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Organic selenium compounds and their modern applications

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REFERENCES

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ANNOTATION

This dissertation work is focused on selenium compounds and their utilization in modern materials sciences. Selected thin film deposition techniques with emphasis on Atomic Layer Deposition (ALD) are briefly introduced along with possible utilization of manufactured nanolayers. The latter part of the thesis is devoted to various organic selenides as potential ALD precursors. Several cyclic silyl-selenides, linear silylselenides, silylselenols, stanylselenides and one silyltelluride were prepared using described, modified, and newly developed synthetic pathways. All target molecules were characterized by GC/MS and multinuclear NMR. DSC and TG analyses were employed to determine fundamental thermal behaviour, as a key parameter of ALD precursors. The last part of the work is dedicated to testing selected selenides in ALD to produce $MoSe_2$ and Sb_2Se_3 thin films.

KEYWORDS

Selenium, synthesis, ALD, depositions, thin films

NÁZEV

Organické sloučeniny selenu a jejich moderní využití.

ANOTACE

Tato disertační práce se zabývá sloučeninami selenu a jejich aplikací při tvorbě tenkých vrstev. První část práce představuje vybrané depoziční metody s bližším zaměřením na technologii Atomic Layer Deposition (ALD), její charakteristiky, využití a obecné požadavky na ALD prekurzor. Ve větším detailu je pak studována příprava a vlastnosti organických sloučenin selenu s již popsaným či potenciálním využitím v ALD. V experimentální části práce bylo připraveno několik silylselenidů, silylselenolů, stanylselenidů a jeden silyltelurid. Charakterizace cílových molekul byla provedena pomocí GC/MS a multinukleární magnetické rezonance. Syntéza a strukturní analýza je doplněna o studii základních termických vlastností (DSC a TGA), které jsou pro využití v ALD zcela klíčové. Vybrané selenidy byly v poslední části práce testovány při tvorbě tenkých vrstev $MoSe_2$ a Sb_2Se_3.

KLÍČOVÁ SLOVA

Selen, syntéza, ALD, depozice, tenké vrstvy

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2. Introduction

Nanotechnology, as a scientific discipline studies the properties, preparation and application of objects with the size up to 100 nm. These unimaginably tiny dimensions possess characteristics that are often completely different from the properties observed in a bulk of the same material. It is unnecessary to describe current fields affected by application of nanotechnologies, because there is almost no domain of human endeavour, where nano-scale materials are not applied in some way.

Very thin layers became irreplaceable in applications as photovoltaics, photo- and electrocatalysis or electronics thanks to their unique abilities easily tenable by composition and thickness of prepared thin film. Nevertheless, preparation of these materials within such a tiny dimension is still challenging. Among other thin film deposition techniques, Atomic Layer Deposition (ALD) became one of the most important, because of its capability to prepare nanolayers with very high level of control of thickness on flat surfaces and also heterostructures like nanotubes and others.

This exceptional control come from the nature of ALD reaction itself, which is based on sequential introduction of ALD precursors ensuring only saturated surface reaction and thus increase of only one atomic layer in one ALD cycle. ALD precursors are chemical substances utilized in the ALD reactor for deposition. Because the ALD reaction is carried out as gas-solid system precursors must possess specific properties such as reactivity, volatility and thermal stability, while finding a trade-off between these properties represents a key point for successful thin film fabrication.

Metal selenides are interesting materials with application in various technologies such as photovoltaics, thermoelectrics or phase change transistors. Nevertheless, selenium ALD precursor portfolio is very limited, to only few options, namely toxic H_2Se, not sufficiently reactive Et_2Se and bis(trimethyl)silyl selenide. The latter is the most established selenium precursor so far. This work aims to focus closer on the existing and potential selenium precursors, their synthetic routes, yields and difficulties during preparation. The most important properties of precursor, such as sufficient reactivity, volatility and thermal stability, are also discussed.

The latter part of this work aims to test prepared selenides in ALD. Thins films of $MoSe_2$ and Sb_2Se_3 are manufactured including analysis of deposited layers and effect of the precursor structure to thin film properties are discussed.

3. Aims of thesis

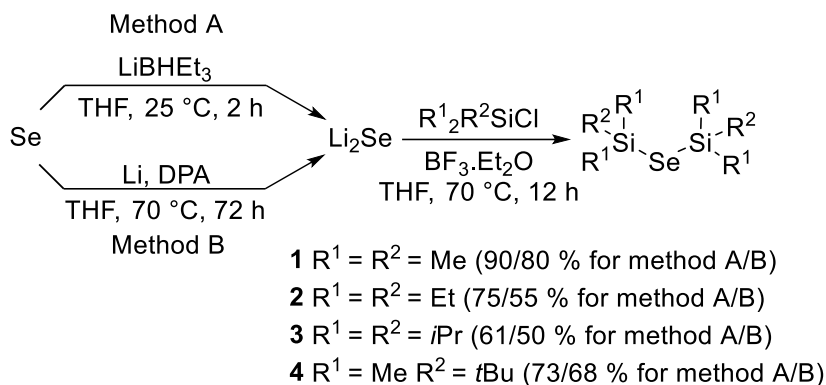The main aims of this work are as follows:

- To perform literature search focusing on principles of ALD and selenium ALD precursors; especially their preparation and utilization.
- To prepare organic selenides with possible application in ALD.
- To characterize prepared organic selenides including their fundamental thermal behaviour.
- To test applicability of the prepared organic selenides in ALD.

4. Results and discussions

4.1. Synthesis

Silyl- and stanylselenides have proven as convenient ALD precursors.[1,2] Their volatility, high reactivity, and thermal stability, however, come with some drawbacks. The most pronounced is high air-sensitivity, which complicates handling during the synthesis, purification, and subsequent deposition. Another questionable limitation is their synthesis. Even though that the established preparation shown on *Scheme 1*[3] utilizing Li_2Se is straightforward, the high price of $LiBHEt_3$ and safety issues connected with the aforementioned hydride or elemental lithium along with high demand for dry solvents and inert atmosphere limit its application beyond the laboratory scale. Hence, the experimental part of this work aims to investigate cyclic silyl-selenides and silylselenoles as an alternative to bis(trialkylsilyl)selenides. These derivatives would potentially bring improved air-sensitivity along with novel synthetic routes using inexpensive starting materials. Thorough structural analysis confirming predicted structure and purity as well as investigation of fundamental thermal properties, as an important characteristic of ALD precursor, are integral part of this experiment work.

Method A
LiBHEt$_3$
THF, 25 °C, 2 h
Se
Li, DPA
THF, 70 °C, 72 h
Method B

Li_2Se $\xrightarrow[\text{THF, 70 °C, 12 h}]{\overset{R^1_2R^2SiCl}{BF_3.Et_2O}}$

1 $R^1 = R^2 = Me$ (90/80 % for method A/B)
2 $R^1 = R^2 = Et$ (75/55 % for method A/B)
3 $R^1 = R^2 = iPr$ (61/50 % for method A/B)
4 $R^1 = Me$ $R^2 = tBu$ (73/68 % for method A/B)

Scheme 1. Synthetic pathways to bis(trialkylsilyl)selenides and their reaction yields.[3]

The most straightforward way to prepare silylselenides is a reaction between Li_2Se and desired alkyldichlorodisilane or dialkyldichlorosilane. In this work, Li_2Se is readily prepared by the established reaction of elemental selenium with $LiBHEt_3$ solution. The alternative reaction of elemental Se with Li is sluggish and usually provides lower yields.

