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Studies on solid state reactions of atomic layer deposited thin films of lithium carbonate with hafnia and zirconia

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In this paper, results on the solid state reactions of atomic layer deposited Li2CO3 with HfO2 and ZrO2 are reported. An Li2CO3 film was deposited on top of hafnia and zirconia, and the stacks were annealed at various temperatures in air to remove the carbonate and facilitate lithium diffusion into the oxides. It was found that Li+ ions are mobile in hafnia and zirconia at high temperatures, diffusing to the film–substrate interface and forming silicates with the Si substrate during heating. Based on grazing incidence x-ray diffraction experiments, no changes in the oxide phases take place during this process. Field emission scanning electron microscopy images reveal that some surface defects are formed on the transition metal oxide surfaces during lithium diffusion. The authors also show that lithium can diffuse through hafnia and react with a potential lithium-ion battery electrode material TiO2 residing below the HfO2 layer, forming Li2TiO3. Published by the AVS. https://doi.org/10.1116/1.5081494

I. INTRODUCTION

Hafnium and zirconium oxides are well-known high-k materials (≈30 for HfO2, ≈25 for ZrO2),1 useful for MOSFETs and memory devices.2 Due to their high electrical resistivity, these oxides could prove useful also in all-solid-state lithium-ion batteries as electrolyte materials. However, electrolyte materials are also required to have a high enough lithium-ion conductivity to be useful. The commonly used solid electrolyte LiPON shows Li-ion conductivities between 10−6 and 10−7 S/cm.3 With the emergence of ever smaller, 3D-structured batteries, geometric reasons could permit the utilization of even somewhat lower ionic conductivities in battery materials. Even though the utilization of hafnia and zirconia as electrolytes in lithium-ion batteries has not been studied as such, some experiments in this area have already been done.4,5 For example, it has been reported that ultrathin HfO2 layers can be used to protect SnO2 nanoparticle anodes, resulting in an improved electrochemical operation of the anode.4 Even after 200 cycles of HfO2 (growth rate ≈1 Å/cycle), the battery performance is improved, without a loss in diffusion kinetics. These results indicate that at least through thin layers of HfO2, lithium diffusion is fast enough for battery application. In addition, simple lithium-ion diffusion into ZrO2 has also been studied.5 It was found that monoclinic ZrO2 is a poor lithium-ion conductor and that lithium diffusivity decreases as the amount of Li+ in the oxide increases.

In this paper, we have studied the interaction of Li2CO3 thin films with HfO2 and ZrO2 thin films. Previously, we have shown that it is possible to form lithium transition metal oxide thin films from lithium carbonate and metal oxides.6 In the current experiments, our goal was to study lithium diffusion into hafnia and zirconia during heating. In addition, we hoped to find out whether lithium hafnates or zirconates could be formed in this manner. Hafnium oxide does not have many well-known lithium containing phases, although at least the structures of two crystalline lithium hafnium oxides are known in the literature, namely, Li2HfO3 and Li3HfO5.7,8 Lithium hafnate Li3HfO5 can be used, for example, as a scintillator material.9 Li3Hf2O7 has also been reported, but very little information on this material is given. However, based on solid-state Li NMR studies, this material was concluded to be a poor Li-ion conductor.10 Lithium zirconates, on the other hand, are much better known in materials science.11–15 Li2ZrO3 has been reported to be a possible tritium breeding material for future fusion reactors.14 In addition, it can be used to protect lithium-ion battery cathode materials,15 and its application as an anode material in lithium-ion batteries has also been studied.13 Doped Li8ZrO6, on the other hand, has been suggested as a possible cathode material for Li-ion batteries.15,16

