UNIVERSITY OF PARDUBICE
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Organometallic compounds for deposition of inorganic materials

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Abstract

The work was focused on the study of single source precursor, which could be used for deposition of thin films II-VI, III-VI and IV-VI materials. The first aim of this dissertation was to investigated whether N → Ga intramolecularly coordinated chalcogenides of gallium element can served as SSP for deposition of thin semiconductor layers of III-VI material. The second aim of the dissertation was focused on the synthesis of new N → M (M = Ga, In) intramolecularly coordinated chalcogenides.or chalcogenolates of the 13th group elements. For this reason either N,C,N- or C,N-chelating ligands $L^{1,2,3}$ *(*L^1 *is* $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}^-$*,* L^2 *is* $\{2\text{-}(Et_2NCH_2)\text{-}4,6\text{-}tBu_2\text{-}C_6H_2\}^-$ *and* L^3 *is* $\{2,6\text{-}(tBuN{=}CH)_2C_6H_3\}^-$*) were used.*

Abstract

Práce byla věnována studiu organokových prekurzorů, které by mohly být využity především pro depozice tenkých vrstev III-VI materiálů. První část disertační práce se zabývala studiem možného využití známých N → Ga intramolekulárně koordinovaných chalkogenidů jako vhodných SSP pro přípravu tenkých polovodičových vrstvev III-VI materiálů. Druhým cílem této práce byla snaho o přípravu monomerních N → M (M = Ga, In) intramolekulárně koordinovaných chalkogenidů a chalkogenolátů prvků 13. skupiny. Pro tento účel byly v této práci využity rozdílné N,C,N- a C,N-chelatující ligandy $L^{1,2,3}$ *(*L^1 *je* $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}^-$*,* L^2 *je* $\{2\text{-}(Et_2NCH_2)\text{-}4,6\text{-}tBu_2\text{-}C_6H_2\}^-$ *a* L^3 *je* $\{2,6\text{-}(tBuN{=}CH)_2C_6H_3\}^-$*).*

Keywords

13th group element • thin films • spin coating • chalcogenides and chalcogenolates • reduction

Klíčová slova

13. skupina prvků • tenké vrstvy • spin coating • chalkogenidy a chalkogenoláty • redukce

Table of Contents

1 Introduction

Semiconducting thin films of II-VI, II-VI and IV–VI materials have optical band gap energy E_g between 1 and 3 eV. Generally, amorphous chalcogenides show numerous unique properties, such as broad optical window from the visible to mid-infrared spectral region, high refractive index, low phonon energy and photosensitivity.[1] Such properties make these materials attractive for a wide range of applications such as sensors, detectors, lasers, optical fibers, light amplifiers, waveguides, phase-change memories (DVD-RAM, Blue-ray discs, PRAM chips), Xerox, high-resolution lithography and absorbing films in photovoltaics.[1,2]

Thin films of II-VI, II-VI and IV–VI materials are usually deposited by physical vapor deposition (PVD), chemical vapor deposition (CVD) together with a solution-based deposition process such as using a chemical bath or by galvanic deposition.[2,3] Effective preparation of semiconducting thin films can also be achieved by spin coating. The growth of thin films by a chemical method became practical with use of volatile metal alkyls such as dimethylcadmium (Me_2Cd) or dimethylzinc (Me_2Zn) in a combination with H_2S, H_2Se, or Me_2Te. Defining the process of metal-organic CVD many films were grown including ZnS, ZnSe, CdS, CdSe, and CdTe.[4] The method involves the delivery of both a metal alkyl and a chalcogenide source in the vapor phase in a mixing chamber on the substrate, but particulate material can be form before the vapors reach the heated substrate, sometimes termed ‘*prereaction*’. To overcome some of these problems, new precursors were developed to control volatility, reduce toxic hazard, improve the quality of the grown layers, and reduce the temperature required for growth. These precursors are termed as ,,single-source precursors’’ (SSP). The deposition of crystalline GaS and Ga_2S_3 films have been studied from 1990 and the most interesting study have been reported by Barron et al. in the study of cubic GaS thin films, which were deposited by use of atmospheric pressure CVD and compounds $[t\text{BuGa}(\mu\text{-S})]_4$ as the SSP.[5]

2 Theoretical part

2.1 Precursors for deposition of III-VI materials by CVD method

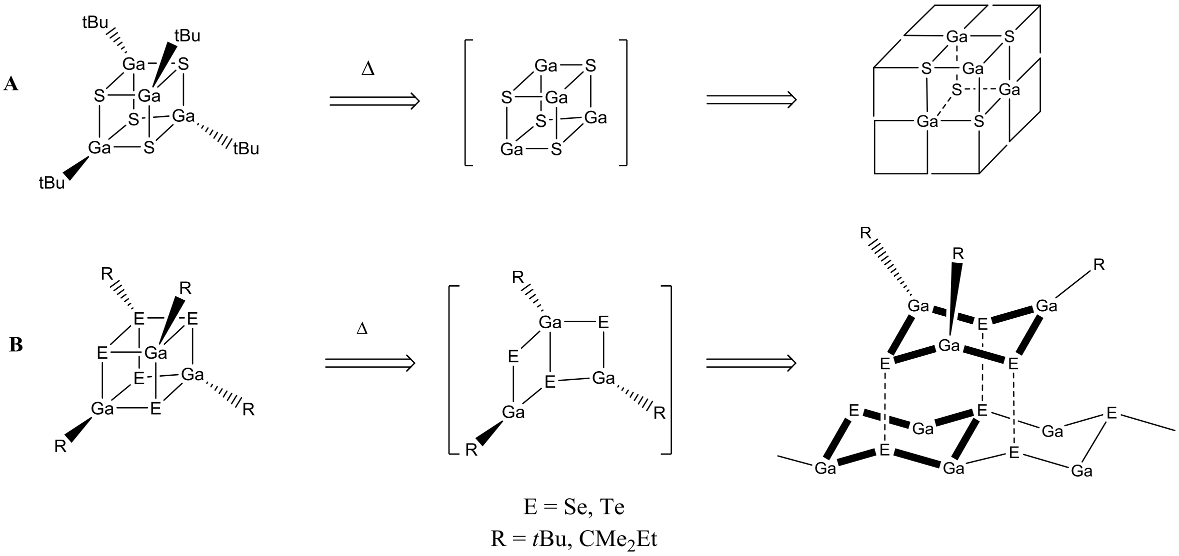
First attempts of thin films grown of III-VI materials go back to the 1990s with the work of Nomura's group. They suggested the alkylindium chalcogenolates $n\mathrm{Bu_2In(S}i\mathrm{Pr)}$ and $n\mathrm{BuIn(S}i\mathrm{Pr)_2}$, which are both liquid at room temperature, as potential SSP for the deposition of InS material.[6] They prepared thin films of tetragonal In_2S_3 material from $n\mathrm{BuIn(S}i\mathrm{Pr)_2}$ by usage of low-pressure horizontal cold-wall reactor on Si substrates. Optimal range of deposition temperature was found for amorphous InS material at 300 °C, crystalline In_2S_3 material in the range at 350 - 400 °C and mix of In_2S_3 material with predominated In_6S_7 material at 450 °C.[7] In 1992, Gysling and Wernberg exemplified the fact that the CVD process could produce metastable phases. They prepared indium selenide films on GaAs substrate by spraying a toluene solution of either $\mathrm{In(SePh)_3}$ or $\mathrm{Me_2In(SePh)}$. The former gave films of hexagonal In_2Se_3. Depending on the temperature the latter gave a new cubic face-centered phase at 365 °C, or the known hexagonal InSe phase with small quantities of the new cubic phase in the range of 400 - 470 °C.[8]

The most striking evidence of the potential to control film stoichiometry and phase, including the possibility of stabilizing phases was given by Barron and co-workers in 1992.[9] Using cubane-type tertbutylgallium sulfide $[t\mathrm{BuGa}(\mu\text{-S})]_4$ in an atmospheric pressure CVD experiment, the authors obtained the deposition of a new metastable cubic GaS. The precursor had previously been shown to be air stable (sublimate at 225 °C under atmospheric pressure) and had a pseudo cubane-type structure with Ga_4S_4 cluster core in the solid state.[10] The author also compared results obtained for the metal-organic CVD of GaS from three structurally distinct precursors, dimeric $[t\mathrm{Bu_2Ga}(\mu\text{-S}t\mathrm{Bu})]_2$, tetrameric $[t\mathrm{BuGa}(\mu\text{-S})]_4$ and heptameric $[t\mathrm{BuGa}(\mu\text{-S})]_7$, in order to gain further insight into phase control by molecular design.[11] As was expected $[(t\mathrm{Bu})\mathrm{Ga}(\mu\text{-S})]_4$ yielded the cubic GaS phase, but in a narrow temperature window at about 400 °C. At the same temperature SSP $[t\mathrm{Bu_2Ga}(\mu\text{-S}t\mathrm{Bu})]_2$ yielded the thermodynamically stable GaS hexagonal phase as poorly crystallized films. The heptameric precursor $[t\mathrm{BuGa}(\mu\text{-S})]_7$ yielded amorphous films only, consistent with the low C_3 symmetry of the Ga_7S_7 core, and with no possibility of ordered close packing. Relationship between precursor core cleavage and deposited phase was also studied with cubane SSP $[\mathrm{RGa}(\mu\text{-E})]_4$ (R = CMe, $\mathrm{CEtMe_2}$, $\mathrm{CEt_2Me}$; E = S, Se, Te). Summary of the gallium chalcogenides thin films deposited by CVD from the cubane SSP is showed in Table 1.[10]

Table 1: Summary of the gallium chalcogenide phases deposited by CVD method from the cubane SSP $[\mathrm{RGa}(\mu\text{-E})]_4$.

Precursor	**Deposited phase**
$[t\mathrm{BuGa}(\mu\text{-S})]_4$	cubic GaS
$[t\mathrm{BuGa}(\mu\text{-Se})]_4$	hexagonal GaSe
$[t\mathrm{BuGa}(\mu\text{-Te})]_4$	hexagonal GaTe

Use of $[RGa(\mu\text{-}E)]_4$ (E = Se, Te) resulted in the growth of the hexagonal GaE In contrast their sulfide analogues allowed grow of metastable cubic GaS. These observations prompted the following questions: First, the precursors had the same Ga_4E_4 core structure, why did the sulfide grows as a cubic phase but the selenide and telluride grow as hexagonal phases? The similarity of the structures for GaSe and GaTe films suggested, that their cubane precursors underwent decomposition via a similar reaction pathway, which was distinct from that of the sulfide precursor.[10]



Scheme 1: Schematic representation of the condensation of cubic Ga_4S_4 fragments to build up the cubic GaS phase (A) and trimeric Ga_3Se_3 fragments to build up the hexagonal GaSe phase (B).[10]

They proved that, growth of cubic GaS from $[RGa(\mu\text{-}S)]_4$ was as a consequence of the retention of the “Ga_4S_4” cubane core during deposition (see scheme 1A). On the other hand deposition from $[RGa(\mu\text{-}Se)]_4$ and $[RGa(\mu\text{-}Te)]_4$ involved decomposition loss of “RGaE”. The „$R_3Ga_3E_3$” moiety rearranged cyclohexane form, which was clearly related to the chair Ga_3E_3 conformation fragment present in hexagonal GaE (see scheme 1B).[10] It was evident, that structure and morphology of prepared film didn’t depend only on deposition method, but also on the structure of used SSP. From this reason, it was desirable to study synthesis of new SSP.

