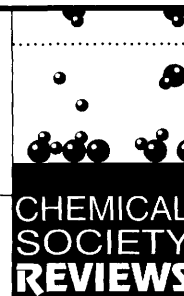


# Developments in metalorganic precursors for semiconductor growth from the vapour phase



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Volatile metalorganic compounds are being increasingly used for the deposition of compound semiconductors from the vapour phase by metalorganic vapour phase epitaxy (MOVPE) or chemical beam epitaxy (CBE). Developments in precursor chemistry, such as improved synthesis and purification techniques and the use of alternative precursors, have been central to the progress of MOVPE and CBE. In this paper some of these recent precursor developments are reviewed and the current thinking on gas-phase and surface mechanisms occurring in MOVPE and CBE is discussed.

## 1 Introduction

Compound semiconductors, based on combinations of elements from Groups III and V and II and VI,<sup>†</sup> have had a significant impact on our everyday lives. Materials such as gallium arsenide (GaAs), aluminium gallium arsenide (AlGaAs), gallium nitride (GaN), indium phosphide (InP) and zinc selenide (ZnSe) have a wide variety of applications in satellite TV receivers, optical fibre communications, compact disc players, bar-code readers and full colour advertising displays.

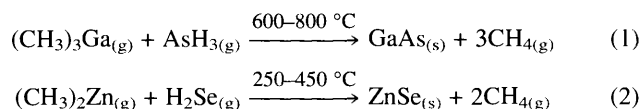
The devices used in these applications require single crystal films of semiconductor material and simple device structures with layer thickness > 10 µm (e.g. light emitting diodes) have been traditionally deposited from mixtures of the molten elements on an appropriate substrate, a process known as liquid phase epitaxy (LPE). However, although LPE can produce high

purity semiconductor films, growth of very thin films (< 0.1 µm) is difficult and there are problems of doping and of interface control during the growth of complex multilayer III-V and II-VI devices. Therefore, a great deal of effort has gone into the development of vapour phase deposition techniques, more suitable for multilayer growth. These include molecular beam epitaxy, using vapour phase mixtures of the pure metals; and metalorganic vapour phase epitaxy (MOVPE) and chemical beam epitaxy (CBE) which use vapour phase mixtures of metalorganic compounds.

The application of metalorganic chemistry has played a vital role in the recent development of MOVPE and CBE semiconductor technology. In this review the use of metalorganic and related compounds in MOVPE and CBE is discussed, with emphasis on chemical interactions occurring in the gas phase and at the semiconductor substrate surface.

## 2 Metalorganic vapour phase deposition techniques

The use of metalorganic compounds to deposit semiconductor materials was first described in detail by Manasevit.<sup>1</sup> He showed that metal alkyls of the Group III A elements (MR<sub>3</sub>; M = Al, Ga, In; R = methyl, ethyl) and the Group II B elements (MR<sub>2</sub>; M = Zn, Cd; R = methyl, ethyl) could be used as volatile precursors for growing III-V and II-VI semiconductors. For example, solid GaAs can be deposited by the pyrolysis of trimethylgallium vapour at 600–800 °C in the presence of arsine (AsH<sub>3</sub>). Manasevit named the technique metalorganic chemical vapour deposition (MOCVD) to describe the vapour transport of the metal as a metalorganic compound. In simple form the deposition of GaAs and ZnSe by MOCVD can be summarised in Scheme 1.



Scheme 1

These semiconductor alloys are generally deposited on single crystal wafer substrates so that each layer assumes the same crystalline orientation as the substrate. This process is called epitaxy and the specific process involving metalorganic precursors is called metalorganic vapour phase epitaxy (MOVPE). MOVPE is an extremely versatile technique which can be used to grow a large range of mixed III-V and II-VI semiconductor materials, (see Table 1). The solid composition of these alloys is controlled simply by varying the concentration of the precursors in the vapour phase. MOVPE is suitable for growing large areas of highly uniform semiconductor layers and allows precise control of layer thickness, purity and doping concentration. Consequently, it is fast becoming the standard technique for producing advanced III-V devices, which often have sophisticated multilayer structures.

The MOVPE process involves a series of gas phase and surface reactions. Although actually a complex process, it can be divided into several steps: (a) evaporation and transport of

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<sup>†</sup> Non-IUPAC nomenclature (i.e. III-V, II-VI rather than 13–15, 12–16) has been universally adopted by the semiconductor industry and is therefore used throughout this review.

precursors, (b) pyrolysis of precursors leading to the semiconductor material and (c) removal of the remaining fragments of the decomposition reactions from the reactor zone. The basic processes which underlie MOVPE or MOCVD processes are shown in Fig. 1. A significant feature of MOVPE is the presence of a layer of hot gas immediately above the substrate. This is termed the boundary layer, and gas phase reactions occurring in this layer play a significant role in MOVPE deposition processes, [see Fig. 2(a)].

The CBE process,<sup>2</sup> shown schematically in Fig. 2(b) is a high vacuum process in which Group III metalorganic precursors are pyrolysed on a hot substrate (450–600 °C) in the presence of Group V atoms. (e.g. As<sub>2</sub> derived from precracked AsH<sub>3</sub>). Under the high vacuum conditions of CBE, the boundary layer is absent and chemical interactions are limited to the substrate surface, which should in principle lead to more uniform semiconductor layers with sharper interfaces. Another advantage of CBE is that the use of high vacuum allows the *in situ* monitoring of layer growth by surface science techniques such as modulated beam mass spectroscopy, reflection high energy electron diffraction, Auger electron spectroscopy *etc.*

Developments in metalorganic precursor chemistry have been central to the progress of MOVPE and CBE. For instance, improvements in synthesis and purification techniques (e.g. adduct purification, see Fig. 3), coupled with the use of increasingly sensitive analytical techniques, have allowed the routine production of ultra-high purity metalorganics (total metal impurities < 1 ppm), necessary for the growth of device-quality semiconductor layers. These advances have been

reviewed elsewhere<sup>3</sup> and will not be discussed here. Another significant chemical contribution to the field of semiconductor growth has been the development of metalorganic precursors, specifically designed for the MOVPE or CBE process, which have improved gas-phase and surface decomposition characteristics, leading to higher quality semiconductor films. These precursor developments form the basis of this review.

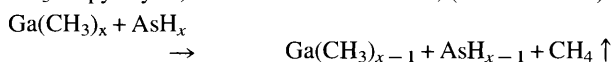
### 3 Precursors for the growth of III–V semiconductors

Both MOVPE and CBE have been widely utilised for the growth of III–V materials. Broadly speaking, there are two approaches to growing these materials; the conventional approach in which separate Group III and V precursors are used (see Table 1); and the use of ‘single-source’ precursor molecules in which both elements of the compound semiconductor are combined. Each of these approaches has inherent advantages and disadvantages, but it is worth noting that many of the original precursors introduced by Manasevit are still favoured today. The single-source precursor approach has yet to make a significant impact on the growth of III–V electronic materials, although this method may find applications in the future, where low temperature growth is important.

#### 3.1 Growth of III–V semiconductors by MOVPE

##### 3.1.1 Conventional precursors

In the development of the MOVPE process, the metalorganic precursors traditionally employed have been those which are readily available commercially, and which have convenient vapour pressures. These include the volatile Group III trialkyls, trimethylgallium (Me<sub>3</sub>Ga), trimethylaluminium (Me<sub>3</sub>Al) and trimethylindium (Me<sub>3</sub>In), in combination with the Group V hydride gases arsine (AsH<sub>3</sub>) and phosphine (PH<sub>3</sub>). To some extent, this choice was fortuitous since the III–V layers grown contained remarkably low levels of carbon contamination, considering that carbon-containing metalorganics were employed. This can be attributed to the large quantity of ‘active’ atomic hydrogen produced by the pyrolysis of AsH<sub>3</sub> or PH<sub>3</sub>, which allows the clean removal of carbon-containing fragments from the growth surface. For GaAs grown from Me<sub>3</sub>Ga and AsH<sub>3</sub>, a mechanism has been proposed<sup>4</sup> for carbon removal which involves the adsorption of [Ga–Me] species (produced by Me<sub>3</sub>Ga pyrolysis) on the substrate surface, (see Scheme 2).



