Atomic Layer Deposition of Crystalline MoS\textsubscript{2} Thin Films: New Molybdenum Precursor for Low-Temperature Film Growth

Miika Mattinen, Timo Hatanpää, Tiina Sarnet, Kenichiro Mizohata, Kristoffer Meinander, Peter J. King, Leonid Khriachtchev, Jyrki Räisänen, Mikko Ritala,* and Markku Leskelä

Molybdenum disulfide (MoS\textsubscript{2}) is a semiconducting 2D material, which has evoked wide interest due to its unique properties. However, the lack of controlled and scalable methods for the production of MoS\textsubscript{2} films at low temperatures remains a major hindrance on its way to applications. In this work, atomic layer deposition (ALD) is used to deposit crystalline MoS\textsubscript{2} thin films at a relatively low temperature of 300 °C. A new molybdenum precursor, Mo(thd)\textsubscript{3} (thd = 2,2,6,6-tetramethylheptane-3,5-dionato), is synthesized, characterized, and used for film deposition with H\textsubscript{2}S as the sulfur precursor. Self-limiting growth with a low growth rate of \( \approx 0.025 \) Å cycle\textsuperscript{-1}, straightforward thickness control, and large-area uniformity are demonstrated. Film crystallinity is found to be relatively good considering the low deposition temperature, but the films have significant surface roughness. Additionally, chemical composition as well as optical and wetting properties are evaluated. MoS\textsubscript{2} films are deposited on a variety of substrates, which reveal notable differences in growth rate, surface morphology, and crystallinity. The growth of crystalline MoS\textsubscript{2} films at comparably low temperatures by ALD contributes toward the use of MoS\textsubscript{2} for applications with a limited thermal budget.

1. Introduction

In the last 10 years, transition metal dichalcogenides (TMDCs) have received considerable attention as a promising material group for a variety of applications. The intriguing layered, 2D crystal structures of TMDCs give birth to unique properties in thin (<10 nm) TMDC layers that are not seen in their bulk form. This is due to quantum confinement effects and the weakness of interlayer interactions in TMDCs.\textsuperscript{[1–4]} To date, molybdenum disulfide (MoS\textsubscript{2}) has been the most extensively studied TMDC material.

Compared to the most well-known 2D material, graphene, which is a semi-metal, the semiconducting 2H phase of MoS\textsubscript{2} is advantageous in having a band gap suitable for electronic applications. In bulk form, MoS\textsubscript{2} has an indirect band gap of 1.3 eV, which increases as a function of decreasing film thickness. In monolayer MoS\textsubscript{2} (thickness <0.6 nm), the band gap becomes direct with a width of 1.8 eV.\textsuperscript{[1]} Importantly, to meet the requirements of different applications, properties of MoS\textsubscript{2} and other TMDCs can be tuned by controlling the thickness,\textsuperscript{[1]} doping and alloying,\textsuperscript{[5–8]} surface modification and functionalization,\textsuperscript{[9–11]} strain,\textsuperscript{[12,13]} and by creating heterostructures with other 2D materials.\textsuperscript{[14–16]}

The appealing properties of TMDCs have led to a wide range of proposed applications. MoS\textsubscript{2} has been extensively studied as a channel material in conventional field-effect transistors,\textsuperscript{[17–21]} as well as phototransistors and other optoelectronic devices.\textsuperscript{[16,21,22]} The 2D structure of TMDCs plays a crucial role in possible applications relying on more exotic quantum phenomena, such as valleytronics,\textsuperscript{[23,24]} MoS\textsubscript{2} has also shown promise in, for example, catalysis\textsuperscript{[25]} batteries,\textsuperscript{[26]} photovoltaics,\textsuperscript{[27]} sensors,\textsuperscript{[28]} and medicine.\textsuperscript{[29]}

The production of high-quality, large-area MoS\textsubscript{2} films with a thickness controllable down to a monolayer, as required in many of the aforementioned applications, still remains a major challenge. Additionally, in many cases, the processing temperature should be kept as low as possible in order to avoid damaging sensitive substrates, such as polymers or nanostructures. Initially, flakes of monolayer MoS\textsubscript{2} were produced from natural MoS\textsubscript{2} crystals using micromechanical exfoliation, a top-down method capable of producing high-quality monolayers, albeit with poor throughput as well as limited control over flake thickness and dimensions.\textsuperscript{[4,30,31]} Liquid-phase exfoliation of bulk crystals, on the other hand, offers good scalability, but often suffers from limited flake size, poor crystallinity, or contamination.\textsuperscript{[4,31,32]}

Bottom-up methods offer a more controllable way to produce MoS\textsubscript{2} films. High-quality MoS\textsubscript{2} thin films are most commonly deposited by chemical vapor deposition (CVD) or sulfurization of metal or metal oxide thin films. The most common
Unfortunately, the low vapor pressure of MoO3 sets limitations to both the deposition temperature (typically 650–850 °C) and deposition area (typically no more than 1 cm²). Sulfurization of Mo or MoO3 films also requires high temperatures, usually 500–1000 °C. Although upscaling of the sulfuration method appears to be easier compared to the MoO3-based CVD, sulfuration tends to produce films of lower quality. Other bottom-up techniques used for the deposition of thin MoS2 films include sputtering, physical vapor transport, pulsed laser deposition, and atomic layer deposition (ALD).