2.2 Intramolecularly coordinated organotin chalcogenides as precursors for IV-VI material deposited by spin coating

Our recent studies have dealt with the synthesis of N→Sn coordinated organotin chalcogenides (see fig. 1) which had well-defined stoichiometry of tin and chalcogens.[12]

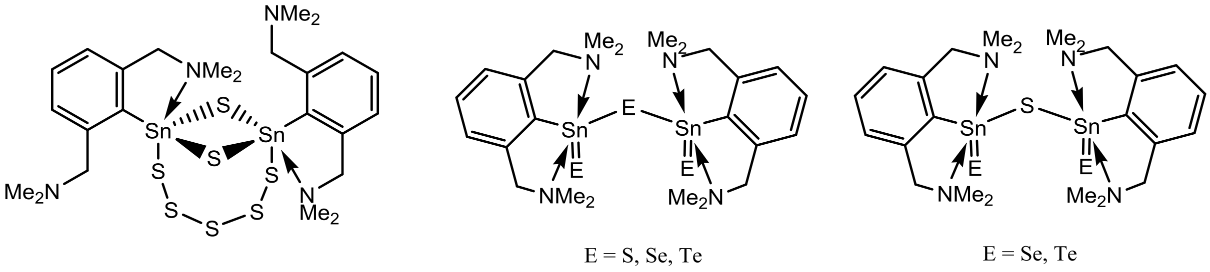


Figure 1: Intramolecularly koordinated organotin chalcogenides.[12]

These compounds were prepared as the products of the oxidation of the distannyne $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Sn]_2$ by chalcogens.[12] The isolation of the latter compounds raised the question of whether they can be applied as useful starting materials for the deposition of thin film. Compounds $[(\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnSe)_2(\mu\text{-}S)]$ a $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnS]_2S_5$ were tested as potential single source precursors for the deposition of SnS, SnSSe semiconducting thin films by using the spin coating method. Molecule structure of compounds is showed in figure 2.[13]

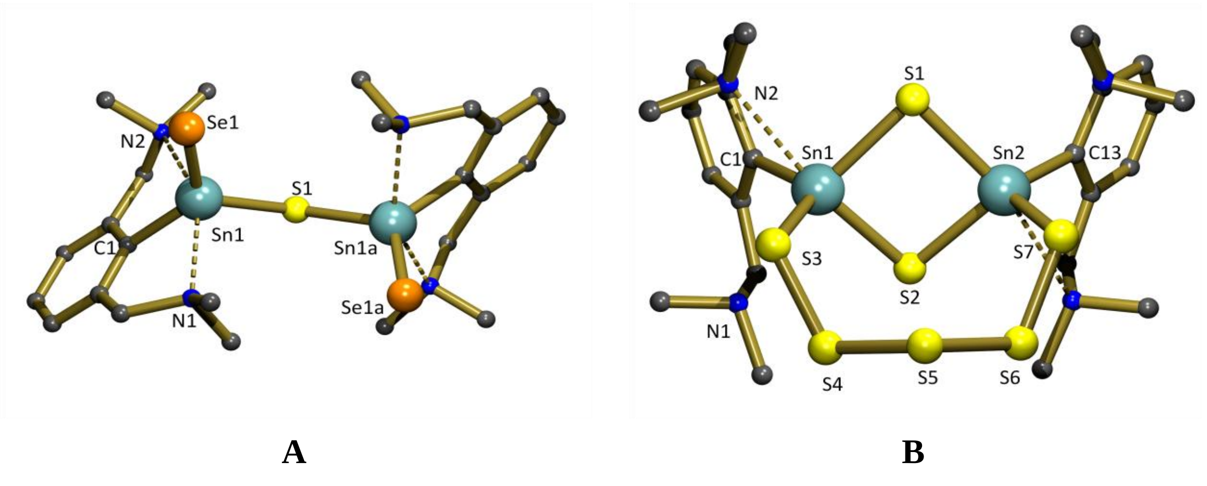


Figure 2: Molecule structure of compounds $[(\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnSe)_2(\mu\text{-}S)]$ (A) a $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnS]_2S_5$ (B).[13]

The thermogravimetric analyses (TG) showed the multistep decomposition of compounds $[(\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnSe)_2(\mu\text{-}S)]$ and $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnS]_2S_5$ (see tab. 2).[13]

Table 2: TG analyses of compounds [({2,6-($Me_2NCH_2)_2C_6H_3$}SnSe$)_2$(μ-S)] and [{2,6-($Me_2NCH_2)_2C_6H_3$}SnS$]_2S_5$ showing expected and observed mass losses (%)

precursor	T_{dec} (°C)	Expected m. l. (%)	Observed m. l. (%)
[({2,6-($Me_2NCH_2)_2C_6H_3$}SnSe$)_2$(μ-S)]	11 - 423	57	59
[{2,6-($Me_2NCH_2)_2C_6H_3$}SnS$]_2S_5$	114 - 281	78	73

Compound [({2,6-($Me_2NCH_2)_2C_6H_3$}SnSe$)_2$(μ-S)] started decomposing at 11 °C and continued till 423 °C. Total expected (57%) and observed (59%) mass losses indicated the formation of $Sn_2S_2Se_2$ material after complete decomposition. Compounds [{2,6-($Me_2NCH_2)_2C_6H_3$}SnS$]_2S_5$ started decomposing at 114 °C and continued till 281 °C, respectively. The total expected (78%) and observed (73%) mass losses indicated formation of SnS_2 material after complete decomposition.[13]

Compound [({2,6-($Me_2NCH_2)_2C_6H_3$}SnSe$)_2$(μ-S)] was deposited by using the spin coating method. X-ray diffraction analysis proved that all the prepared SnSSe thin films were amorphous, and SEM images of the prepared thin films suggested that they are homogeneously spread out on the substrate. The spinning speed strongly influenced the surface roughness of the deposited SnSSe thin films, as indicated by the AFM images (see fig. 3).[13]

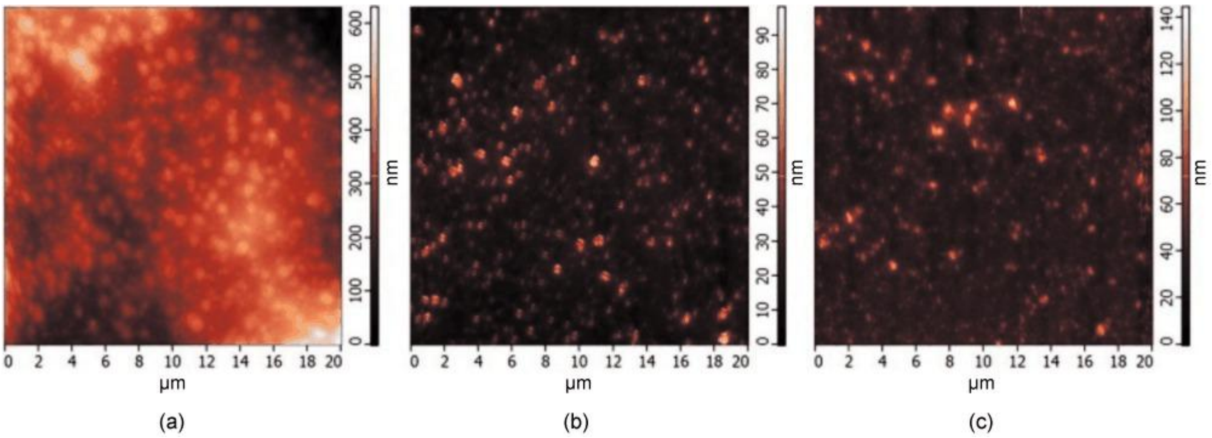


Figure 3: AFM images of the surface of drop-casted (A), spin coated 1500 rpm (B) and spin coated 2500 rpm (C) thin films SnSSe.[13]

While drop-casted films showed the highest peak to peak roughness (see fig. 3A), the surface of spin-coated films revealed reduced roughness. The AFM images showed that the lowest surface roughness of deposited thin films was found for a spinning speed of 1500 rpm (see fig. 3B). EDX spectroscopy also revealed the dependence of the chemical composition of the deposited material on the spinning speed. It was showed that the concentration of Sn and S decreases with the increase of spinning speed and the opposite trend was observed for Se atom content. EDX spectroscopy thus defined that the composition of a SnSSe semiconducting thin film spin coated at 1500 rpm is $Sn_{42}S_{41}Se_{17}$. The optical constants as well as geometric parameters of the 1500 rpm spin coated $Sn_{42}S_{41}Se_{17}$ thin film were further studied by variable-angle spectroscopic ellipsometry, which showed that the thickness of the thin film was approximately 40 nm with calculated optical band gap energy E_g = 1,79 eV.[13]

Compound $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnS]_2S_5$ was deposited by using the spin coating method. The best results were in the case of thin films prepared at a spinning speed of 1500 rpm. EDX spectroscopy of these films revealed a composition $Sn_{32}S_{68}$, which was very close to SnS_2 material. XRD analysis showed that the prepared SnS_2 thin films were amorphous and SEM images indicated the good quality of the thin films which were homogeneously spread out on the substrate surface (see fig. 4).[13]

