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Mechanisms in Metal-Organic Chemical Vapour Deposition [and Discussion]

J. O. Williams, R. D. Hoare, O. Khan, M. J. Parrott, D. J. Cole-Hamilton and R. J. M. Griffiths

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Mechanisms in metal-organic chemical vapour deposition

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The current status of our understanding of mechanistic details of GaAs growth by metal-organic chemical vapour deposition from various starting materials is reviewed. Despite a high level of recent activity in the study of precursor decomposition and reactivity there are still considerable gaps in our knowledge; for example, a clear differentiation between homogeneous (gas phase) and heterogenous (surface-controlled) processes is not yet possible.

The decomposition of trimethylgallium in dihydrogen as carrier gas and the concomitant production of methane may occur by means of a radical process where hydrogen is abstracted by methyl radicals from the trimethylgallium rather than from the carrier gas. Triethylgallium on the other hand also offers the possibility of β-elimination as a facile pathway and this is reflected in the ratio ethene: ethane (3:1). In the presence of arsine there is a more facile pathway for hydrogen abstraction by alkyl radicals, giving rise in the case of triethylgallium and arsine to more ethane than ethene and in the case of trimethylgallium with arsine there is a difference in the reactivity to that found in studies of its decomposition in dihydrogen alone.

Several workers have therefore deduced the participation of an intermediate adduct under growth conditions because arsine and trimethylgallium lower each others' decomposition temperature significantly. However, it should be remembered that arsine is almost certainly a better donor of hydrogen to methyl radicals than is dihydrogen.

Phenylarsine has been found to be a potentially useful alternative precursor to arsine for the preparation of epitaxial GaAs. Thin films with excellent electrical and morphological characteristics have been prepared. Phenylarsine decomposes in dihydrogen to yield benzene and arsine and in the presence of trimethylgallium and triethylgallium mechanisms similar to those found with trimethylgallium and triethylgallium with arsine are suggested. These appear not to involve the dihydrogen carrier gas.

Introduction

Metal-organic chemical vapour deposition (MOCVD) has become an important growth technique for a wide range of semiconductor materials since its discovery in 1968 (Manasevit 1968). The technique can be used to grow epitaxial layers of (group II)–(group VI) and (group III)–(group V) materials suitable for device applications (Dapkus 1984; Razeghi *et al.* 1984; Hersee *et al.* 1984; Thrush *et al.* 1987). Furthermore, multiple quantum wells (MQW) and strained-layer superlattice structures (SLS) may be prepared for selected systems with excellent control of layer thickness, interface widths, dopant incorporation and chemical composition (Leys *et al.* 1984; Roberts 1987; Stringfellow 1988*a*, *b*; Dupuis *et al.* 1984).

It is perhaps surprising that many of these technological innovations have been achieved without a detailed scientific understanding of the fundamental reactions that take place during the MOCVD process. However, the very nature of the thermal processes, involving reactions

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between pyrophoric group II and group III metal alkyl precursors together with hazardous group VI or group V hydrides in an over pressure of dihydrogen makes direct recording of kinetic and mechanistic data and product analysis difficult and it is only recently that such work has been attempted (Larsen *et al.* 1987; Luckerath *et al.* 1987; Williams *et al.* 1989). Previously, the little mechanistic information available had been deduced largely from studies of growth rates against substrate temperature, gas phase ratios of reactants, flow rates, total reactor pressure, etc. (see, for example, Williams 1986).

It is now recognized that both gas phase and surface reactions may well be important in MOCVD. In this respect it is different to molecular beam epitaxy (MBE) where only surface processes control crystal growth (Davies & Andrews 1988). Consequently, to fully understand the mechanistic and kinetic details of MOCVD the active species present in the gas phase *and* at the substrate surface must be identified and the relation between them clarified. It is also accepted that the controlling reactions may well be different in nature and or extent under different pressure régimes within the reactor (typically 10^3–10^5 Pa). Comprehensive studies are, therefore, required under widely varying conditions with a range of analytical techniques.