Scheme 2

**Table 1** MOVPE of III–V and II–VI compound semiconductors

Semi-conductor	Reactants	Typical growth temp/°C	
III–V	GaAs	Me <sub>3</sub> Ga, AsH <sub>3</sub>	600–750
	AlGaAs	Me <sub>3</sub> Al, Me <sub>3</sub> Ga, AsH <sub>3</sub>	600–800
	InP	Me <sub>3</sub> In, PH <sub>3</sub>	650
	InGaAs	Me <sub>3</sub> In, Me <sub>3</sub> Ga, AsH <sub>3</sub>	650
	InGaAlP	Me <sub>3</sub> In, Me <sub>3</sub> Ga, Me <sub>3</sub> Al, PH <sub>3</sub>	750
	GaSb	Me <sub>3</sub> Ga, Me <sub>3</sub> Sb	520
II–VI	ZnSe	Me <sub>2</sub> Zn, H <sub>2</sub> Se	250–350
	ZnSSe	Me <sub>2</sub> Zn, H <sub>2</sub> S, H <sub>2</sub> Se	250–350
	CdSe	Me <sub>2</sub> Cd, H <sub>2</sub> Se	250–350
	CdTe	Me <sub>2</sub> Cd, Pr <sub>2</sub> Te	350–400
	CdHgTe	Me <sub>2</sub> Cd, Hg, Pr <sub>2</sub> Te	350–400

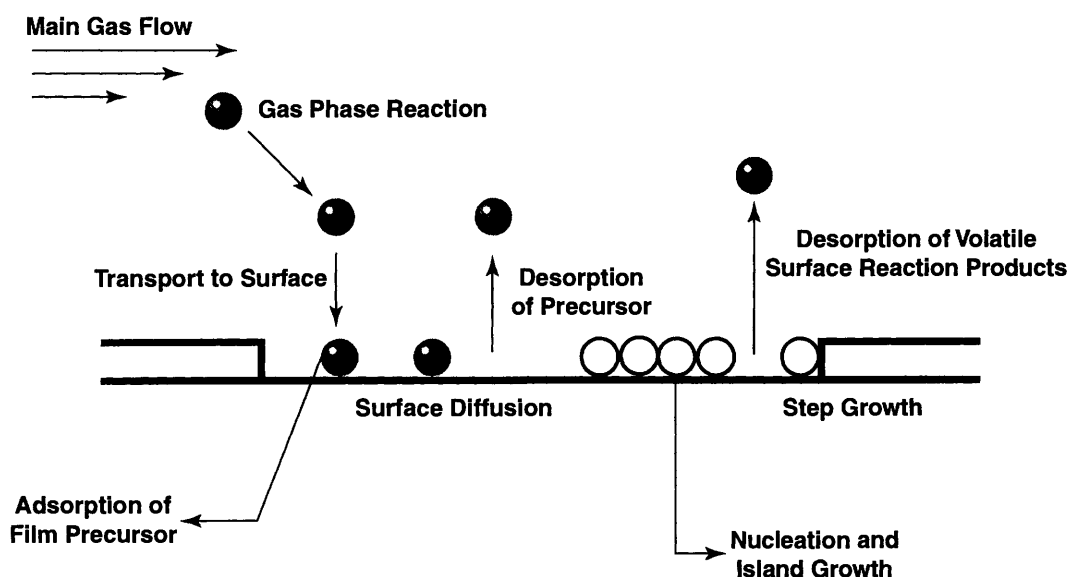


Fig. 1 Scheme to show the transport and reaction processes underlying MOCVD

The vast majority of  $[\text{CH}_3]$  radicals interact with 'AsH<sub>3</sub>' species and are removed as the stable methane molecule. However, a small proportion become more strongly adsorbed and subsequently decompose to incorporate carbon in electrically active form (*i.e.* as a p-dopant) at an arsenic surface site. On the basis of infrared data under UHV conditions, it has been proposed<sup>5</sup> that carbon incorporation proceeds *via* the dehydrogenation of adsorbed methyl radicals to give strongly bound carbene-like species  $[\text{=CH}_2]$ , see Fig. 4. Further dehydrogenation of these species leads to carbon inclusion in the GaAs films.

The concentration of carbon incorporated in GaAs grown from  $\text{Me}_3\text{Ga}/\text{AsH}_3$  is extremely low (*ca.* 0.001 atomic ppm) and the layers are high purity, typically demonstrating high electron mobilities ( $\mu > 100\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  at 77 K) and low n-type residual carrier concentrations ( $n \text{ ca. } 10^{14}\text{ cm}^{-3}$ ). Similarly, high purity InP, essentially free from carbon impurities, can readily be grown from  $\text{Me}_3\text{In}$  and  $\text{PH}_3$ . Using  $\text{Me}_3\text{In}$ , purified

by adduct formation (see Fig. 3) from trace metals like Si or Zn which could act as dopants, InP layers with electron mobilities as high as  $300\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  at 77 K have been grown.<sup>6</sup> This represents some of the highest purity III–V semiconductor material grown by any technique and is suitable for all device applications.

Therefore, with regard to the purity of GaAs and InP layers, there is little requirement for alternative precursors. However, safety and environmental considerations have stimulated research into safer liquid replacements for the toxic Group V hydride gases,<sup>7</sup> and similar reasons have prompted chemists to investigate single source precursors to III–V materials. In other areas of III–V MOVPE, most notably in the growth of AlGaAs, the Group III antimonides, and Group III nitrides, the use of conventional precursors has sometimes proved problematic and alternative precursors have been sought. Some of these developments are highlighted below.

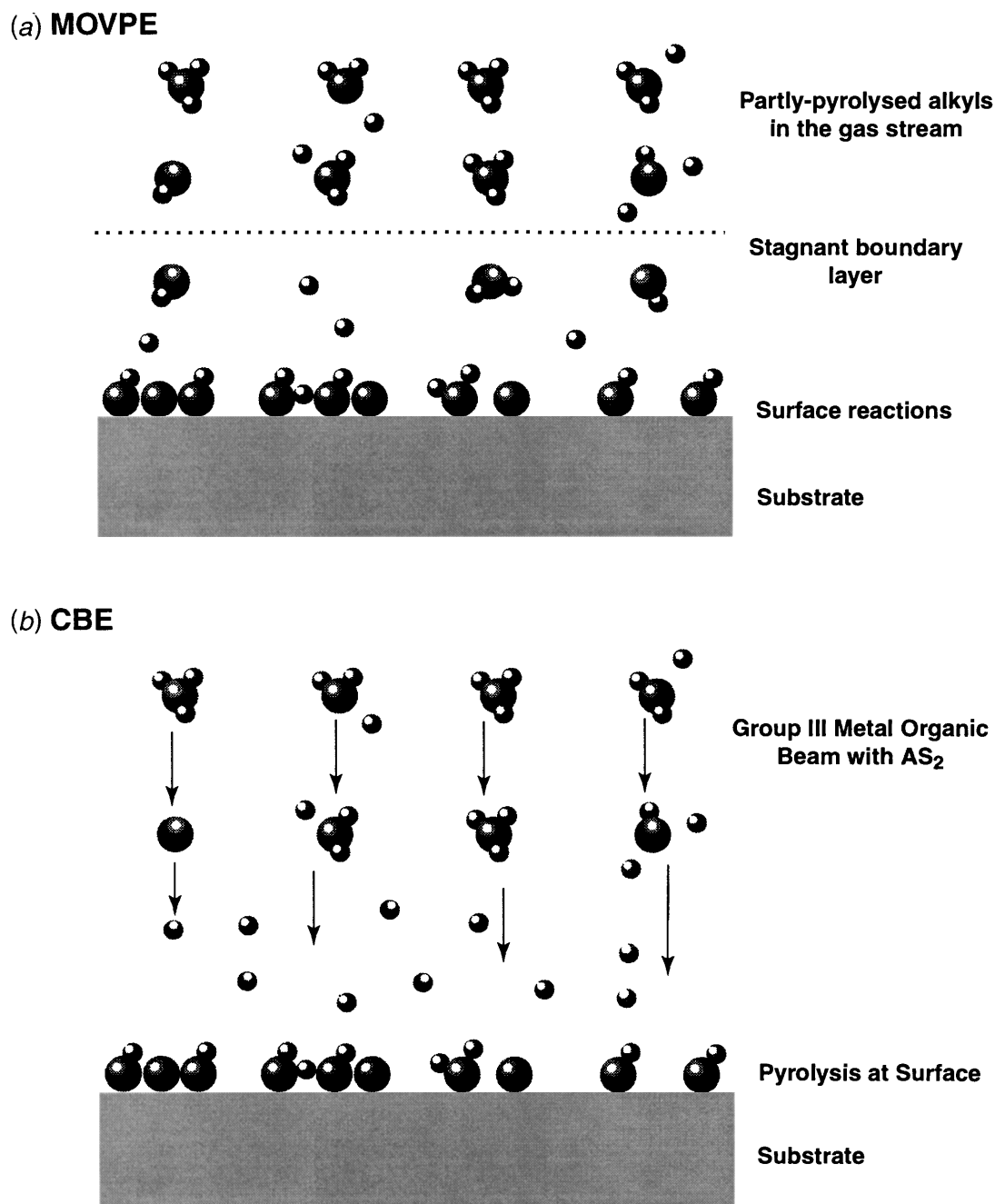


Fig. 2 Schematic representation of growth processes: (a) MOVPE. (b) CBE.