Scheme 2 depicts the first attempts on cyclic silylselenides **9**,[4] **10** and **11**[5] that were formerly reported by Herzog. The synthesis of six-membered cycle **19** was not reported up to date. Whereas products **9** and **19** were prepared with the aid of $BF_3·OEt_2$ as a catalyst in good yields, target compounds **10** and **11** rather decomposed in the presence of $BF_3·OEt_2$. Target compounds were purified by vacuum distillation or crystallization from hexane at –78 °C in the case of **11**. In general, these preparations were without major difficulties.
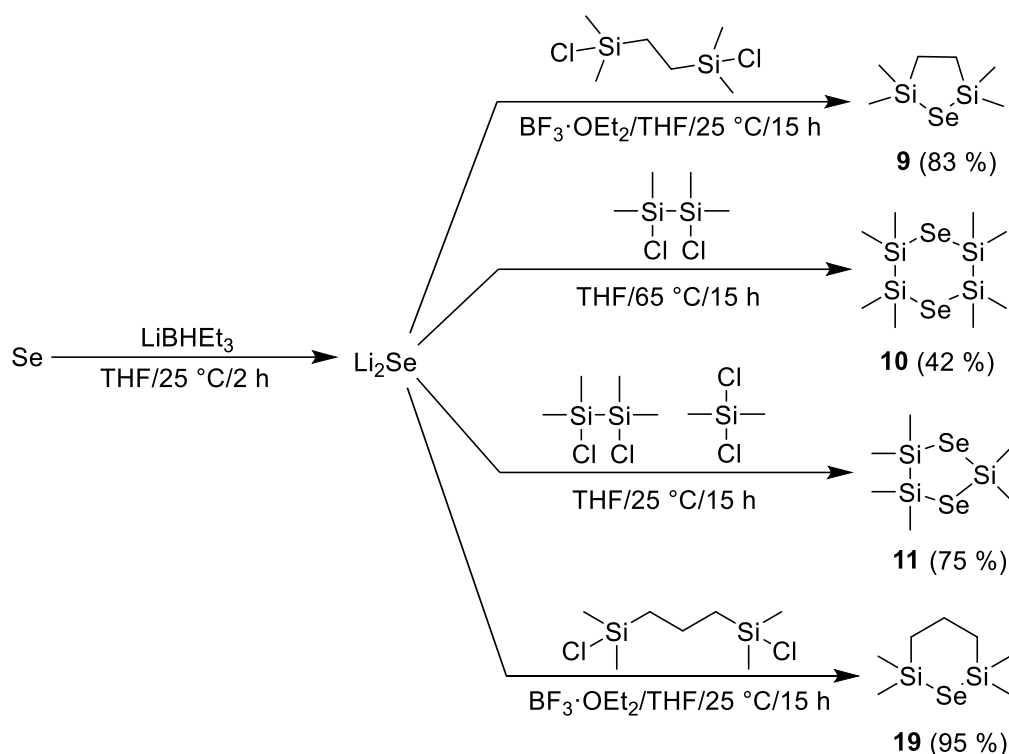
Scheme 2. Preparation of cyclic silylselenides **9–11** and **19**.

In contrast to five- and six-membered cycles, a synthesis of four-membered cyclic silylselenides containing two selenium atoms such as **26** was not reported so far. A reaction between Li_2Se and Me_2SiCl_2 affording six-membered cycle **12** containing three selenium atoms is known from the literature.[5] However, attempts to reproduce this procedure was not successful while a mixture of products was always obtained. Vacuum distillation, fraction vacuum distillation, sublimation, and crystallization from hexane at 0 °C or –78 °C failed to separate single molecules. In addition, *Scheme 3* also shows alternative method towards products **12**, **26**, and **27** by employing Me_2HSiCl, elemental selenium, and $EtNiPr_2$ as a base. As a general feature, these experiments lacked reproducibility and ratios of products usually varied. Heterocycle **27** containing oxygen was always observed as a major impurity (detected on GC/MS), but source of the oxygen was not identified. Hence, motivated by development and synthesis of new selenium precursor in simple and efficient manner, I stopped further investigation of these products.
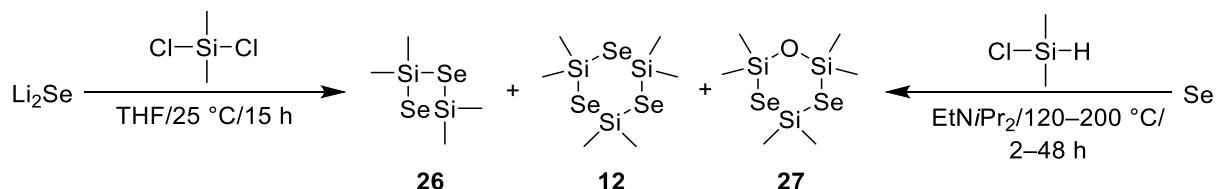
**Scheme 3**. Attempted preparation of selenide **26**.

Thompson[6] reported reaction of Na_2Se (its preparation was not specified) with Et_2SiCl_2 giving mixture of four- (30 % yield) and six-membered (40 % yield) cycles. A separation method was also not specified in this work. Experimental reproduction of this reaction afforded a yellow oil in 43 % yield. However, the yield was significantly improved to 92 % by using Li_2Se. In contrast to GC/MS record detecting only four-membered product **14**, ^1H, ^{13}C, ^{29}Si, and ^{77}Se NMR spectra showed several products. All separation attempts failed; the mixture composition is unknown so far. These difficulties again caused loss of interest in molecule **14**. On the other hand, the corresponding *iso*propyl derivate **20** was prepared quantitatively from Li_2Se, whereas its synthesis from Na_2Se can be carried out with lower yield of 72 %. Newly developed method starting from elemental selenium and iPr_2HSiCl in a basic environment provided **20** in 81 % yield. This method excludes solvent, uses readily available and inexpensive starting materials, and the separation of **20** was very easy. Hence, compound **20** would become an attractive Se-precursor for application in ALD. Analogous *tert*butyl derivative **15** was also examined. Whereas its preparation from Li_2Se completely failed, the synthesis using tBu_2HSiCl provided **15** in 61 % yield.
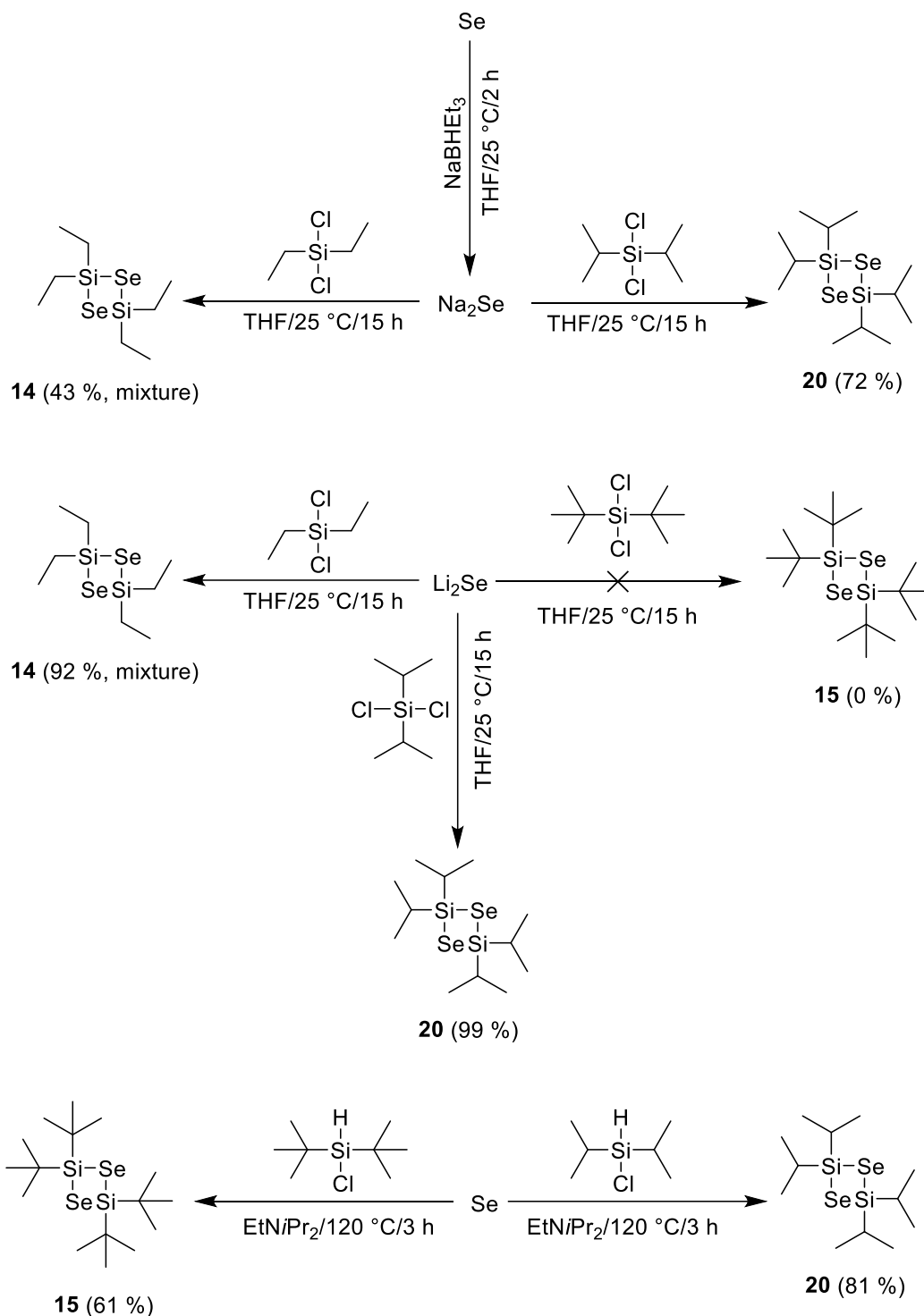
Scheme 4. Preparation of four-membered silylselenides.

