS technology and multifunctional devices.\textsuperscript{18–20}

In this review, we showcase the major achievements in the ALD fabrication of complex oxides, selecting the most representative crystalline structures, and highlight some established doped oxide materials. We will focus on presenting materials that are attractive for a wide selection of applications in microelectronics, and energy conversion and storage. We will also briefly discuss the importance of the precursor and process design in obtaining a material with desired stoichiometry and properties. For a more detailed introduction of the ALD synthesis of multicomponent materials, we refer the reader to a recent review on the topic by Mackus et al.\textsuperscript{17} Finally, we summarize some of the current challenges and future directions in this field.

II. PRECURSORS AND PROCESS DESIGN

A. Precursors for complex oxides

The chemistry of the ALD precursors is an important, if not the most important, stepping-stone to have a well-controlled atomic layer deposition process. The requirements for a precursor to be suitable for the ALD processing are quite demanding: the precursor must be volatile with sufficient vapor pressure to ensure reasonably short pulse lengths, it has to show high reactivity toward the substrate surface, and the precursor attached on the surface must not self-react. Also, the precursor must have sufficiently high decomposition temperature not to decompose during the process. Complementary requirements for an ideal precursor include low toxicity, easiness to handle and synthesize, low production cost, and suitability for up-scaling. The properties of the reaction by-products are also important. They should be volatile for easy purging and not react further with the forming film or etch it.\textsuperscript{21,22} For metal oxides, the precursor can be identified as a metal source and an oxygen source. The metal source typically contains one type of metal atom per precursor. The ligand is also an important part of the metal precursor whose size, heterolepticity, and functionality furnish many

\begin{figure}
\centering
\includegraphics[width=\textwidth]{metal_elements.png}
\caption{Overview of metal elements in ternary metal oxides deposited by ALD. Reproduced with permission from Mackus et al., Chem. Mater. 31(4), 1142 (2019). Copyright 2019 American Chemical Society.}
\end{figure}
opportunities to modify the chemistry of the precursor. The most popular types of ligands are halides (fluorides, chlorides, iodides), alkyls including cyclopentadienyls, alkoxides and metal β-diketonates, amides, and imides. Also, heteronuclear sources are gaining interest in the synthesis of complex oxides for their simplified delivery of the precursors while retaining the precursor stoichiometry. Vehkamäki et al. were the first to report the preparation of SrTa$_2$O$_6$ from SrTa$_2$(OEt)$_{10}$(dmae)$_2$ (dmae = dimethylaminoethoxide). Other examples that can be found are PrAlO$_x$ and NdAlO$_x$ from pure bimetallic alkoxide precursors and more recently Gd–Fe–O.

Regarding the oxygen source, H$_2$O, O$_2$, or O$_3$ are routinely used oxidizers, although the oxygen present in the metal precursor (i.e., when the ligand is an alkoxide or β-diketonate) can also be used as the oxygen source. It is important to note that the use of plasma is an effective approach when more reactive oxygen sources are needed. In this approach, called plasma-enhanced or plasma-assisted ALD (PEALD, PA-ALD), the energetic oxygen plasma can also be used to reduce the deposition temperature and to enhance the film properties, such as crystallinity. However, due to the short lifetime and high recombination probability of the reactive plasma species, it is typically considered inefficient when depositing on 3D-structures.

B. Synthesis of complex oxides by ALD

Synthesis of doped and complex oxides adds complexity to the ALD processing. Commonly, these materials are deposited with an approach where ALD cycles of multiple binary oxides are combined into a supercycle. An ALD supercycle of a ternary oxide is illustrated in Fig. 2. In the supercycle approach, the composition can be varied by tuning the cycle ratio and sequence of each process within the supercycle. For example, by regular alternation of binary cycles AO$_x$ and BO$_y$, a homogeneous film (AB$_z$O$_w$) can be produced [Fig. 2(a)], while repeating each binary cycle multiple times results in a multilayered film of AO$_x$ and BO$_y$, also called nanolamine [Fig. 2(b)]. By fine tuning the cycle ratio, a dopant material can be added to the primary oxide with precise concentrations B:AO$_x$ [Fig. 2(c)].

When considering an ideal supercycle, the film composition and growth should be linear combinations of the applied binary processes, but in reality, the used surface chemistries determine the nucleation and growth. As in the ALD of binaries, the steric hindrance of the precursor molecules limits coverage in a single cycle and the chemisorption is dependent on the density and reactivity of the surface sites, as well as on the reactivity of the precursor. This can cause significant differences on the growth rate of the complex material compared to the growth of binary oxides, as precursors face different surfaces during the deposition. In worst cases of precursor mismatch, the growth can be inhibited or the film can even be etched. A well known example of the latter is AlZnO where TMA (trimethylaluminum) precursor etches the ZnO layer, presumably by surface reactions forming volatile dimethyl zinc. Etching reactions during growth of multicomponent oxides have also been observed with other types of precursor chemistries. For example, β-diketonate precursors Mn(thd)$_3$ and Mg(thd)$_2$ were shown to remove Co atoms during the growth of Mg–Mn–Co–O films. In some rare cases, a precursor cannot

![Fig. 2](https://example.com/fig2.png)

**FIG. 2.** A schematic illustration of the combination of ALD cycles into supercycles. Processes I and II describe ALD cycles for producing binary oxides AO$_x$ and BO$_y$, respectively. With alternating processes I and II, (a) homogeneously mixed film (AB$_z$O$_w$), (b) multilayers of AO$_x$ and BO$_y$, or (c) doped material (B:AO$_x$) can be formed.
be used to grow a binary oxide film but can be used in doping when the primary material surface acts as a catalyst for the reaction and thus promotes the dopant incorporation. The different reactivity of precursors can cause challenges especially in the case of doping, where a uniform lateral and vertical dopant distribution is desired throughout the film whilst maintaining low concentrations. The challenges in the doping arise especially at low dopant concentrations where, according to the supercycle approach, single cycles of the dopant are applied between thick layers of the primary material. This results in inhomogeneous films with too low vertical and too high lateral dopant density. In many cases, the intermixing of the materials can be promoted by postdeposition annealing, but depending on the significance of the concentration gradients to the material functionality and target application, also process tuning may be required. The most straightforward way of doing this is to limit the lateral coverage of the dopant precursor, either by limiting the reactivity or by increasing the ligand size and thus the steric hindrance. This reduces the lateral surface density of the dopant atoms in the films, and fewer cycles of the primary material are required between the dopant cycling in order to achieve the same total volume concentration but with more uniform distribution.

