Deposition and Characterization of Aluminum Oxide Thin Films Prepared by Atomic Layer Deposition

This chapter describes the details of preparation of alumina ($Al_2O_3$) thin films by atomic layer deposition technique and their various structural, optical and electrical characterizations.

5.1 Introduction

Many materials were identified as high-k materials that have higher dielectric constant than $SiO_2$ but not many are compatible with the Si substrate that is used in most of the semiconductor devices. Important concerns include interface quality, film morphology, and reliability. Serious research is still needed in order to identify a promising candidate. In the present work we investigate the high-k dielectric material $Al_2O_3$, which can be used in complementary metal oxide semiconductor (CMOS) transistors and dynamic random access memory (DRAM) capacitors [1,2]. Characterization of these films are also included in this chapter.

5.2 $Al_2O_3$ as gate dielectric

As an alternative to oxide/nitride systems, much work has been carried out on high-k metal oxides as they can provide a substantially thicker (physical thickness) dielectric for reduced leakage and improved gate capacitance. Among the group III oxide candidates, aluminum oxide ($Al_2O_3$) is the most stable and robust material, and has been extensively studied for many applications especially in opto and microelectronics. Regarding its usefulness as an alternate gate dielectric, $Al_2O_3$ has many favorable properties like large band gap, band offset, kinetic stability, thermodynamic stability on Si up to high temperatures, good interface with silicon, low bulk defect density and is amorphous under the conditions of interest [3-5].
Though Al₂O₃ has relatively low dielectric constant (~9), this is more than twice (3.9) that of the widely accepted SiO₂. In particular the high chemical stability, high radiation resistance, high thermal conductivity and low permeability to alkali impurities make it suitable for application in metal oxide semiconductor (MOS) structures even in drastic conditions. Al₂O₃ was commonly used as protective layer, ion barrier layer and as diffusion barriers [4-6]. Al₂O₃ has several other applications such as passivation layers, and dielectric films in chemical sensors [6-10]. All these applications require films with good homogeneity, low surface roughness and good control of thickness for films of the order of 10Å thick or less. Al₂O₃ is one of the best high-k materials which satisfy almost all the guidelines for an ideal gate oxide.

Table 5.1 list the properties of Al₂O₃.

<table>
<thead>
<tr>
<th>Properties of Al₂O₃ gate dielectric [1-2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant value -9.7</td>
</tr>
<tr>
<td>Thermo dynamic stability on Si - good</td>
</tr>
<tr>
<td>Kinetic stability - good</td>
</tr>
<tr>
<td>Crystallization temperature ~1200°C</td>
</tr>
<tr>
<td>Resistivity~ high</td>
</tr>
<tr>
<td>Dielectric Strength &gt;15MV/cm</td>
</tr>
<tr>
<td>Energy band gap ~8.9eV</td>
</tr>
<tr>
<td>Conduction band offset ~2.8eV</td>
</tr>
<tr>
<td>Valence band offset with Si ~3.2eV</td>
</tr>
<tr>
<td>Low interface (Al₂O₃/Si) state density ~10¹⁰eV⁻¹cm⁻²</td>
</tr>
<tr>
<td>Low charge trapping density ~order of 10¹⁰cm⁻²</td>
</tr>
</tbody>
</table>

In the present work we report the deposition of thin aluminum oxide films as gate oxide using the ALD technique in which excellent control of thickness, homogeneity and low value of surface roughness are achieved.

5.3 Review of Atomic Layer Deposited Al₂O₃ thin films

Alumina is the most studied ALD coated material. Still its versatility is not fully explored and large scale research is going on to pioneer new
areas. A brief review of the ALD-Al\textsubscript{2}O\textsubscript{3} is presented in this section, that covers only a small part of the entire work done on this material.

The first reports of ALD-Al\textsubscript{2}O\textsubscript{3} using TMA and H\textsubscript{2}O is by G. S. Higashi and C. G. Fleming in 1989 [11]. Sequential surface reactions of TMA and water vapor were used to deposit Al\textsubscript{2}O\textsubscript{3} on Si(100) surfaces. High quality dielectric films were deposited at deposition temperatures of 100 °C. Resistivity of $10^{17}$Ω-cm, breakdown strengths of 8MV/cm, and interface state densities of $10^{11}$states/eV cm\textsuperscript{2} was achieved and they suggested possible applications of alumina as a gate insulator or a dielectric passivation layer.

C. Soto \textit{et al.} [12] in 1991 discussed the possibility to grow thin films of alumina by the sequential application of TMA and water at room temperature both on high-surface-area alumina and on silicon in ultrahigh vacuum. Both infrared spectroscopy and electron energy-loss spectroscopy (EELS) studies were conducted and proposed a reaction mechanism. Low temperature growth of thin films of Al\textsubscript{2}O\textsubscript{3} by sequential surface chemical reaction of trimethylaluminum and H\textsubscript{2}O\textsubscript{2} was reported by F. Fan \textit{et al.} in 1991 [13]. Trimethylaluminum (TMA) reacts with H\textsubscript{2}O\textsubscript{2} readily at temperatures as low as room temperature, resulted in the identical growth of Al\textsubscript{2}O\textsubscript{3}. Highly insulating and ideally uniform nature of the grown films were also verified.

The surface chemistry of ALD was reported by S.M George \textit{et. al.} in 1996 [14]. He expressed the basic model by the binary reaction sequence approach for Al\textsubscript{2}O\textsubscript{3} atomic layer process using the TMA and H\textsubscript{2}O precursors. Numerous applications of ALD films in the field of microelectronics and optoelectronics were also discussed.

