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A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy

in Chemical Engineering

by

Jea Lyen Cho

2015
ABSTRACT OF THE DISSERTATION

Engineering Lithium Ion Conducting Thin Film Solid Electrolytes by Atomic Layer Deposition

by

Jea Lyen Cho

Doctor of Philosophy in Chemical Engineering

University of California, Los Angeles 2015

Professor Jane P. Chang, Chair

A viable solid state inorganic Li-ion conductor, lithium aluminosilicate (Li$_x$Al$_y$Si$_z$O, LASO), was synthesized by atomic layer deposition (ALD). Investigations of the reaction mechanisms during ALD depositions of the constituent oxides of LASO, Al$_2$O$_3$, LiOH, and SiO$_2$, were first conducted via in-situ Fourier transform infrared spectroscopy (FTIR). The deposition rate of ALD Al$_2$O$_3$ and LiOH were 1.1 and 1.2 Å/cycle respectively while it was not possible to deposit SiO$_2$ by ALD at the conditions studied. The growth of three tertiary oxides, Al$_x$Si$_y$O, Li$_x$Al$_y$O, and Li$_x$Si$_y$O were confirmed by ALD, demonstrating that functionalization through hydroxylated LiOH and Al$_2$O$_3$ surfaces enabled the incorporation of ALD SiO$_2$ at low temperatures. The in-situ FTIR study revealed that presence of electropositive metal atom in vicinity of surface Si-OCH$_2$CH$_3$* specie is essential for the incorporation of ALD SiO$_2$ at low temperatures. No presence of incubation times were found for ALD deposition of each constituent oxide on the other, allowing ALD deposition LASO as a solid solution based on its constituent oxides. The growth rate of ALD LiAlSiO$_4$ was found to be 20.6 Å/global cycle.
The as-deposited ALD LASO films were amorphous with desired physiochemical properties viable for solid electrolyte applications. The calculated values of ionic conductivity were in the range of $1.75 \times 10^{-9}$ to $7.22 \times 10^{-8}$ S/cm, which were tunable by adjusting the number of ALD sub-cycles of the constituent oxides. The activation energy of Li-ion conduction was found to be between 0.46-0.89 eV, which was comparable to that reported in literature. An epitaxial crystallization of the as-deposited amorphous films into $\beta$-LiAlSiO$_4$ was achieved for selected compositions of LASO upon post-deposition rapid thermal annealing, with a relationship of LiAlSiO$_4$ $(1\overline{2}10) \parallel$ Si (100) and $\beta$-LiAlSiO$_4$ $(10\overline{1}0) \parallel$ Si (001) to Si substrate. An exceptional conformality of ALD LASO coating was demonstrated on prospective 3D architectures for electrodes, including high aspect ratio trenches and nanowires.

Integration of ALD Li$_x$Al$_y$Si$_z$O films with electrode materials including carbon electrode (both 2D and 3D), SnO$_2$, and SiGe nanowires were investigated. ALD Li$_x$Al$_y$Si$_z$O coating on 2D carbon electrode improved the coulombic efficiency from 91% to 98%. Integration of 3D carbon array electrodes demonstrated a high areal capacity of 7.36 mAh/cm$^2$, which was 6.75 times higher than the maximum areal capacity obtained from 2D carbon electrodes. *In-situ* HRTEM study on ALD coated SnO$_2$ and Si$_{0.6}$Ge$_{0.4}$ nanowires demonstrated promising prospects of ALD LASO not only as a solid electrolyte but also as a stable artificial solid electrolyte interface layer which can improve both physiochemical and mechanical stability of electrode materials.
The dissertation of Jea Lyen Cho is approved.

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PUBLICATIONS AND PRESENTATIONS

**J. Cho**, T. Kim, T. Seegmiller, and J. P. Chang, “A Mechanistic Study of Atomic Layer Deposition of Li\textsubscript{x}Al\textsubscript{y}Si\textsubscript{z}O thin film via in-situ FTIR Spectroscopy”, in-preparation

**J. Cho**, T. Kim, T. Seegmiller, and J. P. Chang, “A Mechanistic Study of Atomic Layer Deposition of Al\textsubscript{y}Si\textsubscript{z}O thin film via in-situ FTIR Spectroscopy”, in-preparation


Y. Perng*, **J. Cho***, S. Y. Sun, D. Membreno, N. Cirigliano, B. Dunn, and J. P. Chang, “Synthesis of ion conducting Li\textsubscript{x}Al\textsubscript{y}Si\textsubscript{z}O thin films by atomic layer deposition,” Journal of Materials Chemistry A 2014. *These authors equally contributed


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Battery Applications," AVS 60th International Symposium and Exhibition, Long Beach, CA, October 2013


Li-ion batteries (LIBs) are the powering medium of choice for miniaturized electronics as they offer the required power specifications for such devices in cost and energy efficient manner. In contrast to the significant advances made in the field of microelectronics, however, miniaturization of Li-ion technology remained challenging owing to both architectural and materialistic limitations. Even if the current technology is scalable with respect to the size of device, it fails to offer any solution: Under the traditional 2D electrode architecture, LIBs are prone to an inevitable loss of power density when the size of LIBs decreases with respect to decreasing device size. It has been proposed that such loss of power density of 2D battery can be significantly reduced if LIBs can utilize 3-Dimensional (3D) electrode architecture. The utilization of 3D electrode architecture has been limited, however, as the use of traditional liquid-based and/or polymer-based electrolyte fails to provide the required materialistic properties, including electrical insulation between the two electrodes due to compressibility and safety issues. To realize the benefits 3D architecture project to offer, development of novel solid electrolyte with desired physiochemical properties as well as conformality is essential.

Depositions of inorganic-oxide based Li-ion conductors via thin film deposition techniques including chemical vapor deposition (CVD), physical vapor deposition (PVD), and pulsed laser deposition (PLD) have demonstrated their promising results in the development of a 2D thin film Li-ion battery. However, these line-of-sight deposition techniques result in non-conformal films on complex 3D structures. Atomic layer deposition (ALD), a chemical deposition technique based on self-limited surface reactions, could synthesize solid electrolytes
for 3D Li-ion microbattery applications. As such, this work aims to explore the possibility of synthesizing a thin film Li-ion electrolyte by ALD.

1.1 Motivation

There has been growing scientific and technical interests in the recent years in developing an efficient power medium for next-generation miniaturized electronics such as microelectromechanical (MEMS) systems and wireless communication microsystems integrated within less than a cubic centimeter (Tarascon et al. 2001; Mukaibo et al. 2010; Lethien et al. 2011). In contrast to the remarkable exponential advances made in microelectronics, the miniaturization of their powering medium, Li-ion battery has been rather limited. Consequently, the power requirement for these miniaturized electronic devices versus the available battery power per footprint has been diverging, creating a power gap which has been and is projected only to grow in the coming years.

Figure 1.1 Comparison of the increased power required for mobile electronic devices and the actual increase of battery power, showing diverging power gap between estimated power consumption versus Li-ion battery (Jeong et al. 2011)
1.2 Li-ion Battery

Lithium, being the most electropositive and the lightest metal, has led to development of a primary cell based on a lithium metal as an anode. Despite its one time use, Li primary cell was well implemented as power sources for electronics that required low energy density such as watches and calculators (Nishi 2001; Tarascon et al. 2001). A significant technological improvement of Li battery technology was made upon the discovery of reversible alkali metal reactions, which ultimately led to the development of highly reversible, low voltage secondary Li-ion battery (abbreviated as Li-ion batteries or LIBs from hereon) that can be used numerous times (Tarascon et al. 2001). Compared to precedent battery technologies such as lead-acid and nickel-cadmium (Ni-Cd), LIBs offer significant advantages of high capacity, high operating voltage, no memory effect, higher safety and longer cycle life (Armand et al. 2008; Osaka et al. 2010).

Figure 1.2 Comparison of different battery technologies in terms of volumetric and gravimetric energy density (Tarascon et al. 2001)
### Table 1.1 Properties of secondary batteries (Kumar et al. 2010)

<table>
<thead>
<tr>
<th>System</th>
<th>Nominal cell voltage (V)</th>
<th>Specific energy (Wh/kg)</th>
<th>Cycle life (up to 80% of initial capacity)</th>
<th>Charge time (h)</th>
<th>Self-discharge per month (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead-Acid</td>
<td>2</td>
<td>30-50</td>
<td>200-350</td>
<td>8-16</td>
<td>5</td>
</tr>
<tr>
<td>Ni-Cd</td>
<td>1.25</td>
<td>45-80</td>
<td>1500</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>Ni-Mh</td>
<td>1.25</td>
<td>60-120</td>
<td>300-500</td>
<td>2-4</td>
<td>30</td>
</tr>
<tr>
<td>Li-ion</td>
<td>3.6</td>
<td>110-180</td>
<td>500-1000</td>
<td>2-4</td>
<td>10</td>
</tr>
<tr>
<td>Li polymer</td>
<td>3.6</td>
<td>100-130</td>
<td>300-500</td>
<td>2-4</td>
<td>10</td>
</tr>
</tbody>
</table>

As such, LIBs became the battery technology of choice shortly after its first introduction to the market two decades ago. LIBs now power various aspects of our life including the portable electronics, wireless telecommunications, emerging integrated optoelectronic circuits, microelectromechanical systems (MEMS), hybrid electric vehicles (HEV), as well as the storage of renewable energies from photovoltaics (PV) (Bruce et al. 2008). Owing to its wide applications, ever-growing worldwide market of LIBs now exceeds 10 billion dollars per year.

The LIB cell consists of three different active regions, a positive electrode called cathode, a negative electrode called anode, and an electrolyte that is ionically conductive yet electrically insulating. A simplified schematic representation of LIB is depicted in Figure 1.3:

![Figure 1.3 Schematic of Li-ion secondary rechargeable battery. The cell consists of two electrodes (cathode/anode) separated by an electrolyte. (Adapted from (Choi et al. 2011))](image)
The LIB converts the chemical energy within the cell into an electrical energy thorough two thermodynamically favorable chemical half-reactions which involves in intercalation or removal of Li ions from the active host materials. By convention, the electrode that undergoes a reduction (or a gain of electrons and Li ions) during discharge is defined as a cathode. Analogously, the electrode that undergoes oxidation (loss of electrons and Li-ions) is defined as an anode. A selected list of the current and prospective electrode materials being studied for the next-generation Li-ion battery technology is summarized in Table 1.2.

Table 1.2 List of selected electrode materials for Li-ion battery and their specific lithiation capacities

<table>
<thead>
<tr>
<th>Negative Electrode (Anode)</th>
<th>Specific Capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>~300</td>
</tr>
<tr>
<td>Nanostructured Carbon</td>
<td>~260</td>
</tr>
<tr>
<td>$\text{Li}_{3-x} \text{M}_x \text{N}$ (M = Co, Ni or Cu)</td>
<td>~900</td>
</tr>
<tr>
<td>Metal Oxide</td>
<td>~1200 ($\text{Fe}_2\text{O}_3$)</td>
</tr>
<tr>
<td></td>
<td>~790 ($\text{SnO}_2$)</td>
</tr>
<tr>
<td>Germanium (Ge)</td>
<td>~1140</td>
</tr>
<tr>
<td>Silicon (Si) thin film</td>
<td>~4200</td>
</tr>
<tr>
<td>Positive Electrode (Cathode)</td>
<td>Specific capacity (mAh/g)</td>
</tr>
<tr>
<td>$\text{LiCoO}_2$</td>
<td>~110-190</td>
</tr>
<tr>
<td>Li-Manganese (spinel)</td>
<td>~110-120</td>
</tr>
<tr>
<td>$\text{Li-NCM}$ (nickel-cobalt manganese)</td>
<td>~95-130</td>
</tr>
</tbody>
</table>

The operating principle of LIB consists Li-ions moving from the anode through the electrolyte, and lithiated into the cathode during discharge. During this process an electron is also removed from the anode and transferred to cathode through an external circuit (as represented in Figure 1.3) providing current. This discharge process continues until the potential difference between the anode and cathode reaches equilibrium. During charging, the entire processes are reversed when a current at a potential is supplied at a potential higher than that of the cell.

The current commercial LIBs utilize graphite anode with lithium cobalt oxide ($\text{LiCoO}_2$) cathode, as such material combination provides a potential that is relatively close to that obtained from pure lithium metal (Kumar et al. 2010). The overall chemical reaction of graphite/LiCoO$_2$ system can be described by Eq (1.1):
LiCoO$_2$ + 6C = Li$_{1-x}$CoO$_2$ + Li$_x$C$_6$  \hspace{1cm} (1.1)

This overall chemical reaction can be divided into two half-reactions to differentiate the reactions occurring at each electrode, an oxidation half-reaction at the anode (Eq. (1.2)) and reduction reaction at the cathode (Eq. (1.3)):

\[
\text{LiCoO}_2 + \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \hspace{1cm} (1.2)
\]

\[
6\text{C} + x\text{Li}^+ + xe^- = \text{Li}_x\text{C}_6 \hspace{1cm} (1.3)
\]

The amount of energy delivered by LIB is governed by the lithiation capacity of electrode material whereas the rate of electron transfer is controlled by the electrolyte. In the current state-of-the-art LIB, most cells are based on liquid-based electrolytes which provide high Li-ion conductivities up to 1-10 S/cm (Kumar et al. 2010). These electrolytes generally consist of lithium salts such as LiClO$_4$, LiBF$_4$, and LiPF$_6$ dissolved in carbonate organic solvents such as ethylene carbonate (EC), dimethyl carbonate (DMC), or propylene carbonate (PC). Table 1.3 summarizes a list of commonly used liquid electrolyte solutions along with their noteworthy physiochemical properties.
Table 1.3 List of commonly used liquid-based electrolyte for Li-ion batteries (Adapted from (Park et al. 2010))

<table>
<thead>
<tr>
<th>Salt</th>
<th>Solvent</th>
<th>Viscosity (cP)</th>
<th>Conductivity (S/cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiClO₄</td>
<td>PC</td>
<td>2.53 (30 °C)</td>
<td>5.6</td>
<td>• Lithium perchlorate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Satisfactory solubility and high conductivity</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• High anodic stability and generates a lower impedance SEI</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Less hygroscopic and stable to ambient moisture</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Strong oxidant: readily reacts with most organic species at high temperature</td>
</tr>
<tr>
<td>LiBF₄</td>
<td>PC</td>
<td>3.4</td>
<td></td>
<td>• Lithium tetrafluoroborate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Less toxic than LiAsF₆ and safer than LiClO₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Good stability at low and high temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Moderate ionic conductivity</td>
</tr>
<tr>
<td>LiPF₆</td>
<td>PC</td>
<td>5.8</td>
<td></td>
<td>• Lithium hexafluorophosphate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Combination of well-balanced properties: only successfully commercialized salt</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Sensitive to ambient moisture and solvents</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Thermally unstable at high temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Causes tremendous difficulty in preparation and purification</td>
</tr>
</tbody>
</table>

The use of these liquid electrolytes, however, possesses intrinsic disadvantages. When these liquid electrolytes are in direct contact with electrode materials, slow degradations of electrode materials occur even at room temperature, ultimately resulting in detrimental side reactions leading to a defective and unstable cell (Meng et al. 2012).

To discuss the technological challenges of LIBs more effectively, however, it is important to present the technological terminologies and their relationship to each other. The energy capacity represents the energy stored per mass or volume with units of Wh/kg or Wh/L of the lithiation (hosting) lithium ions. Other important Li-ion battery parameters include cell
potential (V), specific energy capacity, rate capability, and cycling ability where their definitions and relationships are summarized in Table 1.4.
<table>
<thead>
<tr>
<th>Battery characteristics</th>
<th>Description</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open-circuit voltage</td>
<td>Maximum voltage in the charged state at zero current. Low currents are characterized by activation losses, while the maximum current is normally determined by mass transfer limitations. The energy that can be derived per unit volume of the weight of the cell. The energy that can be derived per unit weight of the cell (or sometimes per unit weight of the active electrode material).</td>
<td>$E^0$ (cell) $= E^0$ (c) $- E^0$ (a)</td>
<td>Volt (V)</td>
</tr>
<tr>
<td>Current</td>
<td></td>
<td>Ampere (A)</td>
<td></td>
</tr>
<tr>
<td>Energy density</td>
<td>The energy that can be derived</td>
<td>$E = \int V \cdot I , dt$</td>
<td>Watt-hours per liter (Wh/dml)</td>
</tr>
<tr>
<td>Specific energy density</td>
<td>The energy that can be derived per unit weight of the cell (or sometimes per unit weight of the active electrode material).</td>
<td>$E / M$</td>
<td>Watt-hours per kilogram (Wh/kg)</td>
</tr>
<tr>
<td>Power density</td>
<td>The power that can be derived per unit weight of the cell. The theoretical capacity of a battery.</td>
<td>$P = V \cdot I / M$</td>
<td>Watt per kilogram (W/kg)</td>
</tr>
<tr>
<td>Capacity</td>
<td>The quantity of electricity involved in the electrochemical reaction. The time a battery can be stored inactive before its capacity falls to 80%.</td>
<td>$C_{\text{specific}} = n F / M_r$</td>
<td>Ampere-hours per gram (Ah/g)</td>
</tr>
<tr>
<td>Shelf-life</td>
<td>The time a battery can be used at various loads and temperatures.</td>
<td></td>
<td>Hours (usually normalized for ampere per kilogram (A/kg) and ampere per liter (A/l))</td>
</tr>
<tr>
<td>Service life</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycle life</td>
<td>The number of discharge/charge cycles it can undergo before its capacity falls to 80%.</td>
<td></td>
<td>Cycles</td>
</tr>
</tbody>
</table>
The voltage of a cell, \( E^0 \), widely denoted as the theoretical standard cell voltage is defined as the difference of the standard electrode potentials of the cathode and the anode:

\[
E^0 = E^0 \text{ (cell)} = E^0 \text{ (cathode)} - E^0 \text{ (anode)}
\]

(1.4)

For a true estimate of open circuit cell voltage, however, this theoretical voltage equation needs to be modified to account for the nonstandard state of the reacting components (also known as Nernst equation):

\[
E = E^0 - RT \ln Q
\]

(1.5)

where \( Q \) is the chemical quotient for the overall cell reaction, defined as \( Q = \frac{a_{\text{products}}}{a_{\text{reactants}}} \) where \( a \) is the chemical activity, and \( R \) is the universal gas constant, 8.314 J/kmol. For the electrode reaction of

\[
M^{2+} + 2e^- = M
\]

(1.6)

the actual open circuit cell voltage (or the Nernstian potential) is then defined as

\[
E = E^0 - RT \ln \frac{a_M}{a_{M^{2+}}}
\]

(1.7)

It is worth noting that the open circuit voltage shown in Eq. (1.5) changes over time owing to time dependent parameters such as self-discharge, polarization of the electrode, the resistance losses within the cell, et cetera. Therefore the nominal voltage is generally defined as the chemistry of the cell at the given point of time (Kumar et al. 2010).

1.2.1 Li-ion Microbattery

There is strong scientific and technological interest on improving Li-ion battery (LIB) technology to power the next-generation microelectronics, especially those that can be mounted on semiconductor chips under significantly reduced footprint. Unfortunately, as the power density of LIB technology is related to the surface area of electrodes, with the current two-
dimensional (2D) electrode architecture, a significant reduction in footprint translate into an inevitable loss of the power density of the cell. (Long et al. 2004).

![Diagram of energy density and recharge comparison between conventional and miniaturized batteries]

Figure 1.4 Comparison of energy density and recharge between conventional and miniaturized batteries, highlighting the need of higher density batteries in the future (Serrano et al. 2009)

For Li-ion battery technology to be minimized to these significantly reduced footprints/spaces without excessive sacrifice of energy and power density, an extensive redesign of the current 2D planar electrode geometry into novel three-dimensional (3D) electrodes is required. Under such configuration, the surface area of electrodes can be increased simply by increasing the length of electrodes as shown in Figure 1.5.
Figure 1.5 Schematic illustrations of 2-D planar and 3-D interdigitated array electrode architectures both under the same footprint denoted as ‘A’.

To give a quantitative evaluation on this surface area increase from electrode reconfiguration from 2D to 3D, a calculation is presented for the concentric tube 3D electrode configuration shown in Figure 1.5. In this example, the anode consists of an array of pillars with a hexagonal close-packed (HCP) arrangement under a planar footprint of $L^2$. The surface area of 3D electrode ($SA_{3D}$) area of such configuration can then be calculated as:

$$SA_{3D} = L^2 + \pi dh \cdot N_{anode} = SA_{2D} + \frac{\pi d^2}{2} AR \cdot N_{anode}$$

(1.8)

where $SA_{2D} (=L^2)$ is the surface area of 2D planar electrode, $d$ is the diameter of electrode rod, $AR$ is the aspect ratio which is defined as $h/d$. $N_{anode}$ is the number of anodes for a given footprint, where for a HCP arrangement is equal to:

$$N_{anode} = \left( \frac{l - 2D}{P} \right) \left( \frac{l - 2D}{\sqrt{3}} \cdot \frac{P}{2} \right)$$

(1.9)
where P is the pitch, the distance between the center of two rods.

The areal capacity of electrode, $C_{\text{areal}_i}$ (for both anode and cathode material) is given by the relation:

$$C_{\text{areal}_i} = \frac{C_i}{l^2} = \frac{C_i}{M} \rho \frac{V_i}{l^2} = \frac{C_{\text{specific}_i}}{l^2} \rho \frac{V_i}{l^2} \quad (1.10)$$

where the subscript i denotes the electrode material of interest (anode or cathode material), C is the lithiation capacity, $\rho$ is the density, and V is the volume of electrode. The volumes of electrodes for a HCP arranged 3D electrode cell shown in Figure 1.5 can be derived as:

$$V_{\text{anode}} = \pi \left( \frac{d}{2} \right)^2 h \cdot N_{\text{anode}} = \pi \left( \frac{d}{2} \right)^3 \cdot N_{\text{anode}} \cdot \text{AR} \quad (1.11)$$

$$V_{\text{cathode}} = l^2 \cdot h \cdot \pi \left( \frac{d+t}{2} \right)^2 h \cdot N_{\text{anode}} = \left[ l^2 - \pi \left( \frac{d+t}{2} \right)^2 \cdot N_{\text{anode}} \right] \left( \frac{d}{2} \right) \cdot \text{AR} \quad (1.12)$$

As evident from Eq. (1.9)-(1.12), an increase of the aspect ratio (AR) of electrodes increases the volume, which in turn increases the areal capacity of the cell. The increase of areal capacity results in increase of energy and power density of the cell owing to the following relations:

$$E_{\text{cell}} = C_{\text{areal}} \cdot V_{\text{cell}} \quad (1.13)$$

$$P_{\text{cell}} = \frac{E_{\text{cell}}}{t} \quad (1.14)$$

It has to be noted, however, the aspect ratio of the electrodes cannot be increased without limit as there exists a critical length where the increased ohmic resistance of the electrode offsets the advantages from the increased areal capacity. It is therefore essential to design a cell with an architecture that can fully optimize energy content of the cell upon reconfiguration of electrodes into 3D. While a detailed discussion of each component is beyond the scope of this study, a simplified model of LIB cell where the capacity and density of the cell are fully determined by
the charge capacities of electrode materials is discussed briefly to delineate the importance of geometry and material optimization.

Figure 1.6 shows the calculated areal capacity for graphite and LiCoO$_2$ electrodes as a function of the aspect ratio (AR) of the anode. The density values used for calculation are 2.26 g/cm$^3$ (Idota et al. 1997) and 5.06 g/cm$^3$ (Pu et al. 2012) for graphite and LiCoO$_2$ respectively.

![Figure 1.6 Theoretical areal capacity of LiCoO$_2$ and graphite half-cells as a function of aspect ratio (AR) for various pitch values, with anode specifications of d=15 nm, h=400 nm, and t=15 nm. Filled symbols denote LiCoO$_2$ and the empty ones denote graphite.](image)

As evident from the figure above, the areal capacity of electrodes increases with respect to increasing AR. It is important to realize, however, the differences between areal capacities of the electrodes also diverge with increasing AR. Such difference translates to the need of additional anode material (more graphite in this case) in order to match the capacity of the cathode. From the perspective of material optimization, such design is inefficient and uneconomical, however. As such, to design the next-generation LIB in fully optimized fashion, not only the geometrical configurations of electrodes need to be considered, but a deliberate choice of electrode materials with an effective capacity matching also needs to be considered. There exist prospective anode materials with higher lithiation capacities than graphite such as Si,
Ge and SnO$_2$. However, the utilization of these materials in actual cell not been effectively realized owing to pulverizations of active materials following the large (>150 %) volume expansion that follows lithiation. Owing to this reason, graphite still remains as the anode material of choice in commercial 2D architectured LIBs. It is important to mention, however, an effective utilization of 3D architecture is projected to allow the use of these high lithiation capacity anode materials due with improved stress accommodation. Preliminary studies on 3D architectured high capacity anodes includes porous Si (Gowda et al. 2012), SiNW (Liu et al. 2013), Ge spheres (Song et al. 2012), have been beyond promising. Table 1.5 summarizes areal capacity calculations for selected combinations of these prospective high capacity electrodes. The dimensions implemented in the calculations are based on those already attainable for nanowires with current semiconductor fabrication technologies (Nguyen et al. 2011; Surawijaya et al. 2011; Kwong et al. 2012).
Table 1.5 Calculated values of areal capacity and energy of theoretical Li-ion cell with a 3D concentric electrode configuration with attainable dimensions of diameter and heights, with an electrolyte thickness of 15 nm and average cell voltage of 3.5V. The projected areal energy density requirement of 1 J/mm² for on-chip power source is attainable with next-generation anode materials under 3D configuration.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Anode</th>
<th>Volumetric Capacity (mAh/cm³)</th>
<th>Heights H (µm)</th>
<th>Diameter d (nm)</th>
<th>Pitch (nm)</th>
<th>Areal Capacity C_{areal} (mAh/mm²)</th>
<th>Areal Energy E_{areal} (J/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO₂</td>
<td>Graphite (372)</td>
<td>400</td>
<td>150</td>
<td>300</td>
<td>0.009</td>
<td>0.116</td>
<td></td>
</tr>
<tr>
<td>(274)</td>
<td>Si (8500)</td>
<td>400</td>
<td>150</td>
<td>300</td>
<td>0.093</td>
<td>1.168</td>
<td></td>
</tr>
<tr>
<td>LiCoO₂</td>
<td>Ge (9700)</td>
<td>400</td>
<td>150</td>
<td>300</td>
<td>0.106</td>
<td>1.333</td>
<td></td>
</tr>
</tbody>
</table>

As shown in Table 1.5, the footprint-normalized energy capacity from 3D architected LIBs can deliver the required areal density of 1 J/mm² for on-chip power sources for smart dust and related microdevices (Rolison et al. 2009). A 2D architecture or even a 3D cell based on conventional graphite electrode fails to meet such requirement. The 1 J/mm² requirement can also be met not only by the concentric rod architecture (shown in Figure 1.5), but other 3D architectures as well, including trench-shaped electrodes as shown in Figure 1.7. For such trench-shaped architecture, aforementioned 1 J/mm² requirement can be met for the electrode trench lengths longer than 5.3 µm, with Si serving as the anode.
Figure 1.7 A schematic representation of alternative three-dimensional, integrated, solid-state lithium-ion battery. The surface area of the battery has been increased from implementing trench-shaped electrodes rather than planar electrodes. 3D microbatteries are projected to provide enough energy to power smart autonomous network devices related to sensing applications (Armand et al. 2008).

1.3 Need for Solid Electrolyte

The superior advantage of 3D architecture has been well-demonstrated by the recent pioneering work by Pikul et al., where the authors successfully developed a Li-ion microbattery with power densities up to 7.4 mW/cm²μm from 3D meso-porous NiSn and LiMnO₂ electrodes with LiClO₄ in ethylene carbonate-dimethyl carbonate solution (Pikul et al. 2013). This power density was 2000 times higher than the state-of-the-art 2D thin film LIB batteries, demonstrating the promising prospects of 3D LIBs. The size of this 3D NiSn/LiMnO₂ battery, however, was still too large, of ~1mm x 3mm² for applications on micro/nanoscale electronics. As such, further miniaturization of 3D Li-ion cells is critical. The major bottleneck that prohibits further miniaturization of LIB is due to the lack of appropriate electrolyte material that can be implemented on 3D structures under limited footprint. Consequently, the breakthrough advancements in LIBs can only be realized upon the development of a well-engineered, conformal, thin-film electrolyte material, as to be discussed in the following sections.
1.3.1 Li-ion electrolytes

The current state-of-the-art Li-ion cells utilize liquid-based electrolytes, which consists of carbonate organic solvents with lithium salts as where the common choices were previously presented in Table 1.3. The role of an electrolyte is to provide an ionically conductive pathway between the two electrodes, while providing electronic insulation. For the case of liquid electrolytes, the transportable \( \text{Li}^+ \) ions are generated from Li salts such as LiPF\(_6\) which dissolved in a carbonate organic solvent. In such medium, the viscosity of the solution determines the motion of ions, which in turn determines the ionic conductivity. While an accurate prediction of such phenomena is implausible, empirical relations of the Jones-Dole (Eq. (1.15)) and Debye-Huckel-Onsager (Eq.(1.16)) can be implemented to estimate the ionic conductivity of a single solvent system (Park et al. 2010):

\[
\mu_r = \frac{\mu}{\mu_0} = 1 + \frac{AC^{1/2} + BC + DC^2}{2}
\]

\[
\Lambda = \Lambda_0(1/2)SC
\]
where \( \mu_r \) is the relative viscosity, \( \mu \) is the viscosity of solution, \( \mu_0 \) is the viscosity of pure solvent, C is the concentration of salt, and A, B, D are empirical coefficients. \( \Lambda \) is the molar conductivity, \( \Lambda_0 \) is the molar conductivity at infinite dilution, S is parameter based on both the physical properties of the solvent and the nature of the electrolyte (Park et al. 2010). Further discussions on the fundamentals of ionic transport in aqueous electrolytes are omitted hereon as they are beyond from the scope of this study. Detailed discussion of ion transport and ionic conduction can be found elsewhere (Park et al. 2010).

In contrast, the motion of ions in polymer and inorganic glass-ceramic solid electrolytes is described by an activated jump process, for which the diffusion coefficient, \( D \), can be defined as (Tuller 2007):

\[
D = D_0 \exp(-\frac{\Delta G}{k_B T}) = \gamma (1-c)Za^2 v_0 \exp(\Delta S/k) \exp(-\frac{E_m}{k_B T})
\]

(1.17)

where \( a \) is the jump distance, \( v_0 \) is the attempt frequency, and \( E_m \) the migration energy, \( (1-c)Z \) defines the number of neighboring unoccupied sites, \( \gamma \) is the geometric correlation factors. This equation can be further simplified by implementing the definition of ion mobility, \( \mu \), defined as \( \mu = \frac{ZqD_i}{k_B T} \), where \( B \) is the pseudo-activation energy for the conductivity (expressed in units of \( \frac{E_a}{k_B} \)) and \( T_0 \) is the reference temperature. As can be seen from Eq. (1.17), the ion transportation (thus the ionic conduction) in solid electrolytes is a complex function of various physical parameters, including composition and structure of material. As such, in designing a solid electrolyte, the ability to control the composition and structure of material is critical to obtain the desired ionic conductivity.
1.3.2 Solid Electrolytes

Solid electrolytes can be divided largely into two different categories of organic polymers and inorganic ceramics. The main difference between the two lies in their mechanical properties which differentiates their applications. The low elastic moduli of polymer-based electrolytes are better used for flexible battery designs, whereas the high elastic moduli of ceramics make them more suitable for rigid battery designs such as thin film based devices (Fergus 2010). Further comparisons between the two (organic and inorganic ceramics) and to liquid-based electrolytes are summarized in Table 1.6.
Table 1.6 Comparison chart between different types of solid lithium ion electrolytes

<table>
<thead>
<tr>
<th>Subcategory</th>
<th>Ionic Conductivity (Room Temperature)</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous Electrolytes</td>
<td>0.1-18 mS/cm(^{[1]})</td>
<td>Stable to high voltage(^{[2]})</td>
<td>Narrow operation temperature range (Between -20 to 60 °C)(^{[4]})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High ionic conductivity(^{[3]})</td>
<td>Formation of solid-electrolyte interphase which lowers device performance</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>High vapor pressure and flammability</td>
</tr>
<tr>
<td>Solid electrolytes</td>
<td>&gt;10(^{-4}) S/cm(^{[7]})</td>
<td>Very good free-standing properties</td>
<td>Safety concerns</td>
</tr>
<tr>
<td>(Organic)</td>
<td></td>
<td>Cohesive features of solid systems with liquid-like transport properties(^{[7]})</td>
<td>Leakage and corrosion</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Good processibility and flexibility</td>
<td>Limitations for miniaturization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dimensional stability(^{[9]})</td>
<td>Poor room temperature conductivity(^{[10]})</td>
</tr>
<tr>
<td>Ceramic (Inorganic)</td>
<td>10(^{-5})-10(^{-6}) S/cm(^{[7]})</td>
<td>High operating temperature</td>
<td>Low ionic conductivity(^{[7]})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Negligible electrical conductivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stability against chemical reaction with electrodes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Matching thermal coefficients with both electrodes(^{[8]})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Improved safety from large electrochemical stability window and thermal stability</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ease of miniaturization(^{[8]})</td>
<td></td>
</tr>
</tbody>
</table>

\(^{[1]}\): (Lewandowski et al. 2009), \(^{[2]}\): (Wakihara 2001), \(^{[3]}\): (Thokchom et al. 2010), \(^{[4]}\): (Wakihara 2001; Xu 2004), \(^{[5]}\): (Tarascon et al. 2001), \(^{[6]}\): (Scrosati et al. 2010), \(^{[7]}\): (Quartarone et al. 2011), \(^{[8]}\): (Knauth 2009), \(^{[9]}\): (Fergus 2010), \(^{[10]}\): (Patil et al. 2008)
1.3.3 Solid Oxide Li-ion Conductor

Metal oxides play important roles in numerous areas including inorganic chemistry, materials engineering, mechanical engineering, electrical engineering, et cetera. They are the building blocks of the modern electronic devices for applications in high dielectric constant insulators in transistors, magnetic tunnel junctions in spintronic devices, optical coatings, barrier layers, and electrolytes in electrochemical devices. The wide applicability of metal oxides derives from their intrinsic structural, thermal, and chemical stabilities. Additionally, some metal oxides systems offer exotic material properties including piezoelectricity, super conductivity, negative thermal expansion, and ionic conductivity (Gougousi et al. 2005; Fierro 2006). As such, synthesis metal oxide based solid electrolyte has drawn attention in hopes of utilizing the outstanding electrochemical properties of the metal-oxides provide. The development of metal-oxide based solid electrolytes have been successful, and now are implemented in various electrochemical cells including solid oxide fuel cells (SOFCs), proton exchange membrane fuel cells, water hydrolysis cells, chemical sensors and high-energy-density rechargeable batteries (Thangadurai et al. 2006).

Many oxides are known to exhibit ionic conduction, where their structures can be single-crystalline, polycrystalline, or amorphous (Thangadurai et al. 2006). The conducting ions may be Na\(^+\), Ag\(^+\), K\(^+\), Cu\(^+\), H\(^+\), F\(^-\), Li\(^+\), and O\(^2-\). Among these, lithium-ion (Li\(^+\)) conducting metal oxides have drawn attention as Li-ion batteries (LIBs) have become the dominant energy source for microelectronics. With LIBs are projected to remain as the power medium for the next-generation miniaturized electronics including MEMS and on-chip devices, studies on designing Li-ion conducting oxide as a solid electrolyte for such applications have become more important (Zhao et al. 2003).
To be suitable as solid electrolyte in Li-ion microbattery application, the inorganic Li-ion conductor has to meet stringent material criteria. These include a) high ionic conductivity at operating temperature, b) negligible electronic conductivity over the entire employed range of lithium activity and temperature, c) small to none grain-boundary resistance, d) chemical stability with both electrodes, e) matching thermal expansion coefficients of the electrolyte with both electrodes, f) environmental benignity, low cost, and easiness of preparation (Thangadurai et al. 2006). A selected list of inorganic Li-ion conductors that meets these requirements are listed in Table 1.7.
Table 1.7 Structural and conductivity data of various important lithium ion conductors (Thangadurai et al. 2002)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dimension</th>
<th>$\sigma$ (S/cm)</th>
<th>T (°C)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiI</td>
<td>3D</td>
<td>$1.0 \times 10^{-7}$</td>
<td>25</td>
<td>0.43</td>
</tr>
<tr>
<td>LiI (40 mol. %Al$_2$O$_3$)</td>
<td>3D</td>
<td>$1.0 \times 10^{-5}$</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>Li$_3$N</td>
<td>2D</td>
<td>$4.0 \times 10^{-4}$</td>
<td>25</td>
<td>0.30</td>
</tr>
<tr>
<td>Li-β-alumina</td>
<td>2D</td>
<td>$1.3 \times 10^{-4}$</td>
<td>25</td>
<td>0.19</td>
</tr>
<tr>
<td>LiAlSiO$_4$</td>
<td>1D</td>
<td>$4.7 \times 10^{-5}$</td>
<td>400</td>
<td>0.95</td>
</tr>
<tr>
<td>Li$_{1.4}$Zn(GeO$_4$)$_4$(LISICON)</td>
<td>3D</td>
<td>$1.3 \times 10^{-1}$</td>
<td>300</td>
<td>0.50</td>
</tr>
<tr>
<td>Li$<em>{4.4}$Al$</em>{0.4}$Si$_{0.6}$O$_4$</td>
<td>3D</td>
<td>$8.0 \times 10^{-3}$</td>
<td>300</td>
<td>0.56</td>
</tr>
<tr>
<td>LiTi$_2$(PO$_4$)$_3$</td>
<td>3D</td>
<td>$2.0 \times 10^{-6}$</td>
<td>30</td>
<td>0.30</td>
</tr>
<tr>
<td>Li$<em>{1.3}$Al$</em>{0.3}$Ti$_{1.7}$(PO$_4$)$_3$</td>
<td>3D</td>
<td>$7.0 \times 10^{-4}$</td>
<td>30</td>
<td>0.20</td>
</tr>
<tr>
<td>La$<em>{0.55}$Li$</em>{0.36}$M$_{0.09}$TiO$_3$</td>
<td>3D</td>
<td>$1.5 \times 10^{-3}$</td>
<td>30</td>
<td>0.33</td>
</tr>
<tr>
<td>0.2Li$_2$O-0.55SiO$_2$-0.25P$_2$O$_5$</td>
<td>Glass</td>
<td>$8.0 \times 10^{-7}$</td>
<td>150</td>
<td>0.42</td>
</tr>
<tr>
<td>PEO-LiClO$_4$</td>
<td>3D</td>
<td>$1.0 \times 10^{-7}$</td>
<td>25</td>
<td>0.31</td>
</tr>
<tr>
<td>PAN-PC-EC-LiClO$_4$</td>
<td>3D</td>
<td>$1.0 \times 10^{-3}$</td>
<td>25</td>
<td>-</td>
</tr>
</tbody>
</table>

1.3.4 Mechanism of Ion Conduction in Oxides

Ion conduction in oxide compounds occurs by the movement of ions through the ionic point defects and/or diffusion, which increases with increasing temperature. This temperature-dependent characteristic of ionic conduction has led the study of solid electrolytes generally focused in high-temperature applications (>300 °C). With discoveries of ionic conductors of sufficiently high ionic conductivity even at room temperatures, however, their applications at low temperatures are being investigated (Fergus 2010). In this following section, a brief introduction to the ion conduction mechanism and structural design criteria is discussed to underpin the material requirements needed to be considered in designing an inorganic Li-ion conductor.

The basic model of ion transport in oxides can be described as isolated hopping of mobile ions. This hopping mechanism can be divided into two categories of vacancy and interstitial
migration. In the vacancy migration, there exist a number of empty sites that would be occupied in the ideal, defect-free structure. These empty sites are generated due to either a thermally generated Schottky defect (where a cation and anion vacancy pair forms) or upon the presence of charged impurities.

An ion adjacent to this vacancy is then allowed to hop into the vacancy, leaving its previously occupied site empty. Additionally, an interstitial migration can occur when the ions are displaced from their lattice sites into interstitial sites, also known as Frenkel defects. In macroscopic picture, the continuous hopping of ions is what gives rise to ionic conductivity. A summary of available ionic conduction mechanisms in oxide materials is summarized in Table 1.8.
Table 1.8 A summary of diffusion mechanisms in solid (Adapted from (Mehrer 2007))

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacancy (defect)-mediated</td>
<td>Vacancy: Self-diffusion in metals and substitution alloys</td>
</tr>
<tr>
<td>Divacancy</td>
<td>Diffusion via aggregates of vacancies</td>
</tr>
<tr>
<td>Non-vacancy (defect)-mediated</td>
<td>Interstitial: Solute atoms considerably smaller than the host atoms, and atoms are incorporated into interstitial sites of the host lattice to form an interstitial solid solution</td>
</tr>
<tr>
<td>Collective</td>
<td>Collective: Solute atoms similar in size to host atoms involving simultaneous motion of several atoms. Usually substitutional solid solutions are formed</td>
</tr>
<tr>
<td>Interstitialcy</td>
<td>Interstitialcy: A collective mechanism important for radiation-induced diffusion. At least two atoms move simultaneously; however, this mechanism is negligible for thermal diffusion</td>
</tr>
<tr>
<td>Interstitial-substitutional Exchange</td>
<td>Interstitial-substitutional Exchange: Solute atoms are dissolved on both interstitial and substitutional sites and diffuse via interstitial or substitutional exchange mechanisms</td>
</tr>
</tbody>
</table>

By combining the charge of ions, \(z_i q_e\) along with the charge carrier density \(n_i\) and ion mobility, \(\mu\), the ionic conductivity of an oxide system can be described as:

\[
\sigma_{\text{ionic}} = \sum n_i (z_i q_e) \mu_i 
\]  

(1.18)

where \(\mu\), the ion mobility is related to the ion diffusivity, \(D_i\), defined as:

\[
\mu_i = \frac{z_i q_e D_i}{k_b T}
\]  

(1.19)

Substitution of Eq. (1.19) to Eq. (1.18) gives the relationship for ionic conductivity, \(\sigma_{\text{ionic}}\) (Tuller 2007).

\[
\sigma_{\text{ionic}} = \sum \frac{n_i (z_i q_e)^2 D_i}{k_b T}
\]  

(1.20)

The activation energy of ion conduction, \(E_a\), which represents the ease of ion hopping, can be obtained via the Arrhenius equation:

\[
\sigma_{\text{ionic}} = \sigma_0 \exp \left( \frac{-E_a}{k_b T} \right)
\]  

(1.21)
where \( \sigma_0 \) is the pre-exponential factor defined as 
\[
\sigma_0 = \frac{N (Ze)^2 a^2}{k_B} \Gamma_0 f ,
\]
where \( N \) is a number density of the carrier, \( Ze \) is a charge of the carrier, \( a \) is the hopping distance, \( \Gamma_0 \) is the attempt frequency, \( \Delta \) is the activation energy and \( f \) is a correlation factor of about 1 (Furusawa et al. 2008).

A generalized theory in the synthesis of an ion conducting glass lies on the three basic components: network formers, network modifiers, and ionic salts. Network formers are compounds of a covalent nature such as \( \text{SiO}_2 \), \( \text{P}_2\text{O}_5 \), \( \text{B}_2\text{O}_3 \) which forms strongly cross-linked macromolecular chains through an assembly of tetrahedral (\( \text{SiO}_4 \), \( \text{PO}_4 \), \( \text{BO}_4 \)) or triangles (\( \text{BO}_3 \)) by sharing corners or edges. Network modifiers are usually oxides or sulfides which interact strongly with the structure of network formers, through breaking of oxygen or sulfur bridges which links the two network former cations. Lastly, ionic salts are required for ionic conductivity by providing mobile ions in a glass matrix.

