Atomic layer deposition of crystalline molybdenum oxide thin films and phase control by post-deposition annealing

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A B S T R A C T
Molybdenum forms a range of oxides with different stoichiometries and crystal structures, which lead to different properties and performance in diverse applications. Herein, crystalline molybdenum oxide thin films with controlled phase composition are deposited by atomic layer deposition. The MoO2(thd)2 and O2 as precursors enable well-controlled growth of uniform and conformal films at 200–275 °C. The as-deposited films are rough and, in most cases, consist of a mixture of α- and β-MoO3 as well as an unidentified suboxide MoOx (2.75 ≤ x ≤ 2.89) phase. The phase composition can be tuned by changing deposition conditions. The film stoichiometry is close to MoO3 and the films are relatively pure, the main impurity being hydrogen (2–7 at-%), with ≤ 1 at-% of carbon and nitrogen. Post-deposition annealing is studied in situ by high-temperature X-ray diffraction in air, O2, N2, and forming gas (10% H2/90% N2) atmospheres. Phase-pure films of MoO2 and α-MoO3 are obtained by annealing at 450 °C in forming gas and O2, respectively. The ability to tailor the phase composition of MoOx films deposited by scalable atomic layer deposition method represents an important step towards various applications of molybdenum oxides.

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1. Introduction

Molybdenum oxides (MoOx) form a versatile group of materials as their properties vary widely as a function of the molybdenum oxidation state [1]. The most common molybdenum oxides are the monoclinic dioxide (MoO2) and the trioxide (MoO3), the latter of which exists in stable orthorhombic α and metastable monoclinic β phases. In addition, many crystalline mixed-valence suboxides with compositions between MoO2.75 and MoO3 are known, including the γ and η phases of Mo9O11 (x = 2.75), Mo7O47 (x = 2.76), Mo8O14 (x = 2.80), and Mo8O23 (x = 2.88) as well as Mo9O26 (x = 2.89) in the monoclinic and triclinic ("Mo18O52") phases [2–4]. The versatility of molybdenum oxides is reflected in, for example, the electrical properties at room temperature: α and β-MoO3 are relatively insulating with band gaps of approximately 3 eV [5] (resistivity usually >10⁹ Ωcm) [5–7], Mo9O26 is a semiconductor (ρ = 100 Ωcm) [2,8], whereas γ-Mo9O21 (ρ = 10⁻⁴ Ωcm) [8,9] and the well-known MoO2 (ρ = 10⁻⁴ Ωcm) [10] are highly conducting. Additionally, oxygen vacancies or reactions with hydrogen occur easily for MoO3, leading to oxygen deficient, n-type semiconductor MoO3, γ or hydrogen bronzes H2MoO3. Partial reduction of molybdenum is accompanied by an increase in electrical conductivity [4,11–14]. Amorphous MoOx is also common with varying stoichiometries and, consequently, with different properties [15–17].

Due to the possible changes in the structure and oxidation state of molybdenum, molybdenum oxides show changes in optical properties upon excitation by light, heat, or applied voltage, i.e., photochromism [13,15,16,18], thermochromism [18,19], and electrochromism [15], respectively. The most widely studied applications of the chromatic phenomena lie in smart windows and other optical coatings [20], but chromatic metal oxides may also be useful for displays and optical memories, for example [21,22]. Other applications for MoO3 and MoO3-x include catalysts [23,24], gas sensors [25], resistive switching memories [26], and lithium ion...
batteries [27]. Notably, \( \alpha \)-MoO\(_3\) has a two-dimensional crystal structure and a larger band gap than the most known 2D materials, such as transition metal dichalcogenides akin to MoS\(_2\). The 2D \( \alpha \)-MoO\(_3\) has shown promise as a channel [11], contact [28], and electron acceptor [29] material in field-effect transistors. In gas sensors the 2D \( \alpha \)-MoO\(_3\) has shown enhanced performance over its bulk counterpart [30]. Many of the applications of MoO\(_2\) are similar to those of MoO\(_3\) and MoO\(_3\)-y, including catalysis [31] or lithium ion batteries [32]. Reported applications of the crystalline suboxides with \( 2.75 < x \leq 2.89 \) are quite sparse, but some investigations have been made regarding lithium ion batteries [33–35] and catalysis [36,37].

Different MoO\(_x\) phases show varying performance in different applications. For example, the layered structure of \( \alpha \)-MoO\(_3\) allows it to outperform \( \beta \)-MoO\(_3\) in gasochromic applications [38], whereas \( \beta \)-MoO\(_3\) has been suggested to be more active for catalytic oxidation of methanol [39]. Oxygen-deficient MoO\(_3\)-y has also been proposed to exhibit higher activity than MoO\(_3\) in some photo- and electrocatalytic applications [1,40]. It has also been suggested that the crystalline suboxides may, at least in some cases, be the actual thin film catalysts for gas sensors, and lithium ion batteries [32].