### 3.1.2 Alternative Group V sources

AsH<sub>3</sub> and PH<sub>3</sub> are extremely toxic gases, stored in high pressure cylinders so that there is a severe risk of toxic release during transport and use in MOVPE. Much research<sup>7</sup> has therefore been aimed at developing safer liquid alternatives which disperse more slowly in the atmosphere in the case of accidental release.

Trialkylarsine compounds, such as trimethylarsine (Me<sub>3</sub>As) and triethylarsine (Et<sub>3</sub>As) are not useful precursors, as they lead to heavily carbon contaminated GaAs layers due to the absence of active 'AsH<sub>x</sub>' species necessary for carbon removal (*cf.* Scheme 2). Therefore, arsenic precursors which contain one or more hydrogen atoms such as the ethylarsines (Et<sub>2</sub>AsH, EtAsH<sub>2</sub>) or *tert*-butylarsine (Bu<sup>t</sup>AsH<sub>2</sub>) must be used. Bu<sup>t</sup>AsH<sub>2</sub> is by far the most successful liquid arsenic source to date with a convenient vapour pressure (107.2 mbar<sup>‡</sup> at 10 °C) and pyrolysing at a lower temperature than AsH<sub>3</sub>; 50% pyrolysed at

425 °C compared with 575 °C for AsH<sub>3</sub>. The more efficient pyrolysis of Bu<sup>t</sup>AsH<sub>2</sub> relative to AsH<sub>3</sub> allows the growth of GaAs at lower V/III ratios and the increased concentration of active 'AsH<sub>x</sub>' species on the substrate reduces carbon contamination. It is likely<sup>8</sup> that the pyrolysis of Bu<sup>t</sup>AsH<sub>2</sub> proceeds by homolytic fission of the arsenic-carbon bond to give [C<sub>4</sub>H<sub>9</sub>·] and [·AsH<sub>2</sub>]. Subsequent radical disproportionation, recombination and exchange reactions then lead to the formation of C<sub>4</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub> and to a lesser extent, C<sub>8</sub>H<sub>18</sub>.<sup>8</sup> In an alternative mechanism,<sup>9</sup> two competing decomposition pathways were identified. The dominant route was proposed to be an intramolecular hydrogen transfer in Bu<sup>t</sup>AsH<sub>2</sub> leading to the elimination of C<sub>4</sub>H<sub>10</sub> and formation of [AsH] species. However, at substrate temperatures > 350 °C this is accompanied by a minor decomposition route involving the β-hydride elimination of C<sub>4</sub>H<sub>8</sub> and the formation of AsH<sub>3</sub>.

In addition to safety considerations, there are good technological reasons for seeking a replacement for PH<sub>3</sub>. The high thermal stability of PH<sub>3</sub> (only 50% decomposed at 700 °C) in the presence of less thermally stable AsH<sub>3</sub> leads to problems of

<sup>‡</sup> 1 mbar = 1.101325 × 10<sup>2</sup> Pa.

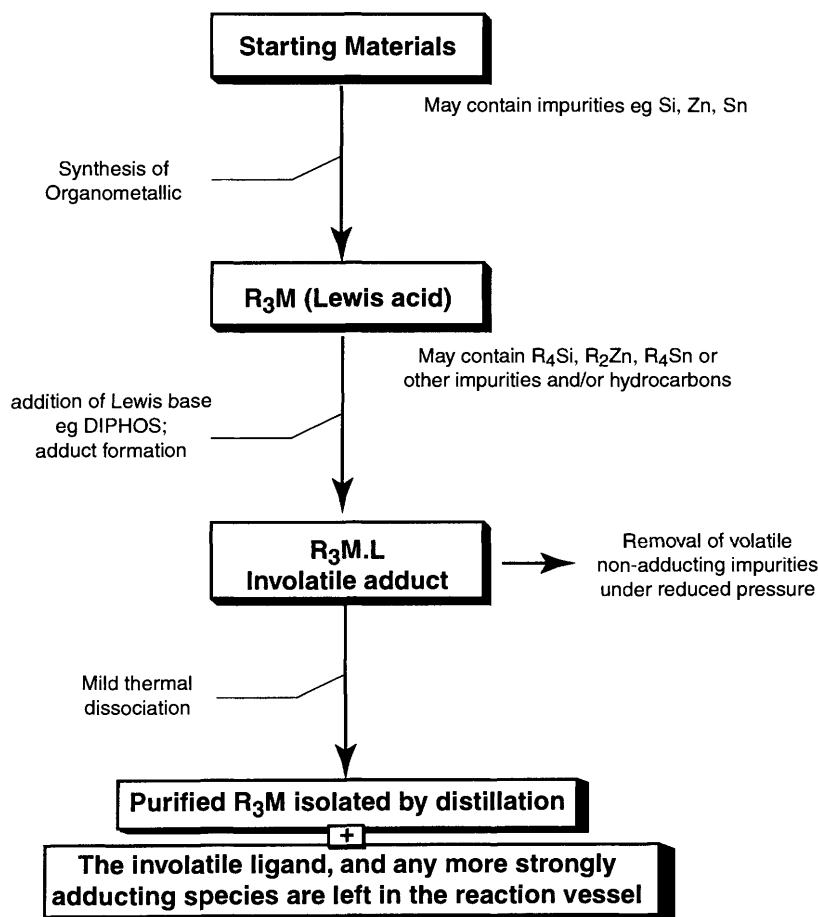


Fig. 3 Principles of adduct purification

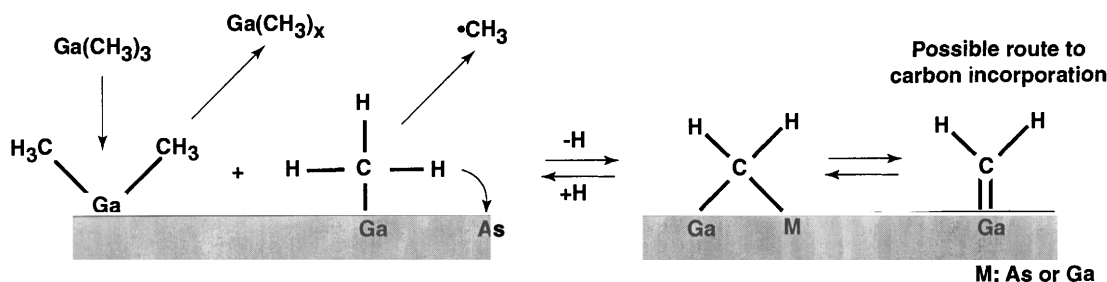


Fig. 4 Mechanism proposed for the decomposition of Me<sub>3</sub>Ga on a GaAs surface. After ref. 5.

composition control in the growth of quaternary alloys such as InGaAsP. The trialkylphosphines (e.g. Me<sub>3</sub>P, Et<sub>3</sub>P) are not useful, as they are more thermally stable than PH<sub>3</sub> and would in any case lead to increased carbon contamination. The most successful alternative phosphorus source to date is *tert*-butylphosphine (Bu<sup>t</sup>PH<sub>2</sub>)<sup>7</sup> which is a liquid with a convenient vapour pressure (184.9 mbar at 10 °C) suitable for a wide range of MOVPE applications. Bu<sup>t</sup>PH<sub>2</sub> (LC<sub>50</sub> > 1000 ppm) also has a much lower intrinsic toxicity than PH<sub>3</sub> (LC<sub>50</sub> = 11–50 ppm) and pyrolyses at a significantly lower temperature (50% pyrolysed at 450 °C), probably by homolytic phosphorus–carbon bond fission. The reduced thermal stability of Bu<sup>t</sup>PH<sub>2</sub> relative to PH<sub>3</sub> allows the growth of InP at lower V/III ratios and leads to big improvements in the uniformity of InGaAsP. As well as these advantages, Bu<sup>t</sup>PH<sub>2</sub> has a more favourable gas phase chemistry than other RPH<sub>2</sub> precursors, which prereact with Me<sub>3</sub>In, even at room temperature to liberate methane and deposit a white solid [probably (MeInPR)<sub>n</sub> polymer],<sup>10</sup> (see Fig. 5). Uniquely, Bu<sup>t</sup>PH<sub>2</sub> undergoes little or no pre-reaction and this effect may be due to the large steric hindrance of the bulky *tert* butyl group, which inhibits the formation of gas-phase adducts such as [Me<sub>3</sub>InPH<sub>2</sub>Bu<sup>t</sup>], likely precursors to the polymeric (MeInPR)<sub>n</sub> deposit.

