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A SIMPLIFIED TECHNIQUE FOR MOCVD OF III-V COMPOUNDS

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ABSTRACT

The use of Lewis acid-base adducts as MOCVD precursors for III-V compounds is described and in particular the use of $\text{InMe}_3 \cdot \text{PEt}_3$ for the growth of InP. A simple, small-scale apparatus, which utilises the safety and handleability of these adducts is described. The InP epitaxial layers obtained were of good crystallographic quality with background carrier concentrations down to $2 \times 10^{15} \text{ cm}^{-3}$. The relative advantages of adducts over conventional metal alkyls is discussed, as well as the ideal requirements of metallo-organic sources for MOCVD. The future potential of both the simplified growth system and the adducts is considered.

1 INTRODUCTION

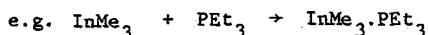
MOCVD has developed rapidly in recent years following the early work of Manasevit and co-workers (1,2). The process has mainly been concerned with gallium arsenide and gallium-aluminium arsenide and the success achieved with these materials has encouraged investigations into the growth of other III-V and II-VI compounds (3). The basis of the MOCVD process is the simultaneous thermal decomposition of volatile compounds containing the constituent elements of the required material. Historically, the metallo-organic compounds used as sources have been the alkyls for the groups III and II elements and the hydrides for the groups V and VI elements. Although these types of sources work well for GaAs and (Ga,Al)As, extension to the growth of indium containing compounds has not been so successful, due to side reactions of the vapour species at room temperature (4). Indium alkyls react with the group V hydrides to form an adduct which is unstable at room temperature; it

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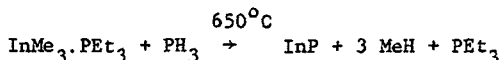
eliminates the corresponding alkane and deposits an involatile polymer on the surfaces of the gas inlet tubes (5), e.g. $\text{InMe}_3 + \text{PH}_3 \rightarrow \text{InMe}_3.\text{PH}_3 + (-\text{InMePH-})_n + 2\text{MeH}$.

The extent of this side reaction is variable, being catalysed by the silica and stainless steel surfaces of the inlet tubes; this causes variable growth rates, poor morphology and poor electrical properties of the desired semiconductor. Furthermore when growing ternary or quaternary compounds containing indium, e.g. $(\text{Ga},\text{In})\text{As}$ and $(\text{Ga},\text{In})(\text{As},\text{P})$, precise composition control is impossible due to the uncontrolled variations in the concentration of the indium alkyl in the vapour resulting from the unwanted side reactions.

We have previously reported (6,7) a technique for completely eliminating the above problem. The indium alkyl vapour is first mixed with a saturated group V Lewis base to form a stable adduct which does not decompose at room temperature nor react with the group V hydride until it reaches the heated zone near the substrate.



Lewis acid Lewis base



We have demonstrated that triethyl phosphine (PEt_3), triethylamine (NEt_3), trimethyl phosphine (PMe_3) and trimethyl arsine (AsMe_3) are all suitable Lewis bases for 'blocking' the reactions of trimethyl indium with either phosphine or arsine. However, they are not all universal reagents: NEt_3 is suitable for the growth of InP , but not $(\text{Ga},\text{In})\text{As}$; AsMe_3 can be used for the growth of arsenides but because it also acts as a source of arsenic (8) it cannot be used for InP . PEt_3 however is sufficiently stable to pass through the reactor without significant decomposition while acting as a blocking agent. It is therefore possible to grow $(\text{Ga},\text{In})\text{As}$ in the presence of PEt_3 without contaminating it with phosphorus (6).

This technique has now been shown to be suitable for growing all compounds of the Ga-In-As-P system at atmospheric pressure using group III alkyls as vapour sources (7). However it involves the 'in situ' formation of an adduct which can be prepared directly by standard chemical synthesis techniques.