Direct insertion of selenium into R_3Si-H bond forming trialkylsilylselenole $R_3Si-SeH$ is another attractive option towards potential Se-precursors as synthetically demonstrated by Grenader.[7] His work reported a reduction of selenium with $cHex_3Si-H$ at 250 ° and also briefly but with no further details mentions preparation of $iPr_3Si-SeH$ **22**. My attempt to prepare **22** starting from iPr_3Si-H afforded only poor yield around 5 % even after heating at 250 °C for 48 hours (*Scheme 5*). Further investigation revealed that the yield can be dramatically increased by adding a Lewis base. When Ph_3P was

used, tri*iso*propylsilylselenole **22** was obtained in 81 % yield. Compound **22** possesses high volatility and very inexpensive synthesis and, therefore, might be an interesting Se-precursor for ALD. Nevertheless, the proton attached to selenium may generate ALD-undesired HX by-product when treated with metal halides. A transformation of **22** to asymmetric silylselenide **23** bearing additional trimethylsilyl group may overcome this drawback. The reaction of selenole **22** with trimethylsilylchloride or one-pot reaction starting from *i*Pr₃SiH gave **23** in 70 or 55 %. Interestingly, using even a large excess of tri*iso*propyl silane gave exclusively **22** and only traces of bis(tri*iso*propylsilyl)selenide, which was detected by GC/MS.
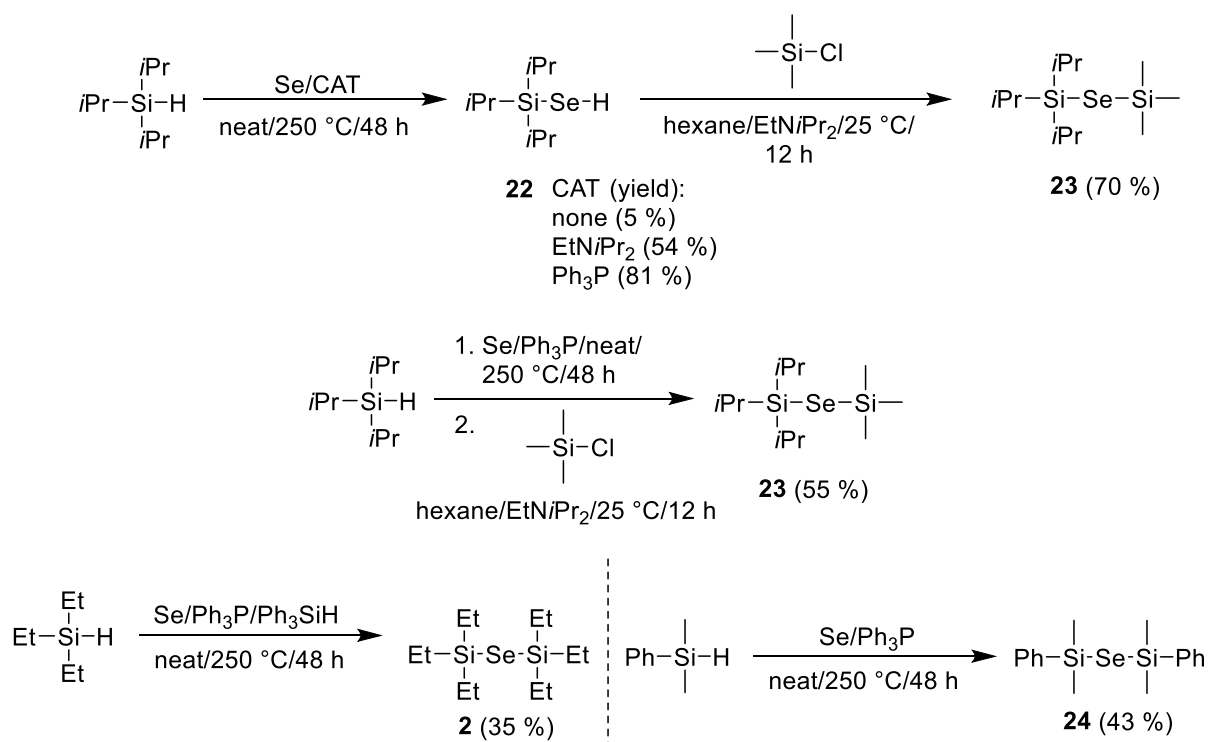

Scheme 5. Reduction of selenides by silanes.

Reduction of selenium with Et_3Si-H was also published by Vyazankin.[8] However, my attempts to reproduce this reaction failed even with addition of Ph_3P, elevated temperature or extended reaction time. Further experiments on preparation of Et_3Si-SeH or $(Et_3Si)_2Se$ via this method led to an idea of employing transmission, which is known phenomenon for 14 group elements. Indeed, when treating two equivalents of Et_3Si-H with selenium and small amount of Ph_3Si-H, bis(triethylsilyl)selenide **2** was obtained in 35 % yield (*Scheme 5*). Only traces of Et_3Si-SeH were detected by GC/MS. Selenide **24** was isolated in 43 % yield along with only minor amount of Me_2PhSi-SeH when treating bulkier silane Me_2PhSi-H with selenium.

Vyazankin[9] described also reduction of selenium with Et_3Sn-H to bis(triethylstanyl)selenide at 120 °C. I have examined this reaction with *n*Bu_3Sn-H (*Scheme 6*). When the reaction temperature was increased to 180 °C, bis(tributylstanyl)selenide **7** was obtained in almost quantitative yield after 12 hours.

Scheme 6 also shows modified synthesis by Han.[10] In this work, selenium is inserted to Sn-Sn bond in a catalytic cycle involving oxidation of triphenylphosphine to $Ph_3P=Se$, which reacts with Me_6Sn_2 at laboratory temperature in benzene to bis(trimethylstanyl)selenide **5** in 47 % yield after 5 hours. Further elaboration with this method revealed, that elevated reaction temperature to 180 °C afforded **5** and **7** in nearly quantitative yields even without catalyst or solvent present. It is wort to note that both starting Me_6Sn_2 and Bu_6Sn_2 are commercially available, air stable, and inexpensive starting materials.

A similar reaction using Me_6Si_2 was also attempted but even at very harsh reaction conditions (250 °C for seven days) and presence of Ph_3P of $EtNiPr_2$ did not afford any product.
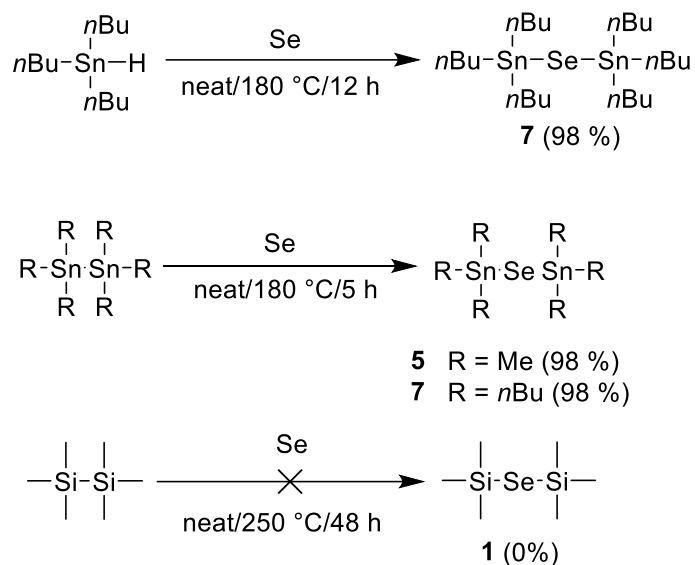
Scheme 6. Insertion of selenium to Sn-Sn/H bond.

