Area-selective atomic layer deposition of molybdenum oxide

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ABSTRACT
Area-selective bottom-up synthesis routes of thin films are required to overcome the current limits in lithography, and such growth can be achieved with high quality and nanometer thickness control by area-selective atomic layer deposition (AS-ALD). However, the current range of materials demonstrated deposited by AS-ALD is limited, and no processes for molybdenum oxide have been available so far. In this work, the authors explore the properties of a new ALD precursor, MoCl₄O, for deposition of molybdenum oxides by ALD. MoCl₄O is administered at room temperature during deposition, making it readily available for use. When reacted with a combination of water and ozone, it leads to an AS-ALD process for deposition of MoOₓ—the first reported. The process is perfectly selective for growth on glass compared to Si(100) substrates for deposition temperatures between 200 and 300 °C, with a growth rate of 0.72 Å/cycle at 300 °C. The process is attempted on a range of substrates proving good growth on soda-lime glass and LiF and no growth on Si(100), silica, Na₂CO₃, CaCO₃, Li₃PO₃, or Li₂SiO₃. The findings of this study indicate an activated process by diffusion of sodium or lithium through the film during growth. The obtained films have further been characterized by x-ray photoelectron spectroscopy, scanning electron microscopy, x-ray diffraction, and atomic force microscopy, revealing films with an RSM roughness of 23 nm with the presence of crystalline MoO₂ (C P/m) when deposited at 300 °C and crystalline Mo₉O₂₆ when deposited at 250 °C. The rough MoOₓ thin films may be applicable for electrocatalysis, gas sensors, or lithium-ion batteries. The findings of this study enable AS-ALD synthesis of molybdenum oxide with excellent selectivity not dependent on intermittent etching cycles during growth.

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I. INTRODUCTION
The semiconductor industry is currently approaching the limits of resolution in lithography—leaving a technology gap that may be filled with precise bottom-up synthesis approaches.¹ One obvious choice to fill this gap is by atomic layer deposition (ALD), or more specifically, area-selective ALD (AS-ALD). ALD, in general, is known to give high quality films with supreme thickness control and conformity. AS-ALD will ease processing in comparison to conventional ALD, as fewer etching steps are required. Despite the fact that the concept has been around for 15 years,² we have not seen a true boom in AS-ALD processes until now.³ This has yet to reach MoOₓ, which takes part in many applications also requiring precise manufacturing, such as catalysis,⁴ nanostructured gas sensors,⁵ injection layers in inverted organic photovoltaics,⁶ antibacterial coatings,⁷ electrochromic devices,⁸ and batteries,⁹ among others. For applications within electrocatalysis,¹⁰ gas sensors,¹¹ or lithium-ion batteries,¹² porous or rough MoOₓ films can be beneficial. A whole range of techniques has already been employed to deposit MoO₃ thin films, although without area selectivity. This includes thermal evaporation,¹³ RF sputtering,¹⁴ flash evaporation,¹⁵ metalorganic chemical vapor deposition,¹⁶ and ALD,¹⁷ which is the subject of this study.

The range of processes for deposition of MoO₃ by ALD is limited, particularly for deposition at higher temperatures as the majority of molybdenum precursors decompose at 180 °C or below. Deposition of MoO₃ by ALD was first reported in 2010 (Ref. 19) using Mo(CO)₆ as the Mo source together with O₃ and H₂O in the
range of 152–172 °C, after which the precursor decomposes. Si(CH3)3cpMo(CO)1(η3–2-methylallyl) is in like manner reported to produce MoO3 together with O3 at 250–300 °C.20 This process does, however, require an initial heating of the Si(100) substrate at 350 °C to prevent a nucleation delay of the following MoOx deposition. Another recent precursor for deposition of MoO3 is bis(ethylbenzene)Mo, which together with H2O shows ALD growth in the range of 135–150 °C.21 Very recently, MoO2(iPr2AMD)2 (Ref. 22) has been demonstrated as a suitable precursor to form MoO3 up to its decomposition temperature of 175 °C using O3 as the oxygen source. (NtBu)2(NMe2)2Mo has also been used as an ALD precursor to form MoO3 with O3 in the temperature range of 100–300 °C23 or 50–350 °C using plasma O2.24 The tungsten counterpart of (NtBu)2(NMe2)2Mo has also been used as an ALD precursor to form WO3 with H2O as the coreactant and in combination with La(thd)3 to form the proton-conducting ternary oxide La28W4+δO54. The same work also mentions using WCl4Oa as a precursor to produce MoO3 together with O3 at 250 °C.25