Atomic layer deposition is an inherently scalable technique that can be regarded as an advanced modification of CVD. It is based on self-limiting surface reactions of vapor-phase precursors that are alternately pulsed to substrates. In order to avoid uncontrolled gas-phase reactions, the precursor pulses are separated by purge or evacuation steps. The self-limiting reactions often allow deposition of high-quality films at comparatively low deposition temperatures, typically 100–400 °C. ALD offers large-area uniformity and precise control over film thickness, as well as unmatched conformality, i.e., uniform thickness over substrates with complex 3D shapes. So far, ALD of MoS2 has been reported using MoCl5 with H2S, as well as Mo(CO)6 with H2S plasma, or dimethyl disulfide. The films deposited with Mo(CO)6 have mostly been amorphous due to the low deposition temperatures of 100–200 °C, although the films deposited with H2S plasma were polycrystalline. Using MoCl5 and H2S, crystalline MoS2 films have been deposited by ALD, but a post-deposition annealing or high deposition temperatures in excess of 500 °C may still be required, in most cases, to obtain films of sufficient quality. Thus, there is a clear need to develop new ALD processes for MoS2.

In this study, we report the preparation of crystalline MoS2 films by ALD at a relatively low temperature of 300 °C, using a new molybdenum precursor, tris(2,2,6,6-tetramethylheptane-3,5-dionato)molybdenum(III), Mo(thd)3, with H2S as the sulfur precursor. We describe the synthesis of Mo(thd)3 and other Mo(III) β-diketonates and evaluate their thermal properties. Growth of MoS2 films shows typical characteristics of ALD: self-limiting growth with linear thickness control and excellent film uniformity. Detailed characterization provides information on film growth, morphology, crystallinity, and composition, as well as optical properties and wettability. Film growth is demonstrated and studied on a range of different substrates.

2. Results and Discussion
2.1. Precursor Selection, Synthesis, and Evaluation
2.1.1. Evaluation of Published MoS2 Processes

We began by evaluating the known MoCl5+H2S process in our commercial hot-wall, flow-type ALD reactor. Despite testing a range of deposition conditions, for example, temperatures from 150 to 500 °C, we either obtained no films at all or the films were highly nonuniform in thickness across the substrates. Increasing the MoCl5 dose decreased the film thickness close to the precursor inlet, which hints toward etching of the deposited film by MoCl5. Later, we also found that Mo(CO)6, the other molybdenum precursor used for ALD of MoS2, suffered from heavy precursor decomposition in our reactor already at 110 °C. This was avoided by lowering the temperature below 100 °C, but no film deposition was found in this case.

We attribute these results to the design of the ALD reactor used in this work, where the precursors undergo multiple collisions with hot walls and substrates, increasing the possibility of film etching and precursor decomposition. Additionally, the precursor source design based on inert gas valving may increase the likelihood of thermal decomposition compared to many other ALD reactors, where the precursors are usually heated in separate containers.

2.1.2. Synthesis and Evaluation of Mo(III) β-Diketonates

Due to the failures with the published processes, we searched for alternative Mo precursors. Interestingly, although metal β-diketonates are commonly used in ALD and CVD, there are, to the best of our knowledge, no reports on using Mo precursors containing only β-diketonate ligands. In general, reports of Mo(III) coordination compounds, especially β-diketonates, are rare. Compared to the more commonly investigated Mo(VI) precursors, the oxidation state +III may be beneficial, as it is closer to the oxidation state +IV in MoS2.

Mo(thd)3 was synthesized using a reaction between MoCl5(THF)3 (THF = tetrahydrofuran) and three equivalents of Kthd or Lithd. Surprisingly, this simple metathesis reaction has not been previously reported for making Mo β-diketonates. After isolation and purification by sublimation, Mo(thd)3 was obtained as dark brown, air sensitive solid with yields up to 83%. Crystal structure of the compound solved by single crystal X-ray diffraction (XRD) shows individual Mo(thd)3 molecules (Figure 1a). Detailed information on the crystal structure and its comparison to the previously reported Mo(III) β-diketonates are provided in the Supporting Information.