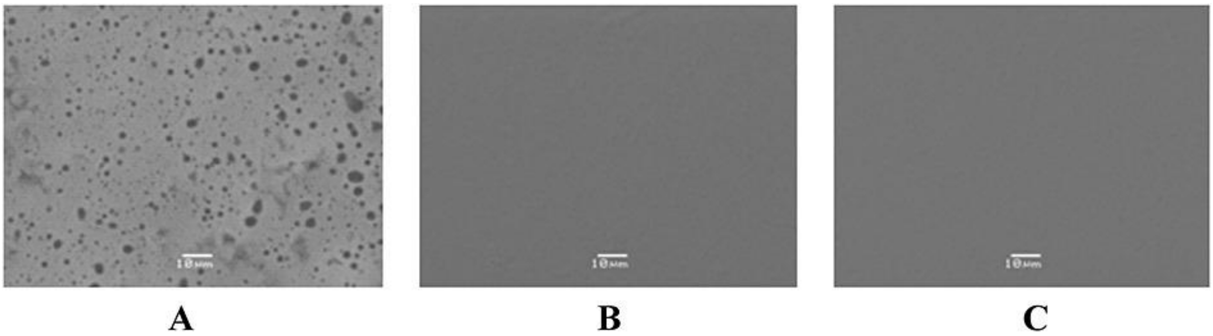


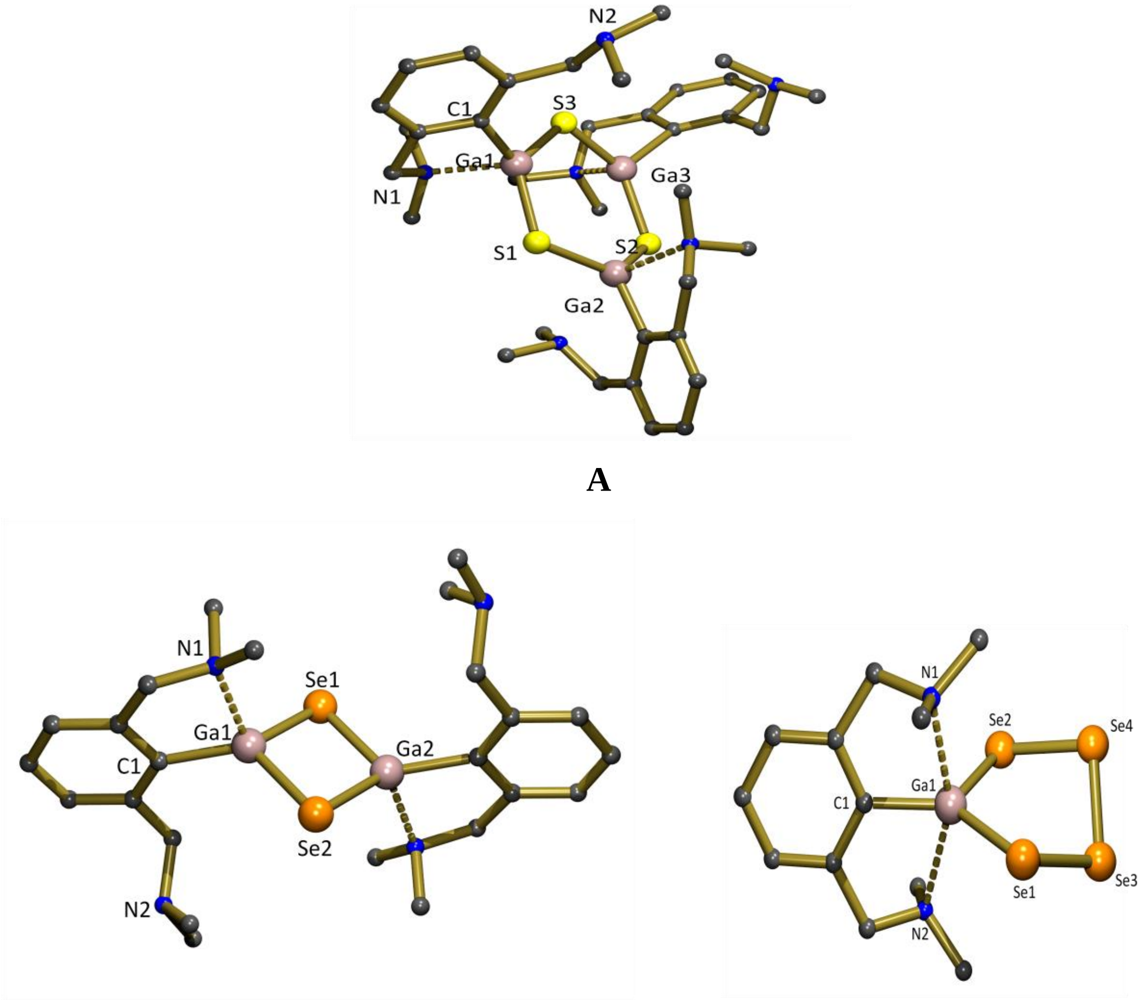
Figure 4: SEM images of the surfaces of drop-casted (A), 3000 rpm spin coated (C) and 5000 rpm spin coated (C) thin films SnS_2.[13]

The thickness of the deposited material depended on spinning speed. The thickness of SnS_2 films decreased with an increase of the spinning speed. The optical constants as well as film thickness of the $Sn_{32}S_{68}$ thin film spin coated at 1500 rpm were further studied using variable angle spectroscopic ellipsometry. The thickness of the thin film SnS_2 spin coated at 1500 rpm was approximately 50 nm (including the surface roughness) with an optical band gap energy E_g = 2.46 eV.[13]

Intramolecularly coordinated organotin chalcogenides $[(\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnSe)_2(\mu\text{-}S)]$ a $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnS]_2S_5$ were successfully used as SSP for the deposition of $Sn_{42}S_{41}Se_{17}$ and $Sn_{32}S_{68}$ thin films by spin coating method. For this reason is desirable to extend study of synthesis of new N→M intramolecularly coordinated (M = Ga, In) organometallic chalcogenides of 13. group elements, which can be further used as potential SSP for deposition of thin film III-VI material.

3 Aim of the dissertation thesis

Amorphous chalcogenide thin films fabricated usually through PVD techniques are today an exciting field for innovations. It was previously shown that the deposition of crystalline III-VI materials from SSP by CVD techniques is already known. In contrast, the deposition of amorphous III-VI layers has been reported infrequently and from this point of view it seems to be reasonable to investigate an alternative route for the fabrication of amorphous chalcogenides thin films. In master thesis we have already investigated synthesis of N→Ga intramolecularly coordinated organogallium chalcogenides. Isolated compounds were differ in their structure and representation of required elements in their structure as is shown in the figure 5.[14]



A

B

C

Figure 5: Molecule structures of compounds [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}Ga(μ-S)]$_3$ (A), [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}Ga(μ-Se)]$_2$ (B) a {2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}Ga(κ^2-Se$_4$) (C).[15]

The molecule structure of compound [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}Ga(μ-S)]$_3$ revealed trimeric structure with a six-membered Ga$_3$S3 ring, whereas compound [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}Ga(μ-Se)]$_2$ revealed a dimeric nature with a central four-membered Ga$_2$S$_2$ ring. The molecular structure of {2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}Ga(κ^2-Se$_4$) showed a monomeric structure with an unusual five-membered GaS_4 ring. The aim of this dissertation thesis was to examine the thermal properties of these prepared N → Ga coordinated organogallium chalcogenides. Based on the measurements, the appropriate SSP were chosen and used for the deposition of thin films III-VI materials by the spin coating method.

Another aim of this work was to synthesize new N → M (M = Ga, In) intramolecularly coordinated organometallic chalcogenides $[L^{1-3}M(\mu\text{-}E)]_n$ (E = S, Se, Te) (see fig. 6A), which were structurally different, depending on used L^{1-3} ligand (see fig. 6B).

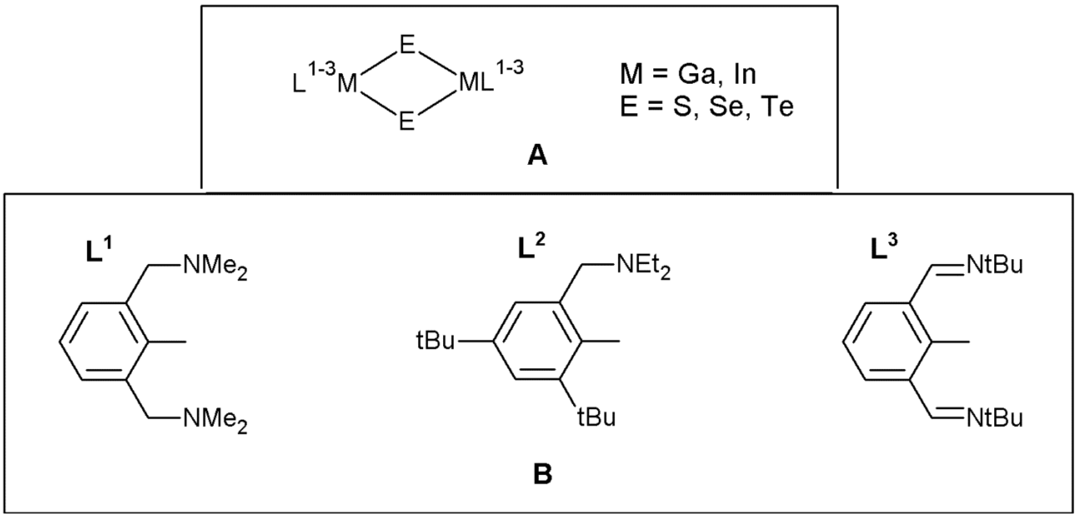
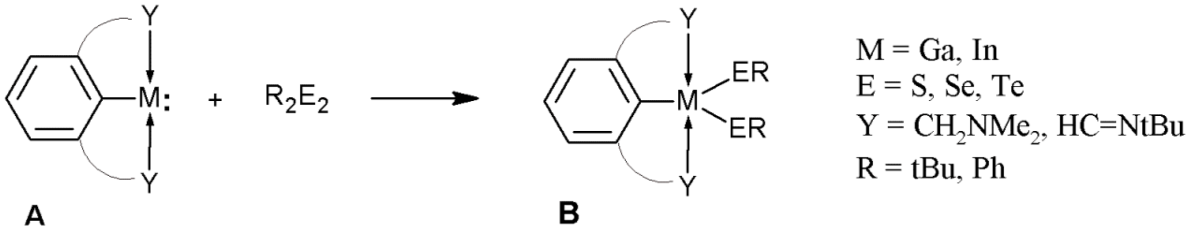


Figure 6: Suggested structure of N → M intramolecularly coordinated compounds $[L^{1-3}M(\mu\text{-}E)]_n$ (E = S, Se, Te) (A) and used chelating ligands $L^1 = \{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}^-$, $L^2 = \{4,6\text{-}t\text{Bu}_2\text{-}2\text{-}(Et_2NCH_2)C_6H_2\}^-$ and $L^3 = \{2,6\text{-}(t\text{BuN=CH})_2C_6H_3\}^-$.

For prepared compounds, we studied their structures, thermal properties and their potential use as SSP for the deposition of thin films III-VI material by the spin coating method.

Literary research has shown that the relatively intensively studied SSP group forms chalcogenolate compounds of the 12th, 13th and 14th groups. However, it was problematic, because these compounds were often involved in higher polymeric units. For this reason, another objective was an attempt to prepare monomeric chalcogenolates of 13th group elements $L^{1,3}M(ER)_2$ (see scheme B). The N → M intramolecular coordination from ligands $L^{1,3}$ to metal centre M could prevented intermolecular interactions between neighbouring molecules, thus the formation of higher polymeric units could be avoided (see scheme 2).



Scheme 2: The synthesis of monomeric chalcogenolates of 13th group elements $L^{1,3}M(ER)_2$ (B) by oxidation reaction of low valent species of 13th group elements $[L^{1,3}M:]$.

As is shown in scheme 2, the synthesis of such compounds $L^{1,3}M(ER)_2$ could be utilized by the oxidation reactions of the low valent species $[L^{1,3}M:]$ with R_2E_2 (E = S, Se, Te; R = *t*Bu, Ph) For this reason, the synthesis of compounds containing $L^{1,3}$ ligands and elements of 13th group in oxidation state + I (see scheme 2A) was also studied in the dissertation thesis. Reaction of such compounds $[L^{1,3}M:]$ with Ph_2E_2 would result in the preparation of monomeric compounds $L^{1.3}M(EPh)_2$ and the finding of a universal process for the preparation of monomeric chalcogenolates of the 13th group elements.