1.3.5 Lithium aluminosilicate (\( \text{Li}_x\text{Al}_y\text{Si}_z\text{O} \), LASO)

One Li-ion conducting oxide that deserves particular attention is lithium aluminosilicate (\( \text{Li}_x\text{Al}_y\text{Si}_z\text{O} \), LASO). This solid solution system consists of \( \text{SiO}_2 \) and \( \text{Al}_2\text{O}_3 \) as the network former, with \( \text{Li}_2\text{O} \) as the network modifier (Jochum et al. 2010). The composition and ionic conductivities of lithium aluminosilicate family are known to vary over a wide range of composition, where a selected list of compositions and their ionic conductivities is shown Table 1.9.
Table 1.9 Compositions and corresponding ionic conductivities of various lithium aluminosilicates

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>$\sigma_{25^\circ C}$ (S/cm)</th>
<th>$E_a$ (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-LiAlSiO$_4$</td>
<td>Bulk Crystal</td>
<td>$1.04 \times 10^{-9}$</td>
<td>0.740</td>
<td>(Alpen et al. 1977)</td>
</tr>
<tr>
<td>Li$<em>{4.4}$Si$</em>{0.6}$Al$_{0.4}$O$_4$</td>
<td>Glass-Ceramic</td>
<td>$2.80 \times 10^{-7}$</td>
<td>0.585</td>
<td>(Shannon et al. 1977)</td>
</tr>
<tr>
<td>Li$<em>{4.6}$Al$</em>{0.6}$Si$_{0.4}$O$_4$</td>
<td>Glass-Ceramic</td>
<td>$2.77 \times 10^{-9}$</td>
<td>0.685</td>
<td>(Shannon et al. 1977)</td>
</tr>
<tr>
<td>Li$_2$O-Al$_2$O$_3$-2SiO$_2$</td>
<td>Glass</td>
<td>$1.70 \times 10^{-8}$</td>
<td>0.680</td>
<td>(Biefeld et al. 1978)</td>
</tr>
<tr>
<td>Li$_2$O-Al$_2$O$_3$-2SiO$_2$</td>
<td>Ceramic</td>
<td>$4.20 \times 10^{-16}$</td>
<td>1.230</td>
<td>(Biefeld et al. 1978)</td>
</tr>
<tr>
<td>Li$_2$O-Al$_2$O$_3$-1.3SiO$_2$</td>
<td>Glass</td>
<td>$8.65 \times 10^{-10}$</td>
<td>0.680</td>
<td>(Biefeld et al. 1978)</td>
</tr>
<tr>
<td>Li$_2$O-Al$_2$O$_3$-2SiO$_2$</td>
<td>Glass</td>
<td>$8.01 \times 10^{-10}$</td>
<td>0.680</td>
<td>(Biefeld et al. 1978)</td>
</tr>
<tr>
<td>Li$_2$O-Al$_2$O$_3$-3.8SiO$_2$</td>
<td>Glass</td>
<td>$4.26 \times 10^{-9}$</td>
<td>0.630</td>
<td>(Biefeld et al. 1978)</td>
</tr>
<tr>
<td>Li$_2$O-Al$_2$O$_3$-3.8SiO$_2$</td>
<td>Ceramic</td>
<td>$7.70 \times 10^{-13}$</td>
<td>0.850</td>
<td>(Biefeld et al. 1978)</td>
</tr>
<tr>
<td>Li$_2$O-Al$_2$O$_3$-7SiO$_2$</td>
<td>Glass</td>
<td>$2.24 \times 10^{-9}$</td>
<td>0.630</td>
<td>(Biefeld et al. 1978)</td>
</tr>
<tr>
<td>Li$_2$O-Al$_2$O$_3$-7SiO$_2$</td>
<td>Ceramic</td>
<td>$4.27 \times 10^{-12}$</td>
<td>0.810</td>
<td>(Biefeld et al. 1978)</td>
</tr>
</tbody>
</table>

While a stoichiometric Li$_4$SiO$_4$ is a modest Li$^+$ ion conductor, it is also a very good host material for doping to engineer desired physiochemical properties. By substituting Si with Al (Eq (1.22)), along Li with Al (Eq (1.23)), Al ions are allowed to occupy Si sites while providing interstitial sites to Li, forming a solid solution of lithium aluminosilicate. The phase equilibrium diagram for lithium aluminosilicate is shown in Figure 1.10.

$$\text{Si}^{4+} \leftrightarrow \text{Al}^{3+} + \text{Li}^+ \quad (1.22)$$

$$3\text{Li}^+ \leftrightarrow \text{Al}^{3+} \quad (1.23)$$
While amorphous Li$_x$Al$_y$Si$_z$O is a moderate Li$^+$ conductive glass electrolyte, a crystalline LiAlSiO$_4$ (where $x=1$, also known as β-eucryptite) deserves particular attention owing to its enhanced ionic conductivity along its c-axis: the crystalline structure consists of the alternating layers of a corner shared AlO$_4$ and SiO$_4$ tetrahedrons, which results in the construction of one-dimensional “quartz channel” along its crystal c-axial direction. In such structure, Li-ions reside in the structural channels to maintain the charge balance (Nagel et al. 1982). The crystalline structure of β-quartz and β-eucryptite and their projection over the c-axial direction ((0001) plane) are shown in Figure 1.11:
LiAlSiO$_4$ first attracted a great deal of interest as a solid electrolyte for high-temperature batteries because of its high ionic conductivity up to 0.1-1 S/cm above 400 °C (Pechenik et al. 1988; Shin-ichi et al. 2004).

Figure 1.11 Crystal structure of β-quartz (above) and β-eucryptite (below) and the corresponding projections onto (0001) plane (Adopted from (Nagel et al. 1982))

Figure 1.12 The ionic conductivities of a bulk, crystalline β-LiAlSiO$_4$ as a function of temperature (left) and Li content (right) (Nagel et al. 1982)
The unique 1D channel of LiAlSiO₄ gives rise to a strong anisotropic ionic conduction along its c-axial direction for LiAlSiO₄ (Shin-ichi et al. 2004). For a bulk LiAlSiO₄, the ionic conductivity is known to be about three orders higher in magnitude in the direction parallel to c-axis than that of the parallel direction. Additionally, for the case of a thin film LiAlSiO₄, its ionic conductivity is reported to increase with decreasing thickness for films with thicknesses on the order of a few tens of nanometers (Shin-ichi et al. 2004). As discussed in previous section (Section 1.3.2), however, the synthesis of Li-ion conductor needs to be demonstrated even on most stringent geometries to be truly viable as a solid electrolyte for 3D LIBs. To meet such requirement, it is essential to implement a non-line-of-sight synthesis technique to synthesize the solid electrolyte of interest, LiₓAlᵧSiₑO₄.

1.4 Atomic Layer Deposition for Li-ion Battery Applications

Atomic Layer Deposition (ALD) is a deposition technique based on saturated surface reactions, allowing the deposition of pinhole-free, conformal, uniform, and homogeneous films (Suntola 1992). ALD is the only thin film deposition technique that allows a high level of thickness control, high uniformity on large, non-planar and/or complex-shaped structures. The advantages of ALD compared to other thin-film deposition technique are summarized in Table 1.10:
## Table 1.10 Comparison of various thin film deposition techniques

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Chemical Deposition</th>
<th>Electrodeposition</th>
<th>Physical Vapor Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursors react chemically at the surface</td>
<td>Precursors react electrochemically at the surface</td>
<td>Vapor precursors condense at the surface</td>
<td></td>
</tr>
<tr>
<td>Available Methods</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atomic Layer Deposition (ALD)</td>
<td>•</td>
<td>• Sputtering and reactive sputtering</td>
<td></td>
</tr>
<tr>
<td>Solution Deposition</td>
<td>•</td>
<td>• Thermal evaporation</td>
<td></td>
</tr>
<tr>
<td>Chemical Vapor Deposition (CVD)</td>
<td>•</td>
<td>• e-beam evaporation</td>
<td></td>
</tr>
<tr>
<td>ALD: Conformal and self-limiting for monolayer</td>
<td>•</td>
<td>• Pulsed Laser Deposition (PLD)</td>
<td></td>
</tr>
<tr>
<td>Thicker films by repeated ALD deposition, or CVD</td>
<td>•</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Key Features</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conformal (to some degree)</td>
<td>•</td>
<td>Generally not conformal</td>
<td></td>
</tr>
<tr>
<td>Limited by electron conduction to the surface</td>
<td>•</td>
<td>Thickness limited only by process time</td>
<td></td>
</tr>
<tr>
<td>Can be self-limiting</td>
<td>•</td>
<td>Good adhesion</td>
<td></td>
</tr>
</tbody>
</table>

ALD has been chosen to be the deposition technology of choice for next generation metal-insulator metal capacitors in DRAM and for the gate oxides in CMOS transistors, demonstrating the superior technological importance of ALD, especially in nanoscales (Marichy et al. 2012). ALD processes have been developed for various classes of materials including metals, metal oxides, metal nitrides, metal sulfides and metal phosphates (Leskelä et al. 2003; Puurunen 2005; Zaera 2008).

Interests on utilizing ALD also have expanded for LIB applications, to engineer and improve the current LIBs technology. ALD is not only explored for synthesis of active materials (cathode, anode, and electrolyte) but also to improve the stability of LIB system via surface engineering of electrode materials at the electrode-electrolyte interface. As such, ALD is well recognized as the essential technology that enables breakthrough advancements in the next-generation LIBs. (Jian et al. 2015)
The recent approaches of implementing ALD for LIB applications can be divided into two categories. One is to synthesize anode and cathode materials that can ultimately engineered into a 3D electrode by depositing ALD synthesized electrode materials onto 3D architecture framework such as metal nanowires, meshes, and carbon nanotubes. The second approach involves the deposition of a thin ALD films onto pre-existing 3D electrodes to improve physiochemical properties of electrode | electrolyte interface.

Significant progresses have been made in the first approach, where various cathode and anode materials have been successfully synthesized by ALD. Cathode materials synthesized by ALD include V$_2$O$_5$ (Chen et al. 2012; Chen et al. 2012; Ostreng et al. 2014), FePO$_4$ (Gandrud et al. 2013), LiCoO$_2$ (Donders et al. 2013), Li$_x$Mn$_2$O$_4$ (Miikkulainen et al. 2013), and LiFePO$_4$ (Liu et al. 2014). Anode materials synthesized by ALD include non-lithiated metal oxides such as TiO$_2$ (Cheah et al. 2009; Kim et al. 2009; Wang et al. 2011; Chunmei et al. 2013), SnO$_2$ (Li et al. 2012; Aravindan et al. 2013), Co$_3$O$_4$ (Donders et al. 2012), ZnO (Martinson et al. 2007; Kim et
al. 2008; Chang et al. 2010; Korhonen et al. 2011; Lin et al. 2011), SnO$_2$ (Heo et al. 2010; Meng et al. 2010; Won-Sik et al. 2010; Marichy et al. 2011; Meng et al. 2011; Meng et al. 2011), and lithiated cathode materials such as Li$_4$Ti$_5$O$_{12}$ (Meng et al. 2013) and Li$_x$Ti$_y$O$_z$ (Miikkulainen et al. 2013).

The second category is in its developing stage, but pioneering works have been rather promising. ALD depositions of the simple binary metal oxides such as Al$_2$O$_3$ or TiO$_2$ directly onto electrodes have reported exceptional enhancements in cyclability and capacity retention of the Li-ion cells. Such improvements are a result of an increased physiochemical stability of electrode materials against the conventional liquid electrolytes by providing an artificial interface between the electrode and liquid electrolyte in which would undergo a slow degradation otherwise. A 33.6% increase in cycling capacity has been reported for ~1 nm of ALD Al$_2$O$_3$ film coated on LiMn$_2$O$_4$ (Guan et al. 2011). Similar improvement has been reported even with two ALD (~2 Å) cycles of Al$_2$O$_3$, where the reversible capacity of nano-LiCoO$_2$ cathode (average particle size: ~400 nm) was increased by 250% (Scott et al. 2010). It has to be noted, however, while results from these direct depositions of binary oxides on electrodes are encouraging, there exists a critical thickness where the benefits provided from the protective ALD layer gets compromised from the impediment of ionic transport which lowers the overall cell performance (Scott et al. 2010; Guan et al. 2011). Given the high versatility and controllability of ALD, however, if a thin oxide electrolyte can be synthesized directly on these electrodes via ALD, the aforementioned enhancements can be utilized without sacrificing the overall performance of the cell. As such, synthesis of a thin film solid-state electrolyte by ALD offers promising opportunities.
Compared to the syntheses of electrode materials by ALD, studies on synthesizing solid electrolytes by ALD have been very recent. Over its short history of about 5 years (as shown in Figure 11.13), the reported studies of ALD synthesized thin film solid electrolyte materials include (Li,La)$_x$Ti$_y$O$_z$ (Aaltonen et al. 2010), Li$_3$PO$_4$ (Hämäläinen et al. 2012), Li$_2$SiO$_3$ (Hämäläinen et al. 2012; Tomczak et al. 2013), and Li$_x$Al$_y$O$_z$ (Aaltonen et al. 2011). Most of these studies focused mainly on the growth behavior of the ALD films and not on their physiochemical properties (e.g.: $\sigma$ and $E_a$). However, a few studies successfully delineated the possibility of ALD synthesized solid electrolytes. Aaltonen et al., have synthesized lithium alumina (Li$_x$Al$_y$O$_z$, LAO) with thicknesses up to 150 nm using lithium tert-butoxide ((CH$_3$)$_3$COLi) and trimethylaluminum (Al(CH$_3$)$_3$) as Li and Al precursors, with ionic conductivities of $9 \times 10^{-4}$ S/cm and $3 \times 10^{-1}$ S/cm at 400 °C and 500 °C respectively (Aaltonen et al. 2011). While the very value of activation energy (2.9 eV) is unusual and perhaps reflects processes other than the Li-ion conduction, their study demonstrated the viability of ALD synthesized thin film Li electrolytes. Liu and his colleagues have synthesized lithium tantalate (Li$_x$Ta$_y$O$_z$, LTO) solid electrolytes using lithium tert-butoxide ((CH$_3$)$_3$COLi) and Tantalum (V) ethoxide (Ta(OC$_2$H$_5$)$_5$) as Li and Ti precursors with tunable compositions of Li$_{0.6}$Ta$_1$O$_z$ to Li$_{12.3}$Ta$_1$O$_z$. A promising value of ionic conductivity of $2 \times 10^{-8}$ S/cm at room temperature with an activation energy of ~0.55 eV have been reported for ~200 nm Li$_{5.1}$Ta$_1$O$_z$ film (Liu et al. 2013). An exceptional conformality of LTO has been demonstrated for a 50 nm thin film Li$_{5.1}$Ta$_1$O$_z$ that was successfully deposited on anodic aluminum oxide (AAO) template with a nominal pore size of 200 nm and an aspect ratio of 300. It has to be noted, however, these studies have yet to demonstrate the feasibility of ALD synthesized solid electrolyte on improving the physiochemical stability of electrode without sacrificing ionic conductivity. However, promising
prospects have been delineated by the study of Liu et al., where a ~5 nm of lithium alumina (LAO, Li\textsubscript{x}Al\textsubscript{y}O) (~5 nm) film formed through lithiation reaction with the native oxide (Al\textsubscript{2}O\textsubscript{3}) on the surface of Al nanowire (NW) electrode resulted in exceptional mechanical robustness while providing efficient ionic conduction. It was also found that the LAO film survived the 100% volumetric expansion of Al NW electrode upon lithiation (Liu et al. 2011). These preliminary results, while limited, offers promising perspectives on ALD synthesized solid electrolytes in which no other deposition techniques can offer.

As previously discussed in Section 1.4, ALD furthermore offers advantage of controlling both composition and thickness in which other thin film deposition techniques such as PLD, sputtering, and CVD fail to offer. For a Li-ion conductor, this translates to a controllable Li-ion concentration to tailor ionic conductivity. The prospects of tunable ionic conductivity have been presented recently by Mane and Elam, where a thin Mo:Al\textsubscript{2}O\textsubscript{3} film was synthesized via ALD with a tunable electrical resistivity over a vast range of 10\textsuperscript{4}-10\textsuperscript{12} Ω-cm (Mane et al. 2013). If a thin film Li\textsubscript{x}Al\textsubscript{y}Si\textsubscript{z}O can be synthesized in a similar manner where the film composition and thickness can be controlled while allowing the direct deposition to 3D electrodes to provide enhanced electrode stability, it allows significant advancements in fabrication of a full solid state, next-generation Li-ion microbattery.

1.4.1 Fundamentals of Atomic Layer Deposition

ALD consists of individual, sequential saturated surface reactions. As result, its growth rate is proportional to the number of reaction cycles instead of the reactant flux or time of the growth (Suntola 1992). Figure 1.14 provides a schematic representation of an ideal ALD process based on saturating surface reactions.
For the case of metal oxides, ALD reaction generally consists of a metal-ligand compound (MLₙ) undergoing a ligand exchange with one or more (y) surface hydroxyl (OH) groups. Once reacted, a gaseous product HL is released and a MLₙ₋y surface specie is formed (Puurunen 2005):

\[
\text{Surface-(OH)}_y + \text{ML}_n (\text{g}) \rightarrow \text{Surface-O-ML} _n _{-y} + y\text{HL} (\text{g})
\]  
(1.24)

The surface adsorbed specie then undergoes a surface reaction upon oxidant exposure, regenerating -OH groups by releasing HL. Water (H₂O) is the most common oxygen source, however, other oxidants such as molecular oxygen, ozone, oxygen radicals, and oxygen peroxide also can be used as oxidant source (Puurunen 2005). Under hydrolytic conditions, the formation of M-O-M bonds (oxo-metal bonds) is completed upon introduction of water:

\[
\text{Surface-O-ML} + \text{H}_2\text{O} (\text{g}) \rightarrow \text{Surface-O-MOH} + \text{HL} (\text{g})
\]  
(1.25)

For ALD of metal oxide thin films, the precursor is generally a metal halide or metal alkoxide with water. It is important to mention that the two half reactions are written in convention which illustrates the new bonds that form and information on the surface being terminated during each half-cycle.
1.4.2 Atomic Layer Deposition of Al₂O₃

ALD deposition of Al₂O₃ is the most studied ALD chemistry owing its applications in semiconductors such as a capacitor dielectric material in dynamic random-access memory (DRAM). As result, the ALD of Al₂O₃ via trimethylaluminum (TMA) and H₂O is now a de facto standard and have demonstrated its growth a wide range of temperatures, from room temperature to 500 ºC. Table 1.11 summarizes the reported studies on ALD of Al₂O₃ with TMA/H₂O chemistry.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Oxidant</th>
<th>Deposition Temperature</th>
<th>Growth Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA</td>
<td>H₂O</td>
<td>100-500 ºC</td>
<td>1.1 Å/Cycle</td>
<td>(Higashi et al. 1989)</td>
</tr>
<tr>
<td>TMA</td>
<td>H₂O</td>
<td>150-450 ºC</td>
<td>1.1 Å/Cycle</td>
<td>(Ott et al. 1996)</td>
</tr>
<tr>
<td>TMA</td>
<td>H₂O</td>
<td>200-400 ºC</td>
<td>1.0 Å/Cycle</td>
<td>(Yun et al. 1997)</td>
</tr>
<tr>
<td>TMA</td>
<td>H₂O</td>
<td>33-137 ºC</td>
<td>1.25 Å/Cycle</td>
<td>(Groner et al. 2004)</td>
</tr>
</tbody>
</table>

The ALD half reactions for TMA/H₂O process can be expressed as:

\[
\text{AlOH}^* + \text{Al(CH}_3\text{)}_3 \rightarrow \text{AlOAl(CH}_3\text{)}_2^* + \text{CH}_4
\]

\[(1.26)\]

\[
\text{AlCH}_3^* + \text{H}_2\text{O} \rightarrow \text{AlOH} + \text{CH}_4
\]

\[(1.27)\]

where the asterisks denote the surface species.

It has to be noted, however, while ALD of Al₂O₃ is considered as the most ideal ALD chemistry, with self-limited surface reactions of 1) formation of Al-CH₃* surface specie during TMA exposure and 2) regeneration of the surface hydroxyl (-OH) group upon H₂O exposure, there still exist non-idealities that are often overlooked. One involves the misconception in the highest obtainable growth per cycle (GPC), which is a function of the number of available reactive surface sites and the steric hindrance of the ligands (Puurunen 2005). While it is generally perceived that one ALD cycle of precursor/oxidant exposure results in one monolayer (ML) of material on the surface, such one ML growth does not happen even for the most ideal
ALD chemistry of Al₂O₃ by TMA/H₂O where island-like growth can be observed (Puurunen et al. 2004). Such island growths of ALD films is not limited to Al₂O₃, but also have been observed for various ALD processes including HfO₂ (Devloo-Casier et al. 2011; Hwang et al. 2011), ZrO₂ (Puurunen et al. 2004), ZnS (Ihanus et al. 1997), Ru (Yim et al. 2006), W (Wind et al. 2009), Cu (Törndahl et al. 2004), et cetera. 

These non-ideal ALD growths should not be overlooked when designing novel ALD chemistries. For atomic layer deposition of lithium aluminosilicate (LiₓAlᵧSi₂O, LASO) in highly controllable manner, it is important to understand these non-idealities. The greatest challenges and non-idealities lie in ALD two of its constituent oxides: SiOₓ and LiOH.

1.4.3 Atomic Layer Deposition of SiOₓ

In contrast to ALD of Al₂O₃, ALD of SiO₂ is well known to be challenging due to lack of an appropriate Si precursor for low temperature processing, especially when H₂O used. Even for the case of tetraethylorthosilicate (TEOS), the most widely used precursor in CVD/PECVD of SiO₂, ALD deposition of SiO₂ does not take place with this precursor and H₂O (Ferguson et al. 2004). Other Si precursors studied for ALD of SiO₂ include tetramethyilsilane (Si(CH₃)₄), tetrabutoxysilane Si(OC₄H₉)₄ and tri-t-butoxysilanol (Si(OC(CH₃)₃)₃). When H₂O is used, however, none of these precursors results in deposition of SiO₂ films at the deposition temperatures up to 500°C (Hämäläinen et al. 2011).
Table 1.12 List of Si precursors implemented with H\textsubscript{2}O to attempt ALD deposition of SiO\textsubscript{2}  

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Oxidant</th>
<th>Deposition Temperature</th>
<th>Growth Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(Obu)\textsubscript{4}</td>
<td>H\textsubscript{2}O</td>
<td>300, 500 °C</td>
<td>No deposition</td>
<td>(Hämäläinen et al. 2011)</td>
</tr>
<tr>
<td>Si(Obu)\textsubscript{4}-SiMe\textsubscript{4}</td>
<td>H\textsubscript{2}O</td>
<td>200, 500 °C</td>
<td>No deposition</td>
<td>(Hämäläinen et al. 2011)</td>
</tr>
<tr>
<td>Si(OEt)\textsubscript{4}</td>
<td>H\textsubscript{2}O</td>
<td>300, 500 °C</td>
<td>No deposition</td>
<td>(Kukli et al. 2004; Hämäläinen et al. 2011)</td>
</tr>
<tr>
<td>(tBuO)\textsubscript{3}SiOH</td>
<td>H\textsubscript{2}O</td>
<td>300, 500 °C</td>
<td>No deposition</td>
<td>(Hämäläinen et al. 2011)</td>
</tr>
</tbody>
</table>

While ALD of SiO\textsubscript{2} with TEOS/H\textsubscript{2}O was known to be feasible in the presence of NH\textsubscript{3} as a catalyst (Klaus et al. 2000), such catalyzed reaction has only been studied at room temperature, limiting its applicability with other ALD processes which require higher deposition temperature. To expand its applicability, ALD deposition of SiO\textsubscript{x} thus has been studied as a constituent in ALD synthesis of a complex oxide, where a suitable silicon precursor is implemented with other ALD process under the same process conditions. Using H\textsubscript{2}O and TEOS as the Si precursor, successful depositions of zirconium silicates (Ritala et al. 2000) (Zr\textsubscript{x}Si\textsubscript{y}O) and halfnium silicates (Kukli et al. 2004) (Hf\textsubscript{x}Si\textsubscript{y}O) have been reported with ZrCl\textsubscript{4} and HfCl\textsubscript{4} as Zr and Hf precursors respectively. For the case of aluminosilicates (Al\textsubscript{x}Si\textsubscript{y}O), alternating pulses of tris-t-butoxysilanol (TTBS) and trimethylaluminum (TMA) have reported to deposit aluminosilicate thin film with a growth rate of up to 12 nm/cycle (Hausmann et al. 2002). Similarly, while ALD process of SiO\textsubscript{2} using hexakis(ethylamino)disilane (Si\textsubscript{2}(NHe\textsubscript{t})\textsubscript{6}) and H\textsubscript{2}O is not attainable, incorporation of the same Si\textsubscript{2}(NHe\textsubscript{t})\textsubscript{6}/H\textsubscript{2}O cycle into ALD process of Al\textsubscript{2}O\textsubscript{3} by TMA/H\textsubscript{2}O results in the deposition of Al\textsubscript{x}Si\textsubscript{y}O film (Tomczak et al. 2012). Table 1.13 summarizes a list of SiO\textsubscript{x} containing complex oxides deposited by ALD with H\textsubscript{2}O.
Table 1.13 List of SiOₓ containing complex oxides and Si precursors deposited via ALD with H₂O as an oxidant

<table>
<thead>
<tr>
<th>Material</th>
<th>Precursors</th>
<th>Oxidant</th>
<th>Deposition Temperature</th>
<th>Growth Rate (Å/Cycle)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrₓSiₓO</td>
<td>ZrCl₄ &amp; Si(OEt)₄</td>
<td>N/A</td>
<td>500 ºC</td>
<td>0.5</td>
<td>(Ritala et al. 2000)</td>
</tr>
<tr>
<td></td>
<td>ZrCl₄ &amp; Si(OBu)₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HfₓSiₓO</td>
<td>HfI₄ &amp; Si (OEt)₄</td>
<td>H₂O</td>
<td>500 ºC</td>
<td>0.56-0.84</td>
<td>(Kukli et al. 2004)</td>
</tr>
<tr>
<td></td>
<td>HfCl₄ &amp; Si(OEt)₄</td>
<td>(not required)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlₓSiₓOₓ</td>
<td>Si(OBu)₄ + AlCl₃ or AlMe₃</td>
<td>H₂O</td>
<td>150-500 ºC</td>
<td>0.50-4.56</td>
<td>(Hämäläinen et al. 2011)</td>
</tr>
<tr>
<td></td>
<td>Si(OEt)₄ + AlCl₃ or AlMe₃</td>
<td>(not required)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(tBuO)₃SiOH + AlCl₃ or AlMe₃</td>
<td>H₂O</td>
<td>200-500</td>
<td>0.57-1.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(not required)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the case of TEOS, the reported studies of SiOₓ containing complex oxides reports only on the growth and the resulting material properties without a detailed study on its surface chemistry. To enable ALD deposition of LiₓAlᵧSiₓO with an accurate composition and thickness control, a detailed mechanistic study on the surface mechanism of SiOₓ deposition via TEOS/H₂O and of its integration to LiₓAlᵧSiₓO is essential.

1.4.4 Atomic Layer Deposition of Li₂O/LiOH

With its first published study in 2009, ALD of LiOH is a recently developing field compared to the conventional ALD materials such as Al₂O₃ and HfO₂. Owing to strong scientific and technological interests of Li-containing complex oxides for LIBs applications, the studies of ALD deposition of LiOH and Li-containing thin films have expanded rapidly since then. While studies report on ALD of LiOH, the results from these studies have been rather inconsistent and controversial. The reported growth rates for ALD of LiOH vary significantly from 0.87 Å/Cycle to 2.2 Å/Cycle, even under similar experimental conditions. The reported growth rates from ALD growth of LiOH via lithium tert-butoxide (LTB) and H₂O is summarized in Table 1.14:
Table 1.14 The growth rate of ALD LiOH by lithium tert-butoxide (LTB)/H$_2$O chemistry in literature

<table>
<thead>
<tr>
<th>Deposition Chemistry</th>
<th>Dep. Temp</th>
<th>Growth Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTB-H$_2$O</td>
<td>225 ºC</td>
<td>0.87 Å/Cycle</td>
<td>(Cavanagh et al. 2010)</td>
</tr>
<tr>
<td>LTB-H$_2$O</td>
<td>250 ºC</td>
<td>~0.87 Å/Cycle</td>
<td>(Meng et al. 2013)</td>
</tr>
<tr>
<td>LTB-H$_2$O</td>
<td>225 ºC</td>
<td>1.7 Å/Cycle</td>
<td>(Aaltonen et al. 2011)</td>
</tr>
<tr>
<td>LTB-H$_2$O</td>
<td>225 ºC</td>
<td>~1.7 Å/Cycle</td>
<td>(Liu et al. 2013)</td>
</tr>
<tr>
<td>LTB-H$_2$O</td>
<td>225 ºC</td>
<td>2.2 Å/Cycle</td>
<td>(Comstock et al. 2012)</td>
</tr>
</tbody>
</table>

Such discrepancy of growth rate leads to an important question of what the differences are in the underlying growth mechanism for ALD of LiOH that results in such vastly different growth rates. Analogous to the studies for ALD deposition of SiO$_x$, the studies of ALD LiOH have been heavily empirical and fell short on providing information of surface mechanisms underlying the deposition process. Consequently, the published studies not only report such different growth rate values, but also various non-idealities observed during the growth of Li-containing complex oxides. The study of Miikkulainen et al. reported the composition and thickness of ALD lithium titanate (Li$_x$Ti$_y$O) do not correlate closely to the ratio of ALD sub-cycles of LiOH and TiO$_2$ with LTB as Li precursor and titanium tetrachloride (TiCl$_4$) or titanium tetra-isopropoxide (Ti(O$^t$Pr)$_4$) as Ti precursor (Miikkulainen et al. 2013). ALD of Li$_x$Al$_y$O (LAO) using LTB and TMA as Li and Al precursors has resulted in similar non-ideal growth where the composition and growth rate diverged significantly from the projected growth behaviors (Aaltonen et al. 2011; Miikkulainen et al. 2015). In some cases, even a non-uniform deposition of LAO was observed in which authors did not investigate in detail. It has been reported that the growth of LAO was significantly affected by unforeseen experimental parameters such as 1) the number of preceding ALD cycles of the other component and 2) presence of purging cycles following each precursor/oxidant exposures (Aaltonen et al. 2011). The study of Comstock & Elam also reported a non-linear growth of Li$_x$Al$_y$O for LiOH:Al$_2$O$_3$ cycle ratios greater than 1 (Comstock et
al. 2012). While some of the studies did offer some insights on the growth mechanisms of LiOH and Li-containing complex oxides via in-situ quartz crystal microbalance (QCM) measurements, an accurate determination of surface species has been limited, as QCM studies offer only the changes in frequencies during the deposition process. Consequently, there still exists the need for a detailed, comprehensive mechanistic study to understand the underlying surface chemistries on Li-containing thin film oxides synthesized by ALD to allow an accurate thickness and composition control.

1.5 Scope and Organization

The scope of this study is to lay the groundwork for ALD of lithium aluminosilicate (Li$_x$Al$_y$Si$_z$O, LASO), starting from an in-depth mechanistic studies on ALD syntheses of its constituents. ALD depositions and the underlying surface mechanisms of LiOH, Al$_2$O$_3$ and SiO$_x$ was investigated first via in-situ Fourier transform infrared spectroscopy (FTIR). Following the detailed understanding on the underlying surface chemistries of its constituent oxides, synthesis and material characterizations on ALD deposited Li$_x$Al$_y$Si$_z$O was investigated, varying compositions and thicknesses. Lastly, integrations of ALD synthesized Li$_x$Al$_y$Si$_z$O to prospective electrode materials was explored to investigate the physiochemical property of electrode | LASO nanocomposite to delineate the applicability of ALD Li$_x$Al$_y$Si$_z$O for solid electrolyte applications.
CHAPTER 2: EXPERIMENTAL SETUP

This chapter presents the schematics of custom made ALD chambers that were used to synthesize and study ALD deposition of lithium aluminosilicate (Li$_x$Al$_y$Si$_z$O, LASO) thin films. The first section includes detailed discussions on the reactor schematics and the experimental parameters and precursors implemented in *in-situ* Fourier transform infrared spectroscopy (FTIR) study. The second section presents the fundamentals of various analytical techniques used to investigate ALD synthesized Li$_x$Al$_y$Si$_z$O thin films. The techniques presented include metrology techniques such as spectroscopic ellipsometry (SE), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), and x-ray reflectivity (XRR), elemental analysis techniques such as x-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray spectroscopy (EDS). The electrochemical properties of ALD synthesized film were obtained through electrochemistry techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

2.1 Thin-Film Deposition Reactors

2.1.1 Atomic Layer Deposition Chamber

ALD Li$_x$Al$_y$Si$_z$O thin films were deposited in a low vacuum ALD reactor under the operating pressure ranges of 30-60 mTorr. The schematic of reactor is shown in Figure 2.1:
Figure 2.1 (a) Schematic and (b) gaslines of ALD Reactor used to deposit Li$_x$Al$_y$Si$_z$O thin films

The reactor consists of 2.75” outer-diameter (OD) six-way cross (MDC, 407002) connected to a loading door (MDC, 665205). All precursors lines were connected through a five-way multiport (MDC, 409004) connected to one of the ports of the six-way cross. One of the ports of the six-way cross was connected to a pumping line and the remaining ports capped by blank flanges (MDC, 110008). A high power heating wire (Ari Industries, BXX09B88-4T) and a type-K thermocouple (Omega Engineering, Inc., CO-K) were installed for a controlled heating of the reactor walls to prevent precursor condensations. Lithium tert-butoxide (LTB, Strem Chemicals, 98%), trimethyl aluminum (TMA, Sigma-Aldrich, 97%), and tetraethyl orthosilicate (TEOS, Sigma-Aldrich, 99.999%) were implemented as lithium, aluminum, and silicon precursors respectively. The vapor from with deionized water was used as the alternating reactant to the organometallic precursors. Implementation of additional Si precursor, Tris(tert-butoxy)silanol (TTBS, Sigma-Aldrich, 99.999%) was also investigated. Detailed information and physiochemical properties of precursors used in this study are summarized in Table 2.1.
Table 2.1 Precursor information for the ALD synthesis of Li₃Al₃Si₂O

<table>
<thead>
<tr>
<th></th>
<th>Lithium tert-butoxide (LTB)</th>
<th>Trimethyl Aluminum (TMA)</th>
<th>Tetraethyl orthosilicate (TEOS)</th>
<th>Tris(tert-butoxy)silanol (TTBS)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Company</strong></td>
<td>Strem Chemicals</td>
<td>Sigma-Aldrich</td>
<td>Sigma-Aldrich</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td><strong>Purity</strong></td>
<td>98%</td>
<td>97%</td>
<td>99.999%</td>
<td>99.999%</td>
</tr>
<tr>
<td><strong>CAS Number</strong></td>
<td>1907-33-1</td>
<td>75-24-1</td>
<td>78-10-4</td>
<td>18166-43-3</td>
</tr>
<tr>
<td><strong>Phase</strong></td>
<td>Solid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Solid</td>
</tr>
<tr>
<td><strong>Formula</strong></td>
<td>LiOC₄H₉</td>
<td>Al(CH₃)₃</td>
<td>Si(OC₂H₅)₄</td>
<td>((CH₃)₃CO)₃SiOH</td>
</tr>
<tr>
<td><strong>Structure</strong></td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td><strong>Melting Pt</strong></td>
<td>-</td>
<td>15 °C</td>
<td>-</td>
<td>63-65 °C</td>
</tr>
<tr>
<td><strong>Boiling Pt</strong></td>
<td>-</td>
<td>125-126 °C</td>
<td>168 °C</td>
<td>205-210 °C</td>
</tr>
</tbody>
</table>

LTB, being a solid precursor in room temperature, was heated to 160°C to ensure a sufficient precursor delivery to the chamber. Analogously, TTBS reservoir was heated to 45 °C with its gas line heated to 75 °C. For liquid precursors, TMA and TEOS, only their gas lines to the reactor were heated to 60°C owing to their high vapor pressure even at room temperature (~1.5 Torr for TMA). The flow rate of TMA was controlled by a mass flow controller (MFC) (Laminar Technologies, UFC-1100A) to 0.15 sccm. The deionized water was enclosed in a 100 mL glass cylinder (MDC, #463000) at room temperature.
The establishment of the deposition parameters was based on the experimental values reported in literature along with precursor flux calculations to ensure that sufficient precursor fluxes were introduced to the chamber to yield self-saturating surface reactions. For a 4 cm² Si (001) substrate (the maximum size of the substrate used in this study) with a fully –OH terminated surface (surface density: 6.8 atoms/nm² (Kim et al. 2011)), the surface density of –OH group is:

\[
\left( \frac{6.8 \text{ atoms}}{\text{nm}^2} \right) \cdot 4 \text{cm}^2 \left( \frac{10^7 \text{nm}}{\text{cm}} \right)^2 = 2.72 \times 10^{15} \text{–OH molecules}
\] (2.1)

The precursor fluxes were calculated based on the ideal gas law, for a chamber with a volume of ~750 mL with its wall temperatures at 100 °C. As evident from Eq. (2.2), a 10 mTorr of precursor pulse was found to introduce precursor molecules three orders magnitude higher than the available reactive –OH surface sites.

\[
n = \frac{PV}{RT} = \left( \frac{100 \text{mTorr}}{1 \text{Torr}} \right) \left( \frac{133 \text{ Pa}}{1 \text{Torr}} \right) \left( \frac{750 \text{mL}}{8.314 \text{ J/mol.K}} (373 \text{K}) \right) \text{–OH} \approx 1.90 \times 10^{18} \text{molecules}
\] (2.2)

where \( N_A \) is Avogadro’s constant \((6.022 \times 10^{23})\). Given a thermodynamically favorable surface chemistry, therefore, a 10 mTorr of precursor flux should ensure sufficient precursors for the saturation of surface.
The impingement rate of gas molecules hitting the substrate surface was calculated to establish the duration of precursor pulses (Jaeger 2002):

\[
\Phi = \frac{2.63 \times 10^{30} \ P}{\sqrt{MT}}
\]  

(2.3)

where \( P \) is the pressure in Pa and \( M \) is the molecular weight.

Table 2.2 summarizes the calculated values of the impingement rate for each reactant used in this study.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Molecular Weight (g/mol)</th>
<th>Impingement Rate (molecules/cm(^2) sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA</td>
<td>114.18</td>
<td>(8.23 \times 10^{15})</td>
</tr>
<tr>
<td>LTB</td>
<td>80.05</td>
<td>(1.17 \times 10^{16})</td>
</tr>
<tr>
<td>TEOS</td>
<td>208.33</td>
<td>(4.50 \times 10^{15})</td>
</tr>
<tr>
<td>TTBS</td>
<td>264.43</td>
<td>(3.55 \times 10^{15})</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>18.02</td>
<td>(5.20 \times 10^{16})</td>
</tr>
</tbody>
</table>

As evident from the table above, a few seconds of exposure at 10 mTorr should result in saturated surface reactions for all precursors and oxidant.

The nomenclatures and cycle sequences implemented for ALD depositions are summarized in Table 2.3.
The Al₂O₃ deposition consisted of a 5 second pulse of TMA with a 5 second water pulse separated by a pump-down time of 45 s. Following each pump-down, a purge cycle consisting of a 10 s N₂ purge and 40 s of purge pump-down were introduced. The TMA pulse time was set at 5 sec owing to its highly favorable reaction mechanism from the strong Al-O bond formation. The duration of water pulse was set to 5 second to keep the pulsing duration to be the same to that of the precursor pulse for each oxide.

The deposition cycle of LiOH was composed of a 10 second LTB pulse and a 10 second H₂O pulse, separated by 50 seconds of pump-down to the base pressure. An extended N₂ purge cycle was introduced after each precursor/oxidant pump-down, of a 20 second N₂ purge and 40 second purge pump-down to eliminate possible gas-phase reactions. The extended purge time was introduced to minimize undesirable reaction between H₂O and LiOH owing to the hygroscopic nature of LiOH, which is known to affect the growth rate of LiOH itself and subsequent growth (Aaltonen et al. 2011; Comstock et al. 2012).

The deposition cycle of SiOₓ was also composed of a 10 second TEOS (or TTBS) pulse and a 10 second H₂O pulse, separated by 50 seconds of pump-down to the base pressure. An
extended N₂ purge cycle was introduced after each precursor/oxidant pump-down, of a 20 second N₂ purge and 40 second purge pump-down to eliminate possible gas-phase reactions.

Multicomponent oxides were synthesized via a solid solution of the constituent oxides, specifically Al₂O₃, LiOH, and SiO₂ with the global cycle sequence of [a(Al-O)-b(Li-O)-c(Si-O)-b(Li-O)]xn. The coefficients a,b,c represent the local ALD cycles of each constituent oxide, and n represents the number of global cycles. The ALD cycle sequences for multicomponent oxides LiₓAlₙSi₂O, LiₓAlₙO, LiₓSiₙO, and AlₓSiₙO are summarized in Table 2.4 below.

<table>
<thead>
<tr>
<th>Material</th>
<th>ALD Cycle Sequence</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiₓAlₙSi₂O</td>
<td>[b(Al-O)-a(Li-O)-c(Si-O)-a(Li-O)]xn</td>
<td>a, b, c &gt; 0</td>
</tr>
<tr>
<td>LiₓAlₙO</td>
<td>[b(Al-O)-a(Li-O)]xn</td>
<td>a, b &gt; 0, c = 0</td>
</tr>
<tr>
<td>LiₓSiₙO</td>
<td>[a(Li-O)-c(Si-O)]xn</td>
<td>a, c &gt; 0, b = 0</td>
</tr>
<tr>
<td>AlₓSiₙO</td>
<td>[b(Al-O)-c(Si-O)]xn</td>
<td>b, c &gt; 0, a = 0</td>
</tr>
</tbody>
</table>

n represents the number of global cycles

For synthesis of LiₓAlₙSi₂O, the Al₂O₃ layer was deposited first because of its aforementioned highly reactive surface mechanism, which facilitates the growth of the subsequent oxides (Riikka 2005). The total number of local ALD cycles for each constituent oxide was held constant at 20, making one global cycle always consist of 20 local constituent oxide cycles. For example, [10(Al-O)-3(Li-O)-4(Si-O)-3(Li-O)]x20 means twenty global cycles were used to deposit an ALD LASO sample with local cycle ratios of (Al-O):(Li-O):(Si-O):(Li-O) set at 10:3:4:3. Syntheses of tertiary oxides LiₓAlₙO, LiₓSiₙO, and AlₓSiₙO were approached in a similar manner, but with the number of ALD cycles of non-participating constituent oxides equal to zero (c = 0).
The films were also prepared on Germanium (Ge) substrates to allow more precise composition analysis on the deposited films, as the deconvolution of Si peak of the film and that from the substrate was found challenging when a Si substrate was used.

2.1.2 In-situ Fourier Transform Infrared Spectroscopy Chamber

The in-situ Fourier transform infrared spectroscopy (FTIR) allows a detailed monitoring of surface species during each half cycles of ALD where the details on the spectroscopic techniques are to be discussed in Section 2.2.3. The schematic and experimental setup of in-situ FTIR chamber is depicted in Figure 2.2.

![Figure 2.2 Schematic of in-situ Fourier Transform Infrared Spectroscopy (FTIR) chamber: (a) front and (b) side view.](image)

The in-situ FTIR chamber consists of a custom-made 2.75” OD six-way cube (MDC, 408001) welded to two 2.75” OD gate valves (MDC, GV-1500V). The gate valves are necessary to isolate the IR transparent KBr windows from the chamber to prevent contamination on the windows during the deposition. Two 2.75” OD IR window flanges (McAllister Technical Services, DPW 275) that are differentially pumped to 30 mTorr were used to install IR
transparent KBr windows to the chamber. The KBr windows (International Crystal Laboratories, 0002C-150) were 38 mm in diameter and 6 mm thick. All metalorganic precursors, oxidant, and nitrogen purge gases are installed through a 2.75” OD 5-multiport flange (MDC, 409004). The base pressure of ~30 mTorr was maintained by a mechanical pump (Alcatel, 2021I) with a nominal pumping speed of 14.6 ft³/min.

The use of high surface area nanoparticles (NPs) is essential for a transmission FTIR spectroscopy to obtain sufficient signals (Ferguson et al. 2000; Yoon et al. 2009; Lee et al. 2012). Therefore, ALD processes monitored by through in-situ FTIR spectroscopy were deposited on a substrate made by nanoparticles as shown in Figure 2.3.