Thermogravimetric analysis (TG) was used to evaluate thermal properties of Mo(thd)3 as well as similarly synthesized Mo(acac)3 (acac = acetylacetone) and Mo(hfac)3 (hfac = 1,1,1,5,5,5-hexafluoroacetylacetone) (Figure 1b). The low residual masses of 0.3% and 2.6%, respectively, for Mo(thd)3 and Mo(hfac)3 imply evaporation of the compounds. In agreement with previous studies, Mo(acac)3 seemed to mainly decompose, which may be explained by the intermolecular O···H interactions found in its crystal structure.

Three steps were found in the TG curve of Mo(thd)3: first, there was a small mass loss between 80 and 150 °C due to evaporation of some free Hthd. Major, 95% weight loss step associated with evaporation of Mo(thd)3, was seen at 150–265 °C. At 265–300 °C a small, 3% weight loss step was seen, likely due to evaporation of an oxidized species MoO2(thd)2. The first and third steps were attributed to decomposition and oxidation of Mo(thd)3, respectively, during loading of the TG sample in air.

The TG curve measured for Mo(hfac)3 was similar to that measured for Mo(thd)3, but the weight losses occurred at
≈100 °C lower temperatures. This indicates that Mo(hfac)₃ is well volatile, but in our studies the thermal stability of the compound seemed to be lower than that of Mo(thd)₃. Also, for thin film growth, fluorinated ligands raise the question of possible F contamination in the resulting films. Thus, Mo(thd)₃ was chosen for the film growth studies.

2.2. Film Growth on Silicon

Based on initial growth trials, 300 °C was chosen as the most promising deposition temperature for ALD of MoS₂ using Mo(thd)₃ and H₂S. In growth experiments on native oxide terminated silicon, saturation of the growth rate was achieved with Mo(thd)₃ and H₂S pulses of at least 0.5 and 2.0 s, respectively (Figure 2a,b). The growth rates were calculated from film thicknesses measured by energy-dispersive X-ray spectroscopy (EDX), assuming smooth and uniform films with bulk density (5.06 g cm⁻³).[59] The saturation indicates that the precursors react with the surface in a self-limiting manner, which is characteristic for ALD. Varying the purge time after each precursor pulse between 0.5 and 2.0 s caused no change in the growth rate, which further confirms the ALD-like behavior of the process. Purge times of 1.0 s and pulse times of 0.5 s for Mo(thd)₃ and 2.0 s for H₂S were used in the following depositions, unless otherwise noted. Film thickness increased linearly with increasing number of deposition cycles, although some nucleation delay appeared to be present, as the line fitted to the thickness values did not pass through the origin (Figure 2c). Growth rate of 0.028 Å cycle⁻¹ and nucleation delay of 150 cycles were determined from the slope and the intersection of the fitted line with the abscissa, respectively.

The lowest temperature where film growth was observed was 250 °C, where the growth rate was only ≈0.005 Å cycle⁻¹ (Figure 2d).

When increasing the deposition temperature, the growth rate increased up to 300 °C, where the majority of depositions were performed, and then decreased again when going to 325 °C. At 350 °C slight Mo(thd)₃ decomposition was visible in the glass source tubes of the ALD reactor, and the extent of decomposition was clearly larger at 400 °C.

The observed growth rate was low, ≈0.025 Å cycle⁻¹. In general, two main reasons have been proposed to limit the growth rate in ALD: steric hindrance between the adsorbed precursor molecules, and limited number of reactive sites on the surface.[53] Relatively low growth rates have often been observed when using bulky metal thd precursors. For example, saturated growth rates of about 0.20 and 0.15 Å cycle⁻¹ were reported using Ni(thd)₂[60] and La(thd)₃[61] respectively, with H₂S.

Figure 1. Mo β-diketonates. a) Molecular structure of Mo(thd)₃ solved by single crystal XRD. Thermal ellipsoids are drawn on the 30% probability level. Hydrogen atoms are omitted for clarity. b) TG curves for synthesized Mo β-diketonates.

Figure 2. MoS₂ film growth. Growth rate versus a) Mo(thd)₃ and b) H₂S pulse length. c) Film thickness versus the number of ALD cycles. d) Growth rate versus deposition temperature. The filled and open symbols refer to single measurements and average values, respectively. Unless otherwise noted, 2000 cycles were applied at 300 °C on silicon substrates, using 0.5 s (c,d) or 1 s (b) Mo(thd)₃ pulses, 2 s H₂S pulses, and 1 s purges.
The much smaller growth rate found in this work suggests that the density of reactive sites is more likely the limiting factor. For many ALD oxide processes, hydroxyl (−OH) groups are the major reactive sites,[62] whereas the analogous thiol (−SH) groups can play an important role for sulfides. As an example, Meng et al.[63] found a rapid decrease in the density of thiol groups, and, consequently, in the ALD growth rate of GaSx, deposited from Ga2(NMe2)6 and H2S, when increasing the deposition temperature from 125 to 225 °C.

