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Reviews

Organometallic Precursors in the Growth of Epitaxial Thin Films of Groups III-V Semiconductors by Metal-Organic Chemical Vapor Deposition

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Metal-organic chemical vapor deposition (MOCVD) can now be used routinely for the preparation of a wide variety of groups III-V semiconductor materials. Ga- and In-based binary (e.g., GaAs, InP), ternary (e.g., $In_xGa_{1-x}As$), and quaternary (e.g., $In_xGa_{1-x}P_yAs_{1-y}$) compounds may be prepared as epitaxial layers ranging in thickness from a few angstroms to several microns for device applications. However, an understanding of the chemistry involved in the gas phase and at growing surfaces during MOCVD is at a primitive level despite the progress of the past few years. In this account we shall review recent progress in the use of organometallic precursors for MOCVD. The purity of these starting materials will be considered in relation to the quality of resulting epitaxial layers. Reaction mechanisms involved in their decomposition and reactivity both in the gas phase and at substrate surfaces will be discussed. Carbon incorporation is comprehensively covered, and growth using alternative group III and group V precursors together with the decomposition reactivity of these reagents is reviewed. The prospects for chemists in this research field are excellent, and in our opinion they are essential to its further development and extension into hitherto unexplored territories.

Introduction

Epitaxial thin films of groups III-V semiconductor materials are playing an increasingly important role in the development of electronic and optoelectronic devices.[1] The results obtained by in-depth investigations not only have been successfully extended to similar families of semiconductor materials (e.g., II-VI) but also appear promising for application in other emerging areas (viz., superconductivity, metal coatings, and ceramic materials).[2] To be suitable for the fabrication of electronic devices, thin epitaxial films of III-V materials must be prepared under very stringent conditions of chemical purity and structural and morphological perfection. Such conditions may be attained only by a few sophisticated deposition methods such as MOVPE (metal organic vapor phase epitaxy, we however will use the more general acronym MOCVD) and MBE (molecular beam epitaxy).[3-5] MOCVD not only fulfills present technological requirements in the field of thin films and superlattices but also shows considerable promise in such areas as atomic layer epitaxy (ALE), selected area deposition, and metastable structures.[6] In addition, very sharp impurity profiles, extreme purity, and alloys with composition inside miscibility gaps with new physical properties, can be obtained by this technique. MOCVD is more attractive than MBE as far as the practical aspects are concerned (cost, operational time, optimization for large-scale production, etc.) and for certain materials systems, e.g., In- and P-containing alloys, has become the method of choice in commercial production of epilayers.[7] It is also interesting to note that protagonists of MBE are increasingly turning to deposition techniques that are hybrids of MOCVD (e.g., gas source MBE (GSMBE), metal organic MBE (MOMBE), and chemical beam epitaxy (CBE)). The MOCVD process is complex and involves both gas-phase and surface reactions (catalysis). It consists of several steps: (a) evaporation of reagents (precursors), (b) pyrolysis of precursors and reaction of decomposition fragments to give the desired material, and (c) elimination of side reactions and unwanted products (e.g., C). As an example, the homoepitaxial growth of GaAs from trimethylgallium ($GaMe_3$) and arsine (AsH_3) precursors in a stream of hydrogen at atmospheric pressure may be schematized by the following reaction:

$$Ga(CH_3)_3 + AsH_3 \xrightarrow[H_2]{550\text{-}650\ ^\circ C} GaAs + 3CH_4 \qquad (1)$$

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Therefore, in principle the precursors must be characterized by suitable volatility and by a pyrolytic decomposition mode leading to the formation of only one solid compound (e.g., GaAs). The other side products must be gaseous at the reaction temperature in order to be easily eliminated from the system. Thus far trimethyl and triethyl derivatives of Al, Ga, and In in combination with AsH_3, PH_3, and SbH_3 (or $SbMe_3$) have been employed for the preparation of III–V semiconductor materials. Their use is, however, ambivalent. On one hand, they have allowed the development of MOCVD, while on the other their use causes problems that hamper the progress of this promising technique. In fact alkyl derivatives of group 13 elements are pyrophoric and sensitive to water and oxygen, and PH_3 and AsH_3 are extremely toxic gases. Consequently, drastic precautions aimed at eliminating fire hazards, contamination of materials by metal oxides, and chiefly removing the danger of poisoning must be taken, raising significantly the cost of the preparation facility. In this context the success of MOCVD is remarkable, and the fact remains that use of these precursors can impart high quality and novel properties to semiconductor materials. The chemistry of the MOCVD process has been largely neglected until recently but is now attracting increasing attention. It is universally recognized that the chemistry of gas-phase and surface processes plays a fundamental role in the overall epitaxy, and many advantages in material production will ensue from an improved knowledge of the pathways leading from volatile precursors to solid materials. The importance of and interest in the chemistry is witnessed by the great number of publications appearing in a growing number of journals (e.g., *Advanced Materials*, *Chemtronics*, *Chemisty of Materials*). The aim of this review, therefore, is to define the role of chemistry in growth by MOCVD and to identify and emphasize in this context the main lines of current research activity. There exist several excellent reviews[1–6,7b,8,9] on MOCVD covering general or particular topics, but none deals specifically with the relationship between chemical aspects on one hand and material properties on the other. Taking this into account we will discuss the following subjects: (a) the purity of precursors and material quality; (b) the reaction and growth mechanisms; (c) the use of new precursors; (d) the future perspectives, on the basis of data published recently and mainly referring to the literature since 1987.

Purity of Precursors and Material Quality

The purity of III–V materials is of fundamental importance in controlling their optical and electrical properties that determine in turn their technological usefulness, i.e., the performance and reliability of devices. Even at low concentrations, ionized impurities degrade electron mobility by scattering[10] and provide nonradiative recombination pathways.[11] Therefore, great efforts have been expended on the problems connected with the presence of extraneous chemical species. It is accepted that the semiconductors normally used are not intrinsic materials, but they must be doped. That is, they must contain electrically active impurities (dopants) different from the main constituents of the compound or of the alloy. Thus, in principle, no difference exists between dopants and impurities normally found in epitaxial films, except that the nature and concentration of dopants are accurately controlled whereas the presence of impurities is not regulated. It is also recognized that the mechanism for incorporation of an element as dopant and/or impurity is analogous. The most common impurities (or dopants) in III–V materials are Zn, Mg, C, Be, Si, Ge, O, S, Sn, and Se, i.e., atoms belonging to groups 12, 14, or 16. These act as substitutional impurities[11,12] in that they occupy lattice sites normally occupied by group 13 atoms (Zn, Mg, or Be for Al, Ga, or In; p-type) or group 15 atoms (O, S, or Se for N, P, As, or Sb; n-type). C, Ge, Si, and Sn may show amphoteric behavior[13] in that they may occupy either group 13 atom and group 15 atom positions. However, C is generally found in group 13 positions (p-type), whereas Si is in group 15 positions (n-type). Technologically important intrinsic (pure) materials generally must have impurities at a level much lower than 10^{15} atoms cm^{-3}. There have been recently reports of carrier concentration (n-type) as low as 10^{13} atoms cm^{-3} and electron mobilities of 335 000 $cm^2\ V^{-1}\ s^{-1}$ for GaAs homoepitaxial layers.[14] As solid materials contain about 10^{22} atoms cm^{-3}, it means that pure materials must contain impurities at a level much less than 1 ppm. Therefore, it is generally accepted that the purity of the precursor alkyls and hydrides currently limits the obtainable purity of the epitaxial layers[15] and an understanding of the origin and of the behavior of residual impurities in the films is an essential issue in MOCVD. The incorporation rate of impurities from the vapor phase of precursors to the epitaxial layer ranges over wide values and depends on the particular system under investigation. Impurities can originate as contaminants of the precursor

Table I. Common Impurities in MOVPE Organometallics and Hydrides

impurity	origin	mater	behavior	ref
CH_3I	$GaMe_3$			18
S	$GaMe_3$–$S(CH_3)_2$		donor	22
Si	$GaMe_3$–$AsMe_3$	GaAs	amphoteric	36
Si	$GaMe_3$	GaAs	donor	25b
Be	$GaMe_3$	GaAs	acceptor	25b
Mg	$GaMe_3$	GaAs	acceptor	25b
Zn	$GaMe_3$	GaAs	acceptor	25b, 17b
Si	$GaEt_3$	GaAs	donor	28
Zn	$GaEt_3$	GaAs	acceptor	27
Mg	$GaEt_3$	GaAs	acceptor	27
Si	$GaEt_3$	GaAs	donor	27
Si	InR_3	InP	donor	30
Zn	InR_3	InP	acceptor	27
O_2	$InMe_3$			20
Zn	$PhAsH_2$	GaAs		15b
Fe	$PhAsH_2$	GaAs		15b
Mg	$PhAsH_2$	GaAs		15b
Mn	$PhAsH_2$	GaAs		15b
Ge	Et_2AsH	GaAs	donor	24c
S	Bu^tAsH_2	GaAs	donor	131
Cu	substrate	GaAs		36
Mn	substrate	GaAs	donor	36

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(8) Very recently MOVPE conferences have been periodically organized. The *Journal of Crystal Growth* has published expansively the works presented, giving a comprehensive and up-to-date picture of this technique. See: (a) ICMOVPE-I Aiaccio, France 1981; *J. Cryst. Growth* **1981**, *55*. (b) IC-MOVPE-II Sheffield, England 1984; *J. Cryst. Growth* **1984**, *68*. (c) IC-MOVPE-II California, USA, 1986; *J. Cryst. Growth* **1986**, *77*. (d) IC-MOVPE-IV, Hakone, Japan 1988; *J. Cryst. Growth* **1988**, *93*.

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source or come from leaks in the reactor (O_2, H_2O) and are incorporated into the material during the growth process (Table I). Alternatively carbon, the prevalent impurity in MOCVD, is a component of the precursor molecule and enters into the material following parasitic side reactions.[16] From the practical point of view, MOCVD precursors must satisfy the conditions of extreme purity and ideally should not lead to the incorporation of C into epilayers. Special and very sensitive analytical methods are used to detect impurity elements in organometallic precursors. ICP (inductively coupled plasma)[17] spectroscopy has been widely used and has proven to be the most powerful tool in detecting even small traces (<1 ppm) of the impurities present in organometallic and hydride sources. Detection using emission lines in the UV region improves sensitivity even further. Mass spectrometry has found variable success in identifying impurities consisting of light hydrocarbons[18,19] or oxygen[20] (in this case the monitored species were methoxide derivatives formed by insertion of O_2 into the M–C bond[21]). Sulfur present in Me_3Ga and Me_3Al has been determined by a luminescence method[22] (detection limit of S is ca. 0.001 $\mu g/cm^3$). However, the most effective method of monitoring impurity problems is by relating the nature and purity of precursors and the growth conditions with the chemical purity and electrical properties of the obtained epitaxial materials and performance of the devices.[12,16] Although rather empirical, this criterion has become of general applicability and is quite effective in giving useful information on the behavior of both precursors and impurities introduced during the growth process. To assess the purity as a function of depth in the epilayer, dynamic SIMS (secondary ion mass spectroscopy) methods have been developed.[16,23] Isotope tracer techniques[24] have assisted in the identification of particular impurities. Low-temperature photoluminescence (PL) spectroscopy[10,16,25] can in certain cases assist in the identification of donor and acceptor impurities on the basis of the band shape and the energy of spectral features. Hall effect measurements yield values of the net carrier concentration and the carrier mobility at both liquid nitrogen and room temperature. In the most favorable cases it is possible to determine N_D (number of donors cm^{-3}), N_A (number of acceptors cm^{-3}), the identification of electrically active impurities, and their incorporation as a function of growth parameters. In Table I we summarize some of the most common impurities present in the commonly used MOCVD precursors and III–V materials.

GaAs Quality. Systematic studies of GaAs growth have been carried out starting from different purity $GaMe_3$ and AsH_3 sources and varying the $[AsH_3]/[GaMe_3]$ ratio and growth temperature (T_G).[25b] Zn and Si originally present as volatile impurities in the precursors (see Figure 1) and C were found in the GaAs layer. Zn behaved as a p-dopant, and its content decreased with increasing temperature, while Si showed n-type behavior, and its content in the epilayer increased with increasing temperature at constant $[AsH_3]/[GaMe_3]$ ratio. As expected on the basis of previously reported data,[26] C decreased with increasing $[AsH_3]/[GaMe_3]$ ratio. The GaAs material with the best electrical properties was grown from the purest precursor sources. In such a way it was possible to establish the optimal growth parameters as shown in Figure 1.

