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Single source molecular precursors for the deposition of III/VI chalcogenide semiconductors by MOCVD and related techniques

Mike Lazell,[a] **Paul O'Brien,***[a] **David J. Otway**[b] **and Jin-Ho Park**[ab]

[a] *The Manchester Materials Science Centre and Department of Chemistry,*
The University of Manchester, Oxford Road, Manchester, UK M13 9PL
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine,*
South Kensington, London, UK SW7 2AY

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There has been a renaissance of interest in Group III/VI (13/16) semiconductor materials because of their potential for use in various electronics applications. The synthesis and characterization of metalorganic and organometallic compounds with Group 16 ligands have as a consequence become topical. Such molecules are used as precursors and contain direct bonds between the metal and the chalcogen. A close interplay between the development of new chemistry and the deposition of novel materials has therefore developed.

Introduction

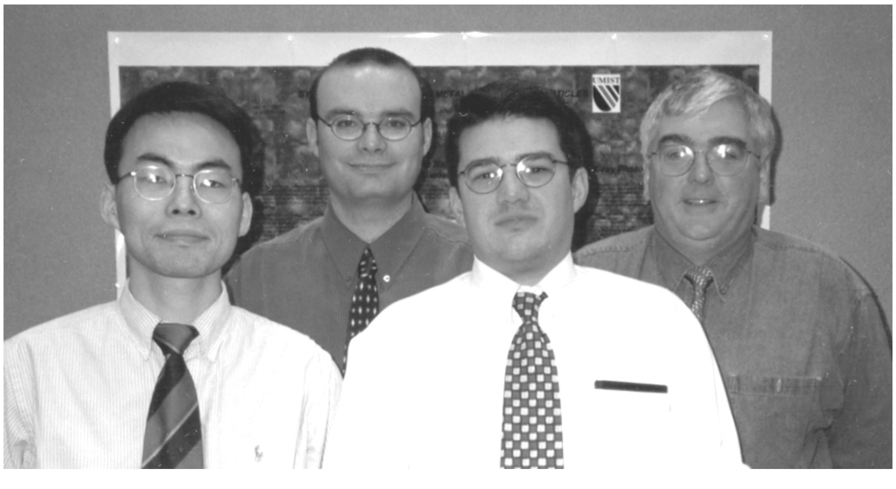
Materials containing a chalcogen and a Group 13 metal (Al, Ga, In or Tl) have been the subject of quite intense study in the last 10 years. The solid phases containing combinations of these elements have a wide range of structural types and potential uses. Developments in the deposition of these materials have seen a close interplay between the invention of new chemistry for precursors and the deposition of new and/or novel phases. Work in this area illustrates the way in which targets, in

Professor Paul O'Brien (back right) graduated from Liverpool University in 1975, obtained his PhD from the University of Wales, Cardiff in 1978 and was immediately appointed as a lecturer at Chelsea College of Science and Technology. Following the University of London re-structuring, he moved to Queen Mary and Westfield College (QMW) in 1984 and was promoted to a chair in 1994. In 1995 he moved to Imperial College of Science, Technology and Medicine (ICSTM) as a Professor of Inorganic Chemistry and Sumitomo STS Professor of Materials Chemistry (1997–1998) and was Reagents Appointed Visiting Professor at Georgia Institute of Technology (1996–1999). At present he is a Professor of Inorganic Materials, a joint appointment between the University of Manchester Chemistry Department and the Manchester Materials Science Centre and the Sumitomo/STS visiting Professor of Materials Chemistry at Imperial College.

Dr David J. Otway (front right) graduated from Imperial College in 1991 and remained there to study for a PhD with Professor D. M. P. Mingos and Dr S. R. Drake. He took a post-doctoral position at Georgia Tech., USA in 1995 with Professor W. S. Rees, Jr. and then in 1996 returned to Imperial College to work briefly with Professor Sir G. Wilkinson, FRS. In 1996 he joined Professor O'Brien's group studying precursors and thin film growth of solar cells and semiconductors. At present he is a fixed-term lecturer in the Department of Chemistry, Imperial College.

Dr Mike Lazell (back left) obtained his BSc Hons in chemistry from QMW, University of London in 1994. In 1997 he completed his PhD working on metallasiloxanes as catalysts and single-source precursors for lithium metal oxides with Professor Alice Sullivan, also at QMW. He then took a post-doctoral position at ICSTM with Professor O'Brien, working on nanoparticulate materials and thin-film deposition. In 1999 he moved with Professor O'Brien to the University of Manchester and the Manchester Materials Science Centre where he is continuing this work.

Jin-Ho Park (front left) obtained his BSc in chemistry from Andong National University in Korea, 1996. He got his MPhil from University of Wales, Cardiff under the supervision of Professors Robert D. Gillard and Mike B. Hursthouse in 1997 and then moved to ICSTM to carry out his PhD with Professor Paul O'Brien from 1998, studying the development of single-source precursors for the deposition of III/VI and metal oxide materials. He is expecting to obtain a PhD from Imperial College in 2000.



Jin-Ho Park **Mike Lazell** **David J. Otway** **Paul O'Brien**

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this case end-point materials, can influence the development of synthetic chemistry.

The materials (most often referred to as III/VI compounds in the materials literature) show great diversity. A number of different stoichiometries are observed for the binary combinations of a Group 13 metal (Ga, In, Tl) and a Group 16 chalcogen (S, Se, Te). Several structural types are found for these compounds including a defect wurzite structure for Ga_2E_3, a defect spinel for In_2E_3 and layered structures for compounds of stoichiometry ME.[1,2] In the solid state, GaS has a hexagonal layered structure; each gallium is co-ordinated to three sulfur atoms (Fig. 1a).[3] Recently Barron and co-workers reported a new simple cubic form of GaS with a lattice constant $a = 5.4$ Å.[4] Both the α and β phases of Ga_2S_3 were proposed to be wurtzite-type hexagonal phases.[5,6] However γ-Ga_2S_3 has now been suggested to be monoclinic with lattice constants $a = 6.38$, $c = 18.09$ Å (Fig. 1b).[7,8] In the case of GaSe, four polytypes have been reported; hexagonal β (isostructural with GaS), hexagonal ε, rhombohedral γ and hexagonal δ.[9] α- and β-In_2S_3 were proposed to be cubic,[5] but β-In_2S_3 was later shown to be a tetragonal phase.[10] In_6S_7 has a monoclinic phase which is isostructural with In_6Se_7.[11,12] α-In_2Se_3 was shown to be hexagonal.[13] The structure of β-In_2Se_3 has been reported as two different phases; hexagonal and rhombohedral. The difference may be due to either a different choice of the *a* axis or weak reflections from the X-ray diffraction. Most ternary I/III/VI chalcopyrite materials tend to be tetragonal; $CuInS_2$, $CuInSe_2$ (Fig. 2) and $CuGaS_2$.