![Figure 2.3 Procedure for making high surface area nanoparticle (NP) substrate for in-situ FTIR spectroscopy: (1) mounting of nanoparticles to a corrosion resistant grid, (2) compression of nanoparticles onto the grid, and (3) mounting of NP substrate to the sample holder.](image)

The nanoparticle substrate consists of nanoparticles (NPs) that were compressed onto a corrosion resistance type grade stainless steel grid (McMaster-Carr, 9317T67) with 100 lines per inch. The NPs were pressed into the grid using stainless steel dies with a hydraulic press under a force of 10,000 lb/ft³ for 10 seconds. The excess nanoparticles on the surface of the grid were removed using a razor blade. Both SiO₂ (Nanostructured & Amorphous Materials, Inc., 99.5% purity) and ZrO₂ (Nanostructured & Amorphous Materials, Inc., 99+ % purity) NPs used in this study had an average particle size of 20 nm, yielding a specific surface area of greater than ~25 m²/g. When compared to a planar substrate, the use of NPs allows a surface area enhancement of 10¹³ over
the same footprint. As result, the use of NPs allow the detection of sufficient IR signals under transmission mode. The high surface area NP substrate was then mounted to the sample holder consisting of a 316 grade stainless steel disc with 18 mm OD and 12 mm ID (McMaster Carr, 90214A527) spot-welded to a Nickel-Chromium wire (Omega Engineering, NI80-040-50) for a resistive heating. A Type-K thermocouple was also spot-welded to the sample holder for an accurate monitoring and PID controlling to the desired deposition temperature.

A Nexus 670 FTIR spectrometer from Thermo Nicolet with germanium (Ge) on cesium iodide (CsI) beam splitter and a deuterated triglycine sulphate (DTGS) pyroelectric IR detector setup was used to collect in-situ FTIR spectra. The detailed schematic of Nexus 670 FTIR spectrometer along with the location of the in-situ FTIR ALD chamber is shown in Figure 2.4:

![Figure 2.4 Schematic of Nexus 670 FTIR spectrometer (Thermo Nicolet) and the IR beam path (dashed line). The location of in-situ FTIR ALD system is also shown (solid rectangle).](image)

The use of CsI beam splitter and DTGS detector allows the detection of IR wavenumbers from 4000 cm$^{-1}$ to 400 cm$^{-1}$. In this region, a detailed surface mechanisms of ALD processes can be
studied by analyzing the IR responses of the surface hydroxyl (4000-3800 cm\(^{-1}\)) and C-H stretching (3000-2800 cm\(^{-1}\)) regions. All of the spectra in this study were obtained at the deposition temperature of 225 °C. The spectrometer setup was purged with dry, CO\(_2\) from a purge gas generator. Spectra were collected with a mirror speed of 3.6 cm/s and averaged over at least 64 scans with a resolution of 4 cm\(^{-1}\). All spectra were normalized using the background scan on initial starting substrate.

2.2 Material Characterization Techniques

2.2.1 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) was utilized to investigate the surface morphology of the thin films deposited by ALD. In AFM, a Si or Si\(_3\)N\(_4\) cantilever tip with a reflective backside coating is brought in vicinity to the sample of interest. In this regime, the AFM tip experiences molecular interactions with the sample surface. This attractive or repulsive molecular interaction results in a deflection of a diode laser when it reaches the photodetector when is reflected off from the back of cantilever. The deflection then is utilized to maintain the tip at a constant force or height above the sample surface based on a PID feedback mechanism. The AFM has three primary modes of operation: contact, non-contact, and tapping mode. Each mode is differentiated based on the interactions between the tip and the sample surface. The contact mode is generally used to image hard surfaces as the tip is dragged along the surface under a close contact to generate the topological features. In the non-contact mode, the tip is kept at ~50-150 Å above the surface and obtains topological information through an attractive interaction between the tip and the sample. Lastly, the tapping mode operates with an objective of minimizing the stress induced by the tip to the sample. This is achieved by tapping the surface with a low force but under high speed, typically at a frequency of 50,000 to 500,000 cycles per second, to generate the
topological image. The topographic information on the sample in tapping mode is obtained by measuring changes of the oscillation amplitude of the tip, resulting in a precise topographic image.

In this work, the surface morphology of the deposited films was examined with a Bruker Dimension Icon AFM machine operating under tapping mode. The Bruker Dimension Icon microscope system allows the AFM investigation over a large sample, up to 210 mm in diameter and 15 mm thick. The X-Y-Z scan range is up to 90 μm × 90 μm × 10 μm. Micron scans (1 μm × 1 μm) were taken at a scan rate of 0.5 Hz with a resolution of ±1 Å. The surface root mean square (RMS) roughness of a sample can be calculated by using the equation:

\[
RMS = \sqrt{\frac{\sum (Z_i - Z_{ave})^2}{N}}
\]  

(2.4)

where \(Z_i\) is the height of sample, \(Z_{ave}\) is the height average of \(N\) samples. The RMS value reported in this work was obtained from analyzing the RMS value of the 1 μm × 1 μm scan within Nanoscope Analysis (Bruker Corporation) AFM analysis software.

Figure 2.5 Atomic force microscope (AFM) image of 28 nm ALD Li\(_x\)Al\(_y\)Si\(_z\)O film deposited with a cycle sequence of \([10(Al-O)-3(Li-O)-4(Si-O)-3(Li-O)]\times20\) on 100 nm Pt/10 nm Ti/Si (100) substrate. The surface root mean square (RMS) is 1.4 nm.
Energy-Dispersive X-ray Spectroscopy (EDS)

Energy-dispersive X-ray spectroscopy (EDS) is an elemental quantification technique that accompanies electron microscopes such as scanning electron microscope (SEM) or transmission electron microscope (TEM). In these electron microscopes, a high voltage electron beam impinges upon the sample, causes the emission of a core electron, leaving the atom in an excited state, which subsequently undergoes de-excitation to generate an x-ray where the energy (thus wavelength) is elemental specific.

![Figure 2.6 Signals generated when a high-energy beam of electrons collide with a thin specimen. (Adapted from (Williams et al. 2009))](image)

This elemental-specific X-ray then can be analyzed through an x-ray energy-dispersive spectrometer (XEDS) which uses either a Si or Ge detector placed in the vicinity of the sample, providing identifications of the elements present in the sample of interest (Williams et al. 2009). The number of excited atoms which generates x-rays is dependent on the atomic number of the atom. Consequently, EDS measurements are better at detecting heavy atoms than light atoms, usually for the elements with Z greater than 10 (Kumar 2014). In this study, EDS was utilized in conjunction with scanning electron microscope (SEM) and transmission electron microscope (TEM). For SEM-EDS, Renishaw’s structural and chemical analyzer (SCA) was used. For TEM-EDS, Oxford’s INCA x-sight was used. Table 2.5 lists the photon energies of K-shell lines from
the elements of interest for this study. Figure 2.7 shows energy-dispersive x-ray spectroscopy (EDS) spectra obtained from ~14 nm ALD Li$_x$Al$_y$Si$_z$O film deposited with a cycle sequence of [10(Al-O)-2(Li-O)-12(Si-O)-2(Li-O)]$\times$5 on a high aspect ratio (AR) silicon nanowire (L: 10 $\mu$m, D: 40-50 nm, AR>200). Increase of Al $K\alpha$ and O $K\alpha$ emissions were well observed from the ALD LASO film.

Table 2.5 Photon energies of K-shell lines for the elements of interest, arranged by increasing energy (Bearden 1967)

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Z</th>
<th>Element</th>
<th>Line</th>
</tr>
</thead>
<tbody>
<tr>
<td>277.0</td>
<td>6</td>
<td>Carbon (C)</td>
<td>K\alpha$_{1,2}$</td>
</tr>
<tr>
<td>524.9</td>
<td>8</td>
<td>Oxygen (O)</td>
<td>K\alpha$_{1,2}$</td>
</tr>
<tr>
<td>1486.3 &amp; 1486.7</td>
<td>13</td>
<td>Aluminum (Al)</td>
<td>K\alpha$_2$ &amp; K\alpha$_1$</td>
</tr>
<tr>
<td>1739.4 &amp; 1740.0</td>
<td>14</td>
<td>Silicon (Si)</td>
<td>K\alpha$_2$ &amp; K\alpha$_1$</td>
</tr>
</tbody>
</table>

Figure 2.7 Energy-dispersive X-ray spectroscopy (EDS) spectra obtained from ~14 nm ALD Li$_x$Al$_y$Si$_z$O film deposited with a cycle sequence of [10(Al-O)-2(Li-O)-12(Si-O)-2(Li-O)]$\times$5 on a high aspect ratio (AR) silicon nanowire (L: 10 $\mu$m, D: 40-50 nm, AR>200).
2.2.3 *in-situ* Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier transform infrared spectroscopy (FTIR) is a spectroscopic technique which utilizes irradiation of an infrared (IR) source (λ: 25-2.5 μm) to the sample. At these wavelengths, the molecular thermal vibrations are triggered upon exposure of sample to the IR light, as the bond strength of the molecule can be in resonance with the wavelength (thus energy) of light. During this resonance process, the photon energy gets absorbed, which results in an increase in the absorption (or a decrease of transmission) signal.

![Figure 2.8 Schematic illustrating the various interactions of energetic radiation with a molecule or atom (Brown 2007)](image)

The interaction force of the atomic pair may be modeled as a set of linear harmonic oscillator, also known as Hooke’s law (Burns et al. 2007):

\[
\nu = k \sqrt{f \left( \frac{m_1 + m_2}{m_1 m_2} \right)} \tag{2.5}
\]

where \( \nu \) is the vibrational frequency, \( k \) is the scaling constant, \( f \) is the force constant, and \( m_i \) are the mass of the atom of in molecule. It has to be noted, however, the IR absorbance of the structure also depends on the local symmetry of the molecule. As such, there are only certain
vibration modes that can be detected (Cotton 1990). The observable modes are generally limited to the stretching and/or bending modes of molecule that result in a change in the dipole of the system.

In this study, in-situ Fourier Transform Infrared Spectroscopy (FTIR) was implemented to investigate the underlying surface mechanism of ALD chemistries. The in-situ FTIR allows a detailed investigation of surface species upon successive half-cycles of ALD through the observation of appearance and disappearance of surface species. Figure 2.9 provides an example of how in-situ FTIR can be implemented to study the surface chemistry during ALD of Al₂O₃ via TMA/H₂O on a hydroxyl surface.

Overall ALD Reaction of Al₂O₃ by TMA/H₂O:

\[
\text{TMA} + \text{H₂O} \rightarrow \text{Al₂O₃}
\]

Half Reaction 1:

\[
\text{Si-OH}^* + \text{Al(CH₃)₃} \rightarrow \text{SiO-Al-(CH₃)₂}^* + \text{CH₄}
\]

Half Reaction 2:

\[
\text{Al-(CH₃)₂}^* + 2\text{H₂O} \rightarrow \text{Al-(OH)₂}^* + 2\text{CH}_4
\]

Figure 2.9 ALD half-reactions and the corresponding surface states observed during ALD of Al₂O₃ via trimethylaluminum (TMA)/water (H₂O) chemistry. The dashed lines indicate the surface species to be investigated via in-situ FTIR.
In ALD, the surface state after each half reaction gets terminated with different ligands. Therefore, a successful acquisition of FTIR spectrum following each half cycles represents an accurate monitoring of the surface chemistry during ALD. In this study, \textit{in-situ} FTIR spectra have been collected from a separate, dedicated chamber built within the FTIR spectrometer where the schematic is shown in Figure 2.2. The infrared vibrational wavenumbers to be studied for \textit{in-situ} FTIR study of ALD Li$_x$Al$_y$Si$_z$O are summarized in Table 2.6.
Table 2.6 Infrared vibrational wavenumbers to be studied during *in-situ* FTIR study of ALD processes with lithium tert-butoxide (LTB), trimethylaluminum (TMA), and tetraethyl orthosilicate (TEOS).

<table>
<thead>
<tr>
<th>Regions</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Regions</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Regions</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H stretching</td>
<td>3720-3320</td>
<td>AIO-H stretching vibration from AIOH* surface specie</td>
<td>3650-3770</td>
<td>SiO-H stretching</td>
<td>3743</td>
</tr>
<tr>
<td>Hydroxyl Stretching form LiOH</td>
<td>3672</td>
<td>O-H stretching vibrations from the added AIOH*</td>
<td>3640-3730</td>
<td>C-H stretching (from Si(OCH(_3))(_3)* surface species)</td>
<td>2979</td>
</tr>
<tr>
<td>H(_2)O from LiOH*H(_2)O</td>
<td>3570-3474</td>
<td>C-H stretching from AlCH(_3)* surface species</td>
<td>2820-2980</td>
<td>SiO(_2) absorbance feature</td>
<td>1075</td>
</tr>
<tr>
<td>C-H stretching</td>
<td>3000-2817</td>
<td>Asymmetric C-O stretching (from some Li(_2)CO(_3) in the LiOH film)</td>
<td>1496</td>
<td>(longitudinal-optical, LO phonon)</td>
<td>1075</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-O stretching vibration (from Li(_2)CO(_3))</td>
<td>1450</td>
<td>(transverse-optical, TO phonon)</td>
<td>1484</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[from carbonate CO(_3)(^2-) ions]</td>
<td>1475</td>
<td></td>
<td>1447</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-O stretching (from unreacted tert-butoxide groups)</td>
<td>1200</td>
<td></td>
<td>1369</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Symmetric C-O stretching (from Li(_2)CO(_3)) [from carbonate CO(_3)(^2-) ions]</td>
<td>1088</td>
<td>Various vibrational modes in the IR spectrum of molecular TEOS</td>
<td>1298</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Out of plane deformation mode [from carbonate CO(_3)(^2-) ions]</td>
<td>870</td>
<td></td>
<td>1170</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bulk Al(_2)O(_3) absorbance feature</td>
<td>~900-1000</td>
<td></td>
<td>1109</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1086</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>970</td>
</tr>
</tbody>
</table>

The FTIR spectra are presented as difference spectra to accentuate the changes resulting from each precursor exposures. A spectrum was acquired after each precursor exposure, and the difference spectrum was generated by subtracting the previous spectrum. Consequently, positive
absorbance features indicate the formation of new surface species, whereas negative absorbances indicate the removal of surface species. Figure 2.10 shows *in-situ* difference FTIR spectra obtained during 11th TMA and H2O exposures ALD cycles of Al2O3 via TMA/H2O chemistry on ZrO2 nanoparticle substrate. The signature absorptions from the generation and/or consumptions of the surface hydroxyl (O-H stretching at 3800-3500 cm\(^{-1}\)) and Al-CH\(_3^*\) (C-H stretching at 3000-2800 cm\(^{-1}\) and Al-CH\(_3^*\) deformation at ~1214 cm\(^{-1}\)) are well observed.

Figure 2.10 in-situ difference FTIR spectra obtained during 11th TMA and H2O exposures during ALD cycles of Al2O3 via TMA/H2O chemistry on ZrO2 nanoparticle substrate. The signature absorptions from the generation and/or consumptions of the surface hydroxyl (O-H stretching at 3800-3500 cm\(^{-1}\)) and Al-CH\(_3^*\) (C-H stretching at 3000-2800 cm\(^{-1}\) and Al-CH\(_3^*\) deformation at ~1214 cm\(^{-1}\)) are well observed.
2.2.4 Spectroscopic Ellipsometry (SE)

Spectroscopic Ellipsometry (SE) is an optical measurement technique which characterizes the reflection of light from the sample to determine the thickness of transparent thin films. SE determines the thickness of a sample by measuring the change of the amplitude ratio $\psi$, and the phase difference $\Delta$, between the two polarized incident light waves that are parallel (p-) and perpendicular (s-) to the sample surface.

![Figure 2.11 Measurement principle of spectroscopic ellipsometry (SE) (Fujiwara 2007)](image)

Upon a reflection from the sample, the amplitude reflection coefficients for p- and s-polarization are changed from the difference in the electric dipole radiation. The refractive index of the sample, $n$ and the extinction coefficient $k$, are then extracted from $\psi$ and $\Delta$ respectively to determine the thickness of a transparent thin film (Fujiwara 2007).

![Figure 2.12 Cross-sectional TEM image of a Si(100) wafer implanted with Si ions and structure obtained from TEM and estimated using spectroscopic ellipsometry. SE allows fast and highly precise measurement while being a nondestructive technique (Fujiwara 2007)](image)
It has to be noted, SE is an indirect thickness measurement technique with one inherent drawback: It requires an appropriate optical model defined with correct optical constants of the sample being measured. As such, if an optical model is unavailable, one has to construct an optical model which may be prone to inaccurate measurements, if the model was constructed with erroneous optical constants.

The deposition rates of ALD deposited films were calculated by measuring the thickness of ALD deposited films by implementing an optical model of air/thin film oxide/substrate as depicted in Figure 2.13:

![Figure 2.13 An example of an optical model that was implemented to determine the thickness of the thin film oxides deposited by ALD in this study](image)

Spectroscopic ellipsometry data in this study were collected with J.A. Woollam M-88 system with a wavelength range of 280–760 nm, analyzed by fitting the empirical correlation of Cauchy or Sellmeier dispersion models available for the material of interest. For transparent materials, the Cauchy dispersion model is defined as:

\[ n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} \]  \( (2.6) \)

where the three terms, \( A_n, B_n, \) and \( C_n \) describe the index of refraction over the range of wavelengths. \( A_n \) is a dimensionless parameter defined as when \( \lambda \to \infty \) then \( n(\lambda) \to A. B_n \) affects the curvature and the amplitude of the refractive index in the visible wavelengths. \( C_n \) affects the
curvature and amplitude in the UV range. The single-term Sellmeier dispersion model (DiDomenico et al. 1969) is defined as:

\[
\frac{1}{(n^2 - 1)} = -\frac{A}{\lambda^2} + B
\]

where \( A \) is the slope of the plot of \((n^2-1)^{-1}\) versus \(\lambda^2\) which gives a measure of dispersion and \( B \) is the intercept of the plot at \(\lambda = \infty\). The optical constants \( A, B, C \) implemented for each dispersion models is listed in Table 2.7.

<table>
<thead>
<tr>
<th>Material</th>
<th>Model</th>
<th>Constants</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3)</td>
<td>Cauchy</td>
<td>( A = 1.62 )</td>
<td>(Langereis et al. 2009)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( B_a = 2.60 \times 10^{-3} ) ( \mu m )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( C_n = 2.00 \times 10^{-6} ) ( \mu m^2 )</td>
<td></td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>Cauchy</td>
<td>( A = 1.46 )</td>
<td>(Fujiwara 2007)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( B_a = 2.38 \times 10^{-3} ) ( \mu m )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( C_n = 9.75 \times 10^{-5} ) ( \mu m^4 )</td>
<td></td>
</tr>
<tr>
<td>LiOH</td>
<td>Sellmeier</td>
<td>( A = 1.10 \times 10^{-6} ) ( \mu m^2 )</td>
<td>(D. Shannon et al. 2002)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( B = 0.96 )</td>
<td></td>
</tr>
</tbody>
</table>

An experimental spectroscopic ellipsometry spectrum obtained from \( \times 70 \) cycles of ALD Al\(_2\)O\(_3\) deposited on a Si(100) substrate via trimethylaluminum/water (TMA/H\(_2\)O) chemistry is shown in Figure 2.14. The Cauchy dispersion fitting to the experimental data is shown in Figure 2.14(b) which determined the thickness of Al\(_2\)O\(_3\) film of 76 Å.
Figure 2.14 (a) Experimental spectroscopic ellipsometry data obtained from x70 cycles of ALD $\text{Al}_2\text{O}_3$ deposited on a Si(100) substrate via trimethylaluminum/water (TMA/H$_2$O) chemistry. (b) Cauchy dispersion fitting of the experimental data. The observed thickness of the ALD $\text{Al}_2\text{O}_3$ was 76 Å.

2.2.5 Photoelectron Spectroscopy (XPS, UPS)

The photoelectron spectroscopy techniques are based on the photoelectric effect, where electrons from the elements in the sample are ejected upon irradiation by a photon source with energy higher than the binding energy of the electrons in the sample of interest. As such, photoelectron spectroscopies offer elemental composition analysis of thin film samples. In x-ray photoelectron spectroscopy (XPS), the ejected electrons are the core electrons. In contrast, in ultraviolet photoelectron spectroscopy (UPS), the electrons are ejected from the valence shells. These ejected electrons have an element specific kinetic energy (KE), thus allowing an atomic identification through the conservation of energy relation:

$$\text{KE} = h\nu - \text{BE} - \phi$$

(2.8)

where $h\nu$ is the energy of the incident photon and $\Phi$ is work function of the spectrometer.
XPS analysis allows both qualitative and quantitative information analysis in the outermost surface of the sample on all elements except hydrogen and helium. The sample probing depth is about three times of the inelastic mean free path (IMFP), the average distance that an electron with a given energy travels between successive inelastic collisions. In this regime, 95% of all photoemission electrons are successfully ejected from the sample (C.J 1988; Ratner et al. 2009). The XPS analysis can also provide qualitative chemical bonding information, as the binding energy of the element is influenced by its molecular environment including as its oxidation state and the electronegativity of the surrounding atoms.

The elemental and surface composition analysis of the ALD deposited thin films in this study were identified using ex-situ XPS, via Kratos Axis Ultra XPS system with Al X-ray source. The excitation energy was 1486.6 eV with a take-off angle of 90° with respect to the sample surface. Survey spectra were collected using a pass energy of 160 eV, yielding a step size of 1 eV. The high-resolution regional scans were collected using a pass energy of 20 eV with a step size of 0.1 eV. The collected spectra were first referenced to the adventitious carbon, by shifting C-C 1s binding energy to 284.8 eV. Figure 2.15 shows a survey XPS spectra of Li$_x$Al$_y$Si$_z$O films deposited by ALD with a cycle ratio of [10(Al-O)-6(Li-O)-4(Si-O)]$\times$10 at $T_{dep}=290$ °C on a Si(100) substrate. Photoemission peaks from all three metal elements of interest, Li, Al, and Si were all present, indicating a successful deposition of ALD Li$_x$Al$_y$Si$_z$O.
Figure 2.15 A survey XPS spectra of Li$_x$Al$_y$Si$_z$O films deposited by ALD with a cycle ratio of [10(Al-O)-6(Li-O)-4(Si-O)] x10 at $T_{dep}$=290 °C on a Si(100) substrate.

The surface composition of the sample of interest can be calculated by analyzing the integrated intensities of the element of interest, normalized to corresponding atomic sensitivity factors (ASF) of the photoemission peak using the correlation:

$$C_i = \frac{I_i / ASF_i}{\sum_{i=1}^{n} I_i / ASF_i}$$  \hspace{1cm} (2.9)

where $I_i$ refers to the integrated intensity of the photoemission peak for element $i$. ASF values corresponding to the elements of this study are listed in Table 2.8. The ASF values listed here are based on the study by Wagner, which accounts the angular dependency and the inelastic mean free path (IMFP) of the photoelectrons accounted for the geometry of Kratos XPS system (Wagner 1983).

<table>
<thead>
<tr>
<th>Table 2.8 ASF values for photoemission peaks used in this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Sensitivity Factors</td>
</tr>
<tr>
<td>Li 1s</td>
</tr>
<tr>
<td>Al 2p</td>
</tr>
<tr>
<td>Si 2p</td>
</tr>
</tbody>
</table>
Additionally, XPS also allows an estimation for film thicknesses 10 nm and below by using the XPS metrology equation developed by Hill et al. (Hill et al. 1976):

$$t = \lambda \sin \theta \ln \left( 1 + \frac{I_o / \text{ASF}_o}{I_{\text{Sub}} / \text{ASF}_{\text{Sub}}} \right)$$

(2.10)

where $\lambda$ is the photoelectron IMFP of the material of interest, $I_{\text{Sub}}$ and $I_o$ are photoelectron intensities of the substrate and the overlayer, and $\text{ASF}_o$ and $\text{ASF}_{\text{Sub}}$ are the corresponding atomic sensitivity factors. The XPS metrology equation offers a simple way to cross-check the film thicknesses obtained by alternative metrology techniques including spectroscopic ellipsometry (SE) where its application is limited for the materials without adequate optical models.

UPS was implemented to complement elemental analysis of the ALD deposited films. UPS uses lower energy light sources than XPS in the range of 16-41 eV for laboratory sized spectrometers and up to extreme ultraviolet energy range of ~130-140 eVs under synchrotron radiation. In this energy range, the photoionization cross section, the probability of the incident light creating a photoelectron upon the irradiation of Li 1s, is 1000 times higher than that of XPS: The atomic cross-section of photoionization for Li 1s 0.8467 Mbarns at photon energy of 130 eV (UPS) in contrast to 0.0007912 Mbarns at 1486.6 eV (XPS) (Yeh et al. 1985). As such, implementation of UPS allows higher sensitivity in the quantification of Li concentration. The difference between the two photoelectron spectroscopy is well represented in Figure 2.16. The signal-to-noise ratio of Li 1s in the XPS spectrum is small, making it more difficult to quantify the Li composition. (Perng et al. 2014) In this study, the UPS spectra were acquired at Stanford Synchrotron Radiation Lightsource, Beamline 8-1 at photon energy range of 120-140 eV.
Figure 2.16 Comparison of photoemission spectra taken by XPS with Al Kα (1486.6 eV) and synchrotron UPS (photon energy of 140 eV) for LiOH films grown by x10 ALD cycles by LTB/H₂O on Si(100) substrate. (Perng et al. 2014)

2.2.6 X-ray Diffraction (XRD)

X-ray diffraction (XRD) was used to investigate the structure and crystallinity of the ALD film. In XRD, the structural information of the sample is analyzed by irradiating a sample with x-rays. In an amorphous sample, the incident beam is diffracted in an aperiodic pattern, resulting in a destructive interference. In a crystalline material, however, the beams can scatter in a constructive manner if the total path difference of the reflected waves is equal to integer multiples of incident wavelengths from the periodically arranged atoms. Such condition for a constructive interference is known as the Bragg’s law:

\[ n\lambda = 2d\sin\theta_B \]  

(2.11)

where \( n \) is an integer known as the order of reflection, \( \lambda \) is the wavelength of incident x-ray, \( d \) is the interspacing distance between two atomic planes, and \( \theta_B \) the Bragg angle, the angle where the constructive interference occurs.
For those angles where the Braggs law is satisfied, the scattered X-rays are completely in phase, giving rise to a strong diffracted beam. By measuring the intensity of the diffracted beam as a function of θ, the diffraction peaks can be obtained at different Bragg angles. These Bragg angles then can be used to calculate the lattice parameter of the deposited film and to investigate the crystallographic information of the sample. The observed diffraction peaks are referenced to Joint Committee on Powder Diffraction Standards (JCPDS) database.

Figure 2.17 Principles of X-ray Diffraction: Constructive interference occurs from two atomic planes if the total path difference of the reflected waves is equal to the integer multiples of incident wavelengths.

XRD also allows an estimate of the mean grain size L of polycrystalline thin films through analyzing the peak profiles via Scherrer equation (Gould 2007):

\[ L = \frac{K\lambda}{\eta\cos\theta} \]  

where \( \lambda \) is the x-ray wavelength, \( \eta \) is the width of a strong peak in radians at half-maximum intensity (also known as FWHM), \( \theta \) is the Bragg angle, \( K \) is a constant which is approximately unity. It has to be noted, however, Scherrer’s equation only gives a mean-size estimate and no information on the size distribution. Figure 2.18 shows X-ray diffractogram obtained from ~23 nm ALD Li\(_x\)Al\(_y\)Si\(_z\)O deposited on Si(100) substrate at 225 °C with ALD cycle sequence of [10(Al-O)-3(Li-O)-4(Si-O)-3(Li-O)]×5. Diffraction peaks from LiAlSiO\(_4\) (100) and (200) planes (JCPDS 01-077-0158) at 2\( \theta \) = 19.8° and 39.6° respectively. The peaks at 19.8° and 39.6° had FWHM value of 2\( \theta \) = 1.51. Using the Scherrer’s formula (Eq.(2.12)), the grain size of 12.2 nm can be then calculated.
Counts (CPS)
LiAlSiO$_4$ (100)
LiAlSiO$_4$ (200)

Figure 2.18 X-ray diffractogram obtained from ~23 nm ALD Li$_x$Al$_y$Si$_z$O deposited on Si(100) substrate at 225 °C with ALD cycle sequence of [10(Al-O)-3(Li-O)-4(Si-O)-3(Li-O)] x5. Diffraction peaks from LiAlSiO$_4$ (100) and (200) planes (JCPDS 01-077-0158) at 2θ = 19.8° and 39.6° respectively.

In this study, the diffraction studies were conducted using either a four-circle diffractometer at Stanford Synchrotron Radiation Lightsource (Beamline 7-2 under a photon energy of 8 keV) or a laboratory scale Panalytical X’Pert Pro X-ray powder diffractometer (40 keV) with a Cu Kα source producing a wavelength of 1.54 Å. The schematic of a four-circle diffractometer is shown in Figure 2.19.
In a conventional diffractometer, only one goniometer is used, thus allowing only one dimensional of freedom (i.e., movement only in $\theta$-direction in Figure 2.19). Under such configuration, only the out-of-plane scans from the planes parallel to the sample surface is obtainable. In contrast, the 4-circle diffractometer allows acquisition of in-plane scans (planes orthogonal to the substrate) from the additional degree of movement from the second goniometer (e.g: movement in $\chi$-direction in Figure 2.19). As such, the 4-circle diffractometer setup allows an in-depth crystallinity study of the sample by conducting diffraction experiments from both the out-of-plane (parallel to the substrate planes) and in-plane (perpendicular to the substrate planes) orientations of the sample.

Figure 2.20 depicts XRD diffractograms that can be acquired using the four circle diffractometer:
Figure 2.20 A schematic illustration of the four-circle diffractometer. The XRD diffractograms obtained for a Silicon substrate and LiAlSiO$_4$ are shown: (a) specular (out-of-plane) scan, (b) in-plane scan and (c) phi (rotational) scan. The diffraction peaks from Si(004) for specular and Si(400) for in-plane scans could not be completed owing to detector saturation. (d) Experimental values of angular positions and d-spacing obtained for Si and LiAlSiO$_4$, compared to the reference (Si: 00-001-0787 & LiAlSiO$_4$: JCPDS 01-077-0158) (Perng 2012)
The 2θ scan corresponds to the out-of-plane scan (Figure 2.20(a)), which is the same with the operational mode of a conventional diffractometer. The extra degree of freedom (χ-direction in Figure 2.19) allows the acquisition of the diffraction responses from the planes parallel to in-plane of the sample surface. In-plane scans are useful in determining the epitaxial relationship of the deposited film to the substrate. The χ axis (Figure 2.20(b)) allows a movement of the sample perpendicular to the θ axis, thereby allowing in-plane scans for the planes perpendicular to the sample substrate. Lastly, the Φ scans (Figure 2.20(c)) on specular reflections are used to determine the symmetry of the planes, and can also be used to determine the degree of misalignment.

2.2.7 X-ray Reflectivity (XRR)

X-ray reflectivity (XRR) is a non-destructive metrology technique which utilizes the grazing X-ray beam reflected off a sample. While XRD measurements are used to obtain crystallographic information such as crystal size, lattice strain and orientation relationship of thin films, XRR allows determination of physical properties of the thin films including thickness, density, surface roughness, and interface roughness (Yasaka 2010). When a flat sample is irradiated with x-rays at a grazing angle, total reflection of the incident beam occurs below the critical angle $\theta_c$ where the x-rays do not penetrate into the sample. When the incident angle is equal to $\theta_c$, the incident x-ray propagates along the sample surface. For the angles just above $\theta_c$, however, a fraction of the incident beam can penetrate into the material through refraction. In these angles, interferences occur between the x-rays reflected from the upper most and those refracted off from the underlying interfaces. These interferences then results in an oscillation profile known as Kiessing fringes as shown in Figure 2.21.
Figure 2.21 (a) Material information that can be studied via X-ray reflectivity (XRR) profile (Adapted from (Yasaka 2010)) and (b) an XRR spectrum obtained from ~32.8 nm ALD Li$_x$Al$_y$Si$_z$O film with ALD cycles of [10(Al-O)-1(Li-O)-4(Si-O)-1(Li-O)] × 14 at T$_{dep}$=225 °C on a Ge(100) substrate (Right).

To accurately determine the film properties such as film thickness, density, and surface roughness of a multilayer film via XRR, a theoretical XRR curve needs to be constructed from a layer structure model and fitted to the experimental parameter (Yasaka 2010). For a single film on a substrate, however, a modified version of Bragg’s equation can be implemented to calculate the thickness of the film (Huang et al. 1993):

$$t = \frac{n\lambda}{2\sqrt{\sin^2 \theta_n - \sin^2 \theta_c}}$$  \hspace{1cm} (2.13)

Where $t$ is the film thickness, $n$ is the integer number of fringe, $\lambda$ is the wavelength of incident X-ray (1.54 Å for Cu Kα), $\theta_n$ is the observed angle of fringe, and $\theta_c$ is the critical angle. For films where both spectroscopic ellipsometry (SE) and x-ray photoelectron spectroscopy (XPS) cannot be used to determine the thickness (upon the lack of applicable optical model for SE and if film thickness is greater than 10 nm for XPS), XRR can be implemented to determine the film thickness. In this study, XRR was used to study the thicknesses of ALD Li$_x$Al$_y$Si$_z$O film. All
XRR spectra were obtained through Panalytical X’Pert Pro X-ray powder diffractometer (40 keV) with a Cu Kα (λ = 1.54 Å) source.

2.2.8 Scanning Electron Microscopy (SEM)

Similar to the operating principle of TEM that was introduced in Section 2.2.8, scanning electron microscopy (SEM) also utilizes accelerated electrons but at lower energy, in the ranges of a few tenths to 30 kV. An electron beam that is generated from the anode gets collimated and focused into a fine spot of 1 to 5 nm by a series of condenser and objective lenses. Upon irradiation on the sample, the interactions with the primary electrons from the atoms in the sample lead to subsequent generation of secondary electrons, which are then detected by a scintillator-photomultiplier device to produce an image that corresponds to the topography of the sample (Alford et al. 2007). In this study, SEM images were obtained using a FEI Nova 600 Dual Beam-SEM/FIB system and a FEI Nova 230 SEM/EDS system under an acceleration voltage of 10 kV. Figure 2.22 shows a scanning electron microscope (SEM) image of a carbon slurry electrode with compositions of 83% mesocarbon microbeads (MCMB), 7% carboxymethyl cellulose (CMC), 8% graphite and 2% Ketjen black, taken under an excitation voltage of 18.0 kV. The rough and porous morphology of the carbon slurry electrode is well observed, in which the optical microscopy techniques cannot offer.
2.2.9 Transmission Electron Microscopy (TEM)

High-resolution transmission electron microscopy (HRTEM) is an electron microscopy technique which utilizes an accelerated electron beam rather than photons used in optical microscopy. In optical microscopy such as visible light microscopy (VLM), the smallest distance that can be resolved, δ, is given approximately by Rayleigh criterion as shown in Eq. (2.14):

\[
\delta = \frac{0.61\lambda}{\mu \sin \beta}
\]

where \( \lambda \) is the wavelength of the radiation, \( \mu \) the refractive index of the viewing medium, and \( \beta \) the semi-angle collection of the magnifying lens. For a green light in the middle of the visible spectrum (\( \lambda = 550\) nm), the best resolution that can be offered by VLM is about ~300 nm, which is about 1000 atom diameters (Williams et al. 2009). By using an accelerated electron beam through a potential drop, however, electron microscopies offer much improved resolution as the wavelength of probing medium is less than 1 Å:
\[ \lambda = \frac{\hbar}{\sqrt{2m_e eV}} \]  

(2.15)

where \( \lambda \) is the electron wavelength, \( \hbar \) is Planck’s constant \((6.626 \times 10^{-34} \text{ Nms})\), \( m_e \) is the mass of electron (or the rest mass, \( 9.109 \times 10^{-31} \text{ kg} \)), and \( V \) is the accelerating voltage of the electron microscope. Under the acceleration voltage of 300 kV, the wavelength of electron is then 2.23 pm, which is a five orders of magnitude difference in the wavelength than that of the VLM. The resolution \( (d) \) of the TEM can be calculated to be (Williams et al. 2009):

\[ d = 0.61\lambda \]  

(2.16)

As evident from Eq. (2.16), using electrons as the probe source increases the resolution limit to the order of Angstroms (Å). TEM therefore allows investigation on the material of interest even to the finest details, down to individual atoms under optimal conditions (Alford et al. 2007).

The schematic and the electron beam path of the TEM are depicted in Figure 2.23. In the TEM, an electron gun produces a beam of monochromatic electrons from a filament through a thermionic or field emission along the optical axis of the microscope. The beam then passes through condenser lenses and strikes the sample. Upon impingement, a portion of the beam is transmitted while others diffract, where the transmitted beam is focused by the objective lens to produce an image.
Figure 2.23 Cross-section schematic of the electron beam path and the operating principle of a transmission electron microscopy (Alford et al. 2007)

The Titan S/TEM used in this study utilizes a carbon nanotube as an emission source with an acceleration voltage of 300 kV, giving an electron wavelength of 2.23 pm and a resolution of 1.36 pm. A Gatan Ultrascan, 2×2k CCD detector is attached to directly collect the transmission spectrum. Figure 2.24 shows a high resolution transmission electron microscope (HRTEM) image of a silicon nanowire (SiNW) with a diameter of ~120 nm. The operating voltage of the electron microscope was 300 kV.
Figure 2.24 A high resolution transmission electron microscope (HRTEM) image of a silicon nanowire (SiNW) with a diameter of ~120 nm. The operating voltage of the electron microscope was 300 kV.

The usage TEM also allows utilization of selected area electron diffraction (SAED), an electron diffraction technique where a portion of the incident beam makes the appropriate angle with a specific set of (hkl) planes such that Bragg’s Law (Eq. (2.11)) is satisfied. Under such condition, information such as lattice parameters and atomic positions in a crystalline sample can be obtained by analyzing the image of reciprocal lattice points as shown in Figure 2.25(a) and Figure 2.25(b). For a single crystalline material, SAED pattern appear as dots owing to periodically ordered planes. For a polycrystalline material, however, SAED pattern appear as a set of concentric rings. The identification of the lattice spacing can be performed by measuring the distance between the diffraction spots in SAED and calculating the inverse of the distance. This lattice spacing is then referred to Joint Committee on Powder Diffraction Standards (JCPDS) reference to identify the corresponding lattice. A SAED pattern obtained from Si$_{0.6}$Ge$_{0.4}$ nanowire is shown in Figure 2.25. The periodic pattern of Si$_{0.6}$Ge$_{0.4}$ nanowire revealed that the wire was homogenous and single crystalline.
Figure 2.25 (a) View of the incident radiation at the Bragg Angle, $\theta_B$, to a set of (hkl) planes and the corresponding diffracted beam. (b) View of the same sample and under the same diffraction conditions showing the reciprocal lattice observed in selected area electron diffraction (SAED). (Alford et al. 2007) (c) The SAED pattern observed from a $\text{Si}_{0.6}\text{Ge}_{0.4}$ nanowire.

One major limitation of the HRTEM is that the sample of interest needs to be thinner than 100 nm, generally in the range of 10-50 nm. As such, TEM in this study has been implemented to study ALD deposited films with thicknesses below 50 nm.

2.2.10 Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) was used to investigate the ionic conductivity of the deposited films. EIS is a powerful characterization technique which allows the study of electrical properties of materials and their interfaces. It also can be used to study the dynamics of mobile charges in the bulk or interfacial regions of various solid materials including ionic, semiconducting, mixed electronic-ionic, and dielectric materials (Macdonald et al. 2005). In EIS, a monochromatic signal (generally voltage) is applied and the resulting steady state output is (usually current) measured over the frequency ranges of 10 mHz to 1 MHz. The obtained impedance data is then analyzed by constructing an equivalent circuit, a representative model of the physical process taking place in the system under investigation. This equivalent circuit consists of passive circuit elements of a resistor (R), capacitor (C), and inductor (L).
Using the fundamental relationships of the passive circuit elements as shown in Table 2.9, the impedance defined as $Z = \Delta V / \Delta I$, of each of the passive circuit elements can be derived.

### Table 2.9 Passive circuit elements and their fundamental relationships

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Unit</th>
<th>Fundamental Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor (R)</td>
<td><img src="image" alt="Resistor" /></td>
<td>Ohm (Ω)</td>
<td>$V(t) = R I(t)$</td>
</tr>
<tr>
<td>Inductor (L)</td>
<td><img src="image" alt="Inductor" /></td>
<td>Henry (H)</td>
<td>$V(t) = L \frac{\partial I(t)}{\partial t}$</td>
</tr>
<tr>
<td>Capacitor (C)</td>
<td><img src="image" alt="Capacitor" /></td>
<td>Farad (F)</td>
<td>$C(t) = \frac{\partial q(t)}{\partial V(t)}$ where $I(t) = \frac{\partial q(t)}{\partial t}$</td>
</tr>
</tbody>
</table>

Starting from a sinusoidal signal AC voltage of

$$V(t) = |\Delta V| \cos wt$$  \hspace{1cm} (2.17)

The current response can then be defined as

$$I(t) = |\Delta I| \cos (wt + \phi)$$  \hspace{1cm} (2.18)

By using the Euler’s relation of

$$\cos (wt + \phi) = \text{Re} \{e^{j(wt+\phi)}\} = \text{Re} \{e^{j\phi} e^{jwt}\}$$  \hspace{1cm} (2.19)

then $I(t)$ can be redefined as

$$I(t) = \text{Re} \{|\Delta I| e^{j\phi} e^{jwt}\} = \text{Re} \{\Delta I e^{jwt}\} \text{ where } \Delta I = |\Delta I| e^{j\phi}$$  \hspace{1cm} (2.20)

Implementing Eq. (2.17) and (2.20) back to the fundamental relationships of the passive circuit elements shown in Table 2.9, the frequency dependent impedance responses of a resistor, inductor, and capacitor can then be derived as:

$$Z_R = \frac{\Delta V}{\Delta I} = R$$  \hspace{1cm} (2.21)

$$Z_L = \frac{\Delta V}{\Delta I} = j\omega L$$  \hspace{1cm} (2.22)
\[ Z_L = \frac{\Delta V}{\Delta I} = \frac{1}{j\omega C} \] \hspace{1cm} (2.23)

These impedance relationships can be used to fit the experimental impedance response of a material by constructing an equivalent circuit. Table 2.10 shows the examples of different equivalent circuits and their simulated impedance responses. It has to be noted, however, when designing an equivalent circuit, a careful model is often required as there are cases where more than one model can fit the same experimental data. A well-designed equivalent circuit not only should fit data, but needs to represent a plausible physical model of the material system under investigation.
Table 2.10 Examples of the equivalent circuits and their simulated impedance responses

| Resistor || Capacitor | Resistor || Capacitor | Resistor || Capacitor |
|-----------|-------------|-----------|-------------|-----------|-------------|
| [Diagram] | [Diagram]   | [Diagram] | [Diagram]   | [Diagram] | [Diagram]   |

- **Resistor || Capacitor**
  - R1=10, C1=0.1
  - R1=100, C1=0.1
  - R1=1000, C1=0.1

- **Resistor || Capacitor – Capacitor**
  - R1=100, C1=0.1, C2=0.01
  - R1=100, C1=0.1, C2=0.1
  - R1=100, C1=0.1, C2=1

- **Resistor || Capacitor - Resistor || Capacitor**
  - R1=1, C1=0.1, R2=1, C2=1
  - R1=0.1, C=0.1, R2=1, C2=1
  - R1=1, C1=1, R2=0.1, C2=1

- **((Capacitor || Resistor) - Resistor) || Capacitor**
  - C1=0.1, R1=0.1, R2=0.1, C2=0.1
  - C1=1, R1=0.1, R2=0.1, C2=0.1
  - C1=10, R1=0.1, R2=0.1, C2=0.1
Electrical characterization of ALD deposited films in this study were conducted by ALD films on a 1 mm thick indium tin oxide (ITO)/quartz substrates (CEC020Q, Präzisions Glas & Optik GmbH, Germany) conductive substrate which served as the back electrode for the measurements. The top electrodes were formed by e-beam deposition of an array of 660 µm diameter dots comprised of a 10 nm adhesion layer of titanium (Ti) followed by 100 nm of Platinum (Pt). Tungsten probes controlled by a Cascade Microtech probe station were attached to the ITO and Pt electrodes and were connected to an HP 4284A LCR meter. Impedance spectra were measured over a frequency range of 20 to $10^6$ Hz using a 13 mV$_{rms}$ signal. Temperature dependent impedance measurement was obtained by carrying out the measurements on a hot plate where the temperatures were observed by Type-K thermocouple that was placed in vicinity to the sample. Figure 2.26 shows the experimental setup and the experimental Nyquist impedance spectra obtained from ~20 nm ALD LASO sample deposited with 10 global cycles with ALD sub-cycle sequence of $[10(Al-O)-3(Li-O)-4(Si-O)-3(Li-O)] \times 1010$ on indium-tin-oxide (ITO) substrate.
Figure 2.26 (a) Experimental setup for EIS measurements. The ALD deposited film is sandwiched between a conducting indium tin oxide (ITO) substrate and platinum electrode (Pt). (b) Nyquist impedance spectra obtained from ~20 nm ALD LASO sample deposited with 10 global cycles with ALD sub-cycle sequence of [(Al-O)-3(Li-O)-4(Si-O)-3(Li-O)]x10 on indium-tin-oxide (ITO) substrate over temperature ranges of 110 to 174 °C. A characteristic semi-circle behavior of an ionic conductor is well observed.

