Communications

Deposition of Thin Films of Gallium Sulfide from a Novel Liquid Single-Source Precursor, Ga(SOCNEt₂)₃, by Aerosol-Assisted CVD**

By *Graeme A. Horley*, *Mike R. Lazell*, and *Paul O'Brien**

Group III chalcogenide materials have been shown to have properties making them potentially useful in photovoltaics and optoelectronics; the ternary material $CuInSe_2$ is of particular interest.[1,2] The parent III/VI materials exhibit a number of stoichiometric forms, e.g., ME or M_2E_3 (M = Ga, In, Tl; E = S, Se, Te), and a range of mid to wide optical bandgaps (e.g., In_2Te_3 [~1.0 eV] and <ga>-Ga_2S_3 [~3.4 eV]).[3,4] Gallium sulfide, as GaS or Ga_2S_3, also has potential applications as a passivating coating on GaAs.[5,6]

The majority of the literature concerned with the deposition of thin films of III/VI materials is based on the use of single-source molecular precursors, such as thiolates,[7,8] selenolates,[9,10] thiocarboxylates,[11] thiocarbonates,[12] and dithio- and diselenocarbamates, which contain group III and group VI atoms.[13–15] These complexes have been used to deposit films at heated substrates by growth techniques such as metal-organic chemical vapor deposition (MOCVD), at either atmospheric (AP-MOCVD) or low pressure (LP-MOCVD), or by assisted methods such as aerosol-assisted (AACVD) or plasma-enhanced (PECVD) chemical vapor deposition. Other routes to III/VI semiconductors, including MOVPE, have also been reported.[16]

A number of gallium chalcogenide complexes have been developed as reliable sources for the deposition of gallium sulfide films. Notably, Barron and co-workers have reported the preparation of a series of complexes with a central cubane core, and suggested that the structure of the precursor has a marked effect on the phase and morphology of the thin films deposited.[17–19] Recently, we have reported the deposition of indium sulfide (β-In_2S_3) thin films by LP-MOCVD, grown from a novel indium monothiocarbamato complex, In(SOCNEt₂)₃.[20] In this communication,

we report the synthesis of the analogous gallium monothiocarbamato complex, Ga(SOCNEt₂)₃, and its use as a novel single-source precursor to deposit thin films of gallium sulfide by AACVD.

X-ray diffraction (XRD) analysis of the thin films grown from Ga(SOCNEt₂)₃ reveal an interesting, highly oriented coating, showing just two peaks at *d*-spacings of 1.41 and 2.81 Å (Fig. 1). The peaks are not consistent with any standard gallium sulfide phase, however, Barron and co-workers have prepared GaS films from [ᵗBuGaS]₄ on GaAs(100) substrates, which give a very similar XRD pattern, with two strong reflections assigned as the 200 and 400 reflections of the face-centered cubic (fcc) GaS phase.[17,18] If we follow the assignment of Barron, the peaks are consistent with the fcc form of GaS: 1.41 Å 400 and 2.81 Å 200. These assignments lead to a lattice parameter, a_0, of 5.6 Å, which may be compared to Barron's lattice parameter, a_0, of 5.4 Å. These oriented films have been suggested to be due to the precursor deposition method, i.e., retention of the precursor's cubane structure,[20] although Barron does state that single-crystal substrates (GaAs) having a similar orientation enhance the growth. Our results suggest a similar degree of preferred orientation but on an amorphous glass substrate, which does not have any effect on growth.
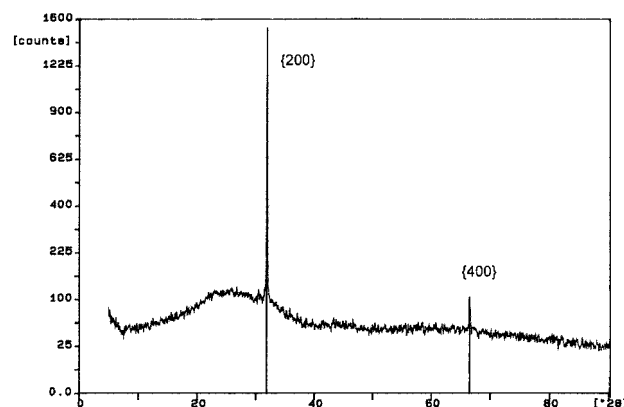

Fig. 1. X-ray diffraction analysis for gallium sulfide film grown from Ga-(SOCNEt₂)₃.