II. EXPERIMENT

A. Film deposition

Li2CO3 thin films were deposited in an ASM Microchemistry F-120 hot-wall flow-type atomic layer deposition (ALD) reactor onto ZrO2 and HfO2 thin films. These films had been deposited by ALD onto single-crystalline silicon wafers using a heteroleptic zirconium precursor and water17 and TEMAH [tetraakis(ethylmethylamino)hafnium] and water.1 Lithd (Volatec oy) and ozone, generated by a Wedeco GmbH Modular 4 HC ozone generator, were used as precursors for the Li2CO3 depositions as previously described in the
The ozone flow rate was 30 l/h, and the concentration was 100 g/Nm³. Lithd was evaporated inside the reactor at 192 °C at a pressure of approximately 5 mbar. The pulse time for Lithd was 1.5 s with a 2 s purge, and ozone was pulsed for 2.5 s with a 3.5 s purge time. The pulsing of the lithium precursor was done by inert gas valving, with gaseous N₂ as the pulse and purge gas. The N₂, obtained from liquid N₂, had as an impurity less than 3 ppm of H₂O and O₂ each. All the Li₂CO₃ deposition experiments were done at 225 °C.

B. Film characterization

A muffle furnace was used for the annealing of the films. All annealing experiments were done in air with a maximum heating rate of approximately 9 °C/min.

The crystallinity of the films was studied by grazing incidence x-ray diffraction (GIXRD) measurements using a PANalytical X’Pert Pro MPD x-ray diffractometer. In situ high-temperature XRD (HTXRD) measurements were also conducted with an Anton-Paar HTK1200N oven. The morphology of the films before and after annealing was studied by field emission scanning electron microscopy with a Hitachi S4800 FESEM instrument. For the FESEM imaging, the samples were coated with approximately 3 nm of Au/Pd by sputtering. No coating was used in the cross-sectional FESEM analyses. Transmission electron microscope (TEM) specimens were prepared using standard focused ion beam lift-out procedures. Bright-field TEM images were taken with an FEI Tecnai F20 microscope operated at 200 kV.

Surface roughness was quantified with atomic force microscopy (AFM) using a Veeco Multimode V instrument. Tapping mode images were captured in air using silicon probes with a nominal tip radius of 10 nm and a nominal spring constant of 5 N/m (Tap150 from Bruker). Images were flattened to remove artifacts caused by sample tilt and scanner bow. Film roughness was calculated as a root-mean-square value (Rₛ).

The composition of the films was studied with time-of-flight elastic recoil detection analysis (ToF-ERDA). The ToF-ERDA measurements were performed with 50 MeV ¹²⁷I and 40 MeV ⁷⁹Br beams from the 5 MV EGP-10-II tandem accelerator at the University of Helsinki. The detection angle was 40° and the sample was tilted 15° relative to the beam direction.
III. RESULTS AND DISCUSSION

A. HfO2 films as substrates

To study whether lithium containing hafnium oxides could be made by similar solid state reactions as we have reported for Li2TiO3, LiTaO3, and LiNbO3,6 a 50 nm hafnium oxide film was covered with 3000 cycles of atomic layer deposited Li2CO3 and the resulting stack was subjected to a high-temperature XRD measurement (Fig. 1). In the temperature range studied, no crystalline lithium hafnate phases formed. At 565 °C, peaks belonging to Li2CO3 have disappeared. At the same time, a peak appears at 2θ = 22.2°. The peak is difficult to index, but it could belong to a lithium silicate phase Li4SiO4.20 Hafnium oxide remains monoclinic during heating. At 655 °C, orthorhombic lithium silicate Li2SiO3 has formed. At the same time, the peak at 22.2° has decreased, possibly indicating a shift from a metastable silicate to a more stable one.

For comparison with previous results on other materials,6 the Li2CO3/HfO2-stack was annealed in air at 650 °C for 2 h and studied with grazing incidence x-ray diffraction at room temperature (Fig. 2). As with the HTXRD measurement, no Li2CO3 or lithium hafnates could be seen after the annealing, with HfO2 remaining monoclinic. For the HfO2 layer, the unit cell parameters change 0.2%–0.4% upon annealing, with a 0.05° change in the β-angle. The literature values for these parameters for the monoclinic HfO2 lie between the results for the as-deposited and the annealed films, meaning that the actual change in the HfO2 structure is smaller than 0.4% despite lithium diffusing through the film. A small increase in the crystallite size can be deduced from the results. Based on the wide peaks visible especially in the as-deposited HfO2 films, the hafnia crystallites reside in an amorphous oxide matrix. After annealing, Li2SiO3 is present in the stack, with no indication of other silicate phases.