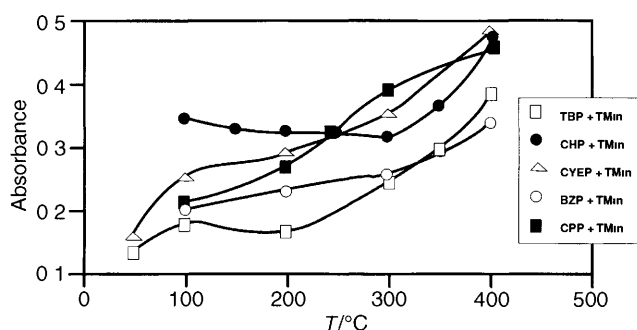


Fig. 5 Plot of methane evolution as a function of substrate temperature for a range of organophosphine precursors in the presence of Me<sub>3</sub>In (□ *tert* butylphosphine ● cyclohexylphosphine △ cyanoethylphosphine ○ benzylphosphine ■ cyclopentylphosphine). After ref. 10.

### 3.1.3 Single-source alternatives

A wide variety of III–V semiconducting materials including GaAs, InAs, InP, GaP and AlAs have been deposited from single source precursors.<sup>11</sup> These compounds potentially exhibit a number of advantages over conventional MOCVD precursors:

- (i) Air and moisture stability
- (ii) Reduced toxicity (AsH<sub>3</sub> and PH<sub>3</sub> are eliminated from the growth process)
- (iii) Pre-reaction is limited, there is only a single source in the supply stream
- (iv) Low temperature growth is often possible

Despite these potential advantages, single source precursors have yet to be commercially developed, mainly due to the following disadvantages:

- (i) Low volatility, which makes them difficult to use in conventional MOCVD equipment
- (ii) Control of stoichiometry can be difficult, especially in the growth of ternary and quaternary alloys (Al<sub>1-x</sub>Ga<sub>x</sub>, As, In<sub>1-x</sub>Ga<sub>x</sub>, As, P<sub>1-x</sub>, etc.)
- (iii) Polynuclear decomposition fragments may have a low surface mobility, inhibiting epitaxial growth

The most widely investigated III–V single source precursors have the dimeric form shown in Fig. 6(a), although a wide range of other types have also been used<sup>12</sup> such as the monomeric GaAs precursor [see Fig. 6(b)] and the dimeric GaP single source molecule, [see Fig. 6(c)].

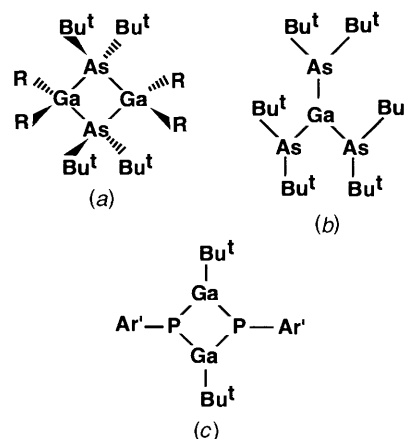


Fig. 6 Single source precursors for GaAs and GaP deposition

Polycrystalline GaAs can be deposited by vacuum MOCVD using the homologous precursors [R<sub>2</sub>Ga(AsBu<sub>2</sub>)<sub>2</sub>] (R = Me, Et, Bu<sup>n</sup>). The methyl-based precursor was found to be the most thermally stable and was not completely decomposed at 350 °C in contrast to the butyl derivative which was fully decomposed at that temperature. The methyl-based precursor also gave GaAs films which were heavily carbon contaminated (10<sup>18</sup>–10<sup>19</sup> cm<sup>-3</sup>), due to the decomposition of surface methyl radicals (cf Fig. 4). An important feature of the dimeric precursors [R<sub>2</sub>Ga(AsBu<sub>2</sub>)<sub>2</sub>] is that they appear to retain the required 1:1 stoichiometry during pyrolysis. This contrasts with the trimeric compounds [Me<sub>2</sub>GaAsMe<sub>2</sub>]<sub>3</sub> and [Me<sub>2</sub>GaAsPr<sub>2</sub>]<sub>3</sub> which liberate unwanted diarsines on pyrolysis at relatively low temperatures (ca. 150 °C), presumably *via* the fission of [Ga–As] bonds. In view of the large investment in research effort and equipment development using conventional multi-source III–V precursors, single-source alternatives are unlikely to have a significant commercial impact unless they show a distinct technological advantage. One possible area of future application is in the low temperature growth of Group III nitrides, discussed in section 3.1.6.

### 3.1.4 Precursors for AlGaAs growth

Carbon is a major acceptor impurity in AlGaAs epitaxial layers grown using Me<sub>3</sub>Al, Me<sub>3</sub>Ga and AsH<sub>3</sub>.<sup>13</sup> This may be due to the increased strength of the aluminium–carbon bond (Al–CH<sub>3</sub>, 65 kcal mol<sup>-1</sup>) (1 cal = 4.184 J) compared with gallium–carbon (Ga–CH<sub>3</sub>, 59 kcal mol<sup>-1</sup>) which leads to an increased concentration of methyl radicals on the growth surface. The minority pathway of methyl radical decomposition (cf Fig. 4) becomes more significant and carbon incorporation (up to 10 ppm) in the AlGaAs layers occurs, *via* the formation of surface [Al=CH<sub>2</sub>] carbene-like species.

Therefore, in order to lower carbon contamination, it is necessary to use Al precursors which do not contain the [Al–Me] group. Triethylaluminium (Et<sub>3</sub>Al) is a dimeric molecule with a very low vapour pressure (0.053 mbar at 27 °C) making it impractical to use in MOVPE. However, the aluminium–hydride adducts trimethylamine alane, AlH<sub>3</sub>(NMe<sub>3</sub>), and dimethylethylamine alane, AlH<sub>3</sub>(NMe<sub>2</sub>Et) are monomeric, with suitable vapour pressures, (ca. 2.6 mbar at room temp.) for MOVPE. High purity AlGaAs epitaxial layers, essentially free from carbon contamination, have been grown using AlH<sub>3</sub>(NMe<sub>3</sub>)<sup>14</sup> or AlH<sub>3</sub>(NMe<sub>2</sub>Et)<sup>15</sup> with Et<sub>3</sub>Ga and AsH<sub>3</sub>. Although carbon-containing ethyl radicals are present on the growth surface, they desorb readily by the β-hydride elimination of ethene from the growth surface, (see Fig. 7). Another advantage of AlH<sub>3</sub>(NMe<sub>3</sub>) precursors is that they do not form volatile oxygen-containing impurities (in contrast to Me<sub>3</sub>Al which can oxidise to form volatile (MeO)AlMe<sub>2</sub> species), which should allow the fabrication of higher efficiency AlGaAs optoelectronic devices.