Equivalent circuit fittings of the measured data were carried out using ZView impedance analysis software (Scribner Associates), where the goodness of fit between the experimental data and the proposed model was validated by chi-squared statistics.

The ionic conductivity, $\sigma_{\text{ionic}}$, for the LASO film was determined by the relation (Kim et al. 2009; Park et al. 2010; Thokchom et al. 2010):

$$\sigma_{\text{ionic}} = \frac{t}{R_{\text{Bulk}}A}$$

(2.24)

where $R_{\text{Bulk}}$ is the extrapolated dc resistance from the fitted circuit model, $t$ is the film thickness and $A$ is the area of the electrodes. It should be noted that the conductivity is measured through the film which enables us to determine accurate values of the ionic conductivity. The observed
values of ionic conductivity from ALD LASO sample shown in Figure 2.26 were $2.38 \times 10^{-7}$ S/cm over the temperature range of 110 to 174 °C.

2.2.11 Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is an electrochemical technique that utilizes potential sweeps of the working electrode at a given rate. The current response during the potential sweep is studied to investigate the reduction/oxidation (redox) responses of the analyte. In the anodic sweep, the potential is swept from negative to positive which decreases the energy of the working electrode. When the potential reaches the oxidation potential of the analyte, a current peak is produced from the oxidation of the analyte. Analogously, in the cathodic sweep, the potential is swept in the positive to negative potential, which increases the energy of the working electrode. When the potential reaches the reduction potential of the analyte, a reduction current peak is produced from the reduction of the analyte (Bard et al. 2001).

![Diagram showing electron energy level comparison](image)

Figure 2.27 The electron energy level of the working electrode compared to the open circuit potential (OCP). Applying a negative bias ($\eta < 0$) increases the electrode energy level, inducing a reduction current. Applying a positive
bias ($\eta > 0$) reduces the electrode energy level, inducing an oxidation current (Cirigliano 2013)

In this work, CV was implemented to study the presence of pinholes in the ALD films through the well-established redox chemistry of ferrocene (bis-(\(\eta\)-cyclopentadienyl) iron (II), FeCp\(_2\)) analyte. The presence of characteristic redox peaks of ferrocene (FcCp\(_2\)) to ferrocinium ion (FcCp\(_2^+\)) served as the indication for the presence of pinholes in ALD films. A 1mM ferrocene solution was prepared using anhydrous propylene carbonate (PC) as the solvent and 100 mM tetrabutylammonium tetrafluoroborate (TBATFB) as the supporting electrolyte to increase the ionic conductivity of the solution. A three electrodes system (Figure 2.28(a)) consisting of an indium-tin-oxide (ITO) working electrode (ITO), a platinum (Pt mesh) counter electrode and a platinum (Pt mesh) reference electrode was used. The reference CV spectrum was obtained using a bare ITO (CEC020Q, Präzisions Glas & Optik GmbH, Germany) serving as the working electrode, in contact with the solution. For the pinhole study of the ALD films, the same ITO substrate with ALD films deposited on top was used as the working electrode. Figure 2.28(b) shows the characteristic current-voltage (IV) curve obtained from the bare ITO substrate.

![Setup of cyclic voltammetry experiment](image)

**Figure 2.28 (a)** Setup of cyclic voltammetry experiment and **(b)** the characteristic IV curve measured on a clean ITO/quartz substrate in a solution of 1 mM Fc and 100 mM TBATFB in PC (Perng 2012).
The characteristic oxidation peak observed during the potential sweep negative to positive potential is from the oxidation of FeCp$_2$ to FeCp$_2^+$. The reduction potential current peak is observed during the potential sweep from positive to negative potential, from the reduction of FeCp$_2^+$ to FeCp$_2$.

For the case of ALD films that are electrically insulating, the presence of redox peak currents should arise only from the presence of pinholes which allow redox molecules to interact with the underlying electrically conductive substrate. Under the assumption that the redox peaks arises from pinholes that act as independent, disk-shaped electrodes, the number density of pinholes of ALD coating can be calculated by (Chailapakul et al. 1995):

$$N = \frac{j}{4nFDC^*r_0}$$  \hspace{1cm} (2.25)

where $N$ is the number density of pinholes, $j$ is the peak current, $n$ is the number of electrons transferred, $F$ is the Faraday constant, $D$ is the diffusion coefficient of the probe molecule, $C^*$ is the concentration of probe molecule, and $r_0$ is the radius of pinhole. The presence of pinholes in ALD deposited LASO films were studied with cobaltocenium hexafluorophosphate (CoCp$_2$PF$_6$) and decamethyl ferrocene (FeCp$_2$) as probe molecules.

2.2.12 Galvanostatic Charge-Discharge Cycling (GV)

Galvanostatic charge-discharge cycling (GV) is a technique in which the current is held constant while the voltage between the working and reference electrodes is monitored. A positive current denotes a flow of electrons from the working electrode to the counter electrode, while a negative current results in electrons flowing from the counter electrode to the working electrode. (Cirigliano 2013) In this study, GVs were performed on various bare electrodes and ALD coated electrodes to study their charge-discharge responses.
The coulombic efficiency (CE) and the irreversible capacity are defined by Eq. (2.26) and (2.27) respectively:

\[
\text{Coulombic efficiency (\%)} = \left( \frac{\text{discharge capacity}}{\text{charge capacity}} \right) \times 100 \quad (2.26)
\]

\[
\text{Irreversible capacity (mAh/g)} = \text{charge capacity} - \text{discharge capacity} \quad (2.27)
\]

In this study, a three electrode cell (as previously shown in Figure 2.28(a)) with 1 M LiClO\textsubscript{4} dissolved in a 50:50 mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) solution was used for GV. The electrodes and ALD coated electrodes were cycled galvanostatically with lithium foil serving as the reference and counter electrodes. Figure 2.29 shows a galvanostatic charge-discharge response of ~20 nm LASO deposited on 2D carbon slurry electrode (where the SEM image of the electrode was previous shown in Figure 2.22) in 1M LiClO\textsubscript{4}, 50:50 EC/DMC solution. Li foils were used as reference and counter electrodes. A successful charge/discharge of 2D carbon is well observed from the voltage changes of E\textsubscript{WE}, from 0.60 V when the electrode is fully discharged, and 0.01 V when fully charged.
Figure 2.29 Galvanostatic charge-discharge response of ~20 nm LASO deposited on 2D carbon slurry in 1M LiClO$_4$ in 50:50 EC/DMC solution with Li foils are reference and counter electrodes.
CHAPTER 3: MECHANISTIC STUDY OF ALD LiₓAlᵧSiₓO

This chapter investigates the growth and the underlying surface mechanisms in ALD synthesis of LiₓAlᵧSiₓO. Detailed studies on the surface mechanism during ALD synthesis of its constituent oxides, Al₂O₃, LiOH, and SiOₓ, are investigated first via in-situ Fourier transform infrared spectroscopy (FTIR), then the complex tertiary oxides of AlₓSiₙO, LiₓAlₙO, and LiₓSiₙO and finally the LiₓAlᵧSiₓO. The mechanistic study on ALD Al₂O₃ by TMA/H₂O and LiOH by LTB/H₂O showed an ideal ALD growth response with a growth rate of ~1.1 and ~1.2 Å/cycle respectively at 225 °C. ALD deposition of SiO₂ by alternating exposures of TEOS/H₂O was found infeasible owing to insufficient hydrolysis of the surface Si-OCH₂CH₃* specie from TEOS exposure when H₂O is used as oxidant. Deposition of SiOₓ in form of complex oxides such as AlₓSiₙO and LiₓSiₙO were demonstrated when the same TEOS/H₂O chemistry was implemented with other ALD chemistries, TMA/H₂O process to synthesize AlₓSiₙO and LTB/H₂O process to synthesize LiₓSiₙO. In-situ FTIR data obtained during ALD depositions of AlₓSiₙO by TEOS/H₂O/TMA/H₂O chemistry and LiₓSiₙO by LTB/H₂O/TEOS/H₂O revealed that the presence of electropositive metal atom in vicinity of surface Si-OCH₂CH₃* specie enhances hydrolysis of ethoxy ligand (-OCH₂CH₃). No presence of incubation times were found for ALD deposition of each constituent oxide on the other, allowing ALD deposition LASO as a solid solution based on its constituent oxides. The mechanistic studies of the constituent oxides and of ternary oxides have provided an in-depth understanding of the chemistry which enabled ALD synthesis of LiₓAlᵧSiₓO.
3.1 Mechanistic Study on ALD of Al₂O₃ by TMA/H₂O Chemistry

The surface mechanism of a well-known ALD chemistry of ALD Al₂O₃ by trimethylaluminum (TMA)/H₂O chemistry was first studied through in-situ Fourier transform infrared spectroscopy (FTIR) to lay the groundwork on studying novel ALD chemistries of LiOH and SiO₂. Figure 3.1 shows in-situ difference FTIR spectra obtained during the first 6 ALD cycles of TMA/H₂O exposure pulses on ZrO₂ nanoparticles (NPs) at 225 °C. The deposition temperature of 225 °C was based on ALD windows reported in literature for Al₂O₃ (Table 1.11).

![Figure 3.1 in-situ difference FTIR spectra of 6 (TMA-H₂O) cycles on ZrO₂ NP substrate at 225 °C. The formation of the surface Al-CH₃* species were well observed upon TMA exposure from the appearances of IR absorbance from Al-CH₃* deformation at 1211 cm⁻¹, C-H stretch at ~2930-2830 cm⁻¹, and disappearance of O-H stretching at 3800-3700 cm⁻¹. Desorption of the surface Al-CH₃* specie and regeneration of the surface O-H group were observed following subsequent H₂O pulse.](image-url)
Following the first TMA exposure, IR absorption responses from the formation of the surface Al-CH$_3$* specie were observed by an increase of absorbance at 1211 cm$^{-1}$ from Al-CH$_3$* deformation and C-H stretching regions at 2929, 2895, 2827 cm$^{-1}$. The negative O-H stretching absorbance at 3725 cm$^{-1}$ indicated consumption of the surface hydroxyl (-OH) groups upon TMA exposure. These observed absorbance matched well with literature reported by Goldstein et al. (Goldstein et al. 2008) and Rai et al. (Rai et al. 2010). Upon subsequent H$_2$O exposure, the IR absorbance observed during TMA exposure were reversed, where negative absorbance were observed for Al-CH$_3$* deformation (1211 cm$^{-1}$) and C-H stretching regions (2929, 2895, and 2827 cm$^{-1}$) indicating a successful desorption of Al-CH$_3$* surface species. The regeneration of surface hydroxyl (-oh) group was well observed from the appearance of positive absorbance at O-H region (3800-3700 cm$^{-1}$). These results conclude that the methyl (-CH$_3$) group of the surface Al-CH$_3$* specie gets effectively removed upon H$_2$O exposure by releasing methane (CH$_4$), regenerating the surface hydroxyl (-OH) groups. These surface hydroxyl group can react readily with the incoming TMA in the next TMA/H$_2$O cycle. The release of methyl (-CH$_3$) ligand and regeneration of the surface hydroxyl (-OH) groups were well demonstrated throughout continuous cycles of TMA/H$_2$O. The integrated absorbance of O-H and C-H stretching regions is shown in Figure 3.2:
Figure 3.2 Integrated absorbance of (a) O-H stretching region at \( \sim 3800-3700 \text{ cm}^{-1} \) and (b) C-H stretch region at 3000-2800 cm\(^{-1}\) during 6 TMA/H\(_2\)O cycles. Consistent and repetitive absorbance are well observed from both regions, demonstrating the ideal ALD growth of Al\(_2\)O\(_3\) via TMA/H\(_2\)O chemistry based on self-limited surface reactions during each ALD half cycles.

As evident from Figure 3.2, both O-H and C-H regions exhibited consistent and repetitive absorbance features throughout continuous TMA/H\(_2\)O cycles: During TMA exposure, the C-H region experiences positive absorbance while the O-H region undergoes negative absorbance. During H\(_2\)O exposures, such responses are reversed, where the C-H region shows negative absorbance and the O-H region showing positive absorbance. From these results, it can be concluded that the ALD growth of Al\(_2\)O\(_3\) by TMA/H\(_2\)O follows the ideal ALD cycle where the growth of Al\(_2\)O\(_3\) by TMA/H\(_2\)O is self-limited by the reactive surface sites in self-saturating manner during each precursor (TMA) and oxidant (H\(_2\)O) exposures. The observed surface mechanism during ALD of Al\(_2\)O\(_3\) via TMA/H\(_2\)O is depicted as in Figure 3.3.
Figure 3.3 A schematic representation of the surface reactions observed during ALD of Al₂O₃ by TMA/H₂O chemistry via *in-situ* FTIR spectroscopy. Regenerations of the surface methyl (-CH₃) groups upon TMA exposure and the surface hydroxyl (-OH) group following H₂O exposure allows the consistent and continuous ALD growth of Al₂O₃.

The growth rate of ALD Al₂O₃ via TMA/H₂O was investigated by spectroscopic ellipsometry (SE) and high resolution transmission electron microscopy (HRTEM). Figure 3.4(a) shows the growth rate of ALD Al₂O₃ on a Si(100) substrate at 225°C, obtained by spectroscopic ellipsometry. A growth rate of ~1.1 Å/cycle was observed, which matched well to literature results previously summarized in Table 1.11. Figure 3.4(b) shows the HRTEM image of a thin Al₂O₃ coating, ~20 Å, on ZrO₂ nanoparticles with 20 cycles TMA/H₂O cycles, consistent with thickness determined from the growth rate of ~1.1 Å/cycle. Figure 3.5 shows XPS spectra obtained from ALD Al₂O₃ deposited by 100 cycles of TMA/H₂O on Si(100). The presence of Al 2p photoemission peak was confirmed at ~74.5 eV, indicating a successful ALD deposition of Al₂O₃.
Figure 3.4 (a) Growth rate of ALD Al₂O₃ by TMA/H₂O on a Si(100) substrate via spectroscopic ellipsometry (b) HRTEM image of ~21 Å Al₂O₃ deposited by x20 TMA/H₂O cycles on a ZrO₂ NP at 225 °C.

Figure 3.5 X-ray photoelectron spectroscopy (XPS) spectra from Al₂O₃ deposited by x100 ALD cycles of TMA/H₂O on a Si(100) substrate at 225 °C: (a) Survey and high resolution regional spectra from (a) Al 2p and (b) O 1s.

Overall, the surface mechanism during ALD growth of Al₂O₃ by TMA/H₂O chemistry was confirmed to alternate between the formation of Al-CH₃* surface species during TMA exposure and the re-generation of –OH upon H₂O exposure.
3.2 Mechanistic Study on ALD of LiOH by LTB/H₂O Chemistry

The growth rate of ALD LiOH by LTB/H₂O chemistry was quantified next. This is an important aspect of this work since literature results vary widely regarding the ALD growth rate of LiOH under the similar experimental conditions, ranging from 0.86 Å/cycle (Cavanagh et al. 2010) to 2.2 Å/cycle (Comstock et al. 2012). Owing to such inconsistency, the growth rate of ALD LiOH by LTB/H₂O chemistry on Si(100) at 225°C was measured by spectroscopic ellipsometry as shown in Figure 3.6.

The observed growth rate of ALD LiOH was found to be 1.2 Å/Cycle at 225 °C, which was in between the growth rates reported by Cavanagh et al. (0.87 Å/Cycle) (Cavanagh et al. 2010) and Aaltonen et al. (1.7 Å/Cycle). It is noteworthy to mention that the observed growth rate of 1.2 Å/cycle was lower than 2.2 Å/cycle reported by Comstock et al. (Comstock et al. 2012). Such difference in growth rate could have resulted from the incorrect optical fit of the deposited LiOH.
film, as LiOH is known to undergo a facile reaction with the ambient CO$_2$ to form Li$_2$CO$_3$ upon a prolonged exposure to air (Putkonen et al. 2009; Aaltonen et al. 2011; Comstock et al. 2012; Kozen et al. 2014). If the spectroscopic ellipsometry studies of LiOH in the study by Comstock were conducted after such prolonged exposure, the resulting film would have been a mixture of Li$_2$CO$_3$ and LiOH. An optical fit of LiOH to such mixture (Li$_2$CO$_3$-LiOH) could be a potential reason as to why the reported growth rate of 2.2 Å/cycle by Comstock differs from other literature values and that observed in this study. The successful deposition of LiOH was confirmed by XPS as shown in Figure 3.7, where a photoemission peak from Li 1s was well observed at ~55 eV.

![Figure 3.7 X-ray photoelectron spectroscopy (XPS) spectra from LiOH deposited by x70 ALD cycles of LTB/H$_2$O on a Si(100) substrate at 225 °C: (a) Survey and detailed high resolution regional spectra of (b) Li 1s and (c) O 1s.](image)

To elucidate the underlying growth mechanism during ALD LiOH by LTB/H$_2$O, in-situ FTIR studies were conducted during the each alternating exposures of LTB and H$_2$O. Figure 3.8 shows in-situ difference FTIR spectra obtained during ALD LiOH growth on ZrO$_2$ NPs at 225 °C with 10 cycles of LTB/H$_2$O.
Figure 3.8 *in-situ* difference FTIR spectra of ALD LiOH on ZrO$_2$ NPs at 225 °C with 10 LTB/H$_2$O cycles. Consistent and continuous IR responses of O-H stretching, C-H stretching, and C-O stretching regions have demonstrated a successful ALD deposition of LiOH by LTB/H$_2$O chemistry.

Upon the first LTB pulse, positive absorptions were observed at 1200 cm$^{-1}$ and 2971 cm$^{-1}$ from C-O and C-H stretching of tert-butoxy (-OC(CH$_3$)$_3$) ligand (Cavanagh et al. 2010; Comstock et al. 2012), indicating successful adsorption of LTB on the surface. The consumption of the surface hydroxyl groups upon the first LTB exposure was well observed from the decrease of O-H stretching absorptions in the regions of ~3800-3700 cm$^{-1}$. These IR absorbance indicate that LTB precursor successfully undergoes a surface reaction with the surface hydroxyl (-OH) group, terminating the surface the butoxy (-OC(CH$_3$)$_3$) ligands. Upon subsequent H$_2$O exposure, the surface hydroxyl groups was regenerated, as evident from the appearances of O-H stretching between ~3800-3700 cm$^{-1}$. The regeneration of the surface hydroxyl group came from oxidation of the butoxy ligand upon H$_2$O exposure, as observed from the negative absorbance features of
C-O and C-H regions following H$_2$O exposure. Continuous alternating exposures of LTB/H$_2$O resulted in the same IR responses to that observed from the first LTB/H$_2$O cycle. The surface mechanism of LTB/H$_2$O for ALD of LiOH based on in-situ FTIR response is depicted in Figure 3.9:

![Figure 3.9](image)

Figure 3.9 Surface mechanism based on in-situ FTIR spectroscopy during ALD LiOH by alternating exposures of LTB/H$_2$O.

During LTB exposure, the LTB precursor is postulated to undergo a molecular adsorption to the surface hydroxyl (-OH) group:

$$\text{M-OH}^* + \text{LiOC(CH}_3)_3 \rightarrow \text{M-OH-LiOC(CH}_3)_3^*$$  \hspace{2cm} (3.1)

where an asterisk is used to denote surface species. Upon subsequent H$_2$O exposure, the tert-butoxy ligand (-OC(CH$_3$)$_3$) undergoes hydrolysis where a tert-butanol (HOC(CH$_3$)$_3$) is released:

$$\text{M-OH-LiOC(CH}_3)_3^* + \text{H}_2\text{O} \rightarrow \text{M-OH-LiOH}^* + \text{HOC(CH}_3)_3$$  \hspace{2cm} (3.2)

The surface reactions presented in Eq. (3.1) and (3.2) are in agreement to those proposed previously (Cavanagh et al. 2010; Aaltonen et al. 2011; Kozen et al. 2014).

Figure 3.10 shows the integrated absorbance of O-H and C-H regions obtained from in-situ difference FTIR spectra of ALD LiOH by LiOH/H$_2$O chemistry. The integrated absorbance of both O-H and C-H region showed consistent and repetitive IR responses similar to that observed previously from ALD of TMA/H$_2$O (Section 3.1). These results indicate that that ALD of LiOH by LTB/H$_2$O undergoes self-limited surface half reactions presented in Eq. (3.1)-(3.2) and exhibits a near-ideal ALD chemistry.
Figure 3.10 Integrated absorbances of (a) O-H stretching region at ~3800-3700 cm\(^{-1}\) and (b) C-H stretch region at 3000-2800 cm\(^{-1}\) during ALD of LiOH with 6 LTB/H\(_2\)O cycles. Consistent and repetitive absorbance were observed from both regions, demonstrating the self-limited growth of ALD LiOH via LTB/H\(_2\)O chemistry.

3.3 Mechanistic Study on ALD SiO\(_2\) by TEOS/H\(_2\)O Chemistry

ALD of SiO\(_2\) is the most challenging task amongst the growth studies of the constituent oxides of LASO. Literature report on ALD of SiO\(_2\) with TEOS as Si precursor is known to require either a highly reactive chemistry such as ozone or use of a catalyst, limiting its applicability if the process were to be combined with other ALD chemistries to synthesize complex oxides.

In this work, ALD of SiO\(_2\) via TEOS/H\(_2\)O chemistry was first studied by spectroscopic ellipsometry (SE). Figure 3.11(a) shows spectroscopic ellipsometry data of up to 150 ALD cycles of TEOS/H\(_2\)O on a Si(100) substrate. No observable thickness changes were present, which agreed with previously reported studies in literature. Figure 3.11(b) shows a high
resolution transmission electron microscope (HRTEM) image of ZrO$_2$ nanoparticles (NPs) exposed to 20 cycles of TEOS/H$_2$O at 225 °C where no deposition of an ALD SiO$_2$ shell was observed.

![Graph](image)

Figure 3.11 (a) Spectroscopic ellipsometry growth data of TEOS/H$_2$O and TEOS/H$_2$O chemistries on a Si(100) substrate and (b) ZrO$_2$ nanoparticles (NPs) exposed to 20 cycles of TEOS/H$_2$O. No growth of SiO$_2$ film was observed by TEOS/H$_2$O chemistry even after x150 cycles.

X-ray photoelectron spectroscopy study on TEOS/H$_2$O chemistry also confirmed that no deposition of SiO$_2$ takes place with TEOS and H$_2$O. Figure 3.12 shows XPS spectra obtained from 60 cycles of TEOS/H$_2$O on a Ge(100) substrate, deposited at 225°C. No photoemission peaks were observed from Si 2p around ~100 eV, supporting SE and HRTEM results that no deposition of SiO$_2$ takes place with TEOS/H$_2$O chemistry at 225°C.
Figure 3.12 X-ray photoelectron spectroscopy spectra of ALD SiO$_2$ obtained from 60 cycles of TEOS/H$_2$O on a Ge(100) substrate at 225$^\circ$C. (a) Survey and (b) high resolution regional spectra for Si 2p region. No photoemission peaks from Si 2p was observed.

To understand as to why alternating exposures of TEOS/H$_2$O do not result in ALD deposition of SiO$_2$ film, \textit{in-situ} FTIR spectroscopy was implemented during each half-cycles of TEOS/H$_2$O chemistry to investigate the underlying surface chemistries. Figure 3.13 shows \textit{in-situ} difference FTIR spectra obtained during ALD of SiO$_2$ with 10 TEOS/H$_2$O cycles on SiO$_2$ NPs.
Figure 3.13 *in-situ* FTIR spectra achieved after 1st, 3rd, 5th and 10th TEOS/Water cycles. Only a selected list of spectra from 1st, 3rd, 5th, and 10th of TEOS/H₂O cycles are presented to save space. The dashed lines at 3800-3600, 3000-2800, and 1394 cm⁻¹ are the guide lines for O-H stretching region, C-H stretching region, and the vibrational mode of molecular TEOS, respectively.

Upon the first TEOS exposure, a negative O-H stretching absorption was observed at 3739 cm⁻¹, indicating that the hydroxyl (-OH) groups of SiO₂ NP have successfully reacted with the incoming TEOS precursor. The adsorption of TEOS is also evident from the appearance of positive absorbance in the C-H stretching regions at 2979, 2937, and 2900 cm⁻¹ from the surface Si(OCH₂CH₃)* species (Ferguson et al. 2004). The positive peak observed at 1394 cm⁻¹ the vibrational mode observed from the molecular TEOS (Mondragón et al. 1995). Following subsequent H₂O exposure, a small decrease in C-H stretching absorbance was observed with a small positive absorbance of O-H stretching region at 3739 cm⁻¹. These IR responses indicate that the H₂O exposure do not result in effective removal of the surface ethoxy (-OCH₂CH₃) ligand. Such incomplete of the hydroxylation of the surface silicon-ethoxy (Si-OCH₂CH₃) group
from di- and triethyl orthosilicate species agreed with other literature results (Ruckenstein et al. 1996; Jitianu et al. 2003; Venkateswara Rao et al. 2004; Sequeira et al. 2007). Consequently, this partial removal of the surface ethoxy group translates to inefficient regeneration of surface hydroxyl group (-OH) to propagate surface reactions upon alternative exposures of TEOS/H$_2$O to deposit SiO$_2$. With increasing number of TEOS/H$_2$O cycles, the changes observed in absorption features for O-H and C-H regions were significantly reduced which are well represented in the integrated absorbance shown in Figure 3.14.

![Figure 3.14](image)

The changes induced upon continuous exposures of TEOS/H$_2$O for both O-H and C-H regions diminished over increasing number of ALD cycles, ultimately reaching a plateau. These results supports the observation that the ethoxy ligand (-OCH$_2$CH$_3$) of the surface TEOS specie (Si(OCH$_2$CH$_3$)$^*$) fails to regenerate the necessary surface hydroxyl groups even after numerous H$_2$O exposures. With increasing number of TEOS/H$_2$O cycles, the partially hydroxylated ethoxy
surface specie is unreactive to both TEOS and H₂O. As such, alternating exposures of TEOS/H₂O chemistry do not result in self-limited surface reactions required to deposit SiO₂ by ALD. The surface reactions observed by in-situ FTIR from continuous alternative exposures of TEOS/H₂O is depicted in Figure 3.15:

![Figure 3.15 Schematic representations of the surface reactions observed during alternating exposures of TEOS/H₂O on SiO₂ nanoparticles via in-situ FTIR spectroscopy. The ALD growth of SiO₂ is unattainable due to incomplete oxidation of the ethoxy (-OCH₂CH₃) ligand and incomplete regeneration of the surface -OH group.](image)

It is noteworthy to mention that the surface chemistry observed for TEOS/H₂O is vastly different from that observed from ALD of Al₂O₃ by TMA/H₂O (Section 3.1) and LiOH by LTB/H₂O (Section 3.2) where ALD growth of both materials was self-limited by the saturated surface reactions during each precursor/oxidant exposure. In summary, while alternating exposures of TEOS/H₂O does not result in ALD growth of SiO₂, in-situ FTIR study on TEOS/H₂O offered valuable insights as to why such growth is unattainable.

3.4 Mechanistic Study on ALD of AlₓSiₙO by TMA/H₂O/TEOS/H₂O Chemistry

The inability to deposit ALD SiO₂ by TEOS/H₂O is then a major bottleneck if the material of interest, lithium aluminosilicate (LiₓAlₙSiₙO, LASO) is to be deposited as a solid solution of constituents. One of potential solution to overcome such problem is to induce ALD deposition of SiO₂ as a complex oxide by implementing a suitable silicon precursor with other ALD chemistries as previous discussed in Section 1.4.3.
With such aim, the growth of SiO\textsubscript{x} film was thus approached as a complex oxide. ALD deposition of Al\textsubscript{x}Si\textsubscript{y}O was investigated by incorporating the well-established ALD process of Al\textsubscript{2}O\textsubscript{3} by TMA/H\textsubscript{2}O to TEOS/H\textsubscript{2}O chemistry. Figure 3.16 shows the growth rates observed by spectroscopic ellipsometry (SE) from alternating exposures of TEOS/H\textsubscript{2}O/TMA/H\textsubscript{2}O on a Si(100) substrate at 225 °C.

![Graph showing growth rate of ALD films obtained by spectroscopic ellipsometry](image)

Figure 3.16 Growth rate of ALD films obtained by spectroscopic ellipsometry by alternating pulses of TEOS/H\textsubscript{2}O (■), TMA/H\textsubscript{2}O (●), and TEOS/H\textsubscript{2}O/TMA/H\textsubscript{2}O (▲) at 225 °C on a Si(100) substrate. An enhanced growth rate of 1.83 Å/cycle was observed for ALD of Al\textsubscript{x}Si\textsubscript{y}O by TEOS/H\textsubscript{2}O/TMA/H\textsubscript{2}O.

Alternative exposures of TEOS/H\textsubscript{2}O/TMA/H\textsubscript{2}O resulted in a growth rate of 1.83 Å/cycle, which was higher than the growth rate of 1.1 Å/cycle previously observed from ALD of Al\textsubscript{2}O\textsubscript{3} by TMA/H\textsubscript{2}O (Section 3.1). To investigate whether such difference is from an incorporation of SiO\textsubscript{2}, XPS spectra were obtained from ALD films deposited by alternating exposures of TEOS/H\textsubscript{2}O/TMA/H\textsubscript{2}O on a Ge(100) substrate.
Figure 3.17 X-ray Photoelectron Spectroscopy (XPS) spectra of ALD films grown by alternating pulses of TEOS/H\textsubscript{2}O (---), TMA/H\textsubscript{2}O (--), and TEOS/H\textsubscript{2}O/TMA/H\textsubscript{2}O (---) on a Ge(100) substrate at 225°C. The deposition of SiO\textsubscript{2} in Al\textsubscript{x}Si\textsubscript{y}O was confirmed from the presence of Si 2p photoemission peak at ~102.3 eV for the ALD film deposited by alternating exposures of TEOS/H\textsubscript{2}O/TMA/H\textsubscript{2}O.

While alternating exposures of TEOS/H\textsubscript{2}O did not show any growth of SiO\textsubscript{2} (as evident from the lack of Si 2p photoemission peak at ~102 eV), alternating exposures of TEOS/H\textsubscript{2}O/TMA/H\textsubscript{2}O resulted in a film that show Si 2p photoemission peak at 102.3 eV. This indicates that the deposition of SiO\textsubscript{2} as a complex oxide of Al\textsubscript{x}Si\textsubscript{y}O is feasible. The Al:Si ratio for ALD Al\textsubscript{x}Si\textsubscript{y}O deposited one cycle of TEOS/H\textsubscript{2}O followed by one cycle of TMA/H\textsubscript{2}O was found to be 1:0.39 by XPS compositional analysis.

To understand the difference in the surface mechanism of TEOS/H\textsubscript{2}O/TMA/H\textsubscript{2}O chemistry that enables the deposition SiO\textsubscript{2} in of a complex Al\textsubscript{x}Si\textsubscript{y}O film, \textit{in-situ} FTIR spectroscopy was performed during each precursor and H\textsubscript{2}O exposures in TEOS/H\textsubscript{2}O/TMA/H\textsubscript{2}O chemistry on ZrO\textsubscript{2} nanoparticles (NPs). The \textit{in-situ} difference FTIR spectra obtained from two global cycles of TEOS/H\textsubscript{2}O/TMA/H\textsubscript{2}O exposures are shown in Figure 3.18.
Figure 3.18 *in-situ* difference FTIR spectra obtained from two global cycles of TEOS/H₂O/TMA/H₂O on ZrO₂ NPs at 225 °C. The FTIR spectra were obtained following each TEOS, H₂O, TMA, and H₂O exposure. Dashed lines at 3800-3700, 3000-2800, 1394, 1214 cm⁻¹ represent O-H stretching region, C-H stretching region, Al-CH₃* deformation and vibrational modes of molecular TEOS respectively.

The IR responses obtained from the 1st TEOS/H₂O cycle (TEOS(1)/H₂O(1)) have shown equivalent IR responses observed for that of TEOS/H₂O chemistry previously presented in Section 3.3. Similarly, TMA exposure that followed (TMA(2)) showed IR responses observed were identical to that previously presented in TMA/H₂O chemistry in Section 3.1. The notable difference in IR response from TEOS/H₂O/TMA/H₂O chemistry (when compared to TMA/H₂O and TEOS/H₂O chemistries themselves) was observed upon H₂O exposure after the preceding TEOS/H₂O/TMA exposures. Figure 3.19 shows a detailed regional *in-situ* FTIR difference spectra obtained after H₂O (Spectrum H₂O (2) of Figure 3.18) that followed preceding TEOS/H₂O/TMA exposures. IR responses obtained from TMA/H₂O (Section 3.2) and TEOS/H₂O (Section 3.3) chemistries as well as a simulated IR spectrum constructed from a linear superimposition of the experimental TMA/H₂O and TEOS/H₂O chemistry with the
relation of 2(TMA/H₂O)+1(TEOS/H₂O) are also shown for comparison. All spectra were normalized to its peak intensity to show all spectra on same graph.

Figure 3.19 Regional in-situ difference FTIR spectra of TEOS/H₂O/TMA/H₂O (—), compared to that of TEOS/H₂O (—) and TMA/H₂O (—) chemistries. The simulated FTIR spectra (—) constructed from a linear superimposition of the experimental TMA/H₂O and TEOS/H₂O chemistry with the relation of 2(TMA/H₂O)+1(TEOS/H₂O) is also shown for comparison.

The detailed IR responses from C-H region of H₂O exposure following the preceding TEOS/H₂O/TMA exposures showed five distinctive negative absorptions at peaks at 2979, 2933, 2902, 2858, and 2831 cm⁻¹. Such IR response is different to that observed for TEOS/H₂O (Figure 3.13) and TMA/H₂O chemistries (Figure 3.1), where both chemistries generate only three absorption peaks in C-H region upon H₂O exposure. The observed IR responses for TMA/H₂O, TEOS/H₂O, and TEOS/H₂O/TMA/H₂O chemistries are summarized in Table 3.1.
Table 3.1 IR absorbances observed during TMA/H₂O, TEOS/H₂O, and TEOS/H₂O/TMA/H₂O ALD cycles and their assignments

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<td>1394</td>
<td>Vibration mode from molecular TEOS[^4]</td>
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[^1]: (Comstock et al. 2012),[^2]: (Rai et al. 2010),[^3]: (Klaus et al. 2000) [^4]: (Mondragón et al. 1995)

Upon a close comparison of C-H responses to TMA/H₂O and TEOS/H₂O chemistry, it was found that C-H stretching responses observed from TEOS/H₂O/TMA/H₂O chemistries consisted of the same peaks observed from both TEOS/H₂O and TMA/H₂O chemistry: the loss of absorption peaks at 2902 and 2831 cm⁻¹ were identical to those observed from the removal of surface methyl group (-CH₃) upon TMA exposure in TMA/H₂O chemistry (previously observed in Section 3.1). The remaining peaks at 2979, 2935, and 2902 cm⁻¹ were identical to those observed from the partial removal of surface ethoxy group (-OCH₂CH₃) in TEOS/H₂O chemistry (in Section 3.3). These results indicate that the H₂O pulse following TEOS/H₂O/TMA exposure not only removes the surface methyl group (-CH₃) but also the ethoxy group (-OCH₂CH₃) which did not undergo hydrolysis from the preceding TEOS/H₂O cycle. This removal of ethoxy (-OCH₂CH₃) should then be the key that enables the deposition of aluminosilicate (AlₓSiᵧO), with SiO₂ incorporation which is unattainable by TEOS/H₂O chemistry itself.
To investigate the surface mechanism of ALD AlₓSiᵧO more closely, integrated absorption responses were analyzed for TEOS/H₂O/TMA/H₂O chemistry for both O-H and C-H regions during two full cycles of TEOS/H₂O/TMA/H₂O as shown in Figure 3.20.

The H₂O exposure following TEOS/H₂O/TMA exposures results in a significant decrease of C-H absorption (3000-2800 cm⁻¹), compared that gained from the preceding TMA cycle. Additionally, the loss of C-H absorption from H₂O exposure following the TMA pulse was 65.4%, which was significantly higher than 20.7% observed from H₂O exposure from 1st TEOS/H₂O cycle. These C-H absorption responses closely correlated with the responses observed from O-H region as well: while the re-generation of the surface hydroxyl (-OH) group after H₂O pulse of TEOS/H₂O cycle was only 24.5%, that observed following H₂O pulse after TEOS/H₂O/TMA pulses was 60.2%. Continuous repetitions of TEOS/H₂O/TMA/H₂O cycles have shown that TEOS/H₂O sub-cycles continuously contributes to ALD cycle to grow SiO₂.
layers in Al$_x$Si$_y$O$_z$ film, where the adsorption and desorption of ethoxy ligands (-OCH$_2$CH$_3$) were repeatedly observed. These results are vastly different from the IR responses observed for TEOS/H$_2$O chemistry in Section 3.3 where the IR absorptions from both O-H and C-H regions become rather inactive after a few TEOS/H$_2$O cycles.

The surface mechanism observed from ALD of Al$_x$Si$_y$O by TEOS/H$_2$O/TMA/H$_2$O chemistry can then be summarized below. Following the first TEOS/H$_2$O exposure, a partial (~24.5 %) hydroxylation of ethoxy (-OCH$_2$CH$_3$) ligand takes place and regenerates the surface hydroxyl (-OH) as shown in Eq. (3.3):

\[
-\text{Si(OCH}_2\text{CH}_3)_3^* + \text{H}_2\text{O} \rightarrow -\text{Si(OCH}_2\text{CH}_3)_{3-x}(\text{OH})_x^* + x\text{CH}_3\text{CH}_2\text{OH}
\]  

where an asterisk (*) denotes surface species.

The subsequent TMA exposure then undergoes a surface reaction with the hydroxyl group of this partially hydroxylated ethoxy surface, generating Si-O-Al bond as observed from the disappearance of O-H stretching mode and appearances of IR responses from the surface Al-CH$_3^*$ during TMA exposure:

\[
-\text{Si(OCH}_2\text{CH}_3)_{3-x}(\text{OH})_x^* + \text{Al(CH}_3)_3 \rightarrow -\text{Si(OCH}_2\text{CH}_3)_{3-x}(\text{OAl(CH}_3)_2)_x^* + \text{CH}_4
\]  

(3.4)

The Al-CH$_3^*$ surface specie can undergo a facile hydroxylation reaction upon H$_2$O exposure, forming a Si-O-Al-OH bond as shown in Eq. (3.5):

\[
-\text{Si(OCH}_2\text{CH}_3)_{3-x}(\text{OAl(CH}_3)_2)_x^* + \text{H}_2\text{O (g)} \rightarrow -\text{Si(OH)}_{3-x}(\text{OAl(OH)}_2)_x^* + \text{CH}_4
\]

\[
+ \text{CH}_3\text{CH}_2\text{OH}
\]  

(3.5)

The presence of this newly formed Al-OH* surface specie also allows the propagation of disproportionation reaction with the nearby ethoxy (-OCH$_2$CH$_3$) ligand, forming a Si-O-Al bond by releasing a CH$_3$CH$_2$OH. Such mechanism is analogous to what have been reported in literature, where ethylamine (-CH$_2$CH$_3$N) ligand of hexakis(ethylamino)disilane (Si$_2$(NHC$_2$H$_5$)$_6$)
and t-butoxy (\(-\text{OC(\(\text{CH}_3\))}_3\)) ligand of tris(tert-butoxy)silanol (\(((\text{CH}_3)_3\text{CO})_3\text{Si}\)) are known to undergo a disproportionation reaction with Al-OH group to generate Al-O-Si bond by releasing C\(_2\)H\(_5\)ND (Tomczak et al. 2012) and (CH\(_3\))\(_3\)OH (Fang et al. 2013). The proposed surface reactions of TEOS/H\(_2\)O/TMA/H\(_2\)O presented in Eq. (3.3)-(3.5) are summarized in Figure 3.21:

![Proposed surface reactions based on FTIR results for Al\(_x\)Si\(_y\)O ALD using sequential exposures of TEOS/H\(_2\)O/TMA/H\(_2\)O at 225 °C.](image)

It is important to understand under what conditions the disproportionation takes place. From the proposed surface reactions (Eq. (3.3)-(3.5)), it can be hypothesized that the presence of a metal atom that is more electropositive than Si (\(\chi_{\text{Al}}=1.61 < \chi_{\text{Si}}=1.90\)) is what enables the disproportionation reaction. To investigate such hypothesis where the incorporation of SiO\(_x\) by removal of ethoxy ligand should only take place under the presence of an electropositive metal in vicinity of ethoxy ligand, the thickness changes in Al\(_x\)Si\(_y\)O films as a function of increasing number of TEOS/H\(_2\)O sub-cycles was studied. Figure 3.22 shows HRTEM images of 20 cycles of TEOS/H\(_2\)O, 20 cycles of TMA/H\(_2\)O, and Al\(_x\)Si\(_y\)O films with ALD cycles relation of [10(Al-O):x(Si-O)]\(\times\)2 on ZrO\(_2\) NPs where (Al-O) and (Si-O) denotes TMA/H\(_2\)O and TEOS/H\(_2\)O sub-cycles.
Figure 3.22 High Resolution TEM images of (a) 20 Cycles of (TEOS/Water), (b) 20 Cycles of (TMA/H$_2$O), and Al$_x$Si$_y$O$_z$ deposited on ZrO$_2$ NPs with ALD cycle ratios of (Al-O):(Si-O) cycle ratios of (c) (10:2) x2, (d) (10:4) x2, and (e) (10:8) x2 where (Al-O) and (Si-O) represent one TMA/H$_2$O and TEOS/H$_2$O cycles respectively. (f) Observed thicknesses of Al$_x$Si$_y$O$_z$ deposited on ZrO$_2$ NPs per one global cycle with as a function of (Si-O) cycles for ALD cycle ratio of 10(Al-O):x(Si-O).
The thickness increase due to TEOS/H₂O cycles saturated after 4 TEOS/H₂O cycles, at 2Å, supporting the hypothesis that desorption of –OCH₂CH₃ via disproportionation reaction only occurs with Al atom (χ_Al = 1.61) present in vicinity of ethoxy ligand.

3.5 Mechanistic Study on ALD of LiₓAlₓO by TMA/H₂O/LTB/H₂O Chemistry

In previous section, it was found that the ALD deposition of SiO₂ in AlₓSiₓO is feasible upon a presence of an electropositive Al atom in vicinity of Si-OCH₂CH₃*. The remaining questions that need to be answered to enable a successful deposition of LiₓAlₓSiₓO by ALD are then to investigate the surface mechanisms of the remaining tertiary oxides, LiₓAlₓO and LiₓSiₓO. This section investigates into the surface chemistry of ALD of lithium alumina (LAO, LiₓAlₓO) by alternating exposures of TMA/H₂O/LTB/H₂O.