The materials exhibit a variety of electronic properties and photo-conduction, semi-metallic behaviour, and even low temperature superconduction (Tl_5Te_3) are known. However, the majority of III/VI materials are mid- to wide-bandgap semiconductors, with a direct electronic transition to the conduction band (see Table 1).

Thin films of III/VI materials have been prepared by various growth techniques and are potential alternatives to II/VI materials for optoelectronic and photovoltaic devices,[14] but also have a potential application as passivating layers for III/V devices.[15] In addition to the simple binary compounds, there are important ternary and quaternary phases such as $CuInE_2$ and $CuIn_{1-x}Ga_xE_2$ (E = S or Se) with uses in solar cells. The groups of Barron, Nomura, Gysling, Hampden-Smith, and Bessergenev, and our own have made contributions to studies of the deposition of III/VI films.

The approaches that have been taken in developing single-source molecular precursors for III/VI materials are similar to those used for II/VI materials for which there is a more extensive literature.[16–21] A wide range of chalcogen containing ligands have been used to prepare complexes with direct metal–chalcogen bonds. The ligands used include thiolates,[22,23] selenolates,[24] thiocarboxylates,[25] dithio- or diseleno-carbamates,[26] and monothiocarbamates.[27–29] There now follows a brief history of

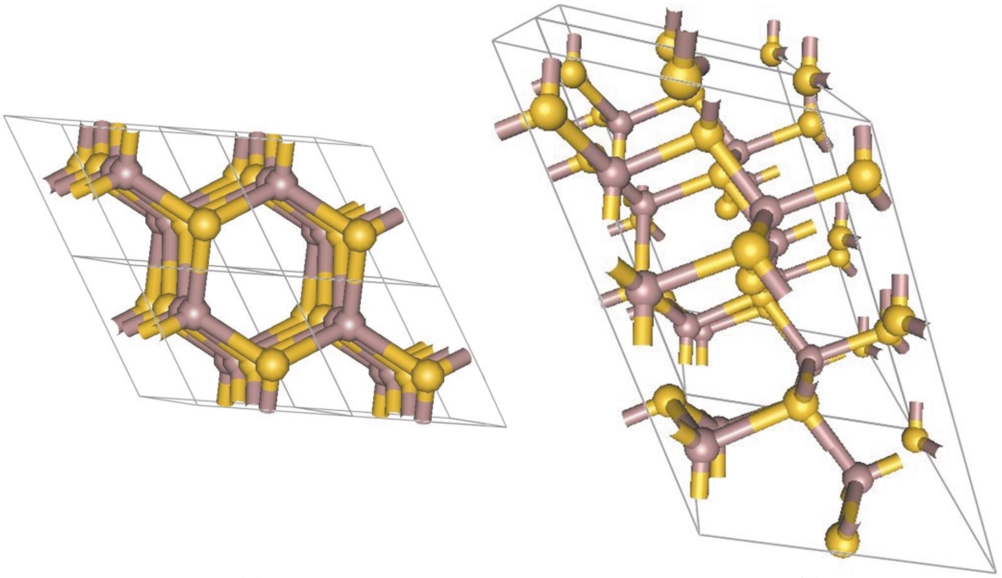
(a) (b)

Fig. 1 Structures of GaS (a) and α-Ga_2S_3 (b).

Table 1 Stoichiometries, structures and selected physical properties of some crystalline chalcogenides of binary and ternary materials (E_{dir} = direct band gap, E_{opt} = optical band gap)

Material	Crystal type	Lattice parameter/Å	Band gap/eV (T/K)[14]	JCPDS
α-Ga_2S_3	Monoclinic	*a* 11.094, *b* 9.578, *c* 6.395	E_{opt} 3.42 (77)	30–577
GaS	Hexagonal	*a* 3.587, *c* 15.492	E_{dir} 3.05 (77)	30–576
β-Ga_2Se_3	Monoclinic	*a* 6.661, *b* 11.652, *c* 6.649	E_{dir} 2.1–2.2 (77)	44–1012
δ-GaSe	Hexagonal	*a* 3.755, *c* 31.990	E_{dir} 2.02 (300)	29–628
Ga_2Te_3	Cubic	*a* 5.899	E_{opt} 1.22 (273)	35–1490
GaTe	Monoclinic	*a* 17.404, *b* 10.456, *c* 4.077	E_{dir} 1.69 (295)	33–571
In_6S_7	Monoclinic	*a* 9.090, *b* 3.887, *c* 17.705	E_{dir} 0.945 (77)	19–587
β-In_2S_3	Tetragonal	*a* 7.619, *b* 32.329	E_{dir} 2.03 (300)	25–390
γ-In_2S_3	Hexagonal	*a* 3.85, *b* 9.15	E_{opt} 1.88 (300)	33–623
InS	Orthorhombic	*a* 3.944, *b* 4.447, *c* 10.648	E_{dir} 2.45 (290)	19–588
InTe	Tetragonal	*a* 8.454, *c* 7.152	Metallic as well as semiconducting	30–636
$CuInSe_2$	Tetragonal	*a* 5.782, *c* 11.619	E_{dir} 1.04–1.27 (77)	40–1487
$CuInS_2$	Tetragonal	*a* 5.53, *c* 11.12	E_{dir} 1.53 (300)	38–777
$CuGaS_2$	Tetragonal	*a* 5.3507, *c* 10.484	E_{dir} 2.43 (300)	24–279

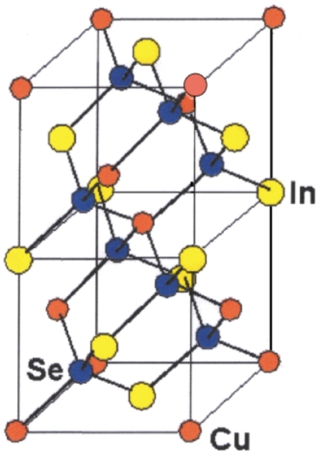

Fig. 2 Structure of $CuInSe_2$.

the chemistry of molecular compounds containing both a metal and a chalcogenide, many of which have been developed later to deposit thin films of III/VI materials.

