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Intramolecularly coordinated gallium sulfides: Suitable single source precursors for GaS thin films

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Abstract: Our studies have been focused on the synthesis of N→Ga coordinated organogallium sulfides $[L^1Ga(\mu\text{-}S)]_3$ (**1**) and $[L^2Ga(\mu\text{-}S)]_2$ (**2**) containing either N,C,N- or C,N-chelating ligands $L^{1,2}$ (L^1 is $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}^-$ and L^2 is $\{2\text{-}(Et_2NCH_2)\text{-}4,6\text{-}tBu_2\text{-}C_6H_2\}^-$). As the result of different ligand, compounds **1** and **2** differ mutually in their structure. To change the Ga/S ratio, unusually N→Ga coordinated organogallium tetrasulfide $L^1Ga(\kappa^2\text{-}S_4)$ (**3**) was prepared and unprecedented complex $[\{2\text{-}[CH\{(CH_2)_3CH_3\}(\mu\text{-}OH)]\text{-}6\text{-}CH_2NMe_2\}C_6H_3]GaS$ (**4**) was also isolated as the minor by-product of the reaction. Compounds **1** - **3** were further studied as potential single source precursors fo amorphous GaS thin film deposition by spi coating method.

Keywords: 13 group element • thin layer • GaS material • NMR • spin coating

Introduction

Amorphous chalcogenide based thin films, fabricated usually via PVD techniques, are today's exciting field for innovations. Their widespread technological applications hold scientists' attention for upcoming challenges and demands in the field of infrared optics, photonics, development of next generation computer memories, and emerging applications in the field of medicine or military.[1] The applications of amorphous chalcogenides are based on their specific properties like broad IR transparency (up to 12 and 16 µm for sulfides and selenides, respectively), photosensitivity, high (non)linear refractive index or low phonon energy (~350 cm^{-1} for sulfides and ~250 cm^{-1} for selenides). From mentioned characteristics, low phonon energy of amorphous chalcogenides results in low probability of multiphonon relaxations among the energy levels of rare earth ions incorporated in chalcogenide-based matrix. Consequently, radiative efficiencies of the most rare earth ions fluorescence emissions in near and mid-IR are improved. It was already shown that the presence of gallium is crucial for the sufficient solubility of rare earth ions in amorphous chalcogenides which is generally low in typical binary compositions (As-S, As-Se Ge-S, Ge-Se, etc.).[2]

While the deposition of crystalline β-Ga_2S_3 films from GaEt and H_2S was reported in 1995 by Smith et al using low-pressur chemical vapour deposition (CVD).[3] Thereafter, Hampden-Smit et al also reported the preparation of crystalline α-Ga_2S_3 films b aerosol-assisted CVD from $Ga(S_2CMe)_2Me(dmpy)$ o $Ga(S_2CMe)_3(dmpy)$ (dmpy = 3,5-dimethylpyridine)[4] and finally O'Brien et al described using $Ga(S_2CNMeHex)_3$ to deposit α-Ga_2S films on GaAs(111) substrates by low-pressure CVD[5] and differen single source precursor (SSP) $[Ga(SiPr)_2(\mu\text{-}SiPr)]_2$ was used fo preparation of high-quality α-Ga_2S_3 and γ-Ga_2S_3 films by CVD method as well. [6] Barron et al have reported synthesis of cubic Ga using atmospheric pressure CVD using $[(tBu)GaS]_4$ as SSP.[7] Th same group has also reported the growth of crystalline GaS films b atmospheric pressure CVD from $(t\text{-}Bu)Ga(S_2CNR_2)_2$ (R = Me, Et as suitable SSP. [8] Therefore, the application of SSP for th deposition of crystalline III/VI materials by CVD techniques i already known. [9] Recently, GaS_x films were prepared by atomi layer deposition (ALD) using $Ga_2(NMe_2)_6$ and H_2S.[10] In addition synthesis of nanoparticles, [11] nanotubes, [12] or flowerlik structures[13] of GaS and Ga_2S_3 have been reported either.

In contrast, the deposition of amorphous GaS layers was reported infrequently and from this point of view, it seems to be reasonable to investigate an alternative way for the fabrication of amorphous chalcogenide thin films containing gallium, which can potentially accommodate rare earth ions. Those are the reasons for the single source precursors' application to develop good quality amorphous GaS thin films presented in this work. In this paper, our studies have been focused on the synthesis of N→Ga coordinated organogallium sulfides $[L^1Ga(\mu\text{-}S)]_3$ (**1**) and $[L^2Ga(\mu\text{-}S)]_2$ (**2**) containing either N,C,N- or C,N-chelating ligands $L^{1,2}$ (L^1 is {2,6-

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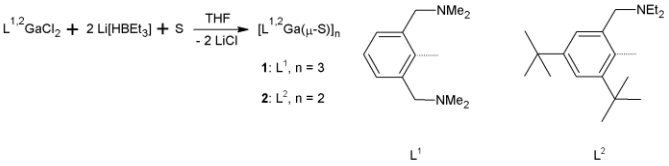
$(Me_2NCH_2)_2C_6H_3\}^-$ and L^2 is $\{2\text{-}(Et_2NCH_2)\text{-}4,6\text{-}t\text{Bu}_2\text{-}C_6H_2\}^-$). As the result of different ligand, compounds **1** and **2** differ mutually in their structure. To change the Ga/S ratio, unusual N→Ga coordinated organogallium tetrasulfide $L^1Ga(\kappa^2\text{-}S_4)$ (**3**) was prepared and unprecedented complex $[\{2\text{-}[CH\{(CH_2)_3CH_3\}(\mu\text{-}OH)]\text{-}6\text{-}CH_2NMe_2\}C_6H_3]GaS$ (**4**) was also isolated as the minor by-product of the reaction. Compounds **1** - **3** were further studied as potential single source precursors for amorphous GaS thin film deposition by spin coating method.

