

# Deposition of Thin Films of Gallium Sulfide from a Novel Single-Source Precursor, $\text{Ga}(\text{S}_2\text{CNMeHex})_3$ , by Low-Pressure Metal–Organic Chemical Vapor Deposition

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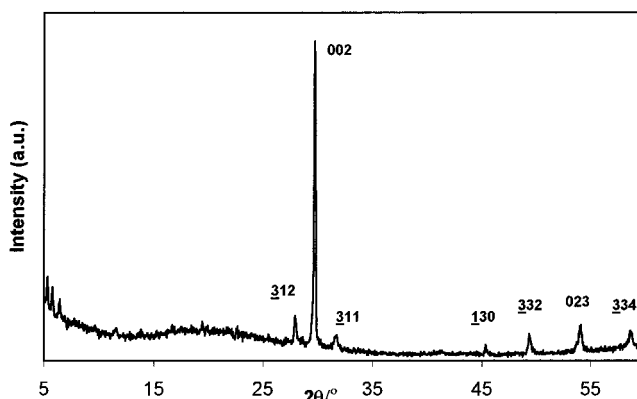
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Group III sulfide and selenides are an interesting class of materials with promise in photovoltaic and optoelectronic applications. The related ternary and quaternary materials  $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_2$  or  $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_2$  are of particular interest for solar cells.<sup>1,2</sup> Binary III/VI materials exhibit a number of stoichiometric forms including ME or  $\text{M}_2\text{E}_3$  ( $\text{M} = \text{Ga}, \text{In}, \text{Tl}$ ;  $\text{E} = \text{S}, \text{Se}, \text{Te}$ ) and have a range of mid- to wide-optical band gaps (e.g.,  $\text{In}_2\text{Te}_3 \sim 1.0$  eV and  $\alpha\text{-Ga}_2\text{S}_3 \sim 3.4$  eV).<sup>3,4</sup> Gallium sulfide has the stoichiometries GaS or  $\text{Ga}_2\text{S}_3$  and has potential application in the passivation of GaAs.<sup>5,6</sup>

A number of single-source precursors have been used for the deposition of thin films of III/VI materials by chemical vapor deposition (CVD) techniques, including thiolates,<sup>7,8</sup> selenolates,<sup>9,10</sup> thiocarboxylates,<sup>11</sup> thiocarbonates,<sup>12</sup> and dithio- and diselenocarbamates.<sup>13–15</sup> Such precursors combine the group III element and chalcogenide in a single molecule. Only quite limited literature is available on gallium sulfide thin films from single-source precursors. Barron et al. have reported the preparation of films from a series of complexes with a



**Figure 1.** XRD pattern of the  $\alpha\text{-Ga}_2\text{S}_3$  film on GaAs(111) deposited from  $\text{Ga}(\text{S}_2\text{CNMeHex})_3$  at 500 °C (Cu K $\alpha$ , 1.541 Å).

cubane core,<sup>17–19</sup> and more recently, we have prepared gallium sulfide films from  $\text{Ga}(\text{SOCNet}_2)_3$  by aerosol-assisted chemical vapor deposition (AACVD) which resulted in cubic GaS.<sup>16</sup> In this communication, we report the synthesis of a related dithiocarbamate complex  $\text{Ga}(\text{S}_2\text{CNMeHex})_3$ ,<sup>18</sup> and its use as a novel single-source precursor to deposit thin films of gallium sulfide by low-pressure metal–organic chemical vapor deposition (LP-MOCVD).