The figure of merit for quantification of the selectivity of a system is termed selectivity, S, and is in Ref. 24 defined as the amount (or rate) of one product relative to the total amount (or rate) of all products formed. S also varies with the number of ALD cycles used and must therefore be reported together.26 An example of a reported selectivity is 2000:1 for Pt versus SiO2 substrates for the previously mentioned Fe2O3 system using 300 cycles.28

In this study, we further explore the effect of different types of substrates on the selectivity of the MoCl4O+(H2O+O3) system to shed light on possible mechanisms behind our observations.

II. EXPERIMENT

A. Atomic layer deposition

All depositions were performed in an F-120 Sat reactor (ASM Microchemistry), in the temperature range of 200–350 °C. The purging gas was N2 at 300 cm3 min−1 from gas cylinders (Praxair, 99.999%, further purified through a Mykrolis purifier) providing a background pressure of ~4 mbar. The depositions were carried out using MoCl4O (Sigma-Aldrich, 97%) as the Mo source and distilled H2O and O3 pulsed simultaneously as the O source. O3 was supplied from an In USA ozone generator (AC-2505) at 15 wt. % O3 in O2, using O2 from a gas cylinder (Praxair, 99.5%). Both MoCl4O and H2O were kept at room temperature in external containers, and MoCl4O was assisted by N2 carrier gas. Standard purging times were 3 s for both MoCl4O and O3, H2O, followed by 3 s purging after MoCl4O and 5 s after O3 + H2O, unless otherwise specified. The times were chosen based on experience with similar systems and gave here uniform films and reproducible data. A standard deposition consisted of 1000 cycles at a deposition temperature of 300 °C. The LiF seeding layers were deposited using LiOtBu (Sigma-Aldrich, 97%) and NH4F (Sigma-Aldrich, 99.9%) based on an internally developed process.27 The LiOtBu and NH4F precursors were kept at 130 and 95 °C, respectively, and pulsed/purged with 5/5 s and 7/3 s, respectively.

Area-selective ALD is an emerging field particularly useful in semiconductor processing for electronics where numerous lithography steps are required.26,27 An overview of the field is given in Ref. 24 and can be summarized as divided into the following approaches: Inherent systems, where no extra measures are taken to make the system area-selective; the use of activators, using catalytic reactions on the surfaces, plasma enhanced areas, etc., such as for deposition of Fe2O3 and NiO by O2 gas with t-buty1 ferrocene/nickelocene on Pt and Ir substrates that dissociate O2, and not on the inert SiO2, Al2O3, and Au substrates;28 the use of inhibitors, such as for deposition of SiO2 on GeO2, SiNx, SiO2, and WO3, and not on Al2O3, TiO2, and HfO2,30 where acetylacetonate chemoselectively inhibits growth by selective adsorption on the latter surfaces. Of these approaches, using inhibitors is by far the most used.

Other examples using inhibitors include the deposition of TiO2 on gold substrates using self-assembled monolayers (SAMs) as inhibitors.31,32 Ru on Cu lines using amino-functionalized SAMs as inhibitors,31,32 and CoO on SiO2/MgO using polystyrene as inhibitors.33 The combination of atomic layer etching (ALE) and ALD is also employed to make thicker films only on the desired substrate. For example, Al2O3 has been deposited selectively on Si and not on octadecylphosphonic acid (OPDA)-SAM inhibited Cu with intermitting acid etch cycles.33

