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Atomic Layer Deposition of Alkaline Earth Oxides: Process Optimization, Characterization, and Application

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Strontium Oxide (SrO) is of interest for the growth of epitaxial perovskite oxides on semiconductors where it acts as a buffer layer between the reactive semiconductor and metal oxide layers. Magnesium oxide (MgO) is widely used as the intervening tunnel barrier to enable efficient spin injection in the magnetic tunnel junctions (MTJs). Due to the strong basicity, MgO and SrO are chemically unstable once exposed to the air, and ex situ chemical and structural analysis tools may not reveal the true properties of MgO and SrO films. Moreover, ex situ optimization of atomic layer deposition (ALD) process parameters, such as saturation curves and deposition temperature windows, becomes a laborious task when multiple films of different thicknesses have to be deposited. Thus, in order to better understand and control ALD processes, in situ thin film analysis techniques are highly desirable. Spectroscopic ellipsometry is an all-optical, non-destructive method, and in situ real time spectroscopic ellipsometry (RTSE) provides a fast and simple way to acquire thickness and optical property data during ALD growth. The objective of this work is to provide insight into the mechanisms of SrO and MgO ALD by using RTSE to study ALD half-cycles, and to learn about nucleation surface chemistry for Sr and Mg precursors reactions with oxide, hydroxide, and metal surfaces. We emphasize the importance of substrate effects in metal oxide ALD processes and establish correlations between the composition and crystallinity of substrates and thin film material properties.
Atomic Layer Deposition of Alkaline Earth Oxides:
Process Optimization, Characterization, and Application

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Atomic Layer Deposition of Alkaline Earth Oxides:
Process Optimization, Characterization, and Application

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Chapter 1 Introduction

1.1 Atomic Layer Deposition (ALD)

1.1.1 Fundamentals of ALD

Thin film deposition may be considered as a series of sequential mechanistic steps.\(^1\) Arriving atoms or molecules must first adsorb onto a surface, followed by surface diffusion before being incorporated into a film; incorporation involves reactions of the adsorbed species with each other and the surface to form chemical bonds of the film material. Then, the film material begins to aggregate in nucleation processes and finally develops a structure and morphology. The crystallography of film materials can range from amorphous to polycrystalline to single-crystal. Also, for thin films, interfaces inevitably exist with the bulk substrate and between layers of different film materials. At many times, abrupt interfaces are desirable, but difficult to achieve. Especially for heteroepitaxy process, interfacial reactions may lead to formation of amorphous or non-stoichiometric layers, which make the target films unlikely to match the underlying substrates in crystalline symmetry or lattice constant.

Like chemical vapor deposition (CVD), ALD also uses precursor vapors and reactant gases as sources of film-forming elements, which eliminates the line-of-sight transport geometry from source to substrate as found in physical vapor deposition (PVD). But different from CVD, ALD is based on sequential, self-limiting surface reactions, avoiding homogeneous gas phase reactions.\(^2\)\(^-\)\(^5\) Therefore, ALD can provide more uniform and conformal coatings on nonplanar structures than CVD. The use of ALD is increasingly common in microelectronics and is extending to other fields including energy conversion, energy utilization, and energy storage.
where it enables new materials. Generally, deposition by ALD consists of the following steps (for simple binary materials):

1. Self-terminating reactions of a first precursor with surface reactive sites;
2. Inert gas purge and/or evacuation to remove unreacted precursor or by-products;
3. Self-terminating reactions of a second precursor with surface reactive sites;
4. Inert gas purge and/or evacuation to remove unreacted precursor or by-products;

Steps (1)-(4) constitute one ALD cycle, and each ALD cycle leads to a small amount of material deposited on a substrate surface, referred to as the growth per cycle (GPC), as shown in Figure 1.1. Ideally, the GPC should be constant under fixed operating conditions (precursor dosing, deposition temperature, etc.), and the thickness of the grown films can be controlled accurately and precisely by running a specific number of ALD cycles.

![ Typical ALD process illustrated for the two half-cycles of the deposition process.](image)

After the full ALD cycle, a submonolayer of film materials is formed and surface groups are again similar to the start of the cycle.
1.1.2 Surface and Interface Reactions in ALD

Due to the small GPC, ALD is mainly targeted at ultra-thin film applications (<10 nm), where interfaces constitute a large fraction of the film material.\textsuperscript{1,3,5} Moreover, the surface chemistry involved is likely to be more complex than implied in the nominal description of ALD processes in the previous section.\textsuperscript{4} Thus, much effort is needed before any ALD process can be commercialized. Firstly, it is urgent to understand the reaction mechanism of adsorbed precursors with both the substrate and deposited film. Also, any interfacial reaction or diffusion should be studied to better control the structure and morphology of deposited ultrathin film materials. To this point, it is also important to develop accurate analytical and metrological techniques to measure the thickness and other properties of materials deposited by ALD, which is covered in the next subsection.\textsuperscript{3}

Generally, it is found that surface hydroxyls are the initiating sites for oxide ALD on most oxide substrates.\textsuperscript{4} In the simplest case, the substrate may only influence the first few ALD cycles, until a monolayer is formed, followed by steady-state growth (homo-ALD). For example, on silicon reaction of HfCl\textsubscript{4} with Si-OH sites is preferred over reaction with Si-H and Si-O-Si surface sites. Nyns and co-workers investigated the relation between the amount of chemisorbed Hf and temperature dependence of OH densities.\textsuperscript{6} For silicon oxide surfaces, they found that with OH density less than 2.2 OH/nm\textsuperscript{2} each HfCl\textsubscript{4} molecule reacts with a single OH site. Above 2.9 OH/nm\textsuperscript{2}, one HfCl\textsubscript{4} may react with two or three OH sites during the first ALD cycle. Their theoretical models and experimental results are shown in Figure 1.2.\textsuperscript{6}
In other cases, the composition of the substrate may be modified during ALD film formation. Interfacial interactions may occur by solid-state diffusion and reaction. Although analytical techniques are needed for accurate examination of these phenomena, it is useful to predict what kind of reactions are likely to occur based on phase diagrams, which give compositions that have reached equilibrium.\(^1,4\) If there are more than one compounds shown in the diagram, all or only some of these may form at a film interface, depending on the thermodynamic favorability of the reaction and kinetic factors. A reaction is favorable if the Gibbs free energy at the relevant temperature is negative. We will examine these aspects in the latter part of this chapter. Because solid-state reaction can only progress by diffusion of one or more of reacting elements through the interfacial layers that are being formed, the extent of interfacial reaction will depend on interdiffusion rates. For example, by studying the ALD of
Al₂O₃ on Ru film surfaces, Tallarida et al., found that RuO₂ present on the substrate participates in reactions with Al(CH₃)₃ reactant and is reduced to Ru, as shown in Figure 1.3.⁷

![Figure 1.3](image)

The authors further pointed out that Al₂O₃ ALD on RuO₂ takes advantage of oxygen present in the substrate in two ways: (i) the steric hindrance is reduced as Al(CH₃)₃ undergoes fast reactions with O surface sites before the H₂O pulse, thus, the first few GPCs are enhanced; and (ii) oxygen vacancies in Al₂O₃ might be reduced as Al(CH₃)₃ reacts with two oxygen sources, one from RuO₂ and the other from H₂O. In the latter case, reduction of RuO₂ to Ru is incomplete probably due to the limited diffusion of oxygen from the substrate to Al₂O₃ layer. Hence, after full coverage of the substrate surface by Al₂O₃, the GPC is defined by properties of Al₂O₃. More importantly, the different substrates (Ru vs. RuO₂) influence different physical properties of the entire system by affecting the band alignments between Al₂O₃ and the substrates.⁷
1.1.3 Analytical Tools for ALD

In the previous subsection, we discussed surface and interface processes involved in ALD. In order to better understand these phenomena, suitable experimental tools are needed. Usually, ultrathin film materials are characterized by means of ex-situ techniques, such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray reflectometry and diffraction (XRR and XRD), second-ion mass spectrometry (SIMS), and x-ray photoelectron spectroscopy (XPS).\(^8\)-\(^{11}\) While these analytical tools can provide useful information on film thickness, microstructure, and chemical composition, in-situ techniques are desirable to control and troubleshoot ALD processes. In-situ tools can also help rapidly establish operating conditions for optimal ALD growth.

Until now, much of the mechanistic information obtained has relied on the use of quartz crystal microbalances (QCM) to follow mass changes upon precursor exposure or mass spectrometry for detection of chemical byproducts released into the gas phase.\(^{12}\) However, it is very difficult to characterize the chemical nature of adsorbed surface species with these methods. For this, the most common technique is infrared spectroscopy, which is sensitive to the molecular details of the adsorbed species. It has been successfully used to follow subtle chemical or structural changes in organic fragments and establish valuable surface chemistry involved in ALD processes.\(^{12}\)

There is also growing interest in applying ellipsometry for in-situ characterization of ALD processes due to its non-intrusive property. Spectroscopic ellipsometry can measure both thickness and refractive index once the substrate polarization ellipse is measured. The versatility of in-situ ellipsometry has been previously reviewed by Kessels et al., where many informative examples of ALD processes were presented, including $\text{Al}_2\text{O}_3$, HfO$_2$, TiO$_2$, and TiN.\(^3\) Due to the
bascity of alkaline earth oxides, in-situ characterization can provide more accurate measurements. And, because many oxides are excellent insulators, they are transparent to probing vis/IR radiation, making optical data interpretation relatively straightforward.

1.2 SrO ALD Process

1.2.1 Sr Precursors

Interest in strontium oxide (SrO) thin films has steadily grown due to the use of these films as buffer layers for the epitaxial growth of strontium titanate (STO) on silicon.\textsuperscript{13} However, a limited choice of Sr precursors has hindered the application of ALD for high-quality Sr-containing thin films. Metalorganic reactants with tmhd ligands (tmhd= 2,2,6,6-tetramethyl-3,5-heptanedionate) have been the most commonly used Sr precursors.\textsuperscript{1} Unfortunately, ALD process with Sr(tmhd)\textsubscript{2} suffer from limited reactivity with H\textsubscript{2}O, and significant carbon contamination has been reported by some.\textsuperscript{14,15} Thus, efforts have been made to develop new Sr precursors.\textsuperscript{16-19} Cyclopentadienyl (Cp) based Sr compounds were earlier considered too moisture-sensitive to handle conveniently, but conformal STO thin films with very low carbon contamination levels (< 0.3 at\%) have been achieved using strontium bis(tri-isopropylcyclopentadienyl) (Sr(C\textsubscript{5}Pr\textsubscript{3}H\textsubscript{2})\textsubscript{2}) with water co-reactant. The dielectric constant has been demonstrated to be as high as 180 with post-annealing in air at 500 °C.\textsuperscript{16} Later studies provided additional evidence that Sr compounds with sterically bulky cyclopentadienyl ligands are good candidates as ALD precursors.\textsuperscript{20,21} The application of Sr bis(penta-methylcyclopentadienyl) (Sr(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}) and Sr bis(tri-tert-butylcyclopentadienyl) (Sr(C\textsubscript{5}tBu\textsubscript{3}H\textsubscript{2})\textsubscript{2}) in ALD of STO have also been reported. Among the three Sr complexes with cyclopentadienyl ligands, Sr(C\textsubscript{5}tBu\textsubscript{3}H\textsubscript{2})\textsubscript{2} was reported to have the best thermal stability and highest reactivity with water. Density functional theory (DFT) studies have
provided further insight into the design of an optimal Sr precursor.\textsuperscript{21} Holme \textit{et al.} suggested that the low reactivity of Sr(tmhd)\textsubscript{2} against water and high concentration of carbon contamination in the as-deposited films can be explained by the strong tmhd ligand to Sr bonds but weaker bonds within the tmhd ligand. By contrast, cyclopentadienyl (Cp) rings have relatively weaker bonds to Sr ions, and when electron donating alkyl groups are substituted for hydrogen on the Cp ring, the Cp to Sr bond is further weakened. Sr(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2} and Sr(C\textsubscript{5}Me\textsubscript{4}Pr)\textsubscript{2} were suggested as the best precursors for Sr-related film growth via ALD.

Despite the numerous studies of ALD grown Sr-containing thin films, fundamental knowledge of the reaction mechanisms of Sr precursor/ H\textsubscript{2}O reaction pairs is limited due to a lack of \textit{in-situ} measurements. Before this work, the basic mechanisms for cyclopentadienyl Sr precursors reacting with oxide surfaces was only studied by isotope labeling and mass spectrometry, and the protonated ligand (C\textsubscript{5}iPr\textsubscript{3}H\textsubscript{3}) was found to be the dominant product.\textsuperscript{22} The authors reported that at 250 °C, more than 70\% of C\textsubscript{5}iPr\textsubscript{3}H\textsubscript{3} molecules were released during each Sr precursor exposure cycle. Based on stoichiometry, it was suggested that there are two kinds of adsorbed Sr species; one bonded to surface oxygen atoms and the other to both oxygen and (C\textsubscript{5}iPr\textsubscript{3}H\textsubscript{2})\textsuperscript{-} surface groups. Nevertheless, some contradictory results are still hard to explain. For example, the growth per cycle (GPC) of SrO thin films using the same precursor varies significantly from one author to another. Early attempts to estimate the GPC of SrO films deposited at 250 °C were based on results from \textit{ex-situ} energy dispersive X-ray spectrometer measurements, which gave a GPC near 0.11 nm/cycle.\textsuperscript{16} In order to acquire more accurate GPCs, Vehkamaki \textit{et al.} deposited thick Ta\textsubscript{2}O\textsubscript{5} barrier layers to protect against reactions with atmospheric moisture and CO\textsubscript{2}.\textsuperscript{23} The re-measured GPC was a smaller 0.042 nm per cycle with 0.6 sec Sr feeding time at 300 °C. Furthermore, the GPC increased to 0.075 nm by doubling the
feeding time. More recently, Black et al. estimate the GPC of SrO grown by Sr(C$_5$H$_9$Pr$_3$H$_2$)$_2$/H$_2$O at 250 °C as 0.023 nm per cycle.$^{24}$ The observed variations are significant and implicitly demonstrate non-idealities of the ALD process. One source of error, which can be eliminated using in-situ measurement techniques, is the formation of multiple layers of carbonate or hydroxide on SrO when the films are removed from the ALD reactor and characterized ex-situ.

Most recently, Lee et al. reported a highly enhanced growth per cycle (GPC) of SrO thin films by Sr(C$_5$H$_9$Pr$_3$H$_2$)$_2$/H$_2$O in a temperature range between 350 and 400 °C.$^{25}$ These temperatures are substantially higher than previous investigations. Based on reported DFT calculations, Lee et al. proposed a possible growth and reaction model for the highly enhanced GPC. The mechanism proposes that isopropyl groups (iPr) on Cp rings may partially decompose to methyl groups (Me) at 350 °C to form smaller surface species that are stable at the high temperatures and prevent CVD contributions to growth. They further propose that the smaller size of these decomposed species reduces steric hindrance and contributes to the enhanced GPC observed during growth. To enable the development of mass-production compatible STO ALD processes, it is important to understand the origin of these contradictory GPC results. Because GPC is directly related with surface reactions between incoming precursors and surface reaction sites, extrinsic effects, such as an imperfect design of the ALD reactor or unsuitable precursor properties as well as intrinsic effects, such as reaction mechanism sensitivity to surface properties, might cause poor control of GPC. The large variations of reported GPCs include experiments done with both home-built and commercial ALD reactors. Based on the discussion above, the capability of Cp-based Sr precursors for ALD growth has largely been established by theoretical modeling and experimental growth studies. Thus, experiments are needed to uncover the origins of the observed discrepancies.
1.2.2 Crystallization Layer in SrTiO$_3$/Ru Interface

Capacitors can be used as electric charge storage and noise reduction components in many microelectronic devices. In brief, dynamic random access memory (DRAM) works with one capacitor and one transistor, where the presence or absence of charge in a cell capacitor is monitored by a select transistor and represents the 1 or 0 digital data. With the shrinking DRAM design rule, higher dielectric constant (k) materials are needed to store charge. Perovskite dielectrics, such as SrTiO$_3$, offer very high k values. However, the integration of SrTiO$_3$ with current DRAM technology is not straightforward due to several issues. Firstly, multi-cation film deposition are quite complex via chemical routes, such CVD and ALD, especially, in order to achieve a stoichiometric crystalline structure to realize high k values. Also, the perovskite oxide may not be compatible with the underlying electrode layers, which results in the presence of dislocations, chemical interactions, and atomic inter-diffusions at the interface. Thus, in order to apply these very high k dielectrics to future DRAM technology nodes, extensive efforts are needed to understand the effects of process parameters on the properties of perovskite thin film materials deposited by ALD and their interaction with metal electrodes.

