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Cyclic Silylselenides: Convenient Selenium Precursors for Atomic Layer Deposition

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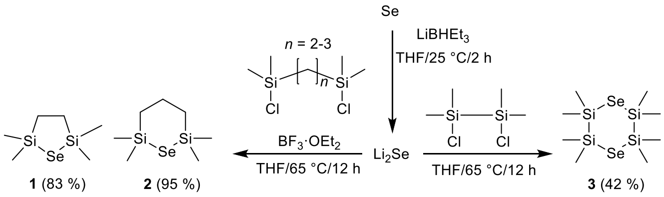
Abstract: Three cyclic silylselenides were prepared in a straightforward manner. Property tuning has been achieved by varying the ring size and the number of embedded selenium atoms. All silylselenides possess improved resistance towards moisture and oxidation as well as high thermal robustness and sufficient volatility with almost zero residues. Especially the six-membered diselenide proved to be superior Se precursors for atomic layer deposition and allowed facile preparation of $MoSe_2$ layers. Their structure and composition has been investigated by Raman and X-ray photoelectron spectroscopy as well as scanning electron microscopy revealing vertically aligned flaky shaped nanosheets.

Atomic layer deposition (ALD) belongs to a family of chemical vapor deposition (CVD) techniques that attracts considerable attention especially in thin-film deposition. It is mainly due to its unique capability of manufacturing highly conformal nanolayers on differently shaped substrates with desired film thickness. [1,2] A simplified ALD process involves a volatile (metallic) precursor, which reacts with a selected substrate. The saturative process allows a sole reaction of unoccupied functional groups of the substrate leading to a deposition of one atomic layer. A subsequent repetition after chamber purging allows to precisely control the film thickness. A variety of materials can be deposited in this way, e.g. metal chalcogenides that offer many interesting properties across a wide variety of scientific fields. For instance, well-studied CuInGaSe (CIGS) solar cells showed total conversion efficiency exceeding 22 %[3] and durability/flexibility in outdoor conditions. [4] Transition metal dichalcogenides (TMDs) may accommodate sodium and magnesium ions, and, besides energy production, found use as a promising electrode material in the energy storage devices.[5] TMDs thin layers often show photocatalytic activity; $MoSe_2$ is a very promising candidate in this respect. It turned out to be very efficient photodegradation catalyst[6,7] that may also replace Pt-based catalysts used in electrochemically-assisted hydrogen evolution techniques.[8,9] The surface area may be further increased by ALD on nanotubes or nanoparticles, which generally lead to pronounced photocatalytic properties. However, the current portfolio of available selenium precursors for ALD is very limited. The most simple precursor is elemental selenium,[10,11] which has unfortunately very low volatility. A direct use of selenium is limited to preparation of simple selenides such as ZnSe or CdSe. On the contrary, very volatile H_2Se represents versatile Se precursor even for larger surfaces, [12] but its wider application is confined by its high toxicity. Diethyl(di)selenide Et_2Se (Et_2Se_2) has also been reported as ALD precursor,[13,14] however its deposition is generally H_2-assisted and, therefore, less controlled. Recently, tetrakis(*N*,*N*-dimethyldithiocarbamate)selenium (SDMDTC) was successfully tested for deposition of Sb_2Se_3 by the reaction with tris(dimethylamino)antimony (TDMASb).[15] This precursor seems to be volatile enough within a range of 100 to 165 °C. Bis(trialkylsilyl)selenides ($R_3Si\text{-}Se\text{-}SiR_3$) were introduced in 2009[16] and were demonstrated as suitable selenium precursors for deposition of various metal selenides. Variation of the R-substituent allowed tailoring volatility and reactivity towards metal halides often used in ALD and provide repeatable results.[17–19] However, linear bis(trialkylsilyl)selenides are generally prone to quick hydrolysis and oxidation and their handling is less comfortable. Hence, we report herein cyclic silylselenides **1**–**3** that preparation is outlined in Scheme 1. The facile synthesis utilizes *in-situ* generation of the lithium selenide by the reaction of elemental selenium with Superhydride. Subsequent treatment of Li_2Se with 1,2-

bis(chlorodimethylsilyl)ethane ($n = 2$) and 1,3-bis(chlorodimethylsilyl)propane ($n = 3$) afforded cyclosilylselenides **1** and **2** in high yields of 83 and 95 %, respectively. The reaction with 1,2-dichlorotetramethyldisilane provided crude **3**,[20] which may be further purified by crystallization or sublimation. Selenides **1**[21] and **2** are viscose liquids that can be easily purified by vacuum distillation. Six-membered cycle **3** represents first solid ALD precursor with more than one Se atom. Complete synthetic details and characterizations are provide in the SI.