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In this study, we further explore the effect of different types of substrates on the selectivity of the MoCl4O+(H2O+O3) system to shed light on possible mechanisms behind our observations.
A variety of substrates were used, including Si(100) with a native oxide layer, Si(100) with the following ALD-deposited thin films—CaCO₃ [from Ca(thd)₂, CO₂ and O₂ (Ref. 35)], Na₂CO₃ [from NaOtBu, H₂O, and CO₂ (Ref. 36)], Li₃PO₃ [from LiOtBu, Me₃PO₃, and water, and x-ray photoelectron spectroscopy (XPS) revealing a surface layer of Li₃CO₃], LiF and Li₂SiO₃ [from lithium trimethylsilanolate and H₂O (Ref. 37)]—conventional soda-lime glass containing 15 mol. % Na₂O₃ (Glaswarenfabrik Karl Heckt), and silica. Si(100), glass, and silica substrates were all washed with ethanol and blown dry prior to deposition. The other substrates were left untouched to not alter the films already deposited on them.

B. Thin film characterization

The thicknesses of the films were measured using a J. A. Woollam α-SE spectroscopic ellipsometer in the range of 390–900 nm, with the COMPLETÉASE software and Cauchy models to analyze the data. The models used two layers, one dense in the bottom and one rough on top, and took into consideration that MoOₓ is absorbing. For each sample, three spots were measured. It was spot dependent how easy it was to model the ellipsometry data, probably due to variations of the roughnesses of the films. Scanning electron microscopy (SEM) was performed using a HITACHI TM3000 SEM with a working distance of ∼9 mm and an acceleration voltage of 15 kV. A Quantax70 energy dispersive x-ray spectrometer equipped with a silicon drift detector and Cu Kα radiation was used for elemental analysis. The acquisition time for each measurement was 5 min. XPS measurements were carried out using a ThetaProbe instrument from ThermoScientific. The incident x-ray beam was Al Kα (1.487 keV) and 4 keV Ar⁺ was used for sputtering. The C1s peak at 285 eV stemming from carbon contamination was used as internal standard for fitting of the XPS spectra. X-ray diffraction (XRD) was performed to study the crystallinity of the samples, using a Bruker D8 Discovery Diffractometer, with Cu Kα1 radiation and a Ge(111) monochromator in a traditional Bragg-Brentano setup. Atomic force microscopy (AFM) was performed using a Park Systems XE-70 AFM equipped with a PPP-CONTSCR cantilever in the contact mode. The AFM micrographs were processed with the GWYDDION software. Four-point probe inline resistivity measurements were performed using a Keithley 2400 SourceMeter.

C. Lithography

The LiF films were patterned using photolithography. A Microposit S1813 positive photoresist was applied using a spin coater, before the sample was baked at 120 °C for 60 s on a hot plate. The pattern was exposed in a Heidelberg μPG501 maskless lithography system and developed in the Microposit MF351 developer diluted with three parts de-ionized (DI) water. Following the development, the sample was rinsed for 1 s in DI water and immediately blown dry in N₂ gas. The exposed LiF was etched by immersing the sample in DI water for 1 min, before the photoresist was stripped by soaking in acetone for 4 min. Unfortunately, 1 min of etching time was found to be excessive, and caused a loss of resolution in the pattern, however, still suitable to prove the possible use within lithography.

D. Selectivity calculations

The selectivity is calculated using the relation given in the Introduction, namely, that selectivity is the “the amount (or rate) of one product relative to the total amount (or rate) of all products formed.” This translates to the following equation where S is the selectivity, n is the number of cycles, and Θ₁ is the measured fraction covered by nuclei at growth surface relative to the measured fraction at an adjacent nongrowth surface, Θ₂. The full derivation of this is found in Ref. 27.

\[
S(n) = \frac{\Theta_1}{\Theta_1 + \Theta_2}
\]

The measured fraction covered by nuclei is directly proportional to the deposited film volume. It is therefore possible to get a measure of this by various characterization methods such as spectroscopic ellipsometry, Auger electron spectroscopy, or electron dispersive x-ray spectroscopy (EDS), which is used in this case. Here, the at. % of Mo versus (Si + Mo) is used as θ for films deposited on both glass and Si(100) substrates.