Additionally, the overlapping of the so-called ALD-windows of the binary processes, a temperature range where the growth is saturated within an ALD cycle, can be challenging due to differences in the ligand chemistries, and the deposition temperature may need to be compromised at a cost of surface saturation. The temperature range is limited by the reactivity and decomposition of the precursors, which can lead to low or uncontrolled growth and result in the increase in impurity content in the films. However, it has also been reported that the viable deposition temperature range of a complex material is wider than the ALD-windows of the constituent binary oxides. For example, Nilsen et al. investigated the growth and composition of La$_{1-x}$Ca$_x$MnO$_3$ films from La(thd)$_3$, Mn(thd)$_3$, Ca(thd)$_2$, and O$_2$. It was observed that the ALD window of the ternary LaMnO$_3$ and CaMnO$_3$, and the quaternary La$_{1-x}$Ca$_x$MnO$_3$ extends up to ∼330 °C, while the growth of binary MnO$_2$ is self-limiting only at 140–240 °C due to the thd ligand detachment at higher temperatures. They attributed the increased stability to the high affinity of surface La/Ca to bind these thd ligands, which limits the formation of additional surface sites and helps maintain the self-limiting growth.

Therefore, the precursor combinations, binary cycle ratios in each ALD supercycle, and the deposition temperature need to be carefully designed for each material. Figure 3 shows an example of possibilities for ALD process design of SrTiO$_3$ from different (a) SrO and (b) TiO$_2$ binary processes. The impact of SrO/TiO$_2$ cycle ratios in the ALD supercycle to the Sr/Ti stoichiometry in the deposited films with different processes is illustrated in Fig. 3(c).

Apart from supercycles, other methods such as precursor mixing and coinjection can be used, with certain precautions, to prepare multicomponent oxides, but these are more common in spatial ALD, where the different stages of the ALD cycle are separated in space rather than in time. Alternatively, the enhanced diffusion of species, such as alkali metals (Li, Na, and K), can be exploited in the fabrication of the multicomponent films via solid state reactions after the deposition.

![Graph](image-url)
Furthermore, the low ALD processing temperatures (<400 °C) generally result in amorphous or polycrystalline films, and therefore, a postdeposition annealing is often needed in order to achieve the desired structure, as well as to promote the intermixing of atoms. Nonetheless, the annealing step can sometimes be avoided by choosing a lattice matched substrate that induces epitaxial growth during the deposition.\textsuperscript{45} The ability to tailor the precursor chemistry and understanding of the surface reaction mechanisms are essential for increasing the breadth of materials to be synthesized by ALD but also to enhance the quality of the deposited film.\textsuperscript{46,47} Computational methods, such as density functional theory (DFT) calculations, are also useful tools in design of new processes.\textsuperscript{48} With the continuous increase in computation capacity, these methods have gained predictive power and have become more widely accessible.

III. DOPED AND COMPLEX OXIDES BY ALD

A. Doped oxides

Doped oxides are the most common family of the ALD grown multicomponent materials. The basic purpose of doping is to tune the material properties (optical, electrical, and structural) to optimize the film for a specific application. Perhaps, the most investigated applications for ALD of doped oxides can be found in microelectronics. A lot of research has been done on high-k dielectrics, where ALD has already been adapted as a state-of-the-art technique for industrial logic and memory processing, including dynamic random access memory (DRAM) and 3D NAND. The majority of these materials are binary oxides (AlO\textsubscript{2}, HfO\textsubscript{2}, ZrO\textsubscript{2}, LaO\textsubscript{2}, TaO\textsubscript{2}, NbO\textsubscript{2}O\textsubscript{5}), but it is possible to tailor the dielectric properties of the material by depositing a mixture of these with a well-defined composition (e.g., Al\textsubscript{2}HfO\textsubscript{4}, Si\textsubscript{2}HfO\textsubscript{5}, and Al\textsubscript{2}TiO\textsubscript{5}) or by forming a nanolaminate structure with alternating thin layers of constituent oxides.\textsuperscript{49} e.g., ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2} also known as “ZAZ.” Also, other cations can be used to improve the film performance. For example, doping with rare-earth elements (Y, La, Ce, Gd, Tb, Er, etc.) leads to higher permittivity of ZrO\textsubscript{2} and HfO\textsubscript{2} via phase stabilization.\textsuperscript{50,51} Other practical examples of nonbinary ALD of high-k oxides include hafnium silicate,\textsuperscript{52} zirconium silicate, and different lanthanide mixtures (LuLaO\textsubscript{5}), as well as ultra-high-k perovskites such as SrTiO\textsubscript{3} and BaTiO\textsubscript{3} discussed later in Secs. III B 1 and III B 4.

