Development of Rutile Titanium Oxide Thin Films as Battery Material Component Using Atomic Layer Deposition

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Herein, growth kinetics, crystal structure, and the uniformity of titanium oxide (TiO$_2$) thin films prepared using atomic layer deposition (ALD) and plasma-enhanced ALD (PE-ALD) are studied. TiO$_2$ thin films are grown using titanium tetrachloride (TiCl$_4$) and water as precursors. Using ALD, TiO$_2$ growth is observed in the temperature range of 270–310 °C thermally and in the range of 300–400 °C with PE-ALD. In spite of the plasma process yielding better uniformity on planar structures, the optimized thermal process provides a remarkable conformal step coverage within deep trenches. In addition, the change in the crystal structure and phase transitions of TiO$_2$ is presented herein. This is attempted at using TiO$_2$ as a component material to grow lithium titanate (LTO) as an electrode material in solid-state lithium-ion batteries (LIBs). Thereby, different substrates are used. In comparison to the silicon (Si) substrate, silicon oxide (SiO$_2$) and titanium nitride (TiN) lead to crystal phase transformation while annealing. Measurements are performed using X-ray diffraction (HT-XRD). It is also shown that when TiN is sandwiched between TiO$_2$ and the silicon substrate, the TiO$_2$ thin film (25 nm) gradually changes from an anatase to a rutile structure.

1. Introduction

Lithium titanate (Li$_4$Ti$_5$O$_{12}$) (LTO) is one of the most promising electrode materials for lithium-ion batteries (LIBs). The spinel structure of LTO has the advantage of undergoing only minor volumetric changes of 0.2% upon cycling, with no structural degradation.[1,2] Furthermore, its spinel structure provides a 3D pathway for Li ions, which lead to higher Li insertion voltage ($\approx$1.5 V vs Li$^+/\text{Li}$) compared with a conventional anode material (e.g., graphite) with a conventional anode material (e.g., graphite) below 0.2 V vs Li$^+/\text{Li}$).[3,4] Considering safety and a longer life cycle, LTO has attracted significant interest recently as an anode material in solid-state LIBs (SSLIBs). LTO can be synthesized with different methods such as sol–gel techniques, magnetron sputtering, pulsed laser deposition, chemical vapor deposition (CVD), and atomic layer deposition (ALD).

In this research, we developed the titanium oxide (TiO$_2$) deposition process on high-aspect-ratio structures (HAR) to be used as a building component for LTO. TiO$_2$ is known to be a polymorphous material that exists in three crystalline structures: two tetragonal variants, anatase and rutile, and one orthorhombic (brookite phase); however, only the anatase and rutile structures are achieved in thin films.[5] The fabrication of TiO$_2$ thin films can be prepared using various techniques, such as the physical vapor deposition, CVD, spin coating, or ALD.[6–9] In comparison with all these methods, ALD offers many advantages, which can be attributed to its growth parameters. In applications which require precise thin-film thickness control, delivering conformal films with precision control over composition and also homogeneous deposition on profiled and 3D substrates at relatively low growth temperatures, ALD shows the most desirable performance among all other techniques.[10–11] A disadvantage of this deposition method is the sequential alternating pulses; it is time-consuming to deposit films thicker than 100 nm. The presented study mainly focuses on the optimization of two processes, thermal and plasma ALD, to identify the most suitable technique to potentially combine with lithium in a sequential ALD process of TiO$_2$ and LiO$_2$ deposition to form the LTO layer.

Studies show that the dual-phase LTO/rutile TiO$_2$ composite has superior electrochemical performance versus that of pure LTO. Particularly, rutile TiO$_2$ nanocoating could improve the low kinetics associated with the electrical performance of LTO.[4,12] In this paper, we report the phase transformation of TiO$_2$ by utilizing an intermediate layer beneath it to induce phase
transformation from anatase to rutile at lower recorded temperatures. In addition, a lithium barrier layer must exist in between the silicon substrate and the anode (e.g., LTO) to prevent lithium ion diffusion from the anode into the Si substrate. Metal nitrides, such as TiN, are often used as a lithium diffusion barrier. TiN is completely electronically conductive and can therefore be used as both a current collector and a diffusion barrier layer. In addition, thermal oxide wafers consisting of a 100 nm-thick SiO$_2$ layer on a bare Si substrate were used, where SiO$_2$ also acts as an intermediate layer beneath TiO$_2$. A massive structural transformation of thermal SiO$_2$ can be used as a barrier for ion diffusion and is widely used as an insulator in electronic devices. Even in HAR structures, it is possible to achieve conformal coverage of the SiO$_2$ layer using plasma-enhanced ALD (PE-ALD).