Results and Discussion

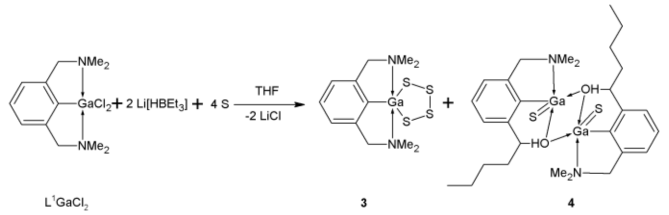
*Synthesis and characterization of compounds **1** - **4***

The treatment of L^1GaCl_2 with one eq. of Li_2S (generated *in situ*, see Scheme 1) yielded the N→Ga coordinated trimeric organogallium sulfide $[L^1Ga(\mu\text{-}S)]_3$ (**1**). In contrast, similar reaction of L^2GaCl_2 provided dimeric organogallium sulfide $[L^2Ga(\mu\text{-}S)]_2$ (**2**).



Scheme 1. Synthesis of N→Ga coordinated organogallium sulfides $[L^1Ga(\mu\text{-}S)]_3$ (**1**) and $[L^2Ga(\mu\text{-}S)]_2$ (**2**).

Despite the different structure, both complexes contain Ga/S atoms in 1/1 ratio. In order to change the stoichiometry of the Ga/S atoms, the reaction of **1** with one eq. of Li_2S_4 (generated *in situ*, see Scheme 2) was run to give N→Ga coordinated organogallium tetrasulfide $L^1Ga(\kappa^2\text{-}S_4)$ (**3**). In addition, from this reaction the by-product **4** was also isolated in very low yield (up to 5 %). Analogous reaction of L^2GaCl_2 provided complex **2** only.



Scheme 2. Synthesis of N→Ga coordinated organogallium tetrasulfide $L^1Ga(\kappa^2\text{-}S_4)$ (**3**) and by-product **4**

Single crystals suitable for X-ray diffraction analysis of **1** and **2** were obtained from saturated toluene-hexane solution at room temperature, while single crystals of **3** and **4** were obtained from toluene solution of **3** at -20°C and THF-hexane solution of **4** at 4°C. The molecular structures of **1** - **4** are shown in Figures 1 - 3, respectively, and selected bond lengths and angles are given in Table 1. Crystallographic data are summarized in Table S1 in Supplementary material.

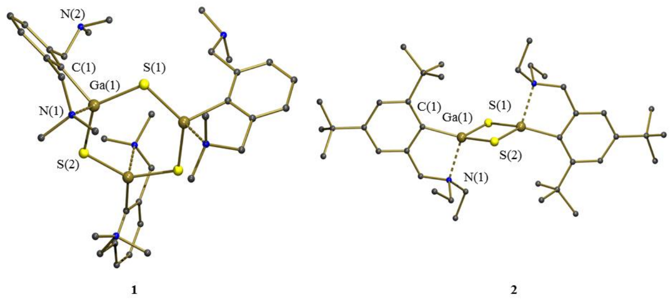


Figure 1. PovRay presentation of molecular structures of $[L^1Ga(\mu\text{-}S)]_3$ (**1**) and $[L^2Ga(\mu\text{-}S)]_2$ (**2**)

The molecular structure of **1** revealed trimeric structure c $[L^1Ga(\mu\text{-}S)]_3$ with central six member Ga_3S_3 core, while compoun **2** with different ligand L^2 revealed dimeric nature of $[L^2Ga(\mu\text{-}S)]$ with central four member Ga_2S_2 core. The coordination environmer of the central Ga atoms in **1** and **2** is, however, similar. The G atoms in **1** and **2** are four-coordinated by one nitrogen (the range c Ga–N distances is 2.1261(19) - 2.321(3) Å), and one carbon atom c the $L^{1,2}$ ligands and by two sulfur atoms (the range of the Ga– distance is 2.2099(8) - 2.2636(6) Å). The Ga atoms show a distorte tetrahedron environment, where the bond angles of C–Ga–N (rang of 78.69(13) - 87.72(8)°) represent the largest deviation from a ideal shape. In the compound **1**, second nitrogen atoms of L^1 ligand are uncoordinated as suggested by Ga–N bond distances with th range of 2.605(3) - 4.791(3) Å.