Besides high-k dielectrics in DRAM, the ALD of doped binary oxides has gained significant interest also as potential materials for emerging nonvolatile data storage applications. Resistive switching random access memory (ReRAM) devices use amorphous or polycrystalline binary oxides (Ta\textsubscript{2}O\textsubscript{5}, TiO\textsubscript{2}, HfO\textsubscript{2}), but doping or fabrication of multilayer stacks by ALD can be used to improve the switching characteristics. Another approach toward low-power programming and long data retention capability is ferroelectric random access memories (FeRAM). Current FeRAM devices use epitaxial Pb(Zr, Ti)O\textsubscript{3}, and the ferroelectric (FE) response of other oxide perovskites such as BaTiO\textsubscript{3} and BiFeO\textsubscript{3} for memory applications has been investigated. However, these materials have a relatively low electronic band gap (<4 eV), leading to a low Schottky barrier height, which makes them susceptible to high leakage currents and breakdown, and thus require high film thickness (>50 nm) to achieve a feasible FE response. ALD of FE HfO\textsubscript{2}-based materials has gained special interest due to their simpler structure, together with CMOS and back end of line (BEOL) compatible processing, meeting the requirements for ferroelectricity in <10 nm films needed for modern devices.\textsuperscript{52-55} FE response after postdeposition annealing has been reported in ALD grown HfO\textsubscript{2} films with several different dopants, including Al,\textsuperscript{56} Si,\textsuperscript{57} Sr,\textsuperscript{58} Y,\textsuperscript{59} Zr,\textsuperscript{60-62} La,\textsuperscript{63} and Gd,\textsuperscript{64} together with durable performance of up to 10\textsuperscript{4} switching cycles of these films in metal-insulator-metal (MIM) capacitors [Figs. 4(a) and 4(b)], both with planar and 3D geometries [Fig. 4(c)]. In some systems, such as Si:HfO\textsubscript{2}, the behavior of the dielectric from ferroelectric and antiferroelectric by changing the dopant concentration.\textsuperscript{65} Zr-doping has been the substituent cation that has been investigated the most. While in other systems the optimum stable dopant concentration is less than 20%, with Zr alloying, the most stable orthorhombic FE phases are observed with the composition of Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}, indicated both by the magnitude of remanent polarization and degree of “wake-up” effect [Fig. 4(d)].\textsuperscript{66,67} The FE response can be measured in films down to 2.5 nm in thickness.\textsuperscript{57} Interestingly, cation intermixing plays no significant role and the FE response can also be detected in the HfO\textsubscript{2}/ZrO\textsubscript{2} nanolaminates, where up to 4 nm thick HfO\textsubscript{2} and ZrO\textsubscript{2} layers can be distinguished also after the postdeposition annealing.\textsuperscript{68} In the perspective of ALD processing, HfO\textsubscript{2} doping with Zr or other group 4 metals is also an advantage, as parallel ligand chemistries such as halides, amides, or cyclopentadienyls can be used for both oxides, which makes the design of the ALD supercycles more straightforward, and the process optimization naturally benefits from the vigorous work done on the precursor and process development for CMOS and DRAM dielectrics.\textsuperscript{69}

In addition to dielectric and ferroelectric thin films, ALD has been used in exploring new chemistries for transparent conducting oxides for displays and optoelectronic and photovoltaic applications. These materials include both doped ZnO and In\textsubscript{2}O\textsubscript{3}, but the ZnO-based materials are demonstrated to have more potential in replacing traditional sputtered indium tin oxide (Sn:In\textsubscript{2}O\textsubscript{3}, ITO), considering material availability and the elimination of plasma damage.\textsuperscript{70} Among the ZnO based compounds, ALD AZO (Al:ZnO) has been shown to be one of the most promising and most investigated candidate with ≈1 · 10\textsuperscript{-3} Ω cm resistivity with ~2% Al content.\textsuperscript{71} Other reported dopants to increase the conductivity of ALD ZnO include B,\textsuperscript{72} Ti,\textsuperscript{73} Ga,\textsuperscript{74} Zr,\textsuperscript{75,76} Y,\textsuperscript{69} Zr,\textsuperscript{69} and Hf,\textsuperscript{69} but systematic studies on these are still sparse. Doped semiconductor oxides by ALD for active channels in thin film transistors (TFTs) have also been investigated. Comparable TFT performance with conventional sputtered films was demonstrated with ALD In\textsubscript{2}GaZnO\textsubscript{5} (IGZO) channel TFTs with a high switching ratio (L\textsubscript{off}/L\textsubscript{on} = 10\textsuperscript{5}), a 90 mV/dec subthreshold slope, and a field effect mobility of 10 cm\textsuperscript{2}/Vs.\textsuperscript{77} Note that ALD deposition of transparent and conducting (p-type) ABO\textsubscript{2} materials with A = Cu and B = Cr, Y, Al will be reviewed in Sec. III B 3.

Other interesting families of materials with a potential for ALD processing are the so-called dilute magnetic semiconductors and dilute magnetic oxides, in which magnetic impurities, e.g., transition metals Mn, Fe, Co, and Ni, are introduced into a semiconducting or a high-k oxide in order to produce a magnetic ground state.\textsuperscript{78} Magnetic properties of some of the dilute magnetic oxide
materials grown by ALD have been investigated, including Fe:ZrO\(_2\),\(^{9,10}\) Co:TiO\(_2\),\(^{91,92}\) and Mn:TiO\(_2\).\(^{92}\) All of these materials exhibit magnetic behavior, although room-temperature ferromagnetism was only confirmed in doped titanium oxide films.\(^{91,92}\)

While the majority of applications for doped oxides by ALD are focused on microelectronics, the potential of these materials for energy storage and conversion applications is also widely explored.\(^{14}\) The safety issues with flammable liquid electrolytes in Li-ion batteries have motivated the research on solid electrolytes and thin film batteries. A selection of electrolytes and electrode barrier/interface layers to mitigate detrimental interfacial effects have been fabricated by ALD, including commonly used LiPON,\(^{93,94}\) different Li(Al, Si)O\(_x\) compounds,\(^{95,96}\) lithium lanthanate titanate,\(^{97}\) lithium lanthanate zirconate,\(^{97}\) and also materials such as lithium tantalate\(^{98}\) and lithium niobate,\(^{99,100}\) which are perhaps better known for their ferroelectric perovskite forms LiTaO\(_3\) and LiNbO\(_3\). Of these, a lithium niobate with a Li:Nb ratio of 1.63 was recently reported with an ionic conductivity of \(6.39 \times 10^{-8}\) S cm\(^{-1}\) at 303 K and 1.62 \times 10^{-8}\) S cm\(^{-1}\) at 353 K with an activation energy of 0.62 eV.\(^{100}\) This corresponds to lithium niobate films grown by ALD to solid oxide fuel cells (SOFCs).\(^{103–106}\)

In Sec. III B 2, the impact of this family of ALD Li-ion based materials for battery applications is further expanded when including spinel structure materials.