The films were imagined with FESEM to study their morphology (Fig. 3). The as-deposited film showed large platelets on the surface, as is common for Li2CO3 films.18 After the annealing, the film showed much smaller, columnar-like crystallites, and a smoother surface in general, somewhat similarly to titanium oxide films reacted with Li2CO3 in our previous study.6 Atomic layer deposited HfO2 has been reported to show columnar-like crystallites after annealing.21 The change in roughness was quantified with AFM measurements (Fig. 4). For the as-deposited film, the rms roughness was as high as 47 nm, with large platelets comprising the surface. After annealing, the roughness of the film stack decreased to 2.9 nm, which is a typical value for polycrystalline ALD HfO2 films.5

In the FESEM images, the annealed film showed some cracking on the surface. This differs from the results obtained for other films studied previously in this same manner.6 One explanation for the surface defects could be the reaction with

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**Table I.** ToF-ERDA results (at. %) of a 3000 cycle Li2CO3 film deposited onto 50 nm HfO2 and measured as-deposited and after annealing at 650 °C for 2 h in air.

<table>
<thead>
<tr>
<th>Element</th>
<th>Li2CO3/HfO2 as-deposited</th>
<th>Li2CO3/HfO2 after anneal at 650 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>18.9 ± 0.4</td>
<td>22.0 ± 0.4</td>
</tr>
<tr>
<td>Hf</td>
<td>11.5 ± 0.1</td>
<td>10.9 ± 0.2</td>
</tr>
<tr>
<td>O</td>
<td>56.1 ± 0.5</td>
<td>63.8 ± 0.5</td>
</tr>
<tr>
<td>C</td>
<td>9.7 ± 0.2</td>
<td>0.94 ± 0.07</td>
</tr>
<tr>
<td>H</td>
<td>2.5 ± 0.5</td>
<td>2.2 ± 0.5</td>
</tr>
<tr>
<td>F</td>
<td>1.25 ± 0.07</td>
<td>0.07 ± 0.03</td>
</tr>
<tr>
<td>Na</td>
<td>0.06 ± 0.03</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Elemental ratios</td>
<td>Assuming stoichiometric</td>
<td>Li:Hf:O = 2.0:1.0:5.9</td>
</tr>
<tr>
<td>HfO2: Li2CO3 ≈ 1:9.5:1:3.4:1</td>
<td>Li2SiO3 = +</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 4. AFM images of Li2CO3/HfO2-stacks before (a) and after (b) annealing in air at 650 °C.

---

**Table II.** X-ray diffraction results for Li2CO3/HfO2 films before and after annealing at 650 °C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Li2CO3/HfO2 as-deposited</th>
<th>Li2CO3/HfO2 after anneal at 650 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ (°)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intensity (a.u.)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Fig. 5. ToF-ERDA depth profiles of an Li2CO3/HfO2 film stack before (a) and after annealing in air at 650 °C (b).

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Fig. 6. X-ray diffractograms of a 3000 cycle Li2CO3 film deposited onto 50 nm HfO2 and measured as-deposited and after annealing at various temperatures. Patterns: Li2CO3 = PDF 22–1141, JCPDS-ICDD, HfO2 = PDF 34–0104, JCPDS-ICDD, Li2SiO3 = PDF 29–0828, JCPDS-ICDD.
the silicon substrate, which could cause strain in the HfO₂ film. Some damage could also be caused by carbon dioxide leaving the film structure, even though this type of damage was not evident in the films forming intermediate lithium transition metal oxide phases. In addition, adhesion problems cannot be completely ruled out, as the samples needed to be cut for the FESEM imaging.