Many researchers studied the structural and morphological aspects of ALD-Al\textsubscript{2}O\textsubscript{3}. In 1996 M. Ritala \textit{et al.} studied [15] the morphological development of Al\textsubscript{2}O\textsubscript{3} films grown by ALD from Al(Cl)\textsubscript{3} and H\textsubscript{2}O by means of AFM. Film surface smoothness and RMS roughness of films were also studied. They reported that there is only a weak tendency towards agglomeration. D. Riiheld \textit{et. al.} [16] developed the optical dielectric multilayer structures using ZnS and Al\textsubscript{2}O\textsubscript{3} as high and low refractive index materials. They also developed various structures include antireflection
coatings, neutral beam splitters, high-reflection coatings and Fabry-Perot filters. The optical performance of the fabricated components were studied by comparing their transmittance and reflectance spectra with those calculated for the ideal structures.

In 1997 S. J. Yun et al. [17] studied the dependence of growth temperature on ALD-Al₂O₃ film characteristics. TMA and H₂O were used as precursors and results obtained were compared with the films grown using AlCl₃ and H₂O. The concentration of impurities in the deposited films were also studied using SIMS and results showed that the contents of C and H in the films grown at 300°C using TMA were approximately six and 10 times higher than those of the film grown at 500°C using AlCl₃. In 2000 Gusev et al. [18] have done the physical and electrical characterization of ALD–Al₂O₃. They used medium energy ion scattering and high-resolution TEM as analysis tools. They successfully deposited Al₂O₃ films over H-terminated Si without forming an interfacial SiO₂ layer. They control the interface reactions successfully.

Several researchers have extended their study to device level. In 2000 Buchanan et al. fabricated [19] nMOSFET with ALD-Al₂O₃ as gate oxide and poly-Si gates. Fabricated structures were treated with standard processing conditions (including a rapid-thermal dopant activation anneal at \( T > 1000°C \)) and electrical characterization. A leakage current of \( J \sim 10^{-1} \) A/cm² at \( V_{\text{bias}} = V_{FB} + 1 \) V was measured for \( t_{eq} = 13 \) Å, showing a reduction in leakage current of two order compared to SiO₂ of the same \( t_{eq} \) value. A trend in fixed charge correlated with Al₂O₃ thickness was also demonstrated, showing that fixed charge increases with decreasing film thickness. They also found that the fixed charge is concentrated near the interface, poly-Si interface. Furthermore, an interfacial layer was identified to contribute \( \sim 8 \) Å to the overall \( t_{eq} \) value. The composition of the interface layer is not known, but apparently has a \( k \) value larger than that of pure SiO₂. At an effective field of 1MV/cm, the channel carrier mobility value for Al₂O₃ was measured to be 200 cm²/Vs. Encouraging drive currents and reliability characteristics were demonstrated for these devices, but the significant mobility degradation clearly indicates some deleterious effects of the ALD-Al₂O₃ which warrant
further investigation. The study by Park et al. [20] in 2000 demonstrated that boron diffuses through ALD Al₂O₃ during dopant activation anneals, and indeed this may be a serious issue for any alternative dielectric. It was reported that dopant activation anneals of 800–900°C performed on boron implanted poly-Si gates on top of ~60 Å Al₂O₃ caused significant diffusion of boron through the Al₂O₃ film and into the n-Si substrate, as evidenced by a flat band shift of ~1.5 V. Secondary Ion Mass Spectroscopy (SIMS) profiles also indicated a significant amount of boron in the substrate after anneal. Furthermore, the addition of an oxynitride layer, grown by an N₂O anneal before Al₂O₃ deposition, greatly reduced the flat band shift to 90 mV.

In a different study by Lee et al. [21] phosphorous diffusion from the n⁺ poly-Si electrode into ALD-Al₂O₃ was observed under reasonable annealing conditions of 850°C for 30 min. C–V analysis showed a flatband shift ∆V_{FB}~670–740 mV depending on the particular dopant incorporation process, which corresponds to >10¹² cm⁻² of negative fixed charge in the film. These results indicate that phosphorous not only diffused through the Al₂O₃ layer, but also introduced fixed charge into dielectric. The authors propose that phosphorous modifies the Al₂O₃ network, causing negatively charged Al–O dangling bonds. It will continue to be extremely important to identify and understand dopant diffusion in any potential alternative gate dielectric.

In 2000 M. Ritala et al. [22] reported a different approach to ALD of oxide thin films. Instead of using water or other compounds for an oxygen source, oxygen is obtained from a metal alkoxide, which serves as both an oxygen and a metal source when it reacts with another metal compound such as a metal chloride or a metal alkyl. These reactions generally enable deposition of oxides of many metals. With this approach, an alumina film has been deposited on silicon without creating an interfacial silicon oxide layer that otherwise form easily. This finding adds to the other benefits of the ALD method, especially the atomic-level thickness control and excellent uniformity. It takes a major step toward the scientifically challenging to implement process of finding promising gate dielectric for the future generations of metal oxide semiconductor field effect transistors. P. I. Räsänen et al. reported in 2002 [23] ALD deposition of Al₂O₃ using AlCl₃
and Al(OiPr)$_3$ precursors. Here also no separate oxygen source is used. In this approach an Al$_2$O$_3$ film gets deposited on silicon without an interfacial silicon oxide layer. The film growth rate was 0.8Å cycle. The residual contents of chlorine, hydrogen and carbon in the film deposited at 300°C were 1.8, 0.7 and 0.1%, respectively. The chlorine content diminished rapidly with increasing growth temperature. The permittivities and leakage current densities were comparable to the conventional Al$_2$O$_3$ ALD processes for thick films, but the permittivity decreased for very thin films. Post deposition annealing is required to improve electrical properties of thin films.