For many of the abovementioned applications, either uniform thin films or nanoparticles with controlled sizes and morphologies are required. Atomic layer deposition (ALD) is an advanced gas phase thin film deposition method, which relies on alternating self-limiting surface reactions. Therefore, ALD is able to coat large areas as well as substrates with complex shapes with a thickness uniformity unmatched by any other method. ALD also typically deposits high-quality films at relatively low deposition temperatures. In addition, due to the cyclic nature of ALD, film thickness and doping can be controlled accurately [44–46].

Reports on ALD of metal oxides have been very common since the 1990s, but the first report on the ALD of molybdenum oxide was published as late as in 2011 by Diskus et al. [47], who used Mo(CO)\(_6\) with “wet oxygen”, i.e. simultaneous exposure to \( O_2 \) and \( H_2O \), as the reactant. Since 2014, a range of new MoO\(_x\) processes have been published, including Mo(CO)\(_6\) with \( O_2 \) plasma [48], Mo(N\(_2\)Bu\(_2\))(NMe\(_2\))\(_2\) with either \( O_3 \) [49] or \( O_2 \) plasma [50,51], MoO\(_2\)(BuAMD)\(_2\) with \( O_3 \) [52], MoO\(_2\)(PR\(_3\)AMD)\(_2\) with \( O_3 \) [53], Mo(CpSiMe\(_3\))(CO)(\( O_2 \))(2-methylallyl) with \( O_3 \) [54] as well as the only \( H_2O \)-based process, Mo(ethylenbenzene)\(_2\) with \( H_2O \) [55]. The composition of the deposited films, if reported, has usually been close to MoO\(_3\) [47,49–51,53,54,56], except for the Mo(VI)oxyxinitride films deposited from MoO\(_2\)(BuAMD)\(_2\) and \( O_3 \) [52].

Deposition of crystalline (\( \alpha \)-MoO\(_3\)) films by ALD has only been reported from Mo\(_x\)(N\(_2\)Bu\(_2\))(NMe\(_2\))\(_2\) and \( O_2 \) plasma at \( 250 \) °C and above [51]. Diskus et al. [56] managed to crystallize the initially amorphous MoO\(_2\) films deposited from Mo(CO)\(_6\) and wet \( O_3 \) to either \( \alpha \)-MoO\(_3\) or a mixture of \( \alpha \)- and \( \beta \)-MoO\(_3\) depending on the annealing temperature. Nevertheless, the aforementioned approaches to produce crystalline films rely on either the use of plasma, which is problematic regarding conformality as well as batch processing, or post-deposition annealing, which is not suitable for temperature-sensitive substrates. Furthermore, to the best of our knowledge, neither MoO\(_2\) nor any of the crystalline suboxide phases \((2.75 < x \leq 2.89)\) have been achieved by ALD, with or without post-deposition annealing. More generally, reports on thin films of the suboxides are also scarce, which hinders their application.

We report the first ALD process capable of depositing crystalline molybdenum oxide films without the use of plasma, using a new ALD precursor MoO\(_2\)(thd)\(_2\) with \( O_3 \) as the reactant. The growth characteristics were studied, followed by detailed film characterization. Post-deposition annealing experiments were performed using \textit{in situ} high-temperature X-ray diffraction in both reducing and oxidizing atmospheres. Annealing was then optimized to produce phase-pure films of \( \alpha \)-MoO\(_3\) and MoO\(_2\).

2. Experimental

2.1. Film deposition

Molybdenum oxide thin films were deposited using a commercial, hot wall flow-type F120 ALD reactor [57]. Nitrogen (\( N_2 \), \( \text{AGA, 99.999\%} \)) was used as both carrier and purge gas at a flow rate of 400 sccm. The reactor pressure was on the order of 5 mbar. The deposition temperature varied by no more than \( \pm 2 \) °C during each deposition, mostly towards higher temperatures due to overshoot during heating of the reactor. The films were deposited on \( 5 \times 5 \) cm\(^2\) silicon (100) and soda lime glass substrates. The glass substrates were cleaned in an ultrasonic bath using successive baths of an alkaline ultrasonic cleaning solution, ethanol, and deionized water. The silicon wafers were used as-received.

Dioxobis(2,6,6-tetramethylheptane-3,5-dionato)molybdenum(VI) (MoO\(_2\)(thd)\(_2\), 99.5%, EpiValence) was evaporated from an open glass boat heated to 135 °C inside the ALD reactor, slightly above the melting point of the precursor, which was about 130 °C under the ALD reactor conditions. A Mettler Toledo STare system equipped with a TGA850 thermobalance was used for simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the precursor. The TGA/DTA measurement was performed at atmospheric pressure of flowing \( N_2 \) using a heating rate of 10 °C/min and a sample size of approximately 10 mg.