GaAs growth has also been investigated by using $GaEt_3$ instead of $GaMe_3$ in a reduced pressure range (18–78 Torr).[27] The dependence of electron mobility and carrier concentration on $[AsH_3]/[GaEt_3]$ ratio was different from the growth using $GaMe_3$; in fact all materials were n-type, and no variation with $[AsH_3]/[GaEt_3]$ ratio was found at T_G = 650 °C, while at 600 °C the mobility decreased with increasing V/III ratio, a behavior opposite to that found with $GaMe_3$ and indicating a low level of acceptor impurities due to the presence of Zn or Mg instead of C. As in ref 25b, Zn content increased with decreasing temperature and increasing $[AsH_3]/[GaEt_3]$ ratio. The impurity responsible for n-type behavior was supposed to be Si, probably coming from Et_3SiH present as a contaminant of the metal source precursor. Si incorporation increased with T_G, presumably due to the high activation energy for the decomposition of the Et_3SiH molecule.[27] On the other hand, Si incorporation decreased with a decrease in the total reactor pressure, and this was explained in terms of Si incorporation being directly dependent on Et_3SiH partial pressure in the gas phase. It was, therefore, concluded that purer GaAs could be obtained by decreasing the reactor pressure. Growth at still lower pressure[28] (0.1–20 Torr compared to 18–78 Torr of ref 27) showed that this prediction did not hold below 10 Torr. In fact the GaAs grown had electrical properties much more independent of the $[AsH_3]/[GaEt_3]$ ratio, and Si was identified as the n-type impurity. Electron mobility on one hand and both N_D and N_A on the other hand showed a maximum and a minimum, respectively, around 2–5 Torr. This fact and a significant content of intrinsic C resulted from a change in growth mechanism at low pressure.

$Al_xGa_{1-x}As$ Purity. Recent experiments in the growth of $Al_xGa_{1-x}As$ have been centered on the role of O_2 or H_2O coming from leaks in the growth system.[16] This effect is ascribed to the presence of Al, which shows a larger oxophilicity than gallium and indium and readily forms Al oxides which can be incorporated as impurities. The stability of metal oxides increases with decreasing temperature, and in the presence of Al at 700 °C O_2 or H_2O should be present at levels lower than fractions of ppb in order to avoid the formation of Al oxides. These conditions are much less stringent for Ga. As it is to be expected that the possibility of system leakage increases with the use of low-pressure reactors, operating at low pressures seems not suitable for growth of high-purity $Al_xGa_{1-x}As$. In any case it has been found that the best $Al_xGa_{1-x}As$ corresponds to the highest x because the greater concentration of $AlMe_3$

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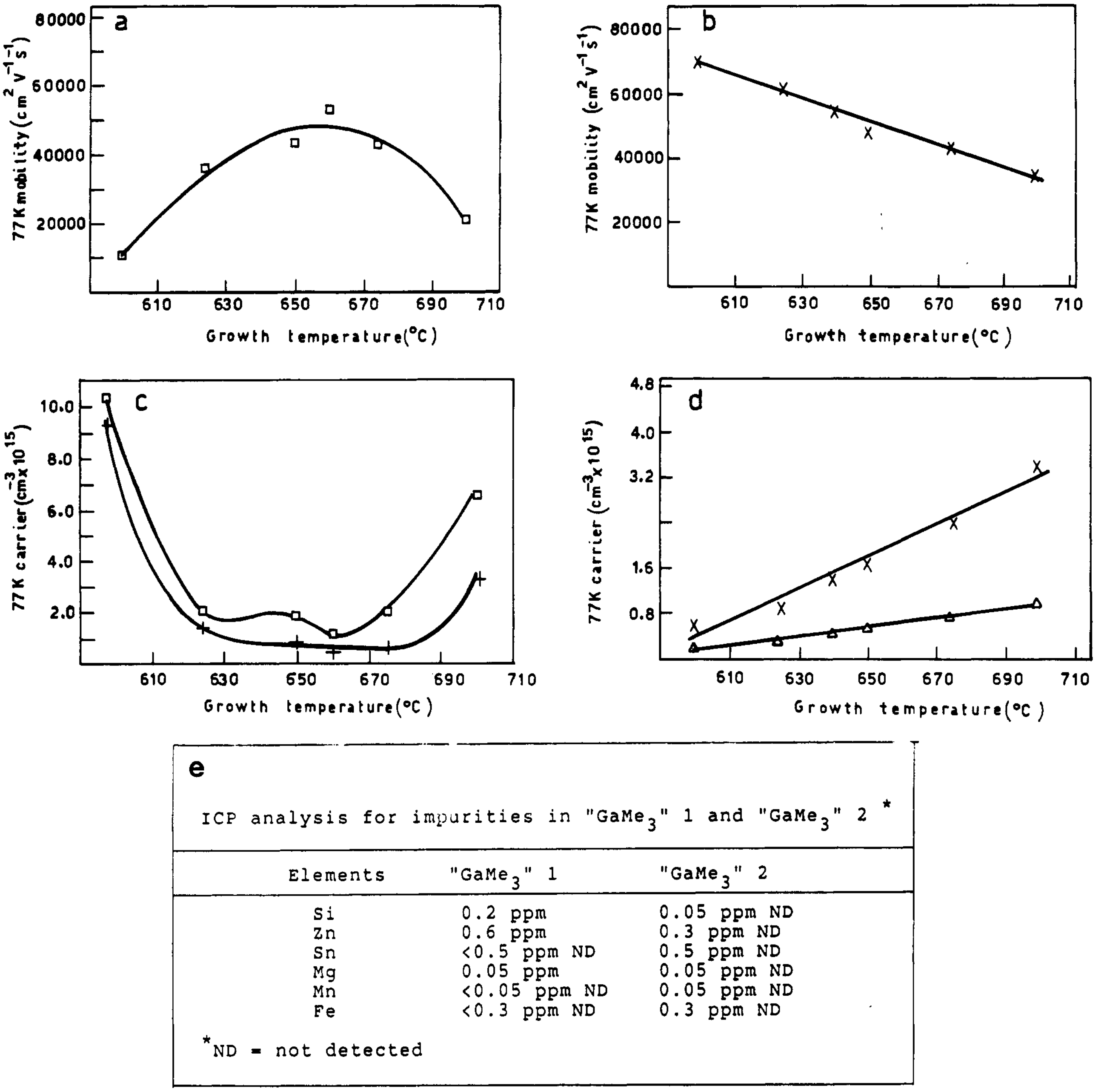

ICP analysis for impurities in "$GaMe_3$" 1 and "$GaMe_3$" 2 *

Elements	"$GaMe_3$" 1	"$GaMe_3$" 2
Si	0.2 ppm	0.05 ppm ND
Zn	0.6 ppm	0.3 ppm ND
Sn	<0.5 ppm ND	0.5 ppm ND
Mg	0.05 ppm	0.05 ppm ND
Mn	<0.05 ppm ND	0.05 ppm ND
Fe	<0.3 ppm ND	0.3 ppm ND

*ND = not detected

Figure 1. Electron mobility and donor/acceptor concentrations versus growth temperature at 77 K for GaAs epitaxial layer grown from two different purity $GaMe_3$ sources ("$GaMe_3$" 1 and "$GaMe_3$" 2) with AsH_3 at V/III ratio of 75/1: a, μ_{77} for "$GaMe_3$" 1; b, μ_{77} for "$GaMe_3$" 2; c, N_D (□) and N_A (+) for "$GaMe_3$" 1; d, N_D (×) and N_A (△) for "$GaMe_3$" 2; e, ICP analysis for the two sources (after Hunt and Williams,[25b] reproduced with the kind permission of Butterworths Scientific).

required was more effective in destroying both O_2 and H_2O. The dependence of $Al_xGa_{1-x}As$ quality on the purity of $AlMe_3$, $GaMe_3$, and AsH_3 has been studied by varying the purity of precursor sources.[29] The quality of the $Al_xGa_{1-x}As$ layers was more strongly affected by the O_2 content of AsH_3 than from the presence of O_2 in $AlMe_3$, where it probably forms $AlMe_2(OMe)$.[21]

Purity of In-Based Materials. The behavior of impurities in the preparation of InP and related materials has been investigated by procedures similar to those reported for GaAs. The quality of InP grown with $InMe_3$ and PH_3 on varying both $[PH_3]/[InMe_3]$ ratio and growth temperature has been studied as a function of the source purity. The best materials have been obtained from purest precursors, and the main impurities identified in $InMe_3$ have been Zn (acceptor) and Si (donor).[30] Zn contamination has been rationalized by taking into account the tendency of Zn to occupy the In vacant sites (V_{In}):

$$Zn(g) + V_{In} \rightarrow Zn_{In} \qquad (2)$$

(where Zn(g) indicates Zn present in the vapor phase probably in the form of ZnR_2, while Zn_{In} indicates a Zn atom occupying In sites in the crystal). $[Zn_{In}]$ increases with decreasing temperature, and this was explained by taking into account Zn desorption increasing with temperature (Zn vapor pressure is 11 Torr at 600 °C and 260 Torr at 800 °C).[3] On the other hand, high $[PH_3]/[InMe_3]$ ratio was found to favour V_{In} and consequently increases the Zn incorporation. On the contrary, Si incorporation

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increases with increasing temperature in line with the higher decomposition temperature of Si organic impurity sources and the low Si vapor pressure[3] (<10^{-11} Torr at 600 °C and 10^{-11} Torr at 800 °C). Similar growth experiments also with a $\mathrm{InMe_3}$ sample prepared[31] by a new method (no details reported on the synthesis) gave similar results. In fact SIMS and PL measurements showed Zn decreasing and Si increasing with growth temperature; it was observed that this behavior parallels that of the hole concentration in GaAs or InP intentionally doped by using $\mathrm{ZnMe_2}$ or $\mathrm{ZnEt_2}$ or that of electron concentration in GaAs and InP intentionally Si-doped with silane. Also in this case the best quality InP was grown by using the purest $\mathrm{InMe_3}$ source. Si in InP can also derive from $\mathrm{SiO_2}$ from a heated silica boat transported as the volatile species SiO, as suggested by Briggs and Butler,[32] through the reactions

$$\mathrm{SiO_2 + H_2 \rightarrow SiO + H_2O} \tag{3}$$

$$\mathrm{SiO + H_2 \rightarrow Si + H_2O} \tag{4}$$

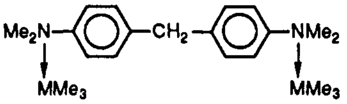
Similar reactions may be also responsible for Si interface contamination during homoepitaxial GaAs growth, where Si "spikes" are observed in dynamic SIMS profiles.[33] However, such Si "spikes" may be explained by Si contamination from the precursors during precleaning and/or pauses in the growth process. The purity of $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ has been studied on varying $[\mathrm{AsH_3}]/\{[\mathrm{InMe_3}] + [\mathrm{GaMe_3}]\}$[34] ratios in the range 20–500 °C. Only n-doped layers were obtained, and the residual carrier concentration increased linearly with T_G; both acceptor and donor impurities increased with the V/III ratio; the main acceptor PL peak was due to Zn, while the identity of donor was not clear even though Si, Ge, or even C were suggested. Thus the behavior of C seems quite unusual here, not only for its donor character but also because its content increases with V/III ratio.