In 2002 Kim et al [24] reported the deposition of Al$_2$O$_3$ using TMA and O$_3$ on Si (100) substrate. In this he reports that the Al$_2$O$_3$ films prepared using O$_3$ have significantly less amount of defect states like Al-Al and OH bonds compared with those prepared by H$_2$O. He also studied the device quality leakage characteristics, and concluded that Al$_2$O$_3$ film prepared with O$_3$ show a leakage current density one or two orders lower and a smaller flatband voltage shift than that of Al$_2$O$_3$ film prepared with H$_2$O, demonstrating improved interface characteristics. In 2003 S. Jakschik et.al. [25] reported the physical characterization of thin ALD-Al$_2$O$_3$. Structural characterizations of these films were done using time-of-flight secondary-ion-mass-spectroscopy, XPS and elastic recoil detection. In 2004 K. K. Seong et. al. [26] has reported about the Atomic-layer-deposited Al$_2$O$_3$ thin films with thin SiO$_2$ layers grown by in situ O$_3$ oxidation. The growth, thermal annealing behaviors, and electrical properties of Al$_2$O$_3$ thin films were studied. The Al$_2$O$_3$ films grown on a bare Si substrate had the highest concentration of excess oxygen which resulted in the largest increase in the interfacial layer thickness during post annealing.

Atomic Layer Deposition of Al$_2$O$_3$ films on Polyethylene Particles was reported by J. D. Ferguson et. al. in 2004 [27]. The presence of an Al$_2$O$_3$ film on the low density polyethylene (LDPE) particles was confirmed using TEM. The TEM images revealed that the Al$_2$O$_3$ coating was very conformal to the LDPE particles. The Al$_2$O$_3$ coating was also thicker than expected from typical ALD growth rates. This thicker Al$_2$O$_3$ coating was explained by
the presence of hydrogen-bonded H$_2$O on the Al$_2$O$_3$ surface that increases the Al$_2$O$_3$ growth rate during Al(CH$_3$)$_3$ exposures. On the basis of these results and additional investigations, a model is proposed for ALD-Al$_2$O$_3$ on polymers. Al$_2$O$_3$ was predicted to be an effective gas diffusion barrier on temperature-sensitive polymeric materials such as LDPE.

Wilson et al. 2005 [28] studied the nucleation and growth during ALD-Al$_2$O$_3$ on a variety of polymer substrates like polyethylene (PE), polystyrene (PS) poly(methyl methacrylate) (PMMA), polypropylene (PP), and poly(vinyl chloride) (PVC) at 85°C. Quartz Crystal Microbalance (QCM) and surface profilometry measurements were used to study the nucleation and growth of Al$_2$O$_3$ ALD on various polymer substrates were studied. This Al$_2$O$_3$ ALD growth occurs without specific chemical species that can react with TMA, such as hydroxyl (-OH) groups, on the surface or in the bulk of the polymer. The nucleation of Al$_2$O$_3$ ALD is facilitated by TMA diffusion into the polymers and the subsequent reaction of the retained TMA with H$_2$O. A model is developed for ALD-Al$_2$O$_3$ on polymers that are consistent with the QCM measurements and recent Fourier transform infrared (FTIR) investigations. This model establishes an initial foundation to interpret ALD on polymers and will be developed further by future studies.

In 2005 R. L Puurunen [29] published a detailed review on surface chemistry of Atomic Layer Deposition in terms of TMA and water reaction. Review includes the basic characteristics of ALD processing, history of ALD, and presented an overview of the two reactant ALD processes investigated up to 2005. Concepts related to the surface chemistry of ALD are formulated and discussed from a theoretical viewpoint. The discussion is generic for compound-reactant-based ALD processes, where the reactions are truly self-terminating and undesired side reactions are absent. The experimental results for the AlMe$_3$/H$_2$O process were reviewed, especially quantitative information about surface chemistry were included in the conclusions section. The historical assumptions, terminology, and effect of experimental conditions on the surface chemistry of ALD were also discussed. In 2006 Puurunen [30] studied the dependence of Growth rate and
refractive index on growth temperature of the Al$_2$O$_3$ films. She concluded that growth rate decreased from 0.20 to 0.08 nm/cycle and refractive index increased from 1.52 to 1.65, with increasing temperature. The dielectric constant slightly increased from 6.8 to 8 with increasing growth temperature. Al$_2$O$_3$ films grown using O$_3$ as oxidant show a smaller hysteresis, lower leakage current density, and higher breakdown field strength compared to those using H$_2$O as oxidant at the same growth temperature. X-ray Photoelectron Spectroscopy results showed that the films grown at lower temperatures have smaller band gap energy. The Al$_2$O$_3$ films grown at a temperature as low as 100°C showed reasonable dielectric properties for dielectric film applications on flexible substrates.

In 2006 S. D. Elliott et al. [31] reported the Ozone-Based ALD of alumina from TMA with emphasis on Growth, Morphology, and Reaction Mechanism. They reported that growth rate decreases with increasing temperature. Morphological characterizations were done and results indicate that O$_3$ as the oxygen source yields lower-quality films than H$_2$O; the films are less dense and rougher, especially at low growth temperatures. In 2006 T.P. Lee [32] reported that OAO (SiO$_2$/Al$_2$O$_3$/SiO$_2$) dielectric film stacks consisting of Al$_2$O$_3$ in place of Si$_3$N$_4$ in conventional ONO stacks have good charge retention capability with high charge to breakdown properties required for flash memory device application.