Ozone (\( O_3 \)) was produced from oxygen (\( O_2 \), \( \text{AGA, 99.999\%} \)) using an ozone generator (Wedeco Ozomax Modular 4 HC). The nominal \( O_3 \) concentration was 100 g/Nm\(^3\) and the flow rate of the \( O_3 \)–\( O_2 \) mixture was typically set to approximately 200 sccm using a needle valve. Unless otherwise noted, films were deposited at \( 250 \) °C using 1 s MoO\(_2\)(thd)\(_2\) and 3 s \( O_3 \) pulses separated by 1 s \( N_2 \) purges.

2.2. Thickness measurements

Film thicknesses were measured by ellipsometry using a Film Sense FS-1 Multi-Wavelength instrument. The model used to fit the data consisted of four layers (silicon, native silicon oxide, dense MoO\(_x\) bottom layer, and rough MoO\(_x\) top layer). The rough top layer was necessary to obtain good agreement between the data and the model and it was implemented using an effective medium approximation with 50% of the layer being void and the other 50% having properties of the dense MoO\(_x\) layer underneath. Cauchy model was used for layers other than the silicon substrate. For comparison, UV–VIS spectroscopy (Hitachi U2000) and energy-dispersive X-ray spectrometry (EDS, Oxford INCA 350 connected to Hitachi S-4800) were also used for some samples to confirm the thicknesses measured by ellipsometry. The high roughness of most films prevented the use of X-ray relectivity (XRR).

2.3. Film characterization

Film morphology was studied by scanning electron microscopy (SEM, Hitachi S-4800) and atomic force microscopy (AFM, Veeco Multimode V). AFM imaging was done in the tapping mode in air using silicon probes (Bruker) with a nominal tip radius of less than 10 nm. The images were flattened to remove artefacts caused by sample tilt and scanner nonlinearity. Film roughness was calculated as a root mean square value (Rq) from \( 2 \times 2 \) \( \mu m \) images.
Film crystallinity was examined by X-ray diffraction (XRD) using a PANalytical X’Pert Pro MPD instrument in grazing incidence (incident angle of 1°) geometry and a Cu Kα (λ = 1.54 Å) X-ray beam. Composition of the surface layers was analyzed by X-ray photoelectron spectroscopy (XPS) using an Argus spectrometer (Omicron Nanotechnology GmbH). The samples were illuminated with X-rays emitted from a standard Mg source (Kα line) at a photon energy of 1253.6 eV. Binding energies were calibrated using the C 1s peak (284.8 eV) of ambient hydrocarbons, and peak fitting was done using the CasaXPS software. Film composition was analyzed by time-of-flight elastic recoil detection analysis (ToF-ERDA) using a 40 MeV 127I7+ ion beam [58].

Micro-Raman spectra were measured in backscattering geometry using confocal Raman microscopes with 100× objectives. Measurements with a 325 nm laser were performed with a Horiba Jobin Yvon LabRam HR 800 instrument, whereas an NT-MDT Ntegra instrument was used with 532 nm and 633 nm lasers. Laser power was adjusted to a level where no deterioration of the sample occurred.

Optical transmission measurements of the films deposited on soda lime glass substrates were conducted using a Hitachi U-2000 UV–Vis spectrophotometer.

2.4. High-temperature X-ray diffraction

In situ high-temperature XRD (HTXRD) measurements were performed using an Anton-Paar HTK1200N oven connected to a PANalytical X’Pert Pro MPD diffractometer with a Cu Kα (λ = 1.54 Å) X-ray source. The measurements were done under atmospheric pressure of air, O2 (AGA, 99.9999%), N2 (AGA, 99.999%, further purified with an Entegris Gatekeeper purifier), or forming gas (10% H2 in N2, AGA). During the experiments, the temperature was increased from 26 up to 666 °C with the temperature stabilized every 40 °C for recording of a grazing incidence diffractogram (incident angle of 1°). Recording each diffractogram took approximately 35 min, and the heating between the measurements was done with a rate of 10 °C/min followed by a two minute stabilization period, which resulted in a total duration of approximately 11 h for each HTXRD experiment.

The Anton-Paar oven was also used to produce annealed films for further analysis. Based on the HTXRD measurements, a temperature of 450 °C and an annealing time of 1 h (O2) or 3 h (forming gas) were selected. The heating rate was 10 °C/min, whereas cooling to room temperature took approximately 30 min. Isothermal measurements with consecutively measured grazing incidence diffractograms were also done under similar conditions to follow the transformation processes in more detail.

3. Results and discussion

3.1. Film growth

Molybdenum oxide thin films were deposited by atomic layer deposition (ALD) using diisobutyl(2,6,6,8-tetramethylpentane-3,5-dionato)molybdenum(VI) [MoO2(thd)3]2 and O3 as precursors. No appreciable film growth occurred using H2O or H2S as the reactant. The lack of reactivity with water is common for precursors containing β-diketonate ligands. In contrast, some of them, including MoO2(thd)3 [59], have been found to react with H2S. To the best of our knowledge, MoO2(thd)3 is a new ALD precursor, whereas it has been used for CVD of MoOx with O2 as a reactant at relatively high temperatures (350–430 °C) [60].