4.2. Structural analysis

The structure of all target compounds and eventual intermediates was studied and determined with a combination of GC/MS and heteronuclear NMR. *Figure 1* shows representative EI-GC/MS record of target molecule **22**, where M^+ peak is observed along with other anticipated fragments caused by the loss of the alkyl groups. The peaks also possess typical isotope pattern.

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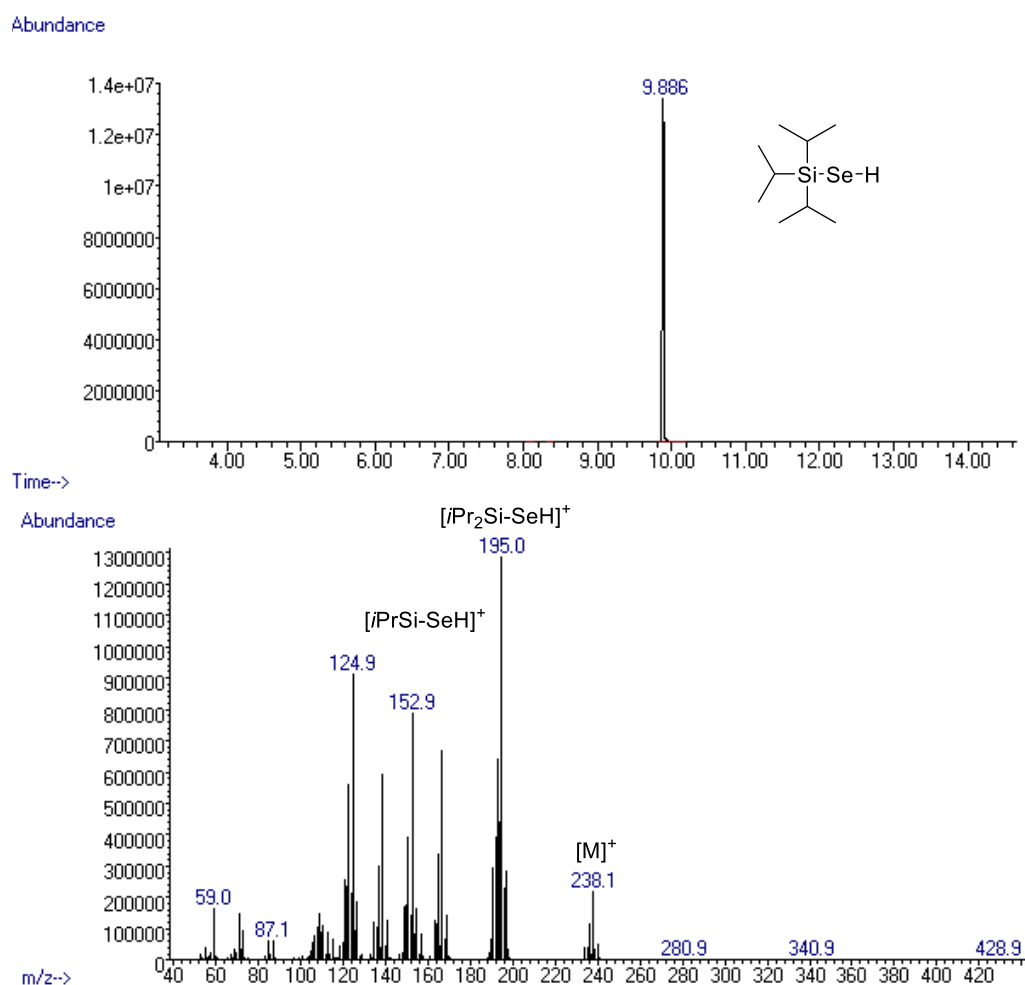
Figure 1. GC/MS record of molecule **22**.

^{1}H-NMR spectra of **22** (*Figure 2*) showed an undistinguished multiplet of the *iso*propyl group at 0.98–1.04 ppm. Singlet with very low chemical shift at –2.81 ppm belongs to the proton attached to the selenium.
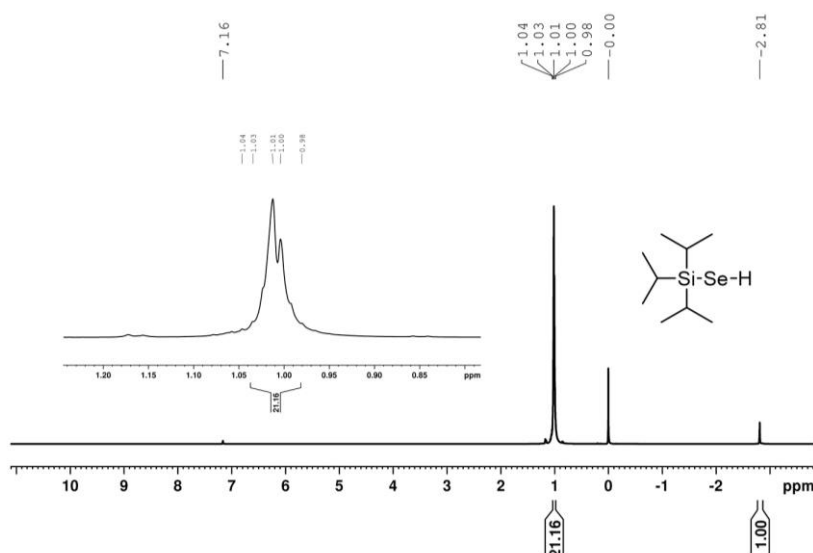
Figure 2. H-NMR spectra (400 MHz, 25 °C, C_6D_6) of **22**.

^{13}C-NMR (APT) spectra were very simple showing two signals at 13.96 and 18.72 ppm. Similarly, only one signal at 32.22 ppm was observed in ^{29}Si-NMR spectra. Both spectra are shown in *Figure 3.*
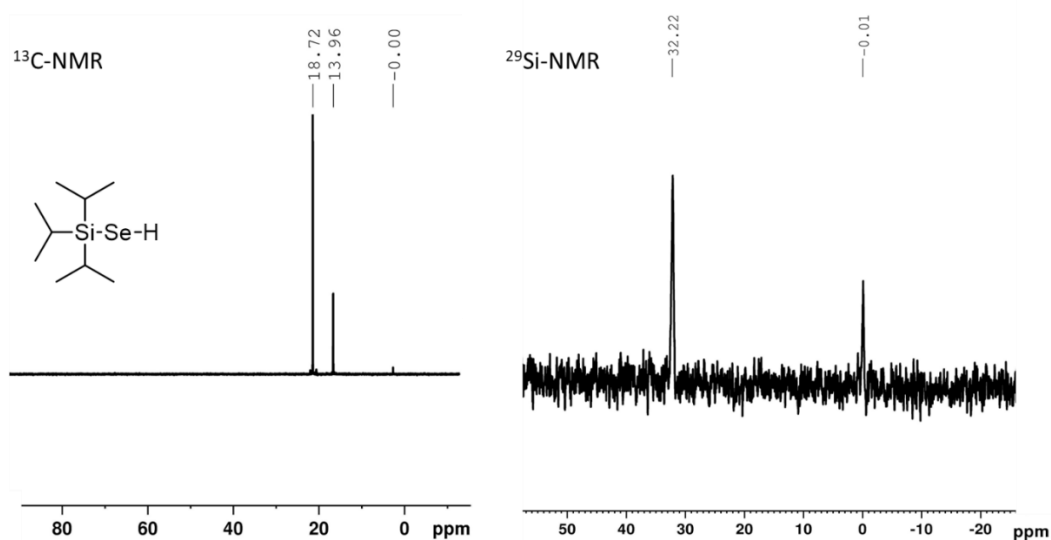
Figure 3. H-NMR spectra (400 MHz, 25 °C, C_6D_6) of **22**.