The compound used in this experiment has two major advantages: it is easy to synthesize, and it is air-stable. Thermogravimetric analysis (TGA) of the compound was carried out at atmospheric pressure with  $\text{N}_2$  as the carrier gas. The heating rate was 10 °C/min. The TGA curve showed that the precursor started to sublime at 180 °C and decomposed at 280 °C, leaving an 18%

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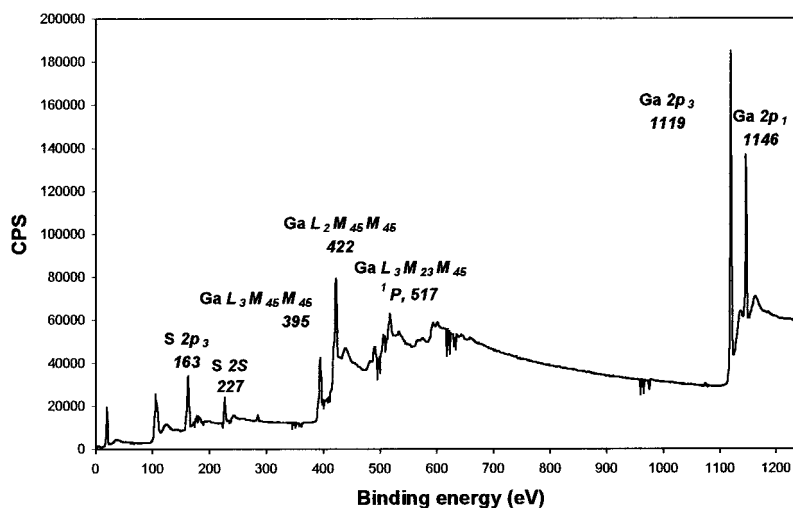
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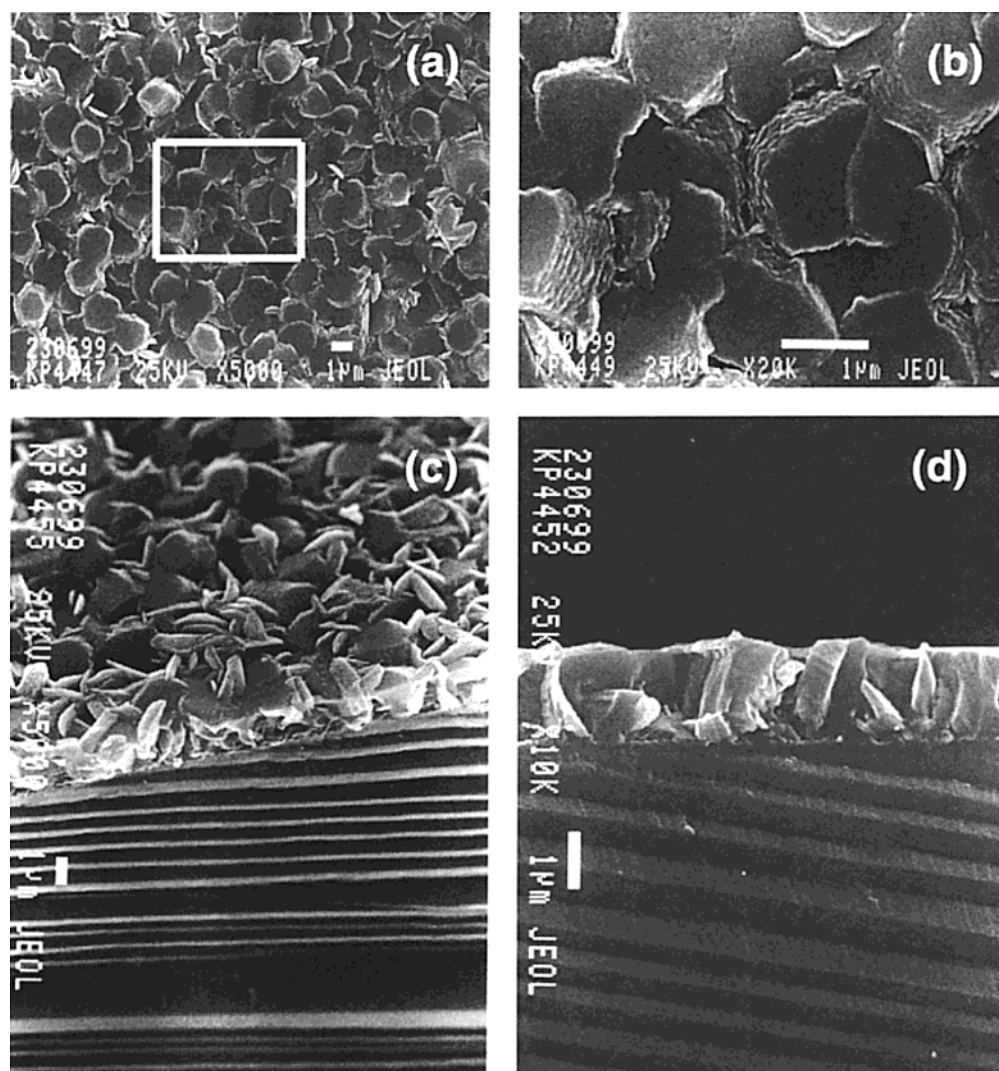
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(18) **Preparation of Tris(methylhexylthiocarbamate)gallium(III),  $\text{Ga}(\text{S}_2\text{CNMeHex})_3$ .** Sodium methylhexylthiocarbamate was prepared by the literature method.<sup>15</sup> Gallium(III) chloride was a gift from Epichem Ltd. Sodium methylhexylthiocarbamate (8.21 g, 46.90 mmol) was dissolved in absolute ethanol (~40 mL). Gallium(III) chloride dissolved in hexane (0.28 M in hexane, 14.7 mL, 15.63 mmol) was slowly added to the solution, and the mixture was allowed to stir for 1 h at room temperature. A