Thermogravimetric analysis (TGA) showed that MoO2(thd)2 volatilized cleanly leaving a residue of less than 2% (Fig. 1). While a solid at room temperature, MoO2(thd)2 melted at approximately 130 °C, which is just below the source temperature used in this work and in agreement with literature values of 129–135 °C [61,62], as indicated by DTA (Fig. 1) and visual observations during heating of the ALD reactor. The favorable thermal properties together with the commercial availability and reactivity with O3 make MoO2(thd)2 an attractive ALD precursor. Most film growth experiments were done at 250 °C, the temperature which yielded the most uniform films and the highest growth rates close to 1 Å/cycle. Due to the roughness of the films, measuring film thicknesses turned out to be rather challenging by ellipsometry and UV–VIS spectrometry, and impossible by XRR. However, a good fit of the ellipsometry data was obtained by using a four-layer model consisting of a Si substrate, a native SiO2 layer, a dense MoO2 layer, and a rough MoOx surface layer (Fig. 2a). Similar thickness values were also measured by UV–VIS spectrometry and EDS (Fig. S1, Supplementary data). The similar trends of the optical thicknesses (ellipsometry, UV–VIS) and the mass thicknesses (EDS) support the use of the ellipsometry-derived total film thicknesses, including both the dense bottom layer and the rough top layer, in the following discussion.

A rather high growth rate of approximately 1.0 Å/cycle was reached with a MoO2(thd)2 pulse of only 0.2 s (Fig. 2b). However, increasing the pulse length above 1.0 s led to a slight increase in the growth rate, which is likely due to precursor decomposition. Nevertheless, pulsing MoO2(thd)2 alone for 1000 pulses of 1 s each resulted in no film growth to the accuracy of the thickness measurements. Thus, the precursor decomposition seems to occur mostly on the surface of the growing MoOx film as opposed to decomposition in the gas phase. From the average slope of the growth rate versus MoO2(thd)2 pulse length from 0.2 to 3.0 s the decomposition was estimated to increase the growth rate by approximately 0.1 Å/cycle per second of MoO2(thd)2 pulsing. Therefore, the decomposition contributed only 2% of the growth rate when using 0.2 s pulses, which already appeared to be long enough to saturate the ALD-like surface reactions. Furthermore, the deposited films were uniform over the 5 × 5 cm2 substrates with non-uniformities below 5%. With ozone, a 2 s pulse was needed to reach saturated growth rate (Fig. 2c).

Interesting effects were observed when the film thickness was varied: during the first 100 cycles the film growth was linear but slow with a growth rate of 0.35 Å/cycle and no apparent nucleation delay (Fig. 2d). The growth was also linear between 250 and 1000 cycles, but with a much higher growth rate of 1.25 Å/cycle. Furthermore, the thinnest films could be modeled as a single, dense
layer, whereas the thicker films required a rough surface layer in the model. The dramatic increase in roughness and growth rate between 100 and 250 cycles is linked to crystallization of the films, as will be discussed in Section 3.2. Indeed, Vos et al. [51] noted a similar effect with their ALD MoO$_x$ films grown from Mo(N-tBu)$_2$(NMe$_2$)$_2$ and O$_2$ plasma at 300 °C, although they measured a growth rate increase of only 25% upon crystallization compared to the 250% increase measured here. The difference may at least partly be explained by the high roughness of our films as well as the different chemical reactions in thermal versus plasma-enhanced ALD. Large, 1.4–4-fold increases in growth rates upon crystallization have also been observed with ALD TiO$_2$ films, which has been suggested to be due to both increased roughness and differences in surface chemistry, such as hydroxyl group coverage [63–65].

Varying the purge times from 1 to 5 s after each precursor pulse had no effect on the growth rate (Fig. 2e), as is expected for ALD. Pulse times of 1 s for MoO$_2$(thd)$_2$, 3 s for O$_3$, and purges of 1 s were selected for further experiments.

The film growth was rather sensitive to the deposition temperature, with the highest growth rates of approximately 1.0–1.1 Å/cycle observed between 245 and 255 °C (Fig. 2f). The growth rate decreased strongly on both sides of this temperature range, which is attributed to slower crystallization at temperatures below 245 °C and, possibly, changes in the crystalline phase composition for films deposited at temperatures above 255 °C. The latter would require different phases to have different growth rates, perhaps due to differing catalytic activity or hydroxyl group coverage. Additionally, the surface area of the films may change with deposition temperature, which would affect the growth rate. The films deposited at 300 °C showed increased non-uniformity, whereas films deposited at other temperatures were visibly uniform over the 5 × 5 cm$^2$ substrates used in this work. Furthermore, despite the slight precursor decomposition at 250 °C, highly conformal films were deposited on trenches with a high aspect ratio of 30:1 within the uncertainty of the thickness measurements of approximately ±5 nm (Fig. 3).
3.2. Characterization