The correlation of the crystal phase with the critical temperature of TiO$_2$, with respect to the deposition temperature, film thickness, and underlying substrate, is studied in this paper. Thin films’ microstructure, composition, and optical properties are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and spectroscopic ellipsometry. These studies help to identify the appropriate conditions for using TiO$_2$ thin films, deposited by ALD, as a potential electrode material for LIB applications.

2. Results and Discussion

2.1. Deposition Process Optimization (ALD Window)

The growth of TiO$_2$ (using TiCl$_4$ and water) is first checked using ellipsometry to determine the ALD process window. The process temperature was changed from 235 to 290, 345, and 400 °C. For the plasma process, the temperature is varied from 150 to 190, 235, 290, 345, and 400 °C. Figure 1 illustrates the relative constant growth rate per cycle (GPC) of 30 and 50 pm per cycle for the thermal and plasma process in the range of the ALD window, respectively. The lower growth rate of TiO$_2$ thermal deposition, in comparison with the plasma process, is mainly due to a significant amount of chlorine that bonds to the surface during TiCl$_4$ adsorption. Aarik et al. mentioned that at temperatures below 200 °C and above 350 °C some chlorine is released in the TiCl$_4$ adsorption step. At intermediate temperatures, however, chlorine is absorbed in the initial stage of the interaction between the TiCl$_4$ and TiO$_2$ surface, which is the main reason for the limited growth rate of TiO$_2$ in the TiCl$_4$/H$_2$O ALD process. The higher growth rate of the thermal process at 345 and 400 °C can also be explained by decomposition processes. In PE-ALD, due to the contribution of plasma, several new parameters will affect the typical ALD behavior. Detecting the ALD window in a plasma process indicates truly ALD mechanisms where surface saturation is the dominant behavior instead of gas phase reaction (CVD effect) or precursor decomposition.

2.2. Pulse Length Optimization (Saturation Curve)

The self-limiting nature of ALD makes it a unique deposition technique that can produce excellent step coverage within HAR structures. However, to demonstrate conclusively that growth indeed operates by an ALD mechanism, saturation curves must be measured for the precursor and oxidant. For each precursor and reactant, the saturation curve is acquired while keeping other parameters, such as, e.g., purging time, deposition temperature, and cycles number, constant.

Figure 2a shows different TiCl$_4$ pulse times containing 150 ms pulses of water. As the pulse time increases between 0 and 50 ms, GPC increases until it plateaus, starting at 50 ms. Increasing the precursor pulse time to 100 ms decreases the standard deviation. This reduction can be explained by the fact that film conformality is enhanced by increasing the dose density of Ti molecules on the film surface after the TiCl$_4$ pulse. A further increase in pulse time may result in nonuniformity on the film surface. Overdosing TiCl$_4$ affects the structural arrangement of the atoms on the surface by releasing a higher amount of byproducts like HCl. Water pulse lengths were changed from 50 to 150 ms, while the TiCl$_4$ pulse lengths and Ar purge times were kept constant at 290 °C. Increasing the water pulse times from 50 up to 150 ms leads to better uniformity, from 2.7% to 2.1%,
respectively, while the growth rate does not see significant changes. Figure 2b illustrates TiCl₄ and plasma saturation curves at the given deposition temperature of 350 °C. The TiCl₄ pulse length was modified from 50 to 150 ms, while the plasma pulse time was kept constant at 5 s. As shown in Figure 2b, after 50 ms for TiCl₄ and after 5 s for the plasma, GPC reaches a plateau. Film thickness uniformity reaches a minimum value at 100 ms (SD of 0.2%) for TiCl₄. Variation in plasma pulse time (from 5 to 11 s) does not change uniformity at higher values.

The uniformity and chemical composition by means of standard deviation of the grown TiO₂ films were checked using ellipsometry and atomic percentage ratio with XPS, respectively. For this purpose, four samples were prepared using both the thermal and plasma processes. Table 1 represents the deposition conditions of each process. With the thermal process (sample no. 1 and 2), a deviation of 2.2% was recorded, and with the plasma process (sample no. 3 and 4) a deviation of 0.6%. In all processes, the measured value for the atomic percentage ratio of O:Ti with XPS is 2:1, that is, the ratio of titanium to oxygen is well above 2.0, which indicates that the oxidation state of titanium is 4⁺ (Ti⁴⁺); therefore, the material is indeed TiO₂ (Table 2). As shown for both plasma processes, a lower amount of carbon is detected in comparison with the thermal process. The plasma removes most of this. Ti 2p½ and Ti 2p¾ spin orbitals for TiO₂ from both ALD processes are located at binding energies of 464.6 and 458.8 eV (Figure 3B), respectively, which is in agreement with the reported literature values [6,7]. All spectra were calibrated based on carbon with a binding energy of 285.0 eV. Furthermore, no chlorine is detected on the surface of the film as shown in Figure 3A.