4 Results and discussion

4.1 Synthesis and characterization of starting organogallium and organoindium dichlorides $L^{1-3}MCl_2$ (M = Ga, In)

The successful isolation of the organogallium and organoindium dichlorides is a key factor for the subsequent preparation of 13th group chalcogenides. For this reason, the first aim of the research was focused on the preparation of the N → M (M = Ga, In) intramolecularly coordinated organogallium and organoindium dichlorides $L^{1-3}MCl_2$ (L^1 = $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}^-$, L^2 = $\{4,6\text{-}t\mathrm{Bu}_2\text{-}(Et_2NCH_2)C_6H_2\}^-$ and L^3 = $\{2,6\text{-}(t\mathrm{Bu}N{=}CH)_2C_6H_3\}^-$) as is shown in figure 7.

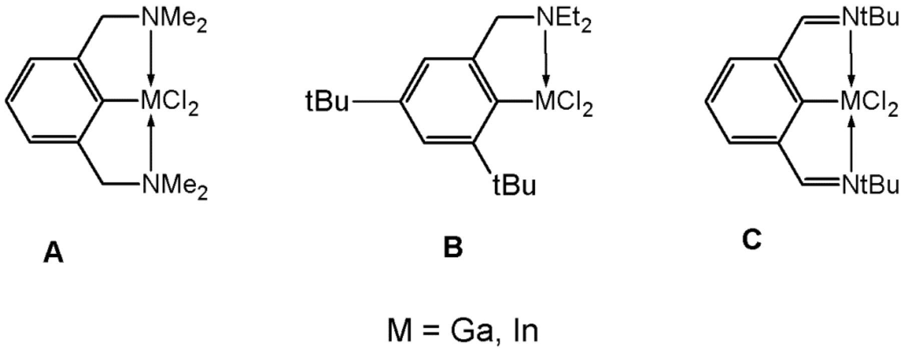


Figure 7: The N → M (M = Ga, In) coordinated organogallium and organoindium dichlorides $L^{1-3}MCl_2$ (L^1 = $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}^-$ (A), L^2 = $\{4,6\text{-}t\mathrm{Bu}_2\text{-}(Et_2NCH_2)C_6H_2\}^-$ (B) and L^3 = $\{2,6\text{-}(t\mathrm{Bu}N{=}CH)_2C_6H_3\}^-$) (C).[15]

The compounds L^1GaCl_2 (**1**),[15] L^1InCl_2 (**2**)[16] and L^2GaCl_2 (**3**)[14] were prepared according to the literature and their structures are shown in figure 8.

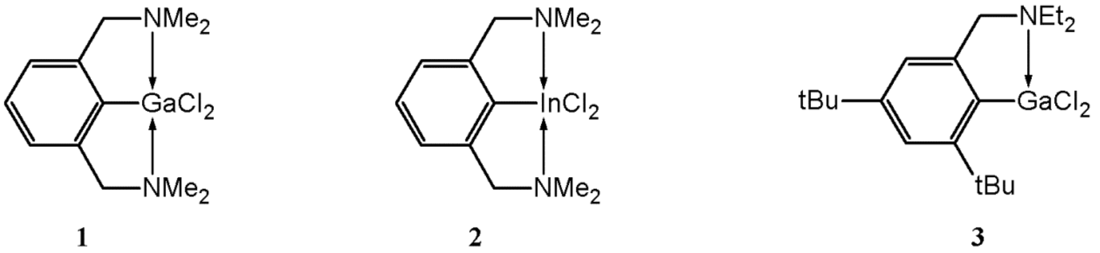
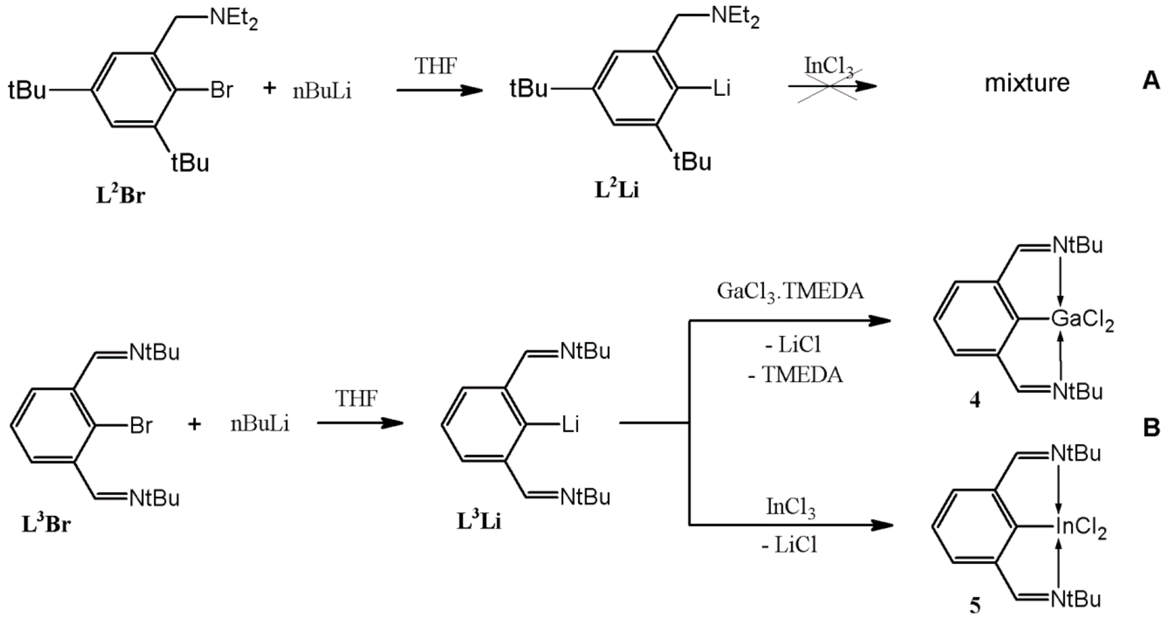


Figure 8: Structure of compounds L^1GaCl_2 (**1**),[15] L^1InCl_2 (**2**)[16] and L^2GaCl_2 (**3**).[14]

Compound L^2InCl_2 has not been published yet, thus the reaction of an organolithium compound L^2Li with $InCl_3$ in THF at -78 °C was performed. However, a mixture of products was isolated (see scheme 3A). Therefore it is obvious that the L^2 ligand is not aqueous for the synthesis of N → In coordinated organoindium dichlorides. Compounds L^3MCl_2 (M = Ga, In) has not been published in the literature as well. For this reason reaction of organolithium compound L^3Li with *in situ* prepared complex [$GaCl_3$.TMEDA] in THF at -90 °C was done and resulted in the isolation of L^3GaCl_2 (**4**) (see scheme 3B). Analogous reaction of organolithium compound L^3Li with $InCl_3$ in THF at -90 °C was carried out and led to the isolation of L^3InCl_2 (**5**) (see scheme 3B).



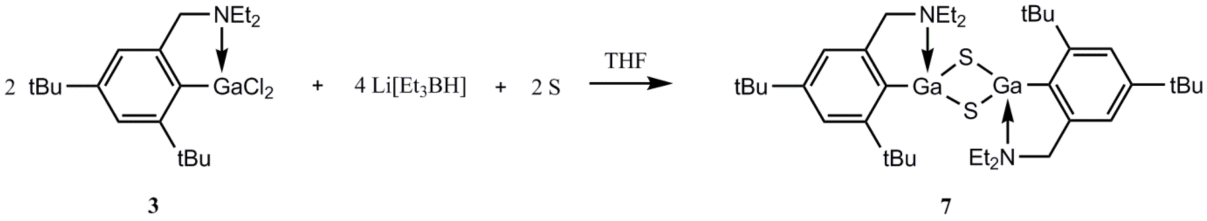
Scheme 3: Synthesis of starting compounds L^3GaCl_2 (**4**) and L^3InCl_2 (**5**).

The prepared compounds **4** and **5** were characterized by ^1H and ^{13}C NMR spectroscopy and were determined by X-ray diffraction analysis. In the ^1H NMR spectra of compounds **4** and **5**, one signal of the methyl $C(CH_3)_3$ groups with a chemical shift δ 1.46 (**4**) and 1.53 (**5**) ppm and one signal of *H*C=N groups with the chemical shift δ 8.06 (**4**) and 8.52 (**5**) ppm were detected. In the ^{13}C NMR spectra of compounds **4** and **5**, one signal of the methyl $C(CH_3)_3$ groups with the chemical shift of δ 30.2 (**4**) and 30.4 (**5**) ppm and the HC=N groups with the chemical shift of δ 158.2 (**4**) and 158.5 (**5**) ppm were presented.

4.2 Deposition of thin film III-VI materials

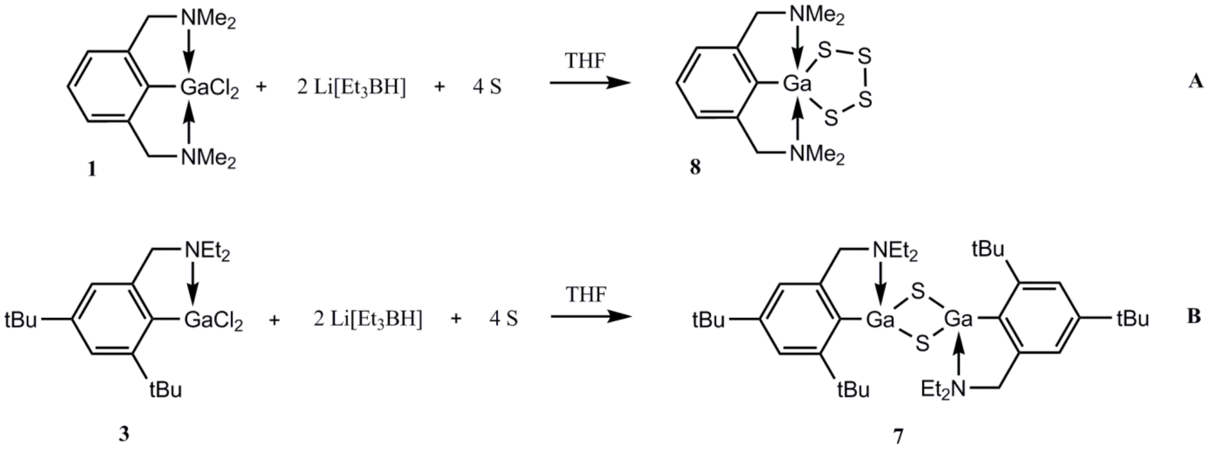
4.3 Intramolecularly coordinated organogallium sulfides as suitable single source precursors for deposition of thin films GaS

The starting compounds $L^{1,2}GaCl_2$ (**1**,**3**) were further used to synthesis of N → Ga coordinated organogallium chalcogenides, due to the easy preparation. As was mentioned earlier, compound $[L^1Ga(\mu\text{-}S)]_3$ (**6**) was prepared according to the literature by reacting of Li_2S with compound **1** in THF.[14] The compound $[L^2Ga(\mu\text{-}S)]_2$ (**7**) was prepared by analogous reaction of starting compound **3** with Li_2S in THF (see scheme 4).