Bridged trimeric structure found for **1** is comparable to that c $[(C_5H_5N)RGa(\mu\text{-}S)]_3$ (R = Me, Et, *t*Bu) analogues, [14] while th dimeric structure found for **2** is analogous t $[\{HC(MeCDippN)_2\}Ga(\mu\text{-}S)]_2$ (Dipp = $C_6H_3\text{-}2,6\text{-}i\text{Pr}_2$).[15] Th average Ga-S bond length of 2.22(1) Å for Ga_3S_3 core as well as c 2.26(1) Å for the Ga_2S_2 is just within the currently known rang (2.20 - 2.27 Å) for organogallium Ga-S species.[7, 14-16]

Table 1. Selected bond lengths (Å) and angles (deg) for **1** – **4**

	1	2	3	4
Ga(1)–C(1)	1.976(3)	1.987(3)	1.935(3)	1.922(2)
Ga(1)–N(1)	2.164(3)	2.1262(19)	2.360(2)	2.2842(18)
Ga(1)–N(2)	4.791(3)	-	2.403(2)	-
Ga(1)–S(1)	2.2181(8)	2.2636(7)	2.2768(8)	2.1881(7)
Ga(1)–S(2)	2.2099(8)	2.2634(7)	2.2829(7)	-
Ga(1)–O(1)	-	-	-	2.2542(14)
Ga(1)–O(1a)	-	-	-	1.8470(15)
N(1)–Ga(1)–S(1)	100.41(7)	105.33(6)	99.72(6)	98.63(5)
C(1)–Ga(1)–S(1)	113.16(8)	129.29(7)	130.70(8)	125.09(6)
C(1)–Ga(1)–N(1)	83.40(10)	87.72(10)	78.49(9)	80.91(7)

The molecular structure of **3** showed monomeric structure of $L^1Ga(\kappa^2\text{-}S_4)$ with an unusual five membered GaS_4 ring.

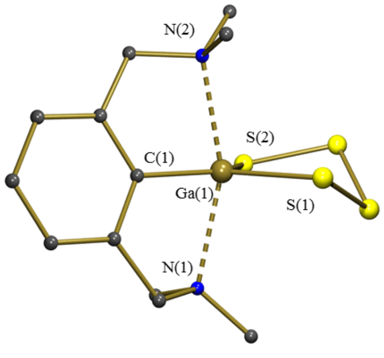


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Figure 2. PovRay presentation of molecular structure of $L^1Ga(\kappa^2-S_4)$ (**3**)

The Ga(1) atom is five-coordinated by two nitrogen and carbon atoms of the ligand L^1 and by two S atoms of (κ^2-S_4) fragment. The coordination geometry is a distorted trigonal-bipyramid with the C(1), S(1), S(2) atoms located in equatorial position (the Ga(1)–S(1) = 2.2768(8) Å and Ga(1)–S(2) = 2.2829(8) Å) and nitrogen N(1) and N(2) atoms in axial positions with bond angle N(1)-Ga(1)-N(2) 155.98(7)°. Both nitrogen atoms are involved in N→Ga coordination as demonstrated by Ga(1)–N(1) = 2.360(2)Å and Ga(1)–N(2) = 2.406(2)Å bond distances. Compound **3** represents the first structurally characterized organogallium complex with GaS_4 fragment and it is thus first evidence for the possible stabilization of polysulfide chains by gallium atom. The polysulfide analogues of group 13 elements are known, however, there are limited numbers of these complexes. Roesky et al reported synthesis of $\{HC[C(Me)N(Ar)]_2\}Al(\kappa^2-S_4)$ (Ar = 2,6-*i*Pr_2-C_6H_3)[17] by the reaction of $\{HC[C(Me)N(Ar)]_2\}Al(SH)_2$ with S_8 while indium analogue $[Tm^{tBu}]In(\kappa^2-S_4)$ (Tm^{tBu} = tris(2-mercapto-1-*t*Bu-imidazolyl)hydroborato) has been prepared by oxidation of $[Tm^{tBu}]In(I)$ precursor by S_8.[18] These complexes take five membered rings with the average S−S bond length 2.07 Å that are comparable to those found in **3**, with S−S bond length ranging from 2.0313(12) - 2.0783(10). [19]

Although the complex **3** is the major product of the reaction several crystals of unexpected compound **4** was isolated from this reaction as well. The NMR data of the original reaction mixture showed the content of **4**. All attempt to prepare complex **4** directly from complex **3**, however, failed (see SI).

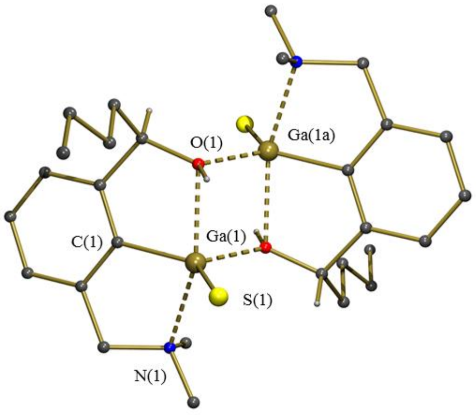

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Figure 3. PovRay presentation of molecular structure of $[\{2-[CH\{(CH_2)_3CH_3\}(\mu-OH)]-6-CH_2NMe_2\}C_6H_3]GaS$ (**4**)

The most interesting feature of **4** is that one CH_2NMe_2 group of the L^1 ligand has been transformed to new $CH_3(CH_2)_3CHOH$ group most probably by attack of the THF molecule and followed by the CH_2-O bond rupture along with the deamination process. As the result, the L^1 ligand was transformed to an unsymmetrical ligand $[\{2-[CH\{(CH_2)_3CH_3\}(OH)]-6-CH_2NMe_2\}C_6H_3]^-$ that is able to stabilize unusual Ga-S terminal bond with Ga(1)-S(1) bond distance of 2.1881(7) Å, that is slightly longer than sum of covalent radii for Ga-S double bond $\Sigma_{cov}(Ga,S)$ = 2.11 Å. [20] The N(1) and O(1) atoms coordinate the central gallium Ga(1) atom by Y→Ga coordination (Ga(1)-N(1) = 2.2842(18) Å and Ga(1)-O(1) = 2.2542(14) Å) and the O(1) atom is also involved in the strong intermolecular O(1)-Ga(1a) coordination (1.8470(15) Å) of the second molecule.