### 2.3. Results on Step Coverage

The TiO₂ thin films were deposited in HAR structures with both thermal and plasma ALD using TiCl₄ to test their conformality. Deposition conditions such as temperature, precursor and reactant pulse time, pressure, and purging times were set to the optimized condition to reach the highest conformality. Figure 4a shows SEM images of a TiO₂ thin film (≈90 nm) deposited by the thermal ALD process. The 9.28 μm-deep HAR structures have a tapered shape, with width decreasing from 0.62 μm at the opening to 0.35 μm at the bottom. The film was deposited at 290 °C, and 2500 cycles were applied in a run. The film shows the conformal coating of the holes with 100% uniformity.

**Table 1.** Summary of TiO₂ samples analyzed with XPS and ellipsometry.

| Sample          | Temperature [°C] | Cycle | Precursor pulse time (TiCl₄) [s] | Reactant pulse time [H₂O] [s] | Ar purge time [s] | Thickness [nm] | Wafer                  |
|-----------------|-----------------|-------|---------------------------------|-------------------------------|------------------|----------------|------------------------|
| Thermal ALD     |                 |       |                                 |                               |                  |                |                        |
| Sample #1       | 290             | 600   | 0.1                             | H₂O: 0.1                      | 5                | 25             | Thermal oxide wafer    |
| Sample #2       | 290             | 600   | 0.1                             | H₂O: 0.1                      | 5                | 22             | Bare Si wafer          |
| Plasma ALD      |                 |       |                                 |                               |                  |                |                        |
| Sample #3       | 350             | 500   | 0.1                             | O₂: 5                         | 5                | 25             | Thermal oxide wafer    |
| Sample #4       | 350             | 500   | 0.1                             | O₂: 5                         | 5                | 26             | Bare Si wafer          |
Table 2. Composition of TiO$_2$ thin films using TiCl$_4$ deposited at 290 and 350 °C in the thermal and plasma ALD process.

| Atom (atomic %)       | F 1s | O 1s | Ti 2p | O/Ti | C 1s | N 1s | Si 2p | Sample #1 | F 1s | O 1s | Ti 2p | O/Ti | C 1s | N 1s | Si 2p | Sample #3 |
|-----------------------|------|------|-------|------|------|------|-------|-----------|------|------|-------|------|------|------|-------|-----------|
| Thermal oxide wafer   |      |      |       |      |      |      |       | Sample #1 |      |      |       |      |      |      |       | Sample #3 |
| Si(100) wafer         |      |      |       |      |      |      |       | Sample #2 |      |      |       |      |      |      |       | Sample #4 |
| TiO$_2$ deposition    |      |      |       |      |      |      |       |           |      |      |       |      |      |      |       |         |
| Thermal ALD process   |      |      |       |      |      |      |       |           |      |      |       |      |      |      |       |         |
| 285 eV)               |      |      |       |      |      |      |       |           |      |      |       |      |      |      |       |         |
| Plasma ALD process    |      |      |       |      |      |      |       |           |      |      |       |      |      |      |       |         |
| 290 °C, 350 °C        |      |      |       |      |      |      |       |           |      |      |       |      |      |      |       |         |

**Figure 3.** High-resolution Cl 2p, Ti 2p XPS spectra from a) TiO$_2$ film deposition using thermal ALD process on top of SiO$_2$; b) TiO$_2$ film deposition using plasma ALD process on top of SiO$_2$; c) TiO$_2$ film deposition using plasma ALD process on Si wafer; and d) TiO$_2$ film deposition using thermal ALD process on Si wafer (calibration based on C binding energy of 285 eV).

SEM images in Figure 4b show the TiO$_2$ thin film deposited with plasma ALD, using TiCl$_4$ and oxygen in an HAR structure (20:1). The film was deposited at 350 °C, with 500 cycles applied in a measurement run, yielding a film thickness of ≈20 nm at the opening of the HAR structure. Depletion of TiO$_2$ at the bottom of the structure denotes poor in trench diffusion of both TiCl$_4$ and plasma radicals during plasma exposure. During plasma exposure pulses, the surface will be exposed to electron and ion bombardment, while only neutrals will be present within the holes. The impact of these nonreactive molecules from plasma radicals significantly reduces the local flux of reactive species to reach deep into the HAR structures. As a consequence, longer pulse times may be required to reach better deposition at the bottom of the holes in the structure.