Gated ^{77}Se-NMR spectra shown in *Figure 4* confirmed direct Se-H coupling resulting in a doublet at –420.7 ppm with interaction constant $J = 47.17$ Hz.

^{77}Se-NMR

Figure 4. ^{77}Se-NMR (95 MHz, 25 °C, C_6D_6, gated) of **22**.

4.3. Thermal properties

High volatility and thermal stability are the key parameters for successful ALD precursor utilization. To study these characteristics, Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TG) were employed. The measurements were performed in N_2 atmosphere and laboratory pressure.

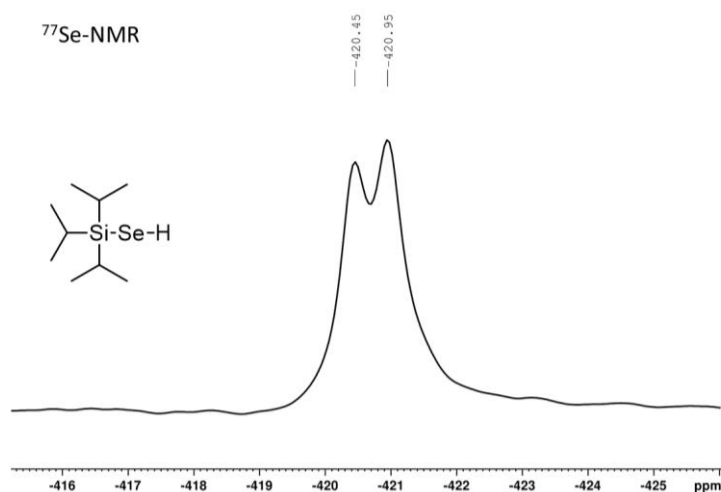Molecules **9**, **10** and **19** exhibited smooth evaporation that decrease with larger molecular weight. Compound **10** is solid at laboratory temperature with melting point at 145 °C and boiling around 275 °C. Compounds **9** and **19** are liquids at 25 °C that boil at 170 or 200 °C, respectively.

DSC curve of **11** revealed glass transition at –55 °C, melting at –21 °C, and complete evaporation at 200 °C. The two revealed melting points and relatively wide evaporation peak of **14** is another proof of this inseparable mixture. Compounds **15** and **20** were evaporated smoothly but at higher temperatures around 285 and 310 °C.

Slightly broadened evaporation peaks seen in DSC curves of **22** and **23** (*Figure 5*) indicates additional thermal process taking place around boiling point. It is more pronounced in TG analysis. I suspected formation of two symmetrical molecules and this idea was confirmed by heating **22** to 180 °C for 15 hours at ambient pressure. Under such condition, a formation of bis(tri*iso*propylsilyl)selenide **3** is observed accompanied by release of H_2Se. Compound **24** underwent glass transition at –35 °C, melting, and subsequent boiling at 345 °C.

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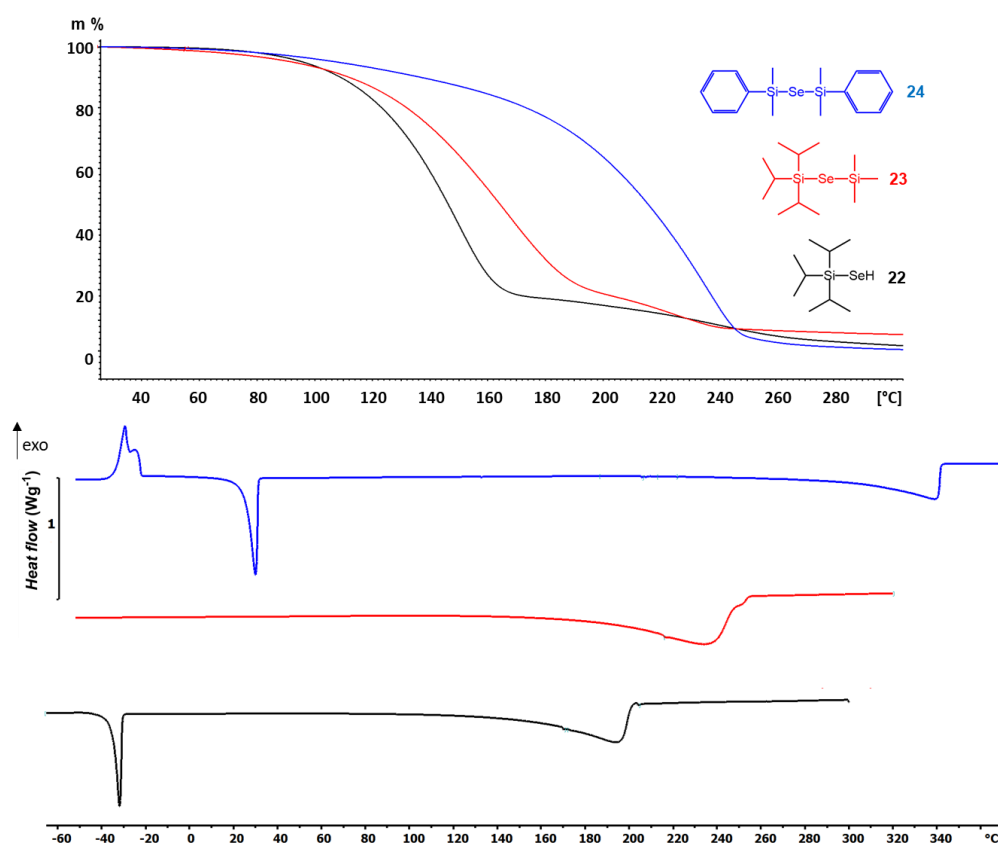
Figure 5. TGA (top) and DSC (bottom) curves of **22** (black), **23** (red) and *24* (blue).

Figure 6 illustrates boiling points determined by DSC as function of the structure, while *Figure 7* contains a complete dataset of obtained thermal properties. It is no surprise, that boiling point steadily increases with extended molecule mass and elongated alkyl chains. Most of the prepared compounds seems to be thermally stable with the exception of **22** and **23** that started to decompose at 160 °C and 185 °C, respectively.

Figure 6. Overview of boiling points of products determined by DSC.

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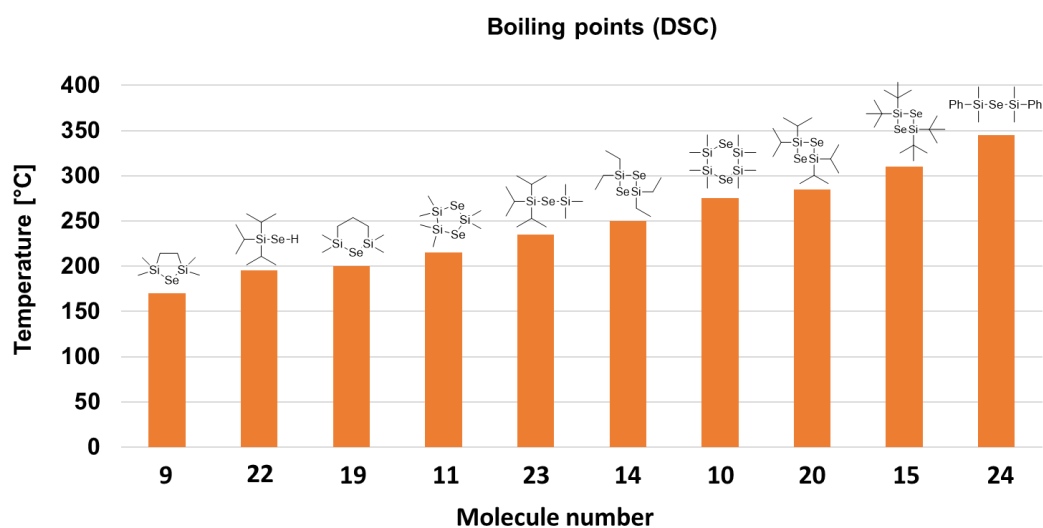| Molecule	Temperature of crystallization (DSC) [°C]	Melting point (DSC) [°C]	Temperature of glass transition (DSC) [°C]	Temperature close to the boiling point (DSC) [°C]	Boiling point (distillation) [°C (pressure)]
9	–62	–27	–90	170	85 (20 torr)
10	-	145	-	275	-
11	–62	–21	–55	215	95–100 (1 torr)
14	–64; 0	–62; 2	-	250	120–140 (1 torr)
15	157	170	-	310	-
19	–85	–32	–89	200	95 (20 torr)
20	3	32	-	285	-
22	–67	–32	-	195	80–85 (5 torr)
23	-	-	-	235	100–105 (2 torr)
24	-	25	–45	345	160–165 (2 torr)

Figure 7. Thermal properties of prepared molecules.