ToF-ERDA measurements revealed that the as-deposited film was close to stoichiometric HfO₂ and Li₂CO₃ (Table 1). After annealing, the film composition was approximately “Li₂HfO₆,” indicating a large excess of oxygen. This excess could be explained by the silicate formation during annealing. Possibly some additional SiO₂ is forming during annealing as a result of the high oxygen diffusivity in HfO₂, and the forming silicon dioxide is further forming silicates. In addition to the lithium silicate seen in the XRD measurements, possibly also some hafnium silicates are forming: a hafnium silicate interfacial layer has been reported to form during annealing of ultrathin HfO₂ layers on silicon. The ToF-ERDA depth profiles corroborate the XRD results in that lithium is indeed concentrated on the film–Si substrate interface after the annealing (Fig. 5). Only a small amount of lithium is incorporated into the HfO₂ film. Moreover, unlike most lithium containing systems, lithium is not concentrated on the outermost film surface.

To study whether it would be possible to mix the lithium ions with hafnia more completely and without silicate formation, a series of annealing experiments was made. 3000 cycles of Li₂CO₃ was deposited onto 50 nm of HfO₂, and the stack was annealed in air at 300, 400, 500, and 600 °C for 2 h. In addition, samples were annealed at 300 °C for 4 h to see whether a longer annealing time could make a difference in the lithium diffusion. After annealing, the films were studied with both GIXRD and ToF-ERDA and the results are collected in Figs. 6 and 7. From Fig. 6, it is apparent that crystalline lithium carbonate has reacted completely only after annealing at 600 °C. Comparing this information with Fig. 7 reveals that the lower temperatures used were not enough to promote full mixing of lithium and hafnium oxide. Some migration has occurred already at 400 and 500 °C, but

![Fig. 7. ToF-ERDA depth profiles of an Li₂CO₃/HfO₂ film stack after annealing in air at 300 °C for 4 h (a), 400 °C for 2 h (b), 500 °C for 2 h (c), and 600 °C for 2 h (d).](image)

![Fig. 8. FESEM and TEM images of a film stack composed of Li₂CO₃, HfO₂, and TiO₂ before (a) and after annealing at 650 °C for 4 h in air (b) and after annealing at 650 °C for 4 h in air (c) and (d).](image)
in these films, lithium is still strongly enriched on the stack surface as the carbonate. In addition, the amount of carbon has not decreased in these samples. Only after annealing at 600 °C has the carbonate been decomposed, and lithium has diffused through the hafnia film to the silicon substrate interface. During the annealing, the carbon impurities were removed from the film. However, this change was accompanied by an increase in the amount of hydrogen, from 2.2 at.% at 500 °C to 6.3 at.% at 600 °C. This could be explained by LiOH formation caused by lithium enrichment on the film surface and reaction with ambient air, similarly to the LiTaO3 sample studied previously.6 Interestingly, despite the large amount of lithium in the silicon substrate surface after the annealing at 600 °C, no crystalline lithium silicates can be found in Fig. 6 at this temperature.

With these experiments, we were able to demonstrate that at elevated temperatures lithium ions can move through the well-known insulating material HfO2 and react with the underlying silicon dioxide and silicon. To show that the reaction is not only limited to the formation of lithium silicates, a sample shown in Fig. 8 was prepared. 3000 cycles of Li2CO3 was deposited onto 50 nm of HfO2, which had been deposited onto approximately 60 nm of TiO2. The TiO2 film was deposited using titanium(IV) iso-propoxide and water. The three-layer stack was annealed in air at 650 °C for 30 min, and 2 and 4 h. The x-ray diffractograms (Fig. 9) show that already after 30 min of annealing, the lithium ions had diffused through the hafnia into the TiO2 layer, forming crystalline Li2TiO3. Some anatase is also present in this layer, based on both Fig. 9 and the metal ratio Li:Ti = 1.4:1, measured with ToF-ERDA. Again, the HfO2 stays monoclinic before and after the annealing. Notably, no lithium silicate phases are detected with XRD. ToF-ERDA depth profiles corroborate the diffraction results by showing that after the annealing lithium is confined to the same layer together with titanium (Fig. 10). In addition, both the depth profile and the FESEM image of the annealed film reveal that the hafnia and titania layers have not mixed, but remain separate despite the lithium diffusion (Figs. 8 and 10).