In 1978 we commenced a programme of research in collaboration with D C Bradley (9), investigating metallo-organic compounds which would act as suitable precursors for MOCVD and be safer to prepare and use than metal alkyls. Amongst those compounds investigated were the dialkylamide compounds of indium e.g. $(\text{CH}_3)_2\text{InN}(\text{CH}_3)_2$ and adducts of the type described above; we have shown that both types of compound can be used as sources for the growth of InP. The higher vapour pressures of the adducts compared with the amido compounds and the success of the method described above have encouraged us to concentrate on the use of adducts as sources for MOCVD.

2 PRE-PREPARED ADDUCTS AS SOURCES FOR MOCVD

We report here on the use of adducts for the growth of InP and (Ga,In)As in a small and simple epitaxial growth system. The use of Lewis acid-base adducts for epitaxial growth has been reported before, Benz et al. in 1980 (10,11) used an indium-phosphorus adduct $(\text{InMe}_3.\text{PMe}_3)$ as a single source for the formation of InP, but decomposition gave a mixture of indium and InP; by adding phosphorus trichloride (PCl_3) to the vapour stream, they were able to eliminate the formation of indium, presumably by forming indium chloride with HCl derived from the PCl_3 . Zaouk et al. (12,13) reported preliminary results on the use of monochlorodialkyl gallium adducted to trialkyl arsines, phosphines and amines for the growth of GaAs and related compounds.

In the present work we have used an adduct as a direct replacement for the group III alkyl, mixing its vapour with a group V hydride and then decomposing the mixture on a hot substrate. This approach avoids the use of chlorine containing compounds and offers considerable advantages over the use of conventional alkyls.

Metal alkyls are pyrophoric materials and consequently hazardous to prepare and handle. Their extreme reactivity also makes purification difficult and they generally need to be contained in stainless steel vessels for safety reasons. Adducts are far less reactive, non-pyrophoric materials which can be purified by a variety of techniques and can be contained safely in glass vessels. Transportation is also easier because of their less hazardous nature.

For the growth of indium containing compounds, indium alkyls present three particular problems: (i) the side-reactions at room temperature discussed above (ii) their thermal instability (iii) their limited commercial availability. There have been reports of several explosions in different laboratories in the preparation of InMe_3 and its commercial availability has been sporadic and unreliable. InEt_3 does not form a sufficiently strong adduct with PEt_3 or NEt_3 to prevent side reactions with PH_3 although it has been used successfully at low pressure by Duchemin et al with prepyrolysis of PH_3 (14). InMe_3 adducts avoid unwanted side reactions; can be made safely by standard chemical techniques (without needing to isolate InMe_3); can be used in conventional MOCVD systems at atmospheric pressures; and, because of their lower reactivity, potentially offer opportunities for obtaining purer source materials.

3 EXPERIMENTAL SYSTEM DESIGN

In order to test the suitability of novel MOCVD source materials, a system was designed in which simplicity and minimum cost, commensurate with safety requirements, were primary considerations. The advantages conferred by the use of adduct precursors considerably assisted in achieving this goal. The apparatus is shown schematically in Fig 1. The adducts are contained in Pyrex glass bubblers, sealed with Teflon valves and maintained at the required temperature ($70 - 100^\circ\text{C}$) with a small oil bath. At these temperatures the adducts are liquid and high purity nitrogen is used as the carrier gas for the vapours. The gas flows are controlled with needle valves and measured with conventional ball flow meters. The main carrier gas flow into the reactor is palladium-diffused hydrogen and the adduct vapours are mixed with this together with a stream of 5% phosphine (or arsine) in hydrogen. The inlet tubes to the reactor are warmed with heater tape to prevent condensation of the adduct. With the exception of the group V hydride line, all the inlet tubes to the reactor are made of glass. The group V hydrides were supplied from cylinders outside the building and piped directly into the vented cabinet housing the equipment. Mass flow controllers, though not essential for the growth of InP or $(\text{Ga}, \text{In})\text{As}$, were used on the hydride lines, since they involved less joints than needle valves and flowmeters.

