Organoselenium Precursors for Atomic Layer Deposition

Jaroslav Charvot, Raul Zazpe, Jan M. Macak, and Filip Bureš*

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ABSTRACT: Organoselenium compounds with perspective application as Se precursors for atomic layer deposition have been reviewed. The originally limited portfolio of available Se precursors such as H_2Se and diethyl(di)selenide has recently been extended by bis(trialkylsilyl)selenides, bis(trialkylstannyl)selenides, cyclic selenides, and tetrakis(N,N-dimethyldithiocarbamate)-selenium. Their structural aspects, property tuning, fundamental properties, and preparations are discussed. It turned out that symmetric four- and six-membered cyclic silyl selenides possess well-balanced reactivity/stability, facile and cost-effective synthesis starting from inexpensive and readily available chlorosilanes, improved resistance toward air and moisture, easy handling, sufficient volatility, thermal resistance, and complete gas-to-solid phase exchange reaction with $MoCl_5$, affording $MoSe_2$ nanostructures. These properties make them the most promising Se precursor developed for atomic layer deposition so far.
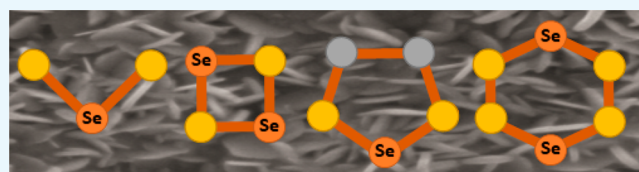
INTRODUCTION

Atomic layer deposition (ALD) belongs to chemical vapor deposition (CVD) techniques that allow deposition of nanoscale thin-film layers.[1] The deposition is based on sequential self-terminating gas—to-solid phase reactions between a gaseous precursor containing deposited atom(s) and a substrate.[2] Since the substrate surface possesses only a certain number of functional groups, the ALD reaction is self-limiting, and the deposition is terminated as soon as the surface is completely covered. This feature makes the ALD process highly controllable and allows adjusting the film thickness by a number of cycles. In contrast to other deposition techniques, ALD is a very efficient tool for performing deposition on variably shaped surfaces such as nanoparticles or nanotubes.[3] Easy combination of different precursors during ALD is another important and very handy feature, which allows the preparation of multilayered structures. A simplified ALD process is outlined in Figure 1. The first step involves transport of the desired precursor into the reaction chamber via a stream of an inert gas or vacuum, and its reaction with the substrate forms the first atomic layer. Excess of the precursor and eventual byproducts are removed by purging the chamber, whereupon the (second) precursor may be loaded to form an additional layer. Whereas the proper combination of precursors accounts for the composition of the resulting layered material, the number of cycles controls its thickness.

Contrary to the aforementioned advantages, gas-to-solid phase reaction represents the main ALD's drawback. In principle, the used precursor must fulfill three basic criteria:

- Volatility to provide sufficient vapor pressure.
- Thermal resistance to withstand temperature used during the deposition (generally above 100 °C).
- Reactivity with the substrate and the second precursor.

In addition, the desired precursor should also possess:

- Chemical resistance toward air and moisture for easy handling.
- Noncorrosive nature including byproducts, especially in relation to ALD equipment.
- Low toxicity.

Last, but not least, the precursor should be produced using cost-effective and large-scale synthesis and should be easily purified. Finding a trade-off between these properties is
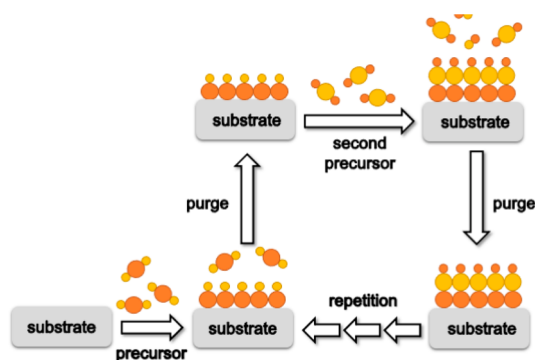