Because currently used TiN is incompatible with SrTiO$_3$, mostly due to interfacial oxidation and reaction, Ru/SrTiO$_3$/Ru-structured capacitors have been explored as alternatives. However, it has been reported that when SrTiO$_3$ was directly deposited on Ru electrodes, the dielectric constant of the SrTiO$_3$ films decreased abruptly from 65 to 16 as film thickness fell below 15 nm, even after post-growth annealing at 600 °C for 10 min.$^{26}$ It was thought that the reason was related to film crystallinity, as shown in Figure 1.4. For 10 nm SrTiO$_3$ films grown directly on Ru, no peak was observed, and only when films are thicker than 15 nm, characteristic XRD peaks show up.$^{26}$
The use of seed layers to promote crystallization has rarely been attempted for DRAM capacitor applications because it is difficult to fabricate perovskite seed layers directly on noble metal electrodes without adverse effects on dielectric properties. SrRuO$_3$ has a pseudocubic perovskite crystal structure with a lattice constant of 0.393 nm. The lattice mismatch between SrRuO$_3$ and SrTiO$_3$ (0.391 nm) is only 0.5%. If crystalline SrRuO$_3$ can be formed on Ru electrodes before growth of SrTiO$_3$, the dielectric constant of SrTiO$_3$ may be enhanced. Ahn and coworker explored this procedure and found that by firstly depositing 3 nm SrO on Ru substrates followed by in-situ annealing, deposited SrTiO$_3$ films can be crystallized with thicknesses as low as 10 nm. The resulting dielectric properties are promising, as evidenced in Figure 1.5. With SrO seed layers, 10 nm SrTiO$_3$ films show crystalline phases. As expected, the dielectric constants of SrTiO$_3$ films with SrO seed layers were higher than films deposited directly on Ru electrodes over the whole thickness range.²⁶

Figure 1.4 XRD patterns of annealed SrTiO$_3$ thin films, thickness range of 10–50 nm without a SrO seed layer on the Ru bottom electrodes.²⁶
1.2.3 Thermal Stability of SrO on Si

High-k gate oxide materials in transistor devices reduce leakage currents because greater physical thickness of the oxide can be used. Because gate stacks are exposed to high-temperature (up to 1000 °C) treatments, interfacial reactions between gate oxides and Si might degrade the performance of the transistors. Thus, it is required that gate oxide materials should be thermally stable in contact with Si or a buffer layer that is stable in contact with both Si and the gate oxide.\(^{27}\) HfO\(_2\) has recently replaced SiO\(_2\) materials as the gate dielectric layers to scale silicon-based field effect transistors (FET). During gate oxide deposition, similar to ZrO\(_2\), an undesirable low-k interfacial layer (amorphous SiO\(_x\) and/or Hf silicide) may form between HfO\(_2\) layers and the Si substrate at elevated temperatures. These interfacial layers degrade the performance of MOSFET devices. This is because the relative dielectric constant of SiO\(_x\) is near 4 and interfacial SiO\(_x\) increases the equivalent oxide thickness (EOT). Hf silicides are also
undesirable because they may contribute to excessive leakage currents. Thus, it is critical to reduce or eliminate these interfacial layers. One possible solution is to insert a relatively high-k layer that forms a good interface with silicon, SrO for example, before deposition of HfO$_2$ gate dielectrics. Frank and coworkers have demonstrated that such inserted SrO interfacial layers improve the electric properties of HfO$_2$/SrO/Si gate stacks compared with HfO$_2$/Si.\textsuperscript{28} For example, the EOT of HfO$_2$/SrO/Si gate stacks can reach as low as 0.5 nm, competitive with the best data reported in the literature before 2011 for HfO$_2$-based FETs. Their structure of HfO$_2$/SrO/Si gate stacks is imaged in Figure 1.6, where the different layers are resolved. As discussed in the original paper, SrO was firstly deposited epitaxially on Si. However, based on the TEM data, after fabrication the interfacial layer became amorphous, which is likely caused by reaction with either silicon or HfO$_2$.

![TEM image of TiN/HfO$_2$/SrO/Si gate stack.\textsuperscript{28}](image)

Experimentally, it has been demonstrated that SrO thin films are thermodynamically unstable in contact with Si at elevated temperatures (>400 °C) and may form Sr silicates (SrSiO$_3$ and Sr$_2$SiO$_4$).\textsuperscript{29} There are several stoichiometric forms of Sr silicates, including SrSiO$_3$, Sr$_2$SiO$_4$, and Sr$_3$SiO$_5$, which are shown in the phase diagram of SrO-SiO$_2$ systems, Figure 1.7.\textsuperscript{30} For experimental studies of a direct solid-state reactions between SrCO$_3$ and SiO$_2$ powders, Sr$_2$SiO$_4$
is the only product observed.\(^\text{31}\) The mechanism was proposed based on the first reaction between SrCO\(_3\) and SiO\(_2\) to form a shell of Sr\(_2\)SiO\(_4\), followed by diffusion of SrO into the core of SiO\(_2\) to thicken Sr\(_2\)SiO\(_4\). However, it has been found that the reaction only took place at temperatures above 600 °C.\(^\text{31}\) These discrepancies call for cautions for interpretation of nanoscale reactions based on thermodynamic data of bulk materials.

![Figure 1.7 Phase diagram of SrO-SiO\(_2\) system.\(^\text{30}\)](image)

**1.2.4 Stoichiometric Control of SrTiO\(_3\): ALD vs. MBE**

The incorporation of both excess Sr and Ti cations have been studied in the MBE of SrTiO\(_3\) because non-stoichiometric regions could lead to locally defective structures and degrade the physical properties of SrTiO\(_3\).\(^\text{32,33}\) It has been observed that slightly Sr-rich films mainly have (001) planar defects with excess Sr cations incorporated. Such Sr-excess films have much lower dielectric constants than stoichiometric SrTiO\(_3\) films. For example, the dielectric constant decreases from 263 in stoichiometric SrTiO\(_3\) to only 44 in Sr\(_2\)TiO\(_4\).\(^\text{32}\) By contrast, excess Ti
cations in slightly Ti-rich films were observed to segregate at grain boundaries and did not affect dielectric properties significantly. As expected, ALD of SrTiO$_3$ shares similar trends. For example, Popovici and coworkers reported that by using Sr(C$_5$Bu$_3$H$_2$)$_2$ and Ti(OMe)$_4$ together with H$_2$O as the oxidant, they obtained stoichiometric SrTiO$_3$ thin films when cycle ratios (Sr-O)/(Ti-O) are 4:3 and 3:2, which resulted in a Sr content ranging between 49 and 52% at 250 °C. Post-annealing experiments showed that all SrTiO$_3$ thin films can be crystallized between 540 and 570 °C, where the lowest temperature of crystallization was found for stoichiometric SrTiO$_3$. The authors also evaluated the dielectric properties of very thin SrTiO$_3$ films (7-20 nm) by using Pt/STO/TiN capacitor structures. A maximum permittivity of 210 was obtained for stoichiometric STO; permittivity decreases when more Sr is incorporated, Figure 1.8.

![Figure 1.8 Permittivity as function of the Sr(Sr+Ti) ratio for SrTiO$_3$ films annealed at 600 °C in N$_2$ ambient for 1 min.](image)

Figure 1.8 Permittivity as function of the Sr(Sr+Ti) ratio for SrTiO$_3$ films annealed at 600 °C in N$_2$ ambient for 1 min.
For MBE of stoichiometric SrTiO$_3$, an ALD-type growth strategy is also applicable, in which the Sr (Ti) flux is alternated between being on (off) and off (on) and full MLs (monolayers) of SrO and TiO$_2$ are sequentially deposited. Growth can be described by the formula (SrO)$_m$(TiO$_2$)$_m$. It has been observed that no artificial structures could be obtained by alternating the growth of identical numbers of SrO and TiO$_2$ MLs, even up to 33 MLs for each. Fisher et al. found that the two layers almost completely inter-reacted to form SrTiO$_3$ perovskite films and only a residual atomic-layer stacking fault exists at the original super-period boundaries. This can be partially explained by considering the large negative Gibbs formation energy for SrTiO$_3$ from the binary oxides. In addition, because the deposition temperature is typically over 700 °C for MBE of SrTiO$_3$, it is reasonable that interdiffusion rates are high for Sr (Ti) in TiO$_2$ (SrO) matrix. However, due to the much lower deposition temperatures in ALD SrTiO$_3$ (< 300°C), the interdiffusion rates should be reduced significantly, which might lead to the formation of SrO/TiO$_2$ multilayers. Indeed, it has been demonstrated that SrO and TiO$_2$ sublayers do not intermix for large $m$ (~20) in (SrO)$_m$(TiO$_2$)$_m$, as shown in Figure 1.9.

![Figure 1.9 TEM image of SrTiO$_3$ grown by 20 cycles SrO followed by 20 cycles TiO$_2$ on Si.](image-url)
For both MBE and ALD, growth rates were observed to vary with the value of m. For example, the thickness of SrTiO$_3$ films deposited by MBE tended to be higher for larger m values than for the m=1 with fixed total cycle numbers.$^{33,34}$ Fisher et al. mentioned this dependency may result from an increase in the sticking coefficients for films with larger m values, from an incomplete solid-state reaction leaving some regions of less dense SrO and TiO$_2$ phases, and/or from decreased densities owing to increased defect populations in the final film structures.$^{33}$ Although large binary cycle numbers were used to ensure ALD growth was carried out on a single component (SrO or TiO$_2$) surface instead of a SrO/TiO$_2$ mixed surface, Riedel and coworkers still discovered that the Sr/Ti atomic ratio for cycle ratios of (Sr-O)/(Ti-O)=10:10 is different from ratios of 20:20.$^{34}$ As a result, the adsorption of Sr/Ti precursors seems to be not only sensitive to the surface compositions, i.e. pure versus mixed oxides, but also the underlying thickness of pure oxides. More work is needed to understand the effect of SrO/TiO$_2$ cycle ratios on the growth rates and atomic compositions of SrTiO$_3$ films deposited by ALD.

1.3 ALD of MgO

Magnesium oxide (MgO) materials are of both scientific and technological importance. With a band gap of 7.8 eV, MgO is widely used as the intervening tunnel barrier to enable efficient spin injection in magnetic tunnel junctions (MTJs).$^{35,36}$ Due to its basicity, MgO is also useful for CO$_2$ adsorption in advanced greenhouse gas capture and storage technologies.$^{33}$ MgO thin films have been deposited by various techniques including physical vapor deposition (PVD), chemical vapor deposition (CVD), and sol-gel process.$^{37-39}$ However, for applications involving nanometer-scale and three-dimensional structures, atomic layer deposition (ALD) provides a simple and superior way to ensure thickness and conformality.
MgO has been deposited by ALD using β-diketonate and cyclopentadienyl (Cp)-based magnesium precursors. In general, β-diketonate precursors have low reactivity toward the most common oxidant sources (H$_2$O and O$_2$). Thus, stronger oxidants such ozone or plasma-assisted processes are needed to activate surface reactions. By contrast, Cp-based magnesium precursors, namely, Mg(Cp)$_2$ and Mg(CpEt)$_2$ (Et=ethyl), are known for their high volatility and reactivity toward H$_2$O. A growth per cycle (GPC) larger than 0.1 nm/cycle has been achieved by using Mg(Cp)$_2$ and Mg(CpEt)$_2$ at 250 °C. The basic mechanism for cyclopentadienyl-based magnesium precursors reacting with oxide surfaces is believed to involve sequential reactions between surface hydroxyl groups and Cp ligands of the Mg precursors.

### 1.4 Thesis Objectives and Scope

The most attractive benefits of thin film deposition with ALD are accurate thickness control and high conformality. For ideal ALD processes, counting cycles should accurately predict and control film thickness. However, because any ALD process starts with a substrate and involves chemical reactions at the surface, it is expected that nucleation effects are inevitable. Issues surrounding nucleation are particularly critical in ALD, since most ALD applications aim for ultrathin films with thickness in the range of 1 - 50 nm. As discussed in previous sections, SrO thin films are of primary interest for semiconductor gate/ memory insulators and other novel nanoelectronics devices and thin film structures. Due to strong basicity, SrO is chemically unstable once exposed to the air, and \textit{ex-situ} chemical and structural analysis tools may not reveal the inherent properties of SrO ALD. Moreover, \textit{ex-situ} optimization of process parameters such as saturation curves and deposition temperature windows becomes laborious when multiple films of different thicknesses have to be deposited. Thus, in order to better understand and
control ALD processes, *in-situ* thin film analysis techniques are highly desirable. Spectroscopic ellipsometry is an all-optical, non-destructive, non-invasive analytical technique, and *in-situ* real time spectroscopic ellipsometry (RTSE) provides a fast and simple way to acquire thickness and optical property data during ALD growth. The objective of this work is to provide insight into the mechanisms of SrO and related MgO ALD using RTSE to study ALD half-cycles to learn about nucleation surface chemistry for Sr and Mg precursor reactions with oxide, hydroxide, and metal surfaces. We emphasize the importance of substrate effects in metal oxide ALD and establish causality between the composition, crystallinity, and material properties.
References


T. Hatanpaa, M. Ritala, and M. Leskela, Crystal structures and thermal properties of Ba(1,2,4-t-Bu\(_3\)C\(_5\)H\(_2\))\(_2\) and Sr(1,2,4-t-Bu\(_3\)C\(_5\)H\(_2\))\(_2\): Precursors for atomic layer deposition, *J. Organomet. Chem.*, **692**, 5256 (2007).


B. Burton, D. Goldstein, and S. George, Atomic Layer Deposition of MgO Using...

Chapter 2 Experimental Techniques

2.1 Spectroscopic Ellipsometry (SE)

2.1.1 Fundamentals of SE

Ellipsometry is an all-optical, non-destructive method that provides a simple and fast way to acquire thickness and optical property data during ALD growth. The fundamental equation of ellipsometry is described by Equation 1,

\[ \rho = \tan \Psi \exp(i\Delta) = \frac{R_p}{R_s} \]

where \( R_p \) and \( R_s \) are the complex Fresnel reflection coefficients for \( p \)- and \( s \)-polarized light, respectively. Here, we refer to plane polarized waves that are in the plane of incidence as \( p \) waves and plane waves polarized perpendicular to the plane of incidence as \( s \) waves. When polarized light is incident on a surface, there is an interaction between the material and the electric fields of the incident wave. The ellipsometric parameter, \( \Delta \), is the change of phase that occurs upon reflection and its value can be from 0 to 360\(^\circ\). \( \Psi \) is the angle whose tangent is the ratio of the magnitudes of the total reflection coefficients. The value of \( \Psi \) ranges from 0 to 90\(^\circ\). The quantities, \( \Delta \) and \( \Psi \) are directly measured by an ellipsometer. The optical properties of thin films are contained in the complex Fresnel reflection coefficients, but extraction of these properties requires a model and fit to experimental data. Whether the calculated optical properties such as thickness and refractive index are correct depends on whether the ellipsometric models applied are correct. Data fitting is achieved by minimizing the mean square error (MSE) between the measured data and the model calculated ellipsometric fit, which
is given by

\[ \text{MSE} = \frac{1}{N} \sum_{i=1}^{N} \left\{ (\Psi_i^{\text{calc}} - \Psi_i^{\text{meas}})^2 + (\Delta_i^{\text{calc}} - \Delta_i^{\text{meas}})^2 \right\} \] (2)

where the sum is taken over all measured wavelengths. In principle, if the incident angle is set near the Brewster’s angle of the film being deposited, \(\Delta\) can detect less than one monolayer of deposition.\(^1\)\(^3\) For example, for a dielectric film with refractive index of 2.0 on a silicon wafer, at an incident angle of 70° and wavelength of 632.8 nm, a change in \(\Delta\) of 0.25° represents a thickness change of about 0.1 nm.\(^2\) A thin metal film will cause a significant change in both light intensity and phase difference, producing a change in both \(\Delta\) and \(\Psi\).\(^2\) As a result, in-situ ellipsometry is suitable for studying adsorption and desorption in ALD of both metal and dielectric thin films.