All compounds were also characterized by ^{1}H and ^{13}C NMR spectroscopy and data are consistent with the structures. Thus ^{1}H NMR spectrum of **1** showed AB spin system and the single resonance of the methylene C*H*$_2$N groups at δ 3.44 and 3.67 ppm respectively, due to the presence of coordinated and uncoordinated CH_2NMe_2 moieties. The ^{1}H NMR spectrum of **2** showed AB spin system of CH_2NEt_2 group at δ 3.54 ppm as the result of N→G interaction and similarly compound **3** provided an AB spin system of CH_2NMe_2 moieties due to the presence of N→Ga coordination o both CH_2NMe_2. Therefore it is evident, that the solid state structure are also retained in the solution of **1** – **3**.

*Deposition of GaS thin films by spin coating using **1** as SSP*

As compounds **1** and **2** differ mutually in their structure with Ga/S atoms in 1 /1 ratio, and complex **3** contains Ga/S atoms in 1/4 ratio, the above mentioned complexes were studied further a potential single source precursors for GaS thin film deposition. Th thermogravimetric analyses showed the multistep decomposition o **1** - **3** (see Figures S1-3 and Table S2 in SI). Compound **1** start decomposing at 160 ºC and continues till 350 ºC. Decomposition i endothermic and it is preceded by melting (around 140 ºC). Tota expected (57%) and observed (55%) mass losses indicate th formation of GaS after complete decomposition. Compounds **2** an **3** start decomposing at 240 ºC and 190 ºC, respectively and continue till 320 ºC and 385 ºC, respectively. It should be noted tha **2** reacted with air both during sample weighing and during heatin up to the decomposition temperature. The decomposition wa endothermic at the beginning but changed to exothermic event a 270 ºC; at this temperature, there is clearly visible slope change o mass-loss curve. After decomposition (above 320 ºC), sligh increase of weight was detected and heat flow signal wa exothermic. For compound **3**, decomposition was exothermic and was preceded by melting (at 140 ºC). Melting and decomposition peaks are well defined and clearly separated. However, the tota expected and observed mass losses (74 and 40% for **2**; 73 and 62% for **3**) did not suggest the formation of GaS as the final product of the thermal decomposition of **2** and **3**.

Therefore compound **1** was tested as potential SSP for the preparation of GaS thin films using the spin-coating method only. When 300 mg of compound **1** was heated at 350°C, the final decomposition product was identified by powder X-ray analysis (XRD) and Raman spectroscopy as amorphous GaS (see Figure S4A in SI). The propylene amine solution of **1** (c = 0.08 mol.l^{-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 (Fig. 4a,b) and AFM (Fig. 4c,d) data showed smooth surface of thin films, without cracks and corrugations. Root mean square roughness determined by AFM was found to be lower than ~ 2 nm.

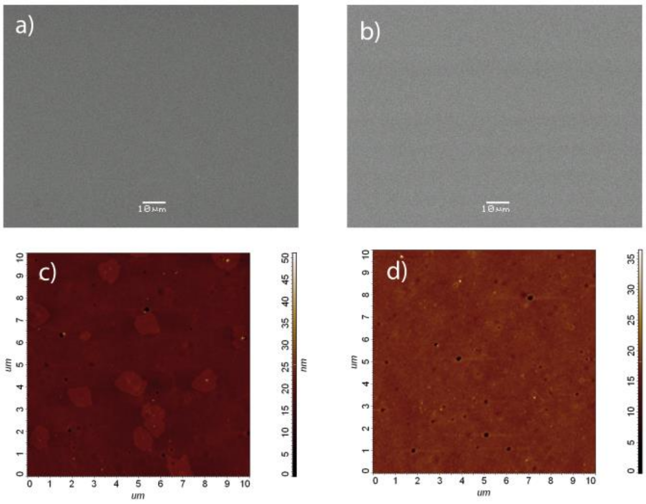

Figure 4. SEM images and AFM images of the surface of 1500 rpm (a, c) and 2500 (b, d) rpm spin-coated GaS thin films from SSP **1**.