Protection of polymer from atomic-oxygen erosion using Al$_2$O$_3$ atomic layer deposition coatings were studied by Russel Cooper et. al. in 2007 [33]. Al$_2$O$_3$ ALD films with varying thicknesses were grown on the polyamide substrates and ALD-coated polyamide materials were exposed to a hyper thermal atomic-oxygen beam. The mass loss versus oxygen-atom exposure time was measured in situ by the QCM. Al$_2$O$_3$ ALD film thicknesses of $\sim$35 Å were capable to protect the polymer from erosion.

The atomic layer deposition (ALD) of Al$_2$O$_3$ using sequential exposures of Al(CH$_3$)$_3$ and O$_3$ was also reported by Goldstein et. al. in 2008 [34]. The in situ Fourier Transform Infrared spectroscopy and QMS (Quadrupole Mass Spectrometry) were also carried out and deposited films were structurally characterized by TEM.
Biocompatibility of atomic layer-deposited alumina thin films studied by D. S. Finch et al. in 2008 [35]. Cell adhesion and growth have been successfully demonstrated on atomic layer-deposited alumina thin films on glass cover slips. The use of an Alamar Blue assay as a measure of biocompatibility suggests that coating glass cover slips with 60nm of ALD alumina results same biocompatibility with the uncoated glass samples.

In 2009 A. S Cavanagh et al. [36] has employed ALD to grow coaxial thin films of Al₂O₃ and Al₂O₃/W bilayers on multi-walled carbon nanotubes. The uncoated and ALD-coated MWCNTs were characterized with TEM and XPS. Al₂O₃ ALD on untreated MWCNTs was found to have nucleation difficulties that resulted in the growth of isolated Al₂O₃ nanospheres on the MWCNT surface. The formation of a physisorbed NO₂ monolayer provided an adhesion layer for the nucleation and growth of Al₂O₃ ALD films. The Al₂O₃ ALD film also served as a seed layer for the growth of W ALD on the MWCNTs. The W ALD films can significantly reduce the resistance of the W/Al₂O₃/MWCNT wire. The results demonstrate the potential for ALD films to tune the properties of gram quantities of very high surface area MWCNTs.

In 2009 P. F. Carcia reported ALD Al₂O₃ as gas diffusion ultra barrier on polymer substrate.[37]. Thermo-mechanical properties of alumina films using atomic layer deposition technique was reported by David C. Miller et al. in 2010 [38]. Inter digitalized humidity sensors with ALD coatings of aluminum oxide demonstrated no leakage current relative to uncoated sensors stored in the ambient, indicating Al₂O₃ may be used to limit the effects of H₂O and other chemical species in miniaturized mechanical and electronic devices. The long term durability of such coatings is not known, but may be predicted from the related material characteristics. The film stress and coefficient of thermal expansion for Al₂O₃ were determined using the wafer curvature method. Film stress was also characterized using thermal cycling up to 500°C.

“Atomic Layer Deposition: An Overview” by S. M George in 2010 [40] reported Al₂O₃ ALD as a model ALD system and ALD Al₂O₃ on carbon
nanotube, graphene substrates, particles and polymers. This review includes general overview of ALD.

In 2011 Dragos Seghete et al. [40] fabricated latterly graded Al₂O₃ layers by using variant ALD techniques for X-ray optical applications. The transformation of conformal Al₂O₃ ALD films into laterally graded layers is achieved by controlling the reactant source location in the ALD reactor.

Armin Richter reported in 2011 [41] that ALD Al₂O₃ of 5Å thickness acts as the surface passivation layer on silicon substrates. He also reported that four ALD cycles of Al₂O₃ are sufficient to reach the full potential of surface passivation, and even with one atomic layer of Al₂O₃ (one ALD cycle) emitter saturation current densities as low as 45 fA/cm² can be reached on boron-diffused emitters.

B. Vermang et al. published a short communication in 2011 about spatially separated atomic layer deposition of Al₂O₃, a new option for high throughput Si solar cell passivation [42].

5.4 Preparation of Al₂O₃ thin films by ALD

Experimental

Atomic Layer Deposition of aluminum oxide was carried out in our homemade ALD reactor. Tri Methyl Aluminum (Sigma Aldrich) and De-Ionized (DI) water were used as precursors and high purity N₂ as the carrier gas. Various substrates used in the present study are glass, quartz and Silicon wafer p(100). Initially the deposition chamber was evacuated to a base pressure of 1×10⁻⁵ mbar using oil diffusion pump and rotary pump. After attaining this base pressure, chamber was filled with N₂ to medium vacuum level and evacuation is directly switched to rotary mode and remaining part of the deposition is done at rotary vacuum. Purge gas was then admitted to the chamber through mass flow meters. The chamber pressure was adjusted by controlling N₂ flow, which was done by combined controlling of needle valve, mass flow meter, butterfly valves and solenoid valves installed in precursor line. Precursors were initially loaded in SS bubblers and delivered to the reaction chamber in alternate sequence separated by N₂ purge. The entire ALD cycle was controlled by a sequence controller which was
interfaced to a desktop computer. Substrate holder was placed over a sealed heater and in our experiments substrate temperature was varied between 30°C to 300°C.