Impurities from Substrate. Substrate preparation is very important for the growth of pure materials[33,35] in that extrinsic impurities can be incorporated by diffusion from the substrate itself. This is the case for Mn and Cu studied by combined SIMS and PL experiments,[36] and it has been shown that these elements occupy Ga sites in GaAs (i.e., they act as acceptors). Moreover, as the diffusion rate is temperature dependent, the luminescence intensity of the Cu peaks increased with growth temperature. Cr, Fe, and Mg as contaminants were also found after surface preparation.[35]

Purity of Precursors. The general observation that the best-quality material corresponded to the highest purity of precursors has stimulated efforts aimed at finding very efficient purification methods and clean preparative routes.[37] In addition to the classical purification procedures of sublimation and distillation,[38] precursors have also been purified by the so-called adduct route.[39] It is well-known that alkyl compounds of trivalent metals M = Al, Ga, and In are electronically unsaturated (only six electrons are formally in the outer shell). Therefore, they show a pronounced Lewis acid behavior. This is reflected in the general tendency of these organometals (a) to occur as oligomeric forms through electron-deficient bonds in which C in the α-position bridges two M atoms sharing its electron pair with them (for Al this takes place also in vapor phase) and (b) to form complexes with Lewis bases. The complex formation can be schematized as follows:[39a]

$$x\mathrm{MR_3(g)} + \mathrm{B(s)} \rightleftarrows [(\mathrm{MR_3})_x\cdot\mathrm{B}](\mathrm{s}) \tag{5}$$

in which x molecules of the $\mathrm{R_3M}$ organometal compound form x coordinative bonds with the Lewis basis B (in B, x atoms with a lone electron pair available for coordinative bonding are present). The reaction represents a particular case in which $\mathrm{MR_3(g)}$ is a volatile compound forming a low volatility $[(\mathrm{MR_3})_x\cdot\mathrm{B}](\mathrm{s})$ complex with the involatile Lewis base B(s). As in general the coordination bond strength is lower than in the covalent bond of the complex molecules, the complex may dissociate at moderately low temperatures (100 °C), releasing the organometallic $\mathrm{MR_3}$ molecule as vapor. The most useful ligands have been proven to be 4,4′-methylenebis(N,N′-dimethylaniline) (I) and 1,2-bis(diphenylphosphino)ethane (diphos, II), which form 1:2 complexes with $\mathrm{MMe_3}$ compounds. The efficient purification of $\mathrm{MMe_3}$ organometallics has been carried out stepwise through the following sequence:[30] (a) Synthesis of $\mathrm{MR_3}$:



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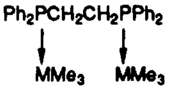

$$\underset{\underset{\mathrm{MMe_3}}{\downarrow}}{\mathrm{Ph_2P}}\mathrm{CH_2CH_2}\underset{\underset{\mathrm{MMe_3}}{\downarrow}}{\mathrm{PPh_2}}$$

II

$$\mathrm{MCl_3 + 3M'R \rightarrow MR_3 + 3M'Cl}$$

$$\mathrm{M = Al, Ga, In;\quad M' = Li\ or\ MgCl} \tag{6}$$

(b) Formation of Lewis complex:

$$\mathrm{2MR_3 + B \rightarrow (MR_3)_2\cdot B} \tag{7}$$

(c) Thermal dissociation:

$$\mathrm{(MR_3)_2\cdot B} \xrightarrow{\text{moderate heating (100 °C)}} \mathrm{2MR_3 + B} \tag{8}$$

Halide impurities ($\mathrm{SiCl_4}$, $\mathrm{SnCl_4}$, $\mathrm{ZnCl_2}$, RX, X = Cl, Br, I) contained in $\mathrm{MCl_3}$ and in M′R are transformed (step a) into $\mathrm{SiR_4}$, $\mathrm{SnR_4}$, and $\mathrm{ZnR_2}$, and hydrocarbons are separated in step b since they do not complex with B. Finally very pure $\mathrm{MR_3}$ can be obtained by thermal dissociation of the adduct $\mathrm{(MR_3)_2\cdot B}$ and subsequent condensation (step c). The efficiency of this method has been demonstrated by ICP analysis before and after adduct formation[17] and by a comparison of the PL spectra and carrier mobility of materials obtained from adduct purified and nonpurified precursors.[30] Other sources of impurity may be $\mathrm{O_2}$ and $\mathrm{H_2O}$ present in $\mathrm{AsH_3}$ and $\mathrm{PH_3}$ or coming from leaks in the reactor lines;[40] these impurities are eliminated by bubbling

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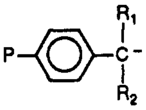
the gases through liquid Al–Ga–In alloy or by using very efficient polymeric resins[41] containing reactive sites of carbanions that remove both H_2O and O_2 (III, where P represents a polymeric chain).



MOCVD Reaction Mechanisms

The knowledge of the chemical reactions involved in the epitaxial growth of III–V materials is of vital importance in that it can provide suitable solutions to some critical problems of MOCVD (parasitic reactions, impurities, safety, etc.). The present availability of information of a fundamental nature is inadequate to explain the bulk of the empirical data. Therefore, great efforts have been recently devoted to investigations aimed at unravelling the chemical nature of the growth process. Difficulties arise mainly from two inherent peculiarities of the MOCVD process: (a) the pyrolysis of both organometallic and hydride sources and reactions between the products can occur both in the gas (homogeneous processes) and at the surface of the reactor walls or substrate surfaces (heterogeneous processes); (b) the chemical species involved are very unstable (radicals, organometallic species with the metal at a formal valence 2, 1, or 0) and present at concentrations that vary depending on the position in the reactor (e.g., near or far from the heated substrate). Accordingly, qualitative and especially quantitative analysis of the reagent species are difficult and can give conflicting results depending upon the experimental techniques employed for sampling the gas mixture and precise conditions employed during the growth process. In situ analysis employing a nonintrusive probe is clearly preferable, but also ex situ experiments are currently proving useful.[42] Suitably modified instrumental techniques such as UV and IR spectroscopies,[43] CARS[44] (coherent anti-Stokes Raman spectroscopy), mass spectrometry,[45] and gas chromatography with proper reactor modifications are under investigation. In addition to the identification of species involved in MOCVD, reference to the extended body of data relating growth rate to other parameters can yield important complementary information about mechanisms. Recent activity has been focused on the following topics: pyrolysis of organometallic precursors, their interaction with hydrides and carrier gas, and pressure effects; carbon incorporation using different precursors; growth rate, etc.

Decomposition of the organometallic and hydride precursors PH_3 and AsH_3, $GaMe_3$, $GaEt_3$, $InMe_3$, and $AlMe_3$ have been studied in connection with the preparation of epitaxial GaAs, InP, and AlGaAs.

GaR_3 Decomposition Studies. $GaMe_3$ decomposition on a GaAs substrate has been studied under three different conditions (Figure 2): (a) alone or in inert ambient with N_2[47] and He[46,48] carrier gases; (b) in H_2 or D_2[45,48,49] ambient; (c) in MOCVD ambient (i.e., in the presence of AsH_3 and H_2).[45,46,48,49] The T_{50} value (temperature at which the compound is 50% decomposed) of 550 °C has been found (in MOMBE, alone $GaMe_3$ decomposes in the range 380–680 °C[50]). In case b T_{50} occurs at 450–500 °C, significantly lower temperatures as compared to case a.

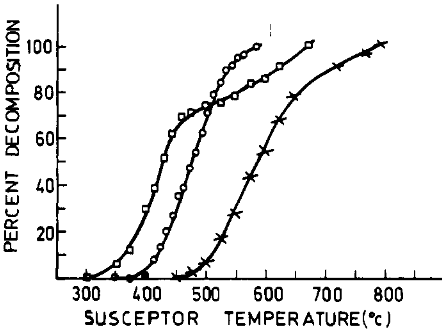
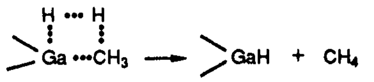
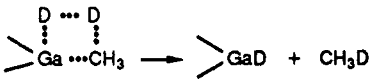


Figure 2. Decomposition temperature profiles for $GaMe_3$ in dihydrogen (○), with AsH_3 (□) at a V/III ratio of 50/1 and for AsH_3 alone in dihydrogen (×) (after Williams et al.;[46] reproduced with the kind permission of Plenum Press).

Such data seem to indicate the participation of the carrier gas in the decomposition of $GaMe_3$, i.e., in assisting the rate-determining step in scission of the metal–carbon bond (eqs 9 and 10).



(9)



(10)

The different T_{50} values between ref 47 (T_{50} = 550 °C) and ref 48 (T_{50} = 480 °C) both obtained in inert ambient (N_2 and He, respectively) may be justified either by the possibility "that the actual temperature at the sampling point could be less than the measured furnace temperature which would lead to an inflated pyrolysis temperature"[48] or by the difference in the operating pressure of the reactor.[49] Moreover, it has been observed that $GaMe_3$ decomposition is mainly homogeneous in the presence of the GaAs surface because its rate is enhanced only slightly by increasing the GaAs surface area.[45] In N_2 or He ambient CH_4 is the predominant decomposition product with little C_2H_6, whereas in H_2 and D_2 the main product is still CH_4 (or CH_3D), with C_2H_6 less than found in N_2 or He.[45,46,48,50] On the basis of the above data the thermal decomposition of $GaMe_3$ may be considered to take place homogeneously involving free radicals (although contribution from heterogeneous reactions cannot be ruled out) and the gaseous products can be accounted for by the reaction sequence in eqs 11–15.

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$$Ga(CH_3)_3 \rightarrow Ga(CH_3)_2 + CH_3^\bullet \qquad (11)$$

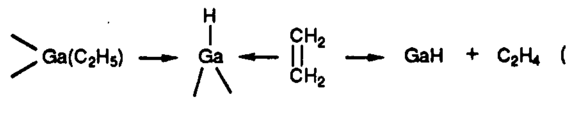
$$Ga(CH_3)_2 \rightarrow GaCH_3 + CH_3^\bullet \qquad (12)$$

$$CH_3^\bullet + H_2 \rightarrow CH_4 + H^\bullet \qquad (13)$$

$$CH_3^\bullet + D_2 \rightarrow CH_3D + D^\bullet \qquad (14)$$

$$CH_3^\bullet + CH_3^\bullet \rightarrow C_2H_6 \qquad (15)$$

$GaMe_3$ decomposition also results in Ga-containing solid products, but the mode of their formation is still[45,48] unclear. Thermal decomposition[46,48] of $GaEt_3$ in H_2 and He (unfortunately D_2 was not investigated) yields C_2H_4 as the main gaseous product accompanied by C_4H_{10} and C_2H_6 (C_2H_6 yield is higher in H_2 than in He). No difference in T_{50} (ca. 420 °C)[48] was observed between H_2 and He ambients. While contribution of heterogeneous reactions again cannot be excluded, the following decomposition pathways have been proposed for explaining the observed gaseous products:



$$>Ga(C_2H_5) \longrightarrow \overset{H}{Ga} \longleftarrow CH_2{=}CH_2 \longrightarrow GaH + C_2H_4 \qquad (16)$$

or

$$>Ga(C_2H_5) \rightarrow >Ga^\bullet + C_2H_5^\bullet \qquad (17)$$

$$2C_2H_5^\bullet \rightarrow C_4H_{10} \qquad (18)$$

$$C_2H_5^\bullet + H_2 \rightarrow C_2H_6 + H^\bullet \qquad (19)$$

Again in this case the formation of solid products containing Ga remained unexplored. Here the β-elimination reaction[17] seems to predominate, and the obvious absence of reaction[19] in He ambient explains the higher concentration of C_2H_6 in H_2, although the contribution of the radical disproportionation (eq 20) may take place.

$$2C_2H_5^\bullet \rightarrow C_2H_4 + C_2H_6 \qquad (20)$$

The decomposition of $GaMe_3$ changes dramatically in the presence of AsH_3 (case c), in that

(1) The T_{50} is depressed both for $GaMe_3$ (from 480 to 360 °C[45]) and for AsH_3 (from 476 to 387 °C in D_2 ambient on GaAs surface) with the ratio $[AsH_3]/[GaMe_3] = 1/2$. A possible explanation is that one $GaMe_3$ molecule and one AsH_3 molecule form a Lewis acid–base complex probably in the gas phase, which subsequently eliminates CH_4 molecules.[51] Whether this reaction is homogeneous or heterogeneous depends on the temperature;[45] at the reported temperature (400–500 °C) it may occur heterogeneously, but under growth conditions ($T_G > 600$ °C) a homogeneous contribution may predominate.[45] The involvement of an adduct originally suggested on the basis of IR evidence[52] has found further experimental support.[53]

(2) The major product, even in D_2 ambient, is CH_4, while CH_3D and $(CH_3)_xAsH_{3-x}$ are present only in traces.

(3) The presence of solid GaAs influences significantly the interaction between $GaMe_3$ and AsH_3. $GaEt_3$ decomposition in the presence of AsH_3 shows evidence of an increasing ethane/ethene ratio in the products.[46]

On the question of the role of carrier gas, a result of fundamental importance has been reported by Gaskill et al.[54] Through IR diode laser experiments they found that CH_3 radicals decay by reaction with AsH_3, even in presence of H_2:

$$CH_3^\bullet \xrightarrow{AsH_3} CH_4 \qquad (21)$$

which is by far predominant over other possible reactions such as $2CH_3^\bullet \rightarrow C_2H_6$ and $CH_3^\bullet + H_2 \rightarrow CH_4 + H^\bullet$; these can take place only in the absence of AsH_3. This is consistent with the fact that arsine acts as an extremely efficient hydrogen donor to alkyl radicals.[42b] This explains the formation of CH_4 as a single product in GaAs growth from $GaMe_3$ and an increase of C_2H_6 over C_2H_4 with $GaEt_3$ and AsH_3.[46] Therefore, even though carrier gases (H_2 and D_2) participate in the thermal decomposition of organometallic compounds alone, their role is extremely reduced under MOCVD conditions, and the material properties are little affected by the nature of the carrier gas.[53] Many experiments using the precursor series $GaMe_3$, $GaEt_3$, and $GaBu^i_3$[55] have been systematically carried out and surveyed with the aim of relating growth rate of GaAs to several factors such as precursor volatility, diffusion coefficient, and thermal stability. Substantial differences, indicating different growth mechanisms, are observed in the behavior of $GaMe_3$ on one hand and $GaEt_3$ and $GaBu^i_3$ on the other, although evidence of direct interaction with AsH_3 has been found for all organogallium compounds. Figure 3 shows growth rate versus temperature dependences under reduced total gas pressure (10^4 Pa) using the three different Ga precursors.