### 2.1.2 In-Situ SE

In order to install an ellipsometer to an ALD chamber, the reactor must be modified to have two ports on either side of the sample holder, with an angle near the Brewster angle.\(^4\) The light source and detector are attached to the two ports. Transparent glass windows separate the ellipsoid from the process. Thus, measurements in an ALD system are most often performed at a fixed angle because the optical geometry is fixed, although, varying the angle of incidence provides more information on a particular structure that enables a more accurate structure model to be achieved.\(^1\)

Different from ex-situ SE measurements, two additional effects must be considered before any measurements: window and temperature effects.\(^4\) Windows can affect the light beam through birefringence, reduced intensity, and possible beam deviation or displacement. Window birefringence will modify the light beam polarization and affect SE measurements, which means
sapphire should be always avoided. Although amorphous fused silica glass can have strain-induced birefringence of a couple of degrees, calibration methods have been developed to correct the small window birefringence effects of common windows used in vacuum applications. Window retardance effects depend not only on the window material but also on dimensions. If windows become coated with deposited materials, signal-to-noise will be affected. Fortunately, coatings do not affect SE accuracy because both p- and s-polarizations are equally absorbed. Windows can also deviate the beam direction if the beam is incident off-normal to a window or if the window is wedge shaped. This effect becomes important only if the ambient index differs significantly on each side of the window, such as for liquid cells where the window is in contact with air on one side and liquid on the other. Because SE is a non-invasive technique, it is not generally affected by process environment, especially in vacuum or air. However, for ultraviolet (UV) SE, oxygen and water vapor will strongly adsorb UV light. Also, CO$_2$ adsorb some bands in the infrared spectrum. Previously, the approach for determing the birefringence parameters and accounting for their effects in interference of the optical properties of bare substrates is as follows:\textsuperscript{5}

(i) Determine the ellipsometric parameters ($\Delta$ and $\Psi$) with both windows removed.

(ii) With only the exit window in position, determine the birefringence parameter of the exit window.

(iii) With both windows in position, determine the birefringence parameters of the entrance window.

(iv) With both windows in position, determine the ellipsometric parameters of the sample ($\Delta$ and $\Psi$) as functions of the temperature. The window parameters are taken as constant with temperature.
In our case, the procedure can be simplified due to the built-in capability of window effect calibration of the COMPLETE EASE software, where a delta model is used with up to four fitting parameters to account for window effects. Briefly, a Si wafer with native oxide (1.65 nm) can be used to fit the window effects at growth temperature by using the known oxide thickness, to fit the delta offset model with up to 4 parameters. After minimizing the MSE, all parameters of delta model are kept constant for future use. The reflected optical wave is sensitive to any physical property or process that affects the optical constants and/or surface or interface conditions. Because optical properties of silicon are temperature-dependent, they can be used to measure the surface temperature of a Si substrate. To extract surface temperature by SE, it is necessary to know the temperature dependent optical constants for the particular materials studies. The range in which the temperature can be measured is limited to the range over which the optical constants are known. In our case, we have used the Si Temp JAW (Temp Library) model to simulate the temperature dependence of Si substrates, as suggested by the manufacturer.

![Graph showing comparison of Si substrate temperature measured by thermocouple and spectroscopic ellipsometer.](image)

Figure 2.1 Comparison of the Si substrate temperature measured by thermocouple and spectroscopic ellipsometer.
As shown in Figure 2.1, the simulated silicon temperature is quite consistent with the one measured by a thermocouple with an error of ± 10 °C.

Our ALD experiments used an M-2000V\textsuperscript{TM} spectroscopic ellipsometer with the COMPLETE EASE 4.32 data analysis software from J. A. Woollam Co., Inc. Ellipsometric Ψ and Δ data were acquired at a fixed angle of incidence (68°) over the spectral range 370–1000 nm (1.20–3.34 eV). Crystalline strontium oxide and magnesium oxide have band gaps larger than 5.5 eV and are transparent (k=0) over the whole photon energy range of our ellipsometer.\textsuperscript{2,6} Thus, a standard Cauchy relationship can be used to describe the dispersion of the refractive index n, as shown in Equation 3.\textsuperscript{1}

\[
n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}
\]

where A, B, and C are Cauchy fitting parameters and λ is the wavelength in nanometer unit. The effects of roughness on ellipsometric measurements may also be considered. Any bulk material has well-defined optical constants and the ambient also has well-defined optical constants. However, rough regions between these two may or may not have well-defined optical constants, and if they do, they will certainly not be the same as those of the bulk material or the ambient. In this case, we can consider this region to be effectively a film with well-defined optical constants, which are different from the bulk material and the ambient. It should be noted that this approximation is only valid when the width of the region is much less than the wavelength of the ellipsometric lights. As a result, it is possible to model the surface roughness as a discrete thin film. There is a broad class of dispersion models, known as effective medium approximations (EMA), which can be used to predict the optical constants of mixtures of materials of known optical constants. The simplest EMA model consists of linearly interpolating between the optical constants of the constituents:
\[ \varepsilon = f_A \varepsilon_A + f_B \varepsilon_B \]  

(4)

where \( \varepsilon \) is the effective complex dielectric function of the composite material, \( \varepsilon_A \) and \( \varepsilon_B \) are the complex dielectric functions of the constituent materials, and \( f_A \) and \( f_B \) are the volume fractions of the two constituent materials (\( f_A + f_B = 1 \)). Another commonly used EMA model is the Bruggeman EMA, in which the effective dielectric function of the composite material is obtained by solving the following equation:

\[ f_A \frac{\varepsilon_A - \varepsilon}{\varepsilon_A + 2\varepsilon} + f_B \frac{\varepsilon_B - \varepsilon}{\varepsilon_B + 2\varepsilon} = 0 \]  

(5)

Generally, unless the roughness on the sample under study is very thick (>10 nm), the choice of EMA model is not critical to the result.

### 2.2 X-Ray Photoelectron Spectroscopy (XPS)

XPS is a surface analysis technique used to probe the chemical composition of roughly the first 5-10 nm of a material. Surface analysis by XPS is accomplished by irradiating a sample with soft x-rays and analyzing the kinetic energy of electrons emitted from the material due to the photoelectric effect. The emitted electrons are collected by electrostatic and magnetic lenses and energy-analyzed by a spectrometer, most commonly a hemispherical electron energy analyzer. From the known photon energy (\( h\nu \)) and the measured kinetic energy (KE), the binding energy (BE) of the electrons can be determined according to Equation 6.

\[ BE = h\nu - KE - \Phi \]  

(6)

where \( \Phi \) is the spectrometer work function. The advantages of XPS for the investigation of thin films are its surface sensitivity and chemical specificity, in which each element has a characteristic set of core-level peaks. Moreover, the binding energy of core-level electrons can show subtle changes induced by variation of the chemical bonding, such as the oxidation state.
For example, the observed chemical shifts for different oxidized Si species can be explained by different degrees of charge transfer from Si to O, which depends on the Si oxidation state. Thus, 2p electrons in the case of Si$^{4+}$ experience a stronger Coulomb attraction to the nucleus than in Si$^{3+}$, resulting in a higher binding energy for Si$^{4+}$.

Mainly, there are two methods to acquire depth-dependent elemental and chemical information using XPS: (1) depth-profiling by Ar sputtering by removing surface layers gradually, where XPS spectra are obtained between sputtering intervals, and (2) non-destructive depth profiling through the variation of the escape-depth of the electrons, either by varying the detection angle relative to the sample surface or by varying the kinetic energies of photoelectrons. Although Ar sputtering can collect information deeper into the sample, it may also alter the chemical states of the sputtered films. Therefore angle resolved XPS is preferable for depth profiling ultra-thin films. If electrons are collected at angles other than 0° with respect to the surface normal, these depths are decreased by a factor of cosθ, as can be seen in Figure 2.2 (left). Figure 2.2 (right) shows schematically the analysis of a thin metal oxide on a metal substrate. In this example, XPS data are collected from the metal at two angles, near normal (the “bulk angle”) and near grazing (the “surface angle”). Near normal emission produces a spectrum in which the metal peak dominates while the oxide peak dominates in the spectrum from the grazing emission.7
In this thesis, XPS studies were carried out using a Kratos Axis-165 XPS instrument equipped with an Al Kα x-ray source monochromated to 1486.6 eV. The base pressures of the transfer and analysis chambers are ~ 10^{-9} and ~10^{-10} Torr, respectively. Pass energies of 160 and 20 eV were used for survey and core-level spectra, respectively, and all spectra were referenced to Si 2p_{3/2} at 99.4 eV. Sensitivity factors used for quantitative analysis were obtained from the XPS instrument manufacturer.

Figure 2.2 (left) Greater surface specificity is achieved by collecting electrons at more grazing emission angles; (right) an illustration of the analysis of a thin metal oxide on a metal. The diagram spectra show the effect of the collection angle on the elemental and oxide peaks of the metal.\(^7\)

2.3 Other Characterization Techniques

2.3.1 Diffraction (XRD, LEED, and RHEED)\(^8\)

Both X-rays and electrons can be diffracted from a crystal when their wavelength corresponds to a periodicity of the crystal lattice, and both are useful for examining thin-film crystallography. Here we briefly discuss three common crystallography techniques: (1) X-ray
diffraction (XRD), which is generally used ex-situ for measuring thick films, (2) low-energy electron diffraction (LEED), where the electron beam is directed perpendicular to the surface and their energies are typically around 100 eV, and (3) reflection high-energy electron diffraction (RHEED), where the electron beam grazes the surface with energies near 10-15 keV.

For XRD, the incident beam penetrates the lattice and scatters from each of the atoms in the 3D array. When the incident and scattering angles are equal as measured from some plane of atoms in the lattice, the path lengths of X-rays scattered off of atoms in that plane will be the same. This results in constructive interference of those X-rays and produces a plane wavefront which may be thought of as having been specularly reflected off of that plane of atoms. In polycrystalline films, the degree of preferential orientation, or texturing, is measured using monochromatic X-rays with Bragg-Brentano geometry, in which the peak intensity is a qualitative measure of the degree of texturing; that is, intensity increases with the fraction of crystallites in the film that have a given atomic plane parallel to the surface. The width of the peak, at half maximum intensity is a measure of the size of the crystal grains. This is because a larger stack of planes contributing to destructive interference at “off-Bragg” angles yields a sharper Bragg peak. Grazing-incidence mode can be used to examine the crystallography within a few nm of the surface.

LEED has been the principal tool for studying atomic reconstructions of surfaces. In principle, the surface diffraction situation is analogous to an optical diffraction grating, and beams will occur at any angle for which the path length difference is an integral number of wavelengths. A 2D pattern of spots on a phosphor screen has the same symmetry as the intersection of the reciprocal lattice with the Ewald sphere. The array of spots, which replicates the symmetry of the surface lattice, expands and contracts as electron voltage is varied, while
spots from different row spacing modulate in brightness at different voltages as they fall into and out of the Bragg condition. In high resolution LEED, the sharpness of the (00) beam can be used as a measure of ordering and smoothness of the top few monolayers.

RHEED is the primary tool used for monitoring surface crystallography during epitaxial film growth by molecular beam epitaxy. In RHEED, incident and diffracted beams both make grazing angles to a surface, so that the electron optics are out of the way of the flux of depositing material. Because the reciprocal lattice rods are almost tangential to the Ewald sphere and because the sphere diameter is very large for a 10 keV beam, the diffraction spots are elongated into streaks on the screen. If the sphere were a shell of zero thickness and the rods were lines of zero cross section, the pattern would be spots. However, the sphere has finite thickness due to some wavelength spread and angular spread in the incident beam, and the rods have finite cross section due to disorder in the surface lattice arising from thermal vibration, atomic steps, and bond strain. Islanded or otherwise roughened surfaces produce spotty RHEED patterns, and this gives a measure of the smoothness of growth to atomic-layer sensitivity. Moreover, spot intensity oscillates with a period exactly equal to the monolayer growth time, allowing one to count the number of monolayers grown for precise construction of quantum well and superlattice structures.

2.3.2 Auger Electron Spectroscopy (AES)  

In AES, a vacancy in the K shell (1s) is filled from the L shell, and an Auger electron is ejected from L. This Auger-electron peak then is designated as KLL; for higher elements, there are also LMM and MNN Auger peaks. The C (KLL) Auger electron escapes with kinetic energy equal to the K-L energy difference less the L well depth (266 eV), which is independent of the
energy of the probe beam. We can also acquire information about the chemical bonding state of
the atom based on the escape energy. For example, the potential-well depth of an atomic inner
shell shifts a few eV with bonding state, since bonding affects the electron density in the valence
shell and thereby affects the screening of the inner shells. It should be noted that quantitative
analysis with AES is less straightforward than XPS.

2.4 ALD System

2.4.1 General Characteristics

![Cross-flow reactor schematic and shower-head reactor schematic.](image)

Figure 2.3 (a) Cross-flow reactor schematic and (b) shower-head reactor schematic.\textsuperscript{11}

The major hardware components of an ALD system are the reactor, reactor heaters, sample heater, gas delivery system, vacuum pumps, abatement, and control systems.\textsuperscript{9,10} Generally, there are two common types of ALD reactor setups: cross-flow and shower-head. Figure 2.3 (a) and (b) show the schematic layouts for these two types of reactors.\textsuperscript{11} In a cross-flow reactor, the reactant and purge gas are introduced into the front side of the reactor via a gas distributor. The gas stream is usually laminar-flow to direct the flow efficiently across the
sample to the vacuum pumps. A large linear velocity is desired for fast reactant switching and rapid purging. In a shower-head design, gas flow is introduced above the wafer and directed radially from the center to the edge of the wafer. Commercial reactors are designed for rapid cycling to enable fast growth, and are not generally equipped with in-situ diagnostics. The introduction of windows and the supporting hardware necessary for in situ-SE studies are contrary to the requirements for fast growth. For this reason, cycle times are longer in the research reactor used in these studies. Fortunately, for true ALD growth conditions, the surface properties are not highly sensitive to the cycle times so that good correspondence between research data and commercial machines may be expected. The major limitation of ALD is its relatively low deposition rate as compared to most conventional CVD and PVD technologies. For very thin films, such as high-k gate dielectrics (~ 3 nm) this is not a problem. For many other applications, much thicker dielectrics in the range of 10-200 nm are needed. Thus, much effort has been spent to improve the productivity of ALD, for example, batch process, spatial gas separation, and atmospheric pressure ALD.\textsuperscript{12}
2.4.2 ALD System for MgO and SrO\textsuperscript{13,14}

The (home-made) ALD system used in this PhD research is shown in Figure 2.4, equipped with our spectroscopic ellipsometer. The Sr-metal precursor was the THF adduct of Sr(C$_5$Pr$_3$H$_2$)$_2$ sold under the brand name Hyper-Sr (Air Liquide). The magnesium metal precursor was bis(cyclopentadienyl)magnesium [Mg(Cp)$_2$, Strem] and purified H$_2$O vapor (Millipore 18 MΩ) was used as the oxidizer. The solid strontium source compound was heated to 150 °C in a glass container where it becomes a light yellow liquid and the solid magnesium source compound was heated to 100 °C in a glass container. The temperature of the H$_2$O container was 25 °C, under which the vapor pressure of water is 23.6 Torr as shown in Figure 2.5. Both inert gas purging and vacuum pumping were used between reactant exposures. Nitrogen or Argon was regulated to maintain 1 Torr reactor pressure using leak valves; vacuum pumping was below 10 mTorr with a dry vacuum pump. The whole ALD system was heated to a temperature
at least 10 °C higher than the precursor temperature used for a specific experiment to prevent precursor condensation on the reactor and tubing walls.

Figure 2.5  H₂O vapor pressure as the function of temperatures.¹⁵
References


Chapter 3 In-Situ Characterization of SrO and MgO ALD

3.1 Introduction

In this chapter, the merits of in-situ real-time SE for studying SrO and MgO thin film deposition by ALD are presented. Firstly, ALD saturation curves can be studied in a single deposition run by determining GPC under various process conditions. Secondly, by increasing the film thickness as a function of ALD cycles, the GPC can be obtained during the ALD process. In addition, by applying real-time mode, submonolayer changes after Sr (Mg) precursor and H$_2$O pulsing can be studied. These aspects are all very relevant for ALD film growth, both in terms of process optimization and control. Furthermore, the combination of in-situ SE and ALD is also useful for fundamental studies of physical and chemical effects related to ultrathin films.