The formation of the Li2TiO3 layer was also studied with TEM [Figs. 8(c) and 8(d)]. Prior to the annealing of the Li2CO3/HfO2/TiO2 film stack, a native silicon oxide layer is present in the TiO2/Si interface [Fig. 8(c)]. The anatase layer is comprised of a single layer of columnar grains. Several structural changes are observed in the annealed specimen [Fig. 8(d)]. Upon annealing, the apparent HfO2 layer thickness increases from 50 to ca. 58 nm. This can be at least in part explained by the increased roughness of both the layer surface and the HfO2/Li2TiO3 interface. It is noteworthy that the HfO2 layer remains continuous, with no cracking or strong mixing with the Li2TiO3 layer taking place. In the TEM image taken after the annealing step, the Li2TiO3 layer thickness is in the range of 80–89 nm, as measured from individual spots along the cross section, corresponding to ca. 50% volume expansion compared to the original TiO2 layer. This is consistent with the expected molar volume expansion upon conversion of anatase TiO2 to Li2TiO3. The Li2TiO3

![Fig. 9. X-ray diffractograms of an Li2CO3/HfO2/TiO2 stack before and after annealing at 650 °C in air. Patterns: Li2CO3 = PDF 22–1141, JCPDS-ICDD, HfO2 = PDF 34–0104, JCPDS-ICDD, TiO2 = PDF 21–1272, JCPDS-ICDD, Li2TiO3 = PDF 33–0831, JCPDS-ICDD.](attachment:fig9.png)

![Fig. 10. ToF-ERDA depth profiles of an Li2CO3/HfO2/TiO2 stack before (a) and after annealing at 650 °C for 2 h in air (b).](attachment:fig10.png)

![Fig. 11. X-ray diffractograms of a 3000 cycle Li2CO3 film deposited onto 54 nm ZrO2 and measured as-deposited and after annealing in air at 500 and 650 °C. Patterns: Li2CO3 = PDF 22–1141, JCPDS-ICDD, ZrO2 = Inorganic Crystal Structure Database (ICSD), collection code 66781, and PDF 37–1484 JCPDS-ICDD, Li2SiO3 = PDF 29–0828, JCPDS-ICDD.](attachment:fig11.png)
layer has two distinct grain heights, a thicker layer with ca. 60 nm tall grains in contact with the HfO2 layer and a lower ca. 25 nm layer in contact with the Si interface. This can be due to the disappearance of the native SiO2 layer, part of which may have been incorporated into the lower part of the Li2TiO3 layer. A 10–15 nm reaction layer, possibly lithium doped Si or amorphous Li silicate, can be seen in the Li2TiO3, with some isolated grains of material which have grown through the mostly smooth Li2TiO3/Si interface layer.

B. ZrO2 films as substrates

Similarly to the study on HfO2, 3000 cycles of Li2CO3 was deposited onto a 54 nm ZrO2 film at 225 °C, and the resulting film stack was annealed at various temperatures in air for 2 h. The x-ray diffractogram (Fig. 11) shows that at 500 °C some Li2CO3 is still present in the film stack. However, at 650 °C, lithium has moved through the ZrO2 film, forming silicates with silicon from the single-crystalline silicon substrate. At the same time, ZrO2 has changed from the tetragonal phase of the as-deposited film to a mixture of tetragonal and monoclinic phases. No lithium zirconate phases formed in these conditions.