Figure 1. Schematic representation of the ALD process.

generally not trivial. Despite the fact that ALD has been known for more than 50 years, its potential began to be exploited only relatively recently along with the boom of materials chemistry and industrial needs.[4] Especially the microelectronics industry is currently significantly influenced by the ALD development. 2D transition-metal dichalcogenide (TMD) monolayers of general formula MX_2, where M stands for transition metal atom (mostly IV to VII group) and X is a chalcogen (S, Se, Te), are greatly prepared with the aid of ALD.[5] TMDs possess a direct band gap and, therefore, very interesting optical and electrical properties accompanied by relative thermal robustness. Hence, TMDs are frequently used as transistors, light emitters/detectors, or electrodes for Li batteries.[6] In addition, ALD-prepared nanoparticles such as nanoflakes found numerous applications in photocatalysis[7] or hydrogen evolution reaction.[3]

Organoselenium Precursors for ALD. In contrast to the well-known ALD of sulfides, metal selenides are much less explored including only Cu, Zn, Ge, Sr, Mo, Cd, In, Sn, Sb, W, Pb, and Bi. When comparing to MoS_2, $MoSe_2$ possesses inherent metallic nature, higher electrical conductivity, narrowed bandgap, layered structure with larger interlayer spacing, higher optical absorbance and resistance to photocorrosion, and larger electrochemically active edges. Unfortunately, selenium possesses only a limited portfolio of Se precursors 1−3 suitable for ALD (Figure 2).
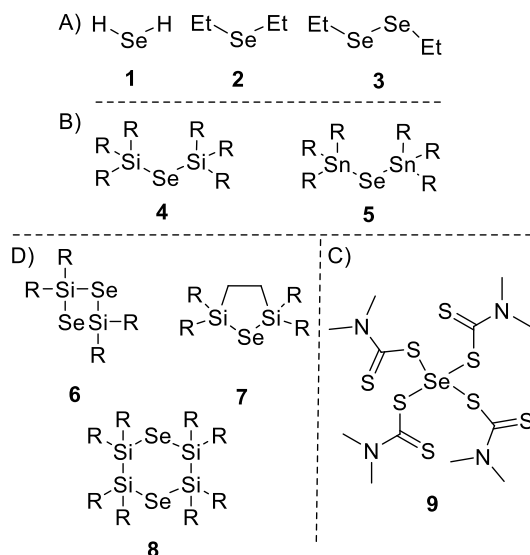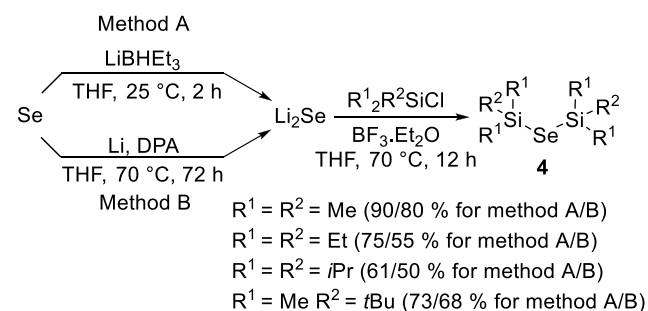

Figure 2. Overview of available Se precursors for ALD: (A) basic selenium compounds, (B) bis(trialkylsilyl/stannyl)selenides, (C) cyclic silylselenides, and (D) SDMDTC. R stands for an alkyl.