3.2 SrO ALD

3.2.1 General characteristics

Originally, it was proposed that strontium oxide (SrO) could be deposited via a Sr(C$_5$\textsubscript{3}Pr$_3$H$_2$)$_2$/H$_2$O process following the overall stoichiometry in Eq. (1).$^{1,2} $

\[
\text{Sr(C}_5\textsubscript{3}\text{Pr}_3\text{H}_2)_2 + \text{H}_2\text{O} \rightarrow \text{SrO} + 2\text{H(C}_5\textsubscript{3}\text{Pr}_3\text{H}_2) \]

(1)

The chemistry of Sr(C$_5$\textsubscript{3}Pr$_3$H$_2$)$_2$/H$_2$O can be divided into two parts. 1) Upon Sr(C$_5$\textsubscript{3}Pr$_3$H$_2$)$_2$ exposure, a Sr(C$_5$\textsubscript{3}Pr$_3$H$_2$)$_2$ molecule may react with one or two surface OH groups presented as 

\[
\text{*Sr-OH} + \text{Sr(C}_5\textsubscript{3}\text{Pr}_3\text{H}_2)_2 \rightarrow \text{*Sr-O-Sr(C}_5\textsubscript{3}\text{Pr}_3\text{H}_2) + \text{H(C}_5\textsubscript{3}\text{Pr}_3\text{H}_2) \]

(2)
2*Sr-OH + Sr(C₅ᵢPr₃H₂)₂ → 2(*Sr-O)-Sr + 2H(C₅ᵢPr₃H₂) \hspace{1cm} (3)

2) Upon H₂O exposure, the surface would be fully hydroxylated as presented in Eq. (4) and (5).

\[ *\text{Sr-O-Sr}(\text{C}_5^i\text{Pr}_3\text{H}_2) + \text{H}_2\text{O} \rightarrow *\text{Sr-OH} + \text{H}(\text{C}_5^i\text{Pr}_3\text{H}_2) \] \hspace{1cm} (4)

\[ 2(*\text{Sr-O})-\text{Sr} + 2\text{H}_2\text{O} \rightarrow 2*\text{Sr-OH} \] \hspace{1cm} (5)

In both equations, the symbol * indicates a surface species. Through this cycle, the surface is regenerated at the beginning of each ALD cycle, and the growth per cycle (GPC) should be steady at a specific deposition temperature. Estimates of the GPC can be obtained by considering the surface density of hydroxyl sites and/ or closest packing of adsorbed species. These two limits represent site limited and steric limited ALD, respectively. However, the Sr(C₅ᵢPr₃H₂)/H₂O process is more complex than revealed by Eqs. (2) - (5), as discussed in the following sections.

### 3.2.2 Saturation Curves and Deposition Window

The ability to extract GPC data by RTSE allows for fast characterization of ALD growth, including verification of saturation of the Sr(C₅ᵢPr₃H₂)/H₂O process with reactant feeding times.³⁴ Figure 3.1 shows GPC measurements at deposition temperatures of 150, 250, and 350 °C as a function of Sr(C₅ᵢPr₃H₂)₂ feeding times (tSr).⁵ The water pulse was sufficient to fully saturate growth due to a fast reaction between the water and adsorbed metal-organic layers. A long purge (120 s) was used to exclude direct reactions between the metal-organic and oxidant. In all three cases, GPCs are self-saturating with respect to Sr precursor feeding time, but they show different saturation characteristics. A constant GPC could be achieved when tSr > 6 s at both 250 and 350 °C. The data at lower temperature show quicker saturation. The GPC at 150 °C was not changed by varying tSr from 3 to 12 s, and the saturated GPC is close to the data
at 250 °C. At 250 °C, the saturated GPC is 0.06 nm/cycle, which is within the range of reported values.\textsuperscript{1,6-8} The saturated GPC is larger than 0.3 nm at 350 °C.

![Graph showing SrO ALD GPC as a function of Sr precursor exposure time at deposition temperatures of 150, 250, and 350 °C. H\textsubscript{2}O dosing time is 0.5 sec, purge time is 120 sec to ensure no direct reactions between Sr precursor and H\textsubscript{2}O, and evacuation time is 70 sec.]

The unusually large GPC at 350 °C is consistent with a highly enhanced rate recently reported by Lee \textit{et al.}\textsuperscript{8} These authors measured GPC via Sr layer density, which is not an in-situ technique. Conversion of their results into thickness increments by assuming the as-deposited films have bulk-like density yields GPCs near 0.06 and 0.26 nm/cycle at 250 and 350 °C, respectively. The data conversions likely underestimate the thickness increment because the as-deposited ALD films usually have a lower density than bulk SrO.\textsuperscript{9} Thus, there is a significant
difference for SrO growth at the lowest and highest temperatures, which suggests a strong effect of temperature on the surface concentration of reacting sites and/or the reaction mechanism.

Self-saturating characteristics of ALD growth were observed over a large temperature range, but with significant variation of the GPC. The saturated GPC is plotted vs. temperature in Figure 3.2. All data are acquired using reactant doses of 12 s Sr(C$_5$Pr$_3$H$_2$)$_2$, 1s H$_2$O, and 120 s purge. These exposure times were verified to be in the saturation region of the GPC versus exposure curves. It is apparent that there are two ALD windows with a transition region between them. There is a low temperature window below 250°C and a high temperature window above

![SrO ALD GPC as a function of temperatures. Sr precursor exposure time is 12 sec, H$_2$O dosing time is 0.5 sec, purge time is 120 sec to ensure no direct reactions between Sr precursor and H$_2$O, and evacuation time is 70 sec.](image)
350°C, both with near constant GPC, and an intermediate region with a temperature dependent GPC. For non-ideal metal oxide ALD, temperature dependence of the GPC might come from the effect of temperature on the number and/or type of surface OH sites for chemisorption of metal precursors. GPC may also increase with temperature because energy barriers may be overcome at higher temperature with reactions that do not occur at lower temperatures. Thus, there is a need to separate the effects of temperature on the reaction mechanism from its effect on the number and/or type of OH groups.

### 3.2.3 Real-Time SE Measurements

In-situ RTSE measurements contribute monolayer-resolved information about the reaction mechanisms, as shown in Figure 3.3. In particular, it is possible to observe chemisorption and reaction steps at different temperatures in each ALD window, as well as the transition region. As expected, thickness vs. time data acquired at 200 and 350°C show significantly different characteristics. At 200°C, the apparent thickness abruptly increases during each Sr(C$_3$Pr$_3$H$_2$)$_2$ feeding step and sharply decreases after reaction with H$_2$O. By contrast, data at 350 °C show qualitatively different characteristics with a larger increase during precursor adsorption, a nearly steady thickness during each purge cycle, and a small, transient, bump-like increase during H$_2$O dosing. The net difference between the two curves accounts for the different GPCs observed during steady growth.
Some groups have suggested that thermal decomposition of Sr(C$_5$iPr$_3$H$_2$)$_2$ may be the reason for the enhanced GPC observed at temperatures above 300 °C.$^{1,2}$ However, our in-situ SE measurements show no sign of thermal decomposition even at deposition temperatures up to 390 °C (limited by our ALD system), as evidenced in Figure 3.4.$^{11}$ Starting with a freshly prepared, OH-terminated surface, five sequential Sr(C$_5$iPr$_3$H$_2$)$_2$ exposure/ purge steps were carried out. Without introducing any additional OH groups (no H$_2$O exposure), the SE results in Figure 3.4 clearly show that thickness only increases after the first Sr(C$_5$iPr$_3$H$_2$)$_2$ exposure cycle. Further precursor exposure leads to negligible thickness increase. If precursor decomposition were occurring on this time scale, a continuous change of thickness would be expected. Our results in Figure 3.4 clearly demonstrate that the self-limited nature of ALD process is preserved.
up to 390 °C, where ligand-exchange reactions and not precursor decomposition control growth.

![Graph showing thickness change as a function of ellipsometric acquisition time in five sequential Sr(C₅Pr₃H₂)₂ exposure-Ar purge steps at deposition temperatures of 350, 370, and 390 °C.](image)

Figure 3.4 Thickness change as a function of ellipsometric acquisition time in five sequential Sr(C₅Pr₃H₂)₂ exposure-Ar purge steps at deposition temperatures of 350, 370, and 390 °C.

### 3.2.4 In Vacuo AES and Ex-Situ XRD Characterization

AES was used to investigate the chemical composition of as-deposited SrO thin films without air exposure; spectra are shown in Figure 3.5. We measured the characteristic Auger peaks for SrO, which are Sr MNN and O KLL, and found that films grown at both 250 and 350 °C have similar peak-to-peak ratios of 2.5 between Sr MNN and O KLL. AES is a very surface-sensitive technique where only the chemical composition of the top few layers are probed. Considering the very thin films studied here (< 5 nm), we conclude based on AES measurements that films grown at both 250 and 350 °C have similar chemical composition, in the sense that they are both SrO and not carbonates or another stoichiometry. However, it should
be noted that SrO is a strong basic oxide that can easily react with water to form Sr(OH)$_2$ (strontium hydroxide).$^{13}$ Under ultra-high vacuum conditions, it is not likely that bulk Sr(OH)$_2$ forms, but hydroxylation of the top few layers might be possible.$^{14}$ During in-vacuo transfer and measurement, the surface chemical composition of as-deposited films might change already. Since any reference material would have the same problem, it was not possible to quantify the Sr/O ratios to differentiate between SrO and Sr(OH)$_2$ with AES alone.

![Figure 3.5 In vacuo AES measurement of SrO films deposited at 250 and 350 °C. The film thicknesses are both around 5 nm. Sr precursor exposure time is 12 sec, H$_2$O dosing time is 0.5 sec, purge time is 120 sec to ensure no direct reactions between Sr precursor and H$_2$O, and evacuation time is 70 sec.](image)
In order to understand the differences of growth characteristics between the low and high deposition temperature windows, we carried out a series of ex-situ XRD measurements. In our early work, we attempted to measure thick SrO samples (> 30 nm) with XRD measurements. However, no characteristic SrO XRD peaks could be observed for samples grown at either 250 or 350 °C. Ex-situ XPS measurements identified significant carbonation of our films with formation of SrCO$_3$ (strontium carbonate). To solve this problem, we integrated ALD Al$_2$O$_3$ with

Figure 3.6 ex-situ GI-XRD measurements of Sr films deposited at 250 and 350 °C. The film thicknesses are both around 50 nm. The growth was carried out in the quartz tube reactor, which has a much smaller reactor volume, leading to much shorter cycle time and saturation was also verified. About 20 nm Al$_2$O$_3$ was deposited in-situ on top of Sr films in order to prevent any hydroxylation or carbonation caused by the air exposure.

In order to understand the differences of growth characteristics between the low and high deposition temperature windows, we carried out a series of ex-situ XRD measurements. In our early work, we attempted to measure thick SrO samples (> 30 nm) with XRD measurements. However, no characteristic SrO XRD peaks could be observed for samples grown at either 250 or 350 °C. Ex-situ XPS measurements identified significant carbonation of our films with formation of SrCO$_3$ (strontium carbonate). To solve this problem, we integrated ALD Al$_2$O$_3$ with
our SrO reactor to cap the films in-situ to protect them from reaction with air. Al₂O₃ is known as an excellent moisture barrier and is expected to also retard CO₂ diffusion into SrO films.²⁰ Twenty nanometer capping layers were found to be sufficient for this purpose.

Crystalline structures of films capped with Al₂O₃ were examined by ex-situ GI-XRD. Figures 3.6(a) and (b) compare XRD spectra of two films grown at 250 and 350 °C, respectively. A 2θ scan from 20° to 55° of films deposited at 250 °C shows major diffraction peaks located at 23.1°, 30.8°, 36.3°, and 46.6°. When compared with reported SrO and Sr(OH)₂ diffraction patterns (JCPDS Nos. 48-1477 and 27-0847), the data show that films deposited at 250 °C consist of crystalline Sr(OH)₂, and no peaks for SrO are observed.¹¹ These results are similar to those reported for BaO ALD where Ba(OH)₂ was found to be deposited for conditions up to 340 °C. They also found that at the lowest deposition temperatures the formation of barium hydroxide hydrates was possible.¹⁵ In the present case of SrO, XRD patterns of films grown at 350 °C show the formation of crystalline SrO films.¹¹ The SrO(111), SrO(200), and SrO(220) diffraction peaks are measured at 29.9°, 34.8°, and 49.9°. These XRD peak positions are close to the reported values for cubic SrO (JCPDS No. 48-1477). No hydrates were observed for our Sr containing films. We conclude that the temperature-dependent GPCs with enhanced growth at 350°C are directly related with chemical composition, which must affect the surface OH density and/or reactivity.

According to Lewis theory, alkaline earth metal hydroxides are weaker bases than their oxides.¹³ The crystal structures are also significantly different. Sr(OH)₂ crystallizes in the Pnam space group with four Sr(OH)₂ units per cell, and belongs to the orthorhombic crystal system. Each Sr ion is coordinated to seven hydroxyl groups.¹⁶ With regard to surface reactivity, two distinct families of hydroxyl groups (O1H and O2H) exist in Sr(OH)₂ with different structural
environments. The first type, O1H, is involved in H-bonding with oxygen sites of neighboring O2H groups. The other type, O2H, is directed perpendicular to the O1H groups. DFT studies have shown that O1H bonds are more ionic than O2H bonds.\(^\text{16}\) Considering that adsorption of Sr precursor molecules involves proton transfer from surface hydroxyl groups to cyclopentadienyl ligands, it is possible that the two OH species have different reactivity, and that a lower density of reactive sites limits the GPC in the low temperature window.\(^\text{11}\) It is also possible that a surface hydrate (Sr(OH)\(_2\)•H\(_2\)O) may form during water pulses at 250 °C, which may also lessen the reactivity towards Sr(C\(_5\)iPr\(_3\)H\(_2\))\(_2\). This effect has been observed for the BaO system where a surface hydrate has been found to lower the catalytic activity of Ba(OH)\(_2\) in organic reactions.\(^\text{13}\) The evidence supports an argument that the nature of the crystal structure and, consequentially, the hydroxyl site density and reactivity are temperature dependent. These factors may explain the temperature dependence of the observed GPC values.

### 3.2.5 Comparison with Theoretical Model

In the present Sr(C\(_5\)iPr\(_3\)H\(_2\))\(_2\)/H\(_2\)O process, a ligand exchange mechanism is expected to be preferred because reactions are driven in the forward direction through removal of volatile reaction products.\(^\text{10}\) On the basis of mass balance relations, Puurunen derived a series of equations to model GPCs caused by either steric hindrance or a limited number of active sites on a surface. These two situations represent two limiting cases that may be encountered. In the case of metal oxide ALD defined by steric hindrance, the number of metal atoms adsorbed on a surface per cycle is described by Eq. (6).

\[
\Delta n_M = \frac{1}{x} \left( \theta \Delta n_{L}^{\text{maxthr}} + f n_{OH} \right)
\]  

\(^\text{6}\)
Where $\theta$ is ligand coverage defined as the ratio of the saturation density of ligands to the maximum density with close-packing; $f$ is the fraction of surface OH groups that react with a metal-bearing precursor during a half cycle; $x$ refers to the ML$x$ stoichiometry of the precursor, and $\Delta n_{L}^{\text{maxthr}}$ is an estimated maximum coverage of ligand L based on close-packing [nm$^2$] as shown in Eq. (7).

$$\Delta n_{L}^{\text{maxthr}} = \frac{2}{\sqrt{3}d_{L}}$$ (7)

In the equation, $d_{L}$ is an effective diameter of a ligand L for close-packing. Puurunen assumed that $\theta$ is 0.7 and independent of deposition temperature, and $n_{\text{OH}}$ decreases linearly from 10 nm$^2$ at 0 °C to zero at 1000 °C. The later is an estimate useful for generic metal oxides where more specific information is not available.