Elemental analysis of the GaS thin layer (see Table S3 in SI) revealed content of carbon and nitrogen in the sample, although the sample was placed in a vacuum oven for 12 hours at 250°C (for further details see SI). From the literature, however, we can learn that this is a common phenomenon for the material deposited from SSPs.[21] 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 $\mathbf{Ga_{51.5}S_{48.5}}$ for 1500 rpm and $\mathbf{Ga_{50.0}S_{50.0}}$ for 2500 rpm respectively. EDX spectroscopy also revealed minimal dependence (if any) of the chemical composition of the deposited material on the spinning speed; the differences are within the error limits of EDX method (Table 2). It is evident that the ratio of Ga/S atoms in SSP **1** is retained in the prepared GaS thin film. As shown in Figure S5 in SI, the S/Ga ratio is strongly dependent on annealing temperatures. The thin GaS layers prepared from SSP **1** were also subject to thermal annealing at higher temperatures (up to 420°C). The S/Ga ratio remained almost constant at 1.0 for lower temperatures of 150−250°C, where the S/Ga ratios are in the expected ratios for GaS (S/Ga = 1.0), but decreased at higher temperatures, down to ~0.25 at 420 °C, due to an easy partial oxidation of the material (see Figure S5 and Table S4 in SI).

Table 2. 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 λ = 1.5 μm), and Root-Mean-Square (RMS) roughness values.

Property	Spinning speed (rpm)		
	1500	2000	2500
Ga (at. %), determined via EDX	48.5	50.2	50.0
S (at. %), determined via EDX	51.5	49.8	50.0
film thickness (nm), determined via VASE	260.9±0.3	209.6±0.4	265.1±0.3
E_{opt} (eV), determined via VASE	3.37±0.01	2.99±0.13	3.03±0.03
refractive index, determined via VASE	1.65±0.01	1.65±0.01	1.65±0.01
RMS (nm), determined via AFM	1.48±0.01	1.97±0.01	0.99±0.01

XRD analysis of deposited thin films indicates that the prepared materials are amorphous (see Figure S4B in SI). Optical functions of prepared GaS layers as well as their thicknesses were obtained from the analysis of variable angle spectroscopic ellipsometry (VASE) data measured using an ellipsometer with automatic rotating analyzer on samples grown on silicon substrates (see Figure S6 in SI). The thickness and optical band gap energy (E_{opt}) of the as-dried GaS thin film are dependent on 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, respectively, (see Table 2).[22] Obtained values of E_{opt} correlate with those found for amorphous GaS thin films prepared by vacuum evaporation of crystalline GaS (2.7eV),[23] and by modulated flux deposition from Ga and S atoms (range 3.2 to 3.6 eV).[24] Similarly, for the hexagonal GaS, the direct band gap E_{dir} = 3.05 eV has bee measured at 77 K.[9]

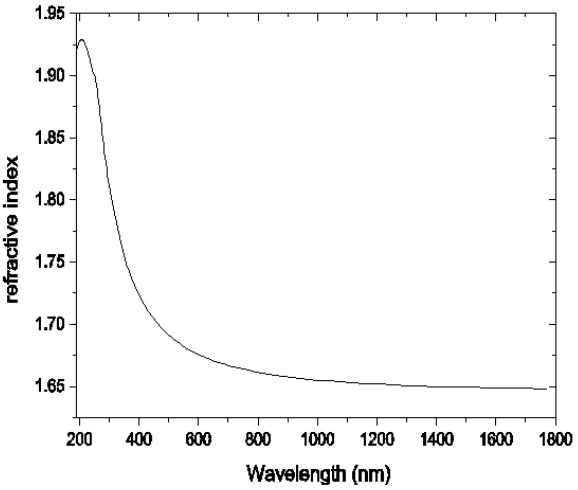

Figure 5. Typical dispersion of the refractive index of spin-coated GaS thin film (250 rpm)

The refractive index for amorphous GaS thin films (n ≈ 1.65 at = 1.5 μm) was independent on spinning speeds (see Table 2, an Figure 5) and the value is close to those found for the ALD GaS films (n ≈ 1.78 at 125°C).[10]

Conclusion

In conclusion, we have showed that N→Ga coordinate organogallium sulfides $[L^1Ga(\mu\text{-}S)]_3$ (**1**) and $[L^2Ga(\mu\text{-}S)]_2$ (2 containing either N,C,N- or C,N-chelating ligands $L^{1,2}$ (L^1 is {2, $(Me_2NCH_2)_2C_6H_3\}^-$ and L^2 is $\{2\text{-}(Et_2NCH_2)\text{-}4,6\text{-}t\text{Bu}_2\text{-}C_6H_2\}^-$) diffe mutually in their structure due to presence of different ligands $L^{1,}$ The ligand L^1 can also stabilize N→Ga coordinated organogalliu tetrasulfide $L^1Ga(\kappa^2\text{-}S_4)$ (**3**) and the unprecedented complex **4** wit Ga-S terminal bond was also isolated as the minor by-product of the reaction. Compounds **1** - **3** having either different structure and Ga/S ratio were further studied as potential single source precursors for amorphous GaS thin film deposition by spin coating method. The thermodynamic behaviour of **1** - **3** strongly depends on their structure and compound **1** has been found as suitable SSP for GaS deposition only. The thin films of GaS materials obtained after thermal annealing are amorphous. The chemical composition, film thickness, refractive Index, E_{opt} and RMS Roughness values were determined from EDX, AFM and SEM measurements on spin coating GaS films deposited at 1500, 2000, and 2500 rpm. The obtained values fall into the regions reported for the GaS materials prepared by different techniques.

Experimental Section

General methods for preparation of 1 - 4.