Elemental selenium represents the simplest precursors; however, due to its low volatility, the ALD process generally requires temperature above 200 °C.[8] Only ZnSe and CdSe were deposited from the elemental selenium so far. H_2Se (1) seems to be an ideal Se precursor due to its gaseous nature at room temperature, which makes it volatile, mobile, and also useful for large-scale deposition.[9] However, its toxicity is a major drawback. A deposition of sulfide layers using less toxic H_2S and subsequent exchange is also an option to avoid using H_2Se.[8a] Diethyl(di)selenides Et_2Se (2) and Et_2Se_2 (3) are organoselenium compounds commonly used in CVD. However, their wider utilization in ALD is hindered by a relatively strong C−Se

bond, which undergoes slow cleavage, generally assisted by H_2, O_3, or plasma.[10]

Bis(trialkylsilyl)selenides (4), first reported by Pore et al. in 2009,[11] represent one of the most promising and widely used groups of organoselenium compounds for ALD. The high reactivity of a triethyl derivative (($Et_3Si)_2Se$) with various metal halides has been demonstrated by depositing Bi_2Se_3, ZnSe, In_2Se, CuSe, and Cu_2Se thin films. Bis(trialkylsilyl)selenides proved to be well-suited for fast exchange reaction with metal chlorides (hard−soft Lewis acid−base pair), forming volatile and noncorrosive trialkylsilyl chloride, which is easily removed by purging. A general synthesis of 4 (Scheme 1) involves *in situ*

Scheme 1. *In Situ* Generation of Li_2Se and Synthesis of Bis(trialkylsilyl)selenides 4[a]

R[1] = R[2] = Me (90/80 % for method A/B)
R[1] = R[2] = Et (75/55 % for method A/B)
R[1] = R[2] = *i*Pr (61/50 % for method A/B)
R[1] = Me R[2] = *t*Bu (73/68 % for method A/B)
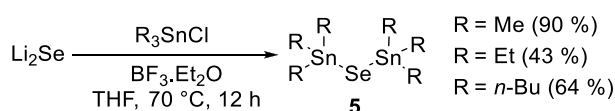
[a]DPA = diphenylacetylene.

preparation of lithium or sodium selenide (either by direct reaction of Li and Se or by treating elemental Se with superhydride ($LiBHEt_3$) − methods B and A). The latter procedure proved to be much faster and provides higher yield of 4 but is also more expensive.

We have further extended the original Pore's work by systematically investigating property tuning of 4 by alkyl variation (Scheme 1).[12] Four derivatives of 4 bearing trimethyl-, triethyl-, tri-isopropyl-, and *tert*-butyldimethylsilyl groups were prepared in the yields of 50−90% by employing both *in situ* generations of Li_2Se. An addition of $BF_3·OEt_2$ significantly accelerated the reaction of Li_2Se with trialkylsilyl chlorides $R^1_2R^2SiCl$. Thermal properties of 4 studied by DSC and TGA proved their sufficient volatility and stability. Bis(trimethylsilyl)-selenide in combination with $MoCl_5$ were successfully applied for deposition of $MoSe_2$ crystalline flakes on fused silica.[13] Subsequent ALD with 4 and commercial Mo precursors $MoCl_5$, $Mo(CO)_6$, and $Mo(NMe_2)_2(NtBu)_2$ was attempted at different substrates. It turned out that 4 undergoes exchange reaction with $MoCl_5$ to form $MoSe_2$ nanostructures,[14] while the other two Mo precursors proved to be ineffective. Moreover, the fundamental properties of 4 can be significantly altered by the appended alkyl chains. Whereas the trimethylsilyl derivative is a very volatile and reactive Se precursor, which is redeemed by its low resistance toward air and moisture, the *tert*-butyldimethylsilyl derivative showed no ALD reaction with $MoCl_5$ due to its high stability. Bis(trimethylsilyl)selenide has further been used for coating 1D TiO_2 nanotube layers with molybdenum oxyselenide (Mo-Se_xO_y).[15] The $MoSe_xO_y$ and TiO_2 interface allows efficient charge transfer, and $MoSe_xO_y$ possesses narrow bandgap, which makes $MoSe_xO_y$-coated TiO_2 nanotubes an efficient photocatalyst for methylene blue degradation. By properly controlling the ALD process, 1D TiO_2 nanotube layers were also successfully covered by $MoSe_2$ by using bis(trimethylsilyl)-

selenide and $MoCl_5$. The prepared $MoSe_2$/1D TiO_2 nanotube heterostructures showed outstanding photo- and electro-catalytic activities for degradation of organic pollutants and hydrogen evolution reaction.[16]

A replacement of silicon by tin in **4** represents another structural tuning enabling bis(trialkylstannyl)selenides **5**.[12] The synthetic strategy toward **5** is similar to that of **4** but is limited to commercially available trialkylstannyl chlorides (Scheme 2).