On the basis of this growth model, the GPC of an ideal SrO ALD process with ligand-exchange reactions can be derived. The distance between the furthest most hydrogen atoms in a cyclopentadienyl (Cp) ring centroid is about 1.15 nm, which is taken as the diameter of an adsorbate ($d_{L}$), if we treat adsorbed molecules as spheres. For the case where only a single Cp ligand is released per reacted Sr(C$_5$H$_3$Pr$_3$H$_2$)$_2$ molecule (assumed monomeric), the number of adsorbed Sr atoms per ALD cycle is 0.61 nm$^2$ for Puurunen’s model, respectively. The thickness increment ($\Delta h$) per ALD cycle with units of nm/cycle is based on the following equation:

$$\Delta h = \frac{M}{\rho N_A} \Delta n$$ (8)

where $\Delta n$ is the number of metal atoms adsorbed per unit surface per cycle [atoms/nm$^2$/cycle], $M$ is the molar mass of the materials [g/mol], $\rho$ is the density of the material [g/nm$^3$], and $N_A$ is Avogadro’s number. Assuming a single ligand exchange reaction, the GPC predicted with Puurunen’s model is about 0.022 nm/cycle, which corresponds to a case where only a fraction of the available hydroxyl sites react during each precursor pulse. Alternatively, a higher GPC is
predicted for the case where all hydroxyl sites react. In that case, the calculated GPC has an upper limit of 0.149 and 0.129 nm per cycle at 250 and 350 °C, respectively. For the low temperature growth region, below 300°C, it is apparent that a single ligand exchange model under-predicts the observed GPC by a factor of 2. A simple explanation for the discrepancy with the single ligand exchange model is that some precursor molecules react with more than a single site, and more than one ligand per molecule is released as a product. The extent of reaction depends on the substrate configuration because accessible OH groups may cause multiple ligand exchanges. This effect has been observed in carefully designed experiments for HfCl₄(g) reaction on water terminated Si(100)-2x1.¹⁸ Even with all OH groups reacted, Puurunen’s model still failed to predict measured GPC of 0.3 nm/cycle above 350 °C. This discrepancy is probably due to the simple assumption of OH group density. Clearly, higher density will contribute to larger predicted GPC. Although formation of bulk Sr(OH)₂ is no longer favorable at 350 °C, basic SrO surface can still be converted into a full monolayer of surface Sr(OH)₂ after H₂O adsorption step.

3.3 MgO ALD

3.3.1 Crystalline Structure of ALD MgO

MgO was studied to compare and contrast with SrO to better understand the role of oxide vs. hydroxide in the alkaline earth metal oxides. MgO (bulk and thin film) has been an ideal model surface for studying molecular and dissociative water adsorption on metal oxides. Dissociative water adsorption is theoretically not favored on a perfect MgO (001) surface.¹⁹ Experimentally, significant hydroxylation of MgO surfaces is attributed to defect sites, such as low-coordinated corners and steps.²⁰ To avoid hydroxylation and carbonation, similar to SrO experiments, 20 nm-thick Al₂O₃ layers were deposited as capping layers on ALD MgO films.
The crystalline structure of films grown at 250 °C was examined by ex-situ GI-XRD. As seen in Figure 3.7, XRD patterns clearly show the formation of polycrystalline MgO. The MgO(111), MgO(200), and MgO(220) diffraction peaks are located at 36.9°, 42.8°, and 62.4°. These XRD peaks are close to the reported values for cubic MgO (JCPDS No. 78-430). No evidence for hydroxide was found. Therefore, we conclude that the tendency for hydroxide formation increases with atomic size in the alkaline earth series.

Figure 3.7 ex-situ GI-XRD measurements of Mg films deposited at 250 °C. The film thicknesses are around 50 nm. The growth was carried out in the quartz tube reactor, which has a much smaller reactor volume, leading to much shorter cycle time and saturation was also verified. About 20 nm Al₂O₃ was deposited in-situ on top of Sr films in order to prevent any hydroxylation or carbonation caused by the air exposure.
3.3.2 Real-Time SE Measurements

Since the films deposited at 250 °C are already MgO instead of Mg(OH)$_2$, similar growth behavior should be expected at deposition temperatures of 250 °C and 350 °C. Indeed, real-time SE shows that thickness changes follow a similar trend during each ALD cycle at both temperatures, as shown in Figure 3.8. Thickness abruptly increases during each Mg(Cp)$_2$ feed step and sharply decreases after switching to H$_2$O feed. For both cases, the change of thickness during purging is negligible following Mg precursor and H$_2$O pulses.

![Figure 3.8](image.png)

Figure 3.8 Thickness change as the function of in-situ SE acquisition time at deposition temperatures of 250 °C and 350 °C. Mg precursor exposure time is 10 sec, H$_2$O exposure time is 2 sec, purging time is 20 sec, and evacuation time before H$_2$O exposure is 10 sec.
The decrease of GPC observed between 250 °C and 350 °C is most likely caused by dehydration that decreases the hydroxyl surface coverage.\textsuperscript{10} Previous investigations of MgO ALD using Mg(CpEt)\textsubscript{2} and H\textsubscript{2}O observed a similar GPC decrease between 250 °C and 350 °C.\textsuperscript{21} In their research, the authors have established the MgO ALD growth mechanism using Mg(CpEt)\textsubscript{2} and H\textsubscript{2}O by combining the QCM, FTIR, and RBS results. Firstly, the QCM results displayed a mass gain during the Mg(CpEt)\textsubscript{2} exposure due to a larger mass being deposited by the Mg-CpEt surface species than is lost by removal of the OH surface groups. The subsequent H\textsubscript{2}O exposure resulted in a mass loss, resulting from a smaller mass being deposited by the OH surface groups than is lost by the removal of the residual CpEt ligand. These observations were supported by FTIR results where CpEt and OH surface species are alternatively present and removed during MgO ALD cycles. Because Mg(Cp)\textsubscript{2} and Mg(CpEt)\textsubscript{2} belong to the same organometallic group, it is reasonable that they also share the same reaction mechanism for depositing MgO thin films. Although SE provides no chemical information, the present real-time results shown in Figure 3.8 display similar trends as observed by QCM where the large thickness changes after Mg(Cp)\textsubscript{2} and H\textsubscript{2}O pulses can be explained by the difference of molecular sizes between absorbed Mg-Cp and OH species. Nevertheless, in order to better understand the real-time SE results and further apply them for real-time process control, chemical-sensitive techniques must be used to probe and verify the reaction mechanism for the specific process. Until now, the application of real-time SE technique in the characterization of the ALD process is still at its early stage. More work is needed to establish the relationship between real-time thickness response and the surface chemistry involved.
Summary

In this chapter, detailed in-situ characterization and understanding of SrO and MgO ALD processes via spectroscopic ellipsometry was described. These data demonstrate that real-time SE is highly suitable for fast understanding and monitoring of ALD film growth, with submonolayer resolution of each half-cycle. For SrO ALD, the Sr(C$_5$Im$_3$H$_2$/H$_2$O process has two temperature windows between 150 and 390°C, and the saturated GPC depends on deposition temperature, ranging from 0.05 to 0.33 nm per cycle. At 250°C films consist of polycrystalline Sr(OH)$_2$ while at 350 °C polycrystalline SrO is observed. The large difference in GPC is believed to be due to reduced accessibility and/or reactivity of OH sites on the hydroxide compared to the more reactive SrO surface. Quantum chemistry calculations may be able to derive activation barriers for the two different surfaces for further understanding, but such work is beyond the current scope.

By also investigating MgO ALD, we have successfully demonstrated the effect of basicity, i.e. the size of alkaline earth ion on the chemical and structural properties of oxide thin films deposited by ALD. The real-time SE data can be are consistent with published results obtained by chemical-sensitive techniques. As a result, once the direct relationship between real-time thickness variation and sequential surface reactions is established, real-time SE can be used as a non-destructive tool for in-line process diagnostics and control. For future experimental work, we suggest in-situ SE studies of other alkaline earth oxide ALD processes (BeO, CaO, and BaO) to gain a systematic view of the adsorption and desorption behaviors during each ALD half-cycle, with emphasis on the role of water. Moreover, we may change H$_2$O to O$_2$ or ozone to study oxidant effects on the density and crystallinity of thin films.
References


9. V. Miikkulainen1, M. Leskelä1, M. Ritala1, and R. Puurunen, Crystallinity of inorganic films grown by atomic layer deposition: Overview and general trends, *J. Appl. Phys.* 113, 021301


4.1 Oxide/Oxide Interface

4.1.1 Sr(OH)$_2$/Al$_2$O$_3$ Interface

Al$_2$O$_3$ thin films (~28 nm) were deposited \textit{in-situ} via Al(CH$_3$)$_3$ and H$_2$O ALD process at 250 °C.\textsuperscript{1} As shown in Figure 4.1, SrO growth is promoted during the first few cycles compared
to later ALD cycles on ALD-grown Al₂O₃ surface at both 200 and 250 °C. It has been well demonstrated that surface hydroxyl groups are the initiating sites for oxide ALD processes on most oxide substrates.¹⁻⁵ Thus, substrate-enhanced growth on Al₂O₃ surface probably indicates that the concentration of OH groups on Sr(OH)₂ is less than on Al₂O₃ at these two deposition temperatures. Because steady growth characteristics of Sr(OH)₂ homo-ALD can be observed after just 5 cycles, the Al₂O₃ substrate is probably unmodified and only influences the first reactive adsorption sites for the incoming Sr precursor. This represents a simple case where the substrate only affects the earliest few ALD cycles, until a complete monolayer is formed, followed by steady-state homo-ALD growth.

4.1.2 Sr(OH)₂ (SrO)/SiO₂ Interface

The substrate nucleation effect is shown in Figure 4.2 for Sr(OH)₂ growth on SiO₂ at 250 °C where the initial GPC shows significantly enhanced growth for approximately 10 cycles. After 10 cycles, the GPC steadily decreases until it reaches its final value (0.05 ± 0.02 nm/cycle) after 25 cycles at 250 °C, which is consistent with previous studies.⁶⁻⁹ By contrast, at deposition temperatures of 350 °C, GPC continuously increases during the first 10 cycles until it reaches a steady value of 0.30 ± 0.02 nm/cycle.⁸ Understanding the nucleation behavior at 250 °C can be assisted by comparing GPCs between the transition region (< 10 cycles) and the normal region (> 30 cycles). It is apparent that films deposited in the transition region have a surface chemistry significantly different from steady SrO growth. It is known that the first-cycle GPC on SiO₂ is mainly determined by OH density and reactivity. The enhanced GPCs in the transition region at 250 °C for the 2ⁿᵈ to 7ᵗʰ cycles are similar to the 1ˢᵗ cycle, which suggests the film surface in this transition region has an OH density similar to SiO₂, and distinct from SrO deposited at 250 °C.
Similar enhancements of initial growth have been observed in ALD studies of TiO$_2$ on SiO$_2$. Methaapanon et al., studied TiO$_2$ ALD on oxide-terminated silicon and proposed that initial growth was accelerated by the formation of Ti-O-Si bonds at the interface.$^{10}$ Therefore, XPS investigations were used here to examine the bonding in layers grown at 250 °C to determine if a similar effect is occurring for SrO ALD. Because SrO films are sensitive to air (CO$_2$ and H$_2$O), a protective layer of Al$_2$O$_3$ was used to encapsulate SrO films to preserve the chemical states at the interface.

Figure 4.2 GPC as a function of ALD cycles on SiO$_2$(1.6nm)/Si surface at deposition temperatures of 250 and 350 °C.
Figure 4.3 (a) C 1s XPS core level spectra for samples (from top to bottom): (□) at 10 ALD cycles and air exposed, (∆) at 10 ALD cycles and capped with Al₂O₃ layer, and (○) after Ar sputtering (10 ALD cycles and capped with Al₂O₃ layer). (b) Si 1s XPS core level Si 1s XPS core level spectra for (∆) clean native SiO₂/Si substrate and sample at 10 ALD cycles, and (□) capped with Al₂O₃ layer. ALD growth was carried out on native SiO₂/Si substrates at 250 °C.
with SiO₂. Figures 4.3(a) and (b) show C 1s and Si 2p XPS core level spectra recorded for films grown at 250 °C. As seen in Figure 4.3(a), no Sr carbonate (~290.3 eV) exists with the protective capping layer and all the carbon signal comes from the surface contamination during sample exposure to air, which can be removed by Ar sputter treatment. Figure 4.3(b) shows Si 2p spectra for samples before and after ALD, which indicates that reaction has occurred between SrO and the underlying SiO₂ layers. The Si 2p peak for the Si-O bonding region has diminished and a new intensity has emerged in the silicate bonding region.

Figures 4.4(a)-(c) show fitting results for the Sr 3d, Si 2p, and O 1s XPS spectra of capped SrO films grown at 250 °C. The binding energy of Sr 3d₅/₂ is 134.2 eV, which is between the energy of pure SrO (133.7 eV) and SrCO₃ (134.9 eV). For O 1s spectra, three peaks can be fitted; they are assigned to residual SiO₂ (533.1 eV), capping Al₂O₃ (532.4 eV), and interfacial silicate (530.8 eV), respectively. For Si 2p spectra, the doublet peaks at low binding energies are assigned to the Si substrate, while the peak located at 103.6 eV is attributed to SiO₂. The peak with intermediate binding energy (101.8 eV) represents the formation of Sr silicate, which is similar to bonding observed in molecular beam epitaxy studies. According to the relative areas of Sr 3d, Si 2p, and O 1s silicate components, the silicate composition is close to Sr₂SiO₄. Unlike the case of TiO₂ ALD on SiO₂, the interface reaction here is quite extensive with several monolayers of Sr silicate formed during the SrO ALD growth. Calculations based on changes in Si 2p and O 1s XPS core level spectra of SiO₂ components indicate that for growth at 250 °C more than 70% and 90% of SiO₂ has converted into Sr silicate after 20 and 30 ALD cycles, respectively. The extensive formation of Sr silicate is probably enabled by facile diffusion of Sr atoms through the top silicate layers into the underlying SiO₂ network, transforming the SiO₂ layer into silicate. Support for this mechanism comes from studies of the...
solid-state reaction between SrCO$_3$ and SiO$_2$ powder that takes place at temperatures above 600 °C where Sr$_2$SiO$_4$ is the only product, without forming any intermediate phases.$^{11}$ The proposed mechanism was reaction between SrCO$_3$ and SiO$_2$ to form a shell of Sr$_2$SiO$_4$, followed by diffusion of SrO into the SiO$_2$ core to thicken the Sr$_2$SiO$_4$ layers. These data provide support for the idea that SrO is the mobile species for silicate formation. The temperature is much lower for the ALD interface reaction studied here, but the length scale is also much smaller and the SrO source does not require decomposition of a carbonate. Surprisingly, spontaneous silicate formation is observed even at the lowest possible deposition temperatures of 150 °C, limited by precursor vaporization. Based on SE data, the silicate has a reactive OH density comparable to SiO$_2$ that leads to a transient enhanced GPC at 250 °C, observed in Figure 4.2.

Figure 4.4 (a) Sr 3d data and fitting for Al$_2$O$_3$/Sr silicate/SiO$_2$ film stack grown at 250 °C, (b) O 1s data and fitting for Al$_2$O$_3$/Sr silicate/SiO$_2$ film stack grown at 250 °C, and (c) Si 2p data and fitting for Al$_2$O$_3$/Sr silicate/SiO$_2$ film stack grown at 250 °C.
In addition to the temperature effects on steady growth, SrO ALD is sensitive to the crystalline structure of the underlying substrate. We observed an unusual effect of under-layer crystallinity on the GPC of SrO films grown with temperatures between 200 and 250 °C. In an experiment designed to study substrate effects, we firstly deposited a 4.0 nm SrO film on native oxide SiO$_2$ substrates at 350 °C, followed by in-situ cooling under conditions of 1.0 Torr Ar flow.

Prior to cooling, the growth displayed the enhanced GPC of 0.3 nm/cycle characteristic of steady growth at 350 °C. After cooling, additional ALD cycles were carried out at 200, 235, and 250 °C. As seen in Figure 4.5, the crystalline SrO template has a significant effect on growth. A transient effect of an enhanced GPC near 0.2 nm/cycle is observed at each of the low temperatures. The

![Figure 4.5](image-url)
effect is short lived for films deposited at 200 °C, but persists for more than 50 and 100 cycles for growth at 235 and 250 °C, respectively. Eventually, the effect attenuates and growth decays back to normal values characteristic for the low temperature regime. These observations show that the GPC is strongly modulated by changes of substrate crystallinity. This interesting ‘memory’ effect shows that the influence of the substrate can persist well beyond the completion of a monolayer.