Group 13 complexes with direct M–E bonds

In 1942, Brown and Davidson[30] prepared a dialkylaluminum thiolate complex, $[AlMe_2(SMe)]$ by the direct reaction of Me_3Al and MeSH. Subsequently, Coates and co-workers developed much important III/VI chemistry. The emphases of many of these studies was on the fact that Group 13 metal alkyls and halides act as strong Lewis acids, and hence readily complex to electron-rich chalcogen containing ligands. Coates and co-workers reported a number of dialkylmetal thiolate complexes *e.g.* $[GaMe_2(SMe)]_2$, $[InMe_2(SMe)]_2$ and $[TlMe_2(SMe)]_2$.[31,32] These compounds were prepared by alkane elimination reactions between the metal trialkyl and the alkanethiol. Coates and Mukherjee later described the preparation of a series of Group 13 dithiophosphinato complexes, $[MMe_2(S_2PMe_2)]$ (M = Al, Ga or In).[33] Many thiolato complexes have been synthesized which incorporate halogen atoms,[34] aryl moieties,[35] and alkylsilyl substituents.[36] Coates also prepared some analogous complexes with selenium or tellurium.[37] Other complexes with direct metal–sulfur interactions were reported by Weidlein, who prepared a number of dialkyldithioacetate ($[MR_2(S_2CMe)]$, R = Me or Et; M = Al, Ga or In)[38] and thiocarboxylate $[MMe_2(OSCMe)]$ complexes.[39] Hausen and Gruder made the analogous diethylindium thiocarboxylate complex, which differed from the earlier complexes reported as the indium centre was found to be five-co-ordinate as opposed to the four-co-ordinate geometry observed in Weidlein's complexes.[40] Dymock *et al.* reported a series of Group 13 metal tris(dialkyldithiocarbamate) compounds, $[M(S_2CNR_2)_3]$ (M = Ga or In; R = Me or Et) (Fig. 3), prepared by reaction of a metal trihalide and a sodium dialkyldithiocarbamate salt.[41] The sodium salt had been prepared by the direct reaction of a secondary amine with sodium hydroxide and carbon disulfide. In the complexes the metal centre is six-co-ordinate. Mixed alkyl Group 13 metal dialkyldithiocarbamates were first prepared by Maeda and Okawara, who described compounds with the formula $[InR_2(S_2CNMe_2)]$ (R = Me or Et), by a salt elimination reaction of a dialkylindium acetate and sodium dimethyldithiocarbamate.[42] Walther *et al.* prepared $[TlMe_2(S_2CNMe_2)]$ by the direct reaction of carbon disulfide and dimethyltellurium dimethylamide; in a formal sense CS_2 was inserted into the metal–nitrogen bond.[43] Haggata *et al.* also reported a number of mixed alkyl Group 13 metal dialkyldithiocarbamates by either the reaction of a sodium salt and dialkylmetal chloride or of tris(dialkyldithiocarbamato)metal(III) and metal trialkyl.[44]

The related dithiophosphinato complexes $[M(S_2PR_2)_3]$ of indium and gallium are known, however no crystal structures of the gallium compounds have been reported. These compounds were prepared by reaction of a sodium salt with the metal chloride. Svensson and Johannson have described the diethyldithiophosphinate (Fig. 4)[45] while Haiduc and co-workers have reported the preparation of the dimethyl- and the diphenyl-dithiophosphinate.[46] The structures show the same geometry at indium as for the gallium dithiocarbamates, with distorted octahedral co-ordination.

The chemical vapour deposition of semiconductors

The deposition of electronic materials is an important and diverse area of contemporary research. Dozens of techniques have been utilized for this purpose, one of the most developed and widely used being metal–organic chemical vapour deposition (MOCVD). However, there are restrictions, imposed by the precursors, on the use of this method. These 'precursor issues' are important for commercial and environmental reasons and include (*i*) The nature of the precursor: the most commonly used precursors were metal alkyls and/or main group hydrides, but such metal alkyls are often pyrophoric and the hydrides are highly toxic. Such precursors therefore require special equipment to guard against safety and environmental hazards. (*ii*) The tendency for homogeneous reaction in the MOCVD apparatus: this so called pre-reaction causes 'snowing' of the film that principally affects the morphology of the growing layer. (*iii*) The need, in many cases, for a large imbalance in the mole ratios of the precursor materials. This is due to differences in volatility, thermal reactivity of the precursors,

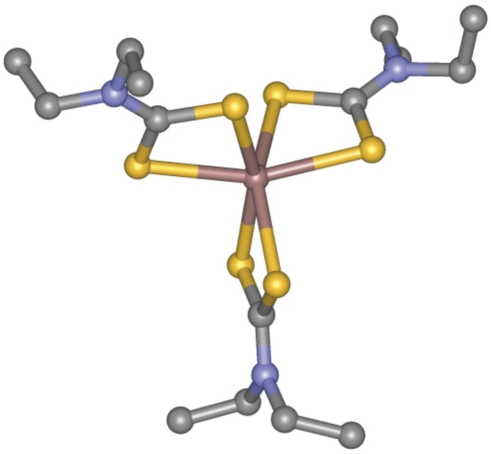

Fig. 3 Crystal structure of $[In(S_2CNEt_2)_3]$.