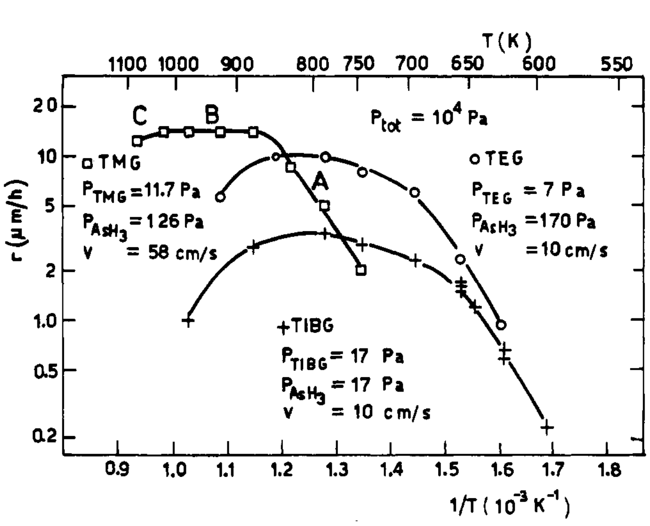


Figure 3. Temperature dependence of growth rate for homoepitaxial GaAs grown using $GaMe_3$ (TMG), $GaEt_3$ (TEG), and $GaBu_3^i$ (TIBG) and AsH_3 (after Balk and Brauer;[90] reproduced with the kind permission of Plenum Press).

Similar dependences are observed at atmospheric pressure with $GaMe_3$. The growth rate versus T shows the typical trend[56] characterized by the three regions A–C. The growth rate increases with increasing temperature until about 600 °C (region A), where it is postulated to depend on the kinetics of the deposition process; it is essentially temperature independent in the range 600–750 °C (region B), where it is diffusion limited, and finally decreases with increasing temperature above 750 °C (region C), probably due to depletion effects or to an enhanced desorption of an organogallium species from the

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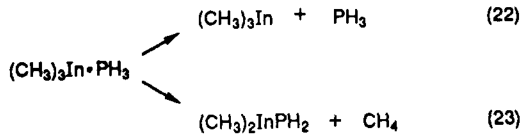
surface. With $GaEt_3$ and $GaBu^i_3$ the region where the rate is determined by decomposition of the precursors is shifted toward lower temperatures, reflecting the lower stability of these alkylgallium compounds.

InR_3 Decomposition Studies. Investigations of InP growth from trimethylindium ($InMe_3$) and phosphine (PH_3) have followed lines similar to those of GaAs. Preliminary results indicated that thermal decomposition of the In precursors depended on the carrier gas (H_2, He)[57] and that the reaction to form InP with PH_3 was affected by parasitic side reactions.[58] The assumptions were that they were caused by initial formation of Lewis complexes of the type $InMe_3{\cdot}PH_3$ and $InEt_3{\cdot}PH_3$, which are stable only at low temperature but could decompose before dissociation, forming polymeric involatile substances deposited on the walls of the reactor. On the other hand, PH_3 can pyrolyze both heterogeneously below 800 °C over InP and GaP and homogeneously above 800 °C. Pyrolysis of $InMe_3$ was homogeneous in H_2, but in N_2 surface effects occurred. The $InMe_3/PH_3$ system was studied by D_2-labeling experiments.[59] It was shown that PH_3 thermal decomposition did not depend on carrier gas.[60] In D_2 ambient, only H_2 was detected as the PH_3 decomposition product by mass spectrometry, with no HD formed in addition to that present as a D_2 trace impurity or as a small contribution from the PH_2D species. Moreover decomposition of PH_3 was found to be first order, indicating P–H bond breaking as the rate-determining step. Addition of $InMe_3$ caused a lowering in the PH_3 decomposition temperature. This temperature decreased with increasing $[InMe_3]/[PH_3]$ molar ratio in a way analogous to the $GaMe_3/AsH_3$ system.[45] Above 300°C the observed slowing down of the decomposition rate was explained by the concomitant formation of $PH_{3-x}(CH_3)_x$ in the vapor by transfer of CH_3 groups from In to P species. The decomposition temperature of $InMe_3$ in the presence of PH_3 was lowered by about 50 °C, and only CH_4 was found as decomposition product even in the presence of D_2. No CH_3D was detected. Thus it has been inferred that an interaction between $InMe_3$ and PH_3 occurs prior to the decomposition of the two single precursors, probably through the formation of an adduct of the type $Me_3In{\cdot}PH_3$ in the vapor phase, which by homogeneous release of a CH_4 molecule, causes the formation of a compound of the type $(CH_3)_2InPH_2$, from which two CH_4 molecules are subsequently liberated either homogeneously or heterogeneously. In any case it has been pointed out that the proposed adduct, reported to be unstable at room temperature,[58] should be short-lived with two possible decay pathways:



Such studies have been repeated with a more detailed analysis of the gaseous products arising from the pyrolysis of $InMe_3$ in He, H_2, and D_2 ambients. In the first case[60] C_2H_6 was the main product, along with a limited amount of CH_4 (a small amount of C deposit was simultaneously observed). C_2H_6 formation was also found in the system $InMe_3/D_2$, where the main product was CH_3D. With the $InMe_3/H_2$ system also, CH_4 is the dominant product (in neither of the two last cases was a C deposit observed). For the three systems the rate constants k_g follow the expressions[61]

$InMe_3/He$

$$\log k_g\ (s^{-1}) = 17.9 - (54.0\ \text{kcal/mol})/(2.303RT)$$

$InMe_3/D_2$

$$\log k_g\ (s^{-1}) = 13.4 - (39.8\ \text{kcal/mol})/(2.303RT)$$

$InMe_3/H_2$

$$\log k_g\ (s^{-1}) = 15.0 - (42.6\ \text{kcal/mol})/(2.303RT)$$

Several decomposition models have been considered. Previous data[58] suggested that homolysis of the first two In–C bonds occurs for the three systems according to $InMe_3 \rightarrow 2CH_3^{\bullet} + InCH_3$, the rate being enhanced in the sequence He < D_2 < H_2. The decomposition involves subsequently the radical reactions $CH_3^{\bullet} + D_2 \rightarrow CH_3D + D^{\bullet}$, $CH_3^{\bullet} + H_2 \rightarrow CH_4 + H^{\bullet}$, and $CH_3^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_6$. The present data may be accounted for, if also the new reactions (24)–(27) (where D may be replaced by H) are

$$D^{\bullet} + In(CH_3)_3 \rightarrow DIn(CH_3)_3 \qquad (24)$$

$$CH_3^{\bullet} + DIn(CH_3)_3 \rightarrow CH_3D + In(CH_3)_3 \qquad (25)$$

$$D^{\bullet} + DIn(CH_3)_3 \rightarrow D_2 + In(CH_3)_3 \qquad (26)$$

$$DIn(CH_3)_3 \rightarrow CH_3D + 2CH_3^{\bullet} + In \qquad (27)$$

postulated to occur in which the "hypervalent" species $DInMe_3$ ($HInMe_3$) plays an important role. Although alternative reactions cannot be ruled out, the overall system proposed seems the most adequate to explain the observed products.[61] Addition of PH_3 to $InMe_3$ in He, H_2, and D_2, respectively, led further to the definition of kinetic parameters for InP growth.[62] In line with previous suggestions[59] it has been deduced that at low temperature the decompositions of $InMe_3$ and PH_3 are strictly interconnected and occur heterogeneously, but on increasing temperature (>400 °C) the homogeneous pathway must gain importance and eventually $InMe_3$ could partially decompose independently as inferred from the formation of C_2H_6 and CH_3D at the lowest (2.1:1) $[PH_3]/[InMe_3]$ ratio.[63] Above 400 °C in the homogeneous regime the reaction sequence (28)–(31) (where $PH_2^{\bullet}$ reflects the role of D in

$$CH_3^{\bullet} + PH_3 \rightarrow CH_4 + PH_2^{\bullet} \qquad (28)$$

$$PH_2^{\bullet} + In(CH_3)_3 \rightarrow PH_2In(CH_3)_3 \qquad (29)$$

$$H_2PIn(CH_3)_3 \rightarrow In + PH_2CH_3 + 2CH_3^{\bullet} \qquad (30)$$

$$PH_2^{\bullet} + CH_3^{\bullet} \rightarrow PH_2CH_3 \qquad (31)$$

(24) and (27)) has been suggested to explain the mechanism on the basis of the experimental data. It has been pointed out that many aspects of the reactivity of $InMe_3$ with PH_3 are reminiscent of the analogous system $GaMe_3/AsH_3$ (and the model proposed by Reep and Gandhi[56]). However in $GaMe_3/AsH_3$ even traces of C_2H_6 and CH_3D were absent. Here the presence of CH_3D and C_2H_6 as reaction products gives an indication that $InMe_3$ may also partially decompose independently before association with PH_3, especially when this ligand is present in low concentration.[63] On the other hand the participation

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[63] It must be noted that here comparison is made between $In(CH_3)_3/PH_3/H_2$ and $Ga(CH_3)_3/AsH_3/H_2$ systems with V/III ratio = 2.1 for the In system and 10 for the Ga system.

of a $Me_3In{\cdot}PH_3$ adduct is important for the growth mechanism. In fact it may lead to the formation of InP but also may cause parasitic reactions with formation of polymeric involatile materials[3] if several parameters such as gas flow rate, point of mixing of precursors, reactor design, reagent purity, etc., are not optimized. The quality and uniformity of InP materials may be compromised because $InMe_3$ is a solid and its sublimation rate varies with the time of use of the precursor container (bubbler). Consequently the quantity of $InMe_3$ supplied to the reaction zone is not constant.[64] Only recently have devices and special procedures been suggested and adopted in order to overcome such difficulties.[65] Originally the liquid $InEt_3$ was preferred to the solid $InMe_3$ as a precursor for InP epitaxial growth particularly at reduced pressures, but currently the improved growth conditions (especially purity and reactor design) have refocused the interest toward $InMe_3$ or its volatile adducts at atmospheric pressure.[66] However, a compromise between trimethyl- and triethylindium has recently given rise to $InMe_2Et$ (dimethylethylindium) as a potential precursor with some advantages over both the individual compounds. Although good-quality InP and $In_xGa_{1-x}As$ materials[67-69] have been grown with $InMe_2Et$, doubt has been cast on the thermal stability of this compound as well as of some analogous heteroleptic Al derivatives that would compromise their use in MOCVD growth. In fact, ^1H NMR spectra of these compounds dissolved in benzene or toluene[70] show evolution of proton signals at variable temperature, which may be consistent with disproportionation equilibria of the type given in eq 32, where $n = 1$, M = In, and $n = 2$, M = Al.

$$3n[(CH_3)_2(C_2H_5)M] \rightleftarrows 2[(CH_3)_3M]_n + [(C_2H_5)_3M]_n \tag{32}$$

Similar disproportionation has been verified also with the corresponding diphos and NMe_3 adducts. If these characteristics are not limited to studies in solution but persisted also in the pure liquids, then the above compounds are not suitable precursors in MOCVD since they would result in mixtures of a range of compounds. From this mixture volatile species are preferentially depleted during the operation, making the control of the flowing precursors unreliable. In the extreme these precursors would be not better than or different from the separate $InMe_3$ and $InEt_3$.

Growth of Semiconductor Alloys. The importance of III–V alloy semiconductors is due to the fact that both energy gap and lattice parameters may be engineered by simple variation of the composition.[71] From the chemical point of view the main problem is to correlate the composition of the solid material with the gas-phase composition and growth conditions in general. Here the specific interactions between the different precursors in the gaseous mixture may affect the characteristics of the growth process and hence the quality of epitaxial materials. The $Al_xGa_{1-x}As$ system grown from $AlMe_3$, $GaMe_3$, and AsH_3 and, in particular, the amount of Al incorporated have been studied by PL (photoluminescence), ERD (elastic recoil detection), and ICPAES (inductively coupled plasma atomic emission spectroscopy).[72] It has been shown that x_s (x in $Al_xGa_{1-x}As$) and x_g ($x_g = [AlMe_3]/\{[AlMe_3] + [GaMe_3]\}$, i.e., the composition of the organometallic gas phase) are interrelated according to the expression $x_s = x_g[1 + (\alpha - 1)x_g]$ derived from a fit to the experimental data. α is a variable that increases with increasing temperature, and so the Al fraction, in the solid phase at a given x_g, increases with T_G. The enrichment in Al of $Al_xGa_{1-x}As$ at high temperature has been rationalized in terms of the stronger Al–As bond with respect to the Ga–As bond and the faster desorption of Ga from the growing surface as compared to Al. Apparent discrepancies with the data of other authors[4] have been ascribed to differences in the adopted growth conditions (temperature, concentration, and velocity profiles). The same Al incorporation trend was found also with the $AlMe_3/GaMe_3/AsEt_3$ system.[73] $In_xGa_{1-x}P$ was grown from $InEt_3$, $GaEt_3$, and PH_3 under vacuum (without any carrier gas).[74,75] The growth rate decreased with increasing growth temperature in the range 500–700 °C probably due to the following effects: (a) the premature decomposition of metalorganic precursors increasing with increasing temperature; (b) the desorption of species involved in the growth is higher at higher temperature.