The density of thiol groups, at least on the most common, sulfur-terminated, (002) basal planes of MoS2 can be expected to be small based on the studies on MoS2 catalysts.[64] The edges of basal plane-terminated, typically plate-like crystallites, on the other hand, contain dangling bonds and may act as reactive sites, as may also other kinds of defect sites. Thus, it is possible that the film growth proceeds mainly on the edges and defects, which could explain the slow growth.

2.3. Characterization of Films Deposited on Silicon

2.3.1. Morphology

The evolution of film morphology with increasing film thickness was analyzed with scanning electron microscopy (SEM; Figure 3a) and atomic force microscopy (AFM; Figure 3b). The surface remained smooth and featureless up to 250 cycles, which may be due to the nucleation delay noted above. After 500 cycles, small crystallites or particles appeared, and the film seemed to be discontinuous at this point. This is expected, as nucleation delay is often connected to island growth in ALD.[65] The flake-like morphology with the crystallites standing up from the substrate became more pronounced with increasing number of deposition cycles. The apparent lateral grain size estimated from the SEM and AFM images increased slightly with increasing number of deposition cycles, from ~10–30 nm.

The evolution of film roughness (Figure 3c) can yield useful information on the film growth. The small grain size and considerable roughness make it difficult to determine from the SEM and AFM images when a continuous or closed film is formed, and although the morphology is also a challenge for ALD film growth by Nilsen et al.[66,67] as well as experimental observations on HfO2[68] and Pt[69] ALD films, for example.

Additional information on the surface morphology can be obtained by examination of line profiles taken from the AFM images (Figure 3d). In a film grown with 500 cycles, for example, there are height differences of up to 3 nm, which is to be compared with the average film thickness of ~1 nm. This shows the extent of film roughness caused by the flakes standing up from the substrate plane, which is detrimental for applications requiring smooth films, for example, electronics. However, some applications, such as electrochemical hydrogen evolution,[25,70] and batteries[26] may also benefit from large film roughness and films exposing the crystallite edges and inter-layer spaces.

In thin film growth the film morphology is first controlled by nucleation and later by grain growth processes. Nucleation of ALD films can be sensitive to the deposition chemistry and conditions, including factors such as precursors and their pulse times, substrate and its preparation, and deposition temperature. The orientation of the formed nuclei can then affect or even determine the film morphology. Furthermore, if the film growth mainly occurs on edges and defect sites of MoS2 crystallites, as suggested in Section 2.2., this could lead to the perceived fairly random orientation of crystallites. Thus, even if the
initially formed nuclei have their basal (002) planes oriented parallel to the substrate, their orientation can change with increasing film thickness.

2.3.2. Crystallinity

We studied the crystallinity of the films using XRD and Raman spectroscopy. In grazing incidence XRD, a peak corresponding to the (002) plane of the desired, semiconducting 2H phase of MoS2\(^\text{[71]}\) was detected after 1000 cycles (Figure 4a). After 4000 cycles, weak peaks corresponding to the (100) or (101) as well as (110) planes were also detected. The improvement of the crystallinity with increasing number of deposition cycles is evident in the decreasing width of the (002) peak.

Raman spectroscopy is a powerful method for studying TMDCs, as it can provide information on crystal structure (phase), electronic structure, strain, and film thickness, among others.\(^\text{[72]}\) The films studied with Raman measurements were deposited on 90 nm SiO\(_2\)/Si substrates, where the SiO\(_2\) layer is close to the quarter-wave thickness of the 488 nm laser, and gives a strong signal enhancement for thin films on top,\(^\text{[73]}\) including MoS\(_2\).\(^\text{[74]}\) We note that the film growth was very evident at 350 °C or above have shown FWHMs as low as 3–4 cm\(^{-1}\).\(^\text{[33,78]}\) On the other hand, for the ALD MoS\(_2\) films deposited from MoCl\(_5\) and H\(_2\)S at 475 °C, the E\(_{1g}\) FWHM was as broad as 18 cm\(^{-1}\), which decreased by sulfur annealing to 12 cm\(^{-1}\) (720 °C) or even 4.2 cm\(^{-1}\) (920 °C).\(^\text{[46]}\) A four-monolayer MoS\(_2\) film, produced by sulfurization of an MoO\(_2\) film, yielded E\(_{1g}\) FWHM of 6.5 cm\(^{-1}\) at 750 °C, whereas a higher sulfurization temperature of 1000 °C reduced the FWHM to 4.6 cm\(^{-1}\).\(^\text{[19]}\) In summary, the Raman spectra indicate comparably good crystallinity, especially considering the low deposition temperature.