The growth rate of LiₓAlₓO was first investigated via spectroscopic ellipsometry (SE). Figure 3.23 shows the growth rate response obtained by SE from alternating exposures of TMA/H₂O/LTB/H₂O on a Si(100) substrate at 225 °C. A growth rate of 2.3 Å/cycle was observed, matched with the expected growth rate of 2.3 Å/cycle from the linear sum of the growth rates of Al₂O₃ (1.1 Å/cycle) by TMA/H₂O (Section 3.1) and LiOH (1.2 Å/cycle) by LTB/H₂O (Section 3.2) chemistries.
Figure 3.23 Growth rate of ALD Li$_x$Al$_y$O obtained by spectroscopic ellipsometry by alternating pulses of TMA/H$_2$O/LTB/H$_2$O at 225°C on a Si(100) substrate. An enhanced growth rate of 2.3 Å/cycle was observed for ALD of Li$_x$Al$_y$O by TMA/H$_2$O/LTB/H$_2$O.

Figure 3.24 X-ray photoelectron spectroscopy spectra obtained from 200 cycles of TMA/H$_2$O/LTB/H$_2$O on a Si(100) substrate at 225 °C. (a) Survey and high resolution regional spectra for (b) Li 1s and (b) Al 2p regions. Photoemission peaks from Li 1s and Al 2p were well observed, indicating a successful ALD deposition of Li$_x$Al$_y$O.

*In-situ* QCM studies on ALD Li$_x$Al$_y$O by Aaltonen et al. and Comstock et al., reported that the TMA pulse following the preceding LTB/H$_2$O subcycle experiences higher reactivity...
than that during ALD of Al$_2$O$_3$ by TMA/H$_2$O, resulting in enhanced growth rate of ALD Li$_x$Al$_y$O (Aaltonen et al. 2011; Comstock et al. 2012). While these in-situ QCM studies offered some insights on the ALD growth of Li$_x$Al$_y$O, they did not provide the detailed surface mechanisms during the deposition. As such, in-situ FTIR spectroscopy studies have been conducted to investigate the underlying surface mechanisms that occur during ALD of Li$_x$Al$_y$O by TMA/H$_2$O/LTB/H$_2$O chemistry. Figure 3.25 shows in-situ difference FTIR spectra obtained during 3 global cycles of ALD Li$_x$Al$_y$O by TMA/H$_2$O/LTB/H$_2$O chemistry.

In contrast to the responses observed from ALD of Al$_x$Si$_y$O by TEOS/H$_2$O/TMA/H$_2$O chemistry (Section 3.4), alternating exposures of TMA/H$_2$O/LTB/H$_2$O showed repetitive, consistent IR responses for each TMA/H$_2$O and LTB/H$_2$O sub-cycles. The integrated absorbance of O-H and
C-H regions during 4 global ALD cycles of TMA/H₂O/LTB/H₂O chemistry is shown in Figure 3.26.

While continuous cycles of TMA/H₂O/LTB/H₂O demonstrated consistent surface mechanism for both O-H and C-H regions, the LTB/H₂O sub-cycle of TMA/H₂O/LTB/H₂O chemistry experienced a different adsorption/desorption mechanism than that observed from LTB/H₂O chemistry itself (Section 3.2).

Starting from TMA/H₂O terminated surface, LTB exposure resulted in a surface reaction shown in Eq. (3.6) where only about half (~56.5%) of the available surface hydroxyl (-OH) groups were consumed by LTB:

$$\text{Al-OH}^* + \text{LiOC(CH}_3)_3 \rightarrow \text{AlOH-LiOC(CH}_3)_3^* \quad (3.6)$$
Upon H₂O exposure, the tert-butoxy (-OC(CH₃)₃) terminated surface from Eq. (3.6) under goes hydrolysis, regenerating -OH group by releasing a tert-butanol (HOC(CH₃)₃):

\[
\text{AlOH-LiOC(CH₃)₃* + H₂O → Al-OH-LiOH* + HOC(CH₃)₃}
\]  
(3.7)

Such fractional adsorption of LTB is different to what was observed for LTB/H₂O chemistry in Section 3.2, where a full adsorption/desorption of tert-butoxy (-OC(CH₃)₃) ligand was observed for LTB/H₂O chemistry. The origin of such difference requires a further study with complementing techniques such as quadruple mass spectroscopy (QMS) or quartz crystal microbalance (QCM), as the surface chemistry of ALD LiₓAlᵧO is known to be a very complex function of various experimental parameters including the number of preceding sub-cycles of Al₂O₃/LiOH (Aaltonen et al. 2011), purge time (Cavanagh et al. 2010; Aaltonen et al. 2011; Kozen et al. 2014), competing surface reactions (Cavanagh et al. 2010; Kozen et al. 2014), et cetera. As ALD growth is known to be highly sensitive to the density of surface hydroxyl groups and steric hindrance experienced by the precursor (Langereis et al. 2006; Kim et al. 2011), it can be speculated the difference in surface mechanism arises from the different steric hindrance experienced by LTB following TMA/H₂O cycle than those experienced in ALD of LiOH by LTB/H₂O chemistry.

The TMA exposure in the following TMA/H₂O sub-cycle results in a complete consumption of all available surface hydroxyl (-OH) group, including those sites that did not react with LTB/H₂O cycle (during Eq. (3.6)) and those regenerated during previous LTB/H₂O cycle (during Eq. (3.7)), creating a methyl (-CH₃) terminated surface as shown in Eq. (3.8) and (3.9).
\[
\text{Al-OH}^* + \text{Al(CH}_3\text{)}_3 \to \text{Al-O-Al-CH}_3^* + \text{CH}_4 \quad (3.8)
\]

\[
\text{Li-OH}^* + \text{Al(CH}_3\text{)}_3 \to \text{Li-O-Al-CH}_3^* + \text{CH}_4 \quad (3.9)
\]

The consumption of both types of hydroxyl groups is apparent in integrated O-H spectra in Figure 3.26, where the changes O-H absorbance observed during H\textsubscript{2}O pulse of TMA/H\textsubscript{2}O cycle (~73%) after preceding TMA/H\textsubscript{2}O/LTB exposure is the sum of the surface -OH unreacted (~44%) during LTB exposure and those regenerated (~29%) from preceding LTB/H\textsubscript{2}O sub-cycle. This consumption of both hydroxyl groups provides detailed insights as to why TMA exposure following the LTB/H\textsubscript{2}O sub-cycle experiences higher reactivity than that observed during ALD of Al\textsubscript{2}O\textsubscript{3} with TMA/H\textsubscript{2}O.

Lastly, the H\textsubscript{2}O exposure that follows TMA pulse hydrolyzes all methyl (-CH\textsubscript{3}) terminated ligands, regeneration the surface hydroxyl group as shown in Eq. (3.10)

\[
\text{M-O-Al-CH}_3^* + \text{H}_2\text{O} \to \text{M-O-Al-OH}^* + \text{CH}_4 \quad (3.10)
\]

where M = Li or Al.

The surface reactions observed (Eq.(3.6)-(3.10)) during ALD of Li\textsubscript{x}Al\textsubscript{y}O by TMA/H\textsubscript{2}O/LTB/H\textsubscript{2}O are summarized in Figure 3.27:
It is noteworthy to mention that the H$_2$O pulse following TMA exposure not only regenerates the hydroxyl groups that was consumed via TMA in Eq. (3.8) and (3.9), but also releases the unreacted tert-butoxy (-OC(CH$_3$)$_3$) ligands that did not undergo hydrolysis after H$_2$O exposure. Such phenomenon is well observed in the integrated absorbance spectra in Figure 3.26(a), where the regeneration of the surface -OH region upon H$_2$O exposure following the precedent TMA/H$_2$O cycle is greater than the consumption of -OH region observed during the TMA exposure. The removal of the unreacted tert-butoxy (-OC(CH$_3$)$_3$) ligands from previous LTB/H$_2$O cycle upon H$_2$O exposure during the following TMA/H$_2$O cycle is speculated due to the shift of electron density of tert-butoxy ligands upon the presence of electropositive Al center, analogous to that observed previously in Section 3.4 for ALD of Al$_x$Si$_y$O via TEOS/H$_2$O/TMA/H$_2$O chemistry. Desorption of the unreacted butoxy ligands is also well observed in \textit{in-situ} difference FTIR spectra in Figure 3.28.
Figure 3.28 *in-situ* difference FTIR spectra observed during H₂O pulse in TMA/H₂O/LTB/H₂O chemistry (—–) in comparison to that observed in TMA/H₂O chemistry (—–) and LTB/H₂O chemistry (——). The guiding lines at 2970, 2902, and 2868 cm⁻¹, are C-H stretching absorbance observed during the removal of surface butoxy groups during LTB/H₂O chemistry.

The C-H IR responses observed from H₂O exposure TMA/H₂O/LTB cycle shows increased negative absorbance at 2970, 2902, and 2968 cm⁻¹ when compared to TMA/H₂O chemistry itself. These regions of increased negative absorbance corresponds to the C-H stretching observed from the removal of surface tert-butoxy (-OC(CH₃)₃) groups in ALD LiOH by LTB/H₂O. As such, it can be concluded that H₂O exposure following TMA exposure in TMA/H₂O/LTB/H₂O cycle results in removal of the unreacted tert-butoxy groups during the precedent LTB/H₂O sub-cycle. In summary, while the underlying surface mechanism of LiₓAlᵧO via TMA/H₂O/LTB/H₂O chemistry was found to be complex, it was found that ALD deposition of LiₓAlᵧO is feasible where the surface reactions are self-limited and continuous.
3.6 Mechanistic Study on ALD of Li₁ₓSi₃O by LTB/H₂O/TEOS/H₂O Chemistry

This section consists of the mechanistic study of Li₁ₓSi₃O, starting with in-situ FTIR study with alternating exposures of TEOS/H₂O/LTB/H₂O. Figure 3.29 shows in-situ difference FTIR spectra obtained during 1, 3, and 7 global cycles of alternating exposures of TEOS/H₂O/LTB/H₂O on ZrO₂ NPs at 225 °C.

Figure 3.29 in-situ difference FTIR spectra obtained during 1, 3, and 7 full cycles of TEOS/H₂O/LTB/H₂O for ALD of Li₁ₓSi₃O on ZrO₂ NPs at 225 °C.

Analogous to IR responses previously observed in Section 3.3 and 3.4, the first TEOS/H₂O cycle have shown the adsorption of TEOS precursor to the surface hydroxyl (-OH) group, followed by the partial hydroxylation of the surface Si-OCH₂CH₃* species. The LTB exposure on this partially hydroxylated ethoxy terminated surface showed no observable changes.

Such result is significantly different to that observed after TMA exposure on the same partially hydroxylated ethoxy surface from Section 3.4, where the formation of Si-O-Al-CH₃* was observed upon first cycle. In contrast, there was no change observed for LTB even after
prolonged exposure, indicating insufficient reactivity of LTB to the partially hydroxylated ethoxy terminated surface.

(a) TMA exposure to partially hydroxylated ethoxy terminated surface

(b) LTB exposure to partially hydroxylated ethoxy terminated surface

![Diagram](image)

Figure 3.30 Surface chemistry observed for (a) TMA and (b) LTB exposure to the partially hydroxylated ethoxy (-OCH$_2$CH$_3$) terminated surface

The IR responses following subsequent H$_2$O pulse did not show any observable changes as shown in Figure 3.29. The IR responses observed from continuous cycle of TEOS/H$_2$O/LTB/H$_2$O converged to the IR responses previously observed from TEOS/H$_2$O chemistry in Section 3.3, where the changes induced from both TEOS and H$_2$O become minimal upon the formation of passivated layer. These results indicate that ALD deposition of Li$_x$Si$_y$O via alternating exposures of TEOS/H$_2$O/LTB/H$_2$O is infeasible.

From ALD of Al$_x$Si$_y$O by TEOS/H$_2$O/TMA/H$_2$O (Section 3.4), it was found that the presence of electropositive metal atom in vicinity of the silicon-ethoxy (Si-OCH$_2$CH$_3^*$) surface specie facilitates the cleavage of the Si-O bond in which remains intact otherwise. To investigate such hypothesis for Li$_x$Si$_y$O system, an alternative approach was taken to study the presence of such phenomenon which may allow ALD deposition of Li$_x$Si$_y$O. ALD of Li$_x$Si$_y$O was therefore approached where LTB/H$_2$O sub-cycle was introduced first, to place Li$^+$ atom in vicinity of ethoxy ligands that should form during the following TEOS/H$_2$O cycle.
Figure 3.31 *in-situ* difference FTIR spectra obtained during the first 3 full cycles of LTB/H$_2$O/TEOS/H$_2$O for ALD of Li$_x$Si$_y$O on ZrO$_2$ NPs at 225 °C.

Figure 3.31 shows *in-situ* difference FTIR spectra obtained during the first 3 global cycles of LTB/H$_2$O/TEOS/H$_2$O exposures in attempt to deposit Li$_x$Si$_y$O by ALD on ZrO$_2$ NPs at 225 °C. The first LTB and subsequent H$_2$O exposure showed standard IR responses observed from successful adsorptions and desorptions of LTB precursor (as previously presented in Section 3.2): positive absorptions at 1200 cm$^{-1}$ and 2971 cm$^{-1}$ from C-O and C-H stretching. The consumption of the surface hydroxyl group was observed from the decrease of O-H stretching absorption between the regions of 3800-3700 cm$^{-1}$. The IR response observed upon subsequent H$_2$O exposure resulted in desorption of LTB ligands and regenerated the surface hydroxyl (-OH) group. The subsequent TEOS exposure showed the same IR responses to what was previously presented in Section 3.3, where positive absorbance in the C-H stretching were observed at 2979, 2937, and 2900 cm$^{-1}$ assigned to the surface Si(OCH$_2$CH$_3$)$^*$ species, with a decrease of surface hydroxyl group at ~3800-3700 cm$^{-1}$. In contrast to IR responses observed upon H$_2$O exposure in
TEOS/H₂O chemistry (Figure 3.13) or TEOS/H₂O/LTB/H₂O (Figure 3.29), the IR responses observed following the H₂O exposure after precedent LTB/H₂O/TEOS exposures showed a desorption of surface ethoxy group (©CH₃CH₃) which is well demonstrated in integrated absorbance shown in Figure 3.32:

Upon the H₂O exposure following LTB/H₂O/TEOS exposures, an enhanced regeneration of surface hydroxyl group was observed as evident from the strong recovery of O-H integrated absorbance, compared to the amount consumed during TEOS exposure. Such increased regeneration of the surface hydroxyl group resulted from an efficient desorption of ethoxy ligand. These results support the hypothesis that the Si-O bond of the silicon-ethoxy (Si-OCH₃CH₃*) surface specie is weakened upon the presence of an electropositive metal atom in vicinity, thus making the Si-O bond more likely to participate in hydrolysis upon H₂O exposure. The
difference in surface chemistry observed from TEOS/H\textsubscript{2}O/LTB/H\textsubscript{2}O versus that observed from LTB/H\textsubscript{2}O/TEOS/H\textsubscript{2}O is summarized in Figure 3.33.

(a) 
(b) 

Figure 3.33 Proposed surface mechanisms during the initial stage of (a) TEOS/H\textsubscript{2}O/LTB/H\textsubscript{2}O exposure and (b) LTB/H\textsubscript{2}O/TEOS/H\textsubscript{2}O exposures based on in-situ FTIR responses observed.

While the alternative exposures of LTB/H\textsubscript{2}O/TEOS/H\textsubscript{2}O resulted in ALD deposition of Li\textsubscript{x}Si\textsubscript{y}O, the reactivity of LTB and the regeneration of surface hydroxyl groups during LTB/H\textsubscript{2}O sub-cycle was significantly decreased with increasing numbers of global cycles of LTB/H\textsubscript{2}O/TEOS/H\textsubscript{2}O. As apparent in Figure 3.31, the changes induced by LTB/H\textsubscript{2}O sub-cycle during the second (LTB(3)/H\textsubscript{2}O(3)) and third (LTB(5)/H\textsubscript{2}O(5)) global cycles of LTB/H\textsubscript{2}O/TEOS/H\textsubscript{2}O was significantly diminished. Such decreased reactivity of LTB/H\textsubscript{2}O sub-cycle is also apparent in integrated absorbance of both O-H and C-H regions in Figure 3.32, where the changes induced by LTB/H\textsubscript{2}O sub-cycles was diminished over increasing numbers of global cycles. Owing to the ineffective regeneration of surface hydroxyl group during LTB/H\textsubscript{2}O
sub-cycle, the IR response observed from the repetitive exposures of LTB/H$_2$O/TEOS/H$_2$O cycle ultimately converges to that observed from TEOS/H$_2$O/LTB/H$_2$O chemistry, where the surface became inactive to both precursors and H$_2$O once the passivated layer is formed. The origin of such decreased reactivity of LTB deserves further studies with complementing in-situ techniques such as quartz crystal microbalance (QCM) and quadrupole mass spectrometers (QMS). Nevertheless, in-situ FTIR studies showed that ALD Li$_x$Si$_y$O is feasible through alternating exposure of LTB/H$_2$O/TEOS/H$_2$O. However, the insufficient regeneration of the surface hydroxyl group during LTB/H$_2$O sub-cycle limits continuous deposition of ALD Li$_x$Si$_y$O only to a first few global cycles. The differences observed from ALD Li$_x$Si$_y$O to that observed from ALD Li$_x$Al$_y$O are speculated due to increased steric hindrance experienced from both TEOS and LTB precursors during ALD of Li$_x$Si$_y$O. In ALD of Li$_x$Al$_y$O, the tert-butoxy ligand of LTB is the only bulky ligand. In ALD of Li$_x$Si$_y$O, however, both Li and Si precursors are based on bulky ligands (tert-butoxy ligand of LTB and tetraethoxy ligand of TEOS), which results in leading to ineffective adsorption of each precursors.

3.7 Investigation on Incubation Times in ALD of Li$_x$Al$_y$Si$_z$O

With detailed knowledge on the surface mechanisms of the constituents (Al$_2$O$_3$, LiOH, and SiO$_2$) and the related complex oxides (Al$_x$Si$_y$O, Li$_x$Al$_y$O, and Li$_x$Si$_y$O), ALD of Li$_x$Al$_y$Si$_z$O was investigated as a solid solution of the three constituents. In designing a multilayered oxide, however, it is essential to investigate the presence of incubation period, an initial growth regime where the growth of one oxide on the other may get inhibited. If ALD of Li$_x$Al$_y$Si$_z$O is to be deposited with a global cycle sequence of b(Al-O)-a(Li-O)-c(Si-O)-a(Li-O), it is important to examine the presence of incubation times of (1) LiOH on Al$_2$O$_3$, (2) SiO$_2$ on LiOH, and (3) LiOH and SiO$_2$. 
From Section 3.5, ALD of LiOH on underlying Al$_2$O$_3$ has been found to initiate from the first LTB/H$_2$O cycle indicating no presence of incubation time. Similarly, the first TEOS exposure on LiOH in TEOS/H$_2$O cycle (Section 3.6) was found to undergo immediate surface reaction with the underlying LiOH layer. Owing to insufficient reactivity of LTB on partially hydroxylated ethoxy terminated surface, however, the study of incubation time of ALD deposition of LiOH on SiO$_2$ was not investigated. To study the presence of incubation time on ALD of LiOH on SiO$_2$, therefore, ALD LiOH was deposited on SiO$_2$ nanoparticles (NPs), studied by in-situ FTIR. Figure 3.34 shows in-situ FTIR spectra obtained during 3 ALD cycles of LiOH by alternating exposures of LTB/H$_2$O on SiO$_2$ at 225 °C.

![FTIR spectra](image)

Figure 3.34 in-situ FTIR spectra obtained during x3 ALD cycles of LiOH by alternating exposures of LTB/H$_2$O on SiO$_2$ at 225 °C. Successful adsorption/desorption of LTB are apparent during the first LTB/H$_2$O cycle.

The IR absorbances obtained from 1$^{st}$ LTB exposure on SiO$_2$ NPs showed distinctive positive absorption C-H stretching peaks observed at 3000-2800 cm$^{-1}$ from the tert-butoxy ligand (Cavanagh et al. 2010; Comstock et al. 2012) indicating a successful adsorption of LTB to the
surface. The consumption of the surface hydroxyl group upon LTB exposure was also well observed, from the decrease of O-H stretching absorption between the regions of ~4000-3700 cm\(^{-1}\). A subsequent H\(_2\)O exposure resulted in desorption of LTB ligand and regeneration of surface hydroxyl groups. These results indicate that ALD of LiOH occurs upon the first LTB/H\(_2\)O cycle on SiO\(_2\) with no presence of incubation time. Table 3.2 summarizes the findings of incubation times for ALD of constituents on the other.

<table>
<thead>
<tr>
<th>Incubation time (cycle)</th>
<th>On Al(_2)O(_3)</th>
<th>On LiOH</th>
<th>On SiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>LiOH</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>1</td>
<td>1</td>
<td>X</td>
</tr>
</tbody>
</table>

The absence of incubation times for all of constituents on the other allows ALD deposition of Li\(_x\)Al\(_y\)Si\(_z\)O in alternating layers of constituent oxides, where the growth of each oxide starts from the first precursor/oxidant cycle. Such absence of incubation time are as expected as the hydroxyl groups on oxide surfaces are known to be reactive to organometallic precursors (George 2009). It has to be noted, however, there exists many ALD processes where incubation times need to be considered when depositing the material of interest. For example, while ALD of Al\(_2\)O\(_3\) via TMA/H\(_2\)O does not exhibit any incubation time when deposited on a hydroxylated oxide surfaces, up to 15 ALD cycles are needed to obtain ALD growth of Al\(_2\)O\(_3\) when deposited on hydrogen terminated silicon substrate (Si-H), (Tsai et al. 2003). Similar responses of low or no growth rate during the incubation stage ALD processes have been observed for ALD of ZrO\(_2\) (Tsai et al. 2003), HfO\(_2\) (Green et al. 2002), B\(_2\)O\(_3\) (Shen et al. 2012), et cetera.
3.8 In-situ FTIR Study of ALD of Li\textsubscript{x}Al\textsubscript{y}Si\textsubscript{z}O

With no incubation time observed for ALD of each constituents of on the other, ALD synthesis of Li\textsubscript{x}Al\textsubscript{y}Si\textsubscript{z}O has been approached as a solid solution of the three constituent oxides: Al\textsubscript{2}O\textsubscript{3}-LiOH-SiO\textsubscript{2}. Figure 3.35 shows an in-situ difference FTIR spectra of Li\textsubscript{x}Al\textsubscript{y}Si\textsubscript{z}O deposited on ZrO\textsubscript{2} NP at 225 °C by alternating exposures of 6(Al-O)-6(Li-O)-6(Si-O).

![Figure 3.35](image)

Figure 3.35 in-situ difference FTIR spectra of Li\textsubscript{x}Al\textsubscript{y}Si\textsubscript{z}O deposited on ZrO\textsubscript{2} NP at 225 °C by alternating exposures of 6(Al-O)-6(Li-O)-6(Si-O). Spectra were obtained during 1\textsuperscript{st}, 3\textsuperscript{rd}, and 6\textsuperscript{th} cycles of each constituents. Depositions of constituents Al\textsubscript{2}O\textsubscript{3}, LiOH and SiO\textsubscript{2} on the other are apparent upon completion of the first cycles.

Starting from ALD of Al\textsubscript{2}O\textsubscript{3} by TMA/H\textsubscript{2}O, the deposition of Al\textsubscript{2}O\textsubscript{3} was successfully obtained as evident from the IR absorbance identical to that presented previously in Section 3.1. ALD deposition of LiOH by LTB/H\textsubscript{2}O above the underlying Al\textsubscript{2}O\textsubscript{3} layer also demonstrated the successful adsorption of LTB precursor starting from the first cycle, followed by desorption of LTB ligands to regenerate the surface hydroxyl groups upon subsequent H\textsubscript{2}O pulse. Continuous cycle of LTB/H\textsubscript{2}O demonstrated stable and consistent deposition of LiOH, in alignment to what
was observed in Section 3.2. Lastly, TEOS/H$_2$O exposure on underlying LiOH layer also showed a successful adsorption of TEOS precursor, followed by regeneration of the surface hydroxyl groups upon H$_2$O exposure. Figure 3.36 shows a survey XPS spectrum obtained from ALD Li$_x$Al$_y$Si$_z$O film deposited on a Si(100) substrate at 225 °C with 15 global cycles with ALD sequence of 6(Al-O)-6(Li-O)-6(Si-O)-6(Li-O). The successful deposition of complex Li$_x$Al$_y$Si$_z$O film was confirmed from XPS spectra as shown in Figure 3.37 where the presence of photoemission peaks from all three metal elements of interest was confirmed: Li 1s at ~55 eV, Al 2p at ~75 eV, and ~102 eV for Si 2p. The observed composition of ALD Li$_x$Al$_y$Si$_z$O deposited with x15 global cycle with ALD sub-cycle sequence of 6(Al-O)-6(Li-O)-6(Si-O)-6(Li-O) was found to be Li$_{0.40}$Al$_{0.32}$Si$_{0.28}$O.

![Figure 3.36 A survey XPS spectrum of Li$_x$Al$_y$Si$_z$O film deposited by x15 global cycles of 6(Al-O)-6(Li-O)-6(Si-O)-6(Li-O) on a Si(100) substrate at 225 °C. Successful ALD deposition of Li$_x$Al$_y$Si$_z$O film was confirmed from the presence of photoemission peaks from all three metal elements at ~55 eV for Li 1s, ~75 eV for Al 2p and ~102 eV for Si 2p.](image-url)
Figure 3.37 High resolution regional XPS spectra of Li$_x$Al$_y$Si$_z$O film deposited by x15 cycles of 6(Al-O)-6(Li-O)-6(Si-O)-6(Li-O) on a Si(100) substrate at 225 °C: (a) Li 1s region, (b) Al 2p region, and (c) Si 2p region.

3.9 Summary

*In-situ* Fourier transform infrared spectroscopy (FTIR) has been successfully implemented to study the surface mechanisms during ALD depositions of Al$_2$O$_3$, LiOH, and SiO$_2$. The growth rate and surface mechanism observed for trimethylaluminum (TMA)/H$_2$O chemistry matched well to literature, demonstrating an ideal ALD chemistry based on self-limited surface reactions. The successful monitoring of ALD Al$_2$O$_3$ by TMA/H$_2$O laid the groundwork for the expansion of mechanistic studies to ALD processes of ALD LiOH and SiO$_2$. The ALD growth and its surface mechanism of LiOH by LTB/H$_2$O chemistry (Section 3.2) also demonstrated a near-ideal ALD growth based on the surface reactions involving adsorption/desorption of LTB precursor followed by the regeneration of the surface hydroxyl groups.

The mechanistic study of TEOS/H$_2$O chemistry (Section 3.3) revealed that ALD of SiO$_2$ by TEOS/H$_2$O is unattainable owing to the limited hydroxylation of the surface Si-OCH$_2$CH$_3$* species with H$_2$O as oxidant. The mechanistic study on the complex oxides of Al$_x$Si$_y$O, Li$_x$Al$_y$O, and Li$_x$Si$_y$O have revealed a presence of an electropositive metal atom in vicinity of metal-
organic ligands could result in enhanced desorption of ethoxy (-OCH$_2$CH$_3$) ligands on surface which does not undergo into hydrolysis upon H$_2$O exposure. While the shift of the electron density of the ethoxy ligand is postulated to be the reason for such results, additional studies should be followed to further understand these complex surface reactions. Nonetheless, the precise monitoring of the surface states following each ALD cycles through *in-situ* FTIR provided a comprehensive mechanistic studies on the novel ALD chemistries. Based on these results, ALD synthesis of lithium aluminosilicate (Li$_x$Al$_y$Si$_z$O) was successfully demonstrated as a solid solution of its constituent oxides.
CHAPTER 4: SYNTHESIS OF LiₓAl₃Si₂O THIN FILMS BY ALD

Lithium aluminosilicate (LiₓAl₃Si₂O, LASO) thin films were successfully synthesized via alternating ALD growth of its constituents, LiOH, Al₂O₃, and SiO₂ with a high thickness and composition control. The as-deposited amorphous ALD LiₓAl₃Si₂O film showed the desired physiochemical properties with tunable ionic conductivity values as close to ~1 × 10⁻⁷ S/cm. The ionic conductivity of as-deposited amorphous LASO was found to be a function of thickness, where its value increased with decreasing thickness. The activation energy for Li-ion transport of ALD LiₓAl₃Si₂O was 0.46-0.89 eV, comparable to that reported in literature. Crystallization of amorphous ALD LiₓAl₃Si₂O films was feasible upon a post-deposition thermal treatment, dependent upon other structural factors. A successful crystallization of β-LiAlSiO₄ was accomplished from ALD LiₓAl₃Si₂O deposited with a cycle sequence of 10(Al-O)-6(Li-O)-4(Si-O) on a Si(100) substrate upon a rapid thermal annealing at 900 °C under N₂. The crystallized β-LiAlSiO₄ had an epitaxial relationship of β-LiAlSiO₄ (1210) || Si(100) and β-LiAlSiO₄ (1010) || Si (001) to a Si substrate. An exceptional conformality of ALD LASO coating has been demonstrated on complex 3D structures including Si trenches, very high aspect ratio SiNWs, and aperiodic carbon nanotube frameworks. Successful synthesis and characterization of ALD LiₓAl₃Si₂O offered promising prospects of ALD synthesized LiₓAl₃Si₂O as a solid electrolyte for 3D Li-ion microbattery applications.
4.1 ALD of LiAlSiO$_4$

The ALD deposition of LiAlSiO$_4$ has been approached as a solid solution of three constituent oxides, LiOH, Al$_2$O$_3$, and SiO with a global ALD cycle sequence of (Al-O)-(Li-O)-(Si-O) where a, b, c represents the numbers of ALD subcycles for LiOH, Al$_2$O$_3$, and SiO$_2$ respectively. Figure 4.1 shows the growth rate observed for ALD LiAlSiO$_4$ film with the global ALD cycle sequence of 10(Al-O)-6(Li-O)-4(Si-O) as a function of global cycle numbers. The LiAlSiO$_4$ film was deposited on a gold-silica (Au|SiO$_2$) nanoparticle at 290 °C with its thickness studied via HRTEM imaging. A linear growth rate of 20.6 Å/global cycle has been observed, demonstrating excellent thickness controllability of ALD LiAlSiO$_4$ film.

![Figure 4.1](image)

Figure 4.1 The thickness of LiAlSiO$_4$ films grown on SiO$_2$/Au nanoparticles at 290 °C as a function of global cycle which composed of 10(Al-O)-6(Li-O)-4(Si-O). The film thickness was determined by HRTEM imaging.

To investigate the composition controllability of ALD Li$_x$Al$_y$Si$_z$O films, a compositional study has been followed by depositing various Li$_x$Al$_y$Si$_z$O films with different sub-cycle coefficients (a, b, c), while keeping the sum of the subcycles (a+b+c) to 20 for one global cycle.
To improve the accuracy in composition analysis, ALD $\text{Li}_x\text{Al}_y\text{Si}_z\text{O}$ films were deposited on a Ge substrate to avoid possible interference that may entail during analysis of Si 2p photoemission peak from $\text{Li}_x\text{Al}_y\text{Si}_z\text{O}$ film to that from the substrate if Si substrate were to be used. Figure 4.2(a) shows ultraviolet photoelectron spectroscopy (UPS) spectra of $\text{Li}_x\text{Al}_y\text{Si}_z\text{O}$ films deposited with 5 global cycles under varying ALD sub-cycle coefficients on a Ge substrate.

![Graph](image1)

**Figure 4.2** (a) UPS spectra of $\text{Li}_x\text{Al}_y\text{Si}_z\text{O}$ on Ge deposited via 5 global cycles of b(Al-O)-a(Li-O)-c(Si-O). (b) Calculated Li contents from the UPS spectra as a function of (Li-O) deposition cycle fraction $(a/(a+b+c))$.

Photoemission peaks from all three metal cations, Li 1s at 55 eV, Al 2p at 75 eV, and Si 2p at 102 eV were observed, demonstrating that ALD depositions of $\text{Li}_x\text{Al}_y\text{Si}_z\text{O}$ for various combinations of ALD sub-cycle coefficients were successful. Figure 4.3(b) shows the calculated atomic percentage of Li as a function of LiOH sub-cycle fraction, defined as the number of LiOH sub-cycle $(a)$ to the sum $(20)$ of ALD sub-cycles in one global cycle $(a/20)$. The Li atomic ratios showed a fairly distributed trend but exhibited a general trend where the Li atomic percentage increased with increasing LiOH ALD cycle fraction. Such result indicates further studies may be required to improve the composition controllability of ALD $\text{Li}_x\text{Al}_y\text{Si}_z\text{O}$ films.
4.2 Electrochemical Characterization of Li$_x$Al$_y$Si$_z$O

To be viable as a solid electrolyte, ALD LASO needs to be electrically insulative to ensure no electrical short occurs between the two electrodes while being ionically conductive. To investigate the electrical resistive response of Li$_x$Al$_y$Si$_z$O films, 6 and 10 nm LASO films ALD sequence of 10(Al-O)-6(Li-O)-4(Si-O) were deposited on a conductive indium-tin-oxide (ITO) substrate to investigate the suppression of redox peaks upon ALD coating. Figure 4.3 shows cyclic voltammogram curve obtained from 6 nm Li$_x$Al$_y$Si$_z$O deposited with the global cycle sequence of 10(Al-O)-6(Li-O)-4(Si-O) on ITO substrate.

Figure 4.3 Cyclic voltammetry characteristics of a clean ITO (dash line) and 6 nm LiAlSiO$_4$ coated ITO (solid line) in a solution of 1 mM ferrocene and 100 mM TBATFB in anhydrous PC.

For a bare ITO substrate, a sigmoidal redox current was present upon potential sweep from owing to electrons generated/lost during the redox reaction of ferrocene solution to the surface of ITO. For LASO coated ITO, however, the redox peaks from ferrocene/ferrocenium solution were completely suppressed by a 6 nm LASO film. Such result indicated that a 6 nm ALD Li$_x$Al$_y$Si$_z$O film was pinhole-free and electrically insulating.
4.3 Ionic Conductivity of Li$_x$Al$_y$Si$_z$O

To investigate ionic conductivity of ALD deposited Li$_x$Al$_y$Si$_z$O, impedance spectroscopy measurements have been performed on LASO films deposited on ITO substrate. Figure 4.4(a) shows Nyquist plots obtained from as-deposited ALD LASO films with 4 global cycles with a:b:c sub-cycle ratios of 16:2:2, 6:10:4, and 2:16:2.

![Nyquist plots](image)

(a) Nyquist plots measured for ~8 nm Li$_x$Al$_y$Si$_z$O films deposited on ITO substrates. The films have different compositions according to the local a, b and c cycles where a:b:c = 16:2:2 (▲), 6:10:4 (●) and 2:16:2 (○).

(b) The measured ionic conductivity for various LASO samples as a function of the lithium content. Lithium contents from various reference compositions are indicated as follows: (1) LiO$_2$-Al$_2$O$_3$-2SiO$_2$ (2) LiO$_2$-Al$_2$O$_3$-1.3SiO$_2$ (3) 1.3LiO$_2$-Al$_2$O$_3$-3.8SiO$_2$ (4) 4.3LiO$_2$-Al$_2$O$_3$-7SiO$_2$ (5) 4.3Li$_2$O-Al$_2$O$_3$-7SiO$_2$

Ionic conductivities of as-deposited LASO films were calculated by fitting an equivalent circuit of one capacitor and resistor in parallel as shown in inset of Figure 4.4(a). The calculated values of ionic conductivities of ALD Li$_x$Al$_y$Si$_z$O were in the range of $1.75 \times 10^{-9}$ to $7.22 \times 10^{-8}$ S/cm. While the observed values of ionic conductivity were lower than that reported for bulk, ALD synthesized Li-ion solid electrolytes demonstrated tunable ionic conductivities by adjusting
the number of ALD sub-cycles, where higher values of ionic conductivity were obtained from ALD LASO films with higher number of (Li-O) sub-cycles.

To study the effect of film thickness on ionic conductivity, ALD LASO films were deposited with varying thicknesses while keeping with the same ALD cycle sequence. Figure 4.5(a) shows Nyquist plots measured from LASO films with a cycle sequence of 10(Al-O)-6(Li-O)-4(Si-O) with thicknesses of 6, 10, and 12 nm.

![Figure 4.5(a) Nyquist plots measured for Li_xAl_ySi_zO films prepared via a global cycle sequence of 10 (Al-O)-6 (Li-O)-4 (Si-O) as a function of thickness (-□-: 6 nm, -●-: 10 nm, -△-: 12 nm), and (b) the thickness dependence of the room temperature ionic conductivity for the films in (a).](image)

The calculated values of ionic conductivity of ALD LASO as a function of thickness are shown in Figure 4.5(b). The ionic conductivity of LASO films was found to increase with decreasing film thickness. Such result is analogous to the results reported previously by Shin-ichi et al., where ionic conductivities of PLD LiAlSiO_4 films increased with decreasing film thicknesses between 7.5-1200 nm (Shin-ichi et al. 2004). The authors attributed increased ionic conductivity to various factors such as the increase of the charge carrier density due to a space charge, decrease in activation energy, modulation of the conductive path originated by a
structural disorder at the boundary, et cetera (Shin-ichi et al. 2004). Further works is still necessary to truly understand the origin of increased ionic conductivity with respect to decreasing thickness, however.

To understand the activation energy \( (E_a) \) of ionic conduction of ALD deposited \( \text{Li}_x\text{Al}_y\text{Si}_z\text{O} \) film, temperature dependent ionic conductivity measurements were conducted. Figure 4.6 shows Arrhenius plot generated from ionic conductivities obtained from ALD LASO film deposited with 5 global cycles of \( 10(\text{Al}-\text{O})-6(\text{Li}-\text{O})-4(\text{Si}-\text{O}) \) sequence as a function of temperature.

![Arrhenius plot](image)

Figure 4.6 Ionic conductivity as a function of temperature for ~10 nm LASO (●-) and LAO (▲-) films prepared via global cycle sequences of \( 10(\text{Al}-\text{O})-6(\text{Li}-\text{O})-4(\text{Si}-\text{O}) \) and \( 10(\text{Al}-\text{O})-6(\text{Li}-\text{O})-4(\text{Al}-\text{O}) \), respectively. The results are compared to LASO (Johnson et al. 1976; Raistrick et al. 1976) and LAO (Glass et al. 1980; Alessandrini et al. 1995) materials reported in the literature.

The \( E_a \) of ALD LASO was 0.89 eV calculated by the Arrhenius equation (Eq. (1.21)), which was in good agreement with reported values in literature for bulk \( \text{LiAlSiO}_4 \) (Nagel et al. 1982; Shin-...
ichi et al. 2004). To investigate the effect of SiO$_2$ content on ionic conductivity, ALD lithium alumina (Li$_x$Al$_y$O, LAO) with the same 5 global cycles but ALD SiO$_2$ sub-cycle was replaced by Al$_2$O$_3$ with a sequence of 10(Al-O)-6(Li-O)-4(Al-O) were also obtained for comparison. The activation energy of conduction, $E_a$ for ALD LAO film was 0.46 eV, which matched well to that of bulk Li $\beta$-Al$_2$O$_3$ (Glass et al. 1980) as well as ALD LiAlO$_2$ layers (Park et al. 2014). The lower value of activation energy for ALD LAO are as expected as the concentration of charge carriers are increases with decreasing SiO$_2$ content in Li$_2$O-Al$_2$O$_3$-SiO$_2$ family (Nagel et al. 1982; Bruce et al. 1997; Li et al. 2004).

4.4 Controlled Crystallization of LiAlSiO$_4$

While the as-deposited amorphous LASO films demonstrate adequate ionic conductive properties solid electrolyte applications for Li-ion microbattery, improvements on ionic conductivity could be made if crystalline $\beta$-LiAlSiO$_4$ films can be synthesized through a post-deposition annealing process. With such aim, studies on post-deposition annealing have been performed to investigate the thermal stability and feasibility inducing of film crystallizations on ALD Li$_x$Al$_y$Si$_z$O films.

Given the right composition, amorphous thin films can undergo crystallization upon post-deposition thermal treatments. To investigate crystallization behavior of ALD Li$_x$Al$_y$Si$_z$O films upon post deposition annealing, ALD Li$_x$Al$_y$Si$_z$O films with varying $a,b,c$ sub-cycle coefficients were deposited on a Si(100) substrate as mapped in a tertiary diagram shown in Figure 4.10(a).
Figure 4.7 (a) A deposition cycle map of LASO films on Si prepared by 5 global cycles of b(Al-O)-a(Li-O)-c(Si-O). (b) The corresponding compositional map, as determined by synchrotron UPS analysis, showing the cation contents varied with in-situ annealing temperatures: as-deposited (●), 500 °C (○), and 900 °C (●).

Figure 4.7(b) shows a compositional tertiary diagram obtained through synchrotron ultraviolet photoelectron spectroscopy (UPS) from ALD LiₓAlᵧSiᵸO samples from three different conditions: as-deposited, in-situ annealing to 500 °C, and in-situ annealing to 900 °C. For all in-situ annealed ALD LASO samples, a significant decrease of Li contents was observed with respect to increase in in-situ annealing temperature. Such decrease of Li content could arise from possible diffusion of Li ions into underlying Si substrate, owing to high intercalation capacity of Si (4200 mAh/g) (Chan et al. 2008). Formation of volatile Li species may play a role as well, as a similar loss of lithium upon a post-deposition annealing has been observed previously for ALD synthesized LiNbO₃ (Østreng 2014) and LiₓTiᵧO₂ (Miikkulainen et al. 2013) thin films.

To minimize the loss of Li upon post-deposition annealing process, a rapid thermal annealing (RTA) was chosen as an alternative to minimize the annealing time. Figure 4.8 shows synchrotron XRD spectra obtained from 10 nm LASO film as-deposited, after RTA annealing at
Figure 4.8: XRD spectra of 10 nm LiAlSiO$_4$ on Si (001) after post-deposition RTA at various temperatures, (1) as-deposited, (2) 500 °C and (3) 900 °C, for 90 seconds in N$_2$: (a) specular scans, (b) in-plane scans and (c) phi scan of 900 °C annealed film. (d) The corresponding UPS spectra to confirm the presence of cations, especially Li. Thin films were prepared using the 10(Al-O)-6(Li-O)-4(Si-O) sequence.
Specular XRD spectra (Figure 4.8(a)) showed that the as-deposited ALD LASO films were amorphous. The films remained amorphous even after RTA annealing at 500 °C. Upon RTA annealing at 900 °C, however, a crystallization of ALD LASO film observed. When aligned to Si (004) plane, ALD LASO after RTA 900 °C showed diffraction peaks at 1.39 Å⁻¹ and 2.78 Å⁻¹ identified as reflections from β-LiAlSiO₄ \((1\overline{1}0\overline{1})\) and \((20\overline{2}0)\) planes (JCPDS 01-077-0158) with d-spacing values of 4.52 Å and 2.27 Å respectively. In-plane XRD measurements on this crystallized ALD LASO film showed reflections from 2.4 Å⁻¹ and 4.8 Å⁻¹, from β-LiAlSiO₄ \((1\overline{2}10)\) and \((2\overline{4}20)\) planes aligned to Si (400) substrate peak. These XRD results indicated that ALD LASO has been crystallized in epitaxial relationship to the underlying Si substrate with a relationship of β-LiAlSiO₄ \((1\overline{2}10)\parallel\text{Si}(100)\) and β-LiAlSiO₄ \((10\overline{1}0)\parallel\text{Si} (001)\). The interfacial epitaxial relationship observed from ALD LASO upon post-deposition RTA treatment is depicted via a crystal model shown in Figure 4.9.

Figure 4.9 Crystal models showing the interfacial epitaxial relationship of β-LiAlSiO₄ on a Si (001) substrate: (a) side-view and (b) top-view.