Scheme 1. Convenient synthesis of cyclic silylselenides.

Thermal behavior of **1**–**3** has been studied by TGA and DSC methods, see Figure 1 and the SI. Whereas the TGA showed very good volatility accompanied by complete evaporation and almost zero residues, the complementary DSC measurements revealed evaporation unaccompanied by a decomposition. Thermal properties of **1**–**3** are mostly dictated by the ring size and the number of embedded Se/Si atoms. For instance, silylselenide **3** with two selenium atoms possesses the melting point of 145 °C, which is close to the boiling points of **1**–**2** (170/200 °C), and significantly shifted boiling point up to 275 °C. Despite high boiling point of **3**, TGA (Figure 1a) revealed its gradual evaporation/sublimation starting at around 120 °C (~60 °C for **1**–**2**, measured at ambient pressure).

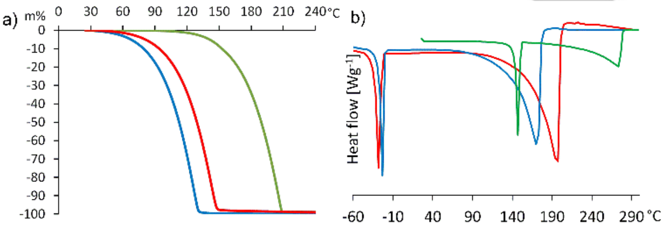


Figure 1. TGA (a) and DSC (b) records for **1** (blue), **2** (red) and **3** (green).

Moisture sensitivity and resistivity towards oxidation on air of silyl selenides **1**–**3** has been examined by keeping their solution in open vials. The NMR and GC/MS spectra (see the SI) have indicated no decomposition up to 28 h; a very small amount of elemental selenium has been deposited after 2 days. As compared to previous linear bis(trialkylsilyl)selenides,[16] the improved stability of **1**–**3** is attributed to cyclic arrangement, which is less prone towards nucleophilic attack (e.g. hydrolysis) or oxygen incorporation. Moreover, the stability is dependent on the ring size and the content of the Se/Si atoms. Elemental selenium and silanoles were identified as the main decomposition products. A reactivity of cyclic selenides **1**–**3** towards metal chlorides such as $MoCl_5$ and $ZnCl_2$ has preliminary been screened. In order to mimic an ALD process, their reactions in dichloromethane afforded immediately dark precipitate, the initial selenium precursor has completely been consumed and the reaction contained only volatile dichlorosilanes (see the SI). Thus, the cyclic silylselenide **1**–**3** showed very good trade-off between stability and reactivity.

Subsequently, all three cyclic selenides were tested as Se precursor in a custom thermal ALD system combined with $MoCl_5$ as Mo precursor (experimental details provided in the SI). The morphologies of the as deposited $MoSe_2$ were characterized by scanning electron microscopy (SEM) images. ALD processes based on the use of cyclic selenides **1** and **3** exhibited abundant, vertically aligned flaky shaped nanosheets, as displayed in Figure 2. These results agree well with the $MoSe_2$ deposited by other techniques.[22–27] Conversely, the six-membered cyclic selenide **2** showed poor reaction rate and negligible amount of material was deposited. This is most likely due to its higher chemical stability and thus resulting lower reactivity under the given deposition conditions - flow reactor mode with time-limited contact between the precursors and kinetically limited reaction

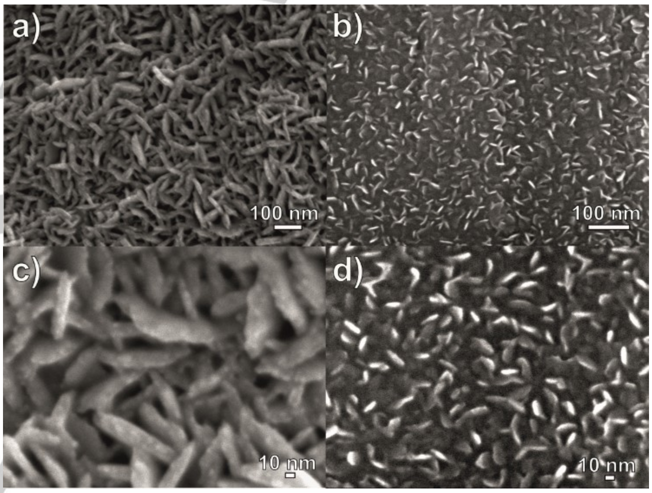


Figure 2. SEM top-view images at different magnification of $MoSe_2$ nanostructures deposited on thin anatase TiO_2 layer using $MoCl_5$ and cyclic selenide **1** (a,c) and **3** (b,d).