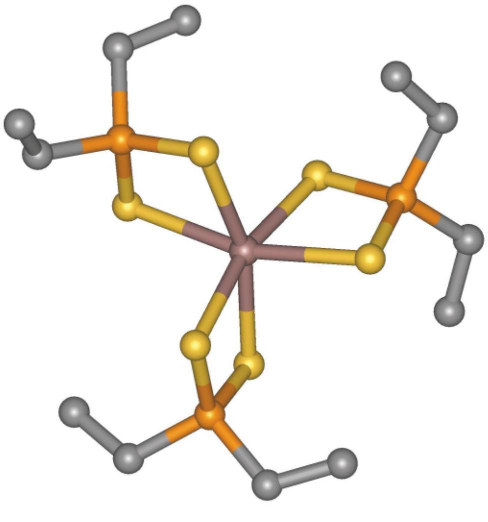

Fig. 4 Crystal structure of $[In(S_2PEt_2)_3]$.

and selective desorption from the growing layer. Furthermore, the large excess of precursor exacerbates problems with waste.

Various modifications have been made to conventional MOCVD methodologies in attempts to overcome such challenges *e.g.* the use of a precursor that has both the metal and the chalcogen in a single molecule.

The conventional CVD process requires volatile precursors, which evaporate and provide steady, reproducible transport rates into the reactor. Another requirement is for a clean thermal decomposition pathway that leads to the deposition of good quality films at high rates and low temperatures. A schematic representation of a CVD process is illustrated in Fig. 5. A volatile precursor is transported to the substrate in the reactor by a carrier gas (1). At the substrate, the precursor sorbs (2) and reacts (3) to liberate the by-products that subsequently desorb (6) and are transported out of the reactor (7). The target atoms then diffuse (4) to form nuclei of the materials (*e.g.* In_2S_3), where subsequent growth occurs (5).

Many MOCVD reactions involving hazardous toxic vapour phase precursors are undertaken at low pressure (LP) partly for reasons of safety; kinetic steps may also be enhanced at low pressure; solid precursors can be sublimed with or without a carrier gas. The vapour pressure (VP) of the precursor may be high enough not to require a carrier gas, for example WF_6 (VP 1000 Torr at 25 °C) can be used without a carrier gas to grow thin tungsten films; feed rate limitations usually do not occur.

In aerosol assisted (AA) CVD an aerosol is injected directly into a vapourizing chamber where the precursor and solution evaporate. In contrast, LP-MOCVD and/or conventional CVD rely on the delivery of precursor at its equilibrium vapour pressure at the source temperature. In general, aerosol delivery systems are suitable techniques where the precursor is thermally sensitive and would slowly decompose if heated for extended periods of time needed to elevate the VP. It is also a useful method for multicomponent systems as several precursors can be dissolved in the same solution and the relative delivery rates of precursors are defined by composition. The AACVD process is illustrated in Fig. 6. A single source precursor is dissolved in an organic solvent (1) and is converted into droplets by a piezoelectric modulator (2). The aerosol of precursor and solvent is then transported by a carrier gas into a hot zone where it evaporates. The vapour of the precursor is then transported to the substrate where it absorbs and reacts to form a film and by-products (3) and (4). AACVD is an example of a family of assisted CVD techniques; liquid injection CVD and spray pyrolysis.

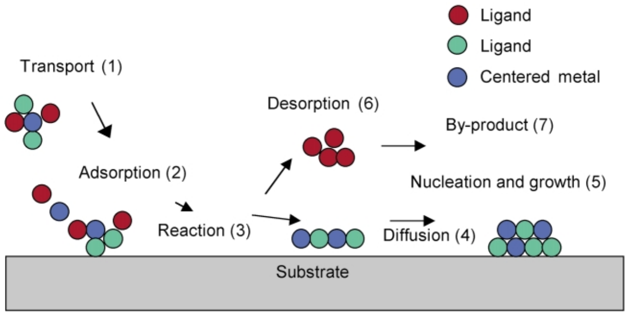

Fig. 5 Schematic diagram of the CVD process.

Developing precursors for applications in CVD

Thin films have many properties that can vary with the phase deposited: degree of crystallinity, crystallographic orientation, composition and impurity (or dopant) concentration are particularly important. All of these factors can be influenced by the precursor chemistry in ways that are far from fully understood. The principal effects of precursor chemistry must lie in the mechanism of decomposition of the compound. The nature of the molecular species present at the surface may influence the morphology, and possibly the structure of the film deposited. This effect is often attributed to the shape of the precursor. However, it must be remembered that when conformal films are grown by CVD there must be significant mobility of the species at the surface (*cf.* Fig. 5) for the deposition of dense films. An alternative way of thinking about the surface reactivity is in terms of the quantities of the various materials provided at the reactive surface. In a classical sense this is equivalent to the fugacities of the materials at the interface and these can have a profound effect on the properties of the phase deposited.[47] These points are particularly important in III/VI systems for which the materials, of a given binary composition, have a wide range of structures and stoichiometries (see Table 1). Some properties of good precursors for CVD can readily be defined. (*a*) The purity of the precursor is essential as extraneous elements, especially those that are electrically active, must not be incorporated into the film. There are several possible sources of impurities in the target materials. These can arise during precursor synthesis (*e.g.* halides from alkyl halides in dimethylzinc) or be incorporated into the material from the decomposition of the precursor (*e.g.* carbon). (*b*) The precursors used in CVD must have significant vapour pressure and should preferably be stable in air. During the decomposition in the reactor the reaction should be facile and lead to a minimum incorporation of impurities (*e.g.* carbon) associated with the precursor. (*c*) Toxicity and toxic hazards should also be minimized by a sensible choice of compound.

Single-source precursors that contain both the metal and non-metal have intrinsic advantages including: improved air/moisture stability, limited pre-reaction and control of stoichiometry.