The variation of the Ga fraction in the solid with the $[GaEt_3]/\{[GaEt_3] + [InEt_3]\}$ ratio deviated from linearity and showed more effective incorporation of Ga than In in the layer. Here the cause was identified as the formation of the adduct between PH_3 and $InEt_3$; such adducts are well-known[3] to undergo premature reaction with ethane elimination and consequently to lower the concentration of $InEt_3$ contributing to the $In_xGa_{1-x}P$ growth. $GaEt_3$ and PH_3 may well form analogous adducts, which, however, do not suffer similar depleting reactions under the adopted growth conditions. On the contrary, In is incorporated in $In_xGa_{1-x}As$ more efficiently than Ga when both In and Ga were supplied from their adducts $InMe_3{\cdot}PEt_3$ and $GaMe_3{\cdot}PEt_3$),[39g,76] and this has been justified in terms of the lower metal–C bond dissociation energy of In–CH_3 (205–218 kJ mol^{-1}) than Ga–CH_3 (259–272 kJ mol^{-1}), in addition to a concomitant enhanced resistance of the In adduct to PH_3-promoted parasitic reactions. In-organometallic compounds undergo such parasitic reactions not only with PH_3 but also with AsH_3, since it has been recently reported that in $In_xGa_{1-x}As$ growth[77,78] interaction between $InEt_3$ and AsH_3 following the equilibrium

$$In(C_2H_5)_3 + AsH_3 \rightleftarrows [In(C_2H_5)_3AsH_3] \tag{33}$$

may occur for which a constant of 30 $Torr^{-1}$ has been determined. In other cases such as $GaAs_xP_{1-x}$[79] it is more difficult to study the compositional variations and dependences because uncontrollable factors (different pyrolysis temperatures of PH_3 and AsH_3, reactions between pyrolysis products and their adsorption/desorption pro-

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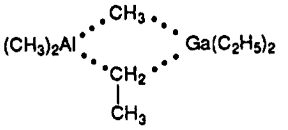
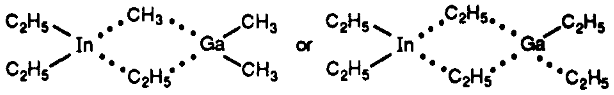
cesses, etc.) may be involved. The control of composition can be considered as the main problem not only with ternary alloys[80,81] but also with quaternary (e.g., $In_xGa_{1-x}P_yAs_{1-y}$, $Al_xGa_{1-x}P_yAs_{1-y}$, $Al_xIn_{1-x}P_yAs_{1-y}$, and $In_xGa_{1-x}Sb_yAs_{1-y}$) alloys.[82,83] The incorporation of the various elements has been treated taking into consideration thermodynamic and kinetic aspects of various hypothetical reactions involved in the growth process.[84] For instance, $InAs_xP_{1-x}$ composition[85] shows a peculiar linear dependence of x versus $[p(AsH_3)]/\{[p(AsH_3)] + [p(PH_3)]\}$ partial pressure ratio in that the As incorporation is very much higher than that of P ($x = 0.35$ occurs at a partial pressure ratio as low as 10^{-2} Torr). It has been suggested that both the difference in pyrolysis rate of AsH_3 and PH_3 and (more effectively) the higher sticking coefficient of As over P may be the cause. Sb-based alloys $GaSb_xP_{1-x}$ and $InSb_xP_{1-x}$[86] are attracting interest because they may be grown in a composition range where equilibrium thermodynamics predicts immiscibility gaps. The growth of such metastable alloys is a demonstration of the wide potential of kinetically driven MOCVD reactions well away from equilibrium. The precursors are generally $GaMe_3$, $InMe_3$, AsH_3, and PH_3 for Ga, In, As, and P, respectively, while $SbMe_3$ is used as Sb precursor. The Sb incorporation has been studied for InP_xSb_{1-x} and is far more efficient than P incorporation, although InP is more stable than InSb. This apparent contradiction is explained by considering that this growth is carried out at moderately low temperature where the decomposition of PH_3 (and then the P incorporation) is very much slower than that of $SbMe_3$[86] and by taking into account an enhanced evaporation rate of P with respect to Sb. Interaction between organometallic precursors in the gas phase prior to materials growth may affect the growth parameters. Thus in the growth of $Al_xGa_{1-x}As$[87] from $AlMe_3/GaEt_3$ and AsH_3, experimental growth rate, and solid-phase composition are found to fit calculated values (based on the values for AlAs and GaAs) only under the hypothesis that a fraction of $GaEt_3$ and $AlMe_3$ did not contribute to the formation of $Al_xGa_{1-x}As$. It was suggested that vapor-phase interaction between $(AlMe_3)_2$ and $GaEt_3$ could lead to a binuclear compound:

$$[Al(CH_3)_3]_2 + 2Ga(C_2H_5)_3 \rightarrow 2(CH_3)_3AlGa(C_2H_5)_3 \quad (34)$$

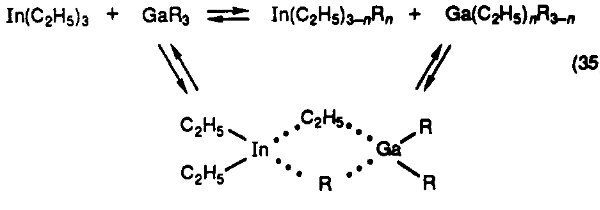
in which Al and Ga are bridged through electron deficient C-centered bonds:



Reaction 34 can be specific for the $AlMe_3$ and $GaEt_3$ system but not for the $AlMe_3$ and $GaMe_3$ system as in this case the growth rate of $Al_xGa_{1-x}As$ has been reported to be the sum of the single growth rate of AlAs and GaAs. The new binuclear Ga–Al compound was assumed to have a low decomposition rate, diffusion efficiency, and vapor pressure in order to explain the reduced growth rate of $Al_xGa_{1-x}As$. On this basis reaction 34 can be considered parasitic. Similar alkyl exchange and interaction between organometallic molecules in the vapor phase have been observed and investigated by mass spectrometry in the systems $InEt_3/GaMe_3$ and $InEt_3/GaEt_3$ used in the growth of $In_xGa_{1-x}As$ films from AsH_3.[88] It was found that both new mononuclear $InEt_{3-n}R_n$ and $GaEt_nR_{3-n}$ species such as



can form through the equilibria



(35)

where R = CH_3 or C_2H_5, $n < 3$.

Interaction of $InEt_3$ with GaR_3 significantly influences its reaction with AsH_3 (leading to In incorporation in $In_xGa_{1-x}As$) and is dependent on the nature of R. In fact in the presence of $GaEt_3$ the reaction of $InEt_3$ with AsH_3 is 40% suppressed with respect to $InEt_3$ alone and 60% in the presence of the same amount of $GaMe_3$. It was concluded that the interaction of $InEt_3$ with $GaMe_3$ was stronger than with $GaEt_3$ and that the reactivity of In toward AsH_3 was reduced because the In atoms in such binuclear compounds were tetracoordinated and then coordinatively saturated and reluctant to undergo further reaction.

It is evident that the studies on reaction mechanisms involved in MOCVD process confirm the previously formulated hypothesis that they are dependent on a large number of physical and chemical parameters and that growth conditions (V/III ratio, total pressure, temperature, gas-flow rate, etc.) may drastically modify the importance of particular reactions. A further complication is that semiconductor growth by MOCVD involves both homogeneous (gas phase) and heterogeneous (surfaces catalyzed) reactions, and it is usually difficult to separate the two components. Furthermore, it is very often hard to correlate the results of experiments in a consistent and correct way since full details are not always available. One particular problem arises from the difference between ex situ and in situ experimental data. CARS investigations,[89] a typical in situ diagnostic technique, show a much lower decomposition temperature for AsH_3 and PH_3 with respect to the corresponding value obtained by ex situ experiments (mainly mass spectrometry); importantly, addition of $GaMe_3$ to AsH_3 and $InMe_3$ to PH_3 does not affect the decomposition temperature of the hydrides.[89] Thus an interaction between organometals and hydrides (such as through formation of Lewis complexes) must be ruled out on the basis of these data.

Incorporation of Carbon and Its Compounds

The incorporation of carbon and its compounds as intrinsic impurities is one of the most debated problems in MOCVD. At first sight it appears quite surprising that

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pyrolysis of compounds containing such considerable numbers of alkyl groups leaves such small amounts of C-containing species (normally less than ppm level) in their decomposition products. This problem is closely connected with the decomposition mechanisms of organometallic precursors and their reactivity with organoarsines and -phosphines and the precise experimental conditions employed during MOCVD. Currently it is possible to prepare GaAs and InP with room-temperature carrier concentrations of the order of 10^{13} cm^{-3} (i.e., 1 ppb impurity level) by using several combinations of reagents and carefully controlled growth conditions.

Carbon Incorporation from Metal (Al, Ga, In) Precursors. It is assumed, sometimes erroneously and without justification, by many researchers that elemental carbon rather than carbonaceous species is the actual impurity.

Early studies[26] concerning GaAs have demonstrated that (a) C incorporation is lower with $GaEt_3$ than with $GaMe_3$; this was ascribed to the different mode of decomposition, which in the case of $GaMe_3$ produces unstable CH_3 radicals while $GaEt_3$ decomposes predominantly via β-elimination, giving stable species such as ethylene and metal hydride; (b) increasing $[AsH_3]/[GaMe_3]$ ratio reduced the carbon content and caused a p–n transition in the conductivity type of GaAs. In fact such an increase is believed to saturate group V sites, thus preventing the adsorption of carbon acceptor impurities; (c) C incorporation from the stable hydrocarbons produced in the reaction growth may be ruled out in view of the SIMS results. These have demonstrated that addition of ^{13}C-enriched gaseous hydrocarbons (CH_4, C_2H_2, C_2H_4, C_3H_6) to the reactor atmosphere had little, if any, influence on C content in GaAs thin films.

Systematic studies on the effect of the nature of R (CH_3, C_2H_5, t-C_4H_9)[55] have shown that ethyl and *tert*-butyl derivatives behave similarly, incorporating far less C than methyl derivatives; this is not unexpected as *tert*-butyl organometallic compounds decompose via β-elimination as do ethyl compounds. In general the same authors[55] concluded that C contamination is an effect of incomplete dissociation of reactants in the gas phase[90] so that the final decomposition of reactants involving high M–C bond strength takes place on the growing layer. This hypothesis is in line with parallel experiments under MOMBE conditions where gas-phase reactions are completely absent and C uptake from $GaMe_3$ is markedly higher than from $GaEt_3$. As a consequence, low thermal stability precursors should be recommended for reduced C incorporation into thin films, and concomitant parasitic reactions that occur before entering into hot reaction zone should be avoided. Pressure effects have been studied by Kimura et al.[28] in the growth of GaAs from $GaEt_3$ and AsH_3. In contrast to expectation,[27] they found increasing C in the layer with decreasing reactor pressure (<5 Torr). They also studied[91] the volatile reaction products during growth of GaAs from the $GaMe_3/AsH_3$ and $GaEt_3/AsH_3$ systems in the pressure range 0.05–100 Torr.