In addition to batteries, solid electrolytes have been applied by ALD to solid oxide fuel cells (SOFCs).\(^{11}\) Thin film ceramic electrolytes such as yttria stabilized zirconia (Y:ZrO\(_2\), YSZ),\(^{103–106}\) doped ceria (Gd:CeO\(_2\), Y:CeO\(_2\),\(^{107,108}\) and yttria doped barium zirconate (BYZ)\(^{109}\) have successfully been demonstrated in SOFCs. Among them, YSZ is considered to be the most suitable in practical applications because it exhibits the best stability against oxidation and reduction at elevated temperatures.\(^{110}\) For example, the superior conformity of the ALD grown YSZ films has been shown to be a key in the improved performance of nanoporous anodized alumina supported thin film SOFCs.\(^{103,111}\) When combined with sputtered electrolyte with high ionic conductivity, it effectively blocks chemical and electrical short circuits, which results in higher power density, measured up to 560 mW cm\(^{-2}\) at 450 °C.\(^{112}\) Even higher values (>1 W cm\(^{-2}\) at 500 °C) have been reported with an ionic conductivity of 6.39 \times 10^{-8}\) S cm\(^{-1}\) at 303 K and 1.62 \times 10^{-8}\) S cm\(^{-1}\) at 353 K with an activation energy of 0.62 eV.\(^{100}\) This corresponds to lithium niobate films grown by ALD to solid oxide fuel cells (SOFCs).\(^{103–106}\) Thin film ceramic electrolytes such as yttria stabilized zirconia (Y:ZrO\(_2\), YSZ),\(^{103–106}\) doped ceria (Gd:CeO\(_2\), Y:CeO\(_2\),\(^{107,108}\) and yttria doped barium zirconate (BYZ)\(^{109}\) have successfully been demonstrated in SOFCs. Among them, YSZ is considered to be the most suitable in practical applications because it exhibits the best stability against oxidation and reduction at elevated temperatures.\(^{110}\) For example, the superior conformity of the ALD grown YSZ films has been shown to be a key in the improved performance of nanoporous anodized alumina supported thin film SOFCs.\(^{103,111}\) When combined with sputtered electrolyte with high ionic conductivity, it effectively blocks chemical and electrical short circuits, which results in higher power density, measured up to 560 mW cm\(^{-2}\) at 450 °C.\(^{112}\) Even higher values (>1 W cm\(^{-2}\) at 500 °C) have been reported.

**FIG. 4.** (a) Remanent polarization (P\(_r\))–endurance plot of ferroelectric undoped and doped ALD HfO\(_2\) films. Reproduced with permission from Park et al., MRS Commun. 8(3), 795 (2018). Copyright 2018 Materials Research Society. (b) Cross-sectional HR-TEM image of Hf\(_{1-x}\)Zr\(_x\)O\(_2\) (HZO) based MIM capacitor (left) and a close-up of the HZO film after annealing at 400 °C (right). Reproduced with permission from Kim et al., Appl. Phys. Lett. 111(24), 242901 (2017). Copyright 2017 AIP Publishing. (c) Top: high-angle annular-dark-field scanning transmission electron microscopy (HAADF-STEM) images of Al\(_2\)O\(_3\) based MIM capacitor showing the cross-sectional morphology of the heterostructure. (left) and a close-up of the Al\(_2\)O\(_3\) film (right). Reproduced with permission from Park et al., Appl. Phys. Lett. 111(24), 242901 (2017). Copyright 2017 AIP Publishing. (d) Polarization–electric field hysteresis curves of Hf\(_{1-x}\)Zr\(_x\)O\(_2\) films with 0.70, 0.51, 0.43, and 0.35 Zr contents (x), respectively. Adapted with permission from Park et al., ACS Appl. Mater. Interfaces 8(24), 15466 (2016). Copyright 2016 American Chemical Society.
been reported on nanostructured Pt/ALD YSZ/Pt membranes.\(^{106}\) Ultrathin ALD films have also shown their capabilities in surface and interface modification of SOFC electrodes,\(^{112,113}\) where materials like Zr:CeO\(_2\) have been used as cathodic interlayers, resulting in significant improvement of the cell operation.\(^{114}\) Ambitiously, processes for SOFC cathode materials including quaternary (La, Sr)CoO\(_{3–δ}\) (LSC),\(^{115}\) (La, Sr)MnO\(_3\),\(^{116}\) and (La, Ca)MnO\(_3\)\(^{116}\) have already been demonstrated. It was recently found out that the performance of SOFCs can be enhanced by surface tuning of the La\(_{0.6}\)Sr\(_{0.4}\)CoO\(_{3–δ}\) /Fe\(_{2}\)O\(_{3}\)–δ (LSCF) cathodes with 1–12 nm ALD-LSC films.\(^{117}\)

### B. Complex oxides

There are many ways to categorize complex oxides, e.g., by their structure, composition, and functionality. Here, we have used the structure to differentiate between materials, focusing on ALD of single oxide perovskites, spinels, delafossites, and scheelites, acknowledging the fact that oxides containing the same metal cations can exist in several stable and metastable structures.\(^{118}\) Regrettably, this differentiation leaves out some of the exciting new advances in the field, such as the first reported ALD grown superconducting complex oxide La\(_{2–x}\)Sr\(_x\)CuO\(_{4–δ}\) with a layered perovskite structure.\(^{119}\) However, we try to cover the fascinating functionalities of these materials as well as their potential in applications ranging from ultra-high-k dielectrics to magnetic memories and ferroelectrics, transparent conducting oxides, and (photo)anodes.