There is an extensive literature detailing the synthesis of bulk III/VI compounds, however there have been relatively few

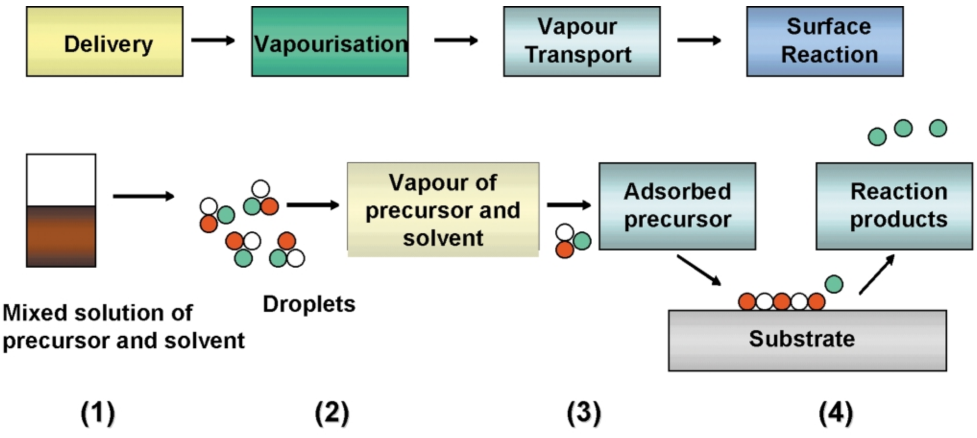

Fig. 6 Schematic representation of the AACVD process.

reports of the deposition of III/VI thin films. For example, the preparation of thin films of β-In_2S_3 by the spray pyrolysis of an aqueous solution of $InCl_3$ and thiourea in methanol–water was reported in 1986.[48] The first studies on the deposition of III/VI materials using single-source precursors were carried out by Nomura and co-workers from the late 1980s. Their studies have mainly involved the growth of indium sulfide,[22,23,49,50] indium oxide,[51,52] and the related copper doped ternary and quaternary materials.[52–54]

III/VI Thin films from single-source precursors

Many of the studies into the preparation of indium sulfide films have been based on the use of a volatile alkylindium alkanethiolate complex with bulky alkyl constituents. Such substituents can lead to an increase in the overall volatility of the precursor, and aid 'clean' decomposition, *e.g.* by enhancing the volatility of by-products generated in the CVD process. The presence of carbon as an element in a single-source organometallic precursor may result in the contamination by carbon of the semiconducting thin film. However, such a disadvantage can be minimized by designing and selecting different ligand groups or changing to bulkier alkyl groups. Complexes such as [In^{i}Bu$_2$(S-^{n}Pr)] are liquids, which is an advantage for conventional CVD.[49] The compound [In^{n}Bu(S^{i}Pr)$_2$], prepared by the reaction of tri-*n*-butylindium and two equivalents of 2-propanethiol, was used to grow films by LP-MOCVD at 300–400 °C on Si(111) and quartz substrates.[23] The films were shown to be tetragonal β-In_2S_3 with a preferred orientation along the (103) plane. However, at higher growth temperatures (450 °C), a sulfur-deficient phase, In_6S_7, was also deposited. [In^{i}Bu$_2$(S^{n}Pr)] was also used to prepare sulfur doped indium oxide thin films by atmospheric pressure (AP) MOCVD.[51] Sulfur deficient phases such as In_6S_7 have different electronic properties from either InS or In_2S_3. Therefore, it is essential to prepare the required stoichiometry. The stoichiometry of the compound can be controlled by changing the growth temperature in this case.

MacInnes *et al.* have suggested that molecular design can play an important and direct role in determining the nature of thin films deposited from single-source precursors.[55] A comparison of the films grown from [In^{t}Bu$_2$(S^{t}Bu)]$_2$ and [InMe$_2$(S^{t}Bu)]$_2$, as well as from the bis-thiolate complex, [InMe(S^{t}Bu)$_2$]$_2$, shows the importance of deposition temperature, decomposition mechanism and the choice of precursor used. At 400 °C the methyl-substituted complex deposited an indium-rich amorphous phase and In_2S_3, whereas the *tert*-butyl substituted complex deposited highly oriented tetragonal InS. This observation suggests that the stronger In–C bond in the former results in fragmentation of the precursor on decomposition, whereas the latter exhibits clean ligand loss. However, the bis-thiolate complex leads to an amorphous phase, though annealing does yield crystalline β-In_2S_3.

In related studies, indium selenide thin films have been prepared from the analogous selenolate complexes.[56] Barron and co-workers also prepared a number of dialkylindium selenolates and alkylindium selenides,[56] and deposited indium selenide films by LP-MOCVD.[57] Whilst [In^{t}Bu$_2$(Se^{t}Bu)]$_2$ deposited indium rich films at temperatures between 230 and 420 °C, [In(CEtMe$_2$)(μ$_3$-Se)]$_4$ gave crystalline films of InSe; however, the film quality depended on the growth temperature. Gysling *et al.* have also prepared thin films of indium selenide from [InMe$_2$(SePh)] or [In(SePh)$_3$], by a spray-assisted MOCVD technique, on GaAs(100).[24] Different phases of InSe were grown at different substrate temperatures, with a cubic phase observed at deposition temperatures between 310 and 365 °C. Pyrolysis of [In(SePh)$_3$] gave hexagonal films of In_2Se_3 at temperatures of 470 to 530 °C. In addition to these, a number of other potential precursors for the growth of indium selenide have been prepared with more bulky alkyl substituents.[58]

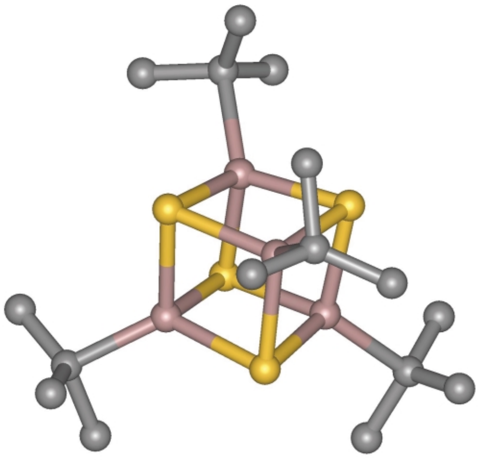

Fig. 7 Crystal structure of [^{t}BuGaS]$_4$.