In recent years there has been increasing interest in replacing group V hydride reactants with less hazardous and more efficient sources. The reagents presently used are highly toxic and are stored in large quantities at high pressures. The MOCVD growth process is inefficient, consuming considerable quantities of the group V reagent. For example, V:III molar ratios of up to 100 are common in the preparation of good quality GaAs (see, for example, Hunt & Williams 1987). In addition, the different pyrolysis behaviour of a pair of hydrides, e.g. AsH_3–PH_3 and H_2S–H_2Se introduce complications when preparing ternary and quaternary materials (Williams 1987; Stringfellow 1988). Often, the alternative precursors are chemically more complex than the hydrides presently used and it is necessary to investigate their decompositions and reactivities under MOCVD conditions to allow rapid optimization of growth parameters. Such studies considered in a wider context can also prove useful in clarifying simpler reactions and aiding the design of further alternative precursors for different uses, e.g. photo-assisted MOCVD and selected-area growth.

In this paper the current status of investigations into the mechanistic details of processes relevant to MOCVD is reviewed. The contributions of the UMIST Solid State Chemistry Group are highlighted and placed in the context of our present understanding of key steps in MOCVD.

To date, few experiments have attempted to identify directly surface species and reactions, hence emphasis will be given to gas phase studies involving both *ex situ* and *in situ* monitoring of reactions relevant to the growth of III–V materials. Product analysis using several experimental techniques has also played an important role and will be discussed but despite this recent progress we still have only a primitive knowledge of the key reaction pathways.

Nature of MOCVD

A consideration of some of the possible MOCVD reactions relevant to GaAs growth assists in identifying the problems to be resolved by mechanistic studies. Reactions that represent the growth of GaAs using trimethyl- and triethylgallium (TMGa, TEGa) and arsine (AsH_3) may be written as follows.

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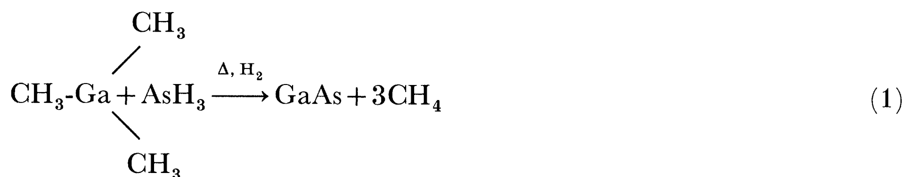
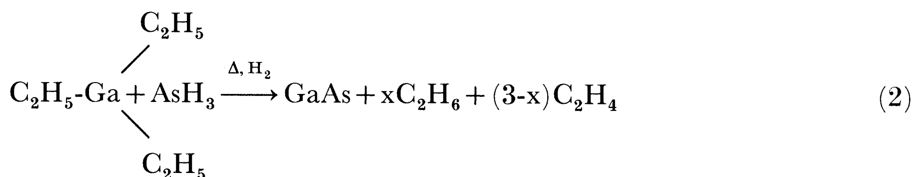


$$CH_3\text{-}Ga(CH_3)_2 + AsH_3 \xrightarrow{\Delta,\,H_2} GaAs + 3CH_4 \quad (1)$$



$$C_2H_5\text{-}Ga(C_2H_5)_2 + AsH_3 \xrightarrow{\Delta,\,H_2} GaAs + xC_2H_6 + (3\text{-}x)C_2H_4 \quad (2)$$

The processes are carried out thermally, usually at atmospheric pressure (reaction (1)) and reduced pressures (reaction (2)) in horizontal or vertical geometry reactors over single-crystalline GaAs substrates (for details see Hunt & Williams 1987; Gerrard *et al.* 1988). The GaAs growth rate is found to be (i) dependent linearly on the concentration of group III precursor, (ii) independent of the group V precursor concentration (but it is present in large excess), (iii) dependent on the total gas flow and pressure in the reactor, (iv) essentially independent of substrate temperature over a wide range including that which gives homo-epitaxial GaAs with optimum morphological, electrical and optical characteristics.

These data are usually interpreted in terms of a growth process that is limited by mass transfer, i.e. diffusion through a boundary layer adjacent to the hot substrate surface, and dependent only on the arrival rate of gallium-containing species at the growth surface. The implication is that catalysis by the surface and incorporation of atoms into the growing layer are relatively fast steps in the overall process. A recent theoretical model for GaAs growth is not inconsistent with this general picture (Tirtowidjojo & Pollard 1988).

Large V:III ratios are used, particularly in reaction (1), to reduce the concentration of carbon impurities that generally occupy As sites, thereby acting as p-type impurities. It has been shown (Kuech & Veuhoff 1984) that using reaction (2) the problem of carbon incorporation is less severe.