4.4. Deposition of MoSe$_2$ with gALD

After first insight into fundamental thermal properties, four candidates **9**, **10**, **19** and **20** were selected to be screened by gALD experiments that were performed by our fellow research group of Dr. J. M. Macák at the University of Pardubice. Sequential introducing of selenium precursor and MoCl$_5$ (with N$_2$ purges in between) were aimed to deposit thin films of MoSe$_2$ according to ligand exchange reaction shown in *Scheme 7*.

Scheme 7. Formation of MoSe$_2$ thin film by reaction of MoCl$_5$ with cyclic precursor **10** as an example.

Figure 8 shows SEM picture with polycrystalline flaky structure, which is typical for MoSe$_2$ and was further confirmed by Raman spectroscopy. Closer surface compositional analysis using XPS unfortunately revealed presence of significant chlorine impurities along with elemental selenium, if precursor **9** was used. This suggest that the reactivity of **9** is not high enough within the used conditions and the exchange of ligands is incomplete. Precursor **10** needed higher temperature for evaporation (120 °C), but the prepared MoSe$_2$ thin films possessed high quality with minimum level of impurities.
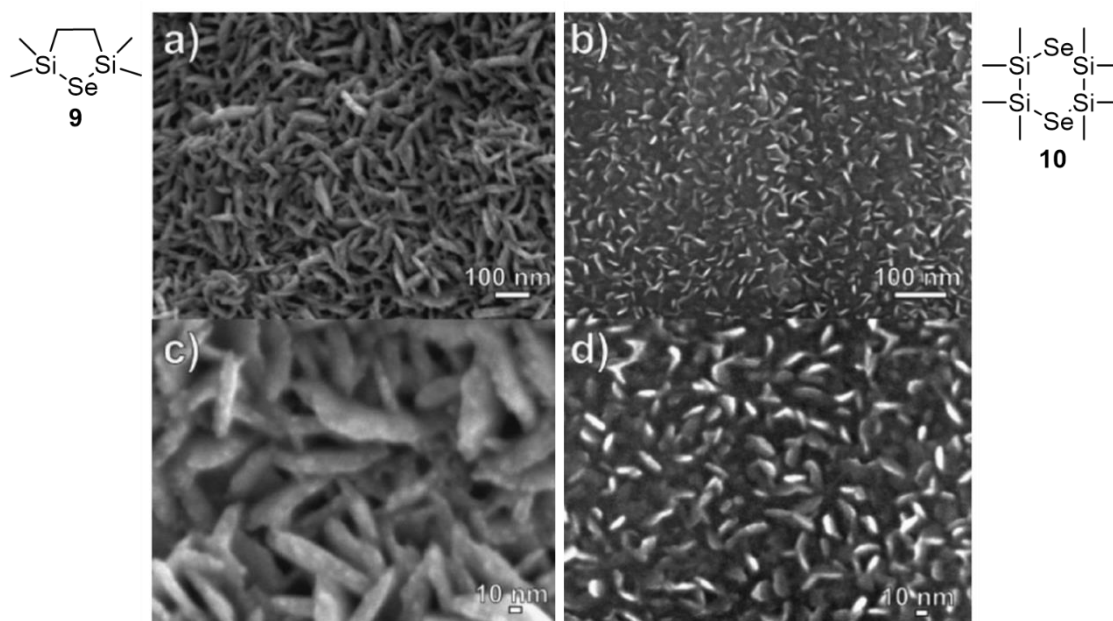
Figure 8. SEM images of $MoSe_2$ (400 cycles) deposited using $MoCl_5$ and **9** (left: a, c) or **10** (right: b, d).

Six-membered silylselenide **19** did not provide any deposition of $MoSe_2$. Increased temperature for evaporation from 45 to even 155 °C, which should ensure large oversaturation of the surface, had no effect. Thus, it seems that **19** is too stable to react at the given conditions.

Four-membered cycle **20** bearing two selenium atoms was the last tested gALD precursor. Its slightly lower volatility required evaporation temperature of 120 °C. *Figure 9* represents SEM images of the as-deposited $MoSe_2$ on two different substrates including cross-sectional SEM. Investigation of different pulse lengths ensures finding the right condition for saturated reaction in ALD regime. If temperature was lowered from 300 to 200 °C, the morphology changed to granular and presence of Se-Se bonds or Se^0 emerged in the XPS spectra. This means that morphology and surface reactions are temperature dependent. Nevertheless, deposition at 300 °C provided high-quality $MoSe_2$ thin films with no residual chlorine detected meaning good ligand exchange.
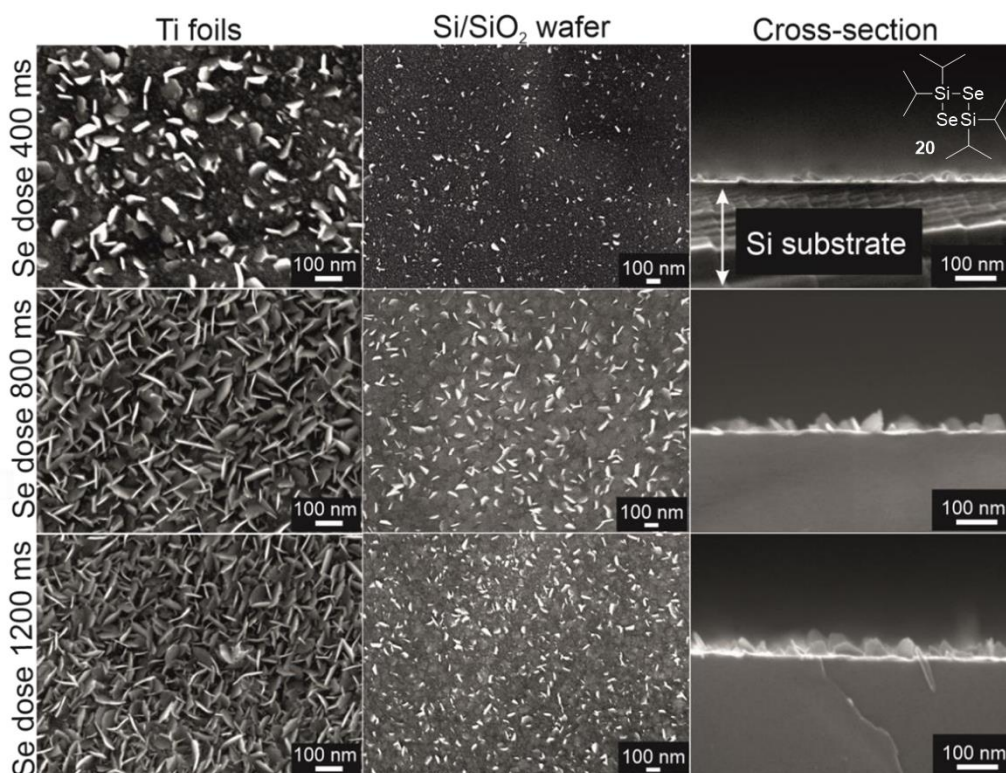
Figure 9. SEM and cross-section SEM images of MoSe$_2$ (800 cycles) deposited using MoCl$_5$ and various pulse lengths of **20** on different substrates.