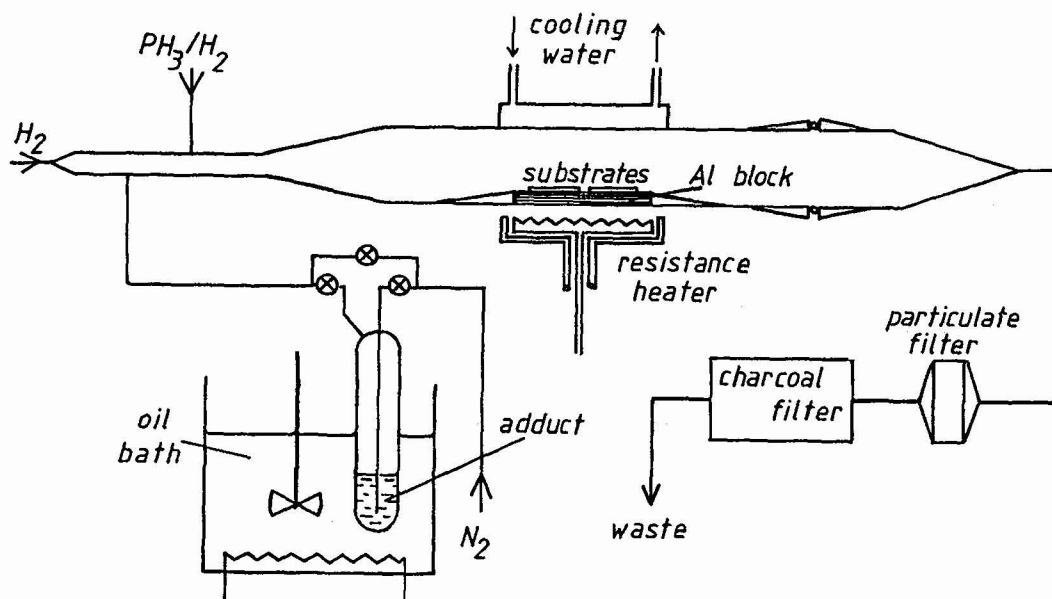


Figure 1. Schematic diagram of system

For greater simplicity a small flat resistance heater, similar in principle to that of Springthorpe et al. (15), was used in preference to an r.f. heater. It was constructed from platinum - 10% rhodium wire on an alumina support and positioned against the lower flat surface of the reactor tube. A small block of aluminium was situated within the reactor to assist in providing a uniform temperature profile for the substrate, which rested on the top surface of the aluminium. No evidence of reaction between the InP substrates and the aluminium support was observed; presumably the oxide layer present on the aluminium surface was sufficient to provide an effective barrier to interdiffusion. The substrate temperature was maintained at 630°C.

The design of the reaction chamber was based on the results of holographic studies of flow patterns in horizontal reactors by Giling (16). In MOCVD it is not possible to maintain the long hot zone at the entrance to the reactor for stabilisation of flow patterns as recommended for silicon CVD systems; such an arrangement would result in substantial depletion of the gas stream due to pyrolysis on the hot reactor walls.

However, Giling showed that stable uniform flow patterns were obtained when a rectangular sectioned tube was used, with the heated susceptor at the bottom and a water-cooled surface at the top. This basic design has been used in the present system: the gas streams are thoroughly mixed then passed along a tube under laminar flow conditions with a smooth transition to the rectangular sectioned reactor. It is possible that the presence of nitrogen in the gas stream may introduce some turbulence above the heated zone, but if this should occur it could be regarded as a replenishable source for transport of the reactants to the substrate (16). How closely the flow patterns in our short reactor approach those observed by Giling can only be ascertained by detailed holographic measurements, but the appearance and quality of the epilayers grown, suggests that the design is appropriate. An additional advantage of the water-cooled top surface of the reactor is that little deposit occurs on it, thus permitting observation of the substrate during growth. The buttress joint used for loading the substrates is sealed using a Viton O-ring. The waste gases are passed through particulate filters before entering an activated carbon filter to remove any unreacted PH_3 or AsH_3 , and then into the exhaust system. The whole apparatus is sufficiently compact to be located in a standard 1.2m chemical work station.