Certain questions arise from these two reaction schemes as written; for example: (i) Does the hydrogen required to form methane in reaction (1) come from dihydrogen or arsine and if so, is this a gas phase or a surface reaction? (ii) What is the ratio ethane:ethene in reaction (2) and is this dominated by gas phase or surface reactions? (iii) If surfaces are involved (catalysis), what is the nature of the chemisorbed state? (iv) What is the nature of the gas phase species?

In mechanistic studies carried out to date and which will be described later, attempts have been made to simplify the problems by investigating, for example, the pyrolysis of TMGa and TEGa separately in dihydrogen and dideuterium and in the presence of arsine in dihydrogen. In this way, some useful information has been obtained from product analysis.

The preparation of InP by routes similar to those represented by reactions (1) and (2) replacing Ga by In and As by P would be expected to follow similar lines because the behaviour of the respective precursors are also similar. However, it is unlikely that these schemes can be carried over to the preparation of AlAs, because the mode of decomposition of the aluminium precursor most often used, trimethylaluminium (TMAl) – a dimer in the solid, liquid and vapour phase up to *ca.* 260 °C – is likely to be very different from that of both TMGa and

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TMIn (Leys *et al.* 1984). The situation relating to the preparation of ternary materials such as $GaAs_{1-y}P_y$, $Al_{1-x}Ga_xAs$ and $Ga_{1-x}In_xAs$ is likely to be even more complex and little mechanistic work has been done on these systems. We therefore restrict our attention in this review to studies relevant to GaAs prepared from different precursors.

Preparation of GaAs

Pyrolysis of TMGa *and* TEGa

Cracking patterns for TMGa and TEGa at molar concentrations similar to those used in crystal growth of GaAs have been obtained by mass spectrometric measurements made on the effluent of an MOCVD reactor and may be compared with corresponding Fourier-transformed infrared (FTIR) spectra and gas chromatography data (Williams 1989). FTIR spectra obtained from the exhaust gases of completely pyrolysed TMGa and TEGa at 800 °C and 700 °C are shown in figure 1 *a*, *b*. In the case of TMGa, bands at 1306 and 3018 cm^{-1} due to methane and in the case of TEGa, bands at 2895 and 2954 cm^{-1} due to ethane and at 950 and 2989 cm^{-1} due to ethene are observed. The corresponding gas chromatography (GC) data confirm the presence of these gases and suggest that in the absence of arsine TMGa exclusively yields methane whereas TEGa yields a mixture of ethane and ethene (ratio 1:3) as hydrocarbon products. A small amount of *n*-butane (typically 1 % of hydrocarbon yield) was also observed in the gases from TEGa pyrolysis.

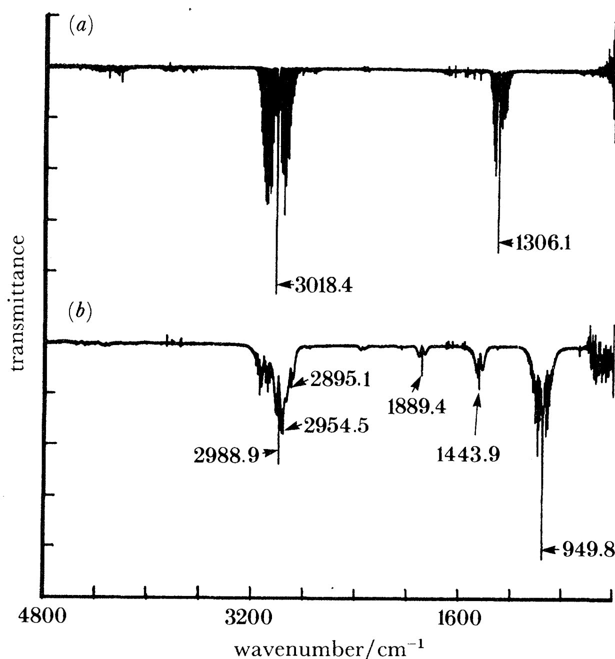

FIGURE 1. FTIR spectra of exhaust gases following pyrolysis of (*a*) TMGa at 800 °C and (*b*) TEGa at 700 °C in dihydrogen respectively. Molar flows are (*a*) 3×10^{-5} mol min^{-1}, (*b*) 10^{-4} mol min^{-1}.