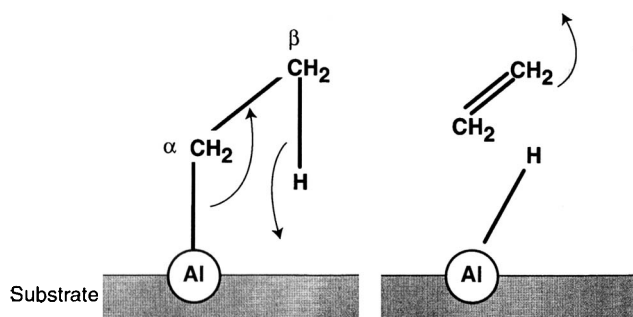


Fig. 7 The desorption of ethyl radicals from an AlGaAs surface by the  $\beta$ -hydride elimination of ethene

Disadvantages associated with the use of  $\text{AlH}_3(\text{NR}_3)$  precursors in MOVPE are their low thermal stability (they decompose to deposit Al at *ca.* 170 °C) and a marked prereaction occurs with  $\text{Et}_3\text{Ga}$ , leading to the formation of highly unstable alkylgallanes (*e.g.*  $\text{Et}_2\text{GaH}$ ,  $\text{EtGaH}_2$ ) resulting in poor AlGaAs layer uniformity.<sup>16</sup> The prereaction problem can be avoided by the use of *tert*-butylaluminium ( $\text{Bu}^t_3\text{Al}$ ). The steric hindrance of the *tert*-butyl groups renders  $\text{Bu}^t_3\text{Al}$  monomeric with an adequate vapour pressure for MOVPE (*ca.* 0.7 mbar at room temp.) and high purity AlGaAs epilayers, with no detectable carbon, have been grown using  $\text{Bu}^t_3\text{Al}$ ,  $\text{Et}_3\text{Ga}$  and  $\text{AsH}_3$ .<sup>17</sup> Pyrolysis studies indicated that surface decomposition of  $\text{Bu}^t_3\text{Al}$  occurs at *ca.* 277 °C, with the evolution of isobutene (see Fig. 8). This shows that the tri-*tert*-butyl radical is readily

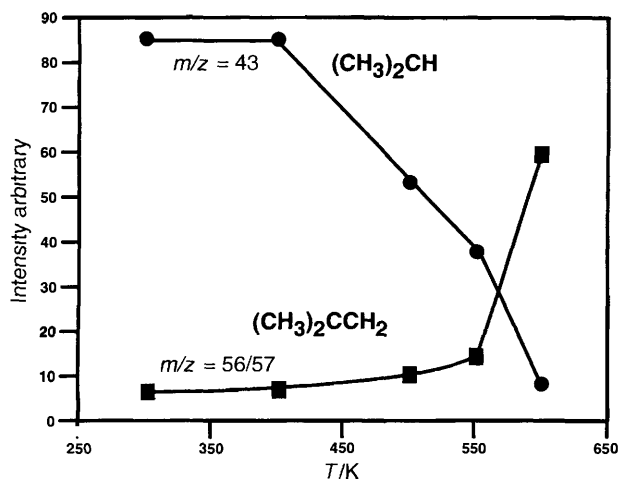


Fig. 8 Surface decomposition of  $\text{Bu}^t_3\text{Al}$  monitored by mass spectrometry.

eliminated from the substrate surface *via*  $\beta$ -hydride elimination (see Fig. 9), making  $\text{Bu}^t_3\text{Al}$  suitable for the growth of carbon-free AlGaAs, as well as high purity Al films by MOCVD.<sup>18</sup>

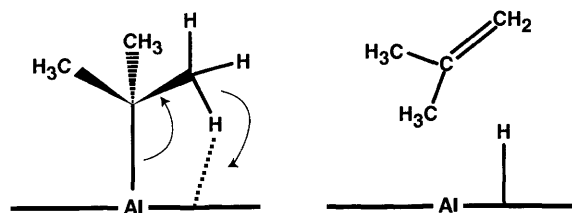


Fig. 9  $\beta$ -Hydride elimination from a coordinated *tert*-butyl radical to give isobutene and surface-bound hydrogen

### 3.1.5 Precursors for Group III antimonides

The MOCVD growth of GaSb, AlGaSb and InSb is complicated by their low melting points (*e.g.* 525 °C for InSb compared with 1240 °C for GaAs) and the very low stability of stibine,  $\text{SbH}_3$ , which decomposes at room temp. Consequently, a range of

trialkylstibine precursors,  $\text{SbR}_3$  (where R = Me, Et, Pr<sup>i</sup>, vinyl, alkyl) have been investigated.<sup>19</sup> The lower alkyls have relatively high thermal stabilities, incompatible with the low melting points of the antimonide alloys (*e.g.*  $\text{Me}_3\text{Sb}$  is only 50% pyrolysed at 525 °C). However, triisopropylstibine ( $\text{Pr}^i_3\text{Sb}$ ) is a promising low temperature source (pyrolysing some 200 °C lower than  $\text{Me}_3\text{Sb}$ ). Unfortunately, although InSb can be grown at temperatures as low as 300 °C, from  $\text{Pr}^i_3\text{Sb}$  and  $\text{Me}_3\text{In}$ <sup>20</sup> the low vapour pressure of  $\text{Pr}^i_3\text{Sb}$  (0.5 mbar at 25 °C) makes it difficult to use in conventional MOVPE. The mixed alkyl source  $\text{Bu}^t\text{SbMe}_2$  has a higher vapour pressure (*ca.* 4.7 mbar at 25 °C), but unfortunately the  $\text{Me}_3\text{In}/\text{Bu}^t\text{SbMe}_2$  combination leads to poor morphology InSb epilayers with very low growth rates.<sup>21</sup> Triis-dimethylaminostibine,  $\text{Sb}(\text{NMe}_2)_3$ , is a more promising Sb source pyrolysing at low temperature (50% decomposed at 340 °C), primarily by antimony–nitrogen bond homolysis.<sup>21</sup> The new  $\text{Sb}(\text{NMe}_2)_3$  source has been used with  $\text{Me}_3\text{In}$  to grow InSb at 275–425 °C with much higher growth efficiency than other  $\text{SbR}_3$  precursors. It was suggested<sup>22</sup> that  $\text{Sb}(\text{NMe}_2)_3$  may accelerate the decomposition of  $\text{Me}_3\text{In}$  by a free-radical mechanism and that carbon contamination is reduced by the reaction of  $[\cdot\text{NMe}_2]$  radicals with  $[\text{Me}\cdot]$  radicals to form the stable volatile molecule  $\text{NMe}_3$ , although a more complex mechanism may be in operation (see later, Fig. 14).

There is also a requirement for alternative Group III precursors. For instance, it has traditionally been very difficult to grow high quality AlGaSb using the conventional precursor  $\text{Me}_3\text{Al}$ . The strong aluminium–carbon bond, and the absence of active hydrogen species required to remove methyl radicals from the growth surface (*cf.* Scheme 2) leads to heavy carbon contamination (as high as *ca.*  $10^{18} \text{ cm}^{-3}$  in  $\text{Al}_{0.2}\text{Ga}_{0.8}\text{Sb}$ ). These hole concentrations are so high that it is impossible to n-dope the AlGaSb layers for device applications. (*e.g.* diode lasers). This problem has been solved by the use of  $\text{Bu}^t_3\text{Al}$  in combination with  $\text{Et}_3\text{Ga}$  and either  $\text{Et}_3\text{Sb}$  and  $\text{Me}_3\text{Sb}$ ,<sup>23</sup> which led to over one order of magnitude reduction in carbon contamination in AlGaSb compared with layers grown using  $\text{Me}_3\text{Al}$ . It has also proved possible to n-dope AlGaSb epilayers grown using  $\text{Bu}^t_3\text{Al}$ , opening up the possibility of producing GaSb/AlGaSb optoelectronic devices.

### 3.1.6 Precursors for Group III nitride growth

The MOCVD of AlN, GaN and InN has traditionally been carried out using mixtures of  $\text{Me}_3\text{Al}$ ,  $\text{Me}_3\text{Ga}$  or  $\text{Me}_3\text{In}$  with ammonia ( $\text{NH}_3$ ).<sup>24</sup> However, the high thermal stability of  $\text{NH}_3$  (only 15% pyrolysed at 950 °C) necessitates the use of high substrate temperatures (typically > 1000 °C) and high V/III ratios (*e.g.* 2000:1) are needed to inhibit nitrogen desorption. This seriously limits the choice of substrate material available and the inefficient use of toxic  $\text{NH}_3$  gas requires the installation of expensive gas-scrubbing systems. Therefore, much research effort has been directed towards the development of alternative precursors which will allow the growth of Group III nitrides at lower temperatures and reduced V/III ratios. One approach has been to use nitrogen precursors which are less stable than  $\text{NH}_3$ , such as hydrazine,  $\text{N}_2\text{H}_4$  (decomposes at *ca.* 400–450 °C) and dimethylhydrazine,  $(\text{MeNH})_2$ . In combination with either  $\text{Me}_3\text{Al}$  or  $\text{Me}_3\text{Ga}$  these allow the growth of AlN and GaN at temperatures down to 500 °C and with low V/III ratios < 20:1. However,  $\text{N}_2\text{H}_4$  and  $(\text{MeNH})_2$  are both toxic and highly unstable, which has restricted their widespread use in MOCVD.