### 1. Perovskites (ABO\(_3\))

Perovskite oxides are materials with a chemical formula of ABO\(_3\), where, generally, A-site cations have 12-fold coordination, and B-site cations are in 6-fold coordination with an octahedron of oxygen anions.\(^{19}\) However, the coordination depends on the relative sizes of the A and B cations. The perovskite material family is not restricted to ternary oxides as the A- and B-site cations can be occupied by more than two metallic elements, creating quaternary- or even higher-order oxides. The ideal perovskite structure is cubic with space group but can also be deviated to tetragonal, octahedral, orthorhombic, or rhombohedral.\(^{120}\) Because of the structural features, oxide perovskite can host almost every metallic element in the matrix structure. Thus, unsurprisingly, they also cover the widest selection of properties, and can be insulating, ionic, or electronic conductors, and possess a range of electrical and magnetic characteristics, depending on the A- and B-site elements.\(^{19,20,121}\)

Like in the case of doped materials, the research of ALD perovskites and perovskitelike oxides has traditionally been driven by the requirements of the microelectronics industry, such as development of ultrathin high-k dielectrics for downscaling of DRAM capacitors. Thus, the majority of published work has been focused on the ALD processing of SrTiO\(_3\) (STO)\(^{108–112,121,122}\) and BaTiO\(_3\) (BTO)\(^124–126\), both covering a wide range of precursors and processes. The challenges in the process development have been the requirement of strong oxidizers due to the poor reactivity of the precursors, narrow overlap of ALD temperature windows of SrO or BaO and TiO\(_2\) processes, and high concentrations of remaining carbon impurities in the films caused by the high bonding energy of the metal-ligand bond.\(^{127}\) To overcome these issues, precursors with cyclpentadienyl complexes such as bis(tri-isopropyl cyclopentadienyl)strontium [Sr(‘Pr\(_2\)Cp\(_2\))] and bis(tert-butyl cyclopentadienyl)barium [Ba(‘Bu\(_3\)Cp\(_2\))] have been developed to replace the more conventional β-diketone precursors.\(^{128}129\)

As the ALD temperature is generally not sufficient to crystallize the films during deposition, a postdeposition crystallization annealing is needed to achieve the high permittivity and low equivalent oxide thickness. The crystallization temperature is strongly dependent on the film thickness and stoichiometry as well as the substrate material, and careful optimization of the annealing conditions is needed to avoid microcrack formation at grain boundaries\(^{130}\) and to prevent the detrimental interdiffusion of the layers, e.g., electrode materials.\(^{131}\) Current records of relative permittivity values of polycrystalline films are 180 and 165 for STO and BTO, respectively,\(^{132}\) and the conformal growth of STO with uniform stoichiometry over high aspect ratio hole structures has also been demonstrated.\(^{133,134}\)

To further improve the film performance and to avoid the increased leakage current through grain boundaries, monolithic integration of the film onto the substrate is needed. Due to the needs of the microelectronic industry, special effort has been put in epitaxial growth of perovskites on semiconductor substrates. Monolithic integration of ALD perovskites on Ge has been demonstrated for STO,\(^135\) BTO,\(^138\) as well as SrZrO\(_3\),\(^{133}\) Sr(HF\(_2\))O\(_3\),\(^{134}\) and Sr(Ti, Hf)O\(_3\).\(^{135}\) Other ALD perovskites have successfully grown also on GaAs.\(^{136}\) However, on silicon, an MBE grown buffer/seed layer is still needed to avoid the formation of the interfacial SiO\(_2\) layer and to facilitate the epitaxial ALD growth, as shown for STO,\(^137\) La:STO,\(^138\) BTO,\(^{139}\) BiFeO\(_3\),\(^{140}\) and LaAlO\(_3\).\(^{140}\) A high effective dielectric constant of 660 was measured from stacks of 7–20 nm ALD BTO films grown on 1.6 nm MBE STO on Si, demonstrating the potential of ALD in future devices.\(^{126}\)

Overall, in the growth of perovskite heterostructures, substantial progress has been made over recent years, including epitaxial multilayers of LaNiO\(_3\)/STO/LaNiO\(_3\) onto a single-crystal STO substrate\(^{141}\) and La:STO/STO/La:STO and La:STO/BTO/La:STO stacks grown on MBE STO buffered Si (100).\(^{121,128}\) A schematic of the process for a La:STO/BTO/STO/Si heterostructure for a quantum metal ferroelectric field effect transistor (QMFefET) is presented in Fig. 5(a). The epitaxial integration was verified by X-ray diffraction and transmission electron microscopy, shown in Figs. 5(b) and 5(c). Besides the aforementioned work on BTO and STO, ALD processes for another high-k dielectric, LaAlO\(_3\), have been investigated.\(^{142–146}\) The discovery of intriguing conduction phenomena, caused by the formation of high-mobility 2D electron gas at the LaAlO\(_3\)/STO interface, sparked motivation to successfully grow epitaxial ALD LaAlO\(_3\) onto STO substrates,\(^{145–147}\) and it was observed that the conductivity in this heterostructure is turned on when the LaAlO\(_3\) layer thickness exceeds four unit cells.\(^{146}\)

Although the main focus has been on dielectrics, recently the research interest has been shifted toward mapping oxide perovskites with known functional properties such as (anti)ferroelectricity, (anti)ferromagnetism, and superconductivity. However, due to the nature of the current ALD research, many of the reported works have been devoted mainly on the proof-of-concept investigation of the viable ALD processes, and the demonstrations of the actual functionality of the films are still fairly rare, as stated in the 2017 review by Sønsteby et al.\(^{148}\) While materials with potential magnetic properties, such as rare-earth manganites RMnO\(_3\)
(R = Y, La, Sm, Yb, Lu), have been grown with ALD, the majority of ALD studies have been focused on thin films with ferroelectric behavior. One of the most investigated functional oxide perovskite systems are lead-based materials, namely, quaternary Pb(Zr, Ti)O$_3$, and its prerequisites PbxZrO$_3$ and PbTiO$_3$. The ferroelectric and piezoelectric properties made this material be commonly used in the ferroelectric applications of the past decades, including FeRAM, and sensors and actuators. There, ALD is considered especially interesting for coating a piezoelectric transducer (PZT) over 3D structures and vertical sidewalls of microelectromechanical systems (MEMS). Despite the challenges in the stoichiometry control both with β-diketonate and alkylamide precursors, ferroelectric polarization and piezoelectric response near the morphotropic phase boundary at composition Pb(Zr$_{0.52}$Ti$_{0.48}$)$_3$ has been confirmed in ALD PZT after crystallization annealing, with film thickness down to 6 nm. The conformity of ALD has also been successfully exploited in the formation of multiferroic composites. Piezoelectric ALD PZT grown on mesoporous magnetostrictive cobalt ferrite leads to changes in the magnetization of the composite, with thinner films (3 nm) leading to more enhanced magnetoelectric coupling, due to the mechanical flexibility caused by the residual porosity. ALD PZT has also been applied to magnetic tunnel junctions (MTJs), and it was shown that a 1.5 nm thick PZT in a MgO tunnel barrier increases the voltage-controlled magnetic anisotropy effect by 40% and possesses a great tunneling magnetoresistance (50%) at room temperature, compared to bare MgO tunnel barriers. These kinds of MTJs are thus potential candidates for future magnetic RAMs with ultralow power consumption and high memory density.