Schemes 1 and 2 outline possible processes by which TMGa and TEGa may pyrolyse in dihydrogen to yield respectively methane and a mixture of ethene and ethane (Fraas *et al.* 1986). From experiments in D_2 and analysis of mass spectra (Larsen *et al.* 1987, 1988) it has been concluded that the pyrolysis of TMGa is a gas phase process with methyl radicals

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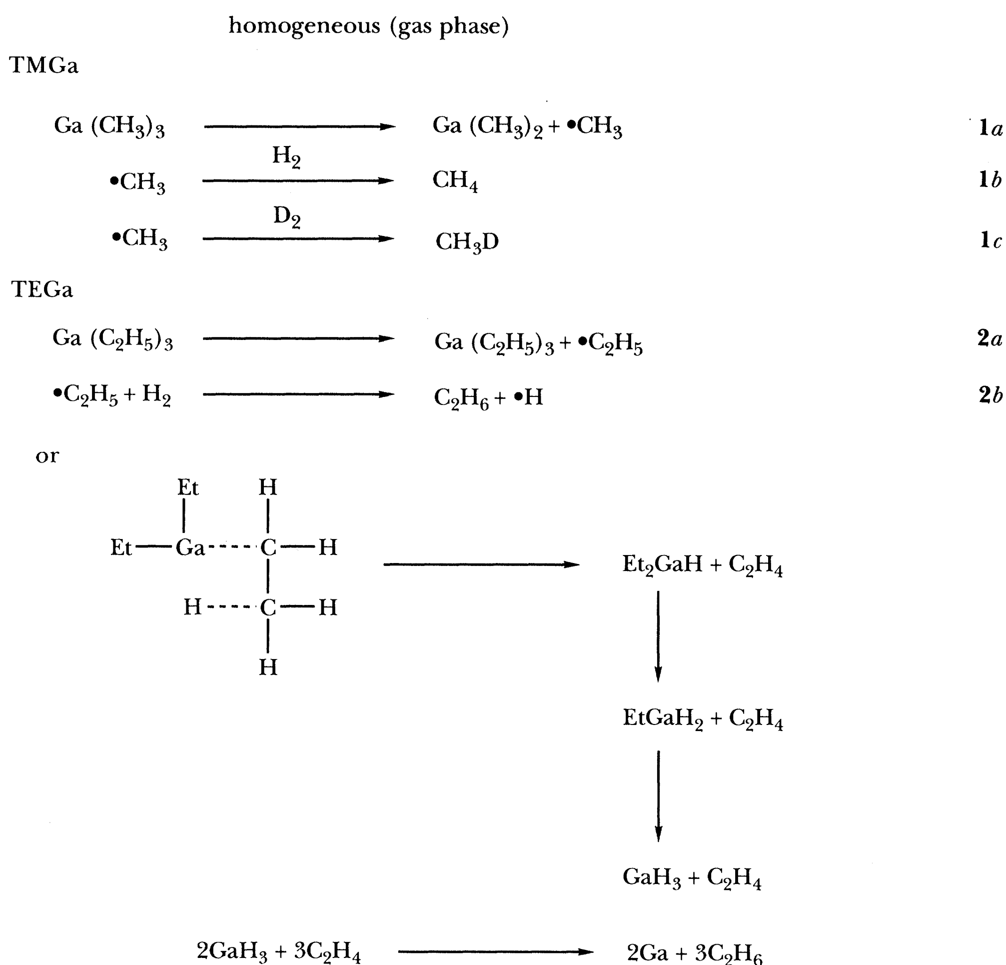

SCHEME 1. TEGa and TMGa mechanisms to consider.

abstracting hydrogen from dihydrogen (dideuterium) and there is evidence of CH_3D as product together with HD. Our results are not inconsistent with this because methane is the only product observed in our pyrolysis experiment with TMGa. We must, however, recognize that these experiments are conducted at much higher alkylmetal concentrations than ours and also that TMGa thermally decomposes in both N_2 and He as carrier gases (albeit at slightly higher temperatures) and is unable in these instances to abstract hydrogen. Thus a different mechanism probably prevails.

It is also likely that TEGa in dihydrogen decomposes in the gas phase but again heterogeneous pathways cannot be ruled out. In fact, ethene is the major product and this may be evidence for a surface dominated β-elimination reaction or a gas-phase, radical β-elimination taking place. The presence of ethane and especially *n*-butane in the product mixture strongly suggests radical pathways and it is interesting that TEGa commences decomposition at a lower temperature than TMGa (see figure 2).