E. Thermodynamic calculations

Thermodynamic calculations were performed using the HSC CHEMISTRY 8 software from Outotec.

III. RESULTS AND DISCUSSION

A. MoOₓ thin film growth

Using the standard pulsing and purging times, MoOₓ was successfully deposited by atomic layer deposition with similar growth rates on glass (0.72 Å/cycle) and LiF (0.69 Å/cycle) substrates. It was possible to obtain a sufficient dose of MoCl₄Oₖ e p t o o m t e m p e r -

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\]
The linearity with respect to the number of ALD cycles was investigated at 300 °C (Fig. 3) proving an overall reduction in growth per cycle with increased film thicknesses. ALD processes are usually regarded as linear with the number of deposition cycles, unless nucleation or evolution of texture affects the available surface area. The current observation with temperature and thickness dependent growth indicates that the process may be controlled by diffusion of an active component from the substrate itself. This also explains why the growth per cycle increases between 300 and 350 °C for 5000 cycles, as the growth of thicker films is more limited by diffusion, which is in turn enhanced at higher temperatures. See the supplementary material for attempts on modeling the evolution in film thickness based on diffusion limited principles.

As this system exhibits clear selectivity with respect to the substrate material, further investigations were performed to gain more insight into its origin. A first step was investigating the oxygen source, if both O3 and H2O play an active part in the growth. When changing the oxygen source to only H2O or O3, a clear reduction of the overall growth rates was observed (Table I). A similar dependency is previously reported for when Mo(CO)6 is used as an Mo source, although at a reduced magnitude. For the Mo(CO)6 process, the effects of omitting H2O was negligible, but a reduction in growth rate of about 75% was observed when omitting O3.

XRD analysis of the films shows a strong dependency of the crystallinity with deposition temperature (Fig. 4). Films deposited at 250 °C match well with Mo9O26 (P 2/C), while the crystallinity is reduced at 275 °C, and at 300 °C, there is only one clear peak present, and this matches well with MoO2 (C 2/m, tugarinovite). Mo9O26 is a Magnéli phase with a structure closely related to the

![FIG. 3. Growth per cycle of MoOx vs number of cycles for the MoCl4O/(O3 +H2O) system at 300 °C. The uncertainties are estimated from the variance in data obtained for 1000 cycles at 300 °C for three separate experiments.](image)

![FIG. 4. XRD diffractograms of molybdenum oxide thin films deposited at varying temperatures using 1000 cycles. Selected reflexes from Mo9O26 (P 2/C, with asterisk) (Ref. 42) and MoO2 (C 2/m, tugarinovite, no asterisk) (Ref. 43) are indexed for comparison.](image)

<table>
<thead>
<tr>
<th>O source</th>
<th>Growth per cycle (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3 + H2O pulsed simultaneously</td>
<td>0.72</td>
</tr>
<tr>
<td>Only O3</td>
<td>0.12</td>
</tr>
<tr>
<td>Only H2O</td>
<td>0.10</td>
</tr>
</tbody>
</table>

![FIG. 2. Growth per cycle on glass vs deposition temperature of MoOx for the MoCl4O/(O3 +H2O) system using 1000 (squares) or 5000 (circles) ALD cycles. The uncertainties are estimated from the variance in data obtained for 1000 cycles at 300 °C for three separate experiments.](image)
more common layered $\alpha$-MoO$_3$, which consists of zig-zag layers of distorted MoO$_6$ octahedra. This is similar for Mo$_9$O$_{26}$, but this structure also includes crystallographic shear planes as described by Magnéli. The crystallographic shear planes reduce the overall oxidation state for Mo from +6 in $\alpha$-MoO$_3$ to approximately +5.8 in Mo$_9$O$_{26}$ without introducing oxygen vacancies. A previous study from our group, using the Mo(CO)$_6$ + (O$_3$ + H$_2$O) process, showed that the films were amorphous as deposited at 167 °C, but crystallized to the metastable $\beta$-MoO$_3$ when annealed at 400 °C for 8 min and as $\alpha$-MoO$_3$ when annealed at 600 °C for 8 min. Another very recent study on MoO$_3$ from our group identifies the crystallization process as both time and temperature dependent proving crystallization of $\beta$-MoO$_3$ at only 185 °C when annealed for an extended amount of time (24 h). The formation of MoO$_2$ is further discussed later in the text.