Table 5.2: Various deposition parameters

<table>
<thead>
<tr>
<th>Pulse time in Seconds</th>
<th>Chamber Pressure (mbar)</th>
<th>Substrate Temp (°C)</th>
<th>Flow rates sccm</th>
<th>Mode</th>
<th>Inference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA 5 Purge 0.5 5</td>
<td>0.790</td>
<td>350</td>
<td>500</td>
<td>thermal</td>
<td>no film</td>
</tr>
<tr>
<td>0.5 5 Purge 0.5 5</td>
<td>0.300</td>
<td>150</td>
<td>500</td>
<td>plasma</td>
<td>Poor</td>
</tr>
<tr>
<td>0.5 10 Purge 0.5 10</td>
<td>0.180</td>
<td>300</td>
<td>500</td>
<td>plasma</td>
<td>good</td>
</tr>
<tr>
<td>0.5 15 Purge 0.5 15</td>
<td>0.270</td>
<td>300</td>
<td>500</td>
<td>plasma</td>
<td>good</td>
</tr>
<tr>
<td>0.5 15 0.5 15</td>
<td>0.260</td>
<td>250</td>
<td>350</td>
<td>plasma</td>
<td>good</td>
</tr>
<tr>
<td>1 5 1 15</td>
<td>0.270</td>
<td>300</td>
<td>500</td>
<td>plasma</td>
<td>good</td>
</tr>
<tr>
<td>1 15 1 15</td>
<td>0.460</td>
<td>250</td>
<td>350</td>
<td>plasma</td>
<td>good</td>
</tr>
<tr>
<td>1 15 1 15</td>
<td>0.220</td>
<td>280</td>
<td>50</td>
<td>plasma</td>
<td>good</td>
</tr>
<tr>
<td>0.5 10 1 10</td>
<td>0.430</td>
<td>250</td>
<td>350</td>
<td>thermal</td>
<td>good</td>
</tr>
<tr>
<td>3 15 2 15</td>
<td>0.096</td>
<td>210</td>
<td>260</td>
<td>plasma</td>
<td>good</td>
</tr>
<tr>
<td>3 15 1 15</td>
<td>0.270</td>
<td>190</td>
<td>260</td>
<td>thermal</td>
<td>good</td>
</tr>
<tr>
<td>3 15 2 15</td>
<td>0.140</td>
<td>210</td>
<td>260</td>
<td>thermal</td>
<td>good</td>
</tr>
<tr>
<td>2 15 2 15</td>
<td>0.190</td>
<td>225</td>
<td>260</td>
<td>thermal</td>
<td>good</td>
</tr>
<tr>
<td>3 15 3 15</td>
<td>0.200</td>
<td>120</td>
<td>260</td>
<td>thermal</td>
<td>good</td>
</tr>
<tr>
<td>3 15 3 15</td>
<td>0.560</td>
<td>225</td>
<td>210</td>
<td>thermal</td>
<td>good</td>
</tr>
<tr>
<td>3 15 3 15</td>
<td>0.270</td>
<td>120</td>
<td>210</td>
<td>plasma</td>
<td>poor</td>
</tr>
</tbody>
</table>

During deposition nitrogen flow, substrate temperature and chamber pressure were kept constant. Each ALD cycle consisted of (I) 3-second dose of metal precursor (II) 15 second nitrogen (argon) purge (III) 2-second dose of water and (IV) another 15 second purge. During purge no precursor was introduced into the reactor. In order to optimize the atomic layer deposition system experiments were repeated at various substrate temperatures, precursor delivery time and purge time and different purge rates. Table 5.1 lists some of the experimental conditions that we have studied in detail.
Effect of precursor delivery on growth rate

The liquid precursors used for ALD - Al₂O₃ has sufficient vapour pressure, Tri Methyl Aluminum (13mbar) and water (31mbar), so that they can be used without a carrier gas. The amount of precursor flow is calculated using pressure in the reactor chamber. The pressure value is also affected by the location of the pressure gauge. We treat pressure value as reference to repeat our experiments at a fixed precursor dosage. Based on ideal gas theory a precursor pulse of a constant flow rate for a particular time contains a fixed number of molecules. ALD is a self limiting growth process and growth per cycle depends on the number of sufficient OH sites and sufficient precursor pulsing[29,43].

Table 5.2 gives the observation by varying TMA, H₂O pulsing time from 0.5 to 3 seconds and purge time from 5 to 15seconds. It is clear that the precursor exposure time and purge time is not much critical as in chemical vapour deposition (CVD). This means ALD has a wide range of deposition parameters.

Successful layer-by-layer deposition in an ALD process with sufficient exposure and purge times and full saturation of the surface, should in principle result in extremely uniform layers. Non-uniformity of the deposited layer can be attributed to one (or more) steps in the ALD cycle. Insufficient purge steps and less amount of precursor may cause some vapor phase reactions which leads to an increase in deposition rate that might be localized. Incomplete saturation of one of the two precursors is easily related to the amount supplied (time or concentration) and usually clearly visible as a decay in thickness in the direction of the precursor flow. Even though, if excess amount of precursor is pulsed that doesn’t vary the growth rate as the excess precursor is purged out in the next sequence. Long purge does not vary the GPC.

Effect of number of cycles on growth per cycle

Thickness of the ALD grown film is often directly proportional to the number of ALD reaction cycles carried out especially when thicker films are grown. This means the amount of material deposited is less, and growth
per cycle is a constant over cycles. During the initial phase of the deposition the growth per cycle is varied over the number of cycles that results variation in GPC. This varying GPC may be due to the fact that, the material deposited by ALD has different surface characteristics than those of the substrate where the film is grown.