Surface characterization using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) was carried out to confirm the chemical composition of the deposited $MoSe_2$. Raman spectroscopy is a paramount method for the structural characterization of layered materials. Figure 3a-b shows the corresponding Raman spectra of $MoSe_2$. Characteristic lattice vibrational modes of $MoSe_2$ were observed, indicating polycrystalline nature of the $MoSe_2$. The distinctive peaks of $MoSe_2$, A_{1g} (out-of-plane) and E^1_{2g} (in-plane) modes were observed for $MoSe_2$ at ~239 and ~288/289 cm^{-1}, respectively. Compared to the peak positions for bulk $MoSe_2$ (242 and 286 cm^{-1}), these lattice vibrational modes exhibited red and blue shift, which indicates few-layered nature of the deposited $MoSe_2$. In addition, the peak at ~350 cm^{-1}, assigned to the Raman-inactive mode A_{2u} points out few-layer 2H-TMDs, as such mode A_{2u} gets active as the crystal symmetry along the c-axis is lost. Furthermore, the clear differences in the relative intensities between the A_{1g} and E^1_{2g} modes indicated the prevailing out-of-plane orientation of the $MoSe_2$ nanosheets.[28]

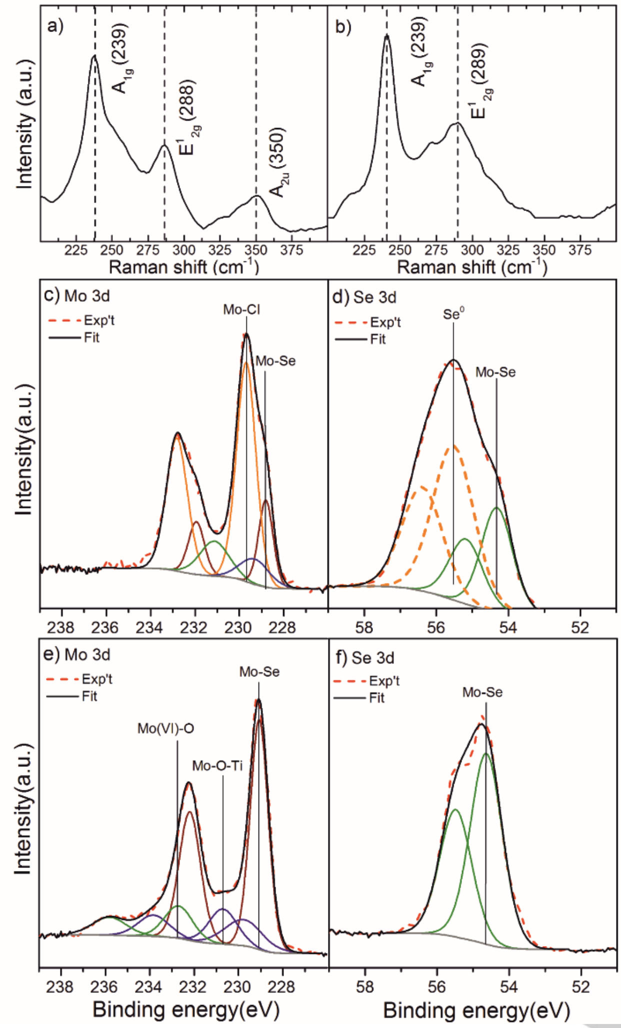


Figure 3. Raman spectra of the $MoSe_2$ deposited using cyclic sylilselenide **1** (a) **3** (b). The main peaks of in-plane and out-of-plane modes are referred. High-resolution XPS spectra of Mo 3d and Se 3d peaks corresponding to the $MoSe_2$ deposited using cyclic silylselenide **1** (c-d) and **3** (e-f), respectively.

These results are in good agreement with the SEM images and confirm the randomly aligned out-of-plane $MoSe_2$ layers.