### 2.4. Crystallographic Characterization (Solid-Phase Transformation)

The ALD processes used to prepare the TiO$_2$ material have shown that the films start to grow amorphously. When the film thickness exceeds 10 nm, the material begins to crystallize and develop into the anatase phase. To investigate crystal phase formation and transformation, TiO$_2$ films were deposited on three different substrates (bare Si(100) wafer, thermal oxide wafer with 100 nm SiO$_2$, and 35 nm TiN) using the thermal ALD process at 290 °C. The crystal structure of each sample is monitored during the annealing process from room temperature up to 715 °C and vice versa with in situ high-temperature XRD (HT-XRD). The results show that the deposited TiO$_2$ (25 nm) on the Si(100) substrate has an anatase crystal phase A(101). Figure 5 shows that the post-annealing and cooling processes grow the anatase phase intensity.

Using a thermal oxide wafer as a substrate influences the crystal structure of the material during the cooling process (Figure 5b); the formation of weak rutile signals combined with the anatase phase is observed in the in situ HT-XRD diffraction pattern while the system cools down. As reported by Pessoa et al., TiO$_2$ ALD deposition using cover glass substrates (composed mainly of SiO$_2$) promotes the synthesis of an almost pure rutile phase. It is mentioned that glass substrates act like SiO$_2$ substrates or even a SiO$_2$ seed layer on another substrate, which could serve as an excellent platform for the growth of good-quality rutile TiO$_2$ phase. Figure 5c shows the diffraction pattern of 25 nm TiO$_2$ deposited on 35 nm TiN. In contrast to other samples, the crystal structure of the as-deposited anatase phase changes when annealed at 600 °C; the rutile phase starts to form, and in parallel, the intensity of the anatase phase decreases. Therefore, using TiN as a substrate can induce the formation of a rutile phase and affect the nucleation process by changing the chemical characteristics of interfaces.

As described by Zhang et al., between 620 and 690 °C, rutile nucleation is predominant at both the interface and surface. At this temperature range, there is no need to have a preexisting rutile structural element to be used as the nucleation site for interface and surface nucleation. Based on this argument, a temperature of 600 °C would not provide sufficient energy to overcome thermal activation energy for bulk nucleation. In spite of this, when TiN is used as a substrate in this research, it is observed that the anatase phase transforms into the rutile phase. Another parameter that affects the crystal phase formation is the oxidation of titanium molecules at the interface of TiO$_2$ and TiN at a high temperature. A redox reaction may oxidize the surface between the amorphous TiO$_2$ and TiN substrate. As reported by Kadoshima et al., during the annealing
Figure 4. Cross-section image of a) a 90 nm TiO$_2$ film deposited at a substrate temperature of 290 °C from the thermal ALD process and b) a 20 nm TiO$_2$ film deposited at a substrate temperature of 350 °C from the plasma ALD process.
process, the diffusion of oxygen ions through the TiO\textsubscript{2} film leads to the growth of interfacial oxide covering the substrate’s surface.\textsuperscript{[22]} Based on the parabolic law for oxygen ion diffusion coefficient in rutile TiO\textsubscript{2}, the diffusion length is calculated to be 0.1 μm at 600 °C (during the first 10 s), which is much larger than the deposited TiO\textsubscript{2} thickness. Due to this fact, oxygen ions could be supplied to induce phase transformation.

Moreover, a comparison between thermal- and plasma-deposited TiO\textsubscript{2} on SiO\textsubscript{2} shows the formation of the rutile phase after post-annealing for the plasma process (as shown in Figure 6). The difference can be attributed to the distinct advantages of plasma ALD-deposited films, such as higher layer densities and a decreased amount of impurities. Comparing the relative densities of these two samples showed a higher value (6%) for plasma-deposited TiO\textsubscript{2}. In addition, XPS results show a higher amount of oxygen (~3%), which can affect crystal structure transformation during post-annealing (see Table 2). The results from the study of samples indicate that the presence of oxygen ions is a compelling factor in phase change.