The film crystallinity was first examined by XRD. For an approximately 100 nm film deposited at 250 °C, multiple reflections originating from both the stable orthorhombic α [66] and metastable monoclinic β [67] phases of MoO3 were detected by grazing incidence XRD (Fig. 4a). In addition, a strong reflection was detected at approximately 22.4° 2θ accompanied by a second reflection close to 46° 2θ, which corresponds to half the d-spacing of the first peak. These peaks could not be indexed to either of the MoO3 phases. Instead, several known suboxide phases, including γ-Mo4O11 [68], η-Mo4O11 [69], Mo7O47 [70], Mo5O14 [71], Mo9O23 [72], Mo8O26 [73], and Mo9O26 [74] have reflections close to these positions. The three partially overlapping peaks at 22.4° (suboxide), 23.0° (β-MoO3 (011)) and 23.3° 2θ (α-MoO3 (110)) were the most intense for each phase also in the 0–20 geometry (Fig. S2, Supplementary data) and the relative peak intensities were also rather similar to the GIXRD measurements. Thus, taking into account the known differences between GIXRD and θ–2θ geometries and the planes detected by them [75], none of the phases appears to be strongly textured.

Raman spectroscopy was also used to study the phase composition. α [76,77] and β [77] phases of MoO3 were detected with UV (325 nm), green (532 nm), and red (633 nm) lasers, although the relative intensities of the peaks were different for each laser (Fig. 4b). However, no signs of any suboxide phase were seen with any of the lasers. Both γ-MoO31 and η-MoO311 have been reported to be relatively weakly Raman active when excited with a green (514.5 or 532 nm) laser [78,79], but increased Raman activity under red (633 nm) laser illumination has been noted for these phases [78,80]. Mo18O52 has been reported to be weakly Raman active under IR (1064 nm), red (633 nm), and UV (244 nm) lasers, whereas relatively strong peaks should result from MoO3C3 when using either a 633 or 244 nm laser [80]. To the best of our knowledge, Raman spectra of other suboxide phases, such as Mo17O47, Mo5O14, or Mo6O62, have not been reported.

Deposition temperature had a strong effect on film morphology (Fig. 5) as well as crystallinity (Fig. 6). The film deposited at 200 °C appeared smooth and nearly featureless, in line with its amorphous structure. At 225 °C rod-like crystallites of an unidentified suboxide phase formed. The films deposited between 240 and 255 °C had rather similar morphologies with rough surfaces composed of both rod and plate-like crystallites, and the films contained both the α and β phases of MoO3 in addition to the suboxide phase(s). At 260 °C plate-like crystallites started to dominate the surface, which was accompanied by a strong decrease in the XRD reflection originating from the suboxide (2θ = 22.4°), while both MoO3 phases were still present. The dominantly plate-like films deposited at 275–300 °C were nearly phase-pure α-MoO3 with slight traces of β-MoO3. In addition, the changes in the relative intensities of the α-MoO3 peaks at temperatures above 260 °C suggest changes in their orientation.

We also observed that precursor pulse times had some effect on the film morphology and phase composition: long MoO2(thd)2 pulses led to more plate-like morphology with increased amount of α-MoO3 compared to the suboxide and β-MoO3 (Fig. S3, Supplementary data), whereas long O3 pulses decreased the amount of the suboxide with a corresponding increase in both the α- and β-MoO3 phases (Fig. S4, Supplementary data). Even purge times affected film morphology (Fig. S5, Supplementary data). There are at least two ways the pulse times may affect the film morphology and crystallinity at doses higher than those needed for saturation of the growth rate. First, longer pulses or purges give more time for processes such as crystallization, phase transformation, and surface diffusion. Second, increasing the dose of especially the reactant, such as ozone, may reduce the impurities, improve the stoichiometry, and affect the film structure.

Notable changes in the film morphology (Fig. 7a and Fig. S6, Supplementary data) as well as crystallinity (Fig. 7b) occurred at 250 °C with increasing film thickness. The thinnest films up to 100 cycles were smooth and amorphous, whereas a crystalline suboxide phase was formed after 250 cycles, which was accompanied by a strong increase in roughness. Thereafter the roughness continued to increase up to 1000 cycles, and changes in phase composition were also observed: both α- and β-MoO3 formed after 500 cycles and their amounts relative to the suboxide seemed to increase with increasing film thickness. The observation of onset of crystallization between 100 and 250 cycles agrees well with the strong increase in the growth rate discussed in Section 3.1. The roughness of the films increases their surface area, which has been found beneficial in many applications of MoO3, as discussed in the Introduction. Based on AFM images, the surface area of the roughest, 1000 cycle film was estimated to be approximately twice the substrate area.