Surface compositional analyses of the $MoSe_2$ deposited using $MoCl_5$ and Se precursor **1** (Figure 3c-d) and **3** (Figure 3e-f) was performed using XPS. In Figure 3c, the deconvoluted spectrum of Mo 3d core level reveals a mixture of Mo(IV)-Se with binding energy E_B (3d$_{5/2}$) = 228.8 eV and E_B (3d$_{3/2}$) = 231.9 eV, Mo-Cl with E_B (3d$_{5/2}$) = 229.7 eV and E_B (3d$_{3/2}$) = 232.8 eV. In addition, Se 3s peaks at 229.3 eV and 231.1 eV agree well with Mo-Se and Se^0 species, respectively, observed in Se 3d. In Figure 3d, the deconvoluted spectrum of Se 3d core level confirms the presence of Se^0 with binding energy E_B (3d$_{5/2}$) = 55.5 eV and E_B (3d$_{3/2}$) = 56.4 eV, and Mo-Se with E_B (3d$_{5/2}$) = 54.3 eV and E_B (3d$_{3/2}$) = 55.2 eV. The presence of Mo-Cl and elemental Se^0 are ascribed to incomplete ligand exchange reaction of the $MoCl_5$ and cyclic sylilselenide **1** or its partial decomposition during the ALD process. A minor deposition of elemental selenium has also been observed during the aforementioned stability tests. The presence of Mo-Cl species was further corroborated by the peak with binding energy E_B (2s)= 269.7 eV from the Cl 2s XPS spectrum (see Figure S11a in the SI). These results indicated that i) the position of Mo(IV)–Se matches well with previous works reported indicating 2H $MoSe_2$[25,29,30] and ii) undesired incomplete ligand exchange reaction leading to residual Cl content. In order to prevent undesired residual contents of ligand precursor, the optimization of the ALD process is compulsory. On the other hand, the XPS spectra of Mo 3d and Se 3d core levels corresponding to the as deposited $MoSe_2$ structures prepared by ALD using $MoCl_5$ and precursor **3** are showed in Figure 3e-f. The Figure 3e shows the detailed analysis of the Mo 3d core levels. Therein, it is disclosed a mixture of Mo(IV)-Se with binding energy E_B (3d5/2) = 229.1 eV and E_B (3d$_{3/2}$) = 232.2 eV, together with Mo(VI)-O with E_B (3d$_{5/2}$) = 232.7 eV and E_B (3d$_{3/2}$) = 233.8 eV, and Mo-O-Ti with E_B (3d$_{5/2}$) = 230.7 eV and E_B (3d$_{3/2}$) = 233.8 eV. The origin of the minor presence of Mo(VI)-O and Mo-O-Ti species can be attributed to $MoSe_2$/Ti substrate interface effect. During the very early ALD stage (initial ALD cycles), it could be expected that $MoCl_5$ reacts with adsorbed hydroxyl groups from the TiO_2 substrate surface. This reaction originates the chemical bonds Mo(VI)-O and Ti-O-Mo, the latter furtherly corroborated by the Ti 2p XPS spectrum from Figure S11b. On the other hand, the used Ti substrates guarantee sufficient reactivity for the ALD reactions presented here, which e.g. pure silicon could not easily offer. In the spectrum of Se 3d core level (Figure 3f), the position of Mo(IV)–Se with E_B (3d$_{5/2}$) = 54.6 eV and E_B (3d$_{3/2}$)=55.5 eV agree with previous works reported indicating 2H $MoSe_2$.[24,28 ,29]

A straightforward synthesis of cyclic silylselenides has been developed. Compared to the limited portfolio of Se precursors, the prepared selenides significantly extent the available selenium compounds for ALD. These can be easily prepared, their purification is very easy, offer facile structural/property tuning, high thermal robustness and volatility, and generally good trade-off between stability and reactivity. Two precursors showed sufficiently fast reaction with metal precursors to allow their direct application in ALD and deposition of $MoSe_2$ nanostructures. The solid cyclic silylselenide **3** bearing two selenium atoms seems to be superior so far. A further structural elaboration on cyclic selenides and optimization of the deposition experiments are ongoing in our lab.

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Keywords: atomic layer deposition • $MoSe_2$ • nanosheets • selenium • transition metal dichalcogenides

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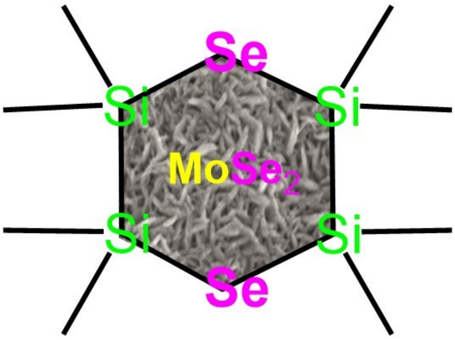

Volatile, sufficiently reactive, and easy-to-synthesized solid Se precursor based on cyclic sylilselenide has been developed and synthesized. It possesses good trade-off between chemical and thermal stability and reactivity towards $MoCl_5$. It has further been used for depositing $MoSe_2$ nanosheets that structure has been confirmed by various techniques.