The full width at half-maximum (FWHM) values of the fitted E\(_{1g}\) and A\(_{1g}\) components were ≈6 and 7 cm\(^{-1}\), respectively, whereas those for the full peaks (i.e., without deconvolution) were around 9 cm\(^{-1}\) for all of the measured films. Mechanically exfoliated as well as the best CVD-grown monolayer MoS\(_2\)-films deposited at 650 °C or above have shown FWHMs as low as 3–4 cm\(^{-1}\).\(^\text{[33,78]}\) In contrast to the typically observed blueshift of E\(_{1g}\) and redshift of A\(_{1g}\) peak with decreasing film thickness in few-layer MoS\(_2\).\(^\text{[71]}\) The lack of peak shifts may result from coexistence of MoS\(_2\) crystallites with different thicknesses, due to the initial island-like film growth.

As we observed asymmetric broadening of the MoS\(_2\) peaks, we used the peak fitting strategy of Mignuzzi et al.\(^\text{[77]}\) to estimate disorder in the films. In addition to the E\(_{1g}\) and A\(_{1g}\) modes, three disorder-induced peaks were fitted, which originate from the transverse optical (≈355 cm\(^{-1}\)), longitudinal optical (≈377 cm\(^{-1}\)), and out-of-plane optical (≈412 cm\(^{-1}\)) branches at the M point of the Brillouin zone (Figure 4c). The relatively large integrated intensity of these modes compared to the E\(_{1g}\) and A\(_{1g}\) modes indicates the presence of disorder in the deposited films, which is expected for a relatively low deposition temperature.

The full width at half-maximum (FWHM) values of the fitted E\(_{1g}\) and A\(_{1g}\) components were ≈6 and 7 cm\(^{-1}\), respectively, whereas those for the full peaks (i.e., without deconvolution) were around 9 cm\(^{-1}\) for all of the measured films. Mechanically exfoliated as well as the best CVD-grown monolayer MoS\(_2\)-films deposited at 650 °C or above have shown FWHMs as low as 3–4 cm\(^{-1}\).\(^\text{[33,78]}\) On the other hand, for the ALD MoS\(_2\) films deposited from MoCl\(_5\) and H\(_2\)S at 475 °C, the E\(_{1g}\) FWHM was as broad as 18 cm\(^{-1}\), which decreased by sulfur annealing to 12 cm\(^{-1}\) (720 °C) or even 4.2 cm\(^{-1}\) (920 °C).\(^\text{[46]}\) A four-monolayer MoS\(_2\) film, produced by sulfurization of an MoO\(_2\) film, yielded E\(_{1g}\) FWHM of 6.5 cm\(^{-1}\) at 750 °C, whereas a higher sulfurization temperature of 1000 °C reduced the FWHM to 4.6 cm\(^{-1}\).\(^\text{[19]}\) In summary, the Raman spectra indicate comparably good crystallinity, especially considering the low deposition temperature of 300 °C.

Finally, multiple measurements were performed from different positions of ≈5 cm\(^2\) SiO\(_2\) substrates (Figure 4d). Identical peak intensities at all positions, including the Si substrate peak, confirm that the films have excellent thickness uniformity, as is expected for ALD.

We also explored how the deposition temperature affects film crystallinity. As noted earlier, self-limiting growth seemed to occur between 250 and 325 °C. The crystallinity of the deposited films seemed to improve with increasing deposition temperature, based on SEM images (Figure 5a) and X-ray diffractograms (Figure 5b). Although a clear increase in grain size was evident at 350 °C, and especially at 400 °C, these films were not deposited under pure ALD conditions. The film deposited at 400 °C consisted of thin flakes standing up from the substrate with a length of ≈100 nm, for a nominal film thickness...
of about 20 nm. Deposition of highly crystalline MoS$_2$ films by ALD appears to call for more thermally stable molybdenum precursors.

2.3.3. Composition

X-ray photoelectron spectroscopy (XPS) was used to study the composition and chemical bonding on the film surface, i.e., no sputtering was done. A survey scan (Figure S2a and Table S3, Supporting Information) revealed peaks originating from Mo, S, O, C, and Sn. Additionally, time-of-flight elastic recoil detection analysis (ToF-ERDA) provided information on film composition averaged throughout the film thickness, detecting also hydrogen and a small amount of nitrogen in addition to the above-mentioned elements (Table S3, Supporting Information). It should be noted, however, that due to the small thickness of the analyzed film (≈10 nm) as well as the rough morphology, the film surface, the film-substrate interface, and the native SiO$_2$ layer likely make a notable contribution to the ToF-ERDA results.

