Synthesis and characterization of gallium thiocarboxylates as novel single-source precursors to gallium sulfide thin films by aerosol-assisted CVD

Guihua Shang, Mark J. Hampden-Smith* and Eileen N. Duesler

Department of Chemistry and Center for Micro-Engineered Materials, University of New Mexico, Albuquerque, NM 87131, USA

The first example of a structurally characterized gallium thiocarboxylate compound, $Ga(SCOMe)_2Me(dmpy)$ 1 (dmpy = 3,5-dimethylpyridine), is synthesized and used to deposit high-purity, crystalline gallium sulfide thin films by aerosol-assisted chemical vapour deposition at low temperatures.

Compounds containing bonds between sulfur and other main-group elements exhibit a rich and interesting structural chemistry due to the wide variety of bonding modes available. In addition, many of these molecules can be used as single-source precursors to produce metal sulfide materials.[1–9] In some cases, it also has been demonstrated that the molecular structure of the metal–sulfur cluster has a strong influence on the composition and crystal structure of the final metal sulfide material.[1,5,10] There has been increasing interest in group 13 chalcogenides, in particular ME and M_2E_3 (M = Ga, In; E = S, Se) phases, due to their potential applications in switching devices,[11] photovoltaics,[12] nonlinear optics[13] and displays.[15,16]

We are interested in synthesizing molecular compounds containing the group 13 elements with sulfur-containing ligands as precursors for the chemical vapour deposition (CVD) of group 13 sulfide thin films. Here we report the synthesis and characterization of the first example of a structurally characterized monomeric gallium thiocarboxylate compound, $Ga(SCOMe)_2Me(dmpy)$ **1**, as well as another gallium tris(thioacetate) compound, $Ga(SCOMe)_3(dmpy)$ (dmpy = 3,5-dimethylpyridine). We have found that the facile elimination of thioacetic anhydride provided a pathway to deposit high purity, stoichiometric, metal sulfide films according to eqn. (1).[17]

$$M(SOCMe)_2{\cdot}L \xrightarrow{\text{heat}} MS + (MeCO)_2S + L \qquad (1)$$

Here, the results of preliminary experiments which demonstrate that these new monomeric gallium thiocarboxylate compounds are suitable for deposition of gallium sulfide films are described.

Trimethylgallium was reacted with 3.0 equiv. of thioacetic acid in toluene in the presence of dmpy. The release of a gaseous product, presumed to be ethane, was observed. After the solvent was removed in vacuum, a light-yellow oily residue was obtained. To the above oily residue, some fresh pentane was added to give a light-yellow clear solution. On storing this solution at room temperature for one day, clear plate-shaped crystals were formed. These were characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis, TGA and single-crystal X-ray diffraction and shown to be $Ga(SCOMe)_2Me(dmpy)$ **1**, the first example of a structurally characterized gallium thiocarboxylate compound.‡ Very few examples of thiocarboxylate compounds of group 13 metals (M = Ga, In) have been reported in the literature.[1,5,21–23] The solid-state molecular structure of **1** is shown in Fig. 1. In the solid state, the Ga centre is tetrahedrally coordinated by two S atoms from two monodentate thioacetate ligands, one C atom from the methyl group and one N atom from neutral dmpy. Note that only two of the methyl groups in the starting material reacted with thioacetic acid, even when more than 3 equiv. of thioacetic acid was used. We speculate that the replacement of the first two methyl groups deactivates the third Ga–Me bond, resulting in the lack of the further reaction. The analytical and spectroscopic data for **1** were all consistent with the solid-state X-ray diffraction results and other structurally characterized Ga compounds.[18–20]

In contrast, the reaction of $GaEt_3$ with 3.0 equiv. of thioacetic acid in toluene in the presence of dmpy gave rise to the formation of $Ga(SCOMe)_3(dmpy)$.§ Compound **2** was characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopies which revealed that all the ethyl groups had reacted.§ We have observed similar subtle differences in the reactions of methyl and ethyl substituted gallium(III) compounds previously as exemplified by their reactions towards S_8.[18]