Solvents were dried by standard methods and distilled prior to use. All moisture and air sensitive reactions were carried out in an argon atmosphere using standard Schlenk techniques. Starting compounds L^2Br and L^1GaCl_2 were prepared according to literature.[25-26] Starting materials S, *n*BuLi, Li[HBEt$_3$] and GaCl$_3$ were purchased from Sigma Aldrich.. The ^{1}H and ^{13}C NMR spectra were acquired on Bruker 400 NMR spectrometer. The ^{1}H, ^{13}C, NMR chemical shifts δ are given in ppm and referenced to external Me$_4$Si (^{13}C, ^{1}H).

Synthesis of L^{2}GaCl$_2$

1.6M *n*BuLi solution in hexane (2.75 mL, 4.41 mmol) was added to a 20 ml Et$_2$O solution of L^{2}Br (1.3 g, 3.67 mmol) at -80 °C and the reaction mixture was allowed to warm to room temperature gradually and stirred for 3 hours. Formed lithium salt L^{2}Li was added to the 15 ml Et$_2$O solution of GaCl$_3$ (0.65 g, 3.67 mmol) under – 78 °C and the reaction mixture was allowed to warm to room temperature gradually and stirred for 3 hours. The Et$_2$O was filtered and evaporated under reduce pressure to give L^{2}GaCl$_2$. Yield: 1.36 g (89 %). m.p. = 148 - 149 °C; Anal. Calcd. for $C_{19}H_{32}Cl_2GaN$ (Mw 415.09) C 55.0 %; H 7.8 %; Found: C 54.5 %; H 7.6 %;. ^{1}H NMR (C$_6$D$_6$, 400.13 MHz): *δ (ppm)* 0.65 (6H, t, CH$_2$*CH$_3$*), 1.31 (9H, s, C(*CH$_3$*)$_3$), 1.59 (9H, s, C(*CH$_3$*)$_3$), 2.30 (2H, m, *CH$_2$*CH$_3$), 2.90 (2H, m, *CH$_2$*CH$_3$), 3.26 (2H, s, *CH$_2$*N), 6.79 (1H, s, *ArH*), 7.59 (1H, s, *ArH*). ^{13}C NMR (C$_6$D$_6$, 100.61 MHz): *δ (ppm)* 7.9 (CH$_2$*CH$_3$*), 31.3 (C(CH$_3$)$_3$), 32.3 (C(*CH$_3$*)$_3$), 34.6 (*C*(CH$_3$)$_3$), 36.7 (*C*(CH$_3$)$_3$), 45.4 (*CH$_2$*CH$_3$), 59.0 (*CH$_2$*N), 119.4 (*C*(3)), 122.8 (*C*(5)), 129.0 (*C*(4)), 140.9 (*C*(6)), 152.4 (*C*(2)), 158.3 (*C*(1)).

Synthesis of [L^{1}Ga(μ-S)]$_3$ (1)

1M Li[HBEt$_3$] solution in THF (25.6 mL, 25.6 mmol) was added to a 25 ml THF solution of S (0.41 g, 12.8 mmol) at room temperature and stirred for 2 hours. The formed lithium sulfide Li$_2$S was added to 25 ml THF solution of L^{1}GaCl$_2$ (4.25 g, 12.8 mmol) at -78°C. The reaction mixture was allowed to warm to room temperature gradually and stirred overnight. The THF was evaporated under reduce pressure and the residue was extracted with toluene-hexane solution (10 ml toluene and 20 ml hexane). This toluene-hexane solution was leaved to crystallize at room temperature to yield colourless crystals of **1** suitable for X-Ray diffraction analysis. Yield: 3.16 g (86 %). m.p. = 160-162 °C; Anal. Calcd. for $C_{36}H_{57}Ga_3N_6S_3$ (Mw 879.25) C 49.2 %; H 6.5 %; Found: C 49.1 %; H 6.7 %; ^{1}H NMR (C$_6$D$_6$, 400.13 MHz): *δ (ppm)* 2.35 (6H, s, N(*CH$_3$*)$_2$), 2.46 (6H, s, N(*CH$_3$*)$_2$), 3.44 (2H, AB system, *CH$_2$*N), 3.67 (2H, s, *CH$_2$*N), 7.07 (2H, d, *ArH*), 7.19 – 7.21 (1H, m, *ArH*). ^{13}C NMR (C$_6$D$_6$, 100.61 MHz): *δ (ppm)* 45.8 (N(*CH$_3$*)$_2$), 45.8 (N(*CH$_3$*)$_2$), 65.4 (*CH$_2$*N), 65.4 (*CH$_2$*N), 125.1 (*C*(3)), 125.3 (*C*(5)), 128.7 (*C*(4)), 144.0 (*C*(2)), 144.8 *(C*(6)), 149.4 (*C*(1)).