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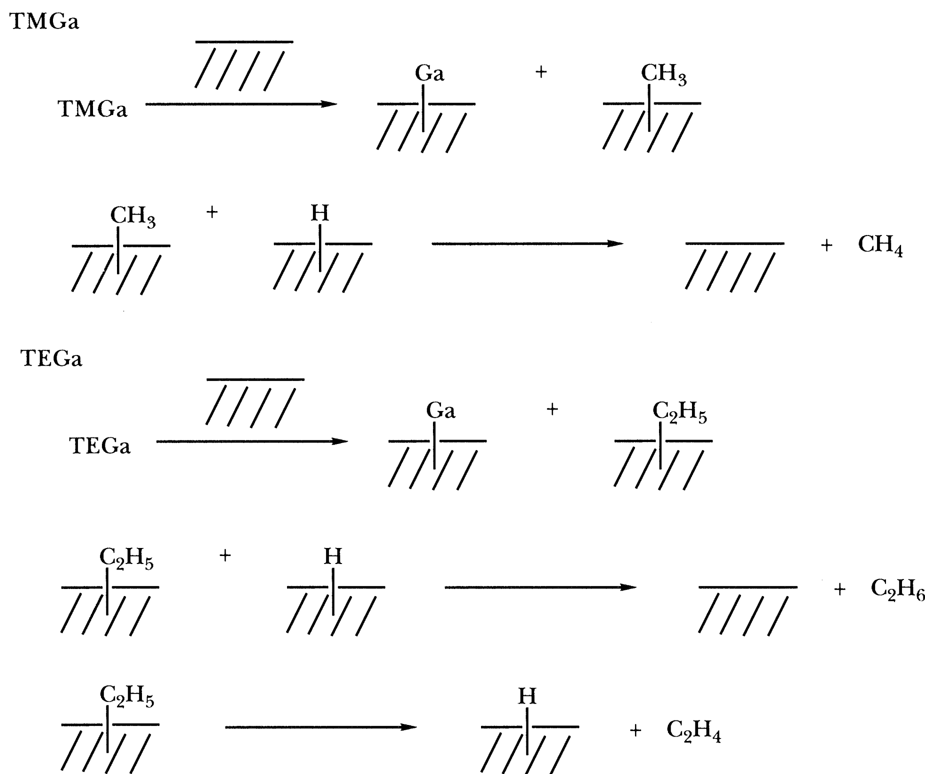

SCHEME 2. Heterogeneous (surface).

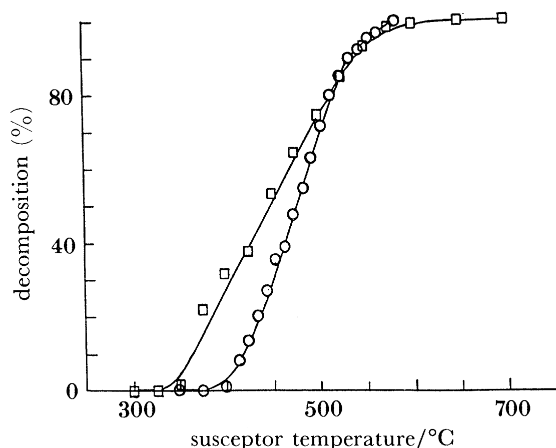

FIGURE 2. Decomposition–temperature profiles for TMGa (○) and TEGa (□) in dihydrogen at molar flow rates of 3×10^{-5} mol min^{-1} and 10^{-4} mol min^{-1} respectively monitored by mass spectroscopy.

Reactions of TMGa *and* TEGa *with* AsH_3

It has been reported on several occasions that the reaction between TMGa and AsH_3 occurs by a very different route to the pyrolysis of the reagents alone (Larsen *et al.* 1987; Den Baars *et al.* 1986; Butler *et al.* 1986). An intermediate or adduct is thought to form either on a surface or in the gas phase although direct experimental confirmation of such a species in the gas phase has only been given on one occasion (Nishizawa & Kurabayashi 1983) and in fact our own researches suggest that the infrared (IR) peak attributed in the latter work to such an

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adduct is more likely to arise from dimethylarsine which we detect by IR in the reactor effluent. Preliminary calculations on the fine structure expected in the IR spectra are further evidence for the presence of both dimethyl and monomethylarsine in the product that clearly suggests that radical transmetallation processes are occurring and serve to further cloud the issues. Hitherto, no confirmation of a surface-bound adduct has been given. It also appears that the involvement of an intermediate depends upon whether *ex situ* or *in situ* techniques are used to monitor reactivity. Accordingly, it is believed (Larsen *et al.* 1988) that the adduct forms since both TMGa and AsH_3 have an effect on the other's pyrolysis whereas CARS studies (Luckerath *et al.* 1987) lead to the conclusion that the process is more complicated and that TMGa does not change the decomposition behaviour of AsH_3. Because our present experiments are *ex situ*, our results should be more in line with those of Stringfellow than Luckerath.