4.5. Deposition of Sb2Se3 using sALD

Suitability of prepared Se-precursors for sALD was examined during my internship at the Friedrich-Alexander-University Erlangen-Nűrnberg under guidance of prof. Julien Bachmann. Sb$_2$Se$_3$ has been chosen as a target material because of its high application potential as photon-absorbing layer in thin film solar cells. It has been prepared by reacting selected Se precursors with SbCl$_3$ according to *Scheme 8*.
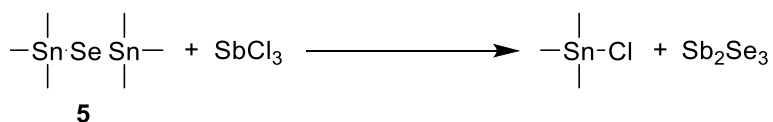
Scheme 8. Reaction of SbCl$_3$ with stanylselenide **5** resulting in Sb$_2$Se$_3$ thin film.

The deposition was carried out using self-made sALD system composed of steel reaction chamber, peristaltic pump, Teflon tubing, and Schlenk flasks connected to the nitrogen filled Schlenk line to maintain the inert atmosphere during the whole process. The deposition was carried out in an injection mode. The length of optimal pulse and purge was determined during ALD study.

Unlike gALD, sALD does not demand high volatility and thermal stability, thus the selection of selenium precursors was based on ease of preparation, handling, and economical aspects, therefore selenides **5** and **7** were the candidates. Hexane was used as solvent.

The initial experiments have shown that reactivity of bis(trimethylsilyl)selenide **1**, a benchmark gALD Se-precursor, is very similar to bis(trimethylstanyl)selenide **5**. Larger bis(tributylstanyl)selenide **7** showed lower growth rate, due to larger and sterically hindered butyls. Although **5** provided slightly larger growth per cycle than **7**, the latter was preferred. The reason is that higher reactivity of **5** caused inhomogeneity during the nucleation and further increasing the number of cycles led to a thickness gradient with thicker film at the side located closer to the solution inlet. Slightly lower reactivity of larger butyl derivate **7** elegantly solved this problem. The saturation behaviour and optimal length of pulse and purge were determined by performing series of experiments using different dosage intervals of precursors and solvent introduction. Si/SiO$_2$ wafer was used as a substrate. The stable, linear growth rate of 0.85 Å/c was achieved with increasing number of cycles, which is a typical feature of ALD growth type. Growth characteristics are highly dependent on substrate type. Substrate effect was observed during deposition on various substrates including Si/SiO$_2$, Si/SiO$_2$ treated with piranha solution before use (mixture of H$_2$SO$_4$ and H$_2$O$_2$), TiO$_2$ (crystalline anatase form), TiO$_2$ dipped in ZnCl$_2$ solution, amorphous Sb$_2$S$_3$, and crystalline Sb$_2$S$_3$ (*Figure 10*). The highest growth rate and also good reproducibility were achieved using both types of TiO$_2$, however *Figure 10b* and *10c* revealed that the difference in growth rates is distinguished only at the initial stage of deposition and stabilize once the whole substrate surface is completely covered. This is further confirmed by SEM images (*Figure 10d* and *e*) showing identical morphology on both substrates.
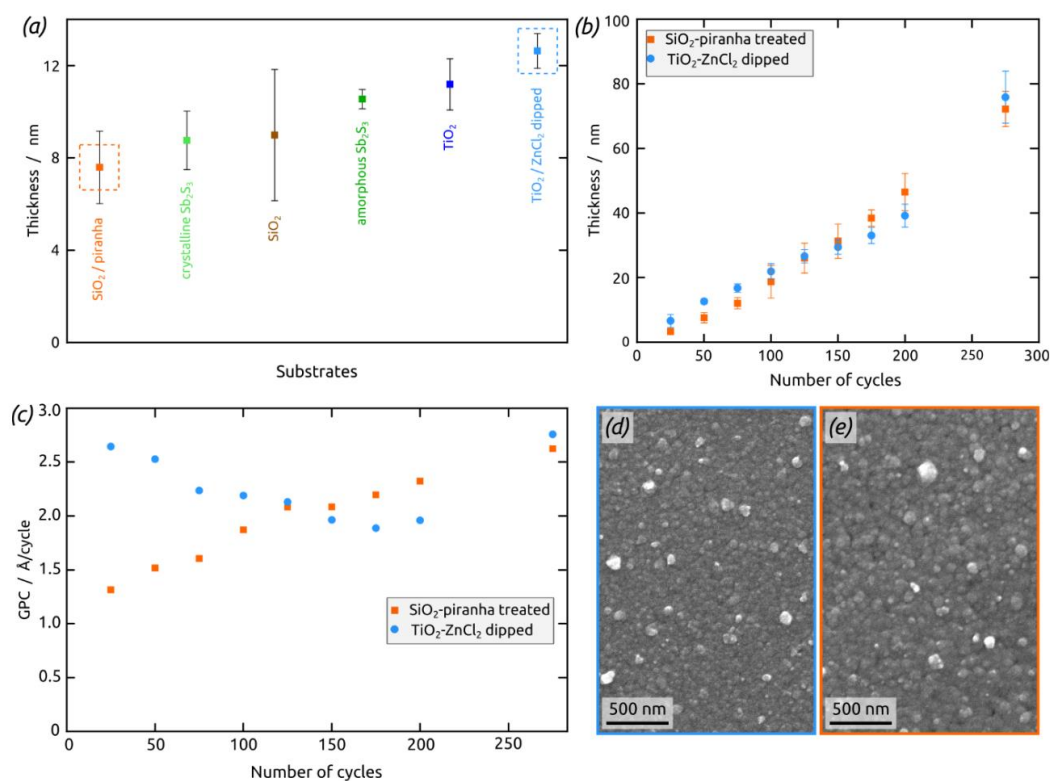

Figure 10. Effect of the substrate to growth characteristics using SbCl$_3$ and **7**. Thickness of films after 50 cycles on six different substrates (a); full growth study on two selected substrates

(b and c); scanning electron micrographs of Sb_2Se_3 films obtained after 275 sALD cycles on piranha-cleaned SiO_2 wafer (d) and a $ZnCl_2$-dipped, TiO_2-coated wafer (e).

EDX analysis of layers prepared by reaction of **7** revealed chlorine incorporation in as-deposited (amorphous) films. This might be caused by incomplete reaction of precursors or leftovers of $SbCl_3$ stuck in film cavities. Incorporation of tin is not observed. Nevertheless, annealing the sample (300 °C for 5 minutes, N_2 atmosphere) resulted in crystallization of the material and a total removal of residual chlorine impurities.

The reaction outcome of sALD can be tuned by varying the used solvent. Increasing relative polarity of the solvent (hexane→chlorobenzene→dichloromethane) decreased the nucleation density on the substrate surface. This is confirmed by SEM and AFM images. Hexane seems to be an ideal choice to achieve good uniformity.

4.6. Upscaling the Sb_2Se_3 sALD deposition

Hence, a homebuilt sALD setup based on a modified slot-die coater has been used for upscaling the Sb_2Se_3 sALD; Less volatile octane was used as a solvent to prevent evaporation from the substrate, which might cause uneven distribution of liquid. This setup allows to perform deposition on up to 10×10 cm substrates or whole 4-inch silicon wafer. The mobility of printing head also ensures even distribution of precursors, which allows to use more reactive bis(trimethylstanyl)selenide 5 without uniformity loss. $SbCl_3$ was used as a source of antimony.

The performed sALD study revealed linear growth with GPC around 1.5 Å per cycle. Detailed characterization of as-grown and annealed Sb_2Se_3 thin films was carried out by means of XRD, SEM, EDX, XPS, and Raman spectroscopy. *Figure 11* shows SEM images of as-deposited and annealed Sb_2Se_3 thin films.