Thermogravimetric analyses of **1** and **2** showed both compounds decomposed at *ca.* 170 °C to give crystalline Ga_2S_3 as determined by X-ray diffraction. In the case of **1**, two distinct steps of mass loss were observed in TGA experiments. The first mass loss was consistent with the loss of dmpy and thioacetic anhydride (calc. 48.7%, found 49.0%) and the second step was consistent with loss of acetone (calc. 16.9%, found, 17.1%). In addition, both thioacetic anhydride and acetone were detected in the ^1H NMR spectrum of cold-trapped by-products from the solid-state thermal decomposition of **1** as shown in Scheme 1

For **2**, quantitative thioacetic anhydride elimination was observed on heating in the solid state, Scheme 2.

Both compounds were employed for aerosol-assisted chemical vapour deposition (AACVD)§ to produce Ga_2S_3 thin films.

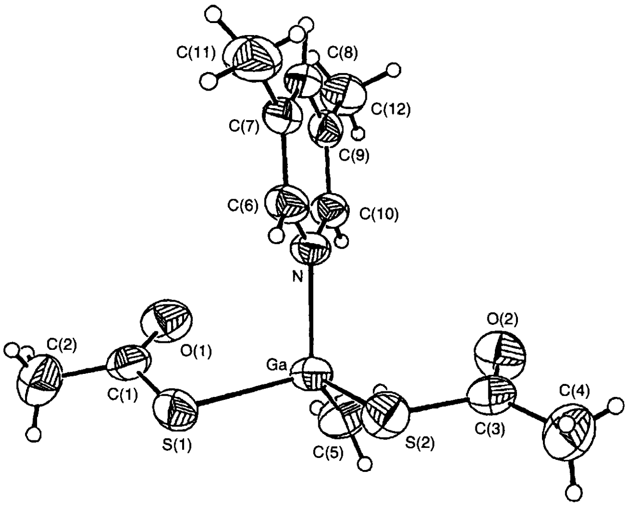
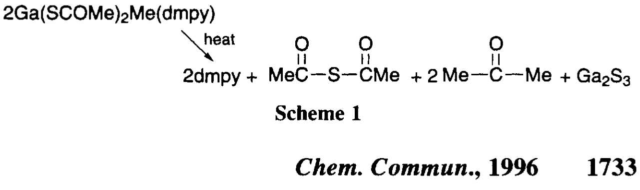
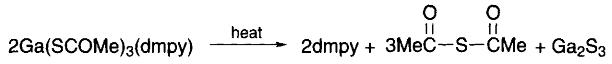


Fig. 1 Molecular structure of $Ga(SCOMe)_2Me(dmpy)$ **1**; relevant bond lengths (Å): Ga–S(1) 2.297(1), Ga–S(2) 2.288(2), Ga–C(5) 1.941(7), Ga–N 2.209(3)



$$2Ga(SCOMe)_2Me(dmpy) \xrightarrow{\text{heat}} 2dmpy + MeC(=O){-}S{-}C(=O)Me + 2\,Me{-}C(=O){-}Me + Ga_2S_3$$

Scheme 1



$$2\mathrm{Ga(SCOMe)_3(dmpy)} \xrightarrow{\text{heat}} 2\mathrm{dmpy} + 3\mathrm{Me}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}-\mathrm{S}-\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{Me} + \mathrm{Ga_2S_3}$$