Scheme 2. Preparation of Bis(trialkylstannyl)selenides 5

$$Li_2Se \xrightarrow[\text{THF, 70 °C, 12 h}]{\underset{BF_3 \cdot Et_2O}{R_3SnCl}} \underset{5}{R_2Sn\text{-}Se\text{-}SnR_2}$$

R = Me (90 %)
R = Et (43 %)
R = n-Bu (64 %)

Unfortunately, thermal properties of **5** revealed lower volatility and thermal stability but higher stability toward air and moisture as compared to **4**. The most volatile trimethyl-stannyl derivative was successfully used for deposition of $MoSe_2$ flakes (Figure 3). Further elaboration with bis(trialkylstannyl)-selenides **5** revealed their alternative preparation, which utilizes inexpensive and readily available hexamethyl(butyl)ditin or tributyltin hydride (Scheme 3).[17]
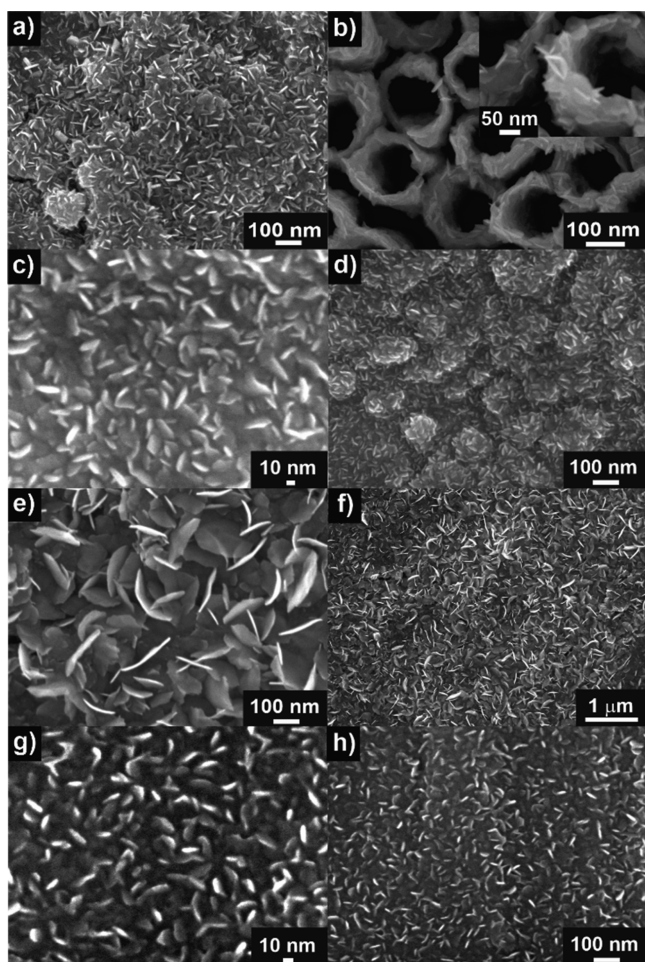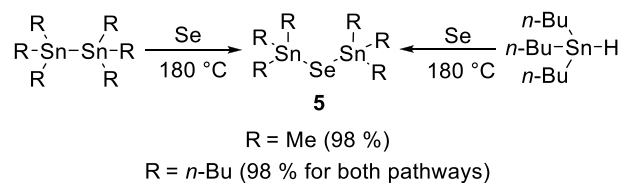

Figure 3. Representative SEM top-view images of $MoSe_2$ nanostructures deposited on planar TiO_2 foils (except SEM image b deposited on TiO_2 nanotube layers) using $(Me_3Si)_2Se$ (a,b),[11,15] $(Me_3Sn)_2Se$ (c,d),[11] and cyclic silylselenides **6** (e,f)[18b] and **8** (g,h).[18a]