white solid was deposited from the light yellow solution. This was filtered off and recrystallized from benzene to give a white crystalline solid: yield = 7.93 g (83%) (based on  $\text{GaCl}_3$ ); mp 86 °C; <sup>1</sup>H NMR ( $\delta$ , DMSO- $d_6$ , 400 MHz) 0.85 [9H, t,  $-\text{CH}_2-\text{CH}_3$ , <sup>3</sup> $J_{\text{H-H}}$  6.8 Hz], 1.27 [18H, m,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ], 1.63 [6H, m,  $\text{NCH}_2\text{CH}_2\text{CH}_2-$ ], 3.27 [9H, s,  $-\text{NCH}_3$ ], 3.68 [6H, t,  $\text{NCH}_2-\text{CH}_2-$ , <sup>3</sup> $J_{\text{H-H}}$  7.5 Hz]; <sup>13</sup>C NMR ( $\delta$ , DMSO- $d_6$ , 100 MHz) 13.87 [ $-\text{CH}_3$ ], 22.03 [ $-\text{CH}_2\text{CH}_3$ ], 25.65 [ $-\text{CH}_2-$ ], 26.13 [ $-\text{CH}_2-$ ], 30.81 [ $-\text{CH}_2-$ ], 42.40 [ $-\text{CH}_2-$ ], 57.10 [ $-\text{CH}_2-$ ], 199.77 [ $\text{N}-\text{C}-\text{S}_2$ ]. IR (Nujol mull,  $\text{cm}^{-1}$ ) 2932(w), 2858(m), 1508(s), 1391(m), 1192(m), 1078(w), 976(s), 727(2), 608(w). Microanalysis: Calculated for  $\text{C}_{24}\text{H}_{48}\text{GaN}_3\text{S}_6$ : C, 45.0; H, 7.5; N, 6.6%. Found: C, 44.4; H, 7.2; N, 6.5%.