Unfortunately, Luckerath has not yet investigated the effect of AsH_3 on the pyrolysis of TMGa.

We clearly see from figure 3 that arsine does have an effect on the decomposition of TMGa at a V:III ratio of 50:1 and even at lower ratios such as 1:1 the effect may be discerned. From figure 4 we see that arsine decomposition in dihydrogen commences at *ca.* 450 °C and at this

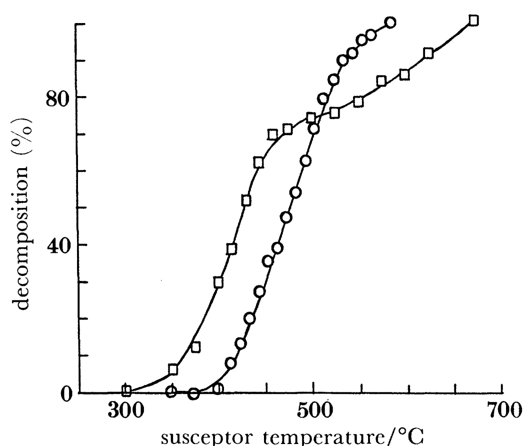

FIGURE 3. Decomposition–temperature profiles for TMGa in dihydrogen alone (○) and with arsine at a V:III ratio of 50:1 (□).

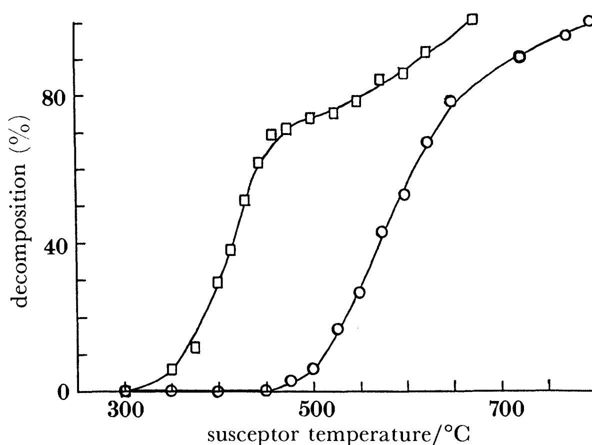

FIGURE 4. A comparison of the decomposition–temperature profiles for TMGa with arsine in dihydrogen (V:III ratio 50:1) (□) and that for arsine alone in dihydrogen (○).

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temperature there is an inflexion in the TMGa profile that is not present in the absence of arsine. It should be noted that up to 450 °C the internal surfaces of the reactor are coated with metallic gallium, whereas above this temperature GaAs has been formed. It is apparent that TMGa pyrolysis is facilitated above 450 °C. Explanations for the inflexion at 450 °C in the TMGa–arsine profile could simply be that (i) the process is catalysed by a GaAs surface and not by a Ga surface or (ii) hydrogen is abstracted from arsine and/or dihydrogen below 450 °C but above 450 °C the thermally decomposing arsine offers easier pathways. However, these suggestions do not rationalize the lowering of the TMGa decomposition temperature. It is possible that an adduct is formed which only participates in the reaction below 450 °C, but we have no direct evidence for such species.

Our data on the reaction between TEGa and arsine are limited at present. However, the observation of a change in the ethene:ethane ratio and the presence of *n*-butane suggest that free radical processes may well be important and indeed can explain the changes of profile described above for both TMGa and TEGa.

The likely initialization step is the homolysis of the gallium–carbon bond of trialkylgallium at temperatures above 300 °C to form alkyl radicals. These alkyl radicals do not necessarily abstract hydrogen from dihydrogen and thus in the absence of arsine, in the case of methyl radicals, the most likely radical-removing pathway is recombination with the gallium species to reform TMGa. However, in the case of TEGa, radicals can abstract hydrogen from TEGa giving rise to ethene by β-elimination and ethane by abstraction. Thus a lower-temperature decomposition is seen for TEGa.