Scheme 3. Improved and Cost-Effective Synthesis of 5

$$R_2Sn\text{-}SnR_2 \xrightarrow[\text{180 °C}]{Se} \underset{5}{R_2Sn\text{-}Se\text{-}SnR_2} \xleftarrow[\text{180 °C}]{Se} n\text{-}Bu_3Sn\text{-}H$$

R = Me (98 %)
R = n-Bu (98 % for both pathways)

The synthesis outlined in Scheme 3 is operationally very simple, excludes solvent, and provides **5** in high yield without further purification.

In general, bis(trialkylsilyl)selenides possess high gas-to-solid phase reactivity toward metal halides, which is unfortunately accompanied by their low resistance toward air and moisture and, therefore, is difficult to handle. Hence, further synthetic attempts were focused on the development of a Se precursor with improved stability and persistent reactivity. Very recently, cyclic silylselenides **6−8** were prepared and tested as ALD precursors.[18] These include four-, five-, and six-membered cycles, whose preparation is shown in Scheme 4. The synthesis

Scheme 4. Synthesis of Cyclic Silylselenides 6−8 and Straightforward Synthesis toward 6
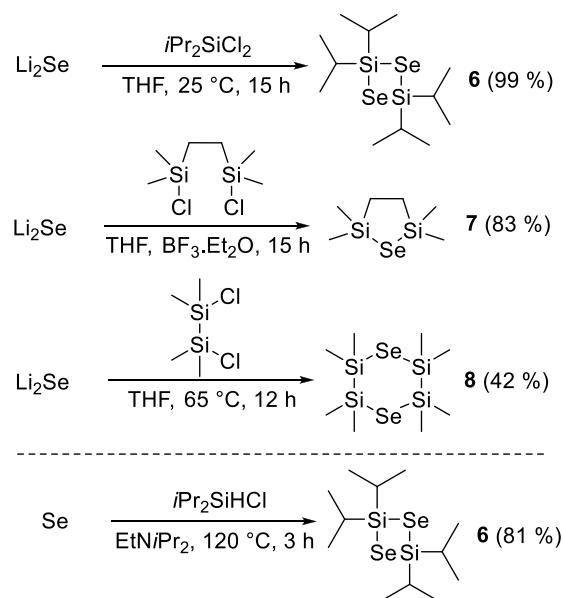
utilizes lithium selenide (Li_2Se) as a reactive intermediate, which undergoes reaction with readily available and inexpensive di-isopropyldichlorosilane, 1,2-bis(chlorodimethylsilyl)ethane, and 1,2-dichlorotetramethyldisilane to afford **6**, **7**, and **8**, respectively.

TGA and DSC analyses of **6−8** revealed volatility similar to linear analogues **4**, but the stability and handling were significantly improved. These derivatives may be stored for several months and even withstand ambient conditions for several hours. Subsequent gas-to-solid phase reaction with $MoCl_5$ revealed the facile formation of $MoSe_2$ layers of different quality. As revealed by XPS, the layer produced from ethyl-bridged **7** showed residual Mo−Cl bonds coming from an incomplete ligand exchange reaction.[18a] On the contrary, application of symmetric four- or six-membered cyclic selenides **6** and **8** afforded $MoSe_2$ of high quality.[18b] These compounds

represent first ALD precursors with more than one Se atom. The remaining drawback of silylselenides and their easy and wide application in ALD may be seen in their synthesis, utilizing organometallic species to generate Li_2Se. Hence, we have recently developed a straightforward preparation of **6**, which starts from elemental selenium and di-*iso*propylchlorosilane (Scheme 4). The main benefits of **6** are as follows: (i) small and symmetric structure; (ii) sufficient vapor pressure and thermal resistance; (iii) high and complete gas-to-solid phase exchange reaction with $MoCl_5$; (iv) improved resistance toward air and moisture; (v) facile synthesis from inexpensive starting materials, which excludes solvent; (v) easy purification (filtration and crystallization); (vi) facile large-scale production; and (vii) a solid compound with easy manipulation and transport. All organoselenium compounds are considered as potentially toxic and, therefore, should be manipulated in a well-ventilated fume hood.