Synthesis of [L^{2}Ga(μ-S)]$_2$ (2)

1M Li[HBEt$_3$] solution in THF (5.10 mL, 5.10 mmol) was added to a 25 ml THF solution of S (0.08 g, 2.55 mmol) at room temperature and stirred for 2 hours to generate Li$_2$S that was added to 25 ml THF solution of L^{2}GaCl$_2$ (1.06 g, 2.55 mmol) at -78°C. The reaction mixture was allowed to warm to room temperature gradually and stirred overnight. The THF was evaporated under reduce pressure and the residue was extracted with toluene-hexane solution (10 ml toluene and 20 ml hexane). The solution was leaved to crystallize at room temperature and provided colourless crystals of **2** suitable for X-ray diffraction analysis. Yield: 0.75 g (78 %). m.p. = 270-273 °C; Anal. Calcd. for $C_{38}H_{64}Ga_2N_2S_2$ (Mw 752.50) C 60.6 %; H 8.6 %; Found: C 60.4 %; H 8.7 %; . ^{1}H NMR (C$_6$D$_6$, 400.13 MHz): *δ (ppm)* 0.93 (6H, t, CH$_2$*CH$_3$*), 1.41 (9H, s, C(*CH$_3$*)$_3$), 1.93 (9H, s, C(*CH$_3$*)$_3$), 3.23 (4H, m, *CH$_2$*CH$_3$), 3.54 (2H, s, *CH$_2$*N), 6.79 (1H, s, *ArH*), 7.59 (1H, s, *ArH*). ^{13}C NMR (C$_6$D$_6$, 100.61 MHz): *δ (ppm)* 9.4 (CH$_2$*CH$_3$*), 31.4 (C(*CH$_3$*)$_3$), 33.3 (C(*CH$_3$*)$_3$), 34.6 (*C*(CH$_3$)$_3$), 37.6 (*C*(CH$_3$)$_3$), 48.2 (*CH$_2$*CH$_3$), 59.2 (*CH$_2$*N), 119.6 (*C*(3)), 121.1 (*C*(5)), 141.8 (*C*(4)), 142.7 (*C*(6)), 150.6 (*C*(2)), 157.6 (*C*(1)).

Synthesis of L^{1}Ga(κ^2-S$_4$) (3) and [{2-[CH{(CH$_2$)$_3$CH$_3$}(μ-OH)]-6-CH$_2$NMe$_2$}C$_6$H$_3$]GaS (4)

1M Li[HBEt$_3$] solution in THF (5 mL, 5 mmol) was added to a 15 ml THF solution of S (0.32 g, 10 mmol) at room temperature and stirred for 2 hours to give Li$_2$S$_4$ that was added to 15 ml THF solution of L^{1}GaCl$_2$ (0.82 g, 2.5 mmol) at -78°C. The reaction mixture was allowed to warm to room temperature gradually and stirred overnight. The THF was evaporated under reduce pressure and the residue was extracted with toluene (15 ml). The toluene solution was leaved to crystallize at -20 °C. Crystal suitable for X-ray diffraction analysis were obtained and identified as compound **3**. Remaining solid insoluble in toluene was re-dissolved in THF-hexane solution (1:1, 15 ml) and the filtrate was leaved to crystalize at 4°C. Crystal suitable for X-ray diffraction analysis were obtained and identified as compound **4**.

for **3**. Yield: 0.72 g (75 %); m.p. = 112-114 °C; Anal. Calcd. for $C_{12}H_{19}GaN_2S_4$ (Mw 389.28) C 37.0 %; H 4.9 %; Found: C 37.0 %; H 4.9 %. ^{1}H NMR (C$_6$D$_6$, 400.13 MHz): *δ (ppm)* 2.04 (12H, s, N(*CH$_3$*)$_2$), 3.03 (2H, s, *CH$_2$*N), 6.75 (2H, d, *ArH*), 7.12 (1H, m, *ArH*). ^{13}C NMR (C$_6$D$_6$, 100.61 MHz): *δ (ppm)* 45.5 (N(*CH$_3$*)$_2$), 63.2 (*CH$_2$*N), 124.5 (*C*(2,6)), 128.1 (*C*(3,5)), 143.1 (*C*(4)), 144.7 (C(1)).

for **4:** Yield: 0.04 g (5 %); m.p. = 215 °C; Anal. Calcd. for $C_{28}H_{46}Ga_2N_2O_2S_2$ (Mw 646.24) C 52.0 %; H 7.2 %; Found: C 52.4 %; H 7.8 %. ^{1}H NMR (C$_6$D$_6$, 400.13 MHz): *δ (ppm)* 0.78 (6H, t, *CH$_3$*(CH$_2$)$_3$CH), 1.18 (4H, m, CH$_3$(*CH$_2$*)$_3$CH), 1.69 (4H, m CH$_3$(*CH$_2$*)$_3$CH), 1.94 (4H, m, CH$_3$(*CH$_2$*)$_3$CH), 2.02 (6H, s, N(*CH$_3$)$_2$*), 2.09 (2H, m CH$_3$(CH$_2$)$_3$*CH*), 2.36 (6H, s, N(*CH$_3$)$_2$*), 2.67 (2H, AX system, *CH$_2$*N), 3.45 (2H, AX system, *CH$_2$*N), 5.79 (2H, s, *OH*), 6.81 (2H, d, *ArH*), 7.13 (2H, d, *ArH*), 7.29 (2H, *ArH*). ^{13}C NMR (C$_6$D$_6$, 100.61 MHz): *δ (ppm)* 16.5 (*CH$_3$*(CH$_2$)$_3$CH), 23. (CH$_3$(*CH$_2$*)$_3$CH), 24.0 (CH$_3$(*CH$_2$*)$_3$CH), 38.7 (CH$_3$(*CH$_2$*)$_3$CH), 43.7 (N(*CH$_3$)$_2$*), 44. (N(*CH$_3$)$_2$*), 64.1 (*CH$_2$*N), 73.2 (CH$_3$(CH$_2$)$_3$*CH*), 123.9 (*C*(3)), 126.7 (*C*(4)), 129.1 (*C*(5) 134.5 (*C*(6)), 141.0 (*C*(2)), 152.5 (*C*(1)).