There are even fewer reports on the deposition of gallium sulfide materials than those of indium. Barron and co-workers have prepared a number of metal chalcogenide complexes with interesting cubane structures, the first was [^{t}BuGaS]$_4$ (Fig. 7), prepared by thermolysing the dimer [Ga^{t}Bu$_2$(μ-SH)]$_2$, which was synthesized by the addition of an excess of H_2S to [Ga^{t}Bu$_3$].[59,60] Much of the impetus for making the complex was that many of the dimeric thiolate complexes, as described above, were prone to yield sulfur-deficient films. The cubane has no direct carbon–sulfur bonds, and is supported by metal–sulfur interactions. [^{t}BuGaS]$_4$ is an air stable white solid and was used to grow gallium sulfide by atmospheric pressure MOCVD at 380–400 °C. The GaS films were deposited on both KBr and GaAs(100) and on the latter a degree of epitaxial growth was observed.[4] The films were of a novel cubic phase of GaS, with good properties as a passivating material for GaAs.[15] The films have a high band gap ($E_g > 3.0$ eV) and were highly insulating ($>2 \times 10^9$ Ω cm). At higher temperatures, >450 °C, there is sulfur loss from the films and an amorphous matrix of gallium resulted. Barron and co-workers also used the dimeric thiolato complex, [Ga^{t}Bu$_2$(S^{t}Bu)]$_2$, to deposit poorly crystalline hexagonal films of GaS. The larger heptameric complex [^{t}BuGaS]$_7$ also deposited amorphous GaS films.[4] They suggested that the cubic nature of the core structure of the [^{t}BuGaS]$_4$ precursor is maintained throughout deposition, and leads to the cubic structure in the as deposited gallium sulfide.

The hypothesis that molecular structure can influence the phase of the as-deposited films was further investigated with the analogous cubane selenide or telluride precursors [GaR(μ$_3$-E)]$_4$ (where E = S, Se or Te; R = CMe$_3$, CEtMe$_2$, CEt$_2$Me or Et$_3$C) (*e.g.* Fig. 8).[61,62] However, in contrast to the sulfides, the hexagonal phase of GaSe was deposited by AP-MOCVD (≈350 °C) and similarly hexagonal GaTe was deposited by LP-MOCVD (at 285–310 °C). An earlier report had suggested that hexagonal GaS could be deposited from [^{t}BuGaS]$_4$, by photochemical cleavage of the central Ga_4S_4 core of the cubane structure, and a similar decomposition pathway was suggested for the deposition of GaSe and GaTe films.[63] Core fragmentation is more apparent for the distorted cubane [Cp*GaS]$_4$.[64] There are also examples of cubanes with indium chalcogenides.[56] However, [^{t}BuInSe]$_4$ was found to give only indium metal films by LP-MOCVD. The complex [(Me$_2$EtC)InSe]$_4$ gave hexagonal InSe in LP-MOCVD, with the best results observed at 290–350 °C.[57] Cubic gallium selenide thin films have also been prepared from the Me$_3$Ga and H$_2$Se or ^{t}Bu$_2$Se precursors.[65]

Another series of complexes that have been studied as precursors for the deposition of III/VI thin films are those containing dialkyldithio- and dialkyldiseleno-carbamato ligands. The tris(dialkyldithiocarbamates) of gallium or indium are monomeric solids,[66] in contrast the bis(dialkyldithiocarbamates) of

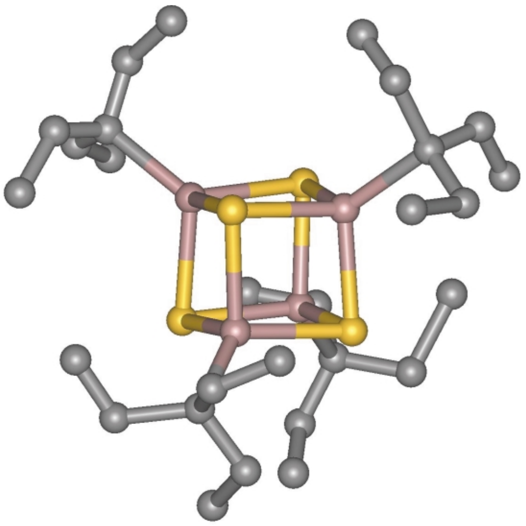

Fig. 8 Crystal structure of $[\text{Ga}(\text{CEt}_3)(\mu_3\text{-S})]_4$.

zinc or cadmium are usually dimers. The symmetrical tris(dialkyldithiocarbamates) are of quite low volatility. The use of asymmetric secondary amines in their preparation was originally developed to improve volatility and O'Brien *et al.* have described some indium tris(dialkyldithiocarbamates) prepared in methanol.[26] Three equivalents of the sodium salt of the asymmetric dithiocarbamate (prepared by the addition of carbon disulfide to a solution of the amine and sodium hydroxide in methanol) added to indium trichloride. Compounds with various asymmetric alkyls groups (R = Me and R′ = Et, ^{n}Bu or ^{n}Hex) were prepared, with the structure of the methyl(ethyl) derivative determined.[67] The other two complexes were used as single-source precursors to grow indium sulfide by LP-MOCVD. The compounds volatilized at 250 °C, and growth at temperatures between 450 and 500 °C was reported. At all temperatures, cubic α-In_2S_3 was deposited on both glass and InP(111), and in both cases the films were strongly orientated in the (111) direction.[26] The fact that In_2S_3 is deposited rather than InS was suggested to be because of the relative contents of indium and sulfur in the precursor molecules. The analogous diselenocarbamate, $[\text{In}(\text{Se}_2\text{CNMe}^n\text{Hex})_3]$, has also been used to deposit thin films of cubic In_2Se_3.[68] At a growth temperature of 450 °C, films of cubic In_2Se_3 were deposited on glass substrates with a preferred (111) orientation. The results are similar to those of Arnold and co-workers who prepared cubic In_2Se_3 films from $[\text{In}\{\text{SeC}(\text{SiMe}_3)_3\}_3]$.[69] In a similar way, gallium sulfide films have recently been prepared by LP-MOCVD from the asymmetric precursors $[\text{Ga}(\text{S}_2\text{CNMeR})_3]$ (where R = Et, ^{n}Bu or ^{n}Hex). The films deposited at 500 °C on GaAs(111) from $[\text{Ga}(\text{S}_2\text{CNMe}^n\text{Hex})_3]$ were shown to be α-Ga_2S_3 by XRD.[70]