Health and environmental concerns have motivated the search for materials which could replace the lead-based ferroelectric and piezoelectric ceramics. Promising materials include BaTiO$_3$, BiFeO$_3$, as well as alkali metal niobates and tantalates. Interestingly, despite the vast exploration of BTO for high-k applications, neither ferroelectric nor piezoelectric response of ALD was reported until 2019, when Lin et al. demonstrated the ferroelectric behavior of the ALD-grown epitaxial BTO films on STO buffered Si by using both piezoresponsive force microscopy (PFM) and electro-optical measurements.

Of these materials, BiFeO$_3$ (BFO) has gained the most interest in the community as room temperature multiferroics, and several processes using different types of Bi and Fe precursors resulting in a large deposition temperature range of 140–520 °C have been developed. The ferroelectric response has been characterized either by PFM or by measuring polarization (P–E) hysteresis from both epitaxial and polycrystalline ALD BFO films, typically after postdeposition annealing. To confirm the multiferroic properties of the ALD BFO, the magnetic characteristics of the films have also been investigated. The ALD process for another lead-free ferroelectric material, SnTiO$_3$, which has been notoriously difficult to fabricate in a thin film form due to the poor control of Sn$^{4+}$ and Sn$^{2+}$ oxidation states at elevated temperatures, have also been proposed. Agarwal et al. showed the room-temperature ferroelectricity of SnTiO$_3$ films. The saturated (P$_r$) and remanent polarization (P$_r$) values measured from 40 nm thick films were found to be 7.5 and 3.3 μC/cm$^2$, respectively. Their results also indicated photocerroelectric behavior, shown as an increase in P$_r$ and P$_r$ values under white light illumination. However, these results have recently been questioned.

Alkali metal containing perovskite and perovskitelike materials, ANbO$_3$ and ATaO$_3$ (A = Li, Na, K), have also been fabricated by ALD, with the demonstrated ferroelectric response in ilmenite-type LiNbO$_3$. More recently, the ALD precursors used are as follows: Sr[(Pr,Ce)$_2$]$_2$−( Bi/iso-propyl cyclopentadienyl)/strontium, La(Pr$_{2}$-fmd)$_3$−(N,N,di-isopropyl formamidinate) lanthanum, TTIP [(Ti(OR)$_3$)$_3$]—titanium tetraisopropoxide, and de-ionized water.

FIG. 5 (a) A schematic representation of processing of the La:STO/BTO/La:STO/STO/Si heterostructure for QMFeFET, the ALD precursors used are as follows: Sr[(Pr,Ce)$_2$]$_2$−(Bi/iso-propyl cyclopentadienyl)/strontium, La(Pr$_{2}$-fmd)$_3$−(N,N,di-isopropyl formamidinate) lanthanum, TTIP [(Ti(OR)$_3$)$_3$]—titanium tetraisopropoxide, and de-ionized water. (b) An asymmetric XRD scan of 6.5 nm ALD BTO/2 nm ALD STO/1.6 nm MBE STO showing BTO (103) and STO (103) reflections. (c) A HAADF-STEM image of the La:STO/BTO/La:STO/STO/Si heterostructure. Reproduced with permission from E. L. Lin, S. Hu, and J. G. Ekerdt, Proc. SPIE 10105, 198 (2017). Copyright 2017 Society of Photo-Optical Instrumentation Engineers (SPIE).
potassium sodium niobate (KNN) films (K_{0.5}Na_{0.5}NbO_{3}) with high compositional uniformity over a large deposition area were grown by ALD. After annealing at 550 °C, the KNN films were highly oriented on the Pt(111) substrate, and the ferroelectric and piezoelectric responses were demonstrated by using in situ synchrotron X-ray diffraction measurements.\(^7\)\(^8\) The strong electro-optic behavior of another similar material, potassium tantalate niobate (KTN), motivated a systematic study of ALD KTa_{1−x}Nb_{x}O_{4}, which showed the importance of composition control of the miscible KNbO\(_3\):KTAO\(_3\) solid system: Stoichiometric or potassium rich KTN forms a pure perovskite phase, while even a slight potassium deficiency induces trace amounts of pyrochlore phase which lacks the electro-optical functionality.\(^9\)

2. Spinels (AB\(_2\)O\(_4\))

The family of spinel oxides, with general formula AB\(_2\)O\(_4\), includes more than 120 compounds. The distribution of the A and B cations within tetrahedrally or octahedrally coordinated sites in the spinel structure strongly determines their properties which can span from ferro-antiferromagnetism, electronic conductivity and transparency, superconductivity, and ferroelectricity.\(^10\) Therefore, it is not surprising that many of them have great technological relevance. The development of ALD processes for complex oxide spinels can impact the field of spintronics and magnetic data storage, which require the preparation of ultrathin films, but will also benefit applications such as batteries, catalysis, and sensors where high aspect-ratio structures are mandatory to improve the device performance.