4.5 Conformality of ALD LASO on complex 3D structures

For ALD LASO to be viable as a solid electrolyte for 3D electrodes (where some electrode configurations were shown previously in Figure 1.8), it should not only have desirable
physiochemical properties such as electrical insulation and sufficient ionic conductivity, but also requires to be synthesized conformally over complex 3D architectures. As such, ALD LASO films were deposited on complex 3D test structures including Si trenches, and very high AR Si nanowires (NWs), and aperiodic carbon nanotube network to study conformality. Figure 4.10 shows cross-sectional scanning electron microscope and high resolution transmission electron microscope (HRTEM) images of ALD LASO coating deposited on Si trench of 6 μm in depth.

Cross-sectional HRTEM images from the sidewall of Si trench showed a conformal ~11 nm thick LASO coating where the presence of ALD coating was also confirmed from Al Kα and O Kα emissions of energy dispersive x-ray spectroscopy (EDS) spectra. High conformality of ALD LASO has been confirmed on very high aspect ratio SiNWs (AR>200, Courtesy of Yang Group,
University of Colorado Boulder) (Figure 4.11, ) as well as aperiodic CNT network (Courtesy of Dunn Group, University of California, Los Angeles) (Figure 4.12).

Figure 4.11 Scanning electron microscope (SEM) image of ALD LASO coated high aspect ratio (AR) silicon nanowire (SiNW) (L: 10 μm, D: 40-50 nm, AR >200) and (b) high resolution transmission electron microscope image of showing conformal ~13 nm coating of ALD LASO on high AR SiNW.

Figure 4.12 Scanning electron microscope (SEM) images of (a) a bare carbon nanotube (CNT) framework and (b) after ~20 nm ALD LASO coating. An excellent conformity of ALD LASO coating has been demonstrated.

4.6 Summary

Lithium aluminosilicate (LiₓAlₓSiₓO, LASO) has been successfully synthesized by atomic layer deposition (ALD) as a solid solution of its constituents, LiOH, Al₂O₃, and SiO₂ with an excellent thickness and composition control. A crystalline β-LiAlSiO₄ film was synthesized
upon a post-deposition rapid thermal annealing for selected compositions of ALD Li$_x$Al$_y$Si$_z$O. The as-deposited amorphous ALD LASO film was pinhole-free on 2D structure, with tailororable Li-ion conductivities, up to $7.22 \times 10^{-8}$ S/cm for a 10 nm film. An excellent conformality of ALD LASO on complex 3D structures including Si trench, high aspect ratio SiNWs, and carbon nanotube (CNT) network was demonstrated. These results offer promising potentials of ALD synthesized LASO to be a viable candidate as a solid electrolyte for all-solid-state 3D Li-ion microbattery.
CHAPTER 5: INTEGRATION OF ALD Li$_x$Al$_y$Si$_z$O TO ELECTRODE MATERIALS

This chapter investigates integration of ALD Li$_x$Al$_y$Si$_z$O films to potential anode materials to delineate the potentials of ALD LASO as a solid electrolyte. ALD Li$_x$Al$_y$Si$_z$O coatings have been deposited on to various electrode materials to investigate physiochemical properties of electrode | ALD LASO nanocomposite system. ALD LASO coated 2D carbon electrode showed 95.7% suppression of redox currents demonstrating an exceptional conformality of ALD coating even on highly rough surface topology of 2D carbon electrodes. Galvanostatic charge-discharge study of 2D carbon | ALD LASO nanocomposite showed improved coulombic efficiency of 97.8%, than 90.9% observed from 2D carbon without ALD LASO coating. Integration onto 3D carbon array electrodes demonstrated high areal capacity of 7.36 mAh/cm$^2$, which was 6.75 times higher than the maximum areal capacity observed from 2D carbon electrode. Preliminary studies on integration of ALD LASO onto prospective high lithiation capacity anodes were investigated. In-situ HRTEM study of a thin (~ 6nm) film ALD LASO deposited SnO$_2$ nanowire showed ALD LASO coating resulted in suppression of the undesired Sn nanoparticles formation during SnO$_2$ lithiation process. In-situ HRTEM studies on ALD coated Si$_{0.6}$Ge$_{0.4}$ nanowire demonstrated that the deposition of a thicker ALD LASO coating may be sufficient to withstand large volumetric expansions of high lithiation capacity anodes. These results demonstrated the promising applicability ALD Li$_x$Al$_y$Si$_z$O coating not only as a solid electrolyte but also as an artificial protective coating that improves physiochemical and mechanical stability of electrode materials. Synthesis of organic-inorganic hybrid thin film solid electrolyte was explored to study the feasibility of developing a hybrid electrolyte system which may offer novel opportunities where a solid electrolyte based on a
single material system cannot offer. Li-ion conductive inorganic-organic hybrid thin film electrolyte was successfully synthesized by combining poly-(tetravinyltetramethylcyclotetrasiloxane) (PV4D4) film synthesized by initiated chemical vapor deposition (iCVD) with ALD synthesized Li$_x$Al$_y$Si$_z$O, with ionic conductivity of $1.76 \times 10^{-8}$ S/cm at 110 °C.

5.1 ALD Li$_x$Al$_y$Si$_z$O coating on 2D carbon slurry electrode

In previous chapter, ALD LASO has successfully demonstrated its ability on providing conformal coating on both 2D and 3D architectures. However, ALD depositions on highly rough surfaces have yet to be investigated. Such question needs to be addressed to implement ALD Li$_x$Al$_y$Si$_z$O coating on conventional electrode materials, which generally consists of high surface area nanoparticles with extremely rough surface topologies, mixed with additives including as a binder and cross-linker. The conventional graphite electrode is no exception, where an example of surface morphology of the carbon electrodes is shown in Figure 5.1(a). The composition of carbon electrode consists of 83% mesocarbon microbeads (MCMB), 7% carboxymethyl cellulose (CMC), 8% graphite and 2% Ketjen black.

![Figure 5.1 Scanning electron micrographs of (a) bare carbon slurry on a stainless steel current collector and (b) after ~20 nm of ALD LASO coating](image)
ALD Li$_x$Al$_y$Si$_z$O has been deposited on this 2D surface carbon electrode to study the conformality of ALD film under its highly rough surface topology. Figure 5.1(b) shows carbon slurry electrode after ~20 nm of ALD LASO deposition prepared via a cycle sequence of 10(Al-O)-6(Li-O)-4(Si-O). The rough morphology of carbon slurry was found to be well-preserved, indicating a conformal coating of ALD LASO. Successful deposition of ALD Li$_x$Al$_y$Si$_z$O on 2D carbon electrode was also confirmed via x-ray photoelectron spectroscopy (XPS) as shown in Figure 5.2.
Figure 5.2 (a) Survey and High resolution regional XPS spectra of Li\(_x\)Al\(_y\)Si\(_z\)O film deposited by [10(Al-O)-6(Li-O)-4(Si-O)]\(_\times\)5 at 225 °C on a carbon slurry electrode on a stainless steel current collector: (a) Li 1s region, (b) Al 2p region, and (c) Si 2p region.

To investigate the presence of pinholes in ALD films on these extremely rough surfaces, electrochemical responses of 2D Carbon | ALD Li\(_x\)Al\(_y\)Si\(_z\)O nanocomposite were investigated by cyclic voltammetry experiments. Figure 5.3 shows cyclic voltammetry responses obtained from both the bare 2D carbon electrode and 2D carbon electrode with ~20 nm of Li\(_x\)Al\(_y\)Si\(_z\)O coating.
Figure 5.3 Cyclic voltammetry characteristics of carbon slurry on a stainless steel current collector (dash line) and ~20 nm Li\textsubscript{x}Al\textsubscript{y}Si\textsubscript{z}O coated carbon slurries on a stainless steel current collector (solid line): (a) 1mM cobaltocenium hexafluorophosphate (CoC\textsubscript{p}\textsubscript{2}PF\textsubscript{6}, D: ~5.5 Å) and (b) 1mM decamethyl ferrocene (FeC\textsubscript{p}\textsubscript{2}\textsuperscript{*}, D: ~7.8 Å) in 100 mM Tetrabutyl ammonium tetrafluoroborate (TBATFB)/acetonitrile solution.

The cyclic voltammetry responses obtained from ALD LASO coated 2D carbon electrode showed excellent suppression of redox currents from both 1mM cobaltocenium hexafluorophosphate (CoC\textsubscript{p}\textsubscript{2}PF\textsubscript{6}, D: ~5.5 Å) and 1mM decamethyl ferrocene (FeC\textsubscript{p}\textsubscript{2}\textsuperscript{*}, D: ~7.8 Å) in 100 mM Tetrabutyl ammonium tetrafluoroborate (TBATFB)/acetonitrile solution. The mass normalized value of current response showed 95.7% suppression of redox currents upon ~20 nm ALD Li\textsubscript{x}Al\textsubscript{y}Si\textsubscript{z}O coating. Such result indicates that ALD Li\textsubscript{x}Al\textsubscript{y}Si\textsubscript{z}O can be deposited conformally even on highly rough and high surface area materials.

Following cyclic voltammetry test, galvanostatic (GV) charge-discharge tests were performed on 2D carbon | 20 nm Li\textsubscript{x}Al\textsubscript{y}Si\textsubscript{z}O film to investigate lithiation responses. Figure 5.4 shows GV responses obtained from 2D Carbon | LASO nanocomposite in 1M LiClO\textsubscript{4} in 50:50
ethylene carbonate (EC)/dimethyl carbonate (DMC) solution, with Li foils as reference and counter electrodes.

![Graph](image)

Figure 5.4 Galvanostatic charge-discharge response of ~ 20nm LASO deposited on 2D carbon slurry in 1M LiClO₄ in 50:50 EC/DMC solution with Li foils as reference and counter electrodes.

The 2D carbon | ALD LASO nanocomposite was able to lithiate and delithiate successfully, with calculated values of lithiation and delithiation capacity of 300.53 mAh/g and 293.91 mAh/g respectively. These values were slightly lower than lithiation capacity of 350.87 mAh/g and delithiation capacity of 318.93 mAh/g, observed from bare 2D carbon electrode. It is important to mention, however, the coulombic efficiency of LASO coated 2D carbon slurry was improved to 97.8%, which was higher than 90.9% observed from the bare 2D carbon slurry. Further studies of ALD LiₓAlᵧSiₓO directly on 2D carbon as a function of both compositions and thickness may offer further optimization of both lithiation/delithiation capacity and coulombic efficiency.
5.2 ALD Li$_x$Al$_y$Si$_z$O coating on 3D carbon array electrodes

With ALD coated LASO on 2D carbon slurry successfully demonstrated its conformal deposition and promising electrochemical results even on highly rough surfaces, studies on ALD coating on carbon electrodes have expanded to 3D carbon electrodes. The 3D carbon array electrodes were fabricated using carbon slurry with the same composition to 2D carbon electrode in Section 5.1. Detailed information on fabrication of 3D electrode can be found elsewhere (Cirigliano et al. 2014). Figure 5.5 shows scanning electron microscope images of a 3D carbon array electrode after ~20 nm of ALD LASO coating. Similar to ALD LASO coating on 2D carbon electrode, the rough surface topology of carbon slurries were found well preserved.

![Figure 5.5](image)

**Figure 5.5** Scanning electron microscope images of ~20 nm ALD LASO coated 3D carbon arrays. (a) Overview of ALD LASO coated 3D carbon arrays and (b) zoomed-in image of 3D carbon posts.

Figure 5.6 shows galvanostatic charge-discharge response obtained from ~20nm ALD LASO coated 3D carbon array electrode over C/50 rate. ALD LASO coated 3D carbon electrodes demonstrated high areal capacity 7.36 mAh/cm$^2$, which was 6.75 times higher than the maximum areal capacity of 1.08 mAh/cm$^2$ observed from 2D carbon electrode. ALD coated 3D carbon obtained 89.4% of areal capacity (7.36 mAh/cm$^2$), compared to the maximum areal capacity of bare 3D carbon electrode (8.23 mAh/cm$^2$). The 3D carbon post array | ALD LASO
nanocomposite showed the coulombic efficiency of 75.6 % which was lower than that observed from ALD LASO coated 2D carbon electrodes. The lower coulombic efficiency is speculated due to the loss of lithium through the formation of silver silicide with the conductive silver paste used to make contact from the base of 3D arrays to the current collector. While further works are necessary to optimize of 3D carbon | ALD LASO nanocomposite, these preliminary results offered promising prospectus of 3D Li-ion battery with ALD LASO as a solid electrolyte for carbon-based electrodes.

![Figure 5.6 Galvanostatic charge-discharge response of ~20 nm ALD LASO coated on CMC carbon arrays cycled obtained over C/50 rate.](image)

5.3 ALD Li$_x$Al$_y$Si$_z$O coating on SnO$_2$ nanowire

Tin oxides (SnO$_2$) have received much attention as attractive anode material owing to their high theoretical capacity (1491 mAh/g), good cyclability, and high coulombic efficiency (Courtney et al. 1997; Brousse et al. 1998; Mohamedi et al. 2001). Applicability of SnO$_2$ as anode material has been rather limited, however, owing to the undesirable formation of metallic
nano-Sn particles in a uniform matrix of Li$_2$O during lithiation via a two-step reaction (Zhang et al. 2012):

\[
\text{SnO}_2 + 4\text{Li}^+ + 4e^- \rightarrow \text{Sn} + 2\text{Li}_2\text{O} \tag{5.1}
\]

\[
\text{Sn} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{Sn} \tag{5.2}
\]

The small Sn particles from Eq. (5.1) are known to undergo agglomeration with if the alloying reaction shown in Eq. (5.2) does not proceed efficiently. The agglomerated Sn particles ultimately result in the loss of its contact with SnO$_2$ electrode, causing a loss of capacity (Li et al. 2011). Figure 5.7 shows in-situ image of a SnO$_2$ nanowire (NW) undergoing lithiation process where such formation and growth of Sn nanoparticles are well observed.

![Image of SnO$_2$ nanowire undergoing lithiation](image)

Figure 5.7 in-situ high resolution transmission electron microscope image SnO$_2$ NW during lithiation. The reaction front is marked with a red arrow. (Zhang et al. 2012)

To investigate whether the direct deposition of ALD LASO on SnO$_2$ could result in suppression of Sn nanoparticle formation, a ~6 nm ALD LASO was deposited over SnO$_2$ NWs with ALD sequence of 10(Al-O)-6(Li-O)-4(Si-O). Figure 5.8 shows a high resolution cross-sectional image of ~6 nm thick ALD LASO coating on SnO$_2$ nanowire.
Figure 5.8 High resolution transmission electron microscope of ~6 nm ALD LASO on SnO₂ nanowire.

Figure 5.9 shows a time-lapse HRTEM image of ALD LASO coated SnO₂ NW during lithiation where the ALD LASO coating demonstrated an exceptional suppression of Sn nanoparticle formation.

Figure 5.9 *in-situ* high resolution transmission electron microscope image of ALD LASO coated SnO₂ NW during lithiation. The reaction front is marked with a red arrow. (Zhang et al. 2012)

It was found that the suppression of Sn particle formation resulted from a fast Li⁺ transport on SnO₂ nanowire surfaces via ALD LASO coating, thus allowing much effective consumption of Sn atoms that formed during the first stage of SnO₂ lithiation (Eq. (5.1)). Such differences are well represented in the selected area electron diffraction (SAED) patterns of bare and ALD LASO coated SnO₂ NW after lithiation as shown in Figure 5.10.
Figure 5.10 Selected area electron diffraction (SAED) patterns from (a) bare SnO$_2$ nanowire (NW) prior to lithiation, (b) bare SnO$_2$ NW after lithiation, and (c) ~6 nm ALD LASO coated SnO$_2$ NW after lithiation. An excellent suppression of Sn particles were well-observed for ALD coated SnO$_2$ (Zhang et al. 2012)

In contrast to bare SnO$_2$ NW, the SAED response from ALD LASO coated SnO$_2$ showed no diffraction patterns from Sn particles. These results indicate that Sn particles formed during (5.1) gets effectively consumed during the second stage of lithiation reaction (Eq. (5.2)). While such result demonstrated promising potentials of ALD LASO on suppressing undesired side-reactions, the ALD coating pulverized upon the large volumetric expansion (~240 %) of SnO$_2$ as shown in Figure 5.11.
To be truly viable as a solid electrolyte, ALD LASO needs to withstand the volume expansion that occurs during lithiation. Deposition of thicker ALD LASO coatings or synthesis of an organic-ALD hybrid thin film electrolytes can be viable options. Nonetheless, ALD coating of SnO$_2$ offered promising potentials of the direct deposition of ALD synthesized solid electrolyte onto electrodes, where the electrochemical responses of electrode | ALD nanocomposite can be tailored to suppress undesired side reactions and/or to engineer desired electrochemical reactions via surface engineering.

5.4 ALD Li$_x$Al$_y$Si$_z$O coating on SiGe nanowire

Silicon is another prospective anode material for next generation Li-ion microbattery, owing to its high lithiation capacity of 3579 mAh/g. The development of Si based Li-ion battery has been lacking, however, owing to its large volumetric expansion upon lithiation, up to ~400%. To alleviate such large volume expansion of Si without sacrificing too much of its high lithiation
capacity, studies on synthesizing Si-alloy anode have been widely investigated. Silicon germanium (SiGe) is one of the promising candidates as germanium (Ge) offers high lithiation capacity of 1384 mAh/g (Bogart et al. 2013) providing improved volume expansion with its larger lattice parameter (5.62 Å) than Si (5.43 Å).

To investigate feasibility ALD LASO film as a solid electrolyte for high lithiation capacity anodes with large volume expansion, in-situ lithiation TEM studies have been conducted on SiGe nanowire (NWs) coated with ALD LASO. For a SiGe NW with similar magnitude of volume expansion, a thicker ALD LASO coating was deposited in attempt to avoid pulverization of ALD LASO film during SiNW lithiation. Figure 5.12 shows HRTEM micrographs obtained from Si_{0.6}Ge_{0.4} nanowire with a conformal ALD LASO coating with a thickness of ~32 nm.

![HRTEM micrographs](a) (b)

Figure 5.12 HRTEM micrographs obtained from an undoped SiGe nanowire with a composition of Si_{0.6}Ge_{0.4} deposited with ALD LASO coating. A conformal ALD LASO coating of ~32 nm is observed throughout the wire.
Upon lithiation of Si<sub>0.6</sub>Ge<sub>0.4</sub> nanowire, a significant volume expansion was observed as shown in Figure 5.13. The overall diameter of Si<sub>0.6</sub>Ge<sub>0.4</sub> ALD LASO nanocomposite increased from ~140 nm before lithiation to ~200 nm, resulting in 42.9% radial expansion.

![Figure 5.13 HRTEM micrographs of ALD LASO coated Si<sub>0.6</sub>Ge<sub>0.4</sub> NW (a) before lithiation and (b) after lithiation. A significant expansion of Si<sub>0.6</sub>Ge<sub>0.4</sub> ALD LASO nanocomposite is well observed.](image)

A close examination of Si<sub>0.6</sub>Ge<sub>0.4</sub> nanowire revealed that a thicker ALD Li<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>O (~32 nm) ALD coating on Si<sub>0.6</sub>Ge<sub>0.4</sub> remained intact even after lithiation, in contrast to what was observed from a thin (~6 nm) LASO coating from previous section. It is noteworthy to mention, however, some regions of Si<sub>0.6</sub>Ge<sub>0.4</sub> ALD LASO experienced morphological change of film as shown in Figure 5.14. The observed changes in film thickness and morphology are suspected due to the stress and elongation of ALD LASO film during volumetric expansion of lithiated Si<sub>0.6</sub>Ge<sub>0.4</sub> NW.
Figure 5.14 HRTEM micrographs of lithiated Si$_{0.6}$Ge$_{0.4}$ nanowire coated with ~32 nm ALD LASO. Changes on ALD LASO coatings are observed following the volume expansion from lithiation.

Selected area electron diffraction (SAED) experiments were conducted to study crystallographic changes of Si$_{0.6}$Ge$_{0.4}$ NW upon lithiation. Figure 5.15 shows SAED patterns obtained from Si$_{0.6}$Ge$_{0.4}$ NW before and after lithiation.

Figure 5.15 Selected area electron diffractions obtained from Si$_{0.6}$Ge$_{0.4}$ ALD LASO nanocomposite (a) before and (b) after lithiation. The crystallographic morphology of Si$_{0.6}$Ge$_{0.4}$ nanowire changes from single crystalline to amorphous upon lithiation.

The SAED features from bare Si$_{0.6}$Ge$_{0.4}$ prior to lithiation showed a crystalline pattern where the observed interplanar spacing values matched well to that projected by Vegard’s law,
which states that the lattice constant of an alloy is equal to a rule of mixtures of the two constituent’s lattice parameters (Vegard 1921):

\[ a_{A_{1-x}B_x} = (1-x)a_A + xa_B \]  

(5.3)

where \( a_{A_{1-x}B_x} \) is the lattice parameter of the solution, \( a_A \) and \( a_B \) are the lattice parameters of the pure constituents, and \( x \) is the concentration of B in the solution. The observed and projected lattice parameters of \( \text{Si}_{0.6}\text{Ge}_{0.4} \) alloy are summarized in Table 5.1.

<table>
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<th>Index</th>
<th>Si(^{[1]}) (Å)</th>
<th>Ge(^{[2]}) (Å)</th>
<th>( \text{Si}<em>{0.6}\text{Ge}</em>{0.4} ) (Projected)</th>
<th>( \text{Si}<em>{0.6}\text{Ge}</em>{0.4} ) (Experimental)</th>
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\(^{[1]}\): JCPDS: 01-080-0018, \(^{[2]}\): JCPDS: 00-004-0545

Crystallographic changes were observed from lithiated \( \text{Si}_{0.6}\text{Ge}_{0.4} \) NW, where its morphology changed from a single crystalline to amorphous, supporting the successful lithiation of \( \text{Si}_{0.6}\text{Ge}_{0.4} \) | ALD Li\(_x\)Al\(_y\)Si\(_z\)O nanocomposite with ALD Li\(_x\)Al\(_y\)Si\(_z\)O serving as a solid electrolyte. Further studies are still necessary to optimize the electrochemical responses of electrode | ALD Li\(_x\)Al\(_y\)Si\(_z\)O films. Nonetheless, a thicker ALD LASO coating demonstrated promising first steps on engineering ALD LASO as a solid electrolyte for high capacity anode materials such as Si and Ge.

5.5 Synthesis of an organic-inorganic hybrid thin film solid electrolyte

Although a thicker ALD LASO coating could be a viable option on implementing LASO as solid electrolyte for high capacity anodes with large volume expansion, there still exists questions on alternative approaches in designing a solid electrolyte that can accommodate the
large volume expansions more effectively. One promising approach involves synthesis of a hybrid inorganic-organic thin film solid electrolyte, where the mechanical and microstructural weaknesses of inorganic films can be accommodated by the organic films. As Li-conductive polymer films and metal oxides have distinct and complementary properties, a hybrid material based on the two may offer the advantages of both classes of materials. With such aim, study on the synthesis of a hybrid composite electrolyte has been explored by integrating ALD Li$_x$Al$_y$Si$_z$O with poly-(tetravinyltetramethylocyclo-tetrasiloxane) (PV4D4) films (Courtesy of Gleason Group, Massachusetts Institute of Technology), synthesized by initiated chemical vapor deposition (iCVD). Further details on the synthesis of iCVD can be found elsewhere (Chen et al. 2015). Figure 5.16 shows AFM topography of iCVD PV4D4 films on ITO substrate along with that of 28 nm thick ALD LASO film and iCVD-ALD hybrid film.

The as-deposited iCVD PV4D4 films had a root mean squared (RMS) roughness of 5.1 nm. In contrast, ALD LASO had much lower RMS roughness of 1.4 nm providing much smoother film on 2D substrate. The iCVD-ALD hybrid sample had RMS roughness of 5.1 nm, indicating that the surface morphology of iCVD sample is well-preserved after ALD coating.
To investigate ionic conductive behavior of a hybrid iCVD-ALD sample, impedance spectroscopy has been conducted. Figure 5.17 shows Nyquist impedance spectra obtained from the hybrid film of 20 nm iCVD PV4D4 with 28 nm ALD LASO film. A characteristic semi-circle was observed, indicating a successful synthesis of ionic conductive hybrid film. The calculated value of ionic conductivity for a \(~48\) nm hybrid iCVD-ALD film was \(1.76 \times 10^{-8}\) S/cm at \(110^\circ\)C which was lower than \(2.38 \times 10^{-7}\) S/cm observed from 28 nm ALD LASO film at the same temperature.

The lower ionic conductivity of iCVD-ALD hybrid film is speculated to be due to the interfacial resistance, analogous to what was observed for a hybrid electrolyte consisting of polymer-Lipon bilayer of poly(methyl methacrylate-co-poly(ethylene glycol) methyl ether methacrylate) (PMMA-EO) or poly[styrene-co-poly(ethylene glycol) methyl ether methacrylate] (PS-EO) with LiPON (Tenhaeff et al. 2011). The hybrid film with the configuration of Polymer-on-Lipon has resulted in a significant interfacial resistance whereas that of Lipon-on-polymer
configuration essentially eliminated the interfacial resistance. Such result delineates the importance of studies on the processing conditions and their effect on the resulting physiochemical property of the hybrid films. While observed ionic conductivity of iCVD-ALD film was lower than that of ALD film itself, the successful synthesis of ionic conductive organic-inorganic hybrid film offered promising prospects. Studies on the effect of different processing conditions are necessary for iCVD-ALD hybrid films to truly utilize merits from both materials while mitigating the shortcomings.

5.6 Summary

This chapter explored integration of ALD synthesized lithium aluminosilicate (Li$_x$Al$_y$Si$_z$O, LASO) thin films to electrode materials to explore their applicability as a solid electrolyte. ALD LASO coatings were conformal even on highly rough surface morphologies of 2D carbon electrode. The 2D carbon | ALD LASO nanocomposite demonstrated improved coulombic efficiency of 97.8% than 90.9% observed from bare 2D carbon electrode. ALD LASO coated 3D carbon electrode demonstrated a high areal capacity of 7.36 mAh/cm$^2$, which was 6.75 times higher than the maximum areal capacity observed from 2D carbon electrodes. Integration of ALD LASO to high capacity anode materials, SnO$_2$ and SiGe nanowires were studied by HRTEM with in-situ lithiation. The formation of undesired Sn nanoparticles that occur during lithiation of SnO$_2$ was completely suppressed for ALD LASO coated SnO$_2$, demonstrating novel opportunities from the direct deposition of ALD coating to electrodes can offer on improving the electrochemical stability of electrode materials. Physical integrity of ALD LASO coating was improved with increasing its thickness, even under the large volume expansion of Si$_{0.6}$Ge$_{0.4}$ NW upon lithiation. Preliminary studies on the synthesis of a hybrid
organic-inorganic thin film electrolyte were promising, where ionic conductive behavior in the order of $10^{-8}$ S/cm was observed for a hybrid film of ALD LASO deposited on iCVD PV4D4.
Atomic layer deposition of lithium aluminosilicate (Li$_x$Al$_y$Si$_z$O, LASO) was investigated, starting with the studies on surface mechanism of its constituents, LiOH, Al$_2$O$_3$, and SiO$_2$. The in-situ Fourier transform infrared spectroscopy (FTIR) studies provided in-depth understanding of ALD depositions of Al$_2$O$_3$ and LiOH. While the ALD deposition of SiO$_2$ by tetraethyl orthosilicate (TEOS) and H$_2$O chemistry was infeasible at low temperature, the depositions of SiO$_2$ containing complex oxides such as Al$_x$Si$_y$O and Li$_x$Si$_y$O were attainable from improved hydroxylation of ethoxy (-OCH$_2$CH$_3$) bond with electropositive atom presence in the vicinity. Studies on incubation time revealed no incubation time for each constituent oxide on another, where the ALD growth starts upon the first precursor/oxidant cycle. In-situ FTIR spectra were successfully obtained for ALD deposition of Li$_x$Al$_y$Si$_z$O, laying the groundwork for investigations on physiochemical properties of ALD synthesized LASO film.

Stoichiometric LiAlSiO$_4$ was synthesized with ALD cycle sequence of 10(Al-O)-6(Li-O)-4(Si-O) at 290°C, with a growth rate of 20.6 Å/global cycle. The as-deposited ALD LASO films were amorphous. ALD LASO films coated on ITO substrate was pinhole-free, confirmed by the suppression of redox current of ferrocene/ferrocenium solution. Ionic conductivities of Li$_x$Al$_y$Si$_z$O films were in the range $1.75 \times 10^{-9}$ to $7.22 \times 10^{-8}$ S/cm which were tunable by adjusting the number of ALD sub-cycles of its constituent oxides. The activation energy of ionic conduction of ALD synthesized films were in the range of 0.46-0.89 eV which was a function of the cation compositions. The as-deposited, amorphous ALD LiAlSiO$_4$ films crystallized to β-LiAlSiO$_4$ upon a post-deposition rapid thermal annealing (RTA) at 900 °C. An epitaxial relationship was realized for β-LiAlSiO$_4$ on Si(100) substrate, with a relationship of
β-LiAlSiO$_4$(1210) || Si(100) and β-LiAlSiO$_4$(1010) || Si(001). ALD LASO films on 3D structures, including Si trenches, Si NWs, and aperiodic CNT networks demonstrated the exceptional capability of ALD on synthesizing conformal LASO films on complex 3D structures.

Integration of ALD LASO films on to conventional and prospective anode materials have been investigated. The 2D carbon | ALD LASO nanocomposite demonstrated an improved coulombic efficiency of 97.8%, than 90.9% observed from 2D carbon electrode. ALD LASO coated 3D carbon electrode demonstrated a high areal capacity of 7.36 mAh/cm$^2$, which was 6.75 times higher than the maximum areal capacity observed from 2D carbon electrodes (1.09 mAh/cm$^2$). Integration of ALD LASO to SnO$_2$ and SiGe with high lithiation capacity was investigated via HRTEM with in-situ lithiation. The formation of undesired Sn nanoparticles that occur during lithiation of SnO$_2$ was completely suppressed for ALD LASO coated SnO$_2$ nanowire (NW), demonstrating promises of novel opportunities the direct deposition of conformal ALD coatings on electrodes can offer. A thicker ALD LASO coating on Si$_{0.6}$Ge$_{0.4}$ NW maintained its mechanical integrity even after the large volume expansion of Si$_{0.6}$Ge$_{0.4}$ NW upon lithiation, providing promising prospects on integration of LASO as a solid electrolyte even on high lithiation capacity electrodes. Successful synthesis of a hybrid organic-inorganic thin film electrolyte was obtained with ionic conductivity as high as 10$^{-8}$ S/cm was observed for a hybrid iCVD PV4D4-ALD LASO film.

Although ALD synthesis of LASO and preliminary results obtained from its integration to electrode materials have been favorable, further studies are necessary to realize the benefits of an ultra-thin film solid electrolyte. Various combinations electrode | ALD electrolyte systems must be investigated with respect to various physiochemical parameters, including their composition, morphology, microstructure, and architecture to develop a fully optimized
electrode-ALD LASO nanocomposite. Some of the major challenges that should not be overlooked in developing 3-D Li-ion microbattery based on electrode-LASO nanocomposite include 1) investigation of additional electrode and LASO combinations that would ensure both structural and cycling stability of the nanocomposite, 2) minimization of interfacial resistance at the electrode-LASO interfaces, 3) protection of short circuit at the edge of the cell, 4) establishing a good contact with the current collector, and 5) development of a final packaging step that is chemically and electrochemically stable with the active materials of the cell. These challenges can be solved effectively only by ALD. A successful synthesis of full-solid-state Li-ion battery where all active materials (anode, cathode, and electrolyte) of the cell are synthesized by ALD should provide new avenues of opportunity for Li-ion 3D microbatteries.
APPENDICES

A1.1 Diagram of LiₙAlₓSi₉O Atomic Layer Deposition Hot Wall Reactor Chamber

University of California, Los Angeles, Department of Chemical Engineering

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A1.2 Diagram of in-situ FTIR Atomic Layer Deposition Hot Wall Reactor Chamber

University of California, Los Angeles, Department of Chemical Engineering

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<td>Cement on Type K Thermocouple</td>
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<td>TT-K-24-100</td>
<td>PFA Insulated, 24 AWG, Type K Thermocouple</td>
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<td>Compact Push-in Connector, Receptacle, 250V AC, for .093” Diameter Pin</td>
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<td>Compact Push-in Connector, Plug, 250V AC, for .093” Diameter Pin</td>
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<td>.093” Diameter Pin, 22-18 AWG, for 250V AC Compact Push-in Connector</td>
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<td>High-Temperature Heat Cable, 36” Length, 125 Watts</td>
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<td>Type K Thermocouple Connector, Male</td>
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<td>USB-Based High-Voltage Relay Output</td>
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<td>5272K292</td>
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<td>5384K51</td>
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<td>Miniature Brass Fitting, 10-32 Thread, Slotted Head Plug</td>
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<td>Front Sleeve for 1/4&quot; Tube OD Brass Yor-Lok Tube Fitting</td>
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<td>Back Sleeve for 1/4&quot; Tube OD Brass Yor-Lok Tube Fitting</td>
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<td>Nut for 1/4&quot; Tube OD Brass Yor-Lok Tube Fitting</td>
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<td>300 VAC/VDC Terminal Block, 10 Circuits, 3/8&quot; Center-to-Center, 20 Amps</td>
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<td>FS-110-20-500</td>
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# A1.4 List of Parts for in-situ FTIR ALD Chamber

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<td>DST-531</td>
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<td>TCG-531</td>
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<td>Molecular Sieve Trap, In-Line</td>
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<td>FT-4-MS</td>
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<td>Molecular Sieve Replacement Material, Zeolite 13-X</td>
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<td>Leybold D16A Mechanical Direct Drive Pump</td>
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<td>DPW 275</td>
<td>Differentially Pumped IR Window Flange, 2.75 in. OD</td>
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<td>2-3/4 to 1-1/3 Zerolength Adapter</td>
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<td>409004</td>
<td>2-3/4&quot; Multiport Flange</td>
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<td>2.75&quot; Gate Valve, 1.5&quot;HV, Manual</td>
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<td>SocketHeadScrew/PlateNut, .75&quot;Lg</td>
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<td>2.75&quot; OD CF to 1/4&quot; MVCR Adapter</td>
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<td>414006</td>
<td>1.33&quot; OD CF to 1/4&quot; MVCR Adapter</td>
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<td>SS Medium-Flow Metering Valve, Vernier Handle</td>
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<td>SS-4BG-V51</td>
<td>SS Bellows-Sealed Valve, Spherical Stem Tip</td>
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<td>SS-DLV51</td>
<td>SS High-Purity High-Pressure Diaphragm-Sealed Valve</td>
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<td>316 SS VCR ¼ in. Female Nut</td>
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<td>SS-4-VCR-4</td>
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<td>SS-4-HCG</td>
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<td>Omega Engineering</td>
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<td>SSR330DC25</td>
<td>Solid State Relay (DC 25 Amp)</td>
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<tr>
<td>McMaster 69295K61</td>
<td>Compact Push-in Connector, Receptacle, 250V AC, for .093&quot; Diameter Pin</td>
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<tr>
<td>McMaster 69295K81</td>
<td>Compact Push-in Connector, Plug, 250V AC, for .093&quot; Diameter Pin</td>
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<tr>
<td>McMaster 69295K23</td>
<td>.093&quot; Diameter Pin, 22-18 AWG, for 250V AC Compact Push-in Connector</td>
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<td>McMaster 69295K33</td>
<td>.093&quot; Diameter Socket, 22-18 AWG, for 250V AC Compact Push-in Connector</td>
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<td>7587K941</td>
<td>Stranded Single-Conductor Wire, UL 1007/1569, 20 AWG, 300 VAC, Black</td>
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<tr>
<td>3641K26</td>
<td>High-Temperature Heat Cable, 96’ Length, 400 Watts</td>
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<td>3641K23</td>
<td>High-Temperature Heat Cable, 24” Length, 100 Watts</td>
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<tr>
<td>3641K24</td>
<td>High-Temperature Heat Cable, 36” Length, 125 Watts</td>
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<td>69145K68</td>
<td>Spade Terminal, Block, Vinyl Insulated, 22-18 AWG, #8 Screw/Stud</td>
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<td>Butt Splice, Nylon-Insulated Double-Crimp, 22-18 AWG</td>
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<td>Type K Thermocouple Connector, Female</td>
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<td>Type K Thermocouple Connector, Male</td>
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<td>Variable Voltage Output Transformer, Bench Top, 1440 VA, 120 VAC Input, 60 Hz</td>
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**Miscellaneous**

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<td>Fisher Scientific</td>
<td>AA10354BY</td>
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<td>International Crystal Laboratories</td>
<td>0002C-144</td>
<td>KBr Polished Disc – 13mm x 2mm</td>
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<td>0002C-150</td>
<td>KBr Polished Disc – 38 mm x 6mm</td>
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<td>UFC-1100A</td>
<td>Mass Flow Rate controller</td>
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<td>9924006</td>
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<td>Moisture-Resistant Polyethylene Vacuum Tubing, 1/16” ID, 1/8” OD, 1/32” Wall Thickness, Semi-Clear White, 50 ft. Length</td>
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<td>Chrome-Plated Brass Thread Pipe Fitting, 1/8 Pipe Size, Square Head Solid Plug</td>
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<td>Miniature Brass Fitting, 10-32 Thread, Slotted Head Plug</td>
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<td>National Instruments</td>
<td>NI USB-9481 USB-Based High-Voltage Relay Output</td>
<td></td>
</tr>
<tr>
<td>Omega Engineering</td>
<td>NI80-020-200 Resistance Heating Wire, Nickel-Chromium Alloy, 80% Nickel/ 20% Chromium, AWG 24</td>
<td></td>
</tr>
<tr>
<td>BARE-20-K-12</td>
<td>Bare wire thermocouple, Type K, 20 AWG</td>
<td></td>
</tr>
<tr>
<td>FS-260-12-500</td>
<td>Single hole fish spine, 500/PK (AWG12/0.081”)</td>
<td></td>
</tr>
<tr>
<td>FS-330-10-500</td>
<td>Single hole fish spine, 500/PK (AWG 10/0.102”)</td>
<td></td>
</tr>
<tr>
<td>FS-110-20-500</td>
<td>Single hole fish spine, 500/PK (AWG 20 / 0.032”)</td>
<td></td>
</tr>
</tbody>
</table>
A1.5 Custom Parts for FTIR ALD Chamber

Set 1: Two Pieces of Purge-Gas Line Fittings

- L: 3/16 inch
- OD: 1.375 inch
- ID: As large as possible
- 1/4 inch OD Pipe Welded
- Length: ~6 inch

Purge gas line fittings are placed between the vacuum chamber and the FTIR spectrometer. This guides the flow of purge gas into the spectrometer.

Set 2: Two Pieces of Alignment Base

- H: 2.263 inch
- L: 2.545 inch
- W: 0.985 inch

The alignment base is placed below the vacuum chamber gate valves to align the FTIR beam through the center of the chamber.

Set 3: Two Pieces of Hold-down Clamps

- W: 0.5 inch
- H: 4.865 inch
- R: 1.365 inch

Clamps are placed on the outside of the gate valves to hold the chamber onto the spectrometer base.
LabVIEW is a graphical programming language that uses nested “For” and “While” loops and sequences in order to accomplish tasks or gather data. A NI-USB 9162 module (which is referred to as DAQ in the program) is used to translate USB signals from LabVIEW to a switch for automation purposes. LabVIEW and the drivers for the DAQ need to be installed before plugging the device into the computer. The DAQ can have up to 4 channels (or switches) active for automating selected pneumatic valves on the chamber.

In LabVIEW programming, the DAQ operates on Boolean (true or false for each channel) within the “For” and “While” loops to activate and deactivate the switch for pneumatic valves on the chamber. Selecting the DAQ wizard in LabVIEW will help set up the module to connect with the program. To verify the DAQ in the program represents the connected controller, right-click the DAQ wizard, select “Properties”. A loading bar will appear to verify that the drivers were installed correctly. At the top of the display (the user-interface), there will be a “Play” button. Press this, and click “OK” to close out of the pop-up box. A loading bar will appear that verifies the program is communicating with the device.

There are two interface screens in LabVIEW that are primarily used to set up an automation program: the Front Panel, and the Block Diagram. The Block Diagram is used to assemble segments of the program to layout the pattern for a precursor deposition. For every precursor, there should be one “For” loop inside a larger “While” loop. For the Lithium Aluminum Silicate (LASO) chamber, each precursor is followed by a nitrogen purge pulse, as well as an oxidizing pulse, followed by another nitrogen purge. The graphic programming schematic of one aluminum precursor cycle is shown in Figure 1.

![Figure 1 - Block Diagram of Aluminum Precursor Deposition](image)

The second interface screen is the user interface for the program, or “Front Panel” (see Figure 2 below). This is where inputs regarding step time, duration, and number of repeats are entered for a deposition set. The steps for one cycle of precursor deposition are listed as follows:

1. Precursor exposure time.
2. Precursor pumpdown time.
3. Nitrogen purge time
4. Nitrogen purge pumpdown time
5. Oxidant (water) exposure time.
6. Oxidant pumpdown time.

The Nitrogen purge pumpdown time should be no less than 40 seconds due to the size of the chamber and limitations with the vacuum pumping system.

Each cycle for the precursor includes the precursor exposure and the oxidant exposure in atomic layer deposition. The number of repeats for each precursor cycle is indicated at the top of each column. There are four columns of precursors that can be used: aluminum (using trimethyl aluminum, or TMA), silicon (tris(tert-butoxy)silanol or TTBS), or lithium (lithium tert-butoxide or LTB). The columns are arranged in the following order: aluminum, lithium, silicon, lithium. This designates a global cycle.

If the precursor cycles are designated 10Al:3Li:6Si:3Li, then the deposition will contain 10 aluminum cycles, 3 lithium cycles, 6 silicon cycles, and lastly 3 lithium cycles. If the number of global cycles is 3, then then the pattern of 10Al:3Li:6Si:3Li will be repeated three times in the total deposition process. The Al capping cycles (the fifth column in the Front Panel view) are activated at the end of the last global cycle. This aluminum capping layer stabilizes the lithium-containing thin film somewhat in ambient atmosphere.
A2.1 Electrical Wiring for Temperature Control Heaters

A2.1.1 Introduction

The heaters on the lithium aluminosilicate (LASO) atomic layer deposition (ALD) chamber rely on high-temperature heat cables controlled by an Omega 7 Channel Temperature Controller (7CC). The Controller has a thermocouple connected to the LASO chamber which monitors the temperature of certain portions of the chamber. The Controller uses standard PID controls to ramp and maintain temperature on the LASO ALD chamber.

The output of the controller is intended to apply the necessary power to heating elements. Unfortunately, because the voltage is 5Vdc, the controller circuit is fed to solid state relays. When the temperature controller activates the circuit, the relay activates the 120Vac circuit containing the heating elements on the chamber.

![Figure 3 - Schematic of electrical wiring for temperature controlled heaters](image)

A2.1.2 Programming the Temperature Controller

Note: Before programming or checking a programmed profile, the Controller must be in “stopped” mode.

1) Enter programming mode of the Temperature Controller by first selecting the channel that needs to be programmed (by pressing CTR SEL on the controller panel).

2) Press and hold the CTR SEL key until the display states “EntEr PASSCOdE”.

3) The front keys are marked with a small digit in the lower right corner. Enter the pass-code combination: 3254.

4) Use the ▲▼ key until “PrOFILE” is displayed.
5) Push the PROG key.

6) The unit will display one of the channels with each push on the \( \updownarrow \) key ("CntrL 1", "CntrL 2", "CntrL 3", "CntrL 4", "CntrL 5", "CntrL 6", "CntrL 7") Select the desired controller, then push PROG to select it.

a) The display will briefly read “Strt SP” for ‘Start Setpoint’, and then the current value of the starting setpoint. Use \( \updownarrow \) and <DIG> keys to enter a desired value. The \( \updownarrow \) key increases and decreases the flashing digit, where the <DIG> key selects the next digit.

b) Press SETUP to go to next function.

c) The display will briefly read SetPt 1 and then the current value of Setpoint #1. Use \( \updownarrow \) and <DIG> to enter the desired value, then press PROG to go to the following function.

d) The display will read “EntEr t” for ‘Enter time’, and show the current time value. Time entered is the ramping time, or the time that it takes to ramp up to the set point (or soak time, if the previous and current setpoints are the same). The value shown for time is in minutes. Use \( \updownarrow \) and <DIG> to enter the desired value, then press PROG to go to the next function.

e) Repeat a-d to program setpoints #2 through #7. Once all 7 segments have been programmed, the display will revert back to the beginning of Programming mode selection. If all the seven segments are not used, the program can be aborted at any segment by pushing the EXT key. The segment in which EXT is pushed will be considered the end of the program. During Verify Program mode, the segment and all following segments are labeled as “PrG End”. \textbf{Note:} After entering the time for the last segment, go to the next segment and then hit EXT.