Arsine is a good hydrogen donor to radical species and so methyl radicals from TMGa readily form methane when arsine is present and the decomposition temperature is lowered; interestingly, to approximately coincide with that of TEGa in dihydrogen because a pathway is offered that allows carbon-centred species to escape from the vicinity of the metal species. Similarly, when arsine is present, ethyl radicals from TEGa will most likely abstract hydrogen from arsine rather than TEGa and so the ethene:ethane ratio is lowered. The inflexion observed in the TMGa–arsine profile is probably a consequence of new pathways emerging because the thermal decomposition of arsine itself offers new reactive species. The reaction complexities shown by CARS (Luckerath *et al.* 1987, 1988) are probably due to the large number of radical species and products that will be involved. For example, hydrogen abstraction from arsine possibly occurs via both arsenyl and arsenanyl radicals.

Decomposition of phenylarsine ($PhAsH_2$)

Phenylarsine ($PhAsH_2$) has been proposed as an alternative source of As to arsine in the growth of GaAs by MOCVD. Recent experiments using TMGa with $PhAsH_2$ at atmospheric pressure (Hoare *et al.* 1989) and using TEGa with $PhAsH_2$ at reduced pressures (Brauers *et al.* 1988, 1989) have yielded device-quality material with low carbon content and low compensation ($n_{77} \approx 1 \times 10^{15}$ cm^{-3}; $\mu_{77} \geqslant 20000$ cm^2 V^{-1} s^{-1}) at relatively low V:III ratios (not more than 23). This is in marked contrast to the comparative unsuccessful use of other, alternative, arsine containing, precursors such as trimethylarsine (Vook *et al.* 1987), triethylarsine (Speckman & Wendt 1987, 1988; Lum *et al.* 1988) although both diethylarsine (Bhat *et al.* 1987) and *tert*-butylarsine ($TBAsH_2$) (Larsen *et al.* 1988) have produced promising GaAs material. The major products of the *t*-$BuAsH_2$ decomposition are isobutane (C_4H_{10}), isobutene (C_4H_3) and AsH_3 (Larsen *et al.* 1988) and the decomposition is believed to proceed

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via two routes: intramolecular coupling to produce C_4H_{10} and β-elimination at higher temperatures to yield C_4H_8.

The decomposition profile (monitored by FTIR) of phenylarsine in dihydrogen is shown in figure 5 and closely follows the formation of benzene monitored by GC and the decomposition of arsine under similar conditions monitored by mass spectrometry (MS). Pyrolysis begins at a temperature of *ca.* 375 °C and is complete at *ca.* 700 °C. The IR spectra of the decomposition products of phenylarsine at 375, 525 and 700 °C are shown in figure 6. Peaks due to the As–H vibrations in arsine are evident at 2122 cm^{-1} in all three spectra, whereas those associated with As–H vibrations in phenylarsine (2100 cm^{-1}) do not appear after 700 °C. These spectra show the formation of arsine and do not contain bands due to any other organic molecule.

The concentration of arsine present in the effluent (monitored by FTIR) is shown in figure 7. The concentration reaches a maximum at 625 °C and rapidly falls off at higher temperatures as the decomposition of arsine becomes dominant over its formation.

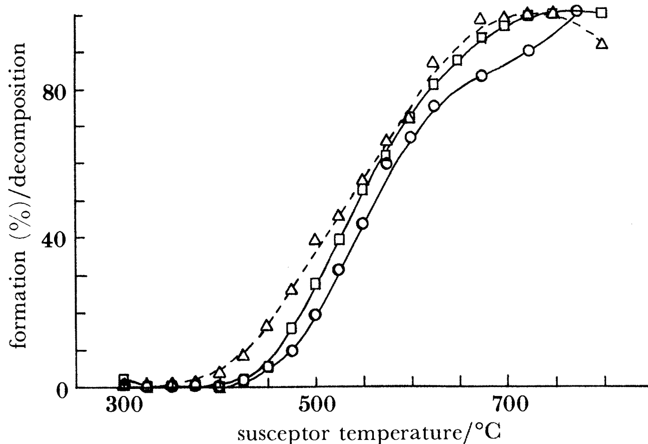

FIGURE 5. Decomposition of $PhAsH_2$ and AsH_3 in dihydrogen and the formation of benzene. △, C_6H_6 formation (GC); □, $PhAsH_2$ decomposition (FTIR); ○, AsH_3 decomposition (MS).