Energy dispersive X-ray analysis (EDAX) of the films at random sites of the film show a gallium to sulfur ratio close to 1:1, with no apparent oxygen contamination, a similar result to that observed for indium sulfide films grown from In(SOCNEt₂)₃ by LP-MOCVD.[21] X-ray photoelectron spectroscopy (XPS) analysis confirms that only gallium ($2p_1$, $2p_3$, and Auger lines $L_2M_{45}M_{45}$, $L_3M_{23}M_{45}$, and $L_3M_{45}M_{45}$) and sulfur (2s and $2p_3$) are present at the surface (Fig. 2). The unassigned peaks are consistent with the borosilicate glass substrate.

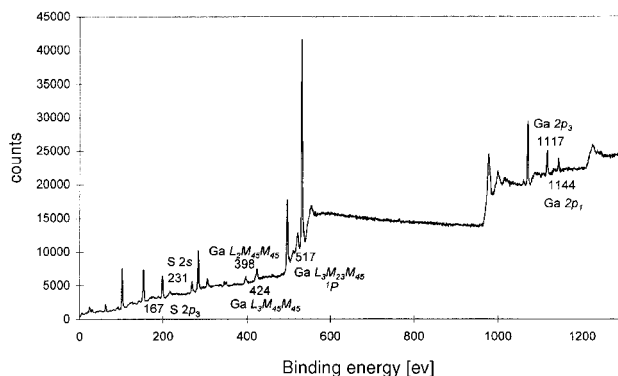Analysis of the films by scanning electron microscopy (SEM) showed an interesting surface structure for the crys-

Fig. 2. X-ray photoelectron spectrum of GaS film deposited from Ga(SOC-NEt$_2$)$_3$.

tallites as deposited by AACVD (Fig. 3). There was no appreciable difference in the gross morphology of the film deposited under various conditions. The individual features observed are less than 1 μm in diameter, close to spherical in shape, and arranged in a reasonably uniform array on the substrate. There also appears to be a small variation of depth to the coating. The growth of near-spherical gallium sulfide crystallites is not unprecedented. Films grown from Et$_2$GaS$_2$CNEt$_2$[13] and [(^{t}Bu)$_2$Ga(S^{t}Bu)]$_2$[17] are also reported to contain spherical particles, the latter showing similar dimensions to those reported here.
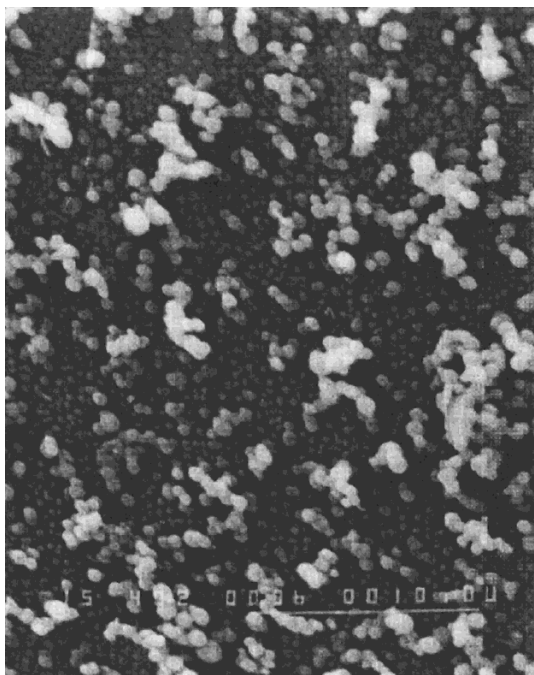

Fig. 3. SEM image of gallium sulfide film grown at 350 °C. Scale bar = 10 μm.