4 RESULTS AND DISCUSSION

Initial experiments were directed towards establishing the growth conditions for InP using the $\text{InMe}_3\text{.PEt}_3$ adduct. Adopting similar concentrations of the adduct vapour and PH_3 to those in the 'conventional' system where the adduct is formed 'in situ' (6), epitaxial layers of good morphology could be readily obtained. Under high power Nomarski microscopy the surface was found to have a slight texture (Figure 2). The substrate quality and preparation prior to growth were also shown to be critical, growth hillocks which appeared to emanate from the substrate-epilayer interface being observed in some cases. Similar features have been noted in the growth of InP and $(\text{Ga,In})\text{As}$ by LPE and VPE. The layers grown were free from gross defects and transmission infra-red microscopy confirmed that there were very few regions of strain the epilayer caused by dislocations or inclusions. X-ray rocking curve line widths

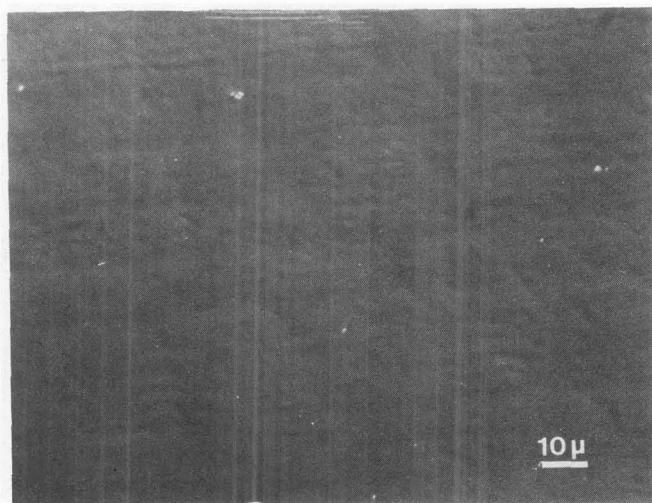


Figure 2. Nomarski interference micrograph of InP

of less than 30 secs of arc also indicate good crystallographic quality.

The layers were n-type and the background carrier concentrations were initially in the range $10^{16} - 10^{17} \text{ cm}^{-3}$, but vacuum redistillation of the adduct samples reduced this and layers with doping levels in the low 10^{15} cm^{-3} region have now been readily obtained. An electrochemical profile plot is shown in figure 3. The room temperature mobilities of samples grown on an iron doped substrate were $\sim 3800 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $N_D = 3 \times 10^{16} \text{ cm}^{-3}$.

A low temperature cathodoluminescence spectrum is shown in figure 4. The results are typical of good quality InP, with narrow peak widths; the small peak at 904 nm is attributed to a zinc acceptor level and is commonly observed in InP.

Generally one concludes that the quality of the InP layers grown using $\text{InMe}_3 \cdot \text{PEt}_3$ adduct precursor is good and comparable with material obtained by other techniques. This is particularly encouraging since little attention was paid to purity aspects during the adduct preparation and a simple vacuum distillation brought significant improvements in background doping levels. Further work on purification and the determination of reliable vapour pressure data is being pursued in conjunction with Bradley and Faktor (9).