(19) **Deposition of Thin Films by LP-MOCVD and Thin-Film Analyses.** Thin films of gallium sulfide were grown on glass, silicon wafer (100), and GaAs (111) single-crystal substrates by low-pressure metal–organic chemical vapor deposition (LP-MOCVD). The reactor was a cold wall, horizontal reactor. The substrate was heated by a tungsten halogen lamp, and the precursor by a Carbolite tube furnace, the system was under a dynamic vacuum at  $\sim 10^{-2}$  Torr. The gallium complex,  $\text{Ga}(\text{S}_2\text{CNMeHex})_3$  (~20 mg), was used in each experiment. The films were then analyzed by X-ray powder diffraction (Siemens D5000, Cu K $\alpha$ ), energy-dispersive X-ray analysis (JEOL J535CM/LINK QX2000), and XPS analysis was performed on a Escalab 220i instrument using focused (500  $\mu\text{m}$  spot size) monochromatic Al K $\alpha$  radiation at a pass energy of 20 eV. Scans were acquired with steps of 20 meV. The binding energies were referenced to the adventitious hydrocarbon C1s peak at 284.8 eV.



**Figure 2.** XPS spectrum of the  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> film deposited on GaAs(111) from Ga(S<sub>2</sub>CNMeHex)<sub>3</sub> at 500 °C (Al K $\alpha$ , 20 eV).



**Figure 3.** SEM images of  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> films deposited on GaAs(111) from Ga(S<sub>2</sub>CNMeHex)<sub>3</sub> at 500 °C: (a and b) top view, (c) tilted view, and (d) cross-sectional view.

residue. Hence, the evaporation temperature for the precursor was set to 230 °C in subsequent deposition experiments. Deposition was attempted by AACVD and LP-MOCVD.<sup>19</sup> AACVD leads to films with a very poor morphology over a range of substrate temperatures

(350–500 °C) on glass, GaAs (111) or silicon wafer (100) substrates. However, the growth of gallium sulfide thin films by LP-MOCVD gave much improved crystallinity and morphology. In all cases the source temperature was maintained at 225 °C. Little or no film growth was

observed at substrate temperatures below 475 °C. However, at a substrate temperature of 500 °C, a crystalline film was obtained but only on the GaAs(111) substrate. EDAX analysis of the film at random sites showed a gallium-to-sulfur ratio of close to 2:3. XRD analysis of the thin film (Figure 1) grown from the compound indicated that  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> (JCPDS 30-577) was deposited on GaAs(111) with a strong reflection for (002) plane. There is no obvious lattice match between the substrate and the oriented film of  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> deposited. The effectiveness of deposition on GaAs, as opposed to glass, may reflect some initial chemical step in the nucleation and growth of the films. The XRD results are much improved over films grown from precursors such as Et<sub>2</sub>-GaS<sub>2</sub>CNEt<sub>2</sub>, which were amorphous.<sup>13</sup> Films obtained from a gallium thiocarboxylate,<sup>20</sup> using AACVD, were found to be of the same phase ( $\alpha$ -Ga<sub>2</sub>S<sub>3</sub>) but with a different preferred orientation ( $\bar{3}12$ ). XPS analysis confirmed that only gallium (2p<sub>1</sub>, 2p<sub>3</sub>, and Auger lines L<sub>2</sub>M<sub>45</sub>M<sub>45</sub>, L<sub>3</sub>M<sub>23</sub>M<sub>45</sub>, and L<sub>3</sub>M<sub>45</sub>M<sub>45</sub>) and sulfur (2s and 2p<sub>3</sub>) are present at the surface (Figure 2). Analysis of the film by SEM (Figure 3) shows average particle sizes of  $\sim 2\ \mu\text{m}$  in plane view in a film of thickness  $\sim 1.5\ \mu\text{m}$  (30 min growth). Films grown from Et<sub>2</sub>GaS<sub>2</sub>CNEt<sub>2</sub>,<sup>13</sup> or [(<sup>t</sup>Bu)<sub>2</sub>Ga(S<sup>t</sup>Bu)]<sub>2</sub>,<sup>17</sup> were dominated by spherical par-

ticles, a quite different morphology from those observed in this study.

It is interesting to note that the precursor [Ga-(SOCNEt<sub>2</sub>)<sub>3</sub>] leads, under similar conditions, to films of the cubic phase of GaS with a 1:1 stoichiometry. The present work leads to the more sulfur-rich phase Ga<sub>2</sub>S<sub>3</sub>. It is tempting to conclude that the different phases depend on the supply of sulfur from the precursor which may suggest that the amount of an element delivered by a single-molecule precursor is one factor important in controlling the phase deposited. These studies demonstrate the formation of dense and relatively thick polycrystalline Ga<sub>2</sub>S<sub>3</sub> films from a precursor which is air stable and relatively easy to synthesize.

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