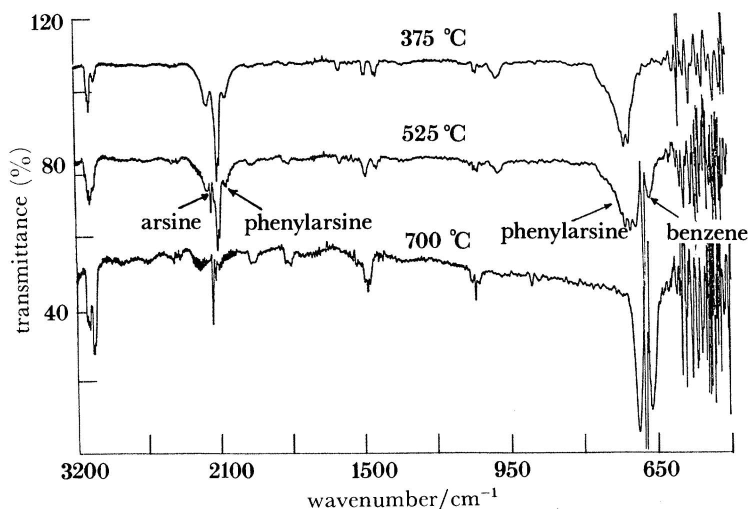

FIGURE 6. FTIR spectra of the decomposition products of $PhAsH_2$ at 375, 525 and 700 °C.

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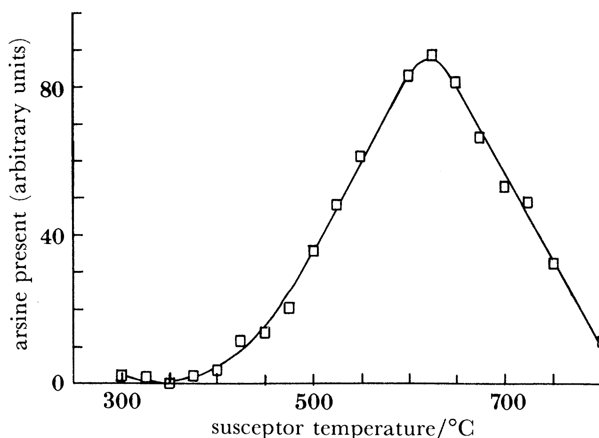

FIGURE 7. Concentration of arsine present in the reactor as a function of temperature during the decomposition of $PhAsH_2$.

Having studied the decomposition of phenylarsine using FTIR, MS and GC, we have only detected benzene and methane as products. No small-chain organic molecules were detected and, because benzene is unlikely to be incorporated into the epitaxial layer, this lends credence to the theory that phenylarsine is unlikely to contribute carbon to GaAs in addition to that emanating from the TMGa. Similar decomposition products and reaction onset temperatures have been observed for phenylarsine in an argon carrier gas.

We thus have shown that benzene and arsine are the major products in the decomposition of phenylarsine and that dihydrogen takes little part in the reaction. The situation may, therefore, be somewhat similar to the decomposition of TMGa, TEGa and t-$BuAsH_2$ where the radicals that are formed do not abstract hydrogen from dihydrogen but prefer to undergo recombination, intramolecular coupling and β-elimination selectively as appropriate.

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Discussion

D. J. Cole-Hamilton (*University of St Andrews, U.K.*). Can Professor Williams be certain that Mn, Fe and Mg in the diphenylarsine do not come from the stainless steel of the bubbler?

Also, how are Me_2AsH and $MeAsH_2$, which are observed in the Me_3Ga–AsH_3 reaction, formed?

J. O. Williams. We can be reasonably certain that the Mn, Fe and Mg detected do not come from the stainless steel. We have shown that starting materials used to prepare phenylarsine contain Fe (22 p.p.m. (by mass)), Mg (5.2 p.p.m.), Si (4 p.p.m.), Mn (1.8 p.p.m.) and Zn (0.99 p.p.m.).

We believe that these two products are formed by attack of methyl radicals on arsine attached to a surface or by rearrangement of an adduct species. Further work is clearly required.

R. J. M. Griffiths (*Plessey Research* (*Caswell*), *Towcester*, *U.K.*). Have free radicals been identified during MOCVD of group III–V materials?

J. O. Williams. In their infrared diode laser probing of MOCVD kinetics Gaskill *et al.* (1988) claim to have monitored the methyl radical concentration against time above the heated GaAs surface. The absorptions ascribed to radicals appear distinct from those due to other species, e.g. CH_4, allowing ready detection.

Additional Reference

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