As well as studies involving Group 13 metal tris(dialkyldichalcogenocarbamate) complexes, there has been some investigation into thin film deposition from mixed alkyl Group 13 metal dialkyldichalcogenocarbamates. A series of mixed alkylindium and gallium diethyldithiocarbamates of formula $[\text{MR}_2(\text{S}_2\text{CNEt}_2)]$ (R = Me, Et or $\text{CH}_2{}^t\text{Bu}$) have been prepared,[44] and were found to be monomeric solids in the case of indium complexes, and liquids in the case of gallium. This observation again differs from the Group 12 mixed alkyl dithiocarbamate complexes, $[\text{ZnR}(\text{E}_2\text{CNEt}_2)]$ (R = ^{t}Bu or $\text{CH}_2{}^t\text{Bu}$, E = S or Se), where a higher degree of association is observed.[71,72]

$[\text{InMe}_2(\text{S}_2\text{CNEt}_2)]$ was first serendipitously isolated by Haggata *et al.*, from the reaction of Me_3In and $[\text{Zn}(\text{S}_2\text{CNEt}_2)_2]$, in attempts to prepare a mixed metal species. Better defined preparations involved either the comproportionation of a metal trialkyl and the appropriate metal tris(dialkyldithiocarbamate), or the reaction of the sodium diethyldithiocarbamate salt with chlorodiethylindium in diethyl ether.[44] The indium complexes were used to deposit indium sulfide films by LP-MOCVD on GaAs(100) substrates at temperatures of 325–425 °C, with the choice of alkyl substituent having an effect on the type of film deposited (Table 2). The molecular structure appears to affect the nature of the as-deposited films, sulfur evaporation and β-hydrogen elimination being possibly important. For example, $[\text{InEt}_2(\text{S}_2\text{CNEt}_2)]$ (Fig. 9) was different from the other two compounds, $[\text{InMe}_2(\text{S}_2\text{CNEt}_2)]$ and $[\text{In}(\text{CH}_2{}^t\text{Bu})_2(\text{S}_2\text{CNEt}_2)]$, in that a single phase, cubic β-In_2S_3, was deposited over the temperature range between 325 and 400 °C. In this case, only the ethyl compound contains β-hydrogen atoms, and the ready elimination of the alkyl fragment may influence the film composition in many ways, including by affecting the amount of carbon incorporation. The analogous gallium precursor $[\text{GaMe}_2(\text{S}_2\text{CNEt}_2)]$ was prepared by Haggata *et al.* and found to be less successful in the growth of gallium sulfide films by LP-MOCVD.[44] In their study no carbon analysis was reported. Barron and co-workers have also pursued the use of dithiocarbamates as precursors. Using $[\text{Ga}^t\text{Bu}_2(\text{S}_2\text{CNR}_2)]$, where R = Me or Et, films of wurtzite GaS, a new phase, were deposited using AP-MOCVD onto GaAs(100). However, the ethyl analogue did deposit amorphous gallium as well as GaS.[73]

The monothiocarbamato $[\text{R}_2\text{NCOS}^-$ (R = alkyl)] moiety has not extensively been studied as a ligand for single-source precursors for the growth of semiconductor thin films. In recent years, some Group 12 and 13 monothiocarbamate compounds have been synthesized and employed for the growth of metal sulfide thin films by CVD techniques. Although there are several routes to prepare monothiocarbamate metal complexes, the reaction of a lithium salt with a metal chloride is simple and gives a high yield. Oxygen incorporation into films grown from monothiocarbamate metal complexes might be thought of as a potential problem. However, in a study of the thermal decomposition of carbonyl sulfide (COS) at temperatures between 350 and 600 °C, COS generated carbon monoxide and sulfur and resulted in CO_2 and CS_2.[74]

The complexes $[\text{In}(\text{SOCNEt}_2)_3]$ (Fig. 10),[27] $[\text{In}(\text{SOCN}^i\text{Pr}_2)_3]$,[28] and $[\text{Ga}(\text{SOCNEt}_2)_3]$[29] have been used in deposition. The films grown from both of the indium precursors were found to be of β-In_2S_3. Using the diisopropyl compound deposition occurred at temperatures as low as 300 °C. However, the gallium monothiocarbamato precursor, deposited cubic GaS at 450 °C, and the film was comparable to those obtained by Barron and co-workers from $[^t\text{BuGaS}]_4$.[59] It was highly

Table 2 Detailed results for the growth of gallium sulfide

Precursor	Deposition temp/°C	Phase observed	Ref.
$(^t\text{Bu}_2\text{GaS}^t\text{Bu})_2$	400	Hexagonal GaS	4
$(^t\text{BuGaS})_4$	380–400	Cubic GaS	4
$(^t\text{BuGaS})_7$	380–400	Amorphous	4
$[\text{GaMe}(\text{SOCMe})_2(\text{dmpy})]$	290	α-Ga_2S_3	78
$[\text{Ga}(\text{SOCNEt})_3]$	450	Cubic GaS	29
$[\text{Ga}(\text{S}_2\text{CNMe}^n\text{Hex})_3]$	500	α-Ga_2S_3	70
$[\text{Ga}^t\text{Bu}_2(\text{S}_2\text{CNMe}_2)]$	375–425	Hexagonal GaS	73

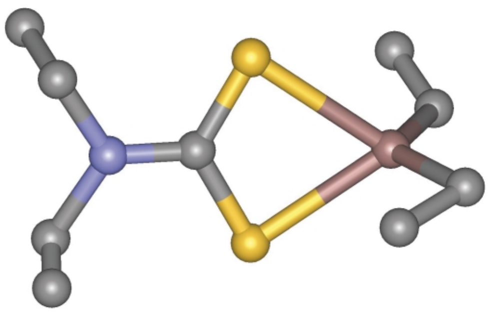

Fig. 9 Crystal structure of $[\text{InEt}_2(\text{S}_2\text{CNEt}_2)]$.