With the first system, CH_3 radicals and CH_4 were formed predominantly and moderate amount of methylarsines $Me_{3-n}AsH_n$ were detected. As the pressure was lowered, an increasing concentration of CH_3 radicals was observed relative to methylarsines. This observation together with previous findings[92] of a higher C content in GaAs grown at reduced pressure suggests that the higher content of CH_3 radicals is responsible for C incorporation. This has been confirmed by Williams et al. in recent studies.[42b] In the ethyl-based system, C_2H_4 probably was the main product of β-elimination above 20 Torr, but below this pressure the dominant species was C_2H_6 and below 1 Torr an increased amount of C_3H_8 appeared in the gas mixture; there a correlation of the C_2H_4 amount with that of C_2H_5 radicals suggested an origin for C_2H_4 different than β-elimination. Concomitantly at these low pressures, C incorporation in GaAs was detected also with the $GaEt_3/AsH_3$ system. Although the number of radical species formed at such low pressures was too high to be identified, experimental evidence indicated that under such conditions, complicated processes may lead to the formation of CH_3 or of monocarbon species such as CH_n (n = 1–3) from $C_2H_5^{\bullet}$ produced from the primary Ga–C_2H_5 homolytic dissociation, as schematized in eqs 36–38.

$$2C_2H_5^{\bullet} \rightarrow C_4H_{10} \tag{36}$$

$$C_2H_5^{\bullet} + C_4H_{10} \rightarrow C_2H_6 + C_4H_9^{\bullet} \tag{37}$$

$$C_4H_9^{\bullet} \rightarrow CH_3^{\bullet} + \text{hydrocarbons} \tag{38}$$

In such a way it was concluded that the C incorporation mechanism at low growth pressures is the same for $GaMe_3$- and $GaEt_3$-based systems, being due to the role of CH_3 radicals in both cases.[42b,91] Moreover, it must be mentioned that at low pressure, surface reactions, probably leading to C incorporation, gain importance over gas-phase reactions.[90]

Reed et al.[93] studied the combined effects of V/III ratio and growth temperature and found that the critical V/III ratio corresponding to p–n transition, i.e., to low C content, varied with growth temperature in the range 550–680 °C, showing a minimum around 600 °C. Below 600 °C the C incorporation was considered to depend on the number of undissociated $GaMe_3$ adsorbed on the substrate, where they subsequently react with adsorbed AsH_3, eliminating C atoms of CH_3 as CH_4. Since the dissociation of $GaMe_3$ increases with temperature (correspondingly the adsorption of $GaMe_3$ diminishes), the amount of AsH_3 necessary to dissociate $GaMe_3$ molecules (and then V/III) increases with decreasing temperature. Above 600 °C the thermal dissociation of AsH_3 becomes important, thus increasing the concentration of gaseous AsH_3 necessary to maintain a sufficient number of adsorbed AsH_3 molecules to break Ga–C bonds. These points are important in that they stress the different role of AsH_3 and $GaMe_3$ in C incorporation, even though they should be integrated by further considerations. In fact above 600 °C, where $Ga(CH_3)_3$ is completely dissociated in gas phase,[45,46,48] the decomposition of AsH_3 supplies As atoms which occupy completely the group V sites and greatly reduce the probability of C atoms coming from CH_3 radicals being incorporated. Both these suggestions are in general agreement with experimental observation reported elsewhere and especially with the role of Bu^tAsH_2 in GaAs growth[94] and Bu^tPH_2 in InP growth.[95] The C incorporation into InP shows aspects analogous to the C incorporation into GaAs, even though it has been generally reported that a smaller difference

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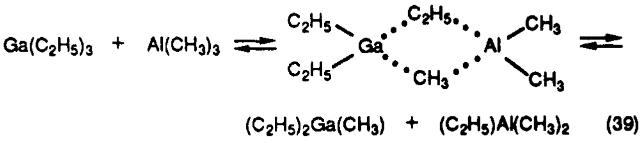
exists between $InMe_3$ and $InEt_3$ than between $GaMe_3$ and $GaEt_3$ systems.[13b] In any case the phenomenon is less relevant than with GaAs, and it has been observed that care must be taken in the identification of the C acceptor peak via low-temperature PL spectra.[25c] With the present status of experimental technique (reactor design, purity of precursors, growth conditions)[96-99] it is possible to obtain InP with extraordinarily high carrier mobility and low carrier concentration.[100] InP is n-type and only moderately contaminated by C even when grown at low V/III ratios or from the $InMe_3/P_4/H_2$ system,[101] i.e., under conditions in which the concentration of P–H species, which are recognized as very efficient scavengers for removing CH_3 radicals through formation of methane, should be relatively low or completely absent.

However, while in GaAs growth using $GaMe_3$ and AsH_3 increasing T_G increases C incorporation, the reverse effect is observed in InP growth[31,95] at least in a comparable temperature regime. This seems due to the higher decomposition temperature of PH_3 relative to that of AsH_3; therefore, the number of P atoms available for InP formation increases with T_G and then reduces the possibility of C occupying the P vacant sites.[31]

C in Alloys. Many studies have concerned AlGaAs, in which C may derive from both Ga and Al precursors. Kuech et al.[16] discussed C incorporation taking into account various parameters such as growth temperature, nature of precursors, gas-phase $[AsH_3]/\{[AlMe_3] + [GaMe_3]\}$ ratio and alloy composition (i.e., x in $Al_xGa_{1-x}As$), whereas Tamamura[102] studied the influence of substrate orientation. C increased with Al content, and the reason was ascribed to the higher Al–C bond strength compared to the Ga–C bond strength. Growth temperature caused a steady increase in C content in the range 600–700 °C, but toward 800 °C the rate of C incorporation was slower. Using $GaEt_3$ (instead of $GaMe_3$) and $AlMe_3$ was found by the same authors[26] to significantly reduce the C content. In this case reactions preliminary to the growth process can cause R-group transfer from Ga to Al and vice versa:[103]



(39)

so that the precursors really involved in the growth may be different from those initially withdrawn by the carrier gas from the metalorganic source. In particular, equilibria 39 may cause the formation of Me_2AlEt, which in turn can give Me_2AlH through β-elimination. It has been reported elsewhere that the $Me_2AlH/GaMe_3/AsH_3$ system produces $Al_xGa_{1-x}As$ with greatly reduced C content.[104]

C from Organophosphine and Organoarsine Sources. In principle, replacement of AsH_3 and PH_3 with their organo derivatives enhances the probability of C uptake by epitaxial layers.[105] This has been confirmed by results obtained with $As(CH_3)_3$ even under precracking[106] vacuum chemical epitaxy conditions or by varying the carrier gas (H_2 and He).[107] C incorporation from $As(^{13}CH_3)_3$ was elegantly studied by Lum et al.[24a,c] using dynamic SIMS. No C from intentionally added $^{13}CH_4$ gas was observed in GaAs grown from the $GaMe_3/AsH_3$ or $GaMe_3/AsMe_3$ systems. Similarly, GaAs (and AlGaAs) grown from the $GaMe_3/AsEt_3$ and $GaEt_3/AsEt_3$ (or $GaMe_3/AlMe_3/AsEt_3$) systems was contaminated by an excess of C[10,19,108-110] relative to the AsH_3-based process. Better results have been attained by adding AsH_3 to the $GaMe_3/AsEt_3$[111] system, but the original purpose of replacing the highly toxic AsH_3 in MOCVD is in this case defeated. PR_3 compounds have been demonstrated not to be useful in MOCVD[105] probably due to their exceedingly high decomposition temperatures. Thus partially substituted phosphines and arsines have been investigated since it was expected that P–H or As–H bonds were essential to completely remove alkyl radicals from organometallics.

C Incorporation and Decomposition Mechanism of Bu^tAsH_2 and Bu^tPH_2. Detailed mechanistic studies have been carried out on GaAs growth from $GaMe_3$ and Bu^tAsH_2[112-120] and $GaMe_3$[42b,110,121] and on GaP growth from $GaMe_3/Bu^tPH_2$[122] systems in which C contamination was found to be particularly low. Jensen et al.[113,114] used $GaMe_3$ and $GaEt_3$ with Bu^tAsH_2 for growing GaAs under reduced total pressure. No interaction with carrier gases was detected, but the deposition process was greatly influenced by gas-phase reactions and flow rate. The decomposition of the GaR_3/Bu^tAsH_2 ($R = CH_3, C_2H_5$) systems was different from that of Bu^tAsH_2 and GaR_3 alone, and the adduct $GaR_3{\cdot}AsBu^tH_2$ was suggested as responsible for parasitic reactions that led to the formation of a low-volatility, polymeric substance with elimination of hydrocarbons. Direct experimental evidence for such an adduct was found only for $GaMe_3$. Stringfellow et al.[115-119] investigated the $GaMe_3/Bu^tAsH_2$ system mainly with the

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Table II. Alternative P and As Precursors Used in MOCVD

compd	vap press., Torr (temp, °C)	group III precursor used in growth	mater	mobility at 77 K, cm^2 V^{-1} s^{-1}	ref
P					
PEt_2H		$InEt_3$	InP		126
PBu^tH_2	286 (23)	$InMe_3$	InP	3800^a	105
PBu^tH_2		$InMe_3$	InP		95
PBu^tH_2		$GaMe_3$	GaP		122
$AsMe_3$	238 (20)	$GaMe_3$	GaAs	7000	106
$AsEt_3$	15.5 (37)	$AlMe_3$–$GaMe_3$	GaAs, AlGaAs	15300	73
$AsEt_3$		$AlMe_3$–$GaMe_3$	GaAs, AlGaAs		111
$AsMe_2H$	176 (0)	$GaMe_3$	GaAs	5000^a	124
$AsEt_2H$	0.6 (18)	$GaMe_3$	GaAs	64600	127
$AsEtH_2$	94 (−16)	$GaMe_3$–$InMe_3$	GaInAs, GaAs	56000	128
$AsBu^tH_2$	96 (−10)	$AlMe_3$, $GaMe_3$	AlGaAs, GaAs	80000	129
$AsBu^tH_2$		$AlMe_3$, $GaMe_3$	AlGaAs, GaAs		130, 131
$AsBu^tH_2$		$InMe_3$	InAs		132
$As(C_6H_5)H_2$	1.7 (20)	$GaMe_3$	GaAs	38000	110
$As(C_6H_5)H_2$		$GaEt_3$	GaAs	20000	15b
$As(C_6H_5)H_2$		$InMe_3$	InAs		132a,b

^{a} At room temperature.

aim of exploring the cause of low C incorporation into GaAs. Two decomposition pathways were suggested for Bu^tAsH_2: (a) intramolecular coupling (or, formally, reductive elimination) (which is the dominant path):

$$As(t\text{-}C_4H_9)H_2 \rightarrow AsH + i\text{-}C_4H_{10} \qquad (40)$$

(b) β-elimination:

$$As(t\text{-}C_4H_9)H_2 \rightarrow AsH_3 + i\text{-}C_4H_8 \qquad (41)$$

whose importance increased with temperature. It has been later suggested that Bu^t radical chain reactions are involved in this mechanism.[119]

Furthermore Lum[123] detected As_2H_4 by mass spectrometry, implying that As_2H_4 species are also produced in the decomposition reactions. Both (a) and (b) have homogeneous and heterogeneous (on GaAs surfaces) contributions. As Bu^tAsH_2 decomposes at a lower temperature than $GaMe_3$, no substantial modifications are introduced by the presence of $GaMe_3$, but conversely Bu^tAsH_2 greatly decreases the decomposition temperature of $GaMe_3$ (by 75 °C). AsH_3 is believed to form adducts[45,51] with $GaMe_3$ in both homogeneous and heterogeneous phases. With Bu^tAsH_2 analogous adduct formation may occur only partially and only in the homogeneous phase since the following were experimentally observed:

(a) The C_5H_{12}/CH_4 ratio is far less than the 1/2 ratio stoichiometrically expected from the decomposition of the adduct:

$$Ga(CH_3)_3{\cdot}As(t\text{-}C_4H_9)H_2 \rightarrow GaAs + 2CH_4 + C_5H_{12} \qquad (42)$$

(b) The C_5H_{12} amount is insensitive to the substrate surface area.