Regarding magnetic spinels, MF\(_2\)O\(_4\) (M = Co, Ni) are interesting ferrite compositions as they show ferromagnetic or ferrimagnetic behavior at room temperature. Their synthesis by ALD allow precise control of the cation stoichiometry and thus tune their magnetic properties. From alternate pulsing of cyclopentadienyl or β-diketonate complexes and ozone at 200−250 °C, polycrystalline films can be routinely achieved on silicon. Annealing of the films improves magnetic properties being comparable to those of the bulk.\(^11\)\(^12\) Interestingly, epitaxial ALD growth of Fe−Co−O films can promote stabilization of metastable phases and control film orientation at already 250 °C, as shown in Fig. 6.\(^13\)\(^14\) In a similar manner, NiFe\(_2−x\)O\(_4\) film orientation can be driven at 250 °C by properly selecting the single crystal substrate (MgO, LaAlO\(_3\), and Al\(_2\)O\(_3\)).\(^15\) Additionally, (Co\(_{1−x}\),Ni\(_x\))\(_2\)O\(_4\) compositions, interesting not only for its magnetic properties but also as a p-type oxide semiconductor, have been also assessed by ALD, resulting in crystalline thin films at 200 °C, with electrical resistivity as low as 0.0014 Ω cm.\(^16\) Resistivity values reported in the literature are quite sparse and strongly dependent on the synthetic process ranging from 0.06 Ω cm for solution deposited films to 0.003 Ω cm for sputtering.\(^17\)\(^18\) Therefore, it is worth emphasizing the high conductivity obtained by ALD considering the low processing temperature. CuCr\(_2\)O\(_4\) have gained a great deal of attention as a ferrimagnetic and p-type semiconductor with a narrow bandgap.\(^19\)\(^20\) The ALD process of this spinel phase has also been proved successful upon annealing at 700 °C under an oxidizing atmosphere.\(^21\)

ZnAl\(_2\)O\(_4\) is a type of spinel oxide material attractive for its use in catalysis. The versatility of ALD enables us to process it as a combination of ZnO/Al\(_2\)O\(_3\) multilayers followed by a high-temperature annealing or, alternatively, by interface reaction depositing ALD-ZnO on nanoporous alumina which is a perfect host for catalytic applications. Analogously, one-dimensional MgAl\(_2\)O\(_4\) nanostructures can be successfully fabricated by depositing ALD-Al\(_2\)O\(_3\) on MgO nanowires.\(^22\)

On the other hand, lithium titanate spinel, with chemical formula Li\(_4\)Ti\(_3\)O\(_12\), is especially suitable for all-solid-state batteries and fuel cells. This compound can be prepared by ALD overcoming the challenging instability of Li-containing materials. The process is based on the meticulous combination of titanium isopropoxide and lithium tert-butoxide chemicals with water as a cocatalyst, followed by a high temperature annealing.\(^23\) Another relevant lithium-based material is lithium manganese, attractive to be processed by ALD for its applications in microbatteries where the reduced film thickness is crucial in order to obtain faster ionic and electronic diffusion. Miikkulainen et al.\(^24\) demonstrated the feasibility of Li\(_x\)Mn\(_2\)O\(_4\) preparation by ALD, showing both promising storage properties with a discharge capacity value of 230 mAh/g with a 50 μA current, being as high as 80% of the theoretical capacity (285 mAh/g), and robustness after cycling activity.

3. Delafossites (ABo\(_2\))

Delafossites have gained tremendous interest since the discovery of both optical transparency and p-type conductivity in CuAlO\(_2\).\(^25\) These findings envisioned a whole new range of applications to be used as transparent electrodes in solar cells, touch screens, thin film transistors, UV light emitting diodes, and gas sensors.\(^26\) Since then, huge efforts have been devoted to prepare delafossite thin films with chemical structure ABo\(_2\) in which A is Cu and B = Al, Ga, Sc, Cr, Fe. CuCrO\(_2\) has been the first composition attempted by ALD.\(^27\) Deposition at <260 °C followed by a postannealing at 800−900 °C ensures the formation of stoichiometric CuCrO\(_2\) films with a direct band gap of 3.09 eV and 75% transparency, in well agreement with density functional theory studies.\(^28\) Additionally, the substitution of Cr by divalent cations in CuCrO\(_2\) has been reported to significantly increase the film...
conductivity using other deposition processes. Other investigated compositions are CuVO\(_3\) and CuAlO\(_3\) where the combination of CuO and Al\(_2\)O\(_3\) or V\(_2\)O\(_3\) with ozone ensures the formation of the delafossite structure although the films were highly resistive. Therefore, ALD may prove useful to further improve the material performance of transparent conducting oxides by offering precise doping in homogeneous and defect free films while being compatible with temperature-demanding substrates.

4. Scheelites (ABO\(_4\))

Compounds with ABO\(_4\) stoichiometry can deliver a wide variety of functionalities. Here, we will focus on those compositions attempted by ALD which have applications in optoelectronics and power electronics.

CuWO\(_4\) (CWO) has emerged as a promising photoanode for photoelectrochemical water splitting because it exhibits visible light absorption, low bandgap energy, and enhanced stability in neutral and moderate basic pH. Conventional ALD by alternate pulsed of the binary oxides leads to unfruitful results as the growth of WO\(_3\) is inhibited on CuO. This enabled the development of a new approach, named atomic layer stack-deposition annealing, in which the deposition sequence is modified by intercalating an annealing step after each supercycle. Crystalline CWO is formed after a final post-annealing at 550°C. For CWO, each supercycle consists of first pulsing ([BuN\(_2\)]\(_2\)(Me\(_2\)N\(_3\))W and water (WO\(_3\)) and then [Cu(‘Bu – amd)]\(_2\) and ozone (CuO) at 250°C. The electrode shows a stability of 4 h with a photocurrent of 0.11 mA cm\(^{-2}\) at 1.23 V versus a reversible hydrogen electrode (RHE). This performance is slightly lower than the state-of-the-art values reported for CWO, and it is attributed to the smaller thickness and lack of film porosity. However, overcoming interfacial effects in these materials is expected to maximize their efficiency.