Table 3 Some precursors successfully used for the deposition of indium sulfide thin films

Precursor	Deposition temp./°C	Phase observed	Ref.
$[In^tBu_2(\mu\text{-}S^tBu)]_2$	380–400	Tetragonal-InS	55
$[InMe_2(S^tBu)]_2$	400	In_2S_3 and amorphous phase	55
$[In^nBu(S^iPr)_2]$	350–400	β-In_2S_3	23
$[InMe_2(S_2CNEt_2)]$	350–425	InS and In_6S_7	44
$[InEt_2(S_2CNEt_2)]$	350–400	β-In_2S_3	44
$[In(CH_2{}^tBu)(S_2CNEt_2)]$	350–400	In_6S_7	44
$[In(S_2CO^iPr)_3]$	250	α- and β-In_2S_3	75
$[In(S_2CNMe^nBu)_3]$	500	α-In_2S_3	26
$[In(S_2CNMe^nHex)_3]$	500	α-In_2S_3	26
$[In(SOCNEt_2)_3]$	450–500	β-In_2S_3	27
$[In(SOCN^iPr_2)_3]$	300–350	β-In_2S_3	28
$[HL]^+[In(SCOMe)_4]^-$	210	β-In_2S_3	77
$[In(SePh)_3]$	470–530	In_2Se_3	24
$[In(CEtMe_2)(\mu_3\text{-}Se)]_4$	230–350	Hexagonal InSe	57
$[InBu_2(\mu\text{-}Se^tBu)]_2$	330–370	Hexagonal InSe	57
$[In(Se_2CNMe^nHex)_3]$	450	Cubic In_2Se_3	68

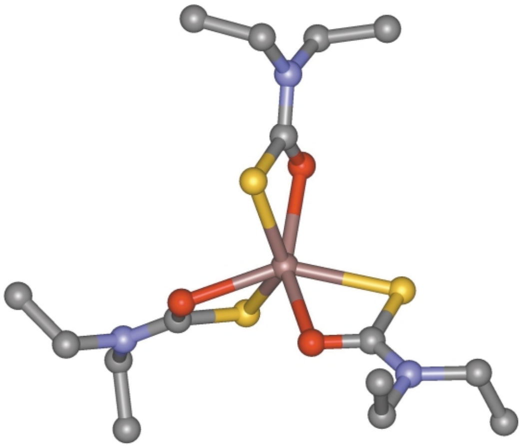

Fig. 10 Crystal structure of $[In(SOCNEt_2)_3]$.

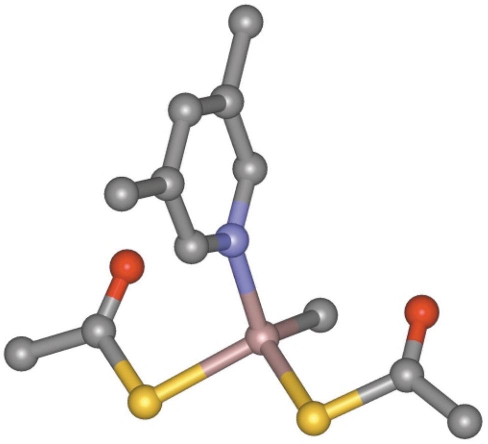

Fig. 11 Crystal structure of $[GaMe(SOCMe)_2(dmpy)]$.

orientated in the (200) direction even though deposited onto glass. The sulfur deficient phase deposited may be due to the Ga:S ratio in the precursor.

There are other reports of single-source routes for Group 13 chalcogenides, see Table 3. Bessergenev *et al.* have reported the deposition of α-In_2S_3 from $[In(S_2CO^iPr)_3]$, by LP-MOCVD at temperatures as low as 250 °C.[75] The same authors have presented a detailed phase analysis study of indium sulfide films grown from both this complex and $[In(S_2CNEt_2)_3]$, focusing on the effects of annealing and deposition temperature by analysing the films by using synchrotron radiation diffraction.[76]

Hampden-Smith and co-workers have used a slightly different approach to single-source deposition.[77] The reaction of triethylindium, thioacetic acid and 3,5-dimethylpyridine (L) yields the indium thiocarboxylate salt $[HL]^+[In(SCOMe)_4]^-$, which has been used to deposit tetragonal β-In_2S_3 by AACVD. The precursor was dissolved in tetrahydrofuran, and passed into the growth chamber, using nitrogen as the carrier gas. The study is notable mainly because films were deposited at substrate temperatures as low as 210 °C, the lowest growth temperature reported for such materials. Auger electron spectroscopy and electron microprobe scanning was utilized to show that oxygen and carbon incorporation was low, although not zero. The gallium compound $[GaMe(SCOMe)_2(dmpy)]$ (where dmpy = 3,5-dimethylpyridine) (Fig. 11) was used in AACVD for the growth of gallium sulfide. This method gave a high-purity, hexagonal α-Ga_2S_3 phase at temperatures as low as 290 °C. These result suggest that the indium and gallium thiocarboxylate compounds undergo quantitative elimination of thioacetic anhydride to give the metal sulfide, resulting in the relatively low growth temperatures (210–290 °C).[78]

Conclusion

The deposition of III/VI materials by CVD has been developed in the last ten years. Many groups emphasize the use of single-source precursors. Single-source precursors based on chalcogen containing ligands include thiols, thiocarbamates, selenocarbamates and thiocarboxylates. The type of ligand has been reported to control the stoichiometry of the as-deposited films, and in some cases may provide routes for the growth of specific phases. Much scope remains for the development of these precursors for lower deposition temperatures and definitive phase control. There is also the possibility to use these complexes as precursors to important ternary and quaternary materials, for example $CuInSe_2$.[79]

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