The deposition of gallium sulfide from Ga(SOCNEt$_2$)$_3$ is significant as it involves the use of a liquid single-source precursor; many related chalcogenide precursors are solids. The use of a liquid source might be some advantage in AACVD growth systems, as problems associated with precursor solubility are eradicated. AACVD uses only a small amount of precursor in each run, enabling the reproducibility of the method to be established on a small batch of precursor. We note that a liquid precursor would be advantageous in more conventional MOCVD applications, in which solid sources can often lead to irreproducible growth results.

Ga(SOCNEt$_2$)$_3$ is a novel liquid gallium complex which has been prepared and utilized as a single-source precursor for the deposition of face centered cubic gallium sulfide (GaS) films on glass substrates by AACVD at 350 °C. The films show a high degree of orientation on an amorphous substrate and an unusual spherical morphology similar to that observed by Barron and co-workers.[17,18] Further studies of novel precursors for the growth of group III chalcogenides are in hand.

Experimental

Sodium diethylmonothiocarbamate was prepared by the literature method [22]. Gallium(III) chloride was a gift from Epichem Ltd. Toluene and hexane (BDH) was distilled over Na/benzophenone and degassed prior to use. All manipulations and reactions were carried out in an inert atmosphere using Schlenk techniques and a vacuum line.

Preparation of Tris(diethylmonothiocarbamato)gallium(III), Ga(SOCNEt$_2$)$_3$: Sodium diethylmonothiocarbamate (1.16 g, 7.49 mmol) was suspended in dry toluene (~10 mL). Gallium(III) chloride (0.28 M in dry hexane, 8.85 mL, 2.48 mmol) was slowly added to the suspension at room temperature, with heat evolved during addition. The mixture was stirred for 4 h, at which point the liquid fraction was separated by filtration, and the solvent was removed in vacuo to yield a slightly opaque, viscous liquid. Yield = 81 % (based on GaCl$_3$). ^{1}H NMR (δ, C$_6$D$_6$, 400 MHz): 0.74 [3H, t, −CH$_2$−, $^3J_{H-H}$ 7.0 Hz]; 0.83 [3H, t, −CH$_2$−, $^3J_{H-H}$ 7.0 Hz]; 2.99 [2H, q, C−CH$_3$, $^3J_{H-H}$ 7.0 Hz]; 3.12 [2H, q, C−CH$_3$, $^3J_{H-H}$ 7.0 Hz]. ^{13}C NMR (δ, C$_6$D$_6$, 100 MHz): 12.88 [CH$_3$]; 41.74 [−CH$_2$−]; 48.53 [−CH$_2$−]; 182.06 [N−C−OS]. Microanalysis: Calculated for C$_{15}$H$_{30}$GaS$_3$O$_3$N$_3$−C: 38.64; H: 6.48; N: 9.01 %. Found: C: 37.98; H: 6.02; N: 8.59 %.

Deposition of Thin Films by AACVD: Thin films of gallium sulfide were grown on borosilicate glass slides by aerosol-assisted chemical vapor deposition (AACVD). The growth apparatus consisted of a flask containing the solution with a pipette connected to a nitrogen flow, which was used as the propellant and carrier gas. The flask was attached, via reinforced tubing, to a silica tube containing the glass substrates, which were heated in a tube furnace.

The gallium complex Ga(SOCNEt$_2$)$_3$ (~20 mg) was dissolved in dry tetrahydrofuran (20 mL) at room temperature, and injected into the growth apparatus, with the substrate at 350 °C. The system was allowed to run for 1 h, with a constant nitrogen flow rate of 100 sccm (carrying the precursor from flask to substrate), at which point the substrates, bearing white, thin coatings were collected. The films were then analyzed by X-ray powder diffraction (Philips PW1700), energy dispersive X-ray analysis (JEOL T220- A/LINK QX2000), X-ray photoelectron spectroscopy (VG ESCALAB-Mk II) and scanning electron microscopy (JEOL J535CM).