In 2019, Sarkar et al. reported atomic layer deposition of Sb_2Se_3 using commercially available tetrakis(*N,N*-dimethyldithiocarbamate)selenium **9** (SDMDTC, Figure 2).[19] Its volatility seems to be high enough at 150 °C; however, TGA showed its decomposition above 165 °C, which indicates a very narrow ALD window. Interestingly, SDMDTC is the only tetravalent selenium compound used as a Se precursor for ALD so far, but its reactivity toward other metal precursors is not known yet.

■ SUMMARY AND OUTLOOK

Significant progress in organoselenium compounds applicable as Se precursors for ALD has recently been encountered. The initially very limited portfolio of useful Se precursors such as H_2Se and Et_2Se (Et_2Se_2) has been extended by novel organoselenium compounds including bis(trialkylsilyl/stannyl)-selenides and cyclic silylselenides. Besides the well-investigated linear bis(trimethylsilyl)selenide (**4**) and eventually analogous bis(trimethylstannyl)selenide (**5**), cyclic selenides **6** and **8** possess well-balanced reactivity/stability, facile synthesis and purification, and most importantly wide application potential in ALD. Molybdenum(IV) selenide layers were successfully deposited using the aforementioned precursors, as shown in Figure 3.

In order to unravel the application potential of the novel precursors **6** and **8**, further ALD experiments are needed, and these are ongoing in our research group.

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

Biographies
Jaroslav Charvot was born in Valašské Meziříčí, Czech Republic (1994), and studies chemistry at the University of Pardubice. He is currently pursuing Ph.D. studies on organoselenium compounds exploitable in material sciences.

Raul Zazpe was born in Pamplona (1978), Spain. He studied chemistry at the University of Navarra and obtained his M.Sc. degree at the University College of Cork (Ireland) in 2005. In 2006 he joined CEIT (Spain) for the development of biosensors. He completed his Ph.D. degree in materials science at CIC Nanogune (Spain) in 2014. Since 2015, he has been a postdoctoral researcher in the Macak group at the Center of Materials and Nanotechnologies of the University of Pardubice (Czech Republic). His research is focused on atomic layer deposition which he uses for the development of various functional coatings and devices, including novel types of solar cells.

Jan Macak was born in Pardubice (1979), Czech Republic. He got his Ph.D. in 2008 at the Friedrich-Alexander University of Erlangen-Nuremberg. Since 2015 he has been a senior researcher and group leader at Center of Materials and Nanotechnologies of the University of Pardubice. Based on his starting ERC grant CHROMTISOL, he leads his R&D group focused on atomic layer deposition of novel chalcogenide-based materials and modifications of high-aspect-ratio nanotubular structures toward various applications. Since 2018, he has also been a group leader at Central European Institute of Technology of the Brno University of Technology.

Filip Bureš was born in Poprad, Slovakia (1979), and studied chemistry at the University of Pardubice where he also obtained his Ph.D. (2005). He subsequently pursued (post)doctoral studies with Prof. P. Knochel (LMU, Munich) and Prof. F. Diederich (ETH, Zurich). In 2010, he was habilitated, and since 2017 he has been a full professor at the University of Pardubice. His working group at the Institute of Organic Chemistry focuses on the design and synthesis of organic molecules with modern applications across various fields.

■ ACKNOWLEDGMENTS

■ ABBREVIATIONS

ALD, atomic layer deposition; CVD, chemical vapor deposition; DPA, diphenylacetylene; DSC, differential scanning calorimetry; SDMDTC, tetrakis(*N,N*-dimethyldithiocarbamate)-selenium; SEM, scanning electron microscope; TGA, thermogravimetric analysis; TMD, transition-metal dichalcogenide; XPS, X-ray photoelectron spectroscopy

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