The films deposited at 225, 250, and 275 °C were all relatively pure. The main impurity was hydrogen, and some carbon and nitrogen were also detected (Table 1). The O/Mo ratios were rather close to 3; this probably results from a balance of the suboxide MoO3 phase (2.75 ≤ x ≤ 2.89) decreasing the ratio and the presence
of residual OH groups increasing it. The highest hydrogen content was measured for the film deposited at 250 °C, which also had the highest O/Mo ratio, suggesting the incorporation of hydrogen as hydroxyl groups. The amount of carbon, which likely originates from the precursor, was low and decreased with increasing deposition temperature. Interestingly, the films contained small amounts of N (0.5–1 at-%). We think this has to be incorporated during the deposition from the usually inert N2 carrier gas, as no nitrogen-containing chemicals were used in the precursor synthesis and the nitrogen appears to be distributed throughout the film thickness. Molybdenum oxides have been reported to incorporate nitrogen relatively easily. For example, films deposited from a nitrogen-containing precursor MoO2(tBuAMD)2 and O3 by ALD were described as Mo(VI)oxynitride [52], partial nitridation of MoO3 has been reported upon N2 annealing at 400 °C [81], and nitrogen impurities have also been found for MoO3 films deposited under nominally nitrogen-free conditions [12].

X-ray photoelectron spectroscopy (XPS) showed that molybdenum on the film surface was mostly present as Mo6+, as evidenced by the Mo 3d5/2 and Mo 3d3/2 binding energies of 233.0 and 236.2 eV, respectively (Fig. 8a). Approximately 10% of molybdenum was identified as Mo5+ represented by a doublet with binding energies of 231.3 (Mo 3d5/2) and 234.5 eV (Mo 3d3/2). The observed binding energies are within the range reported for different MoO3 samples [82], in particular close to the values for crystalline ALD α-MoO3 films deposited by Vos et al. [51] and somewhat higher than those reported for amorphous ALD MoO3 [49,53,56]. The Mo5+/Mo6+ content would be expected to range from 50% (Mo4O11) to 22% (Mo9O26) for the different suboxide phases. However, the similar Mo5+/Mo6+ ratios for the films deposited at different temperatures point to changes on the film surface due to ambient exposure, as XRD showed the films deposited at 225 and 275 °C to be nearly phase-pure suboxide and α-MoO3, respectively.

The majority of oxygen (Fig. 8b) was present as oxide ions (O2−), whereas about 5% (275 °C) or 12% (225 and 250 °C) of oxygen was identified as hydroxyl groups (OH−). The O 1s binding energies of 530.7 (O2−) and 531.9 eV (OH−) are in relatively good agreement with other ALD MoO3 films [49,51,56]. A minor O 1s component at 533.3 eV was attributed to organic species containing oxygen, in accordance with detection of carbonyl species in C 1s spectra (not shown).

Optical properties were evaluated from the films deposited on soda lime glass substrates. Using a Tauc plot, an indirect band gap of 2.8 eV was extracted for a 2000 cycle film deposited at 250 °C (Fig. S7, Supplementary data), which is within the range of band gap values (2.7–3.2 eV) reported for MoO3 [1,7,51,83]. The refractive indices at 580 nm ranged from 2.0 for the amorphous films to 2.2 for the predominantly α-MoO3 films deposited at 275–300 °C and

![Fig. 5. SEM images of MoOx films deposited on silicon at different temperatures using 1000 cycles.](image-url)

![Fig. 6. Grazing incidence X-ray diffractograms of MoOx films deposited on silicon at different temperatures using 1000 cycles. α and β refer to α-MoO3 and β-MoO3, whereas suboxide denotes an unidentified MoOx (2.75 ≤ x ≤ 2.89) phase.](image-url)
even 2.4–2.5 for the mixed-phase films deposited at 250 °C. Refractive indices ranging from 1.8 to 2.2 have been reported for trioxide-like MoO₃ films [7,51,83]. Thus, the highest values measured for the mixed-phase films may be due to the suboxide phase(s).

3.3. Post-deposition annealing

The phase composition of the MoO₃ films could be tuned by changing the deposition conditions. However, the majority of the deposited films were mixtures of three phases. Additional control in phase composition was sought through post-deposition annealing. Approximately 100 nm thick MoO₃ films deposited at 250 °C (1000 cycles), which consisted of a mixture of suboxide, α-MoO₃, and β-MoO₃ phases, were selected for annealing experiments performed in both oxidizing and reducing atmospheres. The effects of annealing were followed in situ by HTXRD.

Upon annealing in O₂ the first changes occurred above 306 and 346 °C, when the suboxide and metastable β-MoO₃ phases, respectively, disappeared (Fig. 9). From 386 to 586 °C the film was phase-pure α-MoO₃, the only changes being peak shifts due to anisotropic thermal expansion and variation in relative peak intensities (preferred orientation). Above 586 °C, the α-MoO₃ film sublimed, leaving a bare silicon substrate, as verified by EDS. The
onset temperature for the sublimation of $\alpha$-MoO$_3$ has been reported to be 500–700 °C depending on experimental conditions [84,85]. Attempts to produce ultrathin, 2D $\alpha$-MoO$_3$ films from amorphous, sub-5 nm MoO$_x$ films were unsuccessful, as no crystallization was detected by either in situ or ex situ XRD after annealing in O$_2$ to 450 °C or higher temperatures.