High-resolution X-ray photoelectron spectra from the Mo 3d region (Figure 6a) showed a doublet corresponding to Mo 3d$_{5/2}$ at 229.9 eV and Mo 3d$_{3/2}$ at 233.1 eV. The observed binding energies are among those reported for thin 2H-MoS$_2$ layers and films (231.6 to 233.2 eV for Mo 3d$_{3/2}$).[39,40,43,44,47–49,51,52] In addition, about 10% of the molybdenum was present as oxidized MoO$_3$ (Mo$^{6+}$) with binding energies$^{[79]}$ of 233.4 and 236.6 eV for Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$, respectively. This implies that the film surface is at least partially oxidized in air. The sulfur/molybdenum atomic ratio of 1.7 (ToF-ERDA) is in agreement with fairly stoichiometric MoS$_2$ with some surface oxidation. S 2s peak was also observed near the Mo 3d doublet at 227.1 eV, in good agreement with the binding energy of S$^2$ in 2H-MoS$_2$.[$^{39,44,47}$]

Binding energies of S 2p$_{1/2}$ (162.7 eV) and S 2p$_{1/2}$ (163.9 eV) seen in Figure 6b are also within the range of values reported for 2H-MoS$_2$.[$^{39,40,43,44,47–49,51,52}$] Additionally, weak doublets at 161.8 and 163.3 eV as well as 163.9 and 165.1 eV were assigned to Sn–S$^{6–}$ and C–S bonding, respectively. Carbon and oxygen were present in multiple chemical environments, as revealed by their broad peaks (Figure S2b,c, Supporting Information). It appears likely that most of the carbon, as well as the hydrogen observed by ToF-ERDA, originates from surface hydrocarbon contamination, although the presence of some residual thd ligands or their fragments cannot be excluded. The oxygen is likely due to surface oxidation, atmospheric contamination, and native SiO$_2$ layer, the last one affecting ToF-ERDA results only.

A small amount of tin present in the films (≈1%–3% of the amount of molybdenum) was assigned to be present as tin(IV)sulfide species (Figure 6b and Figure S2d, Supporting Information). Tin is a residue from the synthesis of the Mo(thd)$_3$ precursor, where metallic tin was used as a reducing agent.

2.3.4. Other Film Properties

We also studied the wettability of the deposited films and observed the water contact angle to increase with increasing...
film thickness from slightly hydrophilic (80° after 100 cycles) to hydrophobic (above 100° after 4000 cycles) as a consequence of increased roughness. More detailed results can be found in the Supporting Information. Optical properties of the films deposited on glass substrates will be discussed in Section 2.4.3.

2.4. Films on Other Substrates

2.4.1. Film Growth

We evaluated a range of different substrates to see how the film growth, surface morphology, and crystallinity are affected by the substrate. As ALD is based on surface reactions, the substrate often has an effect on the film growth in the nucleation stage, which can further alter the resulting film properties. Compared to the already discussed native oxide covered silicon, the other tested substrates can be roughly divided into three groups in terms of the growth rate (Table 1): enhanced growth with more than doubled growth rate was seen on soda lime glass, whereas smaller enhancement was found on ALD-SnS and, surprisingly, HF-treated silicon (Si-H) substrates. On the other hand, ALD-Al₂O₃ and ALD-Ir substrates showed inhibited growth. On majority of the tested substrates (90 or 300 nm SiO₂, borosilicate glass, sapphire, indium tin oxide (ITO) coated glass, ALD-ZnS, and ALD-SnO₂), the growth rate was similar to Si.

We speculate that the enhanced growth on soda lime glass could be due to interfacial mixing, i.e., diffusion of some of the substrate cations, especially Na, into the film. This could affect precursor adsorption and, furthermore, growth rate. We note that borosilicate glass, which was found to contain Al, B, Ba, Ca, Si, Sr, Zn, and W cations, but no alkali metals, yielded growth rate similar to silicon. We also found that film growth saturated on soda lime glass, although with longer Mo(thd)₃ pulses compared to Si, with the saturated growth rate being approximately four times that on silicon (Figure S5a,b, Supporting Information). The growth was also linear with respect to the number of deposition cycles on both silicon and soda lime glass, thus excluding nucleation effects as an explanation for the different growth rates (Figure S5c, Supporting Information).