### 3.1.7 Single-source precursors

An alternative approach to lowering the growth temperature of AlN and GaN is to use single source precursor molecules, which already contain a direct Al–N or Ga–N bond.<sup>25</sup> AlN films, with no detectable carbon (by AES) have been grown by low pressure MOCVD at 400–800 °C from the trimeric precursor  $[\text{Me}_2\text{AlNH}_2]_3$ ,<sup>26</sup> (see Fig. 10). The relatively low levels of carbon in the AlN films can be attributed to the removal of

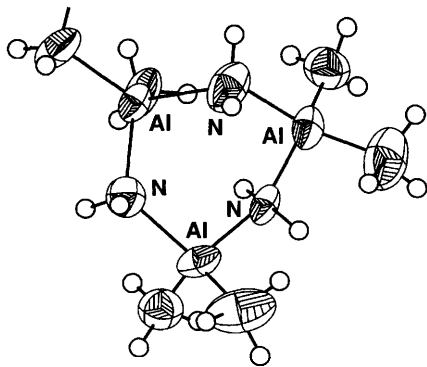


Fig. 10 Molecular structure of the single source AlN precursor,  $(\text{Me}_2\text{AlNH}_2)_3$

$[\text{CH}_3\cdot]$  radicals by the  $\text{NH}_2$  groups bonded to the Al centre. Low temperature AlN growth ( $400\text{--}800\text{ }^\circ\text{C}$ ) has also been achieved from the parent adduct  $[\text{Me}_3\text{AlNH}_3]$ .<sup>25</sup> It is probable that  $[\text{Me}_3\text{AlNH}_3]$  pyrolyses in the hot zone of the MOCVD reactor to form  $[\text{Me}_2\text{AlNH}_2]_3$  species *in situ* prior to layer growth. In contrast,  $[\text{Me}_3\text{GaNH}_3]$  and  $[\text{Me}_2\text{GaNH}_2]_3$  pyrolyse with cleavage of the relatively weak gallium–nitrogen bond to deposit Ga metal rather than GaN.<sup>27</sup> A large range of other single-source precursors have been used for AlN or GaN growth. These have been extensively reviewed elsewhere<sup>28</sup> and include;  $[\text{Me}_2\text{AlNHR}]_2$  ( $\text{R} = \text{Pr}^i, \text{Bu}^t$ ),  $[\text{M}(\text{NR}_2)_3]$  ( $\text{M} = \text{Al}, \text{Ga}$ ;  $\text{R} = \text{Me}, \text{Et}$ ),  $[\text{Et}_2\text{M}(\text{N}_3)]$  ( $\text{M} = \text{Al}, \text{Ga}$ ) and  $[(\text{Me}_2\text{N})_2\text{Ga}(\text{N}_3)]_2$ . However, although these precursors allow the growth of AlN or GaN at low/moderate temperatures ( $400\text{--}800\text{ }^\circ\text{C}$ ) they generally have only very low vapour pressures ( $\ll 1$  mbar) at room temp., which necessitates the heating of source and reactor lines and the use of high vacuum MOCVD equipment. Also, organometallic azides [*e.g.*  $\text{Et}_2\text{M}(\text{N}_3)$ ] are of unknown stability and are possibly hazardous. It has been proposed<sup>29</sup> that the ‘amine-stabilised’ organometallic azides, shown in Fig. 11, are more stable than conventional azides. These have been successfully used for the growth of AlN, GaN and InN at  $< 600\text{ }^\circ\text{C}$ ,<sup>29</sup> although the vapour pressure of these precursors is still very low, requiring the use of high vacuum MOCVD equipment.

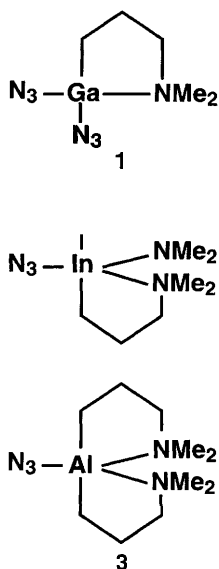


Fig. 11 Monomeric ‘amine-stabilised’ Group III organometallic azides used for the low temperature growth of GaN, InN and AlN. After ref. 29.

In order to combine the advantages of low temperature growth associated with single-source precursors with the benefits of volatile source materials, AlN has been grown from mixtures of  $\text{Me}_3\text{Al}$  or  $\text{Bu}_3\text{Al}$  with the primary alkylamines

$\text{RNH}_2$  ( $\text{R} = \text{Pr}^i, \text{Bu}^t$ ).<sup>25</sup> It is likely that  $[\text{Me}_2\text{AlNHR}]_2$  species (see Fig. 12) are formed in the gas phase, allowing AlN growth at temperatures between  $500$  and  $700\text{ }^\circ\text{C}$ . The films, however, contained high levels of carbon ( $4.7\text{--}17.0$  at %), arising from the decomposition of the organic radical in  $\text{RNH}_2$ .<sup>25</sup>

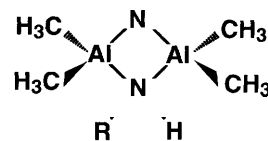


Fig. 12 Likely elimination product formed in the gas phase during AlN growth from mixtures of  $\text{Me}_3\text{Al}$  and  $\text{RNH}_2$  ( $\text{R} = \text{Pr}^i, \text{Bu}^t$ )

### 3.2 Growth of III–V semiconductors by CBE

CBE is a high vacuum technique and, to prevent elemental desorption during semiconductor deposition, growth temperatures are generally lower ( $450\text{--}550\text{ }^\circ\text{C}$ ) than those used in MOCVD.<sup>2</sup> In order to grow good morphology GaAs and AlGaAs epitaxial layers at these low temperatures, the  $\text{AsH}_3$  precursor must be precracked (at *ca.*  $900\text{ }^\circ\text{C}$ ) outside the growth chamber to give  $\text{As}_2$  species (see Fig. 3). However, this leads to a shortage of As–H species, which are needed to remove carbon-bearing alkyl fragments from the growth surface (*cf.* Scheme 2). Therefore, the use of the ‘conventional’ precursors  $\text{Me}_3\text{Ga}$  and  $\text{Me}_3\text{Al}$  results in severe carbon contamination in GaAs and AlGaAs grown by CBE (see mechanism in Fig. 4). This problem is only partly solved by using  $\text{AlH}_3(\text{NMe}_3)$  or  $\text{AlH}_3(\text{NMe}_2\text{Et})$  with  $\text{Et}_3\text{Ga}$ , indicating that an alternative Ga source is required.

Although gallane adducts such as  $\text{GaH}_3(\text{NMe}_3)$  seem to be ideally suited to CBE, these are highly unstable, decomposing in a matter of days at room temperature to deposit Ga metal. A more promising approach is to use  $\text{R}_3\text{Ga}$  compounds containing sterically hindered alkyl groups which can eliminate more readily than ethyl radicals from the growth surface by  $\beta$ -hydride elimination. These include triisopropylgallium ( $\text{Pr}_3\text{Ga}$ ), triisobutylgallium ( $\text{Bu}^i_3\text{Ga}$ ) and tri-*tert*-butylgallium ( $\text{Bu}^t_3\text{Ga}$ ).  $\text{Pr}_3\text{Ga}$  has proved to be a highly successful new Ga source, leading to GaAs and AlGaAs layers with carbon concentrations approximately one order of magnitude less than the equivalent layers grown from  $\text{Et}_3\text{Ga}$ .<sup>30</sup> Similarly, at low substrate temperatures ( $400\text{ }^\circ\text{C}$ ),  $\text{Bu}^i_3\text{Ga}$  leads to reduced carbon contamination in GaAs and AlGaAs. However, at higher substrate temperatures ( $550\text{ }^\circ\text{C}$ ) both  $\text{Bu}^i_3\text{Ga}$  and  $\text{Et}_3\text{Ga}$  lead to similar carbon levels due to the elimination of the  $\beta$ -methyl group from an isobutyl group. This results in surface methyl groups and increased carbon deposition (see Fig. 13). Surprisingly,  $\text{Bu}^t_3\text{Ga}$  is not suitable for GaAs growth by CBE, giving growth rates which were over one order of magnitude less than those given by  $\text{Pr}_3\text{Ga}$  at similar source pressures.<sup>31</sup> This can be attributed to steric hindrance from the bulky and rigid  $\text{Bu}^t$  group which prevents effective chemisorption of  $\text{Bu}^t_3\text{Ga}$ , greatly reducing growth efficiency.