A2.1.3 Verify Mode

1) Verify mode is used to check previously programmed ramp/soak profile, or making small changes to a program. Enter programming mode, and press \( \updownarrow \) until “VErIFY” is displayed.

2) Press PROG.
3) Select the desired controller to verify by pressing ▲▼, then press PROG to step through the profile.
4) Use the ▲▼ and <DIR> as in steps 6a-e of the programming section to edit a program.
5) At any time, pressing EXT to exit Verify mode. Unlike other programming modes, exiting Verify does not mark the end of a profile program.

A2.1.4 Run Mode

1) To run a controller, select the controller by pushing CTR SEL key, followed by a push on RUN/STP.
2) Pushing CTR SEL will display “CntrL 1” for ‘controller 1’.
3) To select another controller, toggle CTR SEL until the desired controller is displayed.
4) To run a controller’s profile, push the RUN STP key until the unit displays “Ctr. rUn”. At this point the desired controller will run its programmed profile.
5) Once running, the controller can be put into an indefinite hold, or stopped.
6) To indefinitely hold a controller at any setpoint, press and hold the CTR SEL key at the desired controller, and simultaneously press SCN/HLD.
7) The controller will display “C# HOLd”.
8) The controller will hold this point until the unit is placed back in Run mode.
9) To stop a controller after it has been put in run mode, select the controller that needs to be stopped using the CTR SEL key to select the controller. Press RUN/STP once.
10) To stop all controllers at the same time, push CTR SEL and RUN/STP keys simultaneously.
A2.2 Electrical Wiring for Automatic Pneumatic Valve Control

The LASO ALD chamber automated deposition is possible through a LabVIEW program on a computer, and a set of circuits to activate a pneumatic valve on the chamber.

A solenoid is used to convert electrical impulses to pressurized air flow. In the LASO ALD chamber, electrical impulses come from an NI-USB-9481 (DAQ) interfaced with the LabVIEW automatic deposition computer program. The pressurized air operate the pneumatic valves on the chamber. A schematic of the solenoid channels are shown in Figure.

When the circuit is closed (by the manual switch on the solenoid box or the DAQ via LabVIEW), the solenoid valve is opened. Pressurized air then flows to the pneumatic valve by plastic tubing. The pneumatic valve opens when pressurized air is available. There are ten solenoid circuits (channels) in the solenoid box that can activate up to ten valves. Each DAQ can operate only four electrical channels. Two DAQ modules are used to operate the LASO ALD chamber.

![Figure 5 - Schematic of Electrical Wiring for Automated Pneumatic Valve Control](image)
A3.1 LASO ALD Hot Wall Reactor Chamber Operational Procedures

A3.1.1 Chemicals Used:

1. Trimethyl Aluminum (TMA)
2. Tetraethyl Orthosilicate (TEOS)
3. Lithium tert-butoxide (LTB)
4. Tris(tert-butoxy)silanol (TTBS)

A3.1.2 EMERGENCY SHUTDOWN:

1. Close all the precursor/reactant valves: LTB (Li), TEOS (Si), TMA (Al), Water
2. Stop LabVIEW program on the computer
3. Close the valves to the chamber (GV1,2,3)
4. Shut down all the electronics: Transformers, Mass Flow Controller control panel
5. Proceed to emergency exit locations

A3.1.3 OPERATING PROCEDURE:

- GV4, V2 and V12 – Valves controlling TMA flowrate, MFC channel 2
- V5, V8, and V11 – Valves controlling N\textsubscript{2} flow rates, MFC channel 4
- V4 – Valve controlling LTB
- M1 and V2 – Valves controlling water flowrate

Figure 6 - LASO Chamber Gas Line Schematic
1. **Initial Check:** Make sure all the valves are closed.

2. **Venting the reactor:**
   a. Isolate the chamber: Turn off V9 of Solenoid box, and close roughing valve. Untighten door so it can be opened.
   b. Flow nitrogen by setting N2 MFC Channel 4 to 10-15%.
   c. Open V10 and V8 on the Solenoid box. Open V5 to vent the chamber.
   d. Purge chamber with nitrogen for 10 minutes, or until the door can open without resistance.
   e. After venting, close V5 on Solenoid Box to the chamber.

3. **Sample loading:**
   a. Open the door of chamber and load the sample into the chamber. Make sure the sample is placed in the center of the reactor holder.
   b. Close the door and tighten the knob.
      Note: After loading, be sure to nitrogen purge before starting experiment. This removes water in the chamber that would interfere with water-sensitive precursors.

4. **Base pressure:** Slowly open the roughing valve, and allow the chamber pressure return to a base pressure lower than 65mTorr.

5. **Nitrogen Purge:** (*)
   a. Set channel 4 of MFC controller to 10-15%.
   b. Open V10 and V8 on the Solenoid box.
   c. Open V5 for 2 seconds, then close V5.
   d. Pressure will go up to 500 mTorr, then wait ~45 seconds until pressure returns to base pressure.
   e. Once base pressure is reached, repeat the procedure (* b-d) at least 2 more times (for a total of 3 times).
   f. Close V5, V8 and V10. Set N2 MFC to 0%.

6. **Heating:** *(Note: Heat chamber, gas lines, and precursor housings concurrently)*
   a. Chamber: Heat the chamber wall to 150°C by activating Ch7 of 7Channel Controller-1 (Denoted as 7CC-1 from now on). Also, activate Ch6 and Ch7 on 7Channel Controller-2 (denoted as 7CC-2 henceforth).
b. Gas Line heating: Heat the gas lines by activating the following channels:
   i. 7CC-1:Ch4: TMA/Water Gas line
   ii. 7CC-2:Ch2: LTB Gas line
   iii. 7CC-2:Ch4: TTBS Gas line

c. Sample stage heating: Heat the sample stage by turning Variable Transformer-1 (Denoted as VT-1 from now on), followed by activating Ch3 of 7CC-1

d. Precursor heating: Heat the precursors by activating corresponding channels of 7CC-1 listed below:
i. Lithium Tert-butoxide (LTB): Ch1 of 7CC-1
ii. Tris(tert-butoxy)silanol (TTBS): Ch3 of 7CC-2

Note: TMA and TEOS is maintained at room temperature

e. Doser heating: Heat the doser by turning Variable Transformer-2 (Denoted as VT-2 from now on), followed by activating corresponding channel of interest on 7-Channel Controller-2 (7CC-2)
   i. Ch1: LTB Doser

f. In summary, the following channels need to be activated for LASO deposition:
   i. 7CC-1: 1, 3, 4, 7
   ii. 7CC-2: 1, 2, 3, 4, 6, 7

Setpoint/ramping info of both 7CC-1 and 7CC-2 are listed below:

<table>
<thead>
<tr>
<th>Channel</th>
<th>Description</th>
<th>Start Pt</th>
<th>SP1</th>
<th>t1</th>
<th>SP2</th>
<th>t2</th>
<th>SP3</th>
<th>t3</th>
<th>SP4</th>
<th>t4</th>
<th>SP5</th>
<th>t5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lithium tert-butoxide (LTB)</td>
<td>25</td>
<td>80</td>
<td>20</td>
<td>80</td>
<td>15</td>
<td>160</td>
<td>20</td>
<td>160</td>
<td>2500</td>
<td>Pg</td>
<td>End</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>3</td>
<td>Sample Heater</td>
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<td>75</td>
<td>20</td>
<td>75</td>
<td>15</td>
<td>225</td>
<td>20</td>
<td>225</td>
<td>2500</td>
<td>Pg</td>
<td>End</td>
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<tr>
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<td>Additional Ch. (Gasline)</td>
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<td>45</td>
<td>20</td>
<td>45</td>
<td>15</td>
<td>60</td>
<td>20</td>
<td>60</td>
<td>2500</td>
<td>Pg</td>
<td>End</td>
</tr>
<tr>
<td>5</td>
<td>Cyclopentadineyl Manganese (Cp2Mn)</td>
<td>25</td>
<td>50</td>
<td>20</td>
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<td>15</td>
<td>75</td>
<td>20</td>
<td>75</td>
<td>2500</td>
<td>Pg</td>
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<tr>
<td>6</td>
<td>Water (H2O)</td>
<td>25</td>
<td>45</td>
<td>20</td>
<td>45</td>
<td>15</td>
<td>60</td>
<td>20</td>
<td>60</td>
<td>2500</td>
<td>Pg</td>
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<tr>
<td>7</td>
<td>Chamber</td>
<td>25</td>
<td>150</td>
<td>20</td>
<td>150</td>
<td>15</td>
<td>150</td>
<td>20</td>
<td>150</td>
<td>2500</td>
<td>Pg</td>
<td>End</td>
</tr>
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</table>
7CC-2 (As of 08/01/2014)

<table>
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<tr>
<th>Channel</th>
<th>Description</th>
<th>Start Pt</th>
<th>SP1</th>
<th>t1</th>
<th>SP2</th>
<th>t2</th>
<th>SP3</th>
<th>t3</th>
<th>SP4</th>
<th>t4</th>
<th>SP5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lithium tert-butoxide (LTB) Doser</td>
<td>25</td>
<td>80</td>
<td>15</td>
<td>80</td>
<td>10</td>
<td>160</td>
<td>20</td>
<td>160</td>
<td>2500</td>
<td>Pg</td>
</tr>
<tr>
<td>2</td>
<td>Lithium tert-butoxide (LTB) Gasline</td>
<td>25</td>
<td>80</td>
<td>15</td>
<td>80</td>
<td>10</td>
<td>160</td>
<td>20</td>
<td>160</td>
<td>2500</td>
<td>Pg</td>
</tr>
<tr>
<td>3</td>
<td>Tris(tert-butoxy)Silanol Gasline</td>
<td>25</td>
<td>50</td>
<td>15</td>
<td>50</td>
<td>10</td>
<td>75</td>
<td>20</td>
<td>75</td>
<td>2500</td>
<td>Pg</td>
</tr>
<tr>
<td>4</td>
<td>Tris(tert-butoxy)Silanol Housing</td>
<td>25</td>
<td>30</td>
<td>15</td>
<td>30</td>
<td>10</td>
<td>40</td>
<td>20</td>
<td>40</td>
<td>2500</td>
<td>Pg</td>
</tr>
<tr>
<td>5</td>
<td>Cyclopentadineyl Manganese (Cp2Mn) Doser</td>
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<td>15</td>
<td>50</td>
<td>10</td>
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<td>100</td>
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<td>15</td>
<td>150</td>
<td>20</td>
<td>200</td>
<td>150</td>
<td>Pg</td>
</tr>
</tbody>
</table>

7. Manual Deposition:

For LiAlSiO$_4$, alternate cycles of Al oxide (b cycles for each global cycle), Li oxide (a cycles for each global cycle), and Si oxide (c cycles for each global cycle). Deposit total of # global cycles. (Note: Aluminum deposit first because have good surface adhesion.)

*The procedures listed below are only for one cycle each! (Note: pump down time can be extended if need be, but cannot extend pulse time.)*

a. Li$_2$O Deposition
   i. Slightly open 45 of lithium precursor Li-t-butoxide, LTB, for 10 seconds. Pressure will increase by 5-10 mTorr.
   ii. Close valve V4 for 50 seconds for pump down time. Make sure chamber goes back to base pressure.
   iii. Before the pump down time of 60 seconds are up, open water valve M1 to setting of 10.
   iv. After the pump down time of 60 seconds, open valve V2 for 10 seconds. Watch the pressure, should increase to 100-200 mTorr, but make sure it does not go above 200 mTorr. (Note: water does not have MFC so vapor pressure can be high.)
   v. Close V2, then close M1 for water.
   vi. Pump down for 60 seconds till base pressure has been reached. (Note: if chamber has not reached the base pressure after pump down time of 60 seconds, then do a Nitrogen Purge Step by pulsing nitrogen in for 10 seconds.)

b. Al$_2$O$_3$ Deposition
   i. Open the valve V1 of Grey Solenoid Box for 5 seconds.
iii. Before the pump down time of 45 seconds are up, open water valve M1 to setting of 10.
iv. After the pump down time of 45 seconds, open valve V2 for 5 seconds. Watch the pressure, should increase to 100-200 mTorr, but make sure it does not go above 200 mTorr. (Note: water does not have MFC so vapor pressure can be high.)
v. Close V2, then close M1 for water.
vi. Pump down for 45 seconds till base pressure has been reached. (Note: if chamber has not reached the base pressure after pump down time of 60 seconds, then do a Nitrogen Purge Step by pulsing nitrogen in for 10 seconds.)

\[ \text{c. SiO}_2 \text{ Deposition} \]
(Note: if nitrogen purge was used in previous deposition, need to reset the MFC channel 4 to 3% before beginning deposition.)
i. Open V3
ii. Half way open the valve GV2 for 20 seconds. Pressure will increase to 200 mTorr.
iii. Close GV2, then close V3. Pump down for 60 seconds. Make sure chamber goes back to base pressure.
iv. Before the pump down time of 60 seconds are up, open water valve M1 to setting of 10.
v. After the pump down time of 60 seconds, open valve V2 for 15 seconds. Watch the pressure, should increase to 100-200 mTorr, but make sure it does not go above 200 mTorr. (Note: water does not have MFC so vapor pressure can be high.)
vi. Close V2, then close M1 for water.
vii. Pump down for 60 seconds till base pressure has been reached. (Note: if chamber has not reached the base pressure after pump down time of 60 seconds, then do a Nitrogen Purge Step by pulsing nitrogen in for 10 seconds.)

8. Automated Deposition
   a. Load LabVIEW program on the computer
      i. Open file “072913 – LASO and Al Capping Layer.vi”
      ii. Set number of cycles for the appropriate element.
         1. Each cycle includes a precursor pulse, nitrogen purge, water pulse, and another nitrogen purge.
         2. Times listed on each pulse step are not normally changed.
      iii. Set number of global cycles on the top of the worksheet. This loops the precursor pulses.
      iv. Check the temperatures on the Channel Controllers.
      v. Check sample in the sample holder.
      vi. Turn V9 on the Solenoid Box to “off”, and open V8 and V10 on the Solenoid box.
      vii. On the computer, press the white arrow on the toolbar to begin the programmed deposition.
9. Finishing the deposition:
   a. Close all MFC and valves.
   b. Turn off all the heating for chamber and precursor containers.
   c. Wait for the chamber to cool down to at least 50ºC. (This will take about ~2 hours; will take ~1 hour to cool down to ~80ºC.)
   d. Nitrogen Purge 3 times (See Step 5).

10. Sample unloading:
    a. Perform Steps 1 and 2.
    b. Open the chamber to unload the sample.
    c. If not loading sample in soon, then pump down the chamber (no need to do nitrogen purge if there is no sample).
A3.2 Operating Procedure of in-situ Fourier Transform Infrared Spectroscopy (FTIR) Chamber

A3.2.1 Chemicals Used:
   1. Trimethyl Aluminum (TMA)
   2. Tetraethyl Orthosilicate (TEOS)
   3. Lithium tert-butoxide (LTB)

A3.2.2 Emergency Shutdown:
   1. Close all the precursor/reactant valves: LTB (Li), TEOS (Si), TMA (Al), Water
   2. Close the valves to the chamber
   3. Shut down all the electronics: Transformers, Mass Flow Controller control panel
   4. Proceed to emergency exit locations

A3.2.3 OPERATING PROCEDURE:

![Overview of FTIR ALD Chamber](image)

Figure 11 - Overview of FTIR ALD Chamber

1. Initial Check: Make sure all the valves are closed
   a. Roughing Valve (RV), both Gate Valves (GV1 & GV2)
   b. Precursor Valves: LTB, TEOS, TMA valves

2. Venting the reactor:
   a. Isolate the chamber by closing the roughing valve (RV1)
   b. Flow nitrogen into the chamber by opening Nitrogen Valve and turning switches V5,V6,V10 of the solenoid box
   c. Wait about ~10 min for the chamber to be vented
3. Sample loading:
   a. Undo the power and thermocouple lines to the feedthrough
   b. After undoing the bolts, rotate the sample stage 60º clockwise to obtain enough clearance to pull the entire sample stage assembly out
   c. Once enough clearance has been obtained, pull the entire sample holder assembly straight out
   d. Using 5/64” Allen key, disassemble the sample mount by undoing the bolts
   e. Load the sample (e.g. KBr or ZrO₂ substrate) and hold the sample into the position by tightening the bolts back
   f. Reassemble the sample stage by following steps a through c in REVERSE (c. → b. → a.)

4. Base pressure: Open the roughing valve, and pump the chamber pressure to the base pressure of ~30mTorr

5. Nitrogen Purge: (*)
   a. Set channel 4 of MFC controller to 45%.
   b. Open the manual valve of N2 line
   c. Open V10, followed by V6, followed by V5 from solenoid
   d. Pressure will go up to 200 mTorr then wait till it goes down to base pressure so line is pumped down.

6. Heating: (Note: Heat chamber and gas lines concurrently)
   a. Chamber & Precursor heating: Heat the system and precursors to the set temperatures by activating the channel of interest. Refer to the table below for the assignment of channels and the corresponding set points.

   b. Sample stage heating: Heat the sample stage by turning Variable Transformer-3, followed by activating Ch7 of 7CC-3
c. At the time of heating, turn on the FTIR spectrometer using the black box at the base of the computer.

Figure 13 - Variable Voltage Transformer

Setpoint/ramping info of 7CC-3 is listed below (as of 11/17/2013)

<table>
<thead>
<tr>
<th>Ch</th>
<th>Description</th>
<th>Start Pt</th>
<th>SP1</th>
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<th>SP2</th>
<th>t2</th>
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<td>2500</td>
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</tbody>
</table>

7. Deposition for in-situ FTIR monitoring of ALD chemistry

*The procedures listed below are only for one cycle each! (Note: pump down time can be extended if need be, but cannot extend pulse time.*)
IMPORTANT: It is important to isolate the KBr windows on both sides by closing the gate valves before pulsing any precursor/oxidant into the chamber. Failure to do so will cause a deposition of precursor/oxidant to the KBr window and affect the measurements.

a. \( \text{Li}_2\text{O} \) Deposition
   i. Close the manual gate valves, and the manual roughing valve.
   ii. Open the manual valve of lithium precursor \( \text{Li-t-butoxide} \), LTB, for 60 seconds.
   iii. Close the LTB manual valve all the way, open the manual roughing pump. Pressure will increase up to ~80mTorr.
   iv. Over the course of nine minutes, pulse nitrogen three times using the solenoid bypass valves (Figure ), pumping down to base pressure in between each pulse. The bypass switches actuate the pneumatic valves shared with the LASO chamber via parallel connection to the LASO solenoid box.
   v. IF, at the end of 10 minutes total, the pressure of the chamber is constant (~30 mTorr), then open the window gate valves. Start acquiring a scan for the deposition.
   vi. After the data has been acquired, close the window gate valves, then close the manual roughing valve.
   vii. Open the water valve for 60 seconds.
   viii. Close the manual valve, open the roughing valve. Watch the pressure, should increase to 100-200 mTorr, but make sure it does not go above 200 mTorr. (Note: water does not have MFC so vapor pressure can be high. Use the needle valve to adjust flow rate - 4 revolutions from closed is standard).
   ix. Over the next nine minutes, purge with N2 three times. Once the chamber pressure is constant, then open the gate window valves.
   x. Pump down for 60 seconds till base pressure has been reached. (Note: if chamber has not reached the base pressure after pump down time of 60 seconds, then do a Nitrogen Purge Step by pulsing nitrogen in for 10 seconds.)

b. \( \text{Al}_2\text{O}_3 \) Deposition
   i. Close the manual gate valves completely, and then the manual roughing valve.
   ii. Pulse TMA by opening TMA Up & TMA Down switch of Solenoid Bypass Box for 60 seconds. The bypass switches actuate the shared pneumatic valves for TMA flow in the LASO chamber.
iii. Turn both switches off, then open the manual roughing valve. Over the next nine minutes, purge chamber with nitrogen three times. Make sure chamber goes back to base pressure.
iv. If the chamber is at steady state, open the window gate valves. Acquire spectra.
v. Close the window gate valves, then close the chamber roughing valve.
vi. After the pumpdown, open the water valve for 60 seconds. Close the water valve, and open the chamber roughing valve. Watch the pressure, should increase to 100-200 mTorr, but make sure it does not go above 200 mTorr. (Note: water does not have MFC so vapor pressure can be high.)
vii. Over the next nine minutes, purge the chamber with nitrogen three times (for ten seconds each nitrogen purge).
viii. If the chamber is at steady state pressure, then open the gate window valves. Acquire spectra.

c. SiO$_x$ Deposition
i. Close the manual gate valves completely, and then the manual roughing valve.
ii. Pulse TEOS by opening the ball valve for 60 seconds.
iii. Close the TEOS precursor, then open the manual roughing valve (the pressure should go up to $\sim$80mTorr).
iv. Over the next nine minutes, purge chamber with nitrogen three times. Make sure chamber goes back to base pressure.
v. If the chamber is at steady state, open the window gate valves. Acquire spectra.
vi. Close the window gate valves, then close the chamber roughing valve.
vi. After the pumpdown, open the water valve for 60 seconds. Close the water valve, and open the chamber roughing valve. Watch the pressure, should increase to 100-200 mTorr, but make sure it does not go above 200 mTorr. (Note: water does not have MFC so vapor pressure can be high.)
viii. Over the next nine minutes, purge the chamber with nitrogen three times (for ten seconds each nitrogen purge).
ix. If the chamber is at steady state pressure, then open the gate window valves. Acquire spectra.

8. Finishing the deposition:
   a. Close all valves.
   b. Turn off all the heating for chamber, water, and precursor containers.
   c. Wait for the chamber to cool down to at least 50ºC or lower. (This will take about ~1 hour roughly)

9. Sample unloading:
   a. Perform Steps 3a. through 3e.
   b. Unload the sample.
   c. Perform Step 3f. then pumpdown the chamber

10. Data Acquisition:
    a. After the spectrometer has warmed up and reached steady-state (turn on spectrometer as chamber heating), open in the OMNIC software on the FTIR computer.
    b. The software will go through two windows to communicate with the spectrometer.
    c. Open "Jay's Experimental Setup."
    d. Make sure "Bench" on top right of window is checked.
    e. Obtain background scan (scans usually take ~8 minutes for 100 scans).
    f. Before running the first precursor pulse, pulse water into the chamber to have hydroxyl surface groups on ZrO$_2$ nanopowder.
    g. Press "Ctr-S" to scan. Confirm the scan, and make sure the peak value should be 5-10 for optimal performance. Post the scan to Window 1.
    h. Save the spectra under the format "[Date][Time] ([Cycle#][Precursor]).spa". The .SPA format includes the experimental parameters of the spectrometer. Save water pulse spectra as "([Cycle#][Precursor]W)".
    i. To make a difference spectra, select the most recent scan, and then select the previous scan. Select "Analyze" and "Subtract". Save the difference spectra as "Subtraction of [Date][Time] ([1st Spectra Cycle Name]-[2nd Spectra Cycle Name])".
Temperature and Temperature Control Related Troubleshooting

Problem: Temperature Controller shows high temperature when housing at room temperature.

Solutions:

- While wearing rubber gloves and de-energize the area, carefully unplug thermocouple input bar at the back of the 7-Channel Controller.
- Wait a few seconds, plug back in very carefully.
- Turn on power, and wait for readout.

Problem: When controller is activated, temperature rapidly rises.

Solutions:

- De-energize the affected channel. Make sure heating wire does not cross over thermocouple.
- Check the adhesion between the thermocouple and the chamber
- Also make sure that the flat of the thermocouple probe is facing the chamber.
- Energize the channel, and activate to verify proper control.

Problem: With controller on, there is no change in temperature on the chamber

Solutions:

- Note: Turn off power to connections before inspecting or changing electrical components.
- Make sure the thermocouple responds to a change in temperature.
- If the light on the appropriate channel's relay is not on, the problem could be between the controller and the relay. De-energize and trace connections between the relay and the controller (this can be done with the resistance setting on a multimeter)
- If the light on the channel is constantly on, make sure there is power from the relay to the heating elements.
- Inspect the fuse to the power components.
- Using a multimeter, inspect the heating element. If there is no resistance (close to 0 Ω on the readout), then the heating wire has shorted. Replace wrap, inspect fuses and solid state relay, and check with multimeter before energizing the system.

Problem: Sample stage does not reach desired temperature.

Solutions:

- Verify thermocouple is connected to the sample holder assembly.
- Make sure power to the heating elements are on.
- Inspect the fuse in the Variable Voltage Transformer (VVT).
- Measure resistance of sample heater assembly.
• Very slowly adjust the VVT to a higher voltage, if more power is needed. *(Note: Should not exceed 4%)*
A5 LASO ALD Chamber Doser Troubleshooting Guide

Problem: No deposition

Solutions:

- Make sure that there is precursor in the housing.
- Switch the lithium housing to the Mn doser assembly side.
  1. Vent chamber.
  2. Turn off heater power, and unwrap heating wires from the precursor housings and the gas lines.
  3. Remove the precursor housing assemblies.
  4. Attach the lithium housing to the doser facing the back of the chamber.
  5. Wrap with heating wires and insulation.
- Clean clogged doser assembly.
  1. Vent chamber
  2. Turn off heater power, and unwrap heating wires from the precursor housings and the gas lines.
  3. Remove the precursor housing assemblies, and the doser assembly.
  4. Rinse gas-lines with copious amounts of isopropyl alcohol.
  5. If a precursor is blocking flow, it must be removed by a combination of physical removal and isopropyl rinses.
  6. Allow chemical solvents to dry out before placing doser assembly back onto the chamber.
  7. Dispose of waste according to proper procedures.

Problem: No doser heating

Solutions:

- Make sure power is on to the doser heating wires.
- Unplug power, and measure resistance of the doser heating assembly with a multimeter.
- If there is not sufficient resistance, or there is too much resistance, then the heating wires may need to be replaced.
  1. Remove doser assembly using the steps in the previous section.
  2. Replace the heating elements and secure them to the doser.
  3. Make sure other electrical connections are maintained.
  4. Replace the assembly, and pump down chamber to base pressure.
A6.1 Atomic Force Microscopy Operational Procedures

1. Open Nanoscope 6.12r2 from the desktop, and open Workspace file.
2. Open the hood to the microscope, and unlock the AFM head by tightening the lock screw. Disconnect the head cables, and pull out the head completely and place it on the table. Do not drop the head. Take the probe carrier off the head.
3. Place a probe carrier onto the carrier holder. Use tweezers to place a probe onto the carrier. Place the carrier back on the AFM head. Place the carrier head back on to the microscope and plug in the cables from the head to the machine.

![Figure 15 - Meter Window](image)

4. Single click on "Meter" on the computer console. The system takes a few minutes to start. The window below will display on one of the computer screens:
5. Pull out the AFM head one more time without disconnecting the cables and hold it upright, observing the projected laser beam. Be careful not to drop the head. Find the tip of the cantilever by looking at the projected laser spot and turning the alignment screws located at the top of the head. This usually results in a diffraction pattern in the projected laser.
6. After the tip has been found, replace the head back onto the machine. Unscrew the screw lock in order to lock the head in position.
7. Check the meter window on the computer screen. The signal level (center blue bar) should be above zero. Maximize the signal by slowly turning the laser alignment screws. Center the red dot on the meter window crosshairs using the detector alignment screws located on the left side of the head.
8. Click on the "Navigate" on the screen. This will display the Real Time Navigate window. Move the stage out so that it completely clears the AFM head (use the arrow buttons on the Navigate window). Place the substrate on the center of the holder plate. Move the stage to approximately the area desired to be scanned. Verify that there is enough vertical clearance. If not, adjust the “Z Motor” upward.
9. Click on the “Locate Tip” button. If the cantilever is not visible on the screen inside the window, click on “Zoom Out” button, or decrease/increase the illumination. Center the tip on the crosshairs using the optical camera adjustment screws (on the side of the camera). Click “Zoom In”, and make sure the tip is centered again. The image should look similar to Figure 16. Click “OK” when done.

10. Low the head slowly using the Z-motor arrows on the Navigate window to move the optics and AFM head down towards the surface of the substrate. When the head is within ~5mm, close the Isolation lid and lock it (to limit acoustic and electromagnetic noise), and turn to the Navigate window on the computer screen. From the drop-down menu on “Focus On”, selected “Tip Reflection.” Using the “Fine” movement selection, slowly move the head toward the surface until the reflection of the tip is in focus. Change the “Focus On” selection to “Substrate” and make sure that the surface is in focus (adjust the Z-motor if needed). Use caution as the probe may break at this step. Do not allow the tip to touch the surface of the substrate. Using the Navigate arrows, adjust the substrate to the desired measurement point.
11. Click on "Scan-Dual" icon and set Microscope Mode to “Tapping”. Click the Tune icon. On the Tune Window, make sure the survey frequencies are larger than the resonance frequency of the probe (usually set between 100 kHz and 500 kHz). Click on “Auto Tune”. Wait a few moments until the probe tuning is completed. Adjust drive frequency by using “Offset” to an appropriate linear response region. Click “Execute” and “Zero Phase.” Record the drive frequency selected (the peak offset should be between 3% and 10%). Exit the window.

12. Click "Dual-Scan" again. In the scan parameters on the right of the window, set an appropriate “Initial Scan Size” (usually 1 μm), “x-“ and “y-offsets” to 0, and the “Scan Angle” to 0. Select appropriate Feedback Controls for the scans. (If not sure what settings to use, set “Integral Gain” to 0.4, “Proportional Gain” to “0.6”, and “Scan Rate” to 1 Hz.)

13. Click on the Engage icon. It takes a few minutes for the microscope to engage. Once the probe engages, the AFM will start scanning. During scanning, check to see if the “Trace” and “Retrace” lines are tracking each other. If they are tracking, the lines should look the same, but they will not necessarily overlap each other. If they are not tracking well, adjust the “Scan Rate”, “Gains”, and/or “Setpoint” to improve the tracking.

14. Change the “Capture” filename under the “Real Time” menu, then “Capture Filename.” Make sure the destination folder is the user. The “Capture” button will capture the image after the scan is complete in the vertical direction. “Capture Now” will secure the image at any point in the scan.

15. After scans are complete, click on the Withdraw icon to withdraw the microscope. Move the AFM head up using the Z-motor on the Navigate window. Open the hood, and move the stage fully away from the AFM head using the Navigate window. Remove the substrate, and move the stage back under the AFM head. Unlock the AFM head by tightening the lock screw. Disconnect the head cables, and pull the head out completely. Place the head on the table, using care not to drop the head. Remove the probe carrier from the head and place on the carrier holder. Remove the probe with tweezers, and slide the head back into the microscope. Loose the lock screw to fix the head to the microscope. Plug cables back in, and close the hood. Close the Nanoscope program window, saving changes to the user’s workspace. Record session in the log book, and sign the AFM out using the LabRunner program.
A6.2 Scanning Electron Microscopy (NOVA 600) Operational Procedures

A6.2.1 Introduction

A beam of high energy electrons bombards the sample and through a series of scattering events, numerous types of particles are ejected from the sample in a limited interaction region. A detector collects specific ejected particles as the beam is scanned across the sample to produce an image.

If the sample is insulating or improperly grounded, it will charge up due to the continuous influx of charged particles from the beam, and will not convey an accurate scanning image. Common charging effects include image drift, over/under-saturation, and the complete reflection of the beam onto the surrounding chamber.

![Figure 18 - NOVA 600 Scanning Electron Microscope](image)

A6.2.2 Guidelines

1) Fill out the logbook when you come into the room and record your logout time upon leaving.

2) The phone in the room can be used by all individuals for matters related to the use and scheduling of the Nova 600 system only.

3) The Nova 600 room is kept in impeccable order. This is not by accident. You are expected to use and maintain the facility in a similar fashion.

4) Never touch the chamber internals, stage mounts, or sample with your bare hands. *Always wear gloves.*

5) Checklist
   a) Check if the chamber is still under vacuum.
   b) Check the vacuum levels
      i) Hold the mouse pointer over the status icon.
ii) FEG IGP < 5E-9 mbar  
iii) E Column IGP < 5E-7 mbar  
iv) I Column IGP < 5E-7 mbar  
v) Chamber < 9E-5 mbar

Figure 19 - Vacuum Status

Note: If the status icon shows that the system is vented and a prior user is not present in the room, contact a Nanolab engineer immediately.

A6.2.3 Sample Loading and Removal

1) Prepare the microscope.  
a) Check that E-beam and I-beam are off (Beam On button should be gray):  
b) Check the navigation page and set the tilt angle to zero if it is not already

2) Vent the chamber.  
a) Click Vent in the beam control page.  
b) Venting takes approximately 5 minutes.  
c) Once a space between the chamber and door become visible, lightly pull on the door handle. Do not pull hard on the door handle. Once the chamber is completely vented, the door will easily slide open.

3) Slowly open the chamber door until the door-stop is hit.

Figure 20 - SEM Door under vacuum (closed) and vented (open)
4) Load or remove your sample. *(WARNING – All screws, nuts, etc. should be tightened to minimum necessary to hold sample rigid)*
   a) Mount the stub holder.
      i) Center the stage by setting the X and Y coordinates to 0 if access to the central threaded hole is difficult.
      ii) Screw the threaded post approximately 1 inch into the base plate if it is not already installed.
      iii) Ensure that the locking nut is sufficiently raised to prevent binding of the nut during movement of the threaded post.
      iv) Rotate the post until the setscrew is visible and easily accessible with a hex driver.
   b) Insert the pin mount stub.
      i) *Gently* insert the pin into the top hole of the threaded post.
      ii) If there is resistance, remove the stub and back the setscrew off 1 turn in the counterclockwise direction. If there is still resistance, your pin diameter may be too large.
      iii) When inserting the pin, you should feel the pin pushing against the D-spring.
   c) Check the sample height.
      i) The height of your sample is extremely important. If it is too high, you may damage the microscope’s internal components when closing the door. If it is too low, you may not be able to raise your sample to the eucentric working distance and will be unable to operate in mode II.
      ii) Place the height measuring guide (found in the Ziploc bag on top of the chamber) on the base plate with the tab near the highest point on your sample. The top of your sample should lie between the top and bottom of the tab.
      iii) To adjust the height of the sample, first remove the height measuring guide and the pin stub mount from the chamber. Rotate the threaded post, reinsert your stub, and recheck the height of the sample. Repeat as necessary.
      iv) *NEVER* leave the height measuring guide in the chamber while rotating the threaded post. This is to prevent knocking it into the chamber.
      v) Return the measuring guide to the Ziploc bag on top of the chamber.

![Figure 21 - Height Measuring Guide](image-url)
d) Secure the pin mount stub.
   i) Lightly tighten the setscrew. **WARNING** – This is the #1 part on the system that is damaged. Users are financially responsible for this part if any damage occurs.
   ii) Finger-tighten the locking nut to the base plate.

5) Pump down the chamber.
   a) Slowly close the chamber door.
   b) Click **Pump**, and gently press against the door for about 5 seconds until the vacuum seal is formed.

A6.2.4 E-Beam Startup

1) Turn on the E-beam.
   a) Select the upper-left quadrant. The data bar should turn blue.
   b) Turn on the high voltage by clicking **Beam On** (button should be yellow).
      i) Default parameters: 10 kV, spot 3 or 4 (0.13 nA or 0.54 nA).
   c) Un-pause the image.
   d) Zero the beam shift: right click the write area of the gauge in the beam control panel and select “zero”.

2) Find your sample.
   a) Reduce the magnification to the minimum value.
   b) Navigate to your sample.
      i) **Important** - When the stage is moved, two distinct 'click' noises will be heard from the cabinets behind the microscope; one before the movement and one following the movement. It is critical that you wait until you hear the second 'click' before proceeding with any additional stage movements.
      ii) Double-click the left mouse button in the imaging window to center a feature.
      iii) Click and hold down the mouse wheel with the pointer in the imaging window and drag the mouse.
      iv) Use the arrow keys to move a single frame over (↑↓←→).
      v) Stage Align Feature: Drag a line in the imaging window on top of the feature which you want to have rotated to either a vertical or horizontal orientation.
      vi) **Navigation Panel → Coordinates Tab**: Coordinates can be manually entered into any of the available axis (X, Y, Z, T, R).
   c) Adjust the contrast, brightness, and focus to optimize the image.
3) Link the stage *(Very Important!)*
   a) After the initial pump-down, the link button should have a question mark on it. This indicates that the software does not know what height the sample is at. In the navigation page the Z value should read zero.
   b) Increase the magnification to >10,000X on a small feature of high contrast (scratches, dirt and defects are a good place).
   c) Adjust the contrast, brightness, and focus to optimize the image.
   d) Press Link Z to FWD and check the navigation page.
   e) *The Z value should now read between 11 and 15 mm. If not, your sample was loaded improperly. You will need to vent and reload your sample.*

4) Adjust the sample height to 5 mm.
   a) Change the Z value to 5 mm. The link button will change indicating that re-linking the stage is recommended. 5 mm is optimal for finding eucentric height and using mode II. *NEVER* decrease the Z value to less than 4 mm.
   b) Repeat the above linking procedure by first refocusing the beam and then pressing Link Z to FWD (ignoring the last bullet). The Z value should update to a value near 5.0000 mm.

A6.2.5 Optimizing an Image

1) Focusing Tools
   a) Course and fine focus knobs are available on the console. Course focus works best for mode I and fine focus best for mode II.
   b) Reduced scanning mode *(F7)* provides a lower noise image ideal for fine focusing. The reduced scanning area can be freely repositioned and resized.
   c) Full screen imaging is accessible by pressing *(F5).*
2) Contrast and Brightness  
   a) The videoscope (F3) presents a graph of the center line scan and how each pixel falls between black and white. It is useful for determining if the grayscale range is being clipped. 
   b) Contrast and brightness numeric values can be found at the Contrast bottom of the beam page (among others). 
   c) Auto contrast and auto brightness buttons are available to you, though not recommended due to their poor results. 

3) Astigmatism  
   a) Identifiable by perpendicular streaking of the image during focusing. It is most visible at higher magnifications. 
   b) Adjust the focus until the image is midway between the two streaking directions and appears blurry but not streaked. 
   c) Optimize the image using the two stigmation adjustment knobs. 
   d) Repeat the process of focusing and adjusting the X and Y stigmation at higher and higher magnification until streaking is no longer apparent and optimal clarity has been achieved. 

4) Mode I and Mode II  
   a) Similar to "low mag" and "high mag" modes on other SEM systems. However, mode I can operate at all magnifications and produce excellent images. 
   b) If mode II is not available, hold the mouse over the Mode button to receive an explanation as to why. There are stage-Z limitations as well as magnification limitations to mode II. 
   c) Course focus works best in mode I and fine focus works best in mode II, though both are operational in either mode. 

5) Dwell Time / Resolution / Averaging  
   a) Each quadrant has its own separate settings for these parameters in both full mode and reduced scanning mode. 
   b) These settings affect the live imaging parameters, not the photo or snapshot parameters. 
   c) Often, samples will charge due to a large dwell time. Reduce it, increase the resolution, and save the paused image for better results. 

A6.2.6 Taking an Image  

1) Basics  
   a) After taking an image, the system will always become paused. Un-pause the image to return to live imaging. 
   b) No images are automatically saved. 
   c) Snapshot (F4): short dwell time image. 
   d) Useful for quick previews of your image optimization settings (see previous section) and for "good-enough" images where precise detail isn’t necessary. Also useful for when your sample is charging.
c) Saving of snapshots must be done manually by going to **File > Save As**.

2) **Photo (F2):** long dwell time image.
   a) Used for taking high detail images.
   b) The **Save As** window will pop open automatically following every photo.
   c) To cancel a photo scan midway, press the pause button twice.

3) **Saving an Image.**
   a) All images are to be saved in the folder for you particular job number in the appropriate month’s folder.
   b) Folder naming convention: [4-digit job number] + space + “-“ + space + [full name]
   c) File naming convention: [sample name] + “_001”. By placing “_001” at the end of the file name, all further files will be saved with the same name and the numeric value increasing incrementally until a new file name is manually input.

4) **Taking your files with you.**
   a) All files are taken via user supplied USB thumb-drive.
   b) *Always* leave the folder behind on the computer even if you decided to delete all of your files from the job.
   c) You are welcome to leave a copy of your images stored on the computer for backup purposes, although file storage cannot be guaranteed beyond 3 months.

A6.2.7 **Eucentric Height**

The eucentric height corresponds to a working distance at which the sample height and tilt axis are coincident. At this position, image displacement will be minimized when tilting the stage.

![Eucentric Height Schematic](image)

Figure 23 – Eucentric Height Schematic

1) **Identify a reference point.**
   a) Set the E-Beam to Mode I if it is not done so already.
b) Link the stage at 5 mm (see the E-beam Startup procedure).
c) Zero the beam shift: right click the gauge and select "zero".
d) Display the crosshair if it is not currently on (Shift + F5).
e) Increase the magnification to >10,000X and bring into focus a high-contrast feature that is at a height close to where you will later be imaging, milling, or depositing material.
f) Center the crosshair onto the feature using stage movement.

2) Initial tilt calibration.
   a) In the navigation page, set the tilt angle to 5°. While the stage tilts, follow the direction in which your feature moves. If you lose sight of the feature, reduce the magnification until it comes back into view. If you still cannot relocate the feature, tilt back to 0° and try again with the magnification properly adjusted.
   b) Select the optical image quadrant (lower-right).
   c) Click the mouse wheel within the optical image quadrant and **SLOWLY** drag the mouse up or down to control the stage's Z position. The further the mouse is dragged from the initial click position, the faster the stage's Z position will change. There is a slight time lag between the time you initially drag the mouse and when you begin to see the stage move. Drag until the feature is back under the crosshair in the E-beam image. Some shift in the x-direction is expected but not of concern.
   d) Return the stage tilt to 0°, refocus, and re-center the stage to where the crosshair is back on top of the original feature if it has shifted.

3) Repeat calibration at 52°.
   a) At 52°, you may find you need to increase the E-beam contrast and adjust the focus.
   b) Your feature should not significantly shift away from the crosshair (**within ~5 nm**) when viewed at both 0° and 52°.

A6.2.8 I-Beam Startup and E-Beam / I-Beam Coincidence

1) Prepare the system.
   a) Select the upper-right quadrant (I-beam). The data bar should turn blue.
   b) In the **Beam Page**, click **Wake Up** if the source bar is grey. It will take approximately 5 minutes for the source bar to become green.
   c) Turn on the high voltage if necessary by pressing **Beam On** (button should be yellow).
   d) Set the I-beam current to the desired value. The lower the current, the less damage. The voltage should be at 30 kV.
   e) Set the stage to the eucentric height and the tilt to 52°.

2) Locate a feature.
   a) Using the E-beam image, navigate to a high contrast feature that can be sacrificed for focusing the I-beam and establishing E-beam/I-beam coincidence.
   b) Pause the E-beam image.
   c) Select the I-beam quadrant and set the I-beam magnification to approximately half that of the E-beam's.
d) Un-pause the I-beam image.
e) Using the I-beam beam-shift, center the feature under the crosshair.
f) Adjust the contrast, brightness, stigmation, and focus to optimize the image.
g) Pause the I-beam image.

3) Verify Coincidence
   a) Un-pause the E-beam image to verify the coincidence of the two beams.
   b) Repeat these steps at higher magnification until you are satisfied with the accuracy of the coincidence.

4) I-Beam imaging notes.
   a) Whenever the I-beam is un-paused, it is damaging your sample. Therefore, you should always leave the I-beam paused when not immediately using it.
   b) When checking your sample position with the I-beam, it is better to use the snapshot feature than to make the image live in order to minimize damage.

A6.2.9 Patterning

When using the ion beam to mill features into your sample, unintended sample damage must always be considered. Be aware that the I-beam, just like the E-beam, must be adjusted for focus, brightness, contrast, and astigmatism before proper milling can be achieved. Note: Basic and advanced parameters will be unavailable until a pattern is drawn in the imaging window.