Inhibited growth on ALD-Al₂O₃ may be explained by surface “poisoning” by β-diketonate ligands, which has been found to hinder nucleation of ALD NiS⁶⁰ and SnS⁸¹ on ALD-Al₂O₃. In other words, Al-thd or Al-Mo-thd surface groups formed after the adsorption of Mo(thd)₃ appear to be unreactive toward H₂S. Interestingly, film growth on sapphire (α-Al₂O₃) was more facile than on amorphous ALD-Al₂O₃, which could be due to different bonding of the thd-ligand to these surfaces. The inhibited growth on ALD-Ir may stem from the high catalytic activity of iridium, as decomposition of Mo(thd)₃ into a carbonaceous layer on iridium could inhibit further adsorption of the precursor, and terminate the film growth.

2.4.2. Film Morphology and Crystallinity

In addition to the growth rate, film morphology, roughness, and crystallinity were also affected by the substrate choice. Morphology was evaluated from SEM (Figure S6, Supporting Information) and, for selected substrates, AFM images (Figure S7, Supporting Information). AFM images were also used for calculating film roughness. Crystallinity was estimated from the FWHM of the (002) XRD reflection of MoS₂ (Figure S8, Supporting Information). As is well known, peak width increases with decreasing crystallite size, although it can also be affected by other factors, such as strain.

Table 1. MoS₂ film growth rate, surface roughness, and XRD (002) FWHM on different substrates. 2000 cycles were applied at 300 °C.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Growth rate [Å cycle⁻¹]</th>
<th>Roughness [nm]</th>
<th>XRD (002) FWHM [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (native oxide)</td>
<td>0.025 ± 0.005</td>
<td>2.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Enhanced growth</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soda lime glass</td>
<td>0.065 (0.11a)</td>
<td>2.4</td>
<td>2.7</td>
</tr>
<tr>
<td>ALD-SnS</td>
<td>0.041</td>
<td>–b)</td>
<td>–c)</td>
</tr>
<tr>
<td>Si-H</td>
<td>0.036</td>
<td>4.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Growth rate similar to Si</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.025</td>
<td>2.1</td>
<td>2.9</td>
</tr>
<tr>
<td>Borosilicate glass</td>
<td>0.025</td>
<td>3.7</td>
<td>3.0</td>
</tr>
<tr>
<td>Sapphire</td>
<td>0.023</td>
<td>2.4</td>
<td>4.5</td>
</tr>
<tr>
<td>ITO-coated glass</td>
<td>0.030</td>
<td>–b)</td>
<td>–c)</td>
</tr>
<tr>
<td>ALD-ZnS</td>
<td>0.023</td>
<td>–b)</td>
<td>–c)</td>
</tr>
<tr>
<td>ALD-SnO₂</td>
<td>0.026</td>
<td>–b)</td>
<td>–c)</td>
</tr>
<tr>
<td>Inhibited growth</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALD-Al₂O₃</td>
<td>&lt;0.005 (6)</td>
<td>1.8</td>
<td>–c)</td>
</tr>
<tr>
<td>ALD-Ir</td>
<td>&lt;0.005 (6)</td>
<td>–b)</td>
<td>–c)</td>
</tr>
</tbody>
</table>

a)With 1 s Mo(thd)₃ pulse, instead of 0.5 s; b) Not measured; c) No peak; d) Film thickness below the detection limit of ≈1 nm.
Films on Si and SiO$_2$ were found to be similar in terms of morphology, roughness, and crystallinity, which is expected considering that our silicon substrates were covered by a native silicon oxide layer. Regarding the substrates with enhanced growth, films on soda lime glass had crystallinity and roughness similar to Si, when comparing films with similar thicknesses. Thus, it appears that if any mixing with soda lime glass substrate occurs, it does not deteriorate film crystallinity. The film grown on hydrogen-terminated silicon (Si-H) was the roughest out of all of the substrates studied by AFM, which may at least partially explain the somewhat higher growth rate compared to Si. In terms of crystallinity, films on Si-H and ALD-SnS also appeared to be similar to Si.

Of the substrates with growth rates similar to Si, films on borosilicate glass and sapphire showed similar and weaker crystallinity, respectively, compared to Si. The film on borosilicate glass was quite rough due to larger flakes scarcely present on the surface. For the films on ALD-SnO$_2$, ALD-ZnS, and ITO-coated glass no signs of crystallinity were detected by XRD. On the substrates with inhibited growth (ALD-Al$_2$O$_3$ and ALD-Ir), no signs of crystallinity were detected, although there were small features visible on ALD-Al$_2$O$_3$ in AFM and SEM images. For some of the substrates, especially ITO-coated glass and ALD-SnO$_2$, and, to a smaller degree, ALD-SnS, ALD-ZnS, and ALD-Ir, the inherent roughness and morphology of the substrates hindered reliable examination of the MoS$_2$ morphology.