Scheme 4: Synthesis of compound $[L^2Ga(\mu\text{-}S)]_2$.[15]

Despite the different structures, both complexes **6** and **7** contain Ga and S atoms in a 1:1 ratio. To change the stoichiometry of the Ga and S atoms in the structure, the reaction of **1** with Li_2S_4 was performed to give N→Ga coordinated organogallium tetrasulfide $L^1Ga(\kappa^2\text{-}S_4)$ (**8**) (see scheme 5A).



Scheme 5: Synthesis of compound $L^1Ga(\kappa^2\text{-}S_4)$.

On the other hand, analogous reaction of compound **3** with Li_2S_4 in THF resulted in the isolation of compound **7** (see scheme 5b). The molecular structure of both prepared compounds **7** and **8** was studied by X-ray structure analysis from monocrystalline materials (see figures 9A, B).

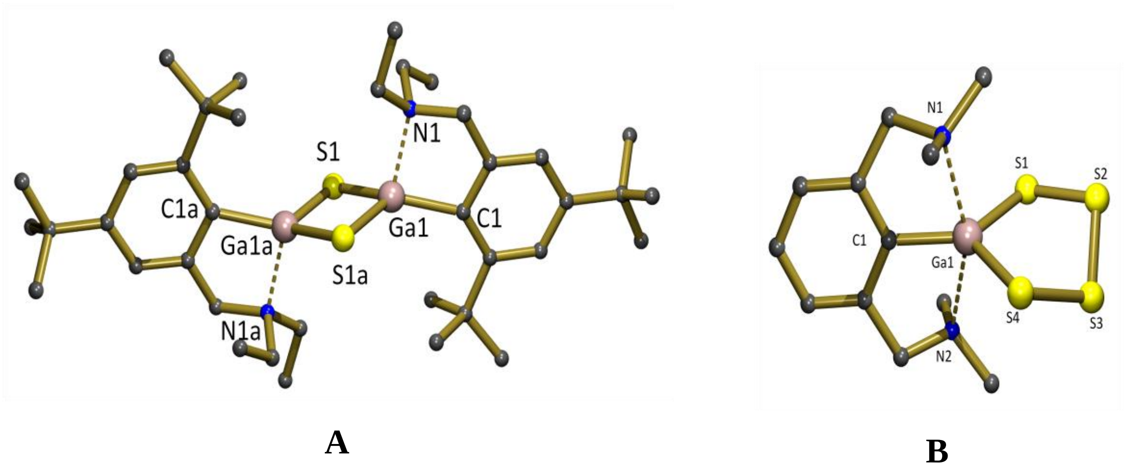


Figure 9: Molecule structure of compounds **7** and **8**.

As compounds **6** and **7** differ mutually in their structures, with Ga:S atoms in the 1:1 ratio, and complex **8** contains Ga:S atoms in the 1:4 ratio. The above mentioned complexes were studied as SSP for GaS thin films deposition and showed the multistep decomposition of compounds. The best result from thermogravimetric analysis (TG) was obtained with compound **6**, which started to decompose at 160°C and continues until 350°C. The total expected (57%) and observed (55%) mass losses indicated the formation of GaS after complete decomposition. For this reason deposition of GaS thin films by spin-coating method was done by use of compound **6** as SSP. The propyleneamine solution of **6** (c = 0.08 molL^{-1}) was used for the preparation of the thin GaS films. The morphology of the layers was of good quality as was indicated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM (see figure 10A, B) and AFM (see figure 10C, D) data showed the smooth surface of thin films, without cracks and corrugations.

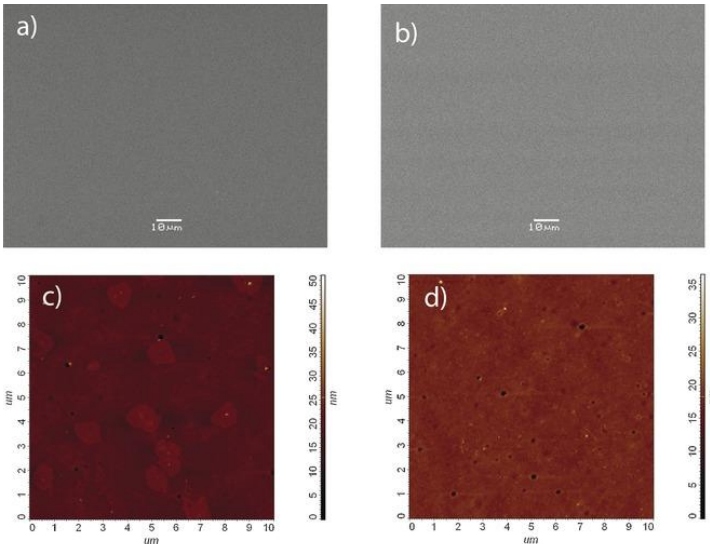


Figure 10: SEM images and AFM images of the GaS thin films surface of 1500 rpm (A, C) and 2500 rpm (B, D) prepared by spin-coating from precursor **6**.

Root mean square roughness determined by AFM was found to be lower than ~2 nm. Energy-dispersive X-ray (EDX) spectroscopy corroborates the results of the elemental analysis and shows that the composition of the resulting semiconducting thin film is approx. $Ga_{50}S_{50}$. EDX spectroscopy also revealed the minimal dependence of the chemical composition of the deposited material on the spinning speed (see tab. 3).

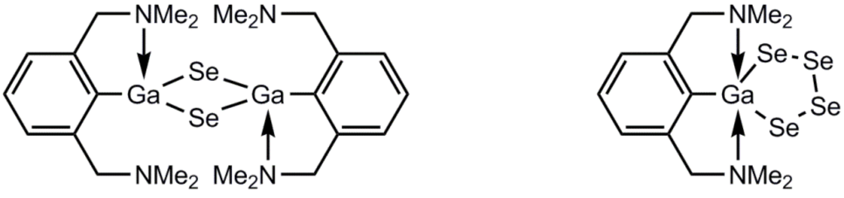
Table 3: Characteristics of spin-coated GaS films deposited at 1500, 2000 and 2500 rpm: chemical composition (±1 at %), film thickness, optical band gap energy (E_{opt}), refractive index (at l = 1.5 mm), and root-meansquare (RMS) roughness values.

Property	**Spinning speed (rpm)**		
	1500	2000	2500
Ga (at%), EDX	48,5	50,2	50,0
S (at%), EDX	51,5	49,8	50,0
Film thickness (nm), VASE	260,9 ± 0,3	209,6 ± 0,4	265,1 ± 0,3
E_g (eV), VASE	3,37 ± 0,01	2,99 ± 0,13	3,03 ± 0,03
Refractive index, VASE	1,65 ± 0,01	1,65 ± 0,01	1,65 ± 0,01
RMS (nm), AFM	1,48 ± 0,01	1,97 ± 0,01	0,99 ± 0,01

It is evident that the ratio of Ga and S atoms in SSP **6** is retained in the prepared GaS thin films. XRD analysis of the deposited thin films indicates that the prepared materials are amorphous. The optical functions of the prepared GaS layers as well as their thicknesses were obtained from the analysis of variable angle spectroscopic ellipsometry (VASE) data measured by using an ellipsometer with automatic rotating analyser on samples grown on silicon substrates. The thickness and optical band gap energy (E_{opt}) of GaS thin films are dependent on the spinning speeds, ranging from 209.6±0.4 to 265.1±0.3 nm and E_{opt} = 2.99±0.13 to 3.37±0.01 eV (see tab. 3). The obtained values of E_{opt} correlate with those found for amorphous GaS thin films prepared by vacuum evaporation of crystalline GaS (2.7 eV),[17] and by modulated flux deposition of Ga and S atoms (3.2 – 3.6 eV).[18]

4.4 Intramolecularly coordinated organogallium selenides as suitable single source precursors for deposition of thin films GaSe

The preparation of crystalline GaSe and Ga_2Se_3 thin films using SSP was the most explored by the prof. Baron who used the CVD method. However, the first amorphous layers of Ga_2Se_3 material were produced recently using pulsed laser deposition on a glass substrate.[19] For this reason, we have focused on the synthesis of new compounds that would serve as precursors for amorphous thin films GaSe and Ga_2Se_3. In the diploma thesis, N → Ga coordinated organogallium selenides $[L^1Ga(\mu\text{-}Se)]_2$ (**9**) and $L^1Ga(\kappa^2\text{-}Se)_4$ (**10**) containing chelating ligand L^1 were synthesized (see figure 11).

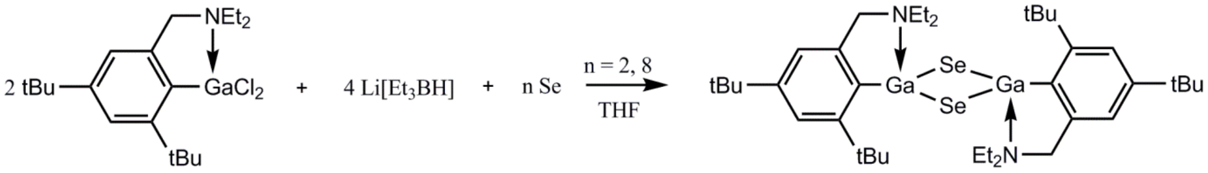


9

10

Figure 11: Structure of synthesized compounds $[L^1Ga(\mu\text{-}Se)]_2$ (**9**) and $L^1Ga(\kappa^2\text{-}Se)_4$ (**10**).

In the dissertation thesis I studied the preparation of N → Ga coordinated organogallium selenides containing chelating ligand L^2. Reaction of starting compound **3** with Li_2Se in THF led to isolation of compound $[L^2Ga\ (\mu\text{-}Se)]_2$ (**11**) (see scheme 6).



3

11

Scheme 6: Synthesis of compound $[L^2Ga(\mu\text{-}Se)]_2$ (**11**).

The molecular structure of compound **11** is shown in figure 12.