FESEM imaging was used to study the morphology of the Li2CO3/ZrO2-stack before and after the annealing at 650 °C (Fig. 12). The as-deposited film shows the same rough, flaky surface as in the case of Li2CO3 on the hafnium oxide films. After the annealing, the surface roughness is decreased dramatically, again similarly as on hafnia. However, the surface shows more defects and is also broken in some places [Fig. 12(c)]. The reason for this difference between hafnia and zirconia is difficult to explain. One possibility could be that the strain caused by lithium insertion is larger in the zirconia film. Another possibility is that during the annealing impurities such as hydroxyls are leaving the zirconia film, causing crater formation and cracks. HfO2 films deposited using TEMAH and water have been reported to contain only very minor amounts of carbon and hydrogen impurities, making crater formation less likely in this material. To study this problem further, we also imagined an annealed ZrO2 film without Li2CO3 deposition. This film did not show similar cracking (not shown here), indicating that impurities in ZrO2 most likely do not completely explain the cracking of the film. It appears that lithium plays a part in the changes in the morphology of the annealed stack.

TABLE II. ToF-ERDA results (at. %) of a 3000 cycle Li2CO3 film deposited onto 54 nm ZrO2 and measured as-deposited and after annealing at 500 and 650 °C for 2 h in air.

<table>
<thead>
<tr>
<th>Element</th>
<th>Li2CO3/ZrO2 as-deposited</th>
<th>Li2CO3/ZrO2 after anneal at 500 °C</th>
<th>Li2CO3/ZrO2 after anneal at 650 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>19.7 ± 1.0</td>
<td>20.2 ± 1.1</td>
<td>25.7 ± 1.3</td>
</tr>
<tr>
<td>Zr</td>
<td>9.4 ± 0.3</td>
<td>9.3 ± 0.3</td>
<td>9.3 ± 0.3</td>
</tr>
<tr>
<td>O</td>
<td>52.0 ± 1.0</td>
<td>54.3 ± 1.1</td>
<td>61.2 ± 1.2</td>
</tr>
<tr>
<td>C</td>
<td>11.9 ± 0.5</td>
<td>11.4 ± 0.6</td>
<td>0.93 ± 0.15</td>
</tr>
<tr>
<td>H</td>
<td>6.2 ± 0.9</td>
<td>4.5 ± 0.7</td>
<td>2.5 ± 0.6</td>
</tr>
<tr>
<td>F</td>
<td>0.50 ± 0.09</td>
<td>0.21 ± 0.06</td>
<td>0.09 ± 0.04</td>
</tr>
<tr>
<td>Cl</td>
<td>0.13 ± 0.04</td>
<td>0.06 ± 0.03</td>
<td>0.07 ± 0.03</td>
</tr>
<tr>
<td>N</td>
<td>0.13 ± 0.05</td>
<td>0.11 ± 0.05</td>
<td>0.09 ± 0.05</td>
</tr>
</tbody>
</table>

Elemental ratios

Assuming stoichiometric ZrO2:

Li2O = 1.71:1:2.8

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Fig. 12. FESEM images of 3000 cycles of Li2CO3 deposited by ALD onto 54 nm of ZrO2, before (a) and after [(b) and (c)] annealing in air at 650 °C.
ToF-ERDA results (Table II) show that Li$_2$CO$_3$ forms close to stoichiometric onto ZrO$_2$. Most likely, the slight deviation from stoichiometry is caused by the calculation not taking into account carbon impurities in the ZrO$_2$ film, which were measured to be of the order of 2.4 at. % before annealing. It is apparent from Table II that annealing the film stack at 500 °C for 2 h is not enough to remove the carbon and hydrogen impurities and to cause lithium migration. However, after annealing at 650 °C, the lithium migration has taken place, with carbon and hydrogen impurities decreasing at the same time. The reaction is evident also in the ToF-ERDA depth profiles (Fig. 13). Lithium has moved into the silicon substrate after annealing at 650 °C, while at the lower annealing temperature, the profile for the most part resembles that of the as-deposited sample. The depth profile of the as-deposited sample also revealed that most of the hydrogen impurities reside in the zirconia layer. Despite being embedded in this bottom layer, these impurities can be removed with annealing.