The microstructure of thin films deposited on glass substrates was investigated with SEM and AFM (Fig. 5). The microstructure was similar for all investigated deposition temperatures (200–350 °C), and the micrographs in Fig. 5 are thus representative for all the investigated samples. The topography appears rough and shows some signs of pinholes. The AFM micrograph further shows that some areas are denser with a thickness around 72 nm, but some areas again have taller grains and more pinholes. The occurrence of pinholes reduces slightly with higher deposition temperatures, but the topography remains rough. The RMS roughness is 23 nm as estimated from the AFM micrograph for a film with total thickness of 72 nm. To shed more light on the film quality, a four-point probe inline resistivity measurement was performed on a 114 nm thick film deposited at 300 °C. The film was insulating at room temperature, i.e., the sheet resistance was above 100 MΩ/sq.

XPS was performed on selected samples to investigate the state of molybdenum and to reveal the presence of any impurities that may be embedded in the growth process. The survey spectrum for a sample deposited at 300 °C on glass is shown in Fig. 6. This shows that beside the expected peaks from oxygen and molybdenum, a large amount of sodium is also found in the films. The Cl p$_{3/2}$ peak, which is the peak primarily used for analysis of chlorine by XPS, is normally found around 200 eV and is absent in the spectrum below.

Two XPS scans were performed on two different spots of a sample deposited at 300 °C to investigate the oxidation state of Mo (Fig. 7). For the Mo 3d$_{3/2}$ peak, the peak positions are at 236.1 and 235.4 eV for the two scans, both within the expected range for the valence being +6. The same goes for the Mo 3d$_{5/2}$ where the peak positions are at 232.8 and 232.1 eV. The observed shift for both Mo 3d peaks between the two scans is less than expected if the valence indeed was different in the two spots.

A depth profile was also obtained by XPS on a MoO$_3$ film deposited on glass at 300 °C, as shown in Fig. 8. It shows a relatively homogeneous distribution of sodium ions throughout the film, probably due to extended diffusion through the 2-h cooling process after the deposition. It should be kept in mind that the

FIG. 5. SEM micrograph (a) of MoO$_x$ deposited on glass at 250 °C and AFM micrograph (b) of MoO$_x$ deposited on glass at 300 °C using 1000 cycles.

FIG. 6. XPS survey scan of MoO$_3$ thin film deposited at 300 °C on glass.
argon sputtering during depth profiling can also affect the distribution of sodium throughout the film. We do observe an accumulation of sodium at the surface of the film with 6.6% Na at zero etch time.

Experiments with prolonged purging times were performed to investigate how diffusion of sodium ions affect the growth rates of the MoOx thin film. If the growth is dependent on diffusion of sodium through the film, the growth rate should be affected by the purging times, leading to increased growth for longer purges, as this allows for more time for diffusion controlled processes.45 The results of such an investigation is shown in Table II and support our hypothesis, although with a higher dependency on the purging times than anticipated from Fick’s laws of diffusion.

B. Area-selective growth

EDS measurements were performed on a number of samples deposited at various temperatures to quantify the selectivity of the process as a function of deposition temperature. Both growth (glass) and nongrowth [Si(100)] surfaces were investigated. As no molybdenum could be detected at the Si(100) surface for depositions at 300 °C or below, the selectivity is here reported as perfect selectivity, i.e., 1. For the film deposited at 350 °C, the selectivity was calculated from the EDS measurements to be 0.85 for glass over Si(100). See the supplementary material50 for details about this calculation.

To illustrate the selectivity of the system further, a pattern was produced by lithography on a 45 nm thick LiF film made by ALD on Si(100). Thus, both growth and nongrowth areas were present on the same substrate. A standard MoOx deposition was then performed on top of this patterned surface. An SEM micrograph of the resulting sample is shown in Fig. 9 where the brighter areas correspond to deposition of MoOx. We found it challenging to perform good lithography on LiF due to its high solubility in water. Yet, samples with clear patterns were obtained.