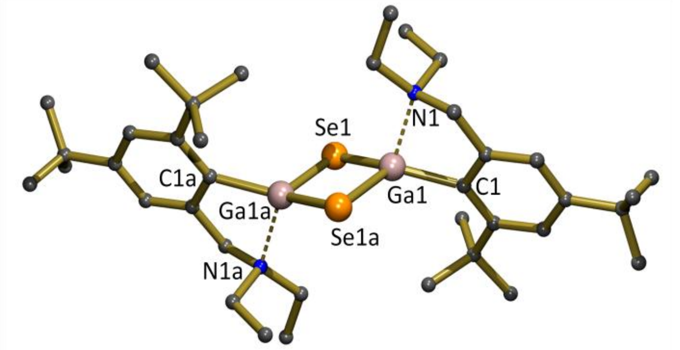


Figure 12: Molecular structure of compound **11.**

While compounds **9** and **11** contained Ga and Se atoms in 1:1 ratio, the complex **10** contained Ga and Se atoms in 1:4 ratio. The TG analyses showed the multistep decomposition of compounds **9** and **10** while compound **11** started decomposing at 250 ºC and continued till 320 ºC as one step decomposition. This clearly demonstrate substantial influence of ligands $L^{1,2}$ on suitability of studied SSPs. For compound **11**, total expected (65%) and observed (62%) mass losses indicate the formation of GaSe after complete decomposition. Initially, compound **11** was tested as potential SSP for the preparation of GaSe thin films using the spin-coating method. The propylamine solution of compound **11** ($c = 0.06\ mol.L^{-1}$) was used for the preparation of the amorphous GaSe thin films. The morphology of the layers was in good quality as was indicated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM (see figure 13 A) and AFM (see figure 13 B) data showed smooth surface of thin films, without cracks and corrugations. Root mean square roughness determined by AFM was found to be lower than ~ 8 nm.

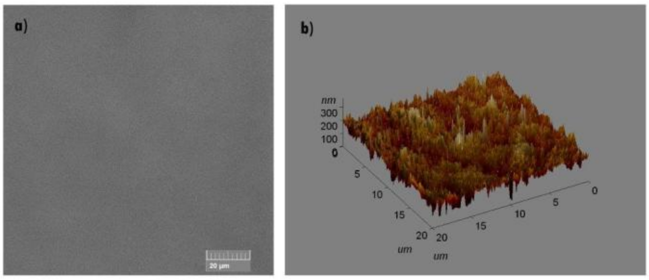


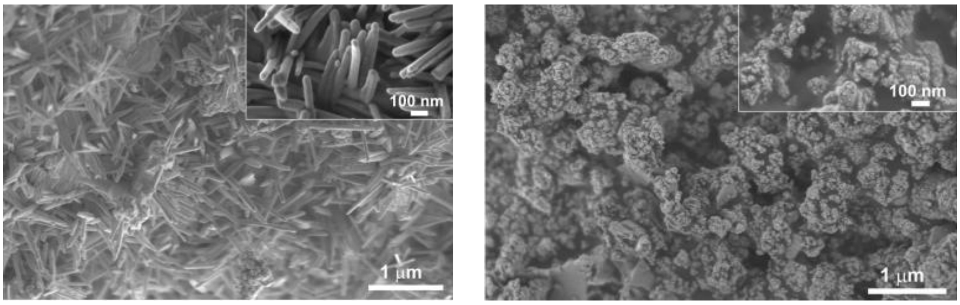
Figure 13: SEM image (A) and AFM (B) image of the surface of 1500 rpm spin-coated GaSe thin films from precursor **11**.

Energy dispersive X-ray spectroscopy (EDX) revealed that the composition of the resulting semiconducting thin films is approx. $Ga_{50}Se_{50}$ respectively. EDX analysis also revealed minimal dependence of the chemical composition of the deposited material on the spinning speed (see tab. 4).

Table 4: Characteristics of spin coated GaSe films deposited at 1500 and 2000 rpm: chemical composition (±1 at. %), film thickness, refractive index (at $\lambda = 1.5\ \mu m$), and root-mean-square (RMS) roughness values.

Property	Spinning speed (rpm)	
	1500	2000
Ga (at. %), determined via EDX	54.9	54.2
Se (at. %), determined via EDX	45.1	45.8
film thickness (nm), determined via VASE	23.7±0.9	50.1±0.5
refractive index, determined via VASE	2.23±0.01	2.26±0.01
E_{opt} [eV], determined by VASE	2.42±0.1	2.41±0.1
RMS (nm), determined via AFM	8.09±0.01	6.39±0.01

It is evident that the ratio of Ga and Se atoms in SSP is retained in the prepared GaSe thin films. XRD analyses of deposited thin films indicated, that the prepared materials are amorphous. Optical functions of prepared GaSe layers as well as their thicknesses were obtained from the analysis of variable angle spectroscopic ellipsometry (VASE). The refractive index for amorphous GaSe thin films (n from 2.23 to 2.26 at $\lambda = 1.5$ µm) was found to be independent on spinning speeds (see tab. 4). In addition, the value is close to those found for amorphous GaSe thin films produced by vacuum evaporation (n ≈ 2.41 at $\lambda = 1.6$ µm).[20] Since the TG analyses suggested low temperature of the decomposition of precursor **11**, the attempts to prepared GaSe material from solution of SSP **11** were carried out. Heating of octadecylamine solution of compound **11** at 350°C provided the crystalline monoclinic Ga_2Se_3. Optical diffuse reflectance UV/Vis/NIR spectroscopy was performed for the $Ga_{34.7}Se_{65.3}$ to estimate the optical band gap energy $E_{\text{opt}} = 2.56$ eV. This value is higher than value for macroscopic cubic single crystal (~2.07 eV)[21] but correspond well to the band-gap values of zigzag-line vacancy-ordered crystal Ga_2Se_3 (~2.56 eV).[22] The SEM analysis indicates that the Ga_2Se_3 material is formed as an interesting needle structure, as shown in fig. 14A. The needles have an average length of 550 ± 150 nm. Moreover, the addition of PVP into the octadecylamine solution of **11** provided the crystalline monoclinic Ga_2Se_3 in the form of agglomerated particles. By analyses of sets of SEM images, it was revealed that the agglomerated particles have an average diameter of 600 ± 150 nm (see figure 14B).



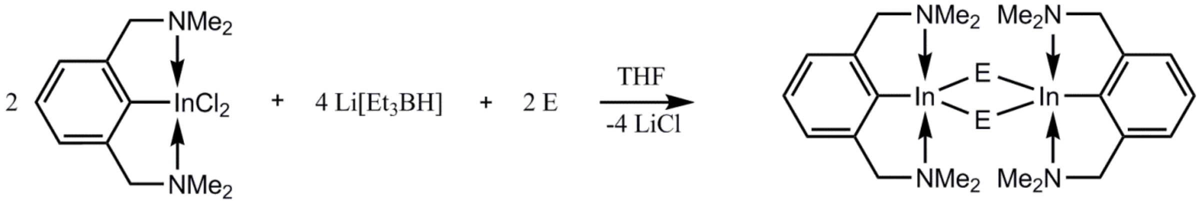
A **B**

Figure 14: SEM images of Ga_2Se_3 material obtained from ODA solution (A) and ODA/PVP solution (B) of compound **11** at 350°C.

During the reaction yielding Ga_2Se_3, PVP influences the structure of the resulting material, but has no influence on the crystallinity of the resulting material. Since the heating of solution of **11** can smoothly provide monoclinic Ga_2Se_3 material, we wondered if SSP **11** can be used as organometallic way of doping of semiconductors.

4.5 Intramolecularly coordinated organoindium chalcogenides as suitable single source precursors for thin films III-VI material

In previous chapters 4.3 and 4.4, we have convinced that N → Ga intramolecularly coordinated organogallium chalcogenides can be used as SSPs for the preparation of thin films of III-VI materials by the spin coating method. For this reason, we decided to extend the study also to the organoindium chalcogenides containing in the structure chelating ligand L^1. Reaction of compound **2** with Li_2E (E = S, Se, Te) in THF resulted in the isolation of poorly soluble intramolecularly coordinated compounds $[L^1In(\mu\text{-}S)]_2$ (**12**), $[L^1In(\mu\text{-}Se)]_2$ (**13**) and $[L^1In(\mu\text{-}Te)]_2$ (**14**) (see scheme 7).

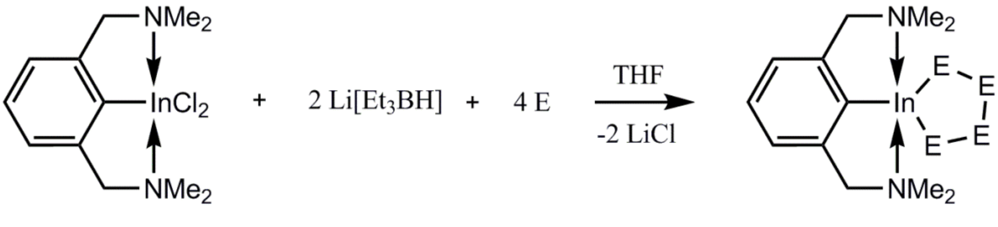


2

E = S (**12**), Se (**13**), Te (**14**)

Scheme 7: Synthesis of compounds $[L^1In(\mu\text{-}E)]_n$ (E = S (**12**), Se (**13**), Te (**14**)).

Compounds **12**, **13** and **14** were characterized by ^1H NMR spectroscopy and **14** by X-ray diffraction analysis Compounds **12**, **13** and **14** were poorly soluble in organic solvents (the highest concentration of c = 9.5.10-3 mol^{-1}) and contained In and E ratio 1:1. In the previous chapters, the preparation of monomeric organogallium tetrachalcogenides **8** and **10** containing a ratio Ga and E 1:4 were done. For this reason, analogous reactions were also performed with compound **2**. Reaction of compound **2** with Li_2E_4 (E = S, Se) resulted in the isolation of $L^1In(\kappa^2\text{-}S_4)$ (**15**) and $L^1In\ (\kappa^2\text{-}Se_4)$ (**16**) (see scheme 8).

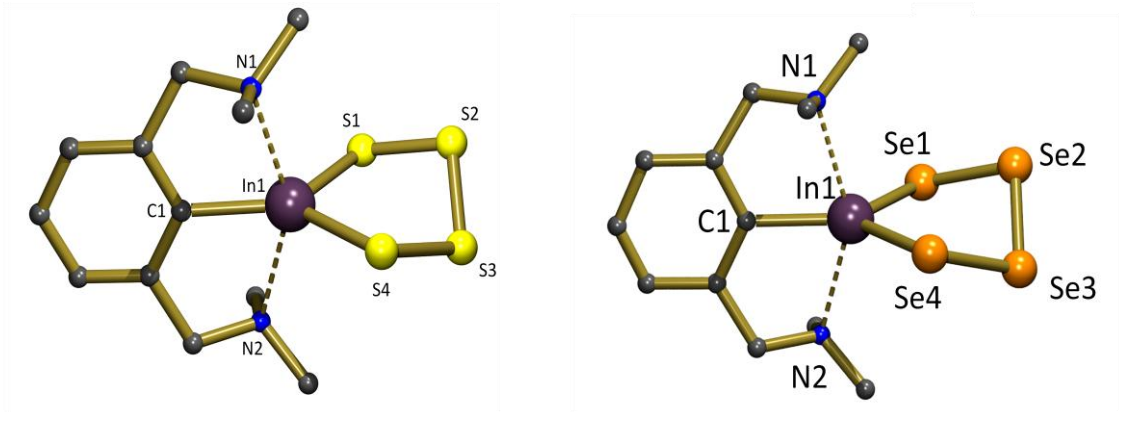


2

E = S (**15**), Se (**16**)

Scheme 8: Synthesis of compounds $L^1In(\kappa^2\text{-}E_4)$ (E = S (**15**), Se (**16**)).