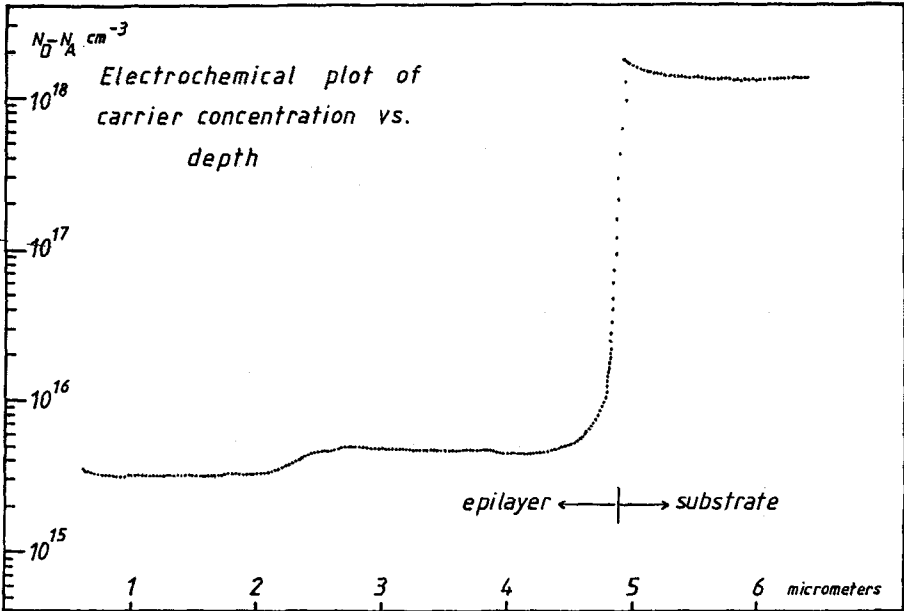


Figure 3. Electrochemical Profile of InP

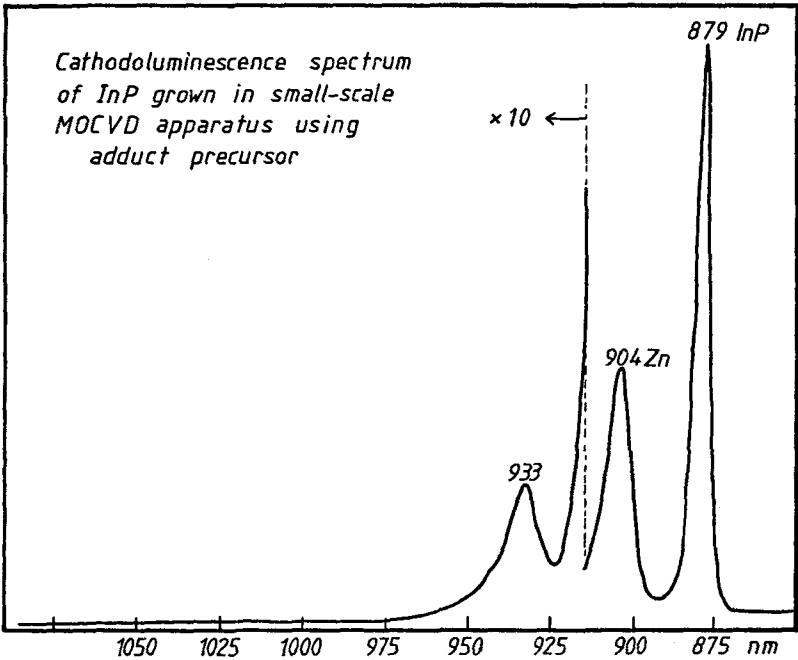


Figure 4. Low temperature cathodoluminescence spectrum of InP

Typical conditions used for the growth of InP were as follows:

Substrate Temperature	: 630°C
Nitrogen flow rate through adduct	: 4.8 l h ⁻¹
Total hydrogen flow rate	: 45 l h ⁻¹
5% PH ₃ in H ₂ flow rate	: 15 l h ⁻¹
Temperature of InMe ₃ .PEt ₃	: 100°C

Under these conditions growth rates of 2-3 $\mu\text{m h}^{-1}$ were obtained and the layer uniformity was better than 5% over a slice $\sim 15 \times 15$ mm.

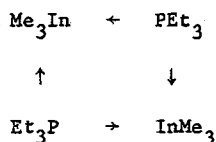
Preliminary results on the growth of (Ga,In)As