To further illuminate the selectivity of the MoCl4O+(H2O+O3) system, EDS mapping was performed on an MoOx film deposited on patterned LiF on Si(100) (Fig. 10). Both molybdenum and fluorine are present within the desired pattern in significant amounts. Attempts to quantify the concentration of molybdenum outside this pattern result in only 0.02 at. %, whereas it revolves around 8 at. % in the pattern itself. The reported values must not be considered absolute concentrations since the EDS analysis volume penetrates through the film and into the substrate. However, they do prove a selectivity for MoOx growth of around 400 times higher growth on the LiF pattern than in the surrounding area, even with imperfect patterning.

C. Discussion

We have here reported using the oxychloride MoCl4O for deposition of MoOx by atomic layer deposition. Equation (2) shows
FIG. 9. SEM micrograph (a, left) illustrating the selectivity of the MoO$_x$ system as deposited on LiF. The pattern is the University of Oslo’s logo (b, right). The LiF film under the lines of the logo shown in (b) was removed with lithography prior to deposition of MoO$_x$. The circle in the micrograph is the area where the EDS measurements in Fig. 10 are taken.

FIG. 10. EDS mapping of molybdenum L$_\alpha$ (a), fluorine K$_\alpha$ as a measure of LiF (b) and silicon K$_\alpha$ (c) in addition to an SEM micrograph of the surrounding area (d) of an MoO$_x$ film deposited at 300 °C on a patterned LiF substrate. The square in subfigure (d) corresponds to the area in which the EDS measurements are performed within.
the proposed reaction between $\text{H}_2\text{O}$ and MoCl$_4$O:

$$\text{MoCl}_4\text{O}(g) + 2\text{H}_2\text{O}(g) \rightarrow \text{MoO}_2(s) + 4\text{HCl}(g). \quad (2)$$

The calculated equilibrium constant, $K$, of this reaction is $2.3 \cdot 10^6$, $8.4 \cdot 10^6$, and $3.7 \cdot 10^7$ at 200, 250, and 300 $^\circ$C, respectively. These values point to a very favorable reaction, which is consistent with our observations. The equilibrium constant decreases one order of magnitude from 200 to 300 $^\circ$C but still remain at a very high level. Even though MoCl$_4$O is known to thermally and photocatalytically decompose to MoCl$_3$O and Cl$_2$ already at room temperature, we still observed MoCl$_4$O’s distinct dark green color also after being connected to the ALD reactor in a glass bubbler with inert gas for weeks during denosition campaigns.  

A possible reason why MoCl$_4$O has not previously been explored as an ALD precursor is the failed attempts to use the tungsten analog, WCl$_4$O, to deposit WO$_3$. The previous attempts of using WCl$_4$O as an ALD precursor showed no growth on Si(100), but signs of growth were seen on La$_2$O$_3$ and Al$_2$O$_3$ when $\text{H}_2\text{O}$ was used as the oxygen source. Likewise, we did not observe growth on Si(100), and based on our study, we would anticipate similar reaction schemes for WCl$_4$O as we observe for our MoCl$_4$O, i.e., a selective growth on alkali-containing substrates. A difference between the WCl$_4$O and our system is that the WO$_3$ films obtained on La$_2$O$_3$ and Al$_2$O$_3$ contained almost as much chloride as tungsten. However, this may be connected with that $\text{O}_3$ was not used together with water in the prior study. Moreover, a very recent work studying ALE of W utilizes WCl$_6$ in combination with $\text{O}_2$ or $\text{O}_3$ to form volatile WCl$_4$O/WCl$_2$O$_2$ in order to etch a W surface and thus the reversed chemistry. Here, thermodynamic modeling reveals that the formation of gaseous WCl$_4$O/WCl$_2$O$_2$ in order to etch a W surface has also been seen for NbCl$_5$ on Nb$_2$O$_5$ from WCl$_4$O and WCl$_2$O$_2$ from WCl$_6$. The growth rate of our MoCl$_4$O+$\text{(H}_2\text{O}+\text{O}_3)$ system showed a sudden increase from 0.13 to 0.71 Å/cycle for 1000 cycles when the deposition temperature was increased from 275 to 300 $^\circ$C. Such a high thermal sensitivity of the growth rate point at a thermally activated process, such as solid-state diffusion, where exponential dependency of diffusion rate with temperature is expected.