Scheme 2

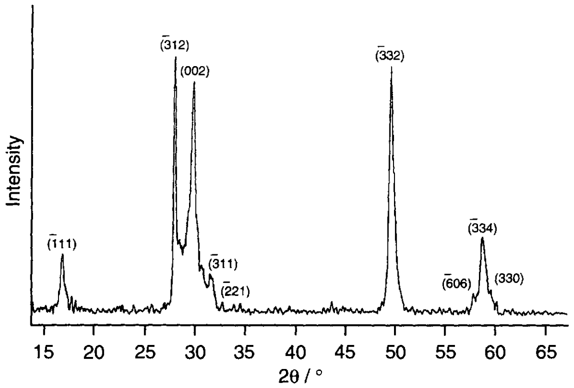


Fig. 2 X-Ray diffraction pattern for the Ga_2S_3 film deposited from **1**

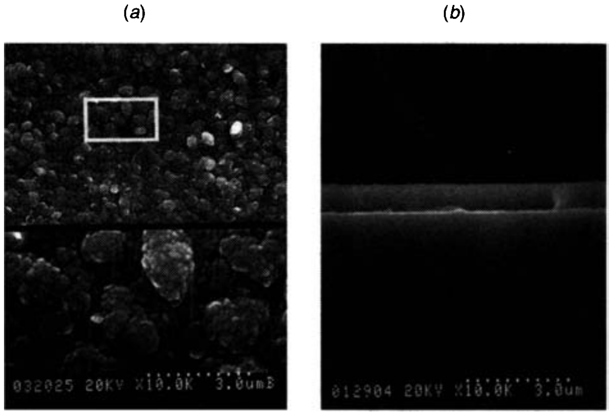


Fig. 3 Scanning electronic micrographs of the Ga_2S_3 film formed at 290 °C from **1**, (*a*) top view, (*b*) cross-section view

At relatively low temperatures (275–310 °C), uniform crystalline Ga_2S_3 films were obtained and characterized by X-ray diffraction to be the hexagonal Ga_2S_3 phase (JCPDS no. 30-0577), see Fig. 2. The electron microprobe results confirmed the film composition to be Ga_2S_3 (40.58% Ga, 59.42% S). Attempts to determine the Ga:S ratio by Auger electron spectroscopy (AES) were thwarted by negative charging of the sample due to the value of the total secondary electron emission coefficient, σ, being < 1.[24] However, no other elements were observed in those samples revealing a high purity level within the limits of this detection method. Scanning electronic microscopy of the surface of the film showed a uniform morphology (Fig. 3). The deposition rate is about 10 nm min^{-1}. These AACVD results demonstrate that **1** and **2** can be used as single-source precursors to make final binary Ga_2S_3 thin films at relatively low temperature.

We thank the Office of Naval Research for funding this research, the National Science Foundation Chemical Instrumentation program for the purchase of a low-field NMR spectrometer and the Dreyfus Foundation and AFOSR for the purchase of a X-ray powder Diffractometer. We thank Dr Paolina Atanasova for obtaining the AES data.

Footnotes

† Synthesis of **1**: To a clear toluene solution of $GaMe_3$ (0.576 g, 0.005 mol) in a glove box, thioacetic acid (1.15 g, 0.015 mol) was added dropwise slowly to form a light-yellow clear solution. The release of gas bubbles was observed. To the solution, 1.0 ml of dmpy was added dropwise. The final light-yellow clear solution was stirred for one day at room temp. under N_2. After the solvent was pumped out, a light orange oily residue was formed. To this residue, 7.0 ml fresh pentane was added and upon storing this pentane solution at room temp. for 1 d, clear plate-shaped crystals formed. After filtration, washing with pentane and pumping dry, 1.2 g of **1** was obtained. The final yield is 70%.

‡ *Characterization data for* **1**: ^1H NMR (250 MHz, 20 °C, C_6D_6): δ 0.97 (s, 3 H, GaMe), 1.47 (s, 6 H, Me of dmpy), 2.19 (s, 6 H, Ga(SCO*Me*)$_2$], 6.31 (s, 1 H, dmpy), 8.55 (s, 2 H, dmpy). ^{13}C NMR (63 MHz, 20 °C, C_6D_6): δ − 4.22 (s, GaMe), 17.62 (s, Me of dmpy), 34.82 [s, Ga(SCO*Me*)], 135.17 (s, dmpy), 141.85 (s, dmpy), 144.85 [s, dmpy), 201.95 [s, Ga(SCOMe)].