ALD process modifies the chemical composition of surface by material deposition. The initial ALD reaction cycles occur usually on the surface of the original substrate and the following cycles on the surface of both the original substrate exposed and ALD deposited material. After few ALD cycles thickness of the film depends on growth per cycle and growth mode. The mechanism of saturating reactions and number of reactive sites may be different on the two materials (substrate and grown material). Thus growth per cycle should vary accordingly with the changes in chemical composition of the surface.

Figure 5.1: Dependence of Growth per cycle on number of cycles (a) linear growth (b) Substrate enhanced growth (c) Substrate inhibited growth of type 1 (d) Substrate inhibited growth of type 2.

ALD process can be divided into four groups (Figure 5.1) on the basis of how growth per cycle varies with number of ALD reaction cycles.
They are (1) linear growth (2) substrate enhanced growth (3) Substrate inhibited growth of type 1 (4) Substrate inhibited growth of type 2 [29].

In all groups the GPC is constant after sufficient number of ALD cycles. In linear growth, number of reactive sites on the surface does not change with number of the deposition cycles and hence GPC is constant over the entire cycles. In substrate enhanced growth the number of reactive sites on the substrate surface is higher than ALD grown material, hence GPC is higher in the initials cycles than at the steady regime. In Substrate inhibited growth of type 1 the number of reactive sites on the substrate surface is lower than that of ALD grown surface and hence GPC is lower during initial cycles than steady regime. But in Substrate inhibited growth of type 2 GPC additionally goes through a maximum before setting to a steady value. Island growth seems to occur in substrate inhibited growth of type 2.

Various ALD growth mechanisms

The amount and type of surface sites also affects how the deposited material is arranged on the surface during ALD growth, defined as the growth mode (Figure 5.2). The growth mode is an important characteristic in ALD as it influences several material characteristics such as layer closure, density and roughness. As for the effect of the starting surface on the GPC, three general classes of growth modes can be distinguished [29]. In two-dimensional growth, the precursors chemisorb preferentially in the lowest unfilled material layer. As a result, one monolayer of the ALD-grown oxide covers the original substrate completely while further growth proceeds monolayer by monolayer. As the GPC is typically less than a monolayer, this growth mode is not evident in ALD. When the precursors chemisorb preferentially on the ALD-grown material instead of on the starting surface, growth is established through microscopic islands. With island growth, the ALD precursors are unreactive towards the starting surface and growth is initiated at reactive defects on the substrate. Further growth proceeds symmetrically around these defects until the islands are large enough and they coalesce into a closed layer. The third growth mode, random deposition, is a statistical growth mode, where material deposits with equal probability
on both the starting surface and the ALD layer. A first indication of the type of growth mode is given by the starting surface dependence of the growth curve as the highest GPC typically implies the most efficient substrate coverage. Strong inhibition during the first ALD cycles, on H-terminated Si, has been associated with island growth while linear and substrate-enhanced growth results in the most two-dimensional surface coverage. Better growth and material characteristics are obtained when reactive Si-OH sites are introduced on the surface, but these sites imply the presence of an interfacial SiO$_2$ layer which adds to the EOT of the gate stack. Figure 5.2 is a schematic representation of the different growth modes in ALD: (a) two-dimensional growth, (b) island growth and (c) random deposition. The arrow indicates the increasing number of ALD cycles. The discussed effects on GPC and growth mode are not strictly related to the type of substrate material, but to any system where the amount and type of available surface sites is not constant during ALD growth. Hence, variations in GPC and deviations from two-dimensional growth are also possible during the ALD of ternary oxides, as their composition determines the type and amount of sites on the exposed surface.

Figure 5.2: Schematic representation of the different growth modes in ALD: (a) two-dimensional growth, (b) island growth and (c) random deposition. The arrow indicates the increasing number of ALD cycles.
thickness measurements were done using ex situ Spectroscopic Ellipsometry. During deposition the substrate temperature and chamber pressure were kept at 210°C and 0.20 mbar respectively.

Figure 5.3: (a) Al₂O₃ film thickness as a function of the number of cycles for thicker (no. of cycles > 100) films. Inset shows GPC curve for thicker films.

Figure 5.3(b): GPC curve for thinner films, inset shows Linear dependence of thickness on number of deposition cycles for thinner (no of cycles <100) films.

As expected, the thickness increases linearly with number of completed cycles. Growth per cycle (GPC) calculated from the linear fit of
the data has a value of 1.17Å/cycle for thicker films and 0.83Å/cycle for thinner films. Insets of Figure 5.2 and Figure 5.3 shows the corresponding GPC and thickness. From the nature of GPC curve we can confirm that the present growth model is substrate inhibited growth of type1.

5. 5 Characterizations of Alumina films

5. 5. 1 Compositional analysis

The chemical composition of the films was evaluated using XPS and EDS.

XPS Analysis

XPS spectra of the deposited samples were recorded using an ULVAC-PHI unit (model: ESCA5600 CIM) employing argon ion sputtering (Voltage = 3 kV, pressure 10⁻⁸ mbar). Al Kα X-ray (1486.6 eV) with a beam diameter of 0.8 mm and power of 400 W was used as the incident beam.