An unusual trait of this ALD process is that the growth rate per cycle is not constant as a function of number of cycles, i.e., on the thickness of the deposited film. The growth rate slows down when the number of cycles is increased and the film becomes thicker. This means that we do not enter a typical steady-state ALD situation where the entire surface is saturated and the material deposits on itself, but rather a situation where a longer distance to the interface of the substrate limits the growth. Studies of growth rates versus purge lengths and a nonlinear relationship between the thickness of the deposited film and number of ALD cycles suggest that the growth is limited by diffusion of Li$^+$/Na$^+$ ions through the film and that the presence of alkali ions is essential for film growth. The fact that soda-lime glass facilitates growth, but silica does not, also supports this. The XPS depth profile of film deposited on glass does show sodium throughout the entire film, proving that diffusion of sodium has taken place. Since Na$_2$CO$_3$, Li$_3$PO$_4$, and Li$_2$SiO$_3$ coated substrates did not induce film growth, the alkali ion cannot be in any arbitrary matrix. The Na$_2$CO$_3$, Li$_3$PO$_4$, and Li$_2$SiO$_3$ were all expected to be terminated by a thin carbonate layer on its surface. A possible denominator is if these carbonate layers themselves lack the feature to initiate MoCl$_4$O+$\text{(O}_3+\text{H}_2\text{O})$ growth. A more thorough understanding of the growth mechanisms will be a topic for more focused studies.

Also, the SEM micrographs of our thin films deposited on glass and LiF show a grainier appearance and do not cover the surface in an optimal manner when grown on LiF. This suggests that the nucleation may be more favorable on glass than LiF, despite the near equal measured growth rate. The selectivity of our system is near perfect for glass over Si (100) with a native oxide layer. This is to the best of our knowledge also the first report of selective area atomic layer deposition of any molybdenum containing compound. Moreover, it is indeed extreme that the selectivity retained even for as much as 1000 cycles. It is rare that a system exhibits selectivity over so many cycles, as 250 cycles is typically reported as the maximum number of cycles before extra measures, such as etching steps, are required. 

Taking the extreme selectivity into account, this work has thoroughly studied the possible MoO$_3$ growth on Si(100). As all data from EDS, SEM, and XPS point to the same conclusion, that MoO$_3$ does not grow on Si(100) using MoCl$_4$O+$\text{(O}_3+\text{H}_2\text{O})$ at temperatures of 300 $^\circ$C or less, we have confidence in that the system indeed is perfectly selective within this temperature range.
IV. SUMMARY AND CONCLUSIONS

We have reported on the use of the novel precursor MoCl₄O⁺ (H₂O+O₃) for deposition of various molybdenum oxides with ALD using deposition temperatures between 200 and 350 °C. The highest growth rate was 0.72 Å/cycle when deposited on soda-lime glass at 300 °C. The MoCl₄O⁺ (H₂O+O₃) process is clearly dependent on the chemistry of the substrate. It shows highly area-selective growth when deposited on substrates containing available lithium or sodium, only growing on glass and LiF and not on Li₃PO₄, CaCO₃, Na₂CO₃, Si(100) with a native oxide layer, or silica. Moreover, the system is perfectly selective as measured by EDS for glass over Si (100) with a native oxide layer in the temperature range of 200–300 °C. XPS analysis showed a large presence of sodium in the film deposited on glass and likewise lithium in the film deposited on LiF. This presence of mobile Li⁺/Na⁺ is most likely the key feature of the nucleation and growth and opens for deposition of patterned structures of molybdenum oxides.

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