Crystal data: $C_{12}H_{18}GaNO_2S_2$, triclinic, space group $P\bar{1}$, $a = 9.173(1)$, $b = 9.935(2)$, $c = 10.748(1)$ Å, $\alpha = 79.30(1)$, $\beta = 65.02(1)$, $\gamma = 63.79(1)$, $U = 796.6(2)$ Å^3, $Z = 2$, $D_c = 1.426$ g cm^{-3}, $T = 25$ °C, Siemens R_{3m}/V, $\lambda_{Mo\text{-}K\alpha} = 0.71073$ Å. Of 5463 data, ($2 < 2\theta < 50.0°$), 2736 were independent and 2024 were observed [3.0σ(*F*)]. The structure was solved by the Patterson method; $R_w = 0.0303$, $R = 0.0327$. SHELXL software used for all computations (G. M. Sheldrick, Siemens, XRD, Madison, WI). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/127.

§ Details available from the authors.

References

1 I. Dance and K. Fisher, *Prog. Inorg. Chem.*, 1994, **41**, 637.
2 B. Krebs, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 113.
3 A. R. Barron, *Mater. Res. Soc. Symp. Proc.*, 1994, **335**, 317.
4 A. R. Barron, *Comments Inorg. Chem.*, 1993, **14**, 123.
5 I. Dance, *Polyhedron*, 1986, **5**, 1037.
6 A. Muller and E. Diemann, *Adv. Inorg. Chem.*, 1987, **31**, 89.
7 M. Draganjac and T. B. Rauchfuss, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 742.
8 O. M. Yaghi, Z. Sun, D. A. Richardson and T. C. Groy, *J. Am. Chem. Soc.*, 1994, **116**, 807.
9 L. E. Maelia and S. A. Koch, *Inorg. Chem.*, 1986, **25**, 1896.
10 N. Herron, J. C. Calabrese, W. E. Farneth and Y. Wang, *Science*, 1993, **259**, 1426.
11 T. Nishino and Y. Hamakawa, *Jpn. J. Appl. Phys.*, 1977, **16**, 1291; R. S. Becher, T. Zheng, J. Elton and M. Saeki, *Sol. Energy Mater.*, 1986, **13**, 97.
12 R. Nomura, K. Kanaya, A. Moritak and H. Matsuda, *Thin Solid Films*, 1988, **167**, L27; W. T. Kim and C. D. Kim, *J. Appl. Phys.*, 1986, **60**, 2631; L. I. Man, R. M. Imanov and S. A. Semiletov, *Sov. Phys. Crystallogr.*, 1976, **21**, 355.
13 A. M. Mancini, G. Micocci and A. Rizzo, *Mater. Chem. Phys.*, 1983, **9**, 29.
14 See for example: J. G. Fan, Y. Kurata and Y. Nannichi, *Jpn. J. Appl. Phys.*, 1989, **28**, L2255; M. S. Carpenter, M. R. MeUoch, M. S. Lundstron and S. P. Tobin, *Appl. Phys. Lett.*, 1988, **52**, 2157.
15 *J. Electron. Mater.*, Special Issue on Wide-Bandgap II–IV Semiconductor Materials, 1993, **22**, 429.
16 N. Braithwaite and G. Weaver, *Electronic Materials*, Butterworth, London 1990.
17 K. Kunze, M. J. Hampden-Smith and E. Duesler, *Adv. Mater.*, 1996, *2*, 105.
18 G. Shang, M. J. Hampden-Smith and E. Duesler, *Inorg. Chem.*, 1996, **35**, 2611.
19 M. B. Power, J. W. Ziller, A. N. Tyler and A. R. Barron, *Organometallics*, 1992, **11**, 1055.
20 M. B. Power, J. W. Ziller and A. R. Barron, *Organometallics*, 1992, **11**, 2783.
21 H. D. Hausen and J. J. Guder, *J. Organomet. Chem.*, 1973, **57**, 243.
22 J. Weidlein, *J. Organomet. Chem.*, 1971, **32**, 181.
23 A. J. Downs, *Chemistry of Aluminium, Gallium, Indium and Thallium*, Blackie Academic & Professional, London, 1993, p. 322.
24 *Practical Surface Analysis*, ed. D. Briggs and M. P. Seah, Vol. 1, Auger and X-ray Photoelectron Spectroscopy, Wiley, New York, 1990.

Received, 10th April 1996; Com. 6/02480G