![Figure 5.4: XPS spectra of the as deposited ALD-Al₂O₃ film](image)

Figure 5.4 shows the XPS spectra of Al₂O₃ film deposited on p-type silicon wafer. All binding energies were referenced to C₁s peak at 284.457
eV. The appearance of Al\textsubscript{2s} at 118.95 eV and Al\textsubscript{2p} at 74.64 eV confirms the formation of Al\textsubscript{2}O\textsubscript{3}. Figures 5.5(a &b) shows XPS peaks of Al\textsubscript{2p} and O\textsubscript{1s}. From the figure it is clear that Al\textsubscript{2p} spectra consists of only a single peak centered around 74.64 eV, which corresponds to Al-O bonds of Al\textsubscript{2}O\textsubscript{3} [44,45]. The absence of shoulder region around 72.5eV confirms that the Al-Al bonds are not present in our film. This higher binding energy of Al\textsubscript{2p} indicated the change of oxidation state of Al from metallic state to Al\textsuperscript{3+} which corresponds to a conversion from sub stoichiometric Al\textsubscript{2}O\textsubscript{x} to Al\textsubscript{2}O\textsubscript{3} [46].

![XPS spectra](image)

Figure 5.5: (a) O\textsubscript{1s},(b) Al\textsubscript{2p} spectra of the as deposited films

**EDS Analysis**

Atomic concentrations of Al, O and Si of the deposited films were studied by EDS analysis and the results were tabulated in Table 5.3. In the samples which were prepared at optimum condition for thermal ALD, the ratio of the atomic percentages of oxygen and aluminum was found to be very close to the ideal value. The samples prepared at wide range of chamber pressures (0.14-0.56 mbar, Table 5.2) show good results for confirm the fact that the chamber pressure is not a critical deposition parameter in ALD as compared to CVD.
EDS was taken from different points on the surface and their mean value was taken as the actual composition of each sample. Since we have prepared samples on Si substrate, definitely an interfacial layer of SiO$_2$ will be present and hence it is difficult to separate the contributions of oxygen from SiO$_2$ or from the environment. The accuracy of EDS measurement is low and it can provide only total percentage of element present in the sample. We have confirmed our results using XPS analysis and obtained a comparable O/Al ratio of 1.40 from XPS data.

Table 5.3: EDS data of Al$_2$O$_3$ film on Silicon wafer

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Element</th>
<th>Mass%</th>
<th>Error%</th>
<th>Atomic%</th>
<th>O/Al ratio</th>
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<tbody>
<tr>
<td>0.180</td>
<td>O</td>
<td>46.08%</td>
<td>0.05%</td>
<td>59.04</td>
<td>1.4414</td>
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<td></td>
<td>Al</td>
<td>53.92</td>
<td>0.07</td>
<td>40.96</td>
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<tr>
<td>0.210</td>
<td>O</td>
<td>33.49</td>
<td>0.01</td>
<td>46.41</td>
<td>1.6736</td>
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<tr>
<td></td>
<td>Al</td>
<td>33.75</td>
<td>0.01</td>
<td>27.73</td>
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<tr>
<td>0.270</td>
<td>Si</td>
<td>32.75</td>
<td>0.01</td>
<td>25.83</td>
<td></td>
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<tr>
<td></td>
<td>O</td>
<td>49.91</td>
<td>0.02</td>
<td>62.69</td>
<td>1.6808</td>
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<tr>
<td></td>
<td>Al</td>
<td>50.09</td>
<td>0.03</td>
<td>37.31</td>
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<tr>
<td>0.320</td>
<td>O</td>
<td>49.54</td>
<td>0.01</td>
<td>62.34</td>
<td>1.6553</td>
</tr>
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<td>Al</td>
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<td>0.02</td>
<td>37.66</td>
<td></td>
</tr>
<tr>
<td>0.400</td>
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<td>15.92</td>
<td>0.01</td>
<td>24.79</td>
<td>1.4943</td>
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<td>0.02</td>
<td>16.59</td>
<td></td>
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<tr>
<td></td>
<td>Si</td>
<td>66.19</td>
<td>0.01</td>
<td>58.70</td>
<td></td>
</tr>
</tbody>
</table>

5.5.2 Structural Analysis

Structural characterizations of the prepared thin films were done using Powder XRD and GXRD (glancing angle at 0.5°) using Cu Kα radiation. The XRD patterns are shown in figure 5.6 and 5.7 respectively. The only peak in the powder XRD is that of silicon substrate.
Figure 5.6: Powder X-ray diffraction pattern of ALD coated Al₂O₃ sample deposited over Si wafer.

Figure 5.7: GXRD pattern of ALD deposited Al₂O₃ samples.

The absence of sharp peak in both patterns confirms the amorphous nature of alumina which is one of the major requirements for a gate dielectric [4].
5. 5. 3 Surface analyses

The surface morphologies of the as-deposited Al₂O₃ films were studied using Scanning Electron Microscopes (FESEM, SEM) and Atomic Force Microscope (AFM). Figure 5.8 (a) shows a comparison between the coated and uncoated surface. (b) & (c) are the surface coated with 200 cycle with 200 and 1000 times magnification respectively. (d) shows the image of a thick sample (1000 cycles). Some particle formation is observed in thick samples.

Figure 5.8: SEM images of Al₂O₃ samples (a) coated and uncoated surface, (b) completely coated surface (200 cycle) (c) higher magnification (200 cycle) (d) 1000 cycle ALD-Al₂O₃.
Figure 5.9: FESEM images of Al$_2$O$_3$ samples (a) 25ALD cycles, (b) 40 ALD cycles.

Figure 5.9 shows FESEM images of two samples prepared after 25 and 40 cycles of ALD respectively. It is clear that sample prepared with 25 cycles has more islands like structure than the second. In random deposition model, new material units have equal probability on all surface sites. This surface smoothness can also be confirmed using atomic force microscope measurement. Figure 5.10 shows AFM images of ALD deposited samples.