Another example of a potential scheelite-like photoanode is BiV\(_2\)O\(_4\). The complexity here relies on the preparation of ALD bismuth-based ternary compounds with well-controlled stoichiometry. The combination of triphenylbismuth (BiPh\(_3\)) with the catalytic effect of vanadium(V)oxy-tri-isoproxiperoxide and water has a tendency to produce nonstoichiometric Bi:V films. An alcohol-based surface functionalization step has been developed to inhibit V\(_2\)O\(_3\) deposition, and it is also effective for the deposition of pure-phase and photoactive BiV\(_2\)O\(_4\) after a calcination step, with average photocurrents of 1.17 mA cm\(^{-2}\) at 1.23 V corresponding to ~56.7% light harvesting efficiency measured under illumination conditions of AM 1.5. Rare earth orthovanadates offer high luminescence efficiency for artificial production of light. This attractive property, highly sensitive to the composition and structure, demands for the production of new materials with improved characteristics compatible with industrial processing. Recently, ALD demonstrated the feasibility to prepare the barely investigated YbV\(_2\)O\(_4\) luminescent material to be used as top coating on solar cells. Optimization of the V\(_2\)O\(_3\):Yb\(_2\)O\(_3\) molar ratio enabled the demonstration of UV to visible and near-infrared (NIR) conversion upon postdeposition treatment at high temperatures (700–1000 °C), thus being an engaging platform for the preparation of more complex systems.

HfSiO\(_3\) offers significant potential to be used as a gate dielectric for Ga\(_2\)O\(_3\)-metal-oxide-semiconductor transistors. This material offers both large dielectric constant (HfO\(_2\)) and wide bandgap (SiO\(_2\)). ALD puts forward an effective way to tune the HfSi molar ratio to modulate the band alignment with β-Ga\(_2\)O\(_3\).

IV. CONCLUSIONS AND FUTURE PROSPECTS

Here, we have reviewed the rapid progress on atomic layer deposited multicomponent oxides from doped to complex oxides focusing on single perovskite, spinel, delafossite, and scheelite structures and highlighting their potential technological applications. This study identified the present limitations as well as unraveled novel opportunities that the synergy of ALD and oxide materials can offer to trigger new research and technology innovations.

Superior film conformality and compatibility with the state-of-the-art manufacturing processes have already made ALD one of the most rapidly developing fields in the microelectronics industry, and ALD has proven itself as a key technology in the down-scaling of novel logic and memory components. New technologies relying on advanced functionalities of the materials set new demands for the high-quality thin films, and ALD has already demonstrated its potential to take on these challenges. For example, ALD of ultrathin HfO\(_2\)-based films is a promising advance for scalable high-density memory devices and other applications requiring ferroelectric thin films, such as negative capacitance transistors. Moreover, with the vast selection of different functionalities, complex oxides are believed to have the potential to overcome some of the current limitations of the CMOS-based technology and enable next generation approaches, such as moving from electronic to electromagnetic devices, as well as neuromorphic computing.

The advances in process development have demonstrated the capability of ALD in monolithic integration of oxide films onto a selection of substrates and even in the fabrication of multilayered heterostructures. These structures are crucial for many emerging applications, for example, in 2D oxide electronics and in spintronics where they can form all-oxide ferroelectric or magnetic tunnel junctions for ultralow power consumption and high-density memory devices. The ability of ALD to coat complex topographies can also be exploited in the design of new multiferroic composites using porous template materials. Besides the oxide electronics, there are other sectors with strong needs for high-quality functional multicomponent thin films and nanoarchitectures, including energy conversion and storage, catalysis, and photonics for which all ALD offers great potential to improve the existing applications, for example, the fabrication of electrolytes and interfacial layers in Li-ion batteries and the use of YSZ thin film electrolytes in SOFC, and the development of photoanodes and transparent electrodes.

Importantly, there is plenty of room to expand the ALD research toward process development and demonstration of functionality. Here, we want to focus on future directions in ALD process development, some of them being common in the development of any ALD-material and others being specific of complex oxides.

ALD of multicomponent oxides is a unique mixture of chemical synthesis, surface science, and process engineering; therefore, true progress can only be achieved with coordinated efforts among these areas. First, the active synthesis of new precursors for even a wider range of deposition materials is required. For example,
development of Ru precursors for fabricating electrodes for microelectronics can also enable the ALD processing of new materials, such as SrRuO$_3$. Also, there is a need to develop novel and more efficient chemistries to broaden the compatible deposition conditions when multisolutes are involved, minimize the use of strong oxidizers, and avoid the incorporation of impurities. Second, it is crucial to understand the gas-solid reactions and reaction mechanisms that take place during the deposition for process optimization. This will be possible by continuous development of theoretical models and simulations of the reactions beyond binary oxides, together with advanced in situ measurements such as Fourier transform infrared spectroscopy, spectroscopic ellipsometry, quadrupole mass spectroscopy, and synchrotron characterization. Absorption calorimetry is a new characterization tool to this field that will provide valuable information on the reaction mechanisms through identifying the heat associated with the half-cycles. Third, the fabrication of nanofeatures of (epitaxial) complex oxides is gaining attention to investigate new physics at the nanoscale and their integration in devices, i.e., multiferroic FETs or silicon microring resonators. There are two very active areas of research in the ALD community tackling device miniaturization: atomic layer etching and area-selective deposition. Expanding this research, which is currently mainly limited to binary elements, to complex oxide will significantly broaden its potential. A pioneering work in this field is the recent demonstration of area selective deposition of epitaxially integrated BaTiO$_3$ on SrTiO$_3$ by Coffey et al. It is also important to adapt the new technologies to ALD reactors incorporating, for example, rapid temperature control of the substrate within the ALD supercycle which would enable new processes where the ALD windows for different binaries do not overlap. The crystalline growth and low growth rates could also be enhanced by equipping ALD reactors with flash lamps, capable of rapid thermal annealing of the films between the deposition cycles, and the use of plasma reactors which would facilitate epitaxy during deposition. Finally, the capabilities of the ALD could be more widely explored, and exploited, beyond the process development and proof-of-concept demonstrations, by expanding the activities even more toward the (volume) manufacturing and engineering. Consequently, there will be great opportunities for ALD of thin film multicomponent oxides both in understanding of fundamental science, as well as in contributions to applied research in construction of improved devices, and generating new uses for these materials supporting the technology development.

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