1) Basic Tab
   a) Application
      i) For milling, should be set to "Si" regardless of what material your sample actually is.
   b) XYZ Size
      i) Double check the units on each dimension.
      ii) Z size determines how deep your pattern will be milled. The value is rarely accurate. Therefore, Z depth must be closely monitored during patterning operations.
   c) Total Time
      i) Most cuts or depositions should take between 30 seconds and 3 minutes. If the total time is more than that, you may need to increase your current.
      ii) If a "Total Time" is not given and the box is grayed out, this indicates that the beam settings are not compatible with the drawn pattern. Magnification or current may need to be adjusted.
2) Advanced Tab
   a) Rotation
   b) X Y Pitch and Overlap
      i) Controls the spacing between milled points.
   c) Passes
      i) This value changes with the Z-Size value. It is an alternate way to control how deep your pattern will be milled

3) Patterning Tools
   a) Shapes
      i) Rectangle: When the mouse pointer is near a corner, you can rotate the pattern.
      ii) Circle: There is both an inner and outer radius setting. Useful for producing sharp tips.
      iii) Line: To produce a line of equally spaced holes, try increasing the pitch.
   b) Polygon Tool
      i) This tool is notorious for crashing the system. Try not to go beyond 6 corners.
   c) Regular Cross Section
      i) Removes material in a stair-step pattern by varying the dwell time over specific portions of the pattern.
   d) Cleaning Cross Section
      i) Removes material one line at a time. The pattern will progress from bottom to top, milling the set depth for the current line before proceeding to the next.
   e) Bitmap File
      i) Bitmap files must be loaded onto the System PC desktop folder labeled "Bitmaps" and should not exceed 2 Mb in size.
      ii) White areas will be milled while black areas will not. If black was properly set
while producing the file, it should appear as transparent upon loading it into the user interface.

iii) Files must be saved in RGB 24-bit mode.

4) Serial and Parallel Patterning
   When patterning multiple patterns at once, the user can choose to have them patterned sequentially or all at the same time. When serial milling is selected, each pattern can have a unique Z depth assigned to it. In parallel mode, all patterns will be set to the same defined Z depth.

A6.2.10 FIB Milling

1) Initial Conditions
   a) Eucentric height
   b) Tilt to 52°
   c) Establish E-Beam/I-Beam coincidence.

2) I-Beam Current
   a) The larger the current, the shorter the milling time, the larger the beam size, and the more difficult to focus.

3) I-Beam Voltage
   a) Should be 30 kV.

4) Milling Monitoring
   a) Take periodic E-Beam snapshots to observe the milling location and depth. The milling can be paused or stopped prematurely before the end of the set patterning time.

5) FIB Deposition
   a) Use Initial Conditions
   b) Gas injection system (GIS)
      i) Warm the appropriate GIS by double-clicking "Cold" if the GIS is not yet "Warm." Heating will take a few minutes.
      ii) Insert the GIS by selecting the checkbox next to the appropriate GIS material.
   c) Pattern Parameters
      i) Application: set to "Pt dep", "W dep", or "C dep".
   d) Current: calculate the area in um² x 6 (in pA) rounded up to the closest current.
      i) Voltage: 30 kV.

6) E-Beam Deposition
   a) Use Initial Conditions
   b) Gas injection system (GIS)
      i) Warm the appropriate GIS by double-clicking "Cold" if the GIS is not yet "Warm." Heating will take a few minutes.
      ii) Insert the GIS by selecting the checkbox next to the appropriate GIS material.
c) Pattern Parameters
   i) Application: set to "Pt dep", "W dep", or "C dep".
   ii) Y-Pitch: Reduce by 50% to minimize row effects.

d) E-Bema Parameters
   i) Current: Spot 6
   ii) Voltage: 5 kV.

Figure 25 - Gas Injection System Panel

7) Cross-section Creation
   a) Stage preparation
      i) Locate the region of interest and rotate the stage to produce a horizontal cross-section.
      ii) Link the stage.
      iii) Set the stage to the eucentric height.
   b) Protection.
      i) If the top 50 nm of your sample are critical for viewing, begin by doing E-Beam deposition to Pt: Z=300 nm.
      ii) On top of your sample, or on top of the E-Beam deposited Pt, deposit with the I-Beam a layer greater than 500 nm of Pt.
A6.3 Basic Transmission Electron Microscopy Using FEI TITAN S/TEM (CNSI)

A6.3.1 Overview

Transmission Electron Microscopy (TEM) is a technique in which a beam of electrons is transmitted through a sample less than 100 nm thick. The image is formed as the electrons interact with the sample, and the image is magnified and focused onto either a fluorescent screen or sensor, such as a CCD camera. TEM is capable of imaging significantly higher resolution than light microscopes, due to the small deBroglie wavelength of electrons.

A6.3.2 Operational Procedures

1) Fill up the Dewar flask with liquid nitrogen and install in place, as shown during microscope training. If the Cold Trap was at room temperature, you may need to allow it to cool for at least 30 minutes. Re-fill liquid nitrogen during the session if needed.

2) Sign in to the logbook.

3) Start the Titan TEM User Interface (UI):
   a) Log on to the Titan computer using your username and password.
   b) Open User Interface (UI) from Windows quick launch toolbar or from start menu. Microscope Control-TEM1 will pop up.
   c) Workset → Setup → FEG Control (User). Make sure that FEG Control parameters are set correctly: HT = 300kV; Extraction voltage = 4300V and Gun lens setting (GL) is 3. If you need to change the extraction voltage value, set the value first and then click the enter button next to the value.
   d) Workset → Setup → Vacuum. Check vacuum in the system: Gun should always be at 1; Octagon (column) vacuum should be below 20 log. Verify that Col. Valves Closed is yellow (valves are closed). The valves should always be closed if the
Octagon vacuum is greater than 20 log, or when microscope is not in use. The field emission gun will be damaged if the column valves are opened when the Octagon vacuum is too high. This will result in an extremely costly and time-consuming repair.

e) The state of the microscope’s vacuum system also may be observed in the Vacuum Overview – Popup panel, right-bottom corner of the UI.

f) Start digital camera controlling software: Digital Micrograph (DM) and/or TIA. Note: TIA requires DM to the running (start DM before TIA).

2) Inert prepared sample into microscope sample holder. (Pay special attention when handling the FEI holders - they ARE really fragile and delicate! Before using the sample holder, check the O-ring for cracks or dust. Check the conical area next to the O-ring - it must be clean and without visual scratches, etc. Do not touch any part of the specimen holder beyond the O-ring. The oil from your fingers will contaminate the vacuum as well as your sample. Inspect the specimen-holding mechanism; make sure it is not damaged. Please report any problem immediately.

a) Single Tilt
   i) Locate the small hole at the base of the clamp.
ii Insert the only the tool into the hole and slowly move the clamp up into a vertical position (make sure the clamp is secured in this position). *Do not apply excessive force!*

iii Insert the sample face down, since the holder undergoes a ~140 degree rotation upon insertion into the column.

iv When clamp is in the vertical position, load the specimen into the carrier; make sure it is centered well and *slowly* move clamp down into the closed position. Do not use tweezers or other instruments to manipulate the clamp mechanism. *Improper operation will damage the mechanism.*

![Figure 28 - Single Tilt Sample Holder](image)

b) Double-Tilt

i Remove plastic cover from the tip of DTSH. Using vacuum tweezers place your sample inside the cup of DTSH.

ii Place sample face down on the sample holder.

iii Put anti-twist washer on top of the sample making sure that both pins on the anti-twist washer go into special notches made in the cup.

iv Place hexring on a flat clean surface, covered with filter paper. Make sure that its wider side is facing up. Grab it with exchange tool, transfer it to the DTSH cup and carefully screw it in (clockwise direction). *Don’t apply extensive force while screwing the hexring.* Note: There is only one turn of thread.

v Turn the holder 180° to flip the cup up-side down and make sure specimen is held in place, though do it while keeping holder above the desk/filtering paper. Keep in mind that it is not a big deal if your sample drops at this point, but it will be a lot of trouble if you lose your sample, anti-twist washer, or the hexring inside the column of the microscope.

![Figure 29 - TEM User Interface](image)

c) Insert specimen-holder into the microscope column.

i Make sure that the Column Valves are closed (Col. Valves Closed button is yellow).

ii Turn ON turbo-molecular-pump by clicking Turbo on. The color of the button will first change from grey to orange, then to yellow. Once it is yellow, the TMP is ready.
iii  Locate the small pin on the end of the holder closer to the tip. Carefully insert the holder into the CompuStage with the small pin on the holder in the 5 o’clock position (large pin at the handle in 11-o’clock position).

iv  The pre-pumping cycle will initiate and the red indicator light will come on. Note: If double-tilt sample-holder is used, plug holder connector to the CompuStage. In the Message window, select double-tilt holder and click enter.

v  When the red light goes off (2-5 minutes - the remaining time may be checked in Vacuum Overview - Popup panel), rotate the specimen-holder counterclockwise until it stops. Then guide the holder into the microscope carefully as it is sucked into the vacuum of the column.

vi  Turn off the turbo pump by clicking Turbo on button (it will turn grey).

vii  Check the vacuum level in Octagon (Workset → Setup → Vacuum). It should be 20 log or less.

3) If Octagon is 20 log or less, open the gun-valve by clicking Col. Valves Closed button. The button will turn gray and the Setup tab will indicate Status shown: liner opened. If everything is fine, you should see the beam on the screen and microscope is ready for operation. If sample is blocking the beam, move it using the X-Y joystick.

4) Set microscope parameters: magnification-5600x, spot size- 3-4; aperture: C1 -50μm and C2 - 100μm (the most common settings).

5) Reset the holder: Workset → Stage → Stage → Control → Reset → Holder. It is a good habit to reset the holder when starting and ending a microscope session. Also, if there is a problem controlling the CompuStage, sometimes resetting the holder may fix the problem.

6) Center the beam: Condense the beam to its smallest size using Intensity knob. Center the beam using multifunction (MF) knobs – Beam Shift X & Y

7) Center the C2 aperture: Spread the beam just beyond the outer circle on the fluorescent screen. Open aperture control panel (Workset → Setup → Motorized Apertures). Check the Center box next to Condenser 2 and use the Mf knobs to adjust the position of the C2 aperture. The C2 aperture is centered well when the beam spreads symmetrically on the center of the screen.

8) If necessary, inset and center objective and/or selected area aperture(s).

9) Conduct the Direct Alignments
   a) Gun tilt alignment.
      i  Click Gun Tilt in the Direct Alignments.
      ii  Using MF, adjust intensity of the beam to its maximum.
      iii  Click Done.

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b) **Gun shift alignment.**
   - Use L3 programmable button to set the spot size to 3.
   - Condense the beam.
   - Select Gun shift.
   - Use MF knobs to bring the beam to the center of the screen.
   - Switch to the spot size 9 (R3 programmable button).
   - Condense the beam.
   - Select Align beam shift.
   - Use MF knobs to bring the beam to the center of the screen.
   - Repeat until beam is in the center for both spot sizes 3 and 9.
   - Click Done.

c) **Beam tilt pivot point X and Y alignment.**
   - Click Beam tilt pp X in the Direct Alignments.
   - The beam will begin to wobble.
   - Using MF knobs, stop beam wobbling, so that beam is stationary in the center of the screen.
   - Click Done button.
   - Select Beam tilt pp Y in Direct Alignments.
   - Repeat the above procedure for the Y pivot points.
   - Click Done.

d) **Rotational center alignment.**
   - Perform this alignment on a visible feature on the sample.
   - Use high magnification for this alignment.
   - Select Rotation center alignment in the Direct Alignments.
   - Image of the feature will start moving.
   - Use MF knobs to minimize the movement.
   - Click Done.

e) **Astigmatism.**
   - Select Stigmators at popup panel (right-bottom corner of the UI).
   - Choose Condenser, Objective or Diffraction.
   - Use the multifunction (MF) knobs to do the correction.
   - For the condenser, adjust the beam shape to become a circle.
   - For the objective, make the granularity of a high magnification image isotropic (use CCD + live FFT for optimal results).
vi  For diffraction, make the central spot of the defocused diffraction pattern circular.

vii Click Done.

10) Observe image on the screen. Adjust Intensity to spread the beam over the screen.

11) Use Digital Micrograph or TIA to record images with the digital camera.

12) In Digital Micrograph (DM):
   a) **Microscope → Global Microscope Info** – fill in the Specimen and Operator name, leave other fields as is.
   b) **File → Global Info → Save Numbered** – set up directory path where your files will be saved (File Directory); create rules for File Name (do not use special symbols like #, /, \, %, @); choose the file format, normally – Gatan Format) in File Content and Format. Choose Save Image As for high-resolution, 16-bit images. Save Display As – low-resolution, 8-bit option. **Note:** Save images on Titan STEM support computer – C support computer on TITANSTEM/Users/[your directory]. **Do not save your data on the Titan computer!**
   c) Make sure that beam is spread: CCD chip of the digital camera will be damaged by condensed beam.
   d) On right (DM) panel – click Camera Inserted to insert the camera.
   e) Uncheck Auto Exposure. Set exposure time manually – 0.1 sec. **Note:** Auto Exposure slows down the camera’s readout. Occasionally, this option may be used in case of difficulties with imaging.
   f) Lift up the microscope’s big screen (usually R1 programmable button).
   g) Choose Preview or Search in **Workset → TV/Camera (UI).** Alternatively, start View in Cameral View (right panel) in DM. Adjust microscope Intensity, so intensity indicator on DM is in the green zone. To accelerate the camera’s refresh rate, use 2x or 4x binning (setup icon). **Note 1:** The CCD chip of the digital camera is very expensive and sensitive to beam damage. Always keep the intensity of the bema so that the DM intensity indicator is in the green zone. **Note 2:** The digital camera may be controlled from either the FEI User Interface (CCD/TV Camera) or DM.
   h) Find area of interest. Adjust magnification; make sure that DM intensity indicator is in the green zone.
   i) Focus the image using the Wobbler button (not the α-wobbler that was used to adjust the z-height) at magnification range up to 50-80Kx. At higher magnification use the “minimal contrast” approach or life FFT (Fast Fourier Transform or “power spectrum”) in DM: **Process → Live → FFT.**
   j) If necessary, use Display Control on the DM left panel to adjust brightness/contrast of the image. The quality of the image may be judged based on the histogram (left panel) shape: a good histogram has smooth, bell-like shape and symmetrical.
k) Take a picture: **Camera Acquire → Start Acquire.** It is a good idea to use Auto Exposure option at this time. If you are planning to take many pictures at the same magnification and under similar illumination conditions - you may uncheck Auto Exposure to accelerate the process of taking pictures. **Note:** All your pictures will be named based on information provided in Global Microscope Info: Specimen name.

l) When sample is changed, do not forget the change Specimen name in **Microscope → Global Microscope Info.** DM will automatically associate typed in Specimen name with all pictures taken after its last change.

m) When all pictures have been collected, save them using “saved numbered” (diskette 1-2-3 icon) option: select the window with the picture and lick Save Numbered, close the window (Ctrl-W), repeat for every picture. All pictures will be saved in the directory specified in **File → Global Info → Save Numbered. Do not save your data on Titan computer!**

### A7.3.3 Shutting Down the System.

1) Bring magnification to 5600x.

2) Spread the beam.

3) Reset the holder (**Stage → Stage2 → open flap-out → Reset → Holder**).
   a) If you are using the double-tilt holder, disconnect the cable from the CompuStage.

4) Close Digital Micrograph and TIA.

5) Close column valves by clicking **Col. Valves Closed** button in **Setup → Vacuum.** The button will turn yellow and the **Setup** tab will indicate **Status shown: liner closed.**

6) Remove the specimen holder from the microscope column.

7) If you are the last person operating the microscope for the day, make sure that you start a **cryo cycle.** Otherwise, proceed to the next step.
   a) Remove the liquid nitrogen Dewar flask from the cold trap as shown during the training session.
   b) Open **Vacuum** tab on the **Workset.** Open its flap-out. Click **Cryo Cycle On** button. The TMP will start its operation and the **Cryo Cycle On** button will turn yellow.
      **Note:** If you are the last user of the day, don’t leave before starting a cryo cycle.

8) Close UI window, log off from Titan computer and complete the record in the logbook.
A7.4.1. X-Ray Photoemission Spectroscopy System

Emergency Shutdown Procedure

1. Move the transfer loading arm all the way out of the XPS chamber, then close the gate valve.
2. Turn off X-ray source by pressing HV button (light will turn off) and then STANDBY button (light will turn on, and OPER button should become unlit). If there is time, wait for water to flow to cool the anode for ~ 1 minute and press COOLING ON button. Then, turn off the main power and chiller power.
3. Turn off energy analyzer by turning off ESCA kV and power switches on boxes from bottom to top (lens, detector, control and display)
4. Turn off software by pressing the Stop Expt/Kill Data switch until experiment stops.
Operating Procedure

1. Before transferring the sample, make sure the x-ray gun is backed out to a setting of about 1.5 mm on the motion manipulator (~1 cm from the Teflon spacer). Move the sample stage towards the gate valve to a setting of 1-2 on the corresponding manipulator). Lower the stage to a setting of ~4 on the corresponding manipulator. Ensure the stage is vertical. **Be careful as the stage rotates easily.**

2. Check the pressure on the XPS using the ion gauge controller (base is ~1 x 10^{-9} Torr, but anything below 3 x 10^{-9} Torr is acceptable. If the pressure is above the 10^{-9} Torr range check the ion pump controller for current reading – should read ~10^{5} – 10^{6} A). Check the pressure on the TT using its ion gauge controller, pressure should be ~4 x 10^{-9} Torr (if it is higher check that the gate valve between the cryo and the TT is open, if it is not, then open it using the controller box (trace the cable to be sure)). Once both pressures are in the requisite range open the gate valve between the TT and XPS using the corresponding controller box (trace the cable if unsure).
3. Slide the transfer arm into the tube **slowly**, checking the viewport occasionally to make sure that you do not collide with the stage or x-ray source. The manipulator settings on the arm should be X-setting = 5.5 (black) and Y-setting = 5 (black). Make sure the stage is aligned with the sample using the lateral manipulator (pictured in Step 1 on previous page). At this point you may have to raise the sample or lower the stage to provide the necessary vertical clearance. Lower the sample onto the stage. You may have to lower the loading arm to a Y-setting of 3-4 in order to remove the fork from the sample – slowly pull out the fork and after each small movement, increase the Y-setting slightly to avoid excessive straining. Retract the fork completely, being cautious to clear the transfer cart, and close the gate valve between the tube and the XPS.

4. Move the sample stage closer to the source and move source in until it is about 0.25 cm away from the Teflon spacer. Select the angle theta, which is the angle between the sample surface and the detector axis, using the rotational control - 240° corresponds to a 90° take off angle and 270° to a 60° take-off angle.

5. Move x-ray source closer if desired and adjust the stage position using the various manipulators until you are satisfied that the beam will illuminate the sample. Check the pressure in the XPS chamber – it should be at or below $3 \times 10^{-9}$ Torr. Turn on the analyzer by turning on the switches labeled in the left picture below – from top to bottom: Display, Control, Detector, Lens, then ESCA kV. Turn on the x-ray source by pressing the power switch on the Control Unit. Press “Cooling On” (this should result in the button beginning to blink with a green light) and then turn on the NESLAB HX-75 Chiller (This should result in the green light becoming steady). Select an anode by pressing the corresponding button (selection will result in the button being illuminated by a green light). At this point none of the Interlock Buttons should be lit red. If they are seek assistance from a senior lab member or cautiously check all connections from electronics to the unit.
Check the chiller setpoint by pushing in the chiller mode switch. This should read 17 degrees. If it has changed adjust the setpoint dial while keeping the mode switch depressed. Check the flow rate by plugging in the BNC/Banana Plug connection to the multimeter. When set to measure DC Voltage the multimeter should give a reading of over 3.4 V. All the electronics to warm up for 10 minutes before running an experiment.

6. Launch the software program SPECTRA by double clicking the icon labeled SPECTRA in the center of the desktop. To save time before the experiment begins you can define your regions (survey, detailed, etc) by clicking the Edit Region Info Button. Also confirm that the software is configured for the anode you selected in Step 5, by clicking the Tools Button, then clicking “Setup Card” in the menu that pops up. In the dialogue box that pops up you can select either Mg (1253.6 eV) or Al (1486.6 eV) in the Excitation field.
7. Once the electronics have warmed up, check that the Spectrometer Control Unit is set to COMP mode and that the Energy Selector corresponds to the Binding Energy (BE) of the anode you selected earlier in Step 5.

8. Press the “I_FIL” button on the X-Ray Source Control Unit, which should light up green. Press the “Stand By” button (display should change to 2.91 A) and monitor the pressure in the chamber, which will rise to as high as 2 x 10^{-8} Torr, but should decrease quickly. When it has returned to 10^{-9} Torr, press the “HV on” button and adjust the dial so that the display reads ~4.00 – 5.00 kV. Monitor the pressure, which should still be in the 10^{-9} range (Note: These values are for Mg anode, Al may be higher). Press the “Oper” button, the value of I_FIL should rise to ~ 3.6 A and the light should blink briefly before becoming steady again. Press the “I_E” button (should light up green) and use the left and right dials to gradually increase the I_E and HV values to the desired reading (14 mA for I_E and 10
kV for HV are standard, 18 mA for $I_E$ and 12 kV are maximum for Mg anode, 14 kV can be used for Al anode). In the SPECTRA window press the circular button marked “Go” to the right of the Edit Regions Button.

9. Once the scans are finished, ramp down the HV and $I_E$ values by turning down the dials slowly until they are at about 4 kV and 5 mA respectively, then Press “Oper” (the light should go off and the “Standby” button should light up. Press “HV” (the light should go off), then press “Standby” (the light should go off). If you are going to do more scans but the pressure has increased significantly over the course of your run, the system can be left in this state while it pumps down. If the pressure has not increased significantly, you can adjust the region info and then run more scans at your discretion without having to turn off the HV/$I_E$ switches.

If you will not run anymore scans, leave the “Cooling On” button on to let the anode cool down for ~5-10 minutes. Press “Cooling On”, then press the power switch. Turn off the chiller. Turn off the analyzer electronics by turning off ESCA kV first, then the boxes from bottom to top (in reverse order from Step 5). Remove your sample from the chamber if desired.
A7.4.2 PHI Photoemission System Operational Procedure

A7.4.2.1 Overview

The PHI Photoemission system at Stanford University uses the Stanford Synchrotron Radiation Lightsource (SSRL) beamline for near-edge X-ray photoemission spectroscopy. The emission system was used to gather data on the composition of the LASO films.

A7.4.2.2 Sample Load Lock Procedure (If load lock is not vented, vent in 1-8.)

1) **VERY IMPORTANT!** Make sure the main chamber/load lock valve is closed!
2) Check to make sure the analyzer is off.
3) Check to make sure the cold cathode gauge (CCG) on turbo cart is off.
4) Turn off the power of the power strip (or unplug the strip) on turbo cart so that the pneumatic valve on top of the turbo is shut off.
5) Turn off the turbo pump. Before proceeding, wait a few minutes and wait for the turbo to stop.
6) Open the N₂ line needle valve. Make sure the N₂ is running and venting out from the relief valve.
7) Open the load lock/pump hose valve if it is closed.
8) Open the N₂ line/turbo valve, so that the N₂ goes into the load lock to vent. Wait a few minutes before proceeding to vent the chamber.
9) Open the load lock door when there is no resistance.
10) Put the aluminum strip under the fork to catch the sample holder in case it falls.
11) Use the hemostat to hold the sample holder and align the sample holder with the fork.
12) Rotate the transfer arm to lock the sample holder on the fork.
13) Release the hemostat.
14) Carefully remove the aluminum strip, not to undo the sample holder from the fork. (May retrieve the fork back and move the aluminum strip so that the aluminum strip does not touch the sample holder).
15) Close the load lock door, making sure the door does not catch any of the glove bag, and seals properly.
16) Close the N₂ line/turbo valve (V3).
17) Close the N₂ needle valve.
18) Make sure the turbo pump is off and already is not spinning (normally takes 5 minutes after it is turned off).
19) Turn on the power of the power strip (plug in the blue plug) on the turbo cart, and the pneumatic valve on the turbo should open.
20) Turn on the turbo pump.
21) Turn on the convection gauge to monitor pressure reduction to 0.1 mTorr.
22) After turbo reaches steady-state, turn on CCG on turbo pump to monitor pressure.
23) Pressure usually takes 30 minutes to pump down.

A7.4.2.3 Transfer sample into chamber

1) Make sure the pressure in the load lock is less than $5 \times 10^{-7}$ Torr.
2) Manipulator should be at a position approximately $x=10.25$, $y=10$, $z=5.5$, $\theta=120$.
3) Close the load lock/pump hose valve.
4) Turn off ion gauge at IOS chamber.
5) Open load lock/main chamber valve.

A7.4.2.4 Sample Annealing Procedure

1) Make sure the electron energy analyzer has been turned off.
2) Make sure the beam valve closest to the chamber is turned off.
   a) IV3 for VL81
   b) IV4 for BL10-1
3) Raise the sample $z$ position from $z=0.45$ to $z=2$.
4) Connect the heating wire if needed.
5) Turn on the multimeter to measure the heating current.
6) Turn on the current power supply, use the coarse adjustment first, and then fine adjustment to reach the desired heating current. See Heater Current Calibration below.
7) Anneal sample.
8) Turn the current down to 0.
9) Turn off the current power supply.
10) Turn off the multimeter.
11) Wait for 5 minutes for the sample to cool down.
12) Lower the sample to $z=0.45$.
13) Make sure the pressure of the chamber is less than $5 \times 10^{-9}$ Torr.
14) Reset the beam line valve control if needed to clear a fault.
   a) A fault will be generated when the pressure gauge is off calibration or pressure is over $5 \times 10^{-9}$ Torr.
15) Open the beam line valve.
16) Turn on electron energy analyzer.
17) Take spectrum

Heater Current – Temperature Calibration

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>70-90</td>
</tr>
<tr>
<td>2.6</td>
<td>150</td>
</tr>
<tr>
<td>3.0</td>
<td>200</td>
</tr>
<tr>
<td>3.6</td>
<td>300</td>
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A7.4.2.5 Change Energy on Beam Line 8-1

1) Find which grating to use: 30-100 eV, then use 822 l/mm; 100-160 eV then use 2400 l/mm.

2) If the grating needs to be changed:
   a) Physically change the grating.
   b) Exit SUPER by typing ‘SUP>exit’ in the computer screen.
   c) Type S081>ics_config grating.
   d) Press “P” for parameter.
   e) Press “Enter” to bring up the window for the first parameter: lines per millimeter on the grating.
   f) Enter the number of the grating (822 or 2400).
   g) Press “E” to exit ics_config program.
   h) Type S081>SUPER to start SUPER.
   i) Change energy by “SUP>mono” then the energy you want. For example, to go to 130 eV, type “SUP>mono 130”.
   j) Maximize the 10 by pitching m1 mirror. “SUP>1mpitch/rel 0.002/-0.002”
   k) Now you are ready to take the spectra.

A7.4.2.6 Change Energy on Beam Line 10-1

1) Find which grating to use: 180-800 eV, use 600 l/mm; 800-1200 eV, use 1000 l/mm.

2) If the grating needs to be changed:
   a) Physically change the grating.
   b) Exit SUPER by typing “SUP>exit”.
   c) Type S101>ics_config grating
   d) Press “P” key for parameter
   e) Press “Enter” to bring up the window for the first parameter: lines per millimeter on the grating.
   f) Enter the number of the grating. (600 or 1000)
   g) Press “E” to exit ics_config program.
h) S101>SUPER to start SUPER  
i) Change energy by “SUP>mono” and the energy desired. For 200 eV, enter “SUP>mono 200”.  
j) Change exit slit position to match the energy. For example, “SUP>eslit 1782”. This is used to obtain optimum resolution. The table for the exit slit positions is at 10-1.  
k) Maximize the 10 by pitching m1 mirror. “SUP>m1pitch/rel 0.002/-0.002”  
l) You are now ready to take the spectra.

A7.4.2.7 Photoemission system - Use SUMMIT software to collect data

1) Open the chamber to the beam line.  
   a) Make sure the chamber pressure is less than 5 x 10^{-9} Torr.  
   b) If there is a fault on the beam line rack, press “reset” to clear the fault.  
   c) Open the beam line valves in the following order: IV3, IV2, IV1, BS.  
   d) Go to the desired photo energy.  

2) Obtaining the Spectrum (simple version)  
   Generally there are already some existing data files. You can open one of the existing data files, modify some parameters and use those settings. If there are no previous data files, you need to start from scratch, and consult the full version below.  
   a) Turn on the Electron Energy Analyzer.  
   b) Start the SUMMIT software. Note you need to start this program after each time the analyzer is turned on to properly initialize the parameters. If the program is already running, you have to shut it down and restart it again.  
   c) Open an existing data file.  
   d) Modify the data region:  
      i) Most of the region parameters are self-explanatory  
      ii) We normally use Pass Energy of 29.35 eV for survey scan, 11.75 eV for detailed scan.  
      iii) We normally use 0.1 eV step size for the survey scan and 0.05 eV for detailed scans.  
      iv) You can adjust the number of repeats with each cycle or time per step so that weaker peaks are scanned for a longer time.  
      v) Note sometimes your change will fail because they are either illegal, (i.e. binding energy >hν), or they depend on some other parameters.  
      vi) You can add more regions or delete regions.  
   e) Modify the number of cycles you need.  
   f) In the “Hardware” section, click “X Ray” and in the “Source Energy” box, input the photo energy.  
   g) Click “folder button”:  

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i) Select the correct folder to save data files.

ii) Enter the prefix for the data file name. Keep it short and free of space and other special characters.

iii) Enter the start number. The full filename will be like, <prefix><number>. The number will automatically increase for the next data file.

iv) Enter comments. Keep it less than one line. Long comments will make the program freeze. To avoid the problem, it is recommended to NOT put comments here. Instead, record everything in a lab notebook.

h) If you want to take a scan without recording the data, click “Test Acquire”.

i) Click “Acquire” to take data.

i) If you want to abort, click “Abort”. No data will be saved.

ii) If you think the data are good, click “Stop”, and the program will finish the current scan and save the data.

iii) At the end of the scan, you will be asked if you want to do more. If you are satisfied with the data, click “no”. If you think you need more scans, click “Yes”. Change number of cycles, and click “Acquire”. More cycles will be added to the existing data.

j) After spectra are collected, click the middle save button to save the data as an ASCII file. The original data files are binary, and not easy to decipher. If you forget, you can always open the file later, and save it as an ASCII.

k) Turn off analyzer and close beam lines after data collection is done. Note: The analyzer sometimes glitches. This causes the spectra to look unusual, or the intensity will be zero. Normally completing test scans until the analyzer resets works (i.e. waiting it out).

3) Taking the spectrum (full version)

a) Turn on the Electron Energy Analyzer.

b) If SUMMIT is already running, exit first and restart the program.

c) If there is already a data file we can use as a template, open the file, make modifications if needed, and start acquisition.

d) If there is no existing file to use, click “Measure (M)” → “Acquisition (A)”. The acquisition window will open.

e) Make sure “Sputter Mode” is “No Sputter”.

f) Make sure “Points/Line/Map” is “Center”.

g) Make sure “AR-XPS” is “No”.

h) In “Hardware” section:

i) Click “Analyzer” and change analysis area to “1 x 3.5 mm”.

ii) Click “X-Ray”.

(1) Change “Anode” to “SR” to stand for Synchrotron Radiation.

(2) Change “Source Energy (eV)” to the desired photon energy.
(3) Make sure the “Work Function (eV) is 4.4 eV.

   iii) Click “OK”

   i) Click “Folder”, specify the directory, prefix of the data file, start number and comment. All data should be stored under subdirectories of C:/XPS data”.

   j) Go back to the top portion of the window to specify data acquisition region. Change the parameters there to the desired value.

   i) NOTE: Remember the x-axis is binding energy. It can start from a negative number, but it cannot exceed or be equal to the photon energy you specified in h(ii)(2). Many times if the parameters refuse to change, this is the reason.

   k) You can add new regions by clicking the “Insert” button and change the parameters there.

   l) Specify “Total Cycles”.

   m) If not sure, click the “Test Acquire” to test the highlighted region. No data file will be saved. Click “Stop” to stop the test acquire.

   n) If the regions are set up correctly, click “Acquire” to start scans.

   o) Click “Abort” to abort the scan without saving.

   p) If noise level is OK, click “Cycle Stop” button to stop after the current scan and save the data, or you can wait until all the cycles are completed.

   q) After the scan is done, go to “File(A)”→”Save as ASCII(A)” to save a text version of the data file.

   r) After all scans are complete:

      i) Turn off the analyzer

      ii) Close the beam line valves in the following order: BS, IV1, IV2, IV3

4) Raw Data Processing

   Absorption measurements are done by measuring the sample drain current. There is a BNC connection on top of the manipulator which is connected to the sample. It is generally grounded by a BNC terminator. It can be used for drain current measurement of applying a bias to the sample.

   a) The ASCII data records spectra parameters, and data. If the data has multiple regions, they are stored in a single file. There is a simple program to break the data file into several data files, one for each region. In addition, the program changes the “y” data from counts to counts per second, so it is easier to compare spectra with different acquisition time.

   b) Open the program called “convSummit.exe”, which is located in “C:/XPSdata”. To run it, copy it into the data folder, double click it and follow the instructions.

A7.4.2.8 Taking the chamber off a beam line
1) Electron Energy Analyzer connection.
   a) Make sure Electron Energy Analyzer is off.
   b) Make sure all the beam line valves are closed.
   c) Disconnect all the cables from the Electron Energy Analyzer.
   d) Shut down the data collection PC.
   e) Move the Analyzer electronics car (with the data collection PC) aside.
      i) Note: Analyzer cables will be reconnected after the chamber is visually aligned using phosphor plate on the beam line.

2) Load lock turbo pump
   a) Close the valve between load lock and the turbo pump hose.
   b) Turn off the Cold Cathode Gauge (CCG) on the turbo.
   c) Turn off the convection gauge if it is on.
   d) Turn off the power for the pneumatic valve between the turbo and the venting manifold. This closes the pneumatic valve.
   e) Disconnect the N₂ line.
   f) Disconnect the compressed air line.
   g) Disconnect the turbo from the load lock.
   h) Move the turbo cart aside.

3) Disconnect chamber from beam line 8-1.
   a) Close the valve between the chamber and beam line bellow. Use 50 ft-lbs. Watch chamber pressure to make sure the valve seals correctly.
   b) Disconnect the chamber from the beam line bellow.
   c) Remove the supporting blocks from the chamber feet.
   d) Remove the chains and eye-bolts which are used for earthquake bracing.
   e) Lower the chamber down by turning the jacks (one in front and two in back). Lower the front a little, then back a little to keep the chamber leveled.
   f) When chamber wheels are close to the floor, make sure the rear wheels do not land on the T.
   g) After the wheels touch the floor, move the T away from the jack legs. Note you cannot totally remove the T because the rear wheels will prevent it.
   h) Put a wood chock under the rear right leg and jack the chamber up a little so that the rear wheels turn freely.
   i) Remove the T.
   j) Lower the chamber down again so the chamber is on all four wheels.
   k) Chock the wheels so that the chamber will not move around.

4) Remove other connections.
a) Put the manipulator in the lowest position so that it can clear the elevator door. The sample surface should face the analyzer to avoid collision.
b) Disconnect the manipulator motor cables, one for rotation, one for vertical.
c) Place the manipulator motor controller on the electronics rack.
d) Disconnect the chamber vacuum gauge interlock cable from the beam line.
e) Turn off the main chamber cold cathode gauge. First press and hold the down arrow button at the front and then flip the power switch at the back of the controller.
f) Disconnect the cold cathode gauge cable from the chamber.
g) Disconnect the BNC cable from the 10 grid to the Ketheley.

5) Manipulator pump
   a) Close the small right angle valve on manipulator rotor, which goes to the vacuum system that pumps the manipulator rotor outer section.
   b) Turn off the manipulator pump.
      i) NOTE: The small manipulator ion pump is not used. It stopped working two years ago. We found that pumping the outer section with a drag pump or small turbo is sufficient. If the pressure in the inner section is too high, it will impact the main chamber pressure. This occurs after a power outage. Open the needle valve between the outer section and inner section so that the inner section can be pumped away. The needle valve should be closed to separate the outer section and inner section.
      ii) NOTE: Normally the outer section is pumped by a alcatel drytel drag pump, which can be placed on the chamber platform to move with the chamber. During operation, it should be placed on the floor so that it does not shake the chamber. Currently, the drag pump is broken. A Varian turbo cart is used instead. It should be disconnected from the chamber because it can not be moved together with the chamber due to size.

6) Main chamber pump.
   a) Turn off the HV on the ion pump controller.
   b) Turn off the power for the ion pump.
   c) Disconnect the ion pump cable. This may be easier to disconnect from the back of the pump controller.
   d) Disconnect the ground cable from the back of the pump controller.
   e) Disconnect the power for the electronics rack.
   f) Disconnect the ground cable for the electronics rack.
   g) Now the chamber can be moved away.
Make sure the analyzer and the transfer clear all the hallways. A person is needed to hold the open button for the B120 elevator so that it does not close when we move the chamber in and out of the elevator.

1) Connecting the chamber to beam line 10-1
   a) Carefully move the chamber around so that it aligns well with the beam line.
      i) The front port should touch the beam line bellow.
      ii) Look from the beam line side, the center of the beam line should align with the chamber manipulator.
   b) Chock the wheels
   c) Place a wood chock under the rear right leg. Turn the jack and raise the back of the chamber a little so that the rear wheels can turn freely.
   d) Insert the T.
   e) Position the rear wheels facing inward so that they do not block the T.
   f) Lower the chamber so that it sits on wheels.
   g) Move the T so that all legs are aligned with the T leg support. (May need to adjust the T so that they are fairly centered to give room to move both ways during the chamber alignment process.)
   h) Drop the chamber legs on the T. Raise the chamber up with the jack. Move front and back up in turn, allowing the chamber to remain level.
   i) Once the chamber reaches the beam line height. Align the chamber front port with the beam line bellow by adjusting the T.
   j) Connect the chamber with the beam line bellow.
   k) Pump down the small connection section and bake out. Set up other items during bake.
   l) After the connection section is baked overnight, burn off bake.
   m) Allow about 3 hours for the connection section to cool.
   n) Open the chamber front port valve so that the connection section is open to the main chamber. Monitor the pressure.
   o) Brace chamber
      i) Put chains on the eye-bolts on the floor to earthquake-brace the chamber.
      ii) For added stability, put support blocks and drop the chamber feet to rest on the support blocks.
      iii) Secure a grounding cable between chamber and the beam line grounding anchor.
   p) Turn on pumps.
      i) Connect the chamber ion pump to pump controller.
      ii) Connect the ground cable from chamber to ion pump controller.
      iii) Ground the electronics rack.
      iv) Turn on ion pump power. Then turn on HV on the controller.
      v) Manipulator pump:
(1) Connect a pump to the manipulator rotor, if there is no pump already connected.
(2) Start the pump. Once the pump reaches full speed, open the manipulator rotor valve so that the outer section is pumped.

vi) Connect the turbo pump cart to the load lock.
   (1) Connect the N\textsubscript{2} line, compressed air line, and power for the turbo cart.
   (2) Turn on the pneumatic valve between the turbo and gas manifold.
   (3) Turn on the turbo. After it pumps for a while, open the valve between the load lock and the turbo pump hose so that the load lock is pumped.

vii) Connect the manipulator motor cables: 1 for vertical, 2 for rotation.

q) Connect the cable for main chamber cold cathode gauge. Turn on the cold cathode gauge by the power switch at the back first, then press and hold the “up arrow” button at the front.
   i) If the pressure is too low (<1 \times 10^{-10} Torr), it will first show “ur”. After a short time, it will turn on and show pressure.
   ii) Connect the pressure interlock cable to the beam line.
   (1) Connect the 10 grid to a Ketheley.

2) Procedures for chamber alignment using phosphor.
   a) Load a sample plate with phosphor powders.
   b) Move x to x=8 so that it is away from the analyzer.
   c) Lower the phosphor plate down to x=4.5, center the analyzer height, and do not rotate the manipulator so that the phosphor plate is still perpendicular to the analyzer.
   d) Open the chamber to the beam line. Observe the zero order beam on the phosphor plate.
   e) Adjust the beam line focus if needed. This is also how to move the beam up and down.
   f) Adjust the chamber height so that the beam spot is approximately at the center of the Electron Energy Analyzer. You may want to first remove the feet support blocks or loosen the chains a little so that the chamber can move.
   g) Place the sample at analysis position, rotate first to 30 degrees on rotor so that sample is facing analyzer. Then set x=y=10, z=0.45. At this position, the sample is at the focal point of the electron energy analyzer. Once we centered the beam on the sample, the beam spot also should be close to the analyzer focal point.
   h) Adjust the back side of the T to twist the chamber sideways so that the beam spot is centered on the phosphor plate. It is useful to rotate the sample to an extreme glancing angle so that the beam spot becomes a horizontal line. It is easier to tell if the beam is centered this way.
i) Note: If the T prevents movement, the chamber can sit on the feet support instead of on the legs. Adjust the T to force the T to change position while the chamber is stationary.

j) Adjust the height so that the beam is centered on the analyzer. Use a flashlight to illuminate the analyzer horizontally, the center of the reflection should be the center of the analyzer, and this should align with the beam spot.

k) Check the alignment using a working energy (400 eV on 10-1, 120 eV on 8-1) instead of zero order. Sometimes the zero order is too bright and true center is difficult to discern.

3) Procedures to align chamber using photoemission peak.
   a) Load a sample into the chamber. (A HF cleaned Si works very well, but any other sample with well defined, strong photoemission peaks should also work.)
   b) Set the beam line energy at the desired value.
   c) Set sample at analysis position x=y=10, z=4.5, angle=30 degree (normal emission). Measure the photoemission peak of interest.
   d) Adjust the back side of the support T. Take a spectra for every turn. Record the intensity for each position.
   e) Set the position at the maximum intensity.
   f) Repeat for the vertical position of the chamber.
   g) Measure each quarter turn of the jack and record the intensity.
   h) Find the height for maximum intensity.
      i) Note: If alignment with phosphor is done well in the vertical direction, the alignment by photoemission peak can be unnecessary. Horizontal alignment is still needed.
      ii) Use “Unscan mode” to take spectra. Use “test scan” instead of “scan” so that it is continuously scanning.

4) Chamber venting procedure.
   a) Close the valve between the main chamber and the ion pump by turning the handle on the back side of the chamber.
   b) Close the manual valve between the main chamber and 10 section to reduce sections to be vented.
   c) Turn off ion pump, cold cathode gauge, and all other equipment.
   d) Open the valve between main chamber and the load lock.
   e) Follow the load lock venting procedure described in the sample transfer section. Because the valve between the main chamber and the load lock is open, the main chamber will be vented as well as the load lock.
5) After the work is done on the chamber:
   a) Cutoff N\textsubscript{2} and separate the N\textsubscript{2} line from the load lock. Follow the procedure described in the sample transfer section.
   b) Pump down the main chamber through the load lock.
   c) After the pressure $1 \times 10^{-6}$ Torr. Open the ion pump valve and the valve between the main chamber and the 10 section.

6) Pump down without bake out:
   a) Pump down by turbo for 2 days.
   b) Turn on ion pump after the pressure drops down. Close the valve between the load lock and the main chamber.
   c) Let the ion pump down for 1-2 days.
   d) Run TSP several times to assist the pumping.

7) Bake out:
   a) Remove the two analyzer electronic boxes from the electron energy analyzer.
   b) Remove motors from the top of the manipulator.
   c) Follow the regular bake out procedures.
BIBLIOGRAPHY


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Jian, L. and S. Xueliang (2015). "Elegant design of electrode and electrode/electrolyte interface in lithium-ion batteries by atomic layer deposition." Nanotechnology 26(2): 024001.


250


Østreng, E. (2014). Atomic layer deposition of thin films containing alkali metals. Doctor of Philosophy, University of Oslo


Riikka, L. P. (2005). Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process. AIP.