Forming gas (10% H$_2$/90% N$_2$) provided a reducing atmosphere in order to produce MoO$_2$ films. The first changes in HTXRD measurements were observed above 226 °C (Fig. 10), when $\beta$-MoO$_3$ disappeared and the initial suboxide phase transformed to a new phase, most likely monoclinic $\eta$-Mo$_4$O$_{11}$ [69]. At 386 °C, $\eta$-Mo$_4$O$_{11}$ may have converted to another suboxide phase and $\alpha$-MoO$_2$ had disappeared with MoO$_2$ starting to form. The formation of $\eta$-Mo$_4$O$_{11}$ is further supported by isothermal measurements presented later in this section. Between 426 and 546 °C, the film was phase-pure, monoclinic MoO$_2$ (tugarinovite) [86]. Starting at 586 °C, MoO$_2$ disappeared and a few broad reflections appeared that most likely originate from molybdenum silicide(s).

An HTXRD experiment was also performed in air, which yielded results very similar to O$_2$ (not shown). Annealing in N$_2$, on the other hand, produced a complex mixture of MoO$_x$ phases (Fig. S8, Supplementary data). MoO$_2$ formed more slowly in forming gas than in O$_2$, where the heating was stopped.

Further insight into the production of phase-pure $\alpha$-MoO$_3$ and MoO$_2$ films in O$_2$ and forming gas, respectively, was obtained through isothermal HTXRD measurements. The transformation to $\alpha$-MoO$_2$ was rapid in O$_2$ atmosphere at 450 °C; only $\alpha$-MoO$_3$ had been reported to occur, although very slowly, at temperatures as low as 500 °C in 10% H$_2$ [87]. MoSi$_2$ is then formed upon reaction of Mo film with the Si substrate, which has been reported to proceed at 500 °C and above [89]. Therefore, it seems that metallic Mo films could be obtained upon reduction in forming gas at approximately 600 °C if the Si substrate was covered by a suitable diffusion barrier layer.

The $\alpha$-MoO$_3$ film produced by annealing in O$_2$ showed lower levels of H and N compared to the as-deposited film, with slightly over stoichiometric O/Mo ratio of 3.15 ± 0.05 (Table 2). The MoO$_2$ film resulting from annealing in forming gas had an O/Mo ratio of 2.11 ± 0.05 and the film was the purest of all analyzed films with sub-at.% carbon, nitrogen, and hydrogen contents. Whereas ToF-ERDA provides results averaged through the whole film thickness, the surface was specifically probed by XPS.

The as-deposited and oxygen-annealed films appeared to have nearly identical surface composition with some 90% of Mo present as Mo$^6+$ and 10% as Mo$^{5+}$ (Fig. S12a, Supplementary data). The O 1$s$ component at 531.9 eV attributed to hydroxyl groups, however, was approximately halved by the O$_2$ annealing (Fig. S12b). Mo$^{4+}$ was expectedly detected after the forming gas annealing with Mo 3d$_{5/2}$ and 3d$_{3/2}$ binding energies of 229.7 and 232.9 eV, respectively, although the relative amounts of Mo$^{4+}$, Mo$^{5+}$, and Mo$^{6+}$ were approximately identical on the surface. This is likely due to surface

3.4. Characterization of annealed films

The MoO$_2$ films formed by annealing in forming gas at 450 °C had a very rough morphology consisting of flower-like structures with widths of about 1 μm (Fig. 11a). Between these structures a smoother area was exposed. The $\alpha$-MoO$_3$ films formed by the O$_2$ annealing at 450 °C consisted of plate-like crystallites on the surface with roughness comparable to the as-deposited film (Fig. 11b). The film formed after the HTXRD measurement in forming gas annealing at 666 °C was found to be a mixture of tetragonal $\alpha$-MoSi$_2$ and Mo$_5$Si$_3$ phases, and the surface was stipped with small triangular crystallites at 676 °C, which was then removed upon further annealing at 700 °C. The morphology and roughness of this film were rather similar to the as-deposited film (Fig. S11b, Supplementary data). The formation of silicides is attributed to reactions between the film and the silicon substrate. It is plausible that MoO$_2$ is first reduced to metallic Mo, which has been reported to occur, although very slowly, at temperatures as low as 500 °C in 10% H$_2$ [87]. MoSi$_2$ is then formed upon reaction of Mo with the Si substrate, which has been reported to proceed at 500 °C and above [89]. Therefore, it seems that metallic Mo films could be obtained upon reduction in forming gas at approximately 600 °C if the Si substrate was covered by a suitable diffusion barrier layer.