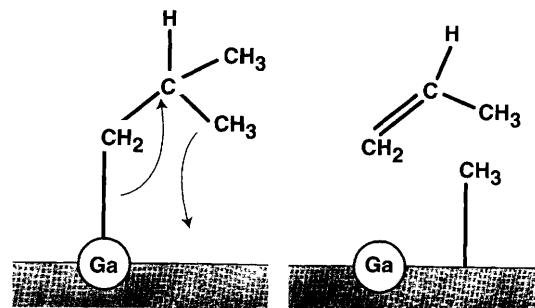


Fig. 13 The pyrolysis (*ca.*  $550\text{ }^\circ\text{C}$ ) of an isobutyl radical in CBE

The use of the alternative As source, tris(dimethylaminoarsine),  $\text{As}(\text{NMe}_2)_3$  also leads to a significant reduction in carbon contamination in GaAs and AlGaAs grown by CBE, even when methyl-based precursors are used.<sup>32</sup>  $\text{As}(\text{NMe}_2)_3$  decomposes at low temperature (*ca.* 300 °C) so that it can be used without precracking. The surface decomposition of  $\text{As}(\text{NMe}_2)_3$  [Fig. 14(a)] involves  $\beta$ -hydride elimination from  $[\text{N}-\text{CH}_3]$  which produces *N*-methylene imine and surface hydrogen.<sup>32</sup> This allows the removal of surface methyl radicals (generated by the pyrolysis of  $\text{Me}_3\text{Ga}$ ) as the stable  $\text{CH}_4$  molecule, thereby reducing carbon contamination in the GaAs and AlGaAs layers [see Fig. 14(b)]. In addition to carbon contamination, oxygen contamination is a particular problem in AlGaAs layers grown at the low temperatures associated with CBE. This can severely reduce the efficiency of AlGaAs-based optoelectronic devices. This oxygen contamination can be correlated directly with traces of diethyl ether (< 0.1%) in the  $\text{R}_3\text{Ga}$  source, deriving from the metalorganic synthesis procedure. This usually involves alkylation of a gallium trihalide  $\text{GaX}_3$  by a Grignard reagent  $\text{RMgX}$  or an alkyllithium compound  $\text{RLi}$ , dissolved in an ether solvent. Therefore, recent research<sup>33</sup> has been aimed at eliminating  $\text{Et}_2\text{O}$  from the synthesis route and the metalorganic adducts  $\text{Pr}_3\text{GaNR}_3$  ( $\text{NR}_3 = \text{NEt}_3, \text{NMe}_2\text{Et}$ ) have been prepared from the reaction between  $\text{GaX}_3$  and  $\text{Pr}^i\text{MgBr}$  in trialkylamine ( $\text{NR}_3$ ) solvent. The use of  $\text{Pr}^i_3\text{Ga}$ -triethylamine adduct prepared in this manner, together with  $\text{AlH}_3(\text{NMe}_2\text{Et})$  (also prepared by an ether-free route) resulted in improved purity AlGaAs with oxygen levels below the SIMS detection limit (*ca.*  $4 \times 10^{16} \text{ cm}^{-3}$ ).<sup>33</sup>

Despite the advances made in the growth of GaAs and AlGaAs by CBE, there are still significant problems associated with the growth of complex indium-containing alloys such as InGaAs and InGaAsP. This is due to the desorption of  $\text{R}_2\text{Ga}$  species, enhanced by the presence of In on the growth surface, which leads to strongly temperature-dependent growth rates and to severe uniformity problems. Unfortunately, all the  $\text{GaR}_3$  and  $\text{GaH}_3(\text{NR}_3)$  precursors investigated to date suffer from this effect, so that alternative solutions are required, such as the precise control of temperature across the substrate wafer.

#### 4 Precursors for the growth of II–VI semiconductors

The wide band gap Zn- and Cd-based chalcogenides have been grown both by conventional MOVPE and the single-source precursor approach. These II–VI materials form defects and interdiffuse at temperatures above *ca.* 500 °C, so that low temperature growth is a major consideration. The introduction

of nitrogen, as an active p-type dopant into ZnSe is another important issue.

##### 4.1 Conventional MOVPE

The growth of ZnSe/ZnS and CdSe/CdS has proved difficult using conventional precursors such as  $\text{Me}_2\text{Zn}$  or  $\text{Me}_2\text{Cd}$  as they prereact in the gas phase with the Group VI hydride ( $\text{H}_2\text{Se}$  or  $\text{H}_2\text{S}$ ) to deposit II–VI material at the MOVPE reactor inlet. A possible mechanism for the prereaction during ZnSe growth is shown in Fig. 15(a). For ZnSe and ZnS growth, this problem has been largely solved by the use of adducts such as  $\text{Me}_2\text{ZnNEt}_3$ , which allow the growth of ZnSe at low to moderate temperatures (*ca.* 250–350 °C) without prereaction. The introduction of an amine (*e.g.*  $\text{NEt}_3$ , pyridine) separately into the gas phase also eliminates the prereaction between  $\text{Me}_2\text{Zn}$  and Group VI hydrides, and it is likely that amines stabilise intermediate elimination products such as  $[\text{MeZnSeH}]$  [Fig. 15(b)], inhibiting prereaction, and allowing the transport of Zn species to the growth zone.<sup>3</sup> This mechanism is strongly supported by the recent isolation and characterisation of the stable pyridine adduct of  $[\text{MeZnSBU}^+]$ ,<sup>34</sup> (see Fig. 16). An effective solution has not yet been found for the elimination of prereaction during CdSe or CdS growth.  $\text{Me}_2\text{Cd}$  is a weaker acceptor than  $\text{Me}_2\text{Zn}$ , so that nitrogen- or sulfur-donors added to the gas phase will not form strong enough complexes with the Cd centre to inhibit prereaction.

Despite the improvements in ZnSe and ZnS purity arising from the use of the  $\text{Me}_2\text{ZnNEt}_3$  adduct, these materials have yet to be commercially exploited, largely due to the difficulty in obtaining p/n junctions, required for optoelectronic devices. Although ZnSe can be easily n-doped using alkyl halides (*e.g.* BuI), reliable p-doping has not proved possible. Nitrogen is the only viable p-dopant for ZnSe, forming a stable acceptor state on a Se site; therefore, much research has gone into methods of incorporating nitrogen in an electrically active form.<sup>35</sup>

For successful nitrogen doping, growth temperatures must be kept low (ideally < 350 °C) so that the p-type conductivity of the ZnSe layers is not counteracted by the generation of intrinsic defects. Although  $\text{H}_2\text{Se}$  does allow low temperature growth, high VI/II ratios are needed for good layer morphology, making the substitution of nitrogen on a selenium site very difficult, and hydrogen deriving from the pyrolysis of  $\text{H}_2\text{Se}$  is likely to deactivate any incorporated nitrogen. Thus  $\text{R}_2\text{Se}$  compounds ( $\text{R} = \text{Me}, \text{Et}, \text{Pr}^i, \text{Bu}^i$ ) have been investigated,<sup>35</sup> with  $\text{Bu}^i_2\text{Se}$  proving the most suitable for low temperature growth. Unfortunately, extensive research into a range of potential nitrogen precursors [*e.g.*  $\text{Et}_3\text{N}$ ,  $\text{RNH}_2$ ,  $\text{Et}_3\text{N}_3$ ,  $\text{Me}_3\text{SiN}_3$ ,  $(\text{allyl})_3\text{N}$ ] has