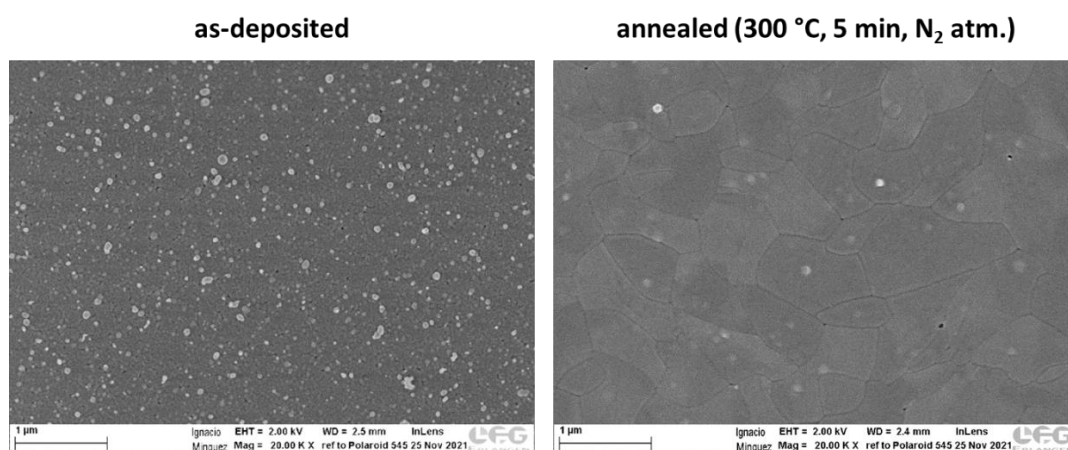**Figure 11**. SEM images of Sb_2Se_3 (350 cycles) on Si/SiO_2 wafer before and after annealing.

The uniformity of deposited layer was determined by ellipsometry area imaging. For this purpose, silicon wafer of 10 cm diameter (4 inch) was decorated with 80 cycles of Sb_2Se_3 using the same conditions, as mentioned above. The mean of obtained thickness corresponds to 11,3 nm (± 0,9 nm) on total area of 7 ×7 cm. *Figure 12* presents

attained results in greater detail. Section *a)* reveals the cut-off and depicts direction of two examined scanning lines, whereas *b)* reveal observed thickness profile. Part *c)* shows thickness graphically. Horizontal thickness is uniform meanwhile slight shift in film thickness is observed in direction of the printing head movement (from top to the bottom).
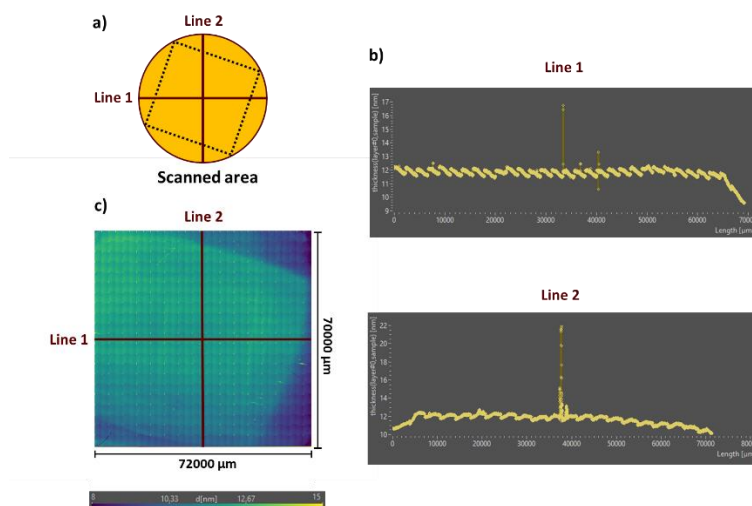

Figure 12. Ellipsometry area imaging of the whole 4-inch wafer scale deposition.

4.7.   Deposition of MoTe2 by gALD

The current portfolio of Te-precursors is very narrow, which significantly complicates ALD of metal tellurides. In 2009, bis(trialkylsilyl)tellurides were reported along with their selenium analogues.[1] Nevertheless, these molecules proved to be extremely sensitive to air and light, thus very difficult to prepare and handle. Based on my gained experience with selenides, cyclic silyltelluride **25** was designed and prepared according to *Scheme 9*. This compound was previously reported by Herzog[5] but I intended to use it as Te-precursor and verify its reactivity to produce metal telluride thin films. Higher stability and easier handling were also expected. DSC measurement of **25** revealed crystallization temperature at 114 °C, melting at 153 °C and smooth evaporation around 255 °C, which is surprisingly a bit lower than its selenium analogue **10** (275 °C). The precursor is stable and does not show any decomposition after one month, when stored under argon atmosphere.
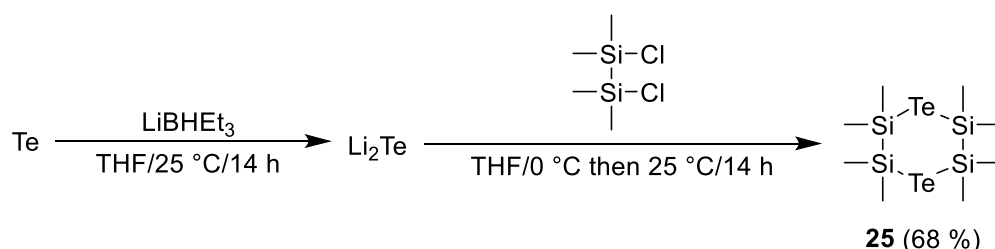
Scheme 9. Preparation of cyclic silyltelluride **25**.

The reaction in gALD performed at J. M. Macák research group was carried out in a custom flow-ALD reactor, where **25** reacted with $MoCl_5$ according to the reaction in *Scheme 10*.

Scheme 10. Reaction of $MoCl_5$ with **25** resulting in $MoTe_2$ thin film.

The used substrates included Si/SiO_2 wafer, TiO_2 foils, and TiO_2 nanotubes; the reaction temperature was 270 °C. The growth rate seems to be somewhat lower, thus relatively high temperature for evaporation of **25** (175 °C) was necessary to provide sufficient vapor pressure. Nevertheless, $MoTe_2$ was successfully deposited using gALD for the first time and demonstrated good efficiencies for electrocatalysis (HER) and photocatalysis (methylene blue photo-decomposition).

5. Conclusion

The dissertation focused on organoselenium compounds and their modern applications, especially in thin film preparation by Atomic Layer Deposition. Its mechanism, characteristics, and challenges were discussed. Preparation and thermal behaviour of existing and possible selenides is described, where most attention is given to cyclic silylselenides, which possess yet unexplored structural properties possibly utilization in ALD technology.

Th experimental part demonstrates synthesis of cyclic silyl-selenides as a potential ALD precursor. The structure-property tuning is directed towards organoselenium molecules with sufficient reactivity, volatility, thermal stability, and improved air-stability; a trade-off between these properties was targeted. Compounds **15** and **20** were prepared via a newly developed reaction pathway. Reported synthesis of silyl-selenoles exploiting trialkylsilanes was modified. By this way, two silyl-selenides **2** and **24** and tri*iso*propylsilyl-selenol **22** were obtained. Precursor **22** was characterized for the first time, while it offers interesting application in ALD due to its high volatility and economical synthesis. Another modification was proposed for stannyl-selenides, where the developed reaction pathway allows to prepare bis(trialkylstanyl)selenides from readily available, air-stable, and inexpensive starting materials in near to quantitative yields.

All of the prepared materials were analysed by GC/MS and heteronuclear NMR. The basic thermal behaviour was studied using DSC and TG analyses.

Testing of the selected selenides **9**, **10**, **19** and **20** in gALD revealed rather lower reactivity of **9** and **19**, while **10** and **20** are good candidates for preparation of $MoSe_2$ thin layers. Bis(trialkylstanyl)selenides **5** and **6** were successfully utilized in sALD for Sb_2Se_3 deposition by the reaction with $SbCl_3$. Using optimized conditions, the deposition process was up-scaled allowing Sb_2Se_3 deposition on 10×10 cm silicon wafer with satisfying uniformity. Properties and composition of the manufactured thin layers were studied and confirmed by ellipsometry, SEM, AFM, EDX, XPS, and XRD. In addition, my further synthetic attempts resulted in preparation of cyclic silyl-telluride **25**, which was characterized and successfully used in gALD. Its reaction with $MoCl_5$ led to deposition of $MoTe_2$, reported for the first time by gALD.

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