Other studies have reported a related effect where GPC varies with film thickness.\textsuperscript{12-14} For example, in TiO\textsubscript{2} ALD, film crystallization is thickness and temperature-dependent, and at higher deposition temperatures, above a critical thickness, the GPC is enhanced by nearly 140% due to an increase in OH density after crystallization.\textsuperscript{12} In this work, no thickness dependent GPC enhancement is observed for film thickness up to 20 nm at 250 °C. In order to further probe the unusual memory effect, GI-XRD was used to investigate the crystalline structures of films in the regimes of low and high GPCs in Figure 4.5. Two films, both grown at 250 °C with transient enhancement are compared. Both films were grown on substrates prepared with a 4 nm SrO surface. One sample was stopped at 100 cycles while growth was still enhanced, and the other was stopped at 300 cycles, well beyond the transient region. Both films were capped with Al\textsubscript{2}O\textsubscript{3} layers to prevent reactions with atmospheric gases such as CO\textsubscript{2} and H\textsubscript{2}O. As seen in Figure 4.6, the film at 300 cycles consists of polycrystalline Sr(OH)\textsubscript{2}, which has main peaks (23.1°, 30.8°, 36.3°, and 46.6°) similar with a 600 cycle film grown directly on SiO\textsubscript{2} surfaces at a constant temperature of 250 °C. The film stopped at 100 cycles is also Sr(OH)\textsubscript{2}, but crystallized with a different crystallographic orientation, where new peaks located at 27.1° and 28.5° appear, while peaks at 23.1° and 30.8° are much weaker. Thus, the underlying crystalline SrO layer has modified the structure of the Sr(OH)\textsubscript{2} deposited layer, and affected the GPC. The precise reason
for the enhanced GPC, whether by increased density and/or reactivity of the hydroxyl sites, is unknown, but it is clear that not only composition and crystal structure, but also orientation may have significant effects on ALD growth. This study is another example of the hidden complexities of ALD and underscores the need for greater understanding of ALD processes where surface chemistry and bulk processes are coupled and may change during growth.

Figure 4.6 GI-XRD patterns of two samples deposited on 4.0 nm 350 °C - grown SrO surfaces at 250 °C: (i) 100 cycles in enhanced transition region and (ii) 300 cycles beyond the enhanced transition region. For comparison, (iii) shows 600-cycle film grown directly on SiO₂ surfaces at a constant temperature of 250 °C.
4.1.4 MgO/SiO$_2$ Interface

Figure 4.7 shows process data for the deposition of MgO thin films on SiO$_2$ at 250 °C where the GPC continuously increases during the first ten cycles until it reaches a steady value of 0.156 ± 0.006 nm/cycle, a value consistent with previous studies. Understanding nucleation behavior at 250 °C can be assisted by comparing GPCs between the 1st and 11th cycles. The lower GPC of the first-cycles likely indicates that MgO surfaces have a much higher OH density than SiO$_2$ surfaces. As expected for heterogeneous growth, during the first 10 cycles, the chemical composition of the growing films continuously changes from SiO$_2$-like to MgO-like.
characteristics, which probably results in a variation of surface hydroxyl densities. Similar with SrO ALD on SiO₂, it is possible that Mg precursor deposition on SiO₂/Si may also lead to a complex layer consisting of various metal silicates and/or silicides.

In order to determine if a similar effect is occurring for MgO ALD, XPS investigations were used to probe the chemical compositions of Mg-containing thin films. Figure 4.8 shows fitting

Figure 4.8 Si 2p XPS core level spectra for (○) clean native SiO₂/Si substrate and samples after 10 ALD cycles at the take-off angles of 0° (□) and 60° (Δ).
results for the Si 2p XPS spectra of MgO films deposited at 250 °C. For all samples, the doublet peaks (cutoff) at low binding energies are from the Si substrate; while the peak located at 103.4 eV is attributed to SiO$_2$. Evidently, after ALD, a peak with intermediate binding energy (102.1 eV) appears in the region expected for formation of Mg silicate, similar to what has been measured in physical vapor deposition studies.$^{15}$ Angle-resolved XPS was used to further identify the position of this formed silicate. The take-off angle was measured between the detector and the normal of the substrate, where a larger angle means higher surface sensitivity. As can be seen in Figure 4.8, with increased angle from 0° to 60°, the intensity ratio between Mg silicate and residual SiO$_2$ increases, which strongly indicates the formation of a Mg silicate/SiO$_2$/Si structure. When combined with $in$-$situ$ SE results shown in Figure 4.7, it is apparent that the Mg silicate formed in the transition region (between the first and tenth cycle) has a reactive hydroxyl density intermediate between SiO$_2$ and ALD MgO surfaces, which results in the transient GPCs observed by $in$-$situ$ SE. Surface atom mobility and / or increased OH reactivity could play a role in the higher GPC for the silicate surface, but increased OH site density is the most plausible explanation.

4.2 Oxide/Metal Interfaces

4.2.1 MgO/Pt Interface

Figure 4.9 shows data for the deposition of MgO thin films on Pt at 250 °C where the initial growth per cycle (GPC) (<8 cycles) continuously changes and the 1st-cycle GPC is relatively large. After 10 cycles, the GPC reaches its steady-state value of 0.15 ± 0.02 nm/cycle, which is consistent with previous studies.$^{16}$ The deposition behavior of MgO thin films on SiO$_2$ is also presented for comparison. The Mg(Cp)$_2$ exposure duration is 6 sec for both processes.
Evidently, steady-state MgO ALD growth can be achieved on both Pt and SiO$_2$ substrates after 8 cycles, but the choice of substrates strongly affects the 1st-cycle GPCs, as illustrated in Figure 4.9.

![Figure 4.9 GPC as the function of the number of MgO ALD cycles on Pt substrate at deposition temperature of 250 °C. Results on SiO$_2$ substrate are also shown for comparison.](image)

Because ellipsometric $\Delta$ signal can detect less than one monolayer of thin film deposition, real-time ellipsometry allows for a fast understanding of the interaction between ALD precursor and substrate. After Mg(Cp)$_2$ exposure, the surface may be terminated by (Cp)$^-$ groups, whose optical properties differ from that of MgO, leading to uncertainty about the thickness increase after Mg(Cp)$_2$ adsorption.$^{17}$ Thus, rather than model thickness, the raw ellipsometric $\Delta$ change may be used to track the effect of substrates (Pt versus SiO$_2$) on the adsorption behavior of Mg precursor, as shown in Figure 4.10. $\Delta$ signal shows adsorption trends with distinctive increment
rates on these two substrates during the first 5 sec, which are consistent with the large difference in 1st-cycle GPCs, shown in Figure 4.9. $\Delta$ increases slowly from 0.8 to 0.9° on Pt, whereas a saturation value of $\sim$ 0.4 degree is quickly reached on SiO$_2$. The dissimilarity suggests a different surface chemistry. Pt may not provide hydroxyl groups as the initiating adsorption sites for the Mg precursor.$^{18}$ Unlike SiO$_2$, Pt may catalyze the breaking of precursor-ligand bonds.$^{19}$-$^{21}$ This could lead to different interfacial properties of ALD MgO films on Pt versus SiO$_2$, which in turn contributes to the distinctive adsorption behaviors of Mg(Cp)$_2$ observed by real-time ellipsometry.

![Figure 4.10](image.png)

Figure 4.10 –$\Delta$ change as the function of Mg(Cp)$_2$ exposure time on Pt surface at 250 °C. Results on SiO$_2$ surface are also shown for comparison.

In order to further understand the real-time ellipsometric results, XPS was used to investigate the chemical composition of MgO layers on Pt and SiO$_2$ surfaces after two ALD cycles. As shown in Figure 4.11(a), two peaks can be fitted for the oxidized Mg states deposited
on SiO₂; they are assigned to MgO (50.2 eV) and MgCO₃ (51.2 eV). It should be noted that MgO films deposited via the Mg(Cp)₂/H₂O process at 250 °C are free of carbon. Therefore, the existence of carbonate is probably due to air exposure during the sample transfer, as seen by others. By contrast, the Mg 2p core-level spectrum is very broad for MgO layers deposited on Pt. Three fitted component peaks are needed to fully capture the characteristics of this spectrum. The lowest peak has the same binding energy as MgO on SiO₂, and the middle peak is assigned to Mg carbonate with a shift of +0.5 eV compared to its counterpart on SiO₂, probably due to stoichiometric variation. The peak located at 53.9 eV, absent for the MgO/SiO₂ interface, is unique to MgO/Pt and appears to result from the interaction between adsorbed Mg species and Pt. The C 1s core-level spectrum provides evidence for interfacial Mg-containing carbon species (peak at 286.7 eV) for MgO films deposited on Pt that is absent for MgO/SiO₂ and also as-received Pt, as shown in Figure 4.11(b). The presence of interfacial Mg-C-O species is in agreement with previous studies of HfO₂/Pt, where XPS showed the existence of interfacial Hf-C species. As pointed out by A. Mackus et al. for ligand decomposition of MeCpPtMe₃ on Pt, the surface reaction should not be considered as a “CVD component” because once all reactive sites are covered by decomposed carbon species, the catalytic Pt surface is deactivated. The adsorption of Mg(Cp)₂ on Pt may also involve self-limiting decomposition. As a result, it can be expected that the increment of ellipsometric Δ from 0.8 to 0.9° after MgCp₂ exposure >5 sec shown in Figure 4.10 is unlikely to be related to continuous adsorption of Mg(Cp)₂. Instead, it may be caused by reorientation or reordering of Mg-containing surface species during the adsorption.
Figure 4.1 (a) Mg 2p XPS core level spectra for the samples after 2 MgO ALD cycles on SiO$_2$ surface (∆) and on Pt surface (□) at 250 °C. (b) C 1s XPS core level spectra for the samples on SiO$_2$ surface (□) and Pt surface (∆) after 2 MgO ALD cycles, and Pt surface (○) before ALD at 250 °C.
4.2.2 Sr(OH)$_2$/Pt or Pd Interface

The Sr($\text{C}_5\text{Pr}_3\text{H}_2$)$_2$/H$_2$O process was carried out on Pt and Pd at 250 °C to investigate nucleation on metallic substrates. Growth up to 40 cycles is shown in Figure 4.12. As seen in other systems, the initial GPC is promoted during the first few cycles compared to later ALD cycles on both Pt and Pd surfaces. Especially, the GPC of the 1st cycle on Pd is significantly larger.

Figure 4.2 GPC as a function of ALD cycles on Pt (a) and Pd (b) surfaces at deposition temperatures of 250 °C.
XPS was used to investigate the chemical composition of Sr films deposited on Pt and Pd surfaces after two ALD cycles. As shown in Figure 4.13, the C 1s core-level spectra of both samples (Pt and Pd) can be fitted with three peaks. The peak with lowest binding energy, 284.6 eV is attributed to C-C/C-H species usually present as a result of air exposure during sample transfer. However, this carbon peak has much larger intensity on Pt versus Pd even if the transfer durations were the same (~15 min.) for both samples. The peaks located at 288.2 eV on Pt and 288.6 eV on Pd belong to Sr carbonate (SrCO$_3$). Both are within the reported binding energy range and the difference of 0.4 eV might result from the composition variation of the carbonates. The middle peak of SrO/Pt has a similar binding energy (286.3 eV) with the one of MgO/Pt. Interestingly, a small shoulder located at 287.8 eV is observable for SrO/Pd, which may also result from interfacial carbon, but with different stoichiometry.

![Figure 4.3 C 1s XPS spectra after two SrO cycles deposited on Pt and Pd surfaces at 250 °C.](image-url)
Sr 3p$_{3/2}$ spectra also show additional peaks for interfacial products as well as SrCO$_3$, Figure 4.14. For both samples, the binding energies of SrCO$_3$ are roughly similar and around 268.9 eV. But, the peak of interfacial Sr is located at 271.8 eV for SrO/Pd, which is +0.8 eV higher than the one for SrO/Pt, again indicating the different stoichiometry between these two interfacial species.

![Figure 4.4 Sr 3p$_{3/2}$ XPS spectra after two SrO cycles deposited on Pt and Pd surfaces at 250 °C.](image)

The initial growth of SrO on Pd can be further understood by examining Pd 3d core-level spectra, which is shown in Figure 4.15. For pre-growth Pd, there are the main metallic peaks (340.9 eV for 3d$_{3/2}$ and 335.2 eV for 3d$_{5/2}$), and additional peaks with higher binding energy. The 3d$_{3/2}$ peak located at 343.2 eV is probably attributed to PdO, and the intermediate 3d$_{3/2}$ peak at
341.9 eV belongs to Pd suboxide (PdO<sub>x</sub>).<sup>23</sup> After 2 ALD cycles, the hydroxide/hydroxyl peaks vanish and the oxide intensity slightly decreases. By contrast, for ALD growth on Pt, no oxides or hydroxides are detectable before and after ALD growth (not shown).

Gibbs free energy of metal oxide formation is used to represent the ability for metal to be oxidized and at 250 °C the Gibbs free energies for SrO and PdO are -530.9 and -133.8 kJ/mole, respectively.<sup>24</sup> Therefore, it is concluded that Sr reacts with oxygen present on the Pd substrate. Scavenging of oxygen from surface PdO could explain the large GPC of the first cycle on Pd, as shown in Figure 4.12.

Figure 4.5 Pd 3d XPS spectra before and after two SrO ALD cycles on Pd surface at 250 °C.
4.3 Summary

The major commercial uses for ALD are ultrathin films with thickness less than 10 nm due to its relatively low deposition rate compared to conventional CVD and PVD technologies. For example, 2-3 nm high-k Hf-based gate dielectrics are currently deposited by ALD.\textsuperscript{25} In this chapter, in-situ spectroscopic ellipsometry has been applied as the principle tool for studying these substrate-induced effects. By combining SE with ex-situ XPS and XRD, possible mechanisms have been proposed to explain in-situ SE results. As extensively discussed in this chapter, the substrate itself usually induces enhanced or inhibited growth behaviors, imposing difficulties for precisely controlling the thickness. GPC can be affected during the very first cycles (\~5) due to simple differences in surface OH densities, such as Sr(OH)\textsubscript{2} growth on Al\textsubscript{2}O\textsubscript{3} at 250 °C. In more complex cases, GPC deviation can last more than 20 cycles, such as Sr(OH)\textsubscript{2} growth on SiO\textsubscript{2} or SrO at 250 °C, where solid-state reaction and diffusion takes place. We find that the effects of crystalline phase and orientation must also be considered to explain ALD growth. For catalytic materials like Pt, it is found that metal (Sr and Mg)-containing carbon species are formed at the oxide/substrate interface. For materials like Pd with reversible oxides, surface oxygen may also contribute to GPC enhancement. In-situ SE serves as a powerful tool for the study of ALD growth, and may also be useful for controlling other thin film properties beyond thickness.
References


5.1 Crystalline Oxides on Silicon by MBE

The challenge for integrating crystalline oxides with silicon is achieving an atomically abrupt interface. The candidate materials for epitaxial growth on silicon should have similar lattice parameters matching closely with silicon and must be compatible without interdiffusion or reaction. Due to the high reactivity of silicon towards oxygen, the oxygen partial pressure and silicon temperature must be manipulated accurately to avoid the formation of amorphous SiO$_2$ layer that would inhibit epitaxy. During the last two decades, the layer-by-layer MBE technique has been extensively applied to fabricate complex oxides on silicon with high degree of crystallinity, especially SrTiO$_3$. It has been demonstrated that metallic Sr can be deposited on silicon to form one monolayer-thick surface phase without the formation of amorphous SiO$_2$. Thus, much effort was made to develop a procedure which ensures Sr-rich initial condition, where a Sr submonolayer is deposited on the clean Si(100) surface as the first step in crystalline oxide epitaxy. For low Sr coverage, below 1/2 ML, Sr atoms sit primary in the troughs between Si dimer rows and two key surface phases were identified, a (2x3) structure at 1/6 ML Sr coverage and a (2x1) structure at 1/2 ML Sr coverage. High Sr coverage, above 1/2 ML, will lead to other complex reconstructions, such as (3x1) and (5x1) surface phases. Among those surface reconstructions, only the (2x1) reconstruction induced by 1/2 ML is known to stabilize the silicon surface and promote epitaxy. This 1/2 ML Sr surface phase was shown to fully passivate the dangling bonds of surface Si dimers and prevent oxidation of silicon when it is exposed to molecular oxygen.
Alternatively, the Sr can be deposited on silicon substrate with native oxide. In this procedure, the thermal desorption of SiO$_2$ has been argued to be catalyzed by elemental Sr, which leads to a lower desorption temperature, shorter heating time, and smoother surface. After the oxide is completely removed, the Si surface is found to be terminated by a submonolayer quantity of Sr with similar surface structures to direct deposition of Sr on clean Si(100) surfaces. This Sr-assisted deoxidation technique has one advantage over other SiO$_2$ removal ones. Although wet chemical cleaning is widely used in the semiconductor industry, such cleaning technique leads to morphologically rough, poor atomic-order Si surface. Moreover, direct desorption of SiO$_2$ on Si surface only takes places at the SiO$_2$/Si interface by the reaction SiO$_2$ + Si $\rightarrow$ 2SiO (g)$^{21-24}$ As a result, high-density pits forms on the Si surface after SiO$_2$ desorption. By comparison, after Sr-assisted deoxidation process, the Si surface is morphologically ordered and smooth. Thus, it was proposed that Sr plays a catalytic role in promoting the decomposition of SiO$_2$(s) into SiO(g) and O(g). The proposed mechanism for decomposition of Sr/SiO$_2$ is illustrated in Figure 5.1.$^7$
The SiO$_2$ desorption process must be monitored with in situ techniques, which should have the capability of confirming oxide-free silicon surface by either chemical or physical methods.\textsuperscript{2,7,12} Typically, LEED, RHEED, AES can fulfill this requirement. For example, a clear surface structure should show up after oxide desorption, which can be detected by LEED and RHEED. For AES, no oxygen peak should exist after complete desorption. By using in-situ SE, we investigated native SiO$_2$ desorption as a function of time, as shown in Figure 5.2. SE measures the average thickness of the investigated sample, so we observe a continuous decrease in SiO$_2$ thickness. After approximately 20 min. at temperature, the SiO$_2$ thickness reaches a minimum value of 0.2 nm and stays constant with further heating (up to 35 min.). The residual
thickness value is interpreted as residual roughness rather than a real oxide thickness since no further decrease is observed. The ability to monitor the oxide desorption process in-situ with SE is critical to achieving sharp dielectric/Si interfaces since the native oxide must be removed before a deposited oxide can be added.