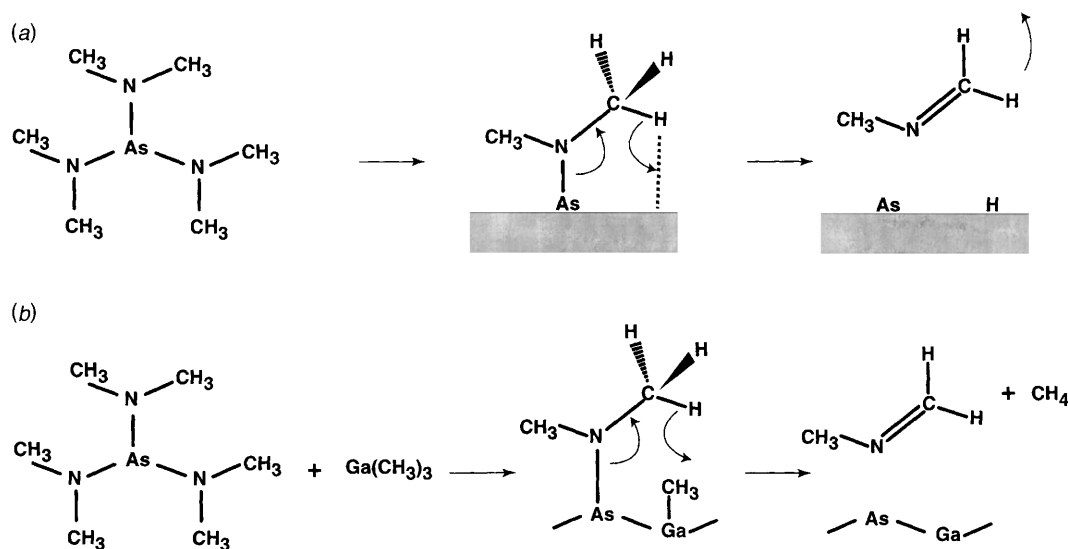


Fig. 14 Decomposition mechanism of  $\text{As}(\text{NMe}_2)_3$ . (a)  $\beta$ -hydride elimination to give surface hydrogen. (b) Removal of surface methyl radicals. After ref. 33.



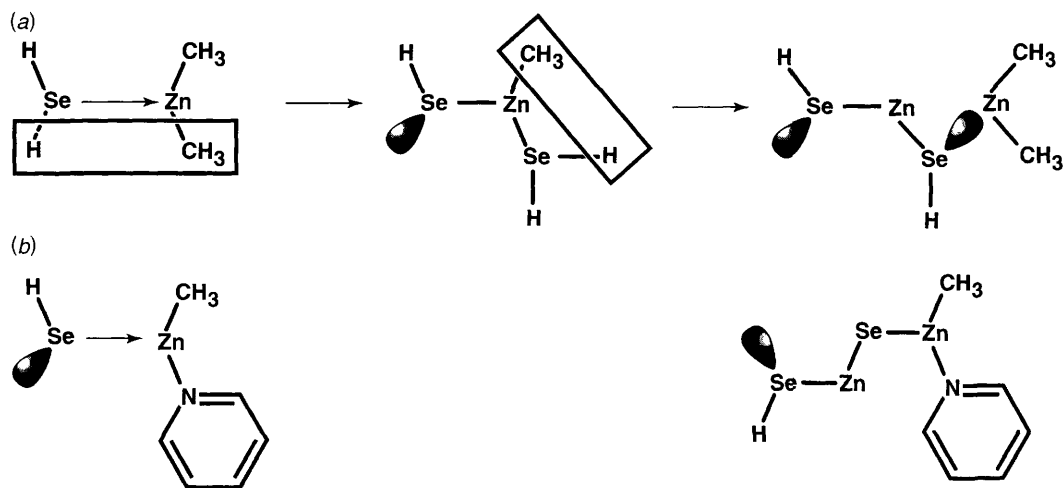


Fig. 15 (a) A possible mechanism for the prereaction between  $\text{Me}_2\text{Zn}$  and  $\text{H}_2\text{Se}$ . (b) Possible mechanisms for the inhibition of prereaction by nitrogen donors such as pyridine.

failed to demonstrate sufficiently high levels of electrically active nitrogen in ZnSe. The single-source precursor  $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ <sup>36</sup> has recently shown more promise, with low temperature photoluminescence spectroscopy indicating the incorporation of significant levels of nitrogen in the ZnSe.<sup>35</sup> However, the layers remained n-type probably due to deactivation of electrically active nitrogen by hydrogen incorporated in the crystal lattice.

#### 4.2 Single-source precursors

The problems in achieving p-type doping in ZnSe coupled with the recent successes in producing commercial blue optoelectronic devices from Group III nitrides<sup>24</sup> may force materials chemists to explore other applications for Zn- and Cd-chalcogenides, such as their use in solar cells and flat panel luminescent displays. Low temperature growth on heat-sensitive substrates (*e.g.* polymers) may be required, for which single-source precursors may be particularly suitable. This area has been comprehensively reviewed<sup>37</sup> and will only be discussed briefly here.

Early studies showed that CdS films could be deposited from precursors such as  $\text{Cd}(\text{S}_2\text{PMe}_2)_2$  whilst recent research has shown that polycrystalline Zn- and Cd-chalcogenide films can be deposited from  $\text{M}(\text{ER})_2$  compounds. [ $\text{M} = \text{Zn}, \text{Cd}; \text{E} = \text{Se}, \text{S}; \text{R} = 2,4,6\text{-Bu}_3\text{C}_6\text{H}_2$  or  $\text{Si}(\text{SiMe}_3)_3$ ]; the presence of bulky R groups inhibits aggregation of  $\text{M}(\text{ER})_2$  units and increases precursor volatility. The other main line of research has involved dithio- or diseleno-carbamates such as  $[\text{M}(\text{E}_2\text{C}-$

$\text{NEt}_2)_2]$  ( $\text{M} = \text{Zn}, \text{Cd}; \text{E} = \text{Se}, \text{S}$ ). However, metal films rather than metal chalcogenide films are sometimes deposited. In contrast, the alkyl complexes  $[\text{RM}(\text{E}_2\text{CNEt}_2)_2]$  lead only to the deposition of the desired metal chalcogenide films.<sup>38</sup> Once again however, it must be noted that these polynuclear compounds have very low vapour pressures and MOCVD must be carried out in high vacuum ( $10^{-2}$ – $10^{-6}$  mbar). This may restrict the widespread application of these precursors.

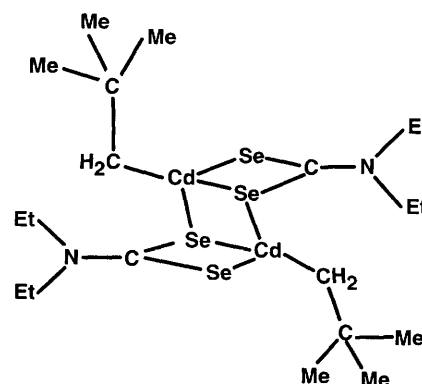


Fig. 17 Typical structure of a mixed alkyl/selenocarbamate of cadmium or zinc

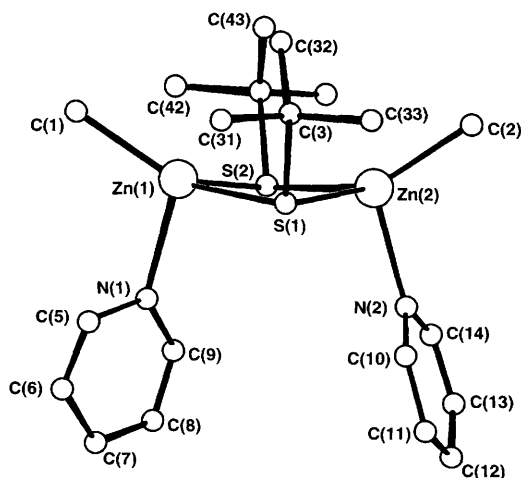


Fig. 16 X-Ray crystal structure of  $[\text{MeZnSBUt}(\text{C}_5\text{H}_5\text{N})_2]$

#### 5 Conclusions

The organometallic chemist has undoubtedly played a major role in the development of methods for depositing semiconductors from the vapour phase. As well as the important developments of improved precursor purity and consistency, alternative precursors specifically designed for use in MOVPE and CBE processes have led to rapid progress, especially in the deposition of AlGaAs, Group III–antimonides and –nitrides and ZnSe/ZnS. Significant contributions have also been made to process safety and environmental awareness by the development of  $\text{Bu}^t\text{AsH}_2$  and  $\text{Bu}^t\text{PH}_2$  as safer liquid replacements for the highly toxic gases  $\text{AsH}_3$  and  $\text{PH}_3$ . Nevertheless, a number of problems still remain such as the need for an effective p-type dopant for ZnSe and related alloys. Also, oxygen contamination remains a problem in high Al-content alloys (*i.e.* those containing > 50% Al) and methods of analysing, and then removing, ppm levels of oxygen impurity need to be devised. These problems will provide continuing challenges for organometallic chemists and materials technologists in the future.

## 6 Acknowledgements

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