Thus methyl groups are eliminated from partially decomposed organometallic Ga species mainly as CH_4 molecules, through reaction with AsH_x species produced by decomposition of Bu^tAsH_2 (see reactions 40 or 41):

$$Ga(CH_3)_x + AsH_x \rightarrow GaAs + xCH_4 \qquad (43)$$

AsH species generated by decomposition of Bu^tAsH_2 are adsorbed on growing GaAs very efficiently at As sites and thus contribute in two ways to avoid C incorporation, i.e., by both occupying positions on the substrate surface where C could be incorporated and eliminating CH_3 groups (possible source of C) through reaction 43. AsH_3 shows the same behavior, but it liberates AsH species at quite higher temperatures (normally at 600 °C) compared to Bu^tAsH_2, which pyrolyzes at about 300 °C; thus fewer As–H species are available to compete for As sites and prevent their occupation by CH_3 radicals (or their decomposition products, e.g., C). It has been reported that Bu^tPH_2 decomposes heterogeneously on a GaP surface[122] through the reaction chain

$$C_4H_9PH_2 \rightarrow C_4H_9^{\bullet} + PH_2^{\bullet} \qquad (44)$$

$$C_4H_9^{\bullet} + C_4H_9PH_2 \rightarrow C_4H_{10} + C_4H_9PH^{\bullet} \qquad (45)$$

$$C_4H_9PH^{\bullet} \rightarrow C_4H_9^{\bullet} + PH \qquad (46)$$

$$C_4H_9^{\bullet} \rightarrow C_4H_8 + H^{\bullet} \qquad (47)$$

This mechanism proposed by Stringfellow et al.[122] is different from one suggested by the same group for the analogous As precursor.[116] An explanation for this could be found in Lum's work, which has been carried out under different reaction conditions (particularly residence times of reactants inside the reactor) and, possibly, greater detection sensitivity.[123]

In the presence of $GaMe_3$, there is the possibility for decomposition fragments such as $Ga(CH_3)_x$ (x = 1–2, probably 1) to be adsorbed on GaP growing surface and there to react with PH_x (x = 1–2):

$$Ga(CH_3)_x + PH_x \rightarrow GaP + xCH_4 \qquad (48)$$

Moreover, adsorption of $Ga(CH_3)_x$ diminishes the number of sites on the surface available for adsorption of Bu^tPH_2 with the effect that the thermal decomposition of Bu^tPH_2 is slowed in the presence of $GaMe_3$, as experimentally observed. Even in this case the availability at low temperature, viz. 400 °C (i.e., much lower than that of PH_3, which decomposes at 600 °C), of PH_x type species very active in removing CH_3 radicals accounts for the low C content in GaP and InP grown with Bu^tPH_2. It is also important that GaAs, GaP, and InP growth from Bu^tAsH_2 and Bu^tPH_2 occurs at a low V/III ratio such as 3:1. Table II summarizes the available data for the growth of III–V materials from alternative As and P precursors. It appears that those compounds possessing EH_x (x = 1, 2; E = P, As) species lead to less C incorporation and consequently higher purity in epitaxial materials. With Me_3As,[106,107] Et_3As,[111] and Me_2AsH[124] poor results have been obtained

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for the growth of GaAs. For Et_3As this is a little surprising since this molecule presumably decomposes thermally via β-elimination[133] in the range 350–430 °C:

$$Et_3As \rightarrow Et_2AsH + C_2H_4 \qquad (49)$$

producing the same As precursors Et_2AsH, which gave good quality GaAs.[105] Optimization of growth conditions may still be necessary in this case. For Me_2AsH[134] high decomposition temperature and excessive production of CH_3 radicals (generally considered responsible for high C incorporation) may be the possible causes of unsatisfactory results.

From the considerable body of results described above the following aspects appear of general importance:

(a) C incorporation from organometallic precursors follows the trend Al > Ga > In. Therefore, it reflects the strength of M–C bond, confirming the hypothesis[90] that organometallic species are not completely decomposed before adsorption when they are adsorbed on the substrate surfaces.

(b) Comparing different organic groups bonded to the metal CH_3 causes more C incorporation than C_2H_5. But this observation is limited to homoleptic compounds; the use of heteroleptic compounds, although promising, is still too limited[104,134] and can lead to complications stemming from alkyl exchange reactions.

(c) High $[EH_3]/[MR_3]$ (E = As, P) ratio reduces C incorporation, but at low reactor pressure C incorporation increases. Concomitantly at these low reactor pressures an increase in the relative amount of CH_3 radicals is observed even when ethyl compounds are used.[91]

(d) Other important growth parameters (T_G, growth rate, gas velocity, etc.) may influence C incorporation, but our knowledge currently is still limited.

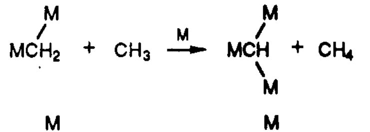
These considerations lead to the conclusion that C incorporation is a quite complicated phenomenon, possibly resulting from a series of different (elemental) processes occurring simultaneously whose importance varies according to growth conditions. In addition, the different C incorporation depending on the substrate orientation strongly indicates a specific interaction between orbitals of atoms on the growing surface and gaseous species impinging on the substrate itself. Certainly one of the dominant processes leading to C incorporation is the interaction between CH_3 radicals and other species resulting from the pyrolysis of organometallic compounds. One such species not hitherto discussed in any detail is MCH_3, i.e., monomethyl metal derivatives, whose formation as a gas-phase species under MOCVD conditions is not inconsistent with experimental results.[49,120] $AlCH_3$ in fact has been observed in UV excimer laser photolysis of $(AlMe_3)_2$,[135] and $GaCH_3$[136] is believed to be rather stable taking into account the values of the bond dissociation energies[137] of $Ga(CH_3)_3$, while $InCH_3$ should be even more stable in view of the increasing stability of monovalent species with atomic number among the group 13 elements. MCH_3 species have been often hypothesized or postulated[138–140] to be involved in the crucial step of formation of ME materials (E = As, P) from $M(CH_3)_3$ and EH_3. Thus in presence both of CH_3 radicals and $E–H_x$ species, MCH_3 can decay through alternative routes:

(a) $MCH_3 + EH \rightarrow ME + CH_4$ (e.g., for x =1) (50)

(b)

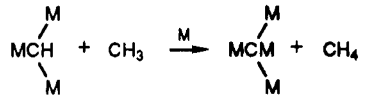
$$MCH_3 + CH_3 \xrightarrow{M} \overset{M}{\overset{/}{MCH_2}} + CH_4$$

(51)



$$\overset{M}{\overset{/}{MCH_2}} + CH_3 \xrightarrow{M} \underset{\underset{M}{\backslash}}{\overset{M}{\overset{/}{MCH}}} + CH_4$$

(52)



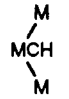
$$\underset{\underset{M}{\backslash}}{\overset{M}{\overset{/}{MCH}}} + CH_3 \xrightarrow{M} \underset{\underset{M}{\backslash}}{\overset{M}{\overset{/}{MCM}}} + CH_4$$

(53)

Route (a) gives the expected material, while route (b) leads stepwise to C incorporation, which on this basis may be considered an intermolecular H abstraction from MCH_3 fragments by CH_3 radicals. H abstraction from MCH_3 organometallic species by CH_3 radicals has been already proposed in MOCVD mechanistic studies[48,141,142] and may be inferred by the fact that even in D_2 ambient a significant amount of CH_4 is formed[45,48] and by the observation[89] that decomposition of $GaMe_3$, even in N_2 ambient, gives an amount of CH_4 (and little C_2H_6) corresponding only to two methyl groups, leaving the third one attached to Ga.[75] Indeed the balance of H atoms requires stripping of at least one H atom from this last CH_3 group:

$$CH_3^{\bullet} + GaCH_3 \rightarrow CH_4 + GaCH_2 \qquad (54)$$

to explain the formation of CH_4 molecules. It is reasonable to hypothesize that bonding between M and C strengthens with concomitant weakening of the C–H bond in the series M–CH_3, M═CH_2 (or M–CH_2–M), and M═CH, or



$$\underset{\underset{M}{\backslash}}{\overset{M}{\overset{/}{MCH}}}$$

as was found for Al.[143,144] In addition, species containing methylene-metal M═CH_2 moiety, in principle, can be formed also via an α-elimination process:

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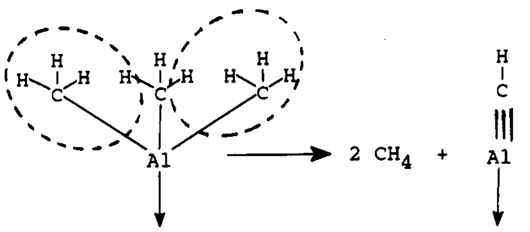
$$M\text{-}CH_3 \rightarrow HM{=}CH_2 \qquad (55)$$

which has been invoked for explaining CH_3I decomposition on an Al(111) surface.[145,146] Moreover, $Ti{=}CH_2$ species have been recently proposed by Girolami et al.[147] as intermediates in TiC preparation via MOCVD from Ti(neopentyl)$_4$. Finally pyrolysis of $AlMe_3$ on a Si(100) surface has been studied[148] by using temperature-programmed desorption, XPS, and EELS techniques. It has been proposed that the observed significant deposit of C (more than one-third of C present in $AlMe_3$) originated from an intramolecular H abstraction formally schematized by the sequence



(56)

which differs from that suggested in reactions 51–53 only by its intramolecular character. Analogous considerations have been proposed for the $GaMe_3$ decomposition on Si(100) studied by a similar method.[149]

C as Dopant. The systematic studies carried out on C incorporation have led to an understanding of certain mechanistic aspects and have initiated recent attempts to control the C content in III–V materials demonstrating the feasibility of using C as a p dopant. This is very advantageous in view of the better properties of C (low volatility, low diffusion) with respect to the other common p dopants (Zn and Mg). Thus GaAs with C levels[150] in the range 10^{16}–10^{19} cm^{-3} has been intentionally obtained by a choice of the proper composition of a mixture of AsH_3 and Me_3As as As precursors and a suitable T_G or by adding CCl_4 to H_2 carrier gas[151] while $Al_xGa_{1-x}As$ ($x = 0.75$) layers in C p-doped quantum well lasers[152]($n = 9 \times 10^{17}$ cm^{-3}) has been grown from $AlMe_3$, $GaMe_3$, and AsH_3 at $T_G = 825$ °C.

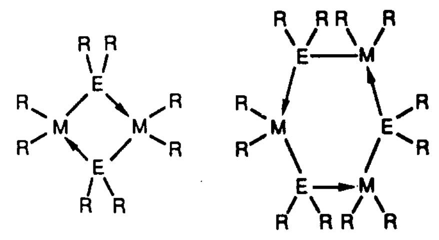
Alternative Precursors

Thus far the classical group III organometallic and group V hydride precursors have provided a basic contribution to the development of MOCVD at the laboratory scale. However, to fully exploit the potential of this technique, it is necessary to overcome the problems that hinder its application on a production level, i.e., the difficulties inherent in the manipulation of air- and moisture-sensitive organometallic compounds and of extremely toxic arsine and phosphine gases that must be used in high-pressure cylinders. It is likely that the above problems will be solved by taking advantage of the improved knowledge of the purity effects and understanding of the reaction mechanisms as well as the wide range of possibilities offered by organometallic and coordination chemistry.

Use of Adducts. A few years ago the use of Lewis complexes in MOCVD was successfully proposed. Coates et al.[153a] showed that combination of trimethyl or -ethyl derivatives of Al, Ga, and In with Lewis bases of the type R_3As and R_3P gave complexes that due to the saturation of the coordination of the central metal were more resistant to hydrolytic decomposition and oxygen attack than the metal alkyls.

Moreover, since they contained As or P in addition to the metals, it was expected that these molecules could act as single precursors and thus avoid the need for AsH_3 and PH_3 as separate precursors.[153b] Although such adducts have been prepared, they have not replaced AsH_3 and PH_3. In the case of the P-based materials, the problem may be that PR_3 is too resistant to thermolysis at temperatures where MR_3 decomposes. In any case, epitaxial deposition has been rarely observed[105] in such conditions.

Use of Compounds Containing Direct M–E Bonds. The use of compounds containing a direct covalent bond between M and E $[R_{3-n}M(ER_2)_n]_m$ (M = Al, Ga, In; E = N, P, As, Sb; n = 1, 2; m = 1, 2, 3][154,155] offers a wide range of possibilities[9] since through a proper choice of R groups and n the molecularity of the compounds (i.e., the value of m) and hence their volatility[159] and resistance to oxygen and moisture can be conveniently controlled. Unfortunately the lone pair of electrons on the E atoms generally does not contribute to a partial double bond in the molecules such as (n = 1) $R_2M{=}ER_2$, in which case monomeric molecule formation would be favored. Instead the lone pair is shared with M atoms of another moiety to form dimeric and trimeric species of the type



through bridges in which the two M–E bonds have the same length and are indistinguishable.[9] As a consequence, these compounds generally show a reduced volatility, and their use in MOCVD has been limited thus far. However, at present they are finding wider and wider application in MOMBE, CBE, or low-pressure MOVPE,[9] where the volatility conditions are less stringent.[160]

Use of Intramolecularly Saturated Compounds. As previously mentioned, the reactivity of Al, Ga, and In toward H_2O and O_2 and consequently the pyrophoricity hazards are due to the coordinative unsaturation of the

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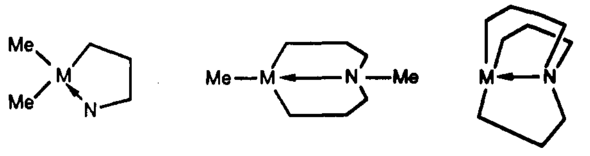
central metal in R_3M compounds. Introduction of donor atoms[125,134,157,161] into the organic group R at a convenient position results in the formation of intramolecularly stabilized compounds of the type



R = C_2H_5 or CH_3 M = Al, Ga, In

which have been easily prepared replacing Cl atoms in Me_2MCl, $MeMCl_2$, and MCl_3 with *N*-alkyl groups. They are liquids or low-melting solids moderately resistant to oxygen and water, nonpyrophoric, and sufficiently volatile to be used in MOCVD growth.[157] Electrical properties of materials prepared by using these alternative N-containing precursors are continuously improving[134] probably as a consequence of more efficient purification methods. It is therefore reasonable to expect in the near future that such electrical and morphological properties will be comparable with those obtained by using the classical precursors. It is significant that materials obtained from these precursors do not contain nitrogen which would be expected to compete with As and P in the formation of bonds to M in view of the fact that the enthalpy of the M–N bonds is higher than those of M–As and M–P bonds. Moreover, the PL spectra reported for InP[157] grown from $Me_2In(CH_2)_3NMe_2$ and PH_3 indicated that the dominant residual acceptor impurity was Zn and not C.