3. Conclusion

This study presented here aimed at establishing an optimum processing condition to grow a conformal TiO\textsubscript{2} thin film layer using TiCl\textsubscript{4} via two methods: thermal and plasma ALD. The plasma process resulted in a higher growth rate compared with the thermal process and showed better conformality on a planar surface of 0.6% in comparison with 2.2% for the thermal process. However, step coverage tests using HAR structures revealed the main challenge that PE-enhanced ALD faces with the depletion of TiO\textsubscript{2} at the bottom of holes. Furthermore, we conducted a survey on the TiO\textsubscript{2} thin-film crystal formation and studied phase transformation by post-annealing on different underlayers. Films with thicknesses higher than 10 nm crystallize to the anatase phase independent of the type of substrate used. Post-annealing processes for TiO\textsubscript{2} films on SiO\textsubscript{2} and TiN as substrates lead to crystal phase transformation. A combined phase of rutile and anatase is observed in the cooling process when using a SiO\textsubscript{2} substrate. The conversion of the crystalline phase from anatase to

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{The in situ HT-XRD diffraction pattern from thermal ALD of 25 nm TiO\textsubscript{2}, annealed up to 715 °C. TiO\textsubscript{2} film is deposited on top of a) silicon substrate, b) 100 nm SiO\textsubscript{2}, and c) 35 nm TiN.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Grazing incidence XRD of thermal and plasma ALD of TiO\textsubscript{2} deposited on SiO\textsubscript{2} after the annealing process up to 715 °C.}
\end{figure}
rutile TiO$_2$ is also observed at high-temperature annealing, whereas using TiN as a substrate reduced the phase transformation temperature. Moreover, this should be considered along with the fact that using TiN as an underlayer between the substrate and anode material has other advantages, such as being an excellent diffusion barrier for Li ions and also as an electron collector.

4. Experimental Section

**ALD Processing: TiO$_2$ ALD Precursor:** The ALD deposition of TiO$_2$ films was done using various precursors at different temperatures, and in turn this influenced the crystal structure of TiO$_2$.[8,9] Halide and alkoxide precursors were widely employed, of which the most commonly used were TiCl$_4$ and propyl alcohol trichlorosilane (TTIP). The main drawback in using TiCl$_4$ was the production of gaseous byproducts resulting from its reaction with hydrogen-based precursors, such as hydrochloric acid (HCl).[8,23,24] HCl resulted in unwanted nonuniformity in film thickness, and due to its corrosive nature, it had the capacity to etch the reactor components, even the grown film, and easily corrode the ALD reactor. Herein, we presented efficient thermal and plasma ALD processes using TiCl$_4$, without resulting in chlorine contamination.

**Deposition Condition:** The ALD processes were done with a FlexAl II ALD tool from Oxford Instruments. For both processes, argon was used as the bubbling gas, with a fixed flow rate of 200 sccm. The minimum manifold temperature was 120 °C, and minimum line temperature was 140 °C. In the reactor, plasma was generated using a radiofrequency source ($f=13.56$ MHz) with a plasma power of 350 W; on the other hand, the thermal process used elevated temperatures to promote deposition on the front surface of the substrate. Oxygen flow rate during plasma exposure was fixed at 60 sccm. The reactor pressure was fixed at 80 mTorr for both processes (optimum process conditions suggested by the tool manufacturer). During plasma stabilization (2000 ms) and plasma exposure, the reactor pressure decreased to 15 mTorr.

**Characterization Techniques:** TiO$_2$ films were characterized by different methods. Physical film thicknesses were measured using spectroscopic ellipsometry via the KLA Tencor Spectra FX100. On each wafer, 49 points were measured with ellipsometry to calculate mean thickness, and uniformity was measured by calculating the standard deviation. The chemical composition was evaluated by Revera VeraFlex inline XPS. XPS measurements were performed using a monochromatic Al-K$_\alpha$ X-ray source (1486.6 eV) and an analyzer pass energy of 141.2 eV. The intensities of the F 1s, O 1s, Ti 2p, C 1s, N 1s, and Si 2p core levels were measured as the peak areas after standard background subtraction according to the Shirley procedure. The spectrometers were fitted using the CasaXPS software. XRD was performed on the multilayer-composed material of TiO$_2$ on top of three different sublayers: a bare Si wafer, SiO$_2$, and TiN. A Cu-K$_\alpha$ radiation source was used to operate at 40 kV/40 mA (Bruker D8 Discover). For HT-XRD analysis, samples were heated from room temperature to 715 °C under constant nitrogen purging in a furnace covered with a hemispherical beryllium dome. During temperature ramp-up and cool-down, in situ GI-XRD measurements were performed.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

anatase/rutile titanium dioxides, atomic layer deposition, phase transformations, plasma-enhanced atomic layer deposition (ALD), titanium tetrachloride

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