### 2.4.3. Optical Properties on Glass Substrates

We studied the optical properties of MoS$_2$ films deposited on soda lime and borosilicate glass substrates. As the film morphology and crystallinity on these substrates were similar to films on silicon, we assume that the optical properties should also be similar. The transmittances of the bare glass substrates were quite similar to each other, as were the general shapes of the transmittance curves of the MoS$_2$-covered substrates (Figure 7a). The two broad features marked with asterisks at 610 and 660 nm were assigned to characteristic A and B exciton peaks of 2H-MoS$_2$, respectively.[82]

Using a Tauc plot we obtained an indirect band gap of 1.2 eV for a 2000 cycle film on borosilicate glass (Figure 7b), in agreement with the generally accepted value of 1.3 eV for bulk MoS$_2$. Band gaps of 1.2 ± 0.2 eV were measured for films of different thickness (1000–8000 cycles, corresponding to ~5–50 nm) on soda lime glass. Band gap determination of films thinner than about 5 nm was not successful using this method and equipment. Therefore, we were unable to observe the increase in band gap with decreasing thickness that is commonly found for few-layer MoS$_2$.[81]

### 3. Conclusion

In this work, we deposited crystalline MoS$_2$ thin films by ALD using a new molybdenum precursor, Mo(thd)$_3$, together with H$_2$S at 300 °C. Self-limiting growth and linear film thickness control, characteristic of ALD, were demonstrated. We characterized the films using a variety of techniques. The films were found to be rather rough, consisting of flake-like grains with size of ~10–30 nm. Raman spectroscopy revealed the film crystallinity to be relatively good, especially taking the low deposition temperature into account. Compositional studies showed some surface oxidation and contamination, but the films themselves were estimated to be close to stoichiometric MoS$_2$. Optical and wetting properties of the films were also analyzed, showing properties expected for MoS$_2$. We deposited MoS$_2$ films on different substrates, and although the growth was successful on most of them, there were marked differences in the film growth, morphology, and crystallinity. The current work offers an alternative for deposition of crystalline MoS$_2$ films at modest deposition temperatures compared to alternative deposition methods.

### 4. Experimental Section

**Precursor Synthesis and Characterization:** All handling and manipulations were done under rigorous exclusion of air and moisture using standard Schlenk techniques and inert gas (N$_2$ or Ar) glove box. Hexane and toluene were dried over 4 Å molecular sieves while Et$_2$O and THF were freshly distilled from sodium benzophenone ketyl. MoCl$_3$ (99.6%, anhydrous, Strem), KH (99%, Strem) were used as received. MoCl$_5$ (THF) was prepared by reacting KH with Hthd in THF. MoCl$_5$(THF)$_3$ was prepared by reacting MoCl$_3$ with Sn pellets using a method modified from the one introduced by Stoffelbach et al.[47]
Thermogravimetric analysis was performed using a Mettler Toledo Star® system equipped with a TGA850 thermobalance. The measurements were done at atmospheric pressure using N2 (50 mL min⁻¹) as the purge gas. Heating rate was 10 °C min⁻¹ and the sample size was 10 ± 1 mg. Melting points were taken from the single differential thermal analysis data measured by the thermobalance. Mass spectra were recorded with a JEOL JMS-SX102 instrument operating in electron impact mode (70 eV) using a direct insertion probe and a sublimation temperature range of 50–300 °C.

\[ \text{Mo(thd)}_2 \text{Cl}_2 \]: In a 600 mL Schlenk bottle MoCl₅(THF)₂ (12.95 g, 30.90 mmol) was suspended in THF (200 mL). This solution was cooled to −10 °C with an ice/acetonate bath and THF solution (200 mL) of Kthd (20.59 g, 92.69 mmol) was added using a Teflon cannula and argon purging. The solution was then heated to a temperature of 160 °C/0.5 mbar. The sublimation being the product, Mo(thd)₂Cl₂, it was collected in a glove box. The yield of the highly air sensitive, dark brown solid was 16.60 g (83%). m.p. 149 °C.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This research was supported by ASM Microchemistry and the Finnish Centre of Excellence in Atomic Layer Deposition funded by Academy of Finland. Mr. Mikko Heikkilä and Dr. Marianna Kemell are thanked for help in trials with the Mo(CO)₆ precursor.

**Keywords**

2D materials, atomic layer deposition, MoS₂, thin films

Received: January 30, 2017
Revised: February 24, 2017
Published online: March 30, 2017