After the creation of Sr/Si template, the next deposition step should involve the formation of a SrO epitaxial layer (monolayer thickness). For MBE, it can be achieved by oxidation using a molecular oxygen source: \( \text{Sr} + \text{O}_2 \rightarrow \text{SrO} + \text{O} \). Once this SrO layer is formed, SrTiO\(_3\) deposition can proceed. It has been found that the deposition temperature must be kept under 300 °C for the initial few SrTiO\(_3\) layers in order to suppress SiO\(_2\) formation. Otherwise, Ti will react with Si to form Ti silicide at the interface.

### 5.2 Opportunities for ALD

Despite the successful MBE-related work on epitaxial growth of oxide thin films on silicon, it is of great interest to develop a more practical and cost-effective method for growth of crystalline oxide on silicon. Different from MBE technique, no elemental Sr ALD process has been reported but ALD of SrO thin films has been developed by many groups. When compared with MBE-related work, it is only plausible to follow a procedure that deposits SrO before removal of SiO\(_2\) to form the 1/2 ML Sr/Si silicate. Recently, our group has used this strategy and successfully achieved well-ordered Sr/Si structures with (3x2) and (2x1) LEED patterns compared well with the Sr template prepared by MBE technique. SrO/SiO\(_2\)/Si structures were investigated by varying the number of ALD cycles and high-temperature annealing (600-900 °C) to form Sr template layers. After cooling to room temperature, the Sr/Si surfaces were investigated by low energy electron diffraction (LEED). It was found that no
LEED pattern is produced below 750 °C. With 5-15 ML SrO deposition, as shown in Figure 5.3(a), a mixed (2x1) with (3x) spot pattern is clearly visible after SiO2 removal above 800 °C, demonstrating the successful formation of an ordered Sr structure. Increase of the coverage to 15-40 ML results in a two domain (3x2) pattern. At coverage of 40-60 ML, a clear (2x1) pattern is observable after annealing at 800 °C. With further increase of the annealing temperature to 850 °C, the (2x1) pattern converts to a (3x2) pattern, probably due to partial Sr desorption at higher temperature. These findings provide proof of concept that ALD deposited layers can be

![Figure 5.3 LEED patterns of the Sr/Si (100) system after SrO deposition and SiO2 deoxidation at high temperature: (a) (3x) obtained after depositing 5-15 ML SrO and annealing at 800 °C. (b) (3x2) obtained after depositing 15-40 ML SrO and annealing at 800 °C, (c) (2x1) obtained after depositing 40-60 ML SrO and annealing at 800 °C, (d) (3x2) obtained after depositing 40-60 ML SrO and annealing above 850 °C.](image-url)
used to grow the $\frac{1}{2}$ ML (2x1) Sr/Si templates for the growth of SrTiO$_3$ on Si. However, a relatively large amount of SrO (more than 20 ML) was required to achieve the 1/2 ML (2×1) reconstruction compared to 2 ML of elemental Sr reported in MBE studies, which indicates that a different mechanism is involved for the ALD route to the template layer. Temperature-programmed desorption experiments have shown that a large portion of SrO directly desorbs from the surface at relatively low temperatures (below 600 °C) and only a small part of the deposited SrO is left to play a role in the complete SiO$_2$ desorption process. Most recently, it has been found that a Sr silicate layer with stoichiometry close to Sr$_2$SiO$_4$ forms spontaneously during SrO ALD growth on SiO$_2$/Si. However, the role of Sr silicate in the formation of Sr/Si template is unknown. In this chapter, we investigate the thermal stability of Sr silicate as the function of annealing temperature and provide some evidence for the mechanism of Sr/Si template by ALD.

5.3 Transformation and Desorption of Sr Silicate

5.3.1 1.5 nm Sample

In situ XPS experiments were performed on 1.5 nm deposited SrO layers (on 1.6 nm SiO$_2$/Si) to observe heating induced interface reactions and SiO$_2$ desorption involved in Sr template formation. XPS results for 1.5 nm sample after annealing at 600, 700, and 800 °C are shown for the Si 2p emission in Figure 5.4(a) and for O 1s emission in Figure 5.4(b). At 600 °C, three peaks can be fitted for the oxidized Si states; they are assigned to SiO$_2$ (103.6 eV), Sr silicate (102.0 eV), and SiO$_x$, with $x \leq 1$ (101.5 eV), respectively. Correspondingly, for the O 1s spectra, the dominate peak at 531.2 eV is attributed to Sr silicate, where the other two peaks at binding energies of 533.2 and 532.8 eV are due to the SiO$_2$ and SiO$_x$, with $x \leq 1$, respectively. At
700 °C, a shift by +0.5 eV for Sr silicate is observable in the Si 2p spectra. However, in the O 1s spectra, the change in binding energy is less 0.2 eV for the Sr silicate. At 800 °C, the desorption of residual SiO$_2$ is complete, as evidenced by the absence of Si 2p peak located at 103.5 eV and O 1s peak at 533.2 eV. By contrast, the SiO$_x$ component is stable up to 800 °C. A new Si 2p peak with binding energy of 100.6 eV shows up after annealing at 800 °C for 1 min, indicating direct bonding between Si substrate and carbon. The formation of silicon carbide is probably assisted by the absence of residual SiO$_2$ after annealing at 800 °C. It should be noted that desorption temperatures for native SiO$_2$ (~1.6 nm) are around 850 °C and a duration of at least 20 min is needed to remove the whole SiO$_2$ layer.

Figure 5.4 (a) Si 2p spectra and (b) O 1s spectra for the 1.5 nm sample at annealing temperatures of 600, 700, and 800 °C.
Further understanding of the effect of annealing temperature on the 1.5 nm sample can be assisted by studying the change in relative intensities of the Sr silicate component, as shown in Figure 5.5. All peak intensities are normalized to the value at 600 °C for Sr 3d, Si 2p and O 1s. According to the relative areas of Sr 3d, Si 2p, and O 1s silicate components, the silicate composition at 600 °C is close to Sr$_2$SiO$_4$, within an error limit of 10%. At 700 °C, the strontium signal stays constant, where both silicon and oxygen signals belonging to silicate components.
increase, indicating a transformation to another silicate. Such transformation has already been confirmed by +0.5 eV shift for the silicate component in Figure 5.4(a). At 800 °C, all three signals sharply decrease, indicating silicate desorption. Above 700 °C, however, the stoichiometry of transformed silicate is not compatible with any known silicate structure, i.e., it is a metasilicate phase.

A separate group of experiments was conducted to study the thickness change as the function of annealing temperature measured by in situ SE. Three samples were studied with nominal SrO thickness of 1.5, 3.0, and 6.0 nm. Because these films are very thin, it is very difficult to simulate each layer (SrO, silicate, or SiO$_2$) only by using in situ SE. Thus, only the total thickness is used to study this temperature effect, differing from the intensity plot which only accounts for the silicate component. As shown for 1.5 nm SrO sample in Figure 5.5, after annealing at 600 °C, the total thickness is 3.2 nm, in consistent with the sum of 1.5 nm of SrO and 1.6 nm of SiO$_2$. After annealing at 700 °C, the total thickness decreases into 2.8 nm, which might be caused by film densification and slight desorption of SiO$_2$ and/or silicate (Figure 5.4). After further annealing at 800 °C, the total thickness is down to only 1.6 nm. At the same time, complete desorption of residual SiO$_2$ and partial desorption of Sr silicate were observed based on Figure 5.4. For such thin films, roughness simulation is not accurate only by using SE and the thickness is averaged over the whole measured area. In other words, SE cannot distinguish uniform desorption from non-uniform one, which is the case for SiO$_2$/Si desorption discussed earlier. Further AFM measurement is needed to studying the film roughness caused by annealing.
5.3.2 3.0 nm Sample

The XPS results for 3.0 nm sample after annealing at 600, 700, and 800 °C are shown for the Si 2p emission in Figure 5.6(a) and for O 1s emission in Figure 5.6(b). At 600 °C, two peaks can be fitted for the oxidized Si states; they are assigned to Sr silicate (102.0 eV) and SiO$_x$, with $x \leq 1$ (101.5 eV), respectively. Thus, SiO$_2$ completely transformed into silicate, which is evidenced by the absence of the peak with binding energy of 103.5 eV. Correspondingly, for the O 1s spectra, the dominate peak at 531.2 eV is attributed to the Sr silicate, where the other small peak at binding energy of 532.8 eV is due to the SiO$_x$, with $x \leq 1$. At higher annealing temperatures, i.e. 700 and 800 °C, different from 1.5 nm sample, Si 2p and O 1s peaks of Sr silicate components show no change in binding energy. Moreover, according to the relative areas of Sr 3d, Si 2p, and O 1s silicate components, the silicate compositions at 600, 700, and 800 °C...
are all close to $\text{Sr}_2\text{SiO}_4$, within an error limit of 10%.

In contrast to the 1.5 nm sample, the temperature dependence of Sr 3d, Si 2p, and O 1s relative intensities of the 3.0 nm samples shows very close coincidence up to 800 °C, as evidenced in Figure 5.7. All peak intensities are normalized to the value at 600 °C for Sr 3d, Si 2p and O 1s. Moreover, Sr silicate slightly desorbs with stoichiometry above 600 °C, where over 78% $\text{Sr}_2\text{SiO}_4$ is still left after annealing at 800 °C for 1 min. The observed results support an
argument that the formation of $\text{Sr}_2\text{SiO}_4$ is thermodynamically favorable up to 600 °C by direct reaction between SrO and SiO$_2$. However, above 600 °C, stoichiometric $\text{Sr}_2\text{SiO}_4$ may transform into a new metasilicate phase by reacting with residual SiO$_2$ (the case for 1.5 nm) and desorption of silicates with both phases is obvious from the decrease in relative XPS intensities of silicate components. More interestingly, once the silicate/Si interface is free of SiO$_2$, the formed stoichiometric $\text{Sr}_2\text{SiO}_4$ is chemically stable in contact with Si up to 800 °C (the case for 3.0 nm), although minor desorption is observed. Figure 5.7 also shows the thickness change as the function of annealing temperatures. As we can see, after annealing at 600 °C, the total thickness is 4.2 nm, which is slightly less than 4.6 nm (3 nm SrO and 1.6 nm SiO$_2$). This variation probably results from different densities between silicate and SrO/SiO$_2$. After annealing at 700 °C, the total thickness only decreases by 0.1 nm, which is consistent with small change in the intensity of Sr silicate. After further annealing at 800 °C, the total thickness is down to 3.5 nm. Because the top film mostly consists of Sr silicate already at 600 °C, the thickness change measured by in situ SE shares the same trend with XPS measurements.

5.3.3 6.0 nm Sample

The XPS results for 6.0 nm sample after annealing at 600, 700, and 800 °C are shown for the Si 2p emission in Figure 5.8(a) and for O 1s emission in Figure 5.8(b). At 600 °C, similar with the 3.0 nm sample, two peaks can be fitted for the oxidized Si states; they are assigned to Sr silicate (102.0 eV) and SiO$_x$, with $x \leq 1(101.5$ eV), respectively. No SiO$_2$ exists at the silicate/Si interface, which is deduced from the absence of a peak with binding energy of 103.5 eV. For O 1s spectra, four peaks can be fitted after annealing at 600 °C for 1 min; the dominate peak at 531.2 eV and a small peak at binding energy of 532.8 eV are attributed to Sr silicate and SiO$_x$, ($x$
≤ 1), respectively. As expected for thick SrO, O 1s peaks for SrO and residual SrCO$_3$ show binding energies of 529.9 and 533.1 eV, respectively.$^{6,9,16}$ The existence of SrCO$_3$ is due to air exposure during sample transfer. Incomplete decomposition of SrCO$_3$ into SrO is probably due to the short annealing period (1 min). At higher annealing temperatures, i.e. 700 and 800 °C, similar to the 3.0 nm sample, Si 2p and O 1s peaks of Si silicate show no change in binding energy. O 1s peaks of both SrO and residual SrCO$_3$ disappear, and both Si 2p and O 1s peak intensities of silicate components increase, indicating the formation of additional silicate. Moreover, according to the relative areas of Sr 3d, Si 2p, and O 1s silicate components, the silicate compositions at 600, 700, and 800 °C are all close to Sr$_2$SiO$_4$, within an error limit of 10%.

Figure 5.8 (a) Si 2p spectra and (b) O 1s spectra for a 6.0 nm SrO sample at annealing temperatures of 600, 700, and 800 °C.
Further support for additional silicate formation is found in the relative XPS intensity change of Sr silicate components, as shown in Figure 5.9. All peak intensities are normalized to the value at 600 °C for Sr 3d, Si 2p and O 1s. Firstly, similarly with the 3.0 nm sample, the temperature dependence of Sr 3d, Si 2p, and O 1s relative intensities of the 6.0 nm sample show very close coincidence up to 800 °C, which suggest a fixed stoichiometry. The amount of $\text{Sr}_2\text{SiO}_4$ sharply increases after annealing at 700 °C for 1 min. As shown in Figure 5.8(a), no $\text{SiO}_2$ exists even at 600 °C, so the formation of the additional silicate must be attributed to

Figure 5.9  Peak intensities as a function of annealing temperatures for Sr silicate components in the 6.0 nm sample. They are normalized to the value at 600 °C for Sr, Si, and O. Filled symbols show the SE thickness data from separate experiments, in which also 6.0 nm SrO was deposited. Only the total thickness of the top films can be measured including SrO, Silicate, and $\text{SiO}_2$. 

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reaction between SrO and underlying Si. Similarly, Muller-Sajak and coworkers have found that 55 ML thick Sr$_{0.3}$Ba$_{0.7}$O film grown directly on Si surface completely transformed into Sr/Ba silicate after annealing at 800 °C. Diffusion of Si atoms through the thick oxide layer was assumed to be responsible for the complete transformation from oxide to silicate. Above 700 °C, Sr$_2$SiO$_4$ is thermally unstable and slowly desorbs. After annealing at 800 °C for 1 min, there is more than 75% silicate left, which is comparable with the 3.0 nm sample. Figure 5.9 also shows the thickness change as the function of annealing temperatures. As we can see, after annealing at 600 °C, the total thickness is 6.2 nm, which is less than 7.6 nm (6 nm SrO and 1.6 nm SiO$_2$). This variation may also be explained by considering different densities between silicate and SrO/SiO$_2$. Because there is SrO left, the top films might become much denser further decreasing the total thickness (SrCO$_3$ should not exist in the in situ SE measurements because of no air exposure during the experiments). After annealing at 700 °C, the total thickness decreases to less than 5 nm, which is different from the large increase in the intensity of Sr silicate. After further annealing at 800 °C, the total thickness decreases to 3 nm, which is consistent with the change of silicate intensity and should be explained by the desorption of silicate.