Compounds **15** and **16** were characterized by multinuclear NMR spectroscopy and X-ray diffraction analysis. The molecular structures of compounds **15** and **16** are shown in figure 15.



A **B**

Figure 15: Molecular structure of compounds **15** (A) and **16** (B).

Unlike compounds **12**, **13** and **14**, compounds **15** and **16** showed sufficient solubility in organic solvents, but compound **16** decomposed in solution. The only potentially suitable precursor was therefore compound **15**. The TG analysis of compound **15** is shown in figure 16.

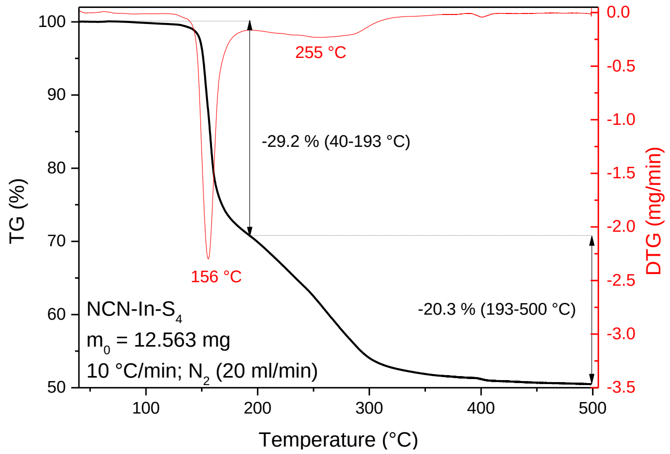
Precursor – TG analysis	**Expected material**
$L^1In(\kappa^2\text{-}S_4)$ (**15**)  	**In_2S_3** Theoretical loss: 38 % **InS** Theoretical loss: 34 % Observed: 49 % 100 – 450 °C

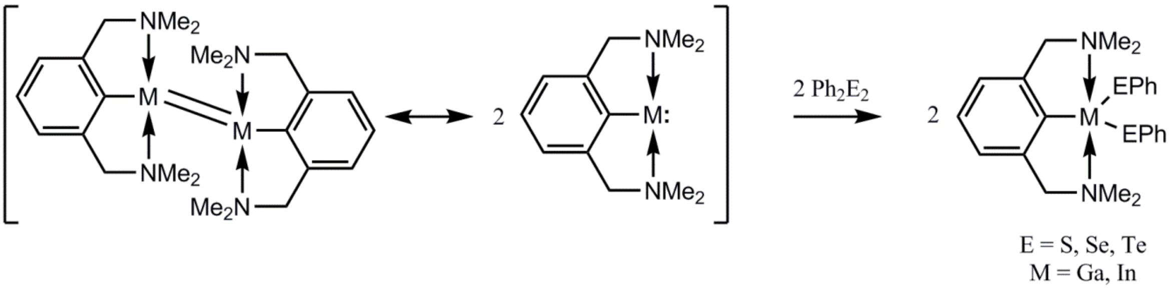
Figure 16: TG analysis of precursors $L^1In(\kappa^2\text{-}Se)_4$ (**15**).

TG analysis showed a multistep decomposition of precursor **15** with decomposition at 100 °C and end at 450 °C. The measurement showed the total weight loss of 49% over expected theoretical weight loss of 66% with complete decomposition and residual InS material. The experimentally determined weight loss did not correspond to the theoretically calculated loss required to prepare InS material. For this reason, compound **15** was not a suitable precursor for the preparation of thin films III-VI material by the spin coating method.

4.6 Preparation of N → M (M = Ga, In) intramolecularly coordinated low valent compounds [$L^{1,3}$M:]

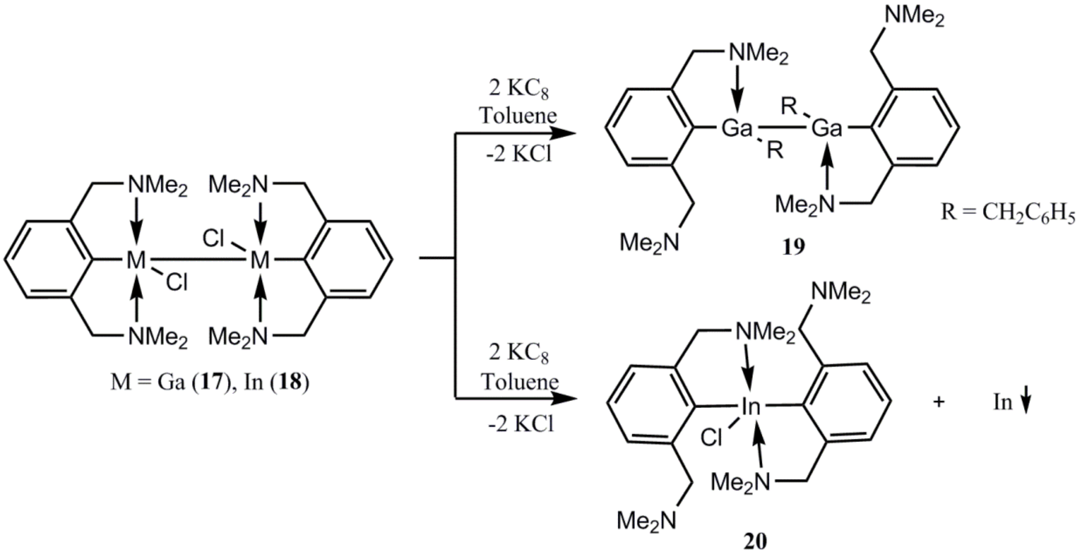
Our recent studies have dealt with the synthesis of organotin chalcogenides [$\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}_2Sn_2(S)_7$] and [$(\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnE)_2E$] (E= Se, Te) which have well-defined stoichiometry of tin and chalcogen.[23] These compounds were prepared as the products of the oxidation of the distannyne [$(\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Sn)_2$] by chalcogen, via organotin(II) chalcogenides [$(\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Sn)_2E$] (E= S, Se).[24] Compounds [$\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}_2Sn_2(S)_7$] and [$(\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnSe)_2S$] found potential as SSP for the deposition of SnS or SnSSe semiconducting thin films by using the spin coating method.[23] Synthesis method of the compounds raised the question, whether would it be possible to prepare similar alkyne analogues of heavier group 13th and oxidize them by chalcogen. The past decades of the investigation of compounds of the heavier group 13th elements in low oxidation state proved possible stabilization of various species. To the best of our knowledge, the field of subvalent derivatives of 13th group elements containing the pincer type ligands is practically unexplored. For example Cowley reported the stabilization of indium(II)-indium(II) compound [L^1(Cl)In]$_2$.[25]

The following chapters were directed to attempts to prepare low valent compounds of the 13th group [$L^{1,3}$M:]. Subsequent reactivity with Ph_2E_2 (E = S, Se, Te) were studied further, in order to isolate monomeric chalcogenolates $L^{1,3}M(EPh)_2$ (M = Ga, In, E = S, Se, Te) by oxidation reaction of the compounds [$L^{1,3}$M:] or [$L^{1,3}$M]$_2$ (see scheme 9).



Scheme 9: Preparation of chalcogenolates $L^{1,3}M(EPh)_2$ (M = Ga, In; E = S, Se, Te) by oxidation reaction of [$L^{1,3}$M:] or [$L^{1,3}$M]$_2$ with Ph_2E_2.

Reaction of compounds **1** and **2** with KC_8 gave the compounds [L^1(Cl)Ga]$_2$ (**17**) and [L^1(Cl)In]$_2$ (**18**) containing a metal(II) - metal(II) bond. Complex **17** was further reduced by KC_8 in toluene, however this reaction provided complex [$L^1(PhCH_2)$Ga]$_2$ (**19**) (see scheme 10). In the case of intramolecularly coordinated indium compound **18** the reduction by KC_8 were done in toluene. However, synthesis led to isolation of compound $(L^1)_2$InCl (**20**) as the result of disproportionation reaction (see scheme 10).



Scheme 10: Synthesis of compounds $[L^1(PhCH_2)Ga]_2$ (**19**) and $(L^2)_2InCl$ (**20**)

Compounds **17** and **19** were characterized by multinuclear NMR spectroscopy and X-ray diffraction analysis. The molecular structures of compounds **17** and **19** are shown in figure 17.

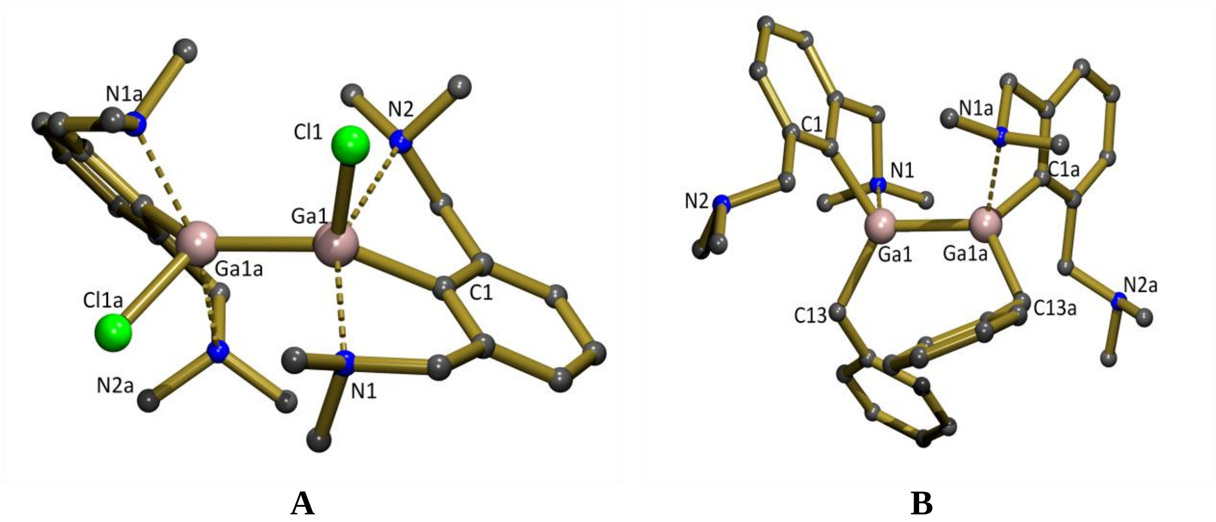
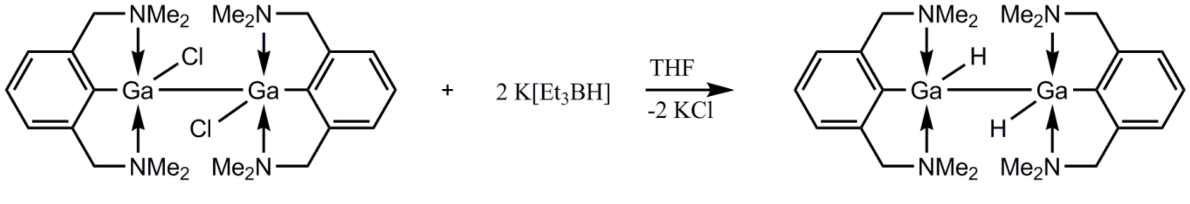


Figure 17: Molecular structure of compounds **17** (A) and **19** (B).