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Detection of H_yInN_x Species in InN Deposition Using the Organoindium Azide Precursor $(N_3)In[(CH_2)_3NMe_2]_2$**

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A new route to organometallic chemical vapor deposited group 13 nitrides—in particular to InN layers—is the single source precursor method, which takes advantage of preformed covalent In–N bonds in the precursor molecule. This method thus provides the possibility of depositing InN layers at substrate temperatures of 350–450 °C, much cooler than is needed for the conventional process (T > 850 K) using $In(CH_3)_3$ and NH_3. With the aim of the rational design and improvement of suitable single source precursors for InN, molecular beam sampling, using quadrupole mass spectrometry, has been used to study the fragmentation of the selected precursor $(N_3)In[CH_2CH_2CH_2N(CH_3)_2]_2$ (**1**). We show that fragments such as H_yInN_x ($y = 0$–2, $x = 0$–3) appear in the boundary layer above the sapphire substrate during thermal decomposition of the precursor $(N_3)In[CH_2CH_2CH_2N(CH_3)_2]_2$ (**1**) in the temperature range 400–1000 K. The temperature dependence of the rel-

ative abundance of the species is shown to be correlated with the growth rate of InN layers.

Thin epitaxial $In_xGa_{1-x}N$ layers serve as optically active components in blue–green light emitting devices.[1] The incorporation of In into group 13 nitride materials grown by organometallic vapor phase epitaxy using simple metal alkyls MR_3 (R = CH_3) and ammonia (NH_3) is, however, difficult to control and requires precise adjustment of the flow rates, as well as a very large excess of ammonia (V/III > 10^4) because of the low-lying onset of the thermal decomposition of InN at 800 K.[2–4] We have demonstrated the growth of polycrystalline InN at low temperatures (600–750 K) without ammonia, using the single molecule precursor $(N_3)InR'_2$ (**1**) with R' = $(CH_2)_3N(CH_3)_2$.[5a,5b] Other related work on azide-type single molecule precursors for group 13 nitrides has been published recently.[6,7] Due to the intramolecular Lewis base adduct stabilization $(N_3)In[CH_2CH_2CH_2N(CH_3)_2]_2$ (**1**) is non-pyrophoric, non-explosive and even air-stable (melting point 340 K). It sublimes readily at 330 K and 10^{-3} torr. In the course of the fragmentation of **1** the indium azide unit InN_3 is thought to generate InN by splitting off N_2 as a leaving group, thus serving as the source for growth relevant species containing a covalent In–N bond. In order to prove this idea and aiming at a further development of this concept we monitored the gas-phase composition of the boundary layer above the substrate as a function of the substrate temperature.

The experimental setup is described in detail elsewhere.[7] Briefly, probing the species from the gas phase in the layer close to the substrate is performed in a molecular beam sampling system that consists of three differential pumped vacuum chambers. The precursor reservoir and the supply of the precursor into the reaction chamber ($p = 6$ hPa) are made of quartz glass and are heated to 350 K during the experiment, whereas Argon (16 sccm) was used to carry the precursor from a reservoir onto a *c*-plane sapphire substrate (0001). The main gas stream is pumped by a mechanical pump, while through a small hole (200 μm diameter) in the sapphire substrate, a molecular beam is formed by species within the gas flow. This beam then passes into the next vacuum chamber ($p = 10^{-1}$ Pa). Subsequently the beam enters through a skimmer into a third vacuum chamber ($p = 10^{-4}$ Pa) and the species within the molecular beam are analyzed by a quadruple mass selector (Balzers QMS 311) with electron impact ionization. The ionization energy in all experiments was fixed at 20 eV and therefore no fragmentation in the mass spectrometer due to electron impact should occur.

Figure 1 depicts the mass spectrum of compound (**1**). The fragmentation of dinitrogen N_2 from the azide group (N_3) or total loss of the azide group is favored at this temperature (500 K; mass peaks at 201, 215, 229, 243, and 287 amu) and so the dominant species are those that have retained the organic group R'. Most interestingly, fragments of the general type H_yInN_x ($y = 0$–2, $x = 0$–3) appear, which do not contain any hydrocarbons. This species should ideally yield pure InN material not contaminated by any

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