General method for the preparation of GaS thin films by spin coating.

0.3 g organogallium precursor **1** was dissolved in 5 ml of propylamine to give solutio with c = 0.08 M. The above mentioned GaS thin layers were prepared by spin coating o as-prepared solution (1 ml per sample) on single-crystalline silicon wafer substrates (c 10 mm x 10 mm x 0.3 mm) using SpinMaster spincoater using one step – 500 - 10k rpm for 60 sec. After spin coating, the layers were vacuum dried at 150°C using vacuum oven at 1 mBar. Afterwards, the layers were subject of thermal annealing for 12 hours a 250°C. The thickness of the as-dried layers was approximately 0.2 – 0.3 μm a determined by SEM.

Characterization methods of GaS material.

The surface of the GaS films and their chemical composition were studied usin scanning electron microscopy (SEM, JSM-5 500 LV Jeol) linked with energy-dispersiv x-ray analyzer (EDX). Standard uncertainty of EDX measurements is ±1 at. % Typically, the EDX measurements were performed at 3 spots per sample and averaged Optical functions of prepared GaS layers as well as their thicknesses were obtaine from the analysis of spectroscopic ellipsometry data measured using an ellipsomete with automatic rotating analyzer (VASE, J. A. Woollam Co., Inc.) on samples grown o silicon substrates. The measurement parameters are as follows: spectral region 190 1770 nm (i.e., 6.49 – 0.7 eV) with wavelengths steps of 10 nm and angles of incidenc 65°, 70° and 75° (see Figure S6 in SI). The measured ellipsometric *Ψ*, *Δ* data were fitte using the following layered model: “Substrate / Thin Film / Roughness”. The optica constants of substrate were known from previous measurement. Optical constants o spin-coated film were determined using the Cody-Lorentz model. This model appropriate for the description of amorphous chalcogenides optical functions.[27] Atomi force microscopy (Solver NEXT, NT-MDT) was used to study topography of GaS thi films within typical scanned area 10 μm × 10 μm in semicontact mode. Phase behavio of all four compounds was studied in the temperature range of 183 to 373 K using DSC Thermal Analysis Q1000 using a heating rate of 2 K·min^{-1} and hermetic aluminium pans, however no phase transitions were observed in this temperature range. TG analysis has been measured at thermogravimetric analyzer SETARAM Setsys Evolutio in an open platinum 100 liters crucible employing temperature range 298 to 573 K or 2 to 500 °C with temperature gradient 10K/min in inert He atmosphere. The crystalline o amorphous state of deposited thin films was studied by X-ray diffraction (XRD analysis employing a diffractometer Bruker AXE D8-Advance using Cu *Kα* radiatio with secondary graphite monochromator. Elemental analyses were performed on a LECO-CHNS-932 analyzer.

Crystallography: The X-ray data for colorless crystals of **1 - 4** were obtained at 150K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K$_\alpha$ radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.[28] The absorption was corrected by integration methods.[29] Structures were solved by direct methods (Sir92)[30] and refined by full matrix least-square based on F^2 (SHELXL97).[31] Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors H$_{iso}$(H) = 1.2 U$_{eq}$ (pivot atom) or of 1.5U$_{eq}$ (methyl). H atoms in methyl, methylene, methine moieties and hydrogen atoms in aromatic rings were placed with C-H distances of 0.96, 0.97, 0.98 and 0.93. In **4**, the hydrogen atoms belonging to the OH group were placed according to the maxima observed on the Fourier difference density map. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 1496647, 1496650, 1496649 and 1496648 for **1, 2, 3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Supporting Information. Crystallographic parameters of compounds **1** - **4** (Table S1), summary of thermogravimetric results (Table S2), TG curves for **1** – **3** (Figures S1-3), XRD data of the GaS material (Figure S4), elemental composition of initial precursor **1** and thin GaS layer sputtered on glass slide (Table S3), Variable Angle Spectroscopic Ellipsometry (VASE) (Figure S6), additional attempts of the preparation of GaS thin films without any contents of carbon and dependence of S/Ga ratio on annealing temperatures (Table S4 and Figure S5).

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Entry for the Table of Contents

Single Source Precursor

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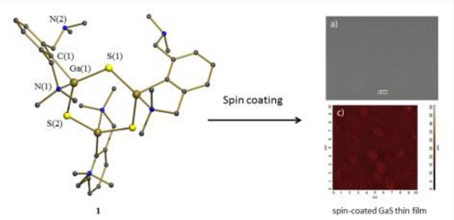
Intramolecularly coordinated gallium sulfides: Suitable single source precursors for GaS thin films



N→Ga coordinated organogallium sulfides containing either N,C,N- or *C*,*N*-chelating ligands were prepared. As the result of different ligands, compounds differ in their structure mutually. To change the Ga/S ratio, an unusually N→Ga coordinated organogallium tetrasulfide was prepared either.

All compounds were further studied as potential single source precursors for GaS thin film deposition by spin coating method and obtained values fall into the regions reported for the GaS materials prepared by different techniques.