The five-coordinate gallium atoms in complex **17** reside in distorted trigonal bipyramidal geometries. Each gallium is connect by two nitrogens and carbon atom of ligand L^1, and by a chlorine and second gallium atom. Complex **19** is again an example of gallium(II)-gallium(II) complex. The four-coordinate gallium atoms in **19** form distorted tetrahedron. Complex **17** has been found as suitable precursor for the synthesis of the 1,2-disubstituted digallane $[L^1(H)Ga]_2$ (**21**) by the substitution reaction of **19** with 2 eq. of $K[BHEt_3]$ (see scheme 11).



17 **21**

Scheme 11: Synthesis of the 1,2-disubstituted digallane $[L^1(H)Ga]_2$ (**21**).

The five-coordinate gallium atoms in **21** reside in distorted trigonal bipyramidal geometries (see figure 18).

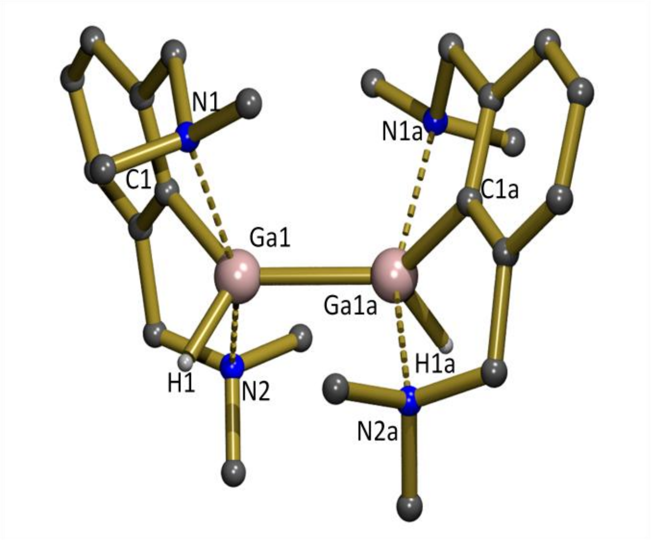


Figure 18: Molecular structure of compound **21**.

Each gallium is connected by two nitrogens and carbon atom of ligand L^1, and by a hydride and second gallium atom. Complex **21** represents rare example of the Ga(II) hydride. Similar complex $[(2,6\text{-Diip}_2C_6H_3)(H)Ga]_2$ has been postulated theoretically, as the possible intermediate of the reaction H_2 with multiple bonded digallene $[(2,6\text{-Diip}_2C_6H_3)Ga]_2$. The final product of this reaction is, however, complex $[(2,6\text{-Diip}_2C_6H_3)(H)Ga(\mu\text{-}H)]_2$ in which both bridging and terminal hydrides are present.[26]

In summary, we have showed the easy stabilization of Ga(II) complexes by the utilization of ligand L^1. The attempts of the stabilization subvalent digallene $[L^1Ga]_2$ by either reduction of $[L(Cl)Ga]_2$ (**17**) or by the hydrogen elimination from $[L^1(H)Ga]_2$ (**21**) failed, but an unexpected complex $[L^1(C_6H_5CH_2)Ga]_2$ (**19**) was isolated. This complex might be the result of the reaction of the parent digallene $[L^1Ga]_2$ with the toluene.

5 Conclusion

The aim of this dissertation thesis was to investigate whether intramolecularly coordinated chalcogenides and chalcogenolates of the 13th group elements can serve as SSP for deposition of thin layers of III-VI materials. For this reason, N → Ga intramolecularly coordinated organogallium sulfides $[L^1Ga(\mu\text{-}S)]_3$ (**6**), $[L^2Ga(\mu\text{-}S)]_2$ (**7**) and $L^1Ga(\kappa^2\text{-}S_4)$ (**8**) were synthesized. The best result was obtained with precursor **6**, which was used for the preparation of thin films GaS by the spin coating method from propylamine solutions on monocrystalline Si. The Ga and S elements were detected in the ratio 1: 1 and value of the band gap E_g was in ranged from 2.99 to 3.37 eV.

Furthermore, N → Ga intramolecularly coordinated organogallium selenides $[L^1Ga(\mu\text{-}Se)]_2$ (**9**), $L^1Ga(\kappa^2\text{-}Se)_4$ (**10**) and $[L^2Ga(\mu\text{-}Se)]_2$ (**11**) were studied. The best result was obtained with the precursor **11**, which was used for the preparation of thin films GaSe material by spin coating method from the propylamine solution on the monocrystalline silicon substrate. The Ga and Se elements were detected in the ration 1: 1 and value of the optical band gap E_g was in the range 2.41 - 2.42 eV. Since TG analysis showed the total degradation of precursor **11** till 350 °C, degradation in octadecylamine solution were investigated. A monoclinic Ga_2Se_3 material was prepared with the optical band gap $E_g = 2.56$ eV.

Analogous organoindium chalcogenides $[L^1In(\mu\text{-}E)]_2$ (E = S (**12**), Se (**13**), Te (**14**)) containing L^1 ligand were prepared. Compounds **12**, **13** and **14** were poorly soluble in organic solvents and therefore were not used as SSP for deposition of thin films. Compounds $L^1In(\kappa^2\text{-}S_4)$ (**15**) and $L^1In\ (\kappa^2\text{-}Se_4)$ (**16**) were also prepared and showed sufficient solubility in organic solvents. However, compound **16** decomposed in solution and only compound **15** was stable. TG experimental data were significantly different from theoretical values, therefore, compound **15** was not further used as SSP for thin films deposition.

An intensively studied SSP group consisted of chalcogenolate compounds of 13th group elements. Successful used N → Sn coordinated distannyn $[2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Sn]_2$ for the synthesis of organotin chalcogenolates L^1SnEPh (E = S, Se, Te) led us to investigate the preparation of intramolecularly coordinated low valent compounds $[L^{1,3}M:]$ and their subsequent reactivity with Ph_2E_2 (E = S, Se, Te). It was found that the starting compounds L^1MCl_2 (M = Ga (**1**), In (**2**)) were not suitable for the preparation of low valent compounds $[L^1M:]$. For this reason, we have prepared starting compounds L^3MCl_2 (M = Ga (**4**), In (**5**)), which contained more sterically hindered L^3 ligand. We have showed the easy stabilization of Ga(II) complexes by the utilization of ligand L^1. The attempts of the stabilization subvalent digallene $[L^1Ga]_2$ by either reduction of $[L(Cl)Ga]_2$ (**17**) or by the hydrogen elimination from $[L^1(H)Ga]_2$ (**21**) failed, but an unexpected complex $[L^1(C_6H_5CH_2)Ga]_2$ (**19**) was isolated. This complex might be the result of the reaction of the parent digallene $[L^1Ga]_2$ with the toluene. Therefore, the stabilization of N→Ga coordinated digallene or N→In coordinated diindene by different *N,C,N*-ligands is of our current interest.

6 References

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7 List of publications

1) T. Ricica, T. Svetlik, L. Dostal, A. Ruzicka, K. Ruzicka, L. Benes, P. Nemec, M. Bouska, R. Jambor, *Chem. Eur. J.*, **2016**, *22(52)*, 18817. Intramolecularly Coordinated Gallium Sulfides: Suitable Single Source Precursors for GaS Thin Films.

2) F. Piana, J. Pfleger, R. Jambor, T. Ricica, J. M. Macak, *J. Appl. Polym. Sci.*, **2017**, *134(37)*, 45236. High-k dielectric composites of poly(2-cyanoethyl vinyl ether) and barium titanate for flexible electronics.

3) J. Vodak, D. Necas, D. Pavlinak, J. M. Macak, T. Ricica, R. Jambor, M. Ohlidal, *Appl. Surf. Sci.*, **2017**, *396*, 284. Application of imaging spectroscopic reflectometry for characterization of gold reduction from organometallic compound by means of plasma jet technology.

4) T. Ricica, L. Dostal, Z. Ruzickova, R. Jambor, *Eur. J. Inorg. Chem.*, **2018**, *2018(14)*, 1620. Synthesis of N→Ga coordinated gallium(II)-gallium(II) compounds.

5) T. Ricica, L. Dostal, Z. Ruzickova, L. Benes, P. Nemec, M. Bouska, J. Macak, P. Knotek, P. Ruleova, R. Jambor, *Chem. Eur. J.*, ***2018,*** 1, Synthesis, structure and application of intramolecularly coordinated gallium chalcogenides: Suitable single source precursors for GaxSey materials.

8 List of conference contributions

Oral presentation

1) T. Ricica, R. Jambor, Z. Ruzickova, *16th International Seminar of PhD Students on Organometallic and Coordination Chemistry*, Schloss Schney, Lichtenfels, Germany, 17 – 21. October **2015**. Reactivity of N→Ga Coordinated Organogallium compounds.

2) T. Ricica, R. Jambor, M. Bouska, *2.konference Pokroky anorganické chemie*, Kutná Hora, 19 -22. July **2016**, *Czech Chem. Soc. Symp. Ser*. **2016**, *14(4)*, 150. Příprava tenkých vrstev SnS_2 a nanočástic $BaTiO_3$,

3) T. Ricica, R. Jambor, Z. Ruzickova, *68. Sjezd chemiků,* Praha, 4 – 7. September **2016**. Příprava prvků 13-té skupiny v nízkém oxidačním stavu.

4) T. Ricica, R. Jambor, Z. Ruzickova, J. Honzicek, *17th international Seminar of PhD Students on Organometallic and Coordination Chemistry*, Czech Republic, Kraskov 2-6. April **2017**, OP42. Reduction of N,C,N-Chelated organogallium and organoindium halides.

Poster presentation

1) T. Ricica; R. Jambor; Z. Ruzickova, *IRIS 14*, Regensburg 26. - 31. July **2015**, P014 page 131. Reactivity of N→Ga Coordinated Organogallium compounds.

2) T. Ricica, R. Jambor, T. Svetlik, M. Bouska, Z. Ruzickova, *27th International Conference on Organometallic Chemistry*, Australia, Melbourne, 17-22. July **2016**, ICOMC poster abstract B n. 261. Deposition of GaS Thin Films by Spin-coating Method and Synthesis of Intramolecularly Coordinated Organogallium Boroxines,

3) T. Ricica, R. Jambor. Z. Ruzickova. J. Honzicek, *EuCheMS International Organometallic Conference XXII*, 9-13. July **2017**, Amsterdam the Netherlands, Poster 202. Reduction pathway dependency of N,C,N-chelated organometallic compounds on central atoms M = Ga or In.

Scholarship abroad - short term grant

Synthesis of new *O,C,O*-Chelated intramolecularly coordinated organometallic compounds of the 13th group elements. Group of prof. Dr. K. Jurkschat, **1.9.2017 – 31.12.2017**, Technische Universität Dortmund, Faculty of Chemistry and Chemical Biology.