Use of Other New Organo–In and –Al Compounds. $(Cp^{Me})In$ (indium η^5-methylcyclopentadienyl), a monovalent indium compound, exhibits chemicophysical properties (relatively high volatility at 20 °C, thermal stability in H_2 to high temperature, >500 °C) suitable for MOCVD.[158] It was used in combination with PH_3 (V:III ratio = 33) for the growth of InP, and the results are very promising at present with $\mu_{77} = 12250$ cm^2 V^{-1} s^{-1}, a C content lower than SIMS detection limits ($<2 \times 10^{17}$ atoms cm^{-3}), and no parasitic reactions observed. In this respect it may be observed that the η^5 mode of ligation of methylcyclopentadienyl tends to electronically saturate the central metal, and premature adduct formation and degradation are thus prevented. Moreover, thermal decomposition leads to stable hydrocarbon fragments (cyclopentadiene isomers, benzene) without leaving residual C. Me_2AlNMe_2 and $Me_3Al{\cdot}NMe_3$[162] have been recently employed in growth of $Al_xGa_{1-x}As$, following the suggestion that their H_2O and O_2 enhanced stability could lead to better material than with $AlMe_3$. However due to their limited vapor pressure only $Al_xGa_{1-x}As$ with $x < 0.13$ was obtained, and the C content was at the same level as with $AlMe_3$. Moreover, in contrast to $AlMe_3$, which may contribute to the elimination of O_2 or H_2O traces present in the reactor, these are rather inert to O_2 and H_2O and then do not eliminate their deleterious effects. Recently Me_2AlBu^t[156] has been used in the growth of $Al_xGa_{1-x}As$ demonstrating a good suitability as MOCVD precursor at low growth temperature notwithstanding the ligand-exchange reaction observed in toluene solution.

Use of Organo–P and –As Compounds. The use of less toxic alternative sources to AsH_3 and PH_3 stimulated interest toward organic As and P derivatives as mentioned before. Trisalkyls (methyl, ethyl) have been demonstrated as not entirely suitable precursors[105] mainly because they pyrolyze at exceedingly high temperatures (higher than AsH_3 and PH_3; e.g., PR_3 failed to give epitaxial material) and C contamination caused by trisalkylarsines was greater than with AsH_3. Compounds containing at least one As–H or P–H bond have proven more promising.[120] Table II reports several of these new compounds with the results obtained in the growth of III–V epitaxial materials. Good morphological and electrical properties of the materials obtained indicate that the replacement of AsH_3 and PH_3 with less toxic and more easily to be handled precursors may be expected in the near future.

Future Directions

The bulk of results reported in the previous sections certainly do not include all recently published data on the role that chemistry plays in MOCVD processes. It is hoped that they give a general picture of the enormous progress that has been made recently in our understanding of the fundamental processes that lead up to the preparation of thin-film III–V semiconductors. In our opinion, a knowledge of the chemical aspects of purity, reaction mechanisms, and alternative precursors will be of crucial importance in the near future and will allow the MOCVD technique to improve and develop into new materials systems.

Purity. In this area the development of analytical methods and equipment for the assessment of impurities both in precursors and in deposited materials is one important objective. Even though ICP and SIMS are presently very sensitive techniques, they must be improved to compare with levels of detection presently achievable on deposited layers by electrical measurements and photoluminescence spectroscopy. Progress in synthetic methods has improved the purity of precursors, but better techniques and greater efficiency are required in purification methods. In addition to improvement of classical physical separation techniques (distillation and sublimation), adduct-based systems offer considerable promise for further progress.

Reaction Mechanisms. The results obtained in this field have a fundamental impact on many aspects of MOCVD technology. Recently, knowledge of parasitic reactions have stimulated appropriate modifications of reactor system design. Studies of C incorporation are now allowing C to be used as a reliable p-type dopant in GaAs. In addition the peculiar features of atmospheric pressure and low-pressure regimes are now becoming clearly understood, and this will lead not only to a choice between APMOCVD (atmospheric pressure MOCVD) and LPMOCVD (low-pressure MOCVD) but also further development of ALE, MOMBE, and CBE. Although thermal decomposition of organoaluminum compounds has been extensively investigated,[163] no specific mechanistic studies of AlAs or AlP formation analogous to those on GaAs or InP growth have been carried out (e.g., Jensen[44b] and Stringfellow[45,49] under D_2 atmosphere). There is also much to do in adopting the most suitable analytical techniques in order to correctly detect the species involved in the growth process[42] at the substrate surfaces. Sophisticated instrumental methods for in situ studies (which are expected to give more reliable information than ex situ experiments) should be tested more extensively,[164,165] and

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Table III. Some Alternative Organometallic Precursors Used Recently in MOCVD

compd	phys properties (partial press./mpt/bpt)	mater prepared	mobility, $cm^2 V^{-1} s^{-1}$	ref
$[R_2M-EBu^t{}_2]_2$		GaAs, InP		155
R = Me, M = Ga, E = As				
R = Me, M = Al, Ga, In, E = As, P				
$[Me_2AlBu^t]$	$P_{29°C}$ = 0.17 Torr	$Al_xGa_{1-x}As$ (x = 0.1–0.3)		156
$Me_2In(CH_2)_3NMe_2$	mp = 12 °C, bp_{500Pa} = 67 °C	InP	49 000	157
$(CH_2)_5Ga(CH_2)_3NMe_2$		GaAs	51 000	134a
$(CH_2)_5Ga(CH_2)_3NMe_2 + AlEt_3$		AlGaAs	8 000	134a
$(CH_2)_5Ga(CH_2)_3NMe_2 + (CH_2)_5Al(CH_2)_3NMe_2$		$Al_{0.28}Ga_{0.72}$	15 000	134a
$GaEt_3 + (CH_2)_5Al(CH_2)_3NMe_2$		$Al_{0.19}Ga_{0.81}As$	6 900	134a
$InMe_2Et$	$P_{17°C}$ = 1.12 Torr	Ga In As	45 000	68
$InMe_2Et$		InP	109 000	68
$InCp^{Me}$	$P_{20°C}$ = 0.4 Torr	InP	12 250	158

reasons for discrepancies between in situ and ex situ experiments clarified. A diagnostic level similar to that in MBE process is required for both surface and gas-phase reactivity. For instance, spectroscopic techniques such as FTIR, optical second harmonic generation (SHG), and reflectance-difference spectroscopy (RDS) need further development for the determination of surface species participating in the growth process. Lessons learned from heterogeneous catalysis could profitably be applied to semiconductor studies.[166]

Alternative Precursors. Solution of the two most difficult problems in MOCVD (sensitivity of MR_3 to O_2 and H_2O and toxicity of AsH_3 and PH_3) appears close in that some RPH_2 and $RAsH_2$ derivatives (expecially for R = Bu^t) are able to replace PH_3 and AsH_3,[167] while new organometallic precursors (e.g., the so called "internally coordinated" compounds) are generally more resistant to O_2 and H_2O[161] (Table III).

Moreover, the fact that N is not incorporated into $Al_xGa_{1-x}As$ and InP when N-based precursors are used[157,162] suggests the use of compounds such as $R_{3-n}M(NR_2)_n$ (n = 1–3),[168] which are also less sensitive to O_2 and H_2O than classical R_3M precursors. New clean synthetic reactions based on Me_3Si group transfer with prospects of leading to III–V semiconductors at low temperatures are under investigation, and promising results have been recently reported by several authors on the preparation of InP, InAs, and GaAs.[169–172]

Finally, it is reasonable to expect that technology will drive toward the preparation of new III–V materials, i.e., new alloys with new properties. At present, interest is directed toward alloys with composition corresponding to immiscibility ranges, i.e., metastable alloys, and toward N-based materials.[173] In fact N-based materials exhibit inviting optical and electronic properties[174] and offer the possibility of fabricating alloys ($In_xGa_{1-x}N$, $In_xAl_{1-x}N$, $Al_xGa_{1-x}N$) with a range of energy gaps from 2 to 6 eV (E_g are 2, 3.5, and 6 eV for InN, GaN, and AlN, respectively). A few examples[175–178] of epitaxial growth have demonstrated the feasibility but also the difficulties that will be met especially for InN.[179] This material readily decomposes themally, and MOCVD, with its relatively low temperature growth, is one of the most suitable techniques that can be employed in its preparation.[180] At present it is limited by the paucity of organometallic precursors bearing N ligands, which upon thermal decomposition give MN as the final product. The recent successful preparation of AlN[181,182] will no doubt encourage attempts also in the growth of similar Ga- and In-based materials.

Conclusion

Intense activity in MOCVD is now producing an enormous amount of experimental data which, although often difficult to explain and contradictory, testify to the inherent complexity of the chemical processes involved. In such a situation the active participation of chemists from a variety of backgrounds is crucial to further development of the field. It is quite amazing that barely understood complex chemical reactions are currently producing high-quality materials with designed electrical and optical properties for industry. Further detailed understanding can only improve the situation.

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List of Abbreviations

MOCVD	metal organic chemical vapor deposition
MOVPE	metal organic vapor-phase epitaxy
MBE	molecular beam epitaxy
MOMBE	metal organic molecular beam epitaxy
ALE	atomic layer epitaxy

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Chem. Mater. 1991, *3*, 242-252

CBE	chemical beam epitaxy
R	alkyl group
Me	CH_3, methyl
Et	CH_2CH_3, ethyl
Bu^i	$CH(CH_3)(C_2H_5)$, isobutyl
Bu^t	$C(CH_3)_3$, *tert*-butyl
Neop	$CH_2C(CH_3)_3$, neopentyl
Cp^{Me}	$C_5H_4CH_3$, methylcyclopentadienyl
Ph	C_6H_5, phenyl
ERD	elastic recoil detection
ICPAES	inductively coupled plasma atomic emission spectroscopy
ICP	inductively coupled plasma
μ	electron mobility
SIMS	secondary ion mass spectrometry
N_D	number of donors cm^{-3}
N_A	number of acceptors cm^{-3}
PL	photoluminescence
CARS	coherent anti-Stokes Raman Spectroscopy
TMG	trimethylgallium, $Ga(CH_3)_3$
TEG	triethylgallium, $Ga(C_2H_5)_3$
TMA	trimethylaluminum, $Al(CH_3)_3$
TEA	triethylaluminum, $Al(C_2H_5)_3$
TMIn	trimethylindium, $In(CH_3)_3$
TEIn	triethylindium, $In(C_2H_5)_3$
T_G	temperature at which the material is grown
T_{50}	temperature corresponding to 50% decomposition of a particular precursor
XPS	X-ray photoelectron spectroscopy
SHG	second harmonic generation
EELS	electron energy loss spectroscopy
RDS	reflectance difference spectroscopy

α'-Sialon Ceramics: A Review

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α'-Sialons are a relatively new class of ceramics that promise excellent high-temperature mechanical properties and thermal shock resistance. This report reviews the current status of research on α'-sialons, including phase equilibria, formation, sintering, and properties.

Introduction

Silicon nitride and oxynitride ceramics have attracted interest for high-temperature engineering applications for nearly 40 years,[1-4] because of their excellent properties: (1) high strength; (2) wear resistance; (3) high decomposition temperature; (4) oxidation resistance; (5) thermal shock resistance; (6) low coefficient of friction; (7) resistance to corrosive environments.

The formation of silicon nitride (Si_3N_4) was reported about a century ago.[5-7] However, fully dense silicon nitride ceramics were obtained by hot-pressing only in 1961.[8] Huge efforts on the investigation of silicon nitride ceramics have been made in the past three decades, resulting in a tremendous progress.[9,10]

Good mechanical properties of silicon nitride ceramics are achieved only in fully dense materials. But as a highly covalent compound, silicon nitride exhibits a very low diffusivity[11-15] and therefore cannot be densified by using conventional solid-state sintering methods. Instead densification has been achieved by means of liquid-phase sintering. To this end sintering additives are used, for instance, metal oxides, such as MgO, Al_2O_3, Y_2O_3, and Ln_2O_3,[16-23] but some metals, carbides, and nitrides have been tried as well.[24-27] At high temperatures these additives react with both the oxygen-rich layer, which is always present at the surface of each silicon nitride particle,[28,29] and a small fraction of silicon nitride to form an

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