Figure 5.10: AFM image of ALD-Al$_2$O$_3$ films on Si(100): (a) 25 cycle (2D), (b) 25 cycle (3D)
AFM examination reveals that there is sharp island or particles formation observed in deposited films with sufficient thickness variation. Root-mean-square (RMS) surface roughness was found to be 1.128nm (over an area of $2 \times 2 \mu m^2$) which indicate that the present $Al_2O_3$ samples on silicon are relatively smooth on an atomic-scale. Some particles formation was observed on thick films prepared at 1000 cycles.

Figure 5.10: AFM image of $Al_2O_3$ film deposited on Si(100): (c) 50 cycles (2D), (d) 3D

Figure 5.11: AFM images of thick ALD-$Al_2O_3$ films on Silicon(100) (a)1000 cycles (2D),(b) 3D
5.5.4 Optical properties

Optical Characterization of Al\textsubscript{2}O\textsubscript{3} thin films are very important due to their increasing applications as protective and ion barrier layers in electronic and optoelectronic devices. Above 90\% transmittance is obtained for 170nm thick samples for whole visible range, which is comparable to that of the best quality films produced by other techniques [46, 47].

![Transmission spectra of Al\textsubscript{2}O\textsubscript{3} samples](image)

Figure 5.12: Transmission spectra of Al\textsubscript{2}O\textsubscript{3} samples

![FTIR spectra of ALD coated Al\textsubscript{2}O\textsubscript{3} film](image)

Figure 5.13: FTIR spectra of ALD coated Al\textsubscript{2}O\textsubscript{3} film
Figure 5.13 shows the FTIR spectra of Al$_2$O$_3$ film (174nm) deposited at 210°C. In literature FTIR results from thick and amorphous Al$_2$O$_3$ samples present a wide band centered around 700 cm$^{-1}$. This band corresponds to the overlapping of the Al-O stretching mode (750-850 cm$^{-1}$) and O-Al-O bending mode (650-700 cm$^{-1}$) [27,48-52]. Atomic layer deposited Al$_2$O$_3$ usually show a characteristic Al-O-Al band centered around 620 cm$^{-1}$ and samples intensity of this band is small. Absence of absorption peak at 1050-1100 cm$^{-1}$ (Si-O stretching mode) clearly indicates that there is no interfacial SiO$_2$ formed during deposition. It has been reported in the literature that it is very difficult to get rid of these native SiO$_2$ formation during deposition. The existence of SiO$_2$ increases EOT of the films and reduces the effective dielectric constant of the alternate high-k dielectric [52].

Film thicknesses were measured using a spectroscopic ellipsometer (Horiba Jobin Yvon–UVISEL and J. A. Woolman Co. M 2000U) and related parameters like dielectric constant and refractive indices were extracted using a simulation software (Delta Psi). The values of $\Psi$ and $\Delta$ were obtained over a spectral range of 200nm-830nm at an incidence angle of 70°. The best fit model was obtained using a three-layer model that included a roughness layer at the sample surface.

![Figure 5.14: Extracted dielectric constant from ellipsometric studies](image-url)
The figure 5.14 shows the extracted dielectric constant (k) from ellipsometric studies and obtained a value of 9.7 which is very close to experimentally reported values [4,53,54]. Figure 5.15 shows the extracted refractive index versus thickness of the samples. A mean refractive index value of 1.645 was observed at wave length of 550nm which is very close to the reported values [55].

![Refractive Index vs Thickness](image)

**Figure 5.15: Variation of refractive index with thickness**

### 5.5.5 Electrical properties

Aluminum oxide (Al$_2$O$_3$) is one of the best stable dielectric material. In order to study the dielectric properties of the ALD alumina MIM capacitors were fabricated as shown in Figure 5.16. Aluminum was used as metal electrodes, which were thermally evaporated at a thickness of 100 nm.
The dielectric properties of the fabricated MIM capacitor were studied using LCR meter (Fluke PM6306).

Variation of capacitance with frequency is shown in Figure 5.17. As frequency increases, capacitance decreases. The decrease in capacitance value with frequency is more pronounced at low frequencies. The dielectric constant of the different samples were calculated from measured capacitance at a frequency of 10 KHz. The results were tabulated in Table 5.3.

![Figure 5.17: Variation of capacitance with frequency](image)

**Table 5.3: Dielectric data of MIM capacitors**

<table>
<thead>
<tr>
<th>No of ALD cycles</th>
<th>Thickness of dielectric layer (nm)</th>
<th>Measured capacitance (nF)</th>
<th>Capacitance density</th>
<th>Dielectric constant calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>11</td>
<td>68.61</td>
<td>857.63</td>
<td>9.348</td>
</tr>
<tr>
<td>200</td>
<td>22</td>
<td>220.7</td>
<td>380.52</td>
<td>9.797</td>
</tr>
<tr>
<td>300</td>
<td>33</td>
<td>23.10</td>
<td>256.67</td>
<td>9.570</td>
</tr>
<tr>
<td>400</td>
<td>44</td>
<td>60.40</td>
<td>172.71</td>
<td>9.746</td>
</tr>
</tbody>
</table>
5.6 Conclusions

$\text{Al}_2\text{O}_3$ thin films were grown by Atomic Layer Deposition using TMA and water as precursors. The deposition conditions were optimized. Linear dependence of thickness over the number of cycles was verified. The growth per cycle was experimentally calculated and has a value of 1.17Å/cycle. Stoichiometric composition of grown films were studied using XPS and EDAX. Deposited films were structurally, optically and electrically characterized.

References

43. R. L Puurunen, Chemical Vapor Deposition, 9, 5, 249 (2003).