The $\alpha$-MoO$_3$ film produced by annealing in O$_2$ showed lower levels of H and N compared to the as-deposited film, with slightly over stoichiometric O/Mo ratio of 3.15 ± 0.01 (Table 2). The MoO$_2$ film resulting from annealing in forming gas had an O/Mo ratio of 2.11 ± 0.05 and the film was the purest of all analyzed films with sub-at.% carbon, nitrogen, and hydrogen contents. Whereas ToF-ERDA provides results averaged through the whole film thickness, the surface was specifically probed by XPS.

The as-deposited and oxygen-annealed films appeared to have nearly identical surface composition with some 90% of Mo present as Mo$^6+$ and 10% as Mo$^{5+}$ (Fig. S12a, Supplementary data). The O 1$s$ component at 531.9 eV attributed to hydroxyl groups, however, was approximately halved by the O$_2$ annealing (Fig. S12b). Mo$^{4+}$ was expectedly detected after the forming gas annealing with Mo 3d$_{5/2}$ and 3d$_{3/2}$ binding energies of 229.7 and 232.9 eV, respectively, although the relative amounts of Mo$^{4+}$, Mo$^{5+}$, and Mo$^{6+}$ were approximately identical on the surface. This is likely due to surface

Fig. 9. High-temperature grazing incidence X-ray diffractograms (left) of a MoO$_3$ film heated in O$_2$ from 26 to 666 °C, where white and black represent low and high intensities, respectively. On right, peaks between 20 and 30 °2θ are identified at selected temperatures to highlight the phase transitions. $\alpha$ and $\beta$ refer to $\alpha$-MoO$_3$ and $\beta$-MoO$_3$, whereas suboxide denotes an unidentified MoO$_x$ ($2.75 \leq x \leq 2.89$) phase.
Fig. 10. High-temperature grazing incidence X-ray diffractograms (left) of a MoOx film heated in forming gas (10% H2/90% N2) from 26 to 666 °C, where white and black represent low and high intensities, respectively. On right, peaks between 20 and 35 °2θ are identified at selected temperatures to highlight the phase transitions. a and b refer to α-MoO3 and β-MoO3, whereas suboxide denotes an unidentified MoOx (2.75 ≤ x ≤ 2.89) phase.

Fig. 11. Grazing incidence X-ray diffractograms (top row) and SEM images together with roughness values measured by AFM (bottom row) of (a) MoO2 film produced by annealing in forming gas (450 °C, 3 h) and (b) α-MoO3 film produced by annealing in O2 (450 °C, 1 h).

Table 2
Elemental compositions of annealed MoOx films analyzed by ToF-ERDA. The films were deposited on silicon at 250 °C using 1000 cycles.

| Treatment                        | Mo (at-%) | O (at-%) | O/Mo | C (at-%) | H (at-%) | N (at-%) |
|----------------------------------|-----------|----------|------|----------|----------|----------|
| As-deposited (250 °C)            | 22.0 ± 0.5 | 70.1 ± 1.3 | 3.19 ± 0.10 | 0.47 ± 0.15 | 6.6 ± 1.1 | 0.92 ± 0.15 |
| O2 annealed (450 °C, 1 h)        | 23.5 ± 0.6 | 74.0 ± 1.5 | 3.15 ± 0.11 | 0.53 ± 0.13 | 1.9 ± 0.6 | 0.12 ± 0.04 |
| Forming gas annealed (450 °C, 3 h)| 31.8 ± 0.6 | 67.1 ± 1.3 | 2.11 ± 0.05 | 0.59 ± 0.16 | 0.12 ± 0.03 | 0.40 ± 0.11 |
oxidation of the MoO₂ film, as has been previously observed [82]. Interestingly, the relative intensity of the 5319 eV O 1s peak attributed to the OH- groups increased after the forming gas annealing, although the hydrogen content throughout the film analyzed by ToF-ERDA was negligible. This suggests that the hydroxyl groups may have been exclusively present on the film surface in the forming gas annealed film, perhaps due to exposure to ambient air.

4. Conclusions

Atomic layer deposition of crystalline molybdenum oxide thin films was demonstrated using a new, commercially available precursor MoOₓ(Td)₂ with O₂. Well controlled film growth with good uniformity and conformality was achieved although complete saturation was not reached with MoOₓ(Td)₂. Most of the films were mixtures of α-MoO₃, β-MoO₃, and an unidentified suboxide MoOₓ phase (2.75 ≤ x ≤ 2.89). The film composition was close to MoO₃ and the films had fairly low levels of impurities. Relative amounts of the different phases could be controlled by changing the deposition conditions. Post-deposition annealing treatments studied by high-temperature X-ray diffraction enabled further control of film composition. In particular, single-phase α-MoO₃ and MoO₂ films were achieved by annealing in O₂ and forming gas, respectively. As the thickness, crystallinity, morphology, and phase composition strongly affect the performance of MoOₓ films, the presented ALD process constitutes an important step towards the use of MoO₃ in various applications such as sensing, energy storage, and catalysis.

Declarations of interest

None.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.mtchem.2018.04.005.

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