Based on these results, it is clear that hafnium and zirconium oxides behave quite similarly when annealed with a lithium carbonate film on top. This is somewhat surprising considering the large amount of literature on lithium zirconates: one could assume that producing lithium zirconates with solid state reactions would be more straightforward than obtaining lithium hafnates. To still study whether we could synthesize lithium zirconates with this solid state reaction process, a thinner ZrO$_2$ film of 30 nm was used, together with 3000 cycles of Li$_2$CO$_3$. The idea behind this experiment was to drive lithium into the thinner zirconia layer at a lower temperature than above so that lithium would not react with the substrate but instead with zirconia, producing a crystalline lithium zirconate. Figure 14 shows a ToF-ERDA depth profile and an x-ray diffractogram of a film stack deposited at 225 °C and annealed at 500 °C. It is evident that with the thinner zirconia film, lithium mixing occurs throughout the film already after annealing at 500 °C. This has to do with the smaller thickness of the zirconia film promoting faster lithium diffusion. At 500 °C, our previous sample was tetragonal, whereas the thinner sample showed peaks belonging to both tetragonal and monoclinic zirconia, which might also mean that the ionic conductivity is different in this sample. In any case, it is evident that only crystalline ZrO$_2$ is present in the diffractogram of the annealed sample. The atomic percentages in the annealed film, as determined by ToF-ERDA, were Li 25.3, Zr 7.2, O 53.7, C 5.8, H 7.3, F 0.6, and N 0.1. The excess oxygen is most likely in the form of lithium carbonate, since not all carbon has been removed at this temperature.

FIG. 13. ToF-ERDA depth profiles of an Li$_2$CO$_3$/ZrO$_2$ film stack as-deposited (a) and after annealing at 500 °C (b) and 650 °C (c) for 2 h in air.

FIG. 14. ToF-ERDA depth profile (a) and x-ray diffractogram (b) of an Li$_2$CO$_3$/ZrO$_2$ film stack after annealing at 500 °C for 2 h in air. The ZrO$_2$ film thickness was 30 nm, and Li$_2$CO$_3$ was applied for 3000 cycles. Patterns: ZrO$_2$ = Inorganic Crystal Structure Database (ICSD), collection code 66781, and PDF 37-1484 JCPDS-ICDD.
temperature. Based on these results, the closest lithium zirconate phase possible would be either Li$_2$ZrO$_3$ or Li$_3$Zr$_2$O$_7$. However, the phase cannot be unambiguously recognized in the x-ray diffractogram in Fig. 14(b). Still, the small, broad peak at 22.1°–22.9° (2θ) could originate from a zirconate phase.26–28 Further identification of the phase was impossible at this time, which is why we believe that making lithium zirconate films with this process is not feasible.

It has been reported that forming Li$_2$ZrO$_3$ from either LiOH or Li$_2$CO$_3$ and ZrO$_2$ using solid state reactions involves much higher temperatures than, for example, in the case of Li$_2$TiO$_3$.14,29 Therefore, we are faced with a similar problem with Li$_2$ZrO$_3$ as we were previously with producing Li$_2$Ti$_5$O$_{12}$;6 the temperature range available for our system is limited due to lithium reactivity with silicon. The chemical potential of lithium silicate formation appears to drive the potential of lithium silicate formation appears to drive the lithium migration through the zirconium oxide layer to the interface with the substrate before any reaction with the zirconia can occur.

IV. SUMMARY AND CONCLUSIONS

In this paper, we have studied the reactions between atomic layer deposited Li$_2$CO$_3$ and HfO$_2$ or ZrO$_2$. After annealing the films at 650 °C, lithium silicates have formed with no indication of lithium hafnate or zirconate phases. Thus, it appears that these materials behave differently from TiO$_2$, Ta$_2$O$_5$, and Nb$_2$O$_5$, which we have studied previously and found to form lithium containing ternary phases. After annealing, the films showed a relatively smooth surface with some defects. We postulate that these defects are formed when impurities are removed from the metal oxide layer and when lithium is inserted into the silicon substrate. Next, when impurities are removed from the metal oxide layer and some defects. We postulate that these defects are formed when lithium migration through the zirconium oxide layer to the interface with the substrate before any reaction with the zirconia can occur.

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