### 5.4 Summary

For 1.5, 3.0, and 6.0 nm samples, the stoichiometry of Sr silicates is Sr$_2$SiO$_4$. Both chemical and thermal stabilities of this Sr$_2$SiO$_4$ depend on thickness and temperature. It has been found that the Sr$_2$SiO$_4$ of 1.5 nm sample transforms into a metasilicate whose stoichiometry is not compatible with any known silicate structure after annealing at 700 °C. Meanwhile, 1.5 nm SrO cannot consume all SiO$_2$ and the left SiO$_2$ desorbs after annealing at 800 °C. The metasilicate also desorbs with only 50% left after annealing at 800 °C. With SrO thickness
increased to 3.0 nm, no SiO$_2$ exists after annealing at 600 °C and all SiO$_2$ is reacted with SrO to form Sr$_2$SiO$_4$. With further annealing at 700 and 800 °C, Sr$_2$SiO$_4$ is chemically stable without transformation into metasilicate and only desorbs slightly. For 6.0 nm sample, SrO amount is abundant. After all SiO$_2$ is consumed, there are still ~50% SrO (SrCO$_3$) left in the top film after annealing at 600 °C. Evidently, all left SrO (SrCO$_3$) transformed into Sr$_2$SiO$_4$ after annealing at 700 °C, probably indicating Si diffusion into the top layer and further reaction with SrO. Similarly with 3.0 nm sample, the thick Sr$_2$SiO$_4$ is chemically stable after annealing at 800 °C and suffers minor desorption.

According to our group’s previous work, further annealing at 850 °C would finally lead to the formation of Sr/Si template, with the amount of Sr depending on SrO ALD cycles. Therefore, there may be several reaction pathways from Sr silicate to elemental Sr. Firstly, Sr silicate can decompose back to SrO and SiO$_2$, which will react with Si to form Sr and gaseous SiO. Probably, at such high temperature, SrO may suffer from desorption, competing with the reaction process. If it is true, it may partially explain the large amount of SrO needed in the ALD process to achieve 1/2 ML Sr coverage. Also, Sr silicate may react directly with Si to form Sr and gaseous SiO or O. During this process, Sr silicate itself will also desorb as it has already happened at 700 °C. Further study is needed to understand the detailed mechanism behind the formation of Sr/Si template involving Sr silicate.
References


6. Summary and Future Work

6.1 Towards the Understanding of SrO ALD

One factor that strongly affects the properties of ALD films in actual applications is the crystallinity of the grown film: is the film amorphous or, if it is crystalline, which phase is present.\textsuperscript{1} Until now, the general trend in the development of SrO ALD film crystallinity as function of its process parameters is incomplete. Although SrO has a very simple rock-salt structure, it is very basic and chemically unstable in contact with H\textsubscript{2}O and CO\textsubscript{2}.\textsuperscript{2} As the result, ex-situ structural and compositional characterizations are challenging without protective layers. Moreover, as demonstrated in Chapter 3 and 4, surface or even bulk hydroxylation complicates the true reaction mechanism in the Sr(C\textsubscript{5}Pr\textsubscript{3}H\textsubscript{2})\textsubscript{2}/H\textsubscript{2}O process.\textsuperscript{3,4} This is further illustrated by comparing with the Mg(C\textsubscript{5}H\textsubscript{5})\textsubscript{2}/H\textsubscript{2}O process. For example, as shown in Figure 3.8, RTSE clearly indicates a similar growth behavior of MgO ALD at 250 and 350 °C, while deposition temperatures strongly impact the adsorption/reaction behaviors of SrO ALD (Figure 3.3). Consistently, both temperatures lead to polycrystalline MgO films, while Sr(OH)\textsubscript{2} and SrO are crystallized at 250 °C and 350 °C, respectively. This strong structure/composition-temperature correlation in the Sr(C\textsubscript{5}Pr\textsubscript{3}H\textsubscript{2})\textsubscript{2}/H\textsubscript{2}O process will further contribute to the complexity of related SrTiO\textsubscript{3} ternary oxide ALD.\textsuperscript{5,6} To this end, it is highly desirable to simultaneously investigate both GPC and surface chemical reactions with in situ SE and FTIR, directly linking between surface chemistry and thickness variation during each SrO ALD cycle.
6.2 From SrO to SrTiO₃: Stoichiometric Control

ALD has demonstrated itself as a production worthy thin film deposition method. The main strength of ALD is its ability to deposit films with excellent control of thickness, composition and microstructure, even over complex topographies and over large surface areas. Currently, there are several ALD-deposited oxide materials being successfully applied in industry, such as Al₂O₃, HfO₂, ZrO₂, and SiO₂.¹,⁷ Before being transferred into mass production, these processes were extensively researched in order to achieve the best film properties. As introduced in Chapter 1, SrO, MgO, and related materials have been proposed to be useful in many applications, especially in semiconductor industry. Recently, the driving force behind Sr-based ALD processes is the need for SrTiO₃ thin films with ultra high dielectric constant (over 100) and thickness less than 10 nm as the dielectric capacitor in semiconductor memory devices.⁸ Because TiO₂ itself is also a high-k oxide (~40), the development of Ti-based ALD process has received much attention too.⁸ By contrast, research in SrO ALD is much delayed and the number of suitable Sr precursors is very limited. Among the limited choices, Cp-based Sr precursors, such as Sr(C₅Pr₃H₂)₂ and Sr(C₅Bu₃H₂)₂, have been reported to be compatible with certain Ti precursors to deposit stoichiometric SrTiO₃ thin films with reasonable electrical properties.

The first step to deposit a ternary oxide, such as SrTiO₃, is to find the deposition temperatures where both Sr and Ti precursors are thermally stable. Then, the atomic composition ratios between Sr and Ti should be examined carefully as a function of SrO/TiO₂ cycle ratios in order to achieve stoichiometric films. However, the latter step has been proved to be complex and almost unpredictable when based on the growth behaviors of individual binary oxide ALD process. For example, even though SrO/TiO₂ cycle ratios of 20:20 and 10:10 are mathematically equal, the deposited films may have different thicknesses and atomic ratios even
when the total number of cycles is the same, i.e. when 20:20 process is repeated twice, 10:10 process is repeated four times.\textsuperscript{5} Since ALD of SrTiO\textsubscript{3} always involves deposition of SrO onto TiO\textsubscript{2} and vice versa, substrate effects contribute to stoichiometric variations in the case of 20:20 and 10:10 cycle ratios. Clearly, if the value of subcycle becomes smaller (20 to 10), more interfaces (3 to 7) are present and more substrate effects should be expected. Nevertheless, detailed understanding of the SrTiO\textsubscript{3} ALD process is still very limited. The most valuable in situ characterization was carried out by Rahtu and coworkers in 2001, where the reaction mechanisms were studied with QCM and QMS. Precursors were Sr(C\textsubscript{5}iPr\textsubscript{3}H\textsubscript{2})\textsubscript{2}, Ti(O\textsubscript{i}Pr)\textsubscript{4}, and D\textsubscript{2}O.\textsuperscript{9} Most interestingly, the authors found the GPC of SrO on TiO\textsubscript{2} was significantly higher during the first cycle than during the subsequent cycles. Over 90\% of the (C\textsubscript{5}iPr\textsubscript{3}H\textsubscript{2})\textsuperscript{−} ligands were released already during the initial Sr(C\textsubscript{5}iPr\textsubscript{3}H\textsubscript{2})\textsubscript{2} pulse onto TiO\textsubscript{2}, as shown in Figure 6.1. By contrast, enhanced growth of TiO\textsubscript{2} on SrO occurred to a much lesser extent. The authors attributed the significantly enhanced growth of SrO on TiO\textsubscript{2} to the thermodynamically favorable

![Figure 6.1 QCM mass change in an ALD process where at first ten cycles of TiO\textsubscript{2} are deposited and after that ten cycles SrO at 325 °C.\textsuperscript{9}](image-url)
SrTiO$_3$ formation. However, the unequal effect of SrO on the GPC of TiO$_2$ suggests that this is not the whole picture. Further explanation calls for more detailed in situ experiments.

Most recently, it has been demonstrated that crystalline SrTiO$_3$ films grow at a higher GPC than amorphous SrTiO$_3$ films under the same deposition conditions. For example, the average GPC of as-deposited crystalline films was found to be 0.11 nm/subcycle (0.22 nm/supercycle) using a 1:1 (Sr:Ti) cycle ratio, while the average GPC is only 0.076 nm/subcycle (0.15 nm/supercycle) using the same recipe but grown on SiO$_2$/Si(100) native oxide substrates.$^{10}$ Because 1:1 cycle ratio was applied, a mixed Sr/Ti surface should be expected instead of pure SrO or TiO$_2$. This crystallization effect might increase the density of surface OH groups on the mixed oxide surface. Different from Al$_2$O$_3$, which is always amorphous at typical ALD deposition temperatures (<300 °C), crystallization of SrTiO$_3$ films either by substrate or temperature effects adds complexities for accurate thickness and composition control. More systematic work, such as the methods demonstrated in this thesis, is needed to fully understand this ternary oxide ALD process.

It is also worth mentioning another Sr-based ternary oxide, SrRuO$_3$, which has become the most popular electrode for complex oxide heterostructures.$^{11}$ Although there have been successful ALD growth of both SrO and RuO$_2$ films from Sr(C$_5$H$_{13}$H$_2$)$_2$/O$_2$ and Ru(DMPD)(EtCp)/O$_2$ [DMPD=2,4-(dimethylpentadienyl) and EtCp=ethylcyclopentadienyl]] chemistry, the growth of the Ru-O layer was greatly retarded on Sr-O.$^{12}$ It was proposed that the ALD mechanism of RuO$_2$ using Ru(DMPD)(EtCp) involves reaction between Ru precursor and surface oxygen atoms to form Ru-O bonds. However, once the substrate is covered with SrO, the very strong bond between Sr and O does not allow surface oxygen to react with incoming Ru precursors, so that no Ru-O layer can be incorporated into the film. In other words, to deposit
SrRuO$_3$ by ALD, it is necessary to find an alternative Ru precursor that reacts with surface OH groups. This case clearly demonstrates the importance of surface chemistry for growing technologically useful thin film materials.

6.3 Single-Crystalline Epitaxial Thin Films by ALD

It is widely held that ALD is not applicable for attaining high-quality complex oxide films in single-crystalline epitaxial form. However, even though ALD involves low vacuum and low deposition, it is still possible to achieve single-crystalline epitaxial films of perovskite oxides on some substrates comparable to those obtained using high-temperature chemical or physical vapor deposition approaches. The key is to choose an appropriate combination of precursors with similar temperature windows and compatible surface chemistry on alternatively terminated surfaces during deposition. In this section, three examples are discussed to demonstrate recent research progress and challenges for epitaxial growth by ALD: (1) La$_{2-x}$Y$_x$O$_3$ on GaAs(111)$^{13}$, (2) BiFeO$_3$ on SrTiO$_3$(100)$^{14}$, and (3) SrTiO$_3$ on Si(100) buffered by MBE-grown SrTiO$_3^{10}$. The ternary oxide, La$_{2-x}$Y$_x$O$_3$, can be considered as a mixture of La$_2$O$_3$ and Y$_2$O$_3$. The lattice constant of cubic La$_2$O$_3$ is slightly larger than 2 times the GaAs lattice constant, while the lattice constant of cubic Y$_2$O$_3$ is $\sim$6% smaller than that of La$_2$O$_3$. Therefore, Wang and coworkers adjusted the lattice constant of the ternary compound, La$_{2-x}$Y$_x$O$_3$, to study the effect of mismatch by varying the ratio of La and Y.$^{13}$ Precursors included lanthanum tris(N,N-diisopropylformamidinate), yttrium tris(N,N-diisopropylacetamidinate) and H$_2$O. If deposition is carried out on amorphous substrates like SiNx, only amorphous La$_{2-x}$Y$_x$O$_3$ films can be achieved. By contrast, high quality crystallized epitaxial films, including La$_2$O$_3$, La$_{1.8}$Y$_{0.2}$O$_3$, La$_{1.9}$Y$_{0.1}$O$_3$, and Y$_2$O$_3$, can be grown on GaAs(111). Figure 6.2 shows a cross-sectional TEM
image and XRD 2θ scan of a La$_{1.8}$Y$_{0.2}$O$_3$/GaAs(111) sample. The interface is atomically abrupt without interlayers and the lattice mismatch is only -0.64% for La$_{1.8}$Y$_{0.2}$O$_3$ with respect to GaAs. As discussed in Chapter 5, the starting surface is critical for initiating epitaxial growth. In this case, achieving clean GaAs is relatively easy. HCl can be used to efficiently remove any native oxide on GaAs surface and (NH$_4$)$_2$S can be further used for sulfur passivation.

![Cross-sectional TEM image and XRD 2θ scan](image)

Figure 6.2 (left) the cross-sectional TEM image and (right) XRD 2θ scan of a La$_{1.8}$Y$_{0.2}$O$_3$/GaAs(111) sample.$^{13}$

BiFeO$_3$ is attractive among ferroelectric materials for solar energy conversion due to its large photovoltage and visible photon energy bandgap (~2.7 eV). The precursors used for BiFeO$_3$ ALD include Bi(mmp)$_3$ [mmp=tris(1-methoxy-2-methyl-2-propoxy)], Fe(Cp)$_2$, and O$_3$. Different from the first case, as-deposited BiFeO$_3$ is amorphous even with lattice-matched SrTiO$_3$ as substrate. Post-annealing was used to crystallize the films, where epitaxial crystallization of the pure perovskite phase occurs above 660 °C. The major challenge of
BiFeO$_3$ thin film synthesis is phase degradation at high temperatures due to volatilization of Bi$_2$O$_3$. Indeed, some nanoinclusions of the sillenite phase were identified by TEM, but mostly on the surface. Nevertheless, the interface between film and the substrate is free of misfit dislocations even after high-temperature annealing. This example demonstrates that even when an as-deposited film is amorphous, high-quality single-crystalline films can be obtained after post-annealing on lattice-matched substrates.

For epitaxial growth of oxide on Si, as discussed in Chapter 5, amorphous SiO$_2$ must be removed to initiate epitaxy. Our group has made significant contribution to achieving passivation templates on Si by ALD. The next step is to examine whether this template is stable during ALD oxide growth. Recently, the Ekerdt group from UT Austin has demonstrated that MBE-grown SrTiO$_3$ can serve as a buffer layer for the epitaxial growth of SrTiO$_3$ on Si by ALD. This buffer layer can be as thin as 8 MLs (4-unit-cell SrTiO$_3$). The precursors used were Sr(C$_5$Pr$_3$H$_2$)$_2$, Ti(O$i^i$Pr)$_4$, and H$_2$O.$^{10}$ Different from the previous example, direct crystallization of SrTiO$_3$ can be achieved at 250 °C. When compared with standard MBE growth as discussed in Chapter 5, this mixed MBE/ALD approach provides an advantage when thicker epitaxial SrTiO$_3$ films are desired. Nevertheless, for cost-effective large-scale fabrication of multifunctional perovskites integrated with Si technology, MBE-based steps must be eliminated and all-ALD approach is needed.

**6.4 Conclusion**

In this dissertation, we explored the capability of real-time spectroscopic ellipsometry (SE) for understanding reaction mechanisms in SrO and MgO ALD. Submonolayer sensitivity of SE allowed us to monitor adsorption/desorption during growth of these two alkaline earth oxides. Because SrO is more basic than MgO, growth behaviors of SrO ALD are complicated by
H₂O and GPCs strongly depend on deposition temperatures. MgO ALD can be considered simpler as it follows a ligand exchange reaction mechanism. Furthermore, we carefully studied the effect of substrate on the structural and chemical properties of as-deposited SrO and MgO ALD films. It has been demonstrated that solid-state reactions and diffusion play important roles in the initial growth of SrO and MgO films on SiO₂. Thermodynamically, formation of Sr and Mg silicates from mixtures of SrO/MgO and SiO₂ is favorable. In order to understand the role of Sr silicate in the formation of Sr/Si template, the thermal stability of Sr silicate with different thicknesses were carefully studied. XPS results indicated competitive desorption and transformations of Sr silicate during high-temperature annealing. Further studies are needed to fully understand and control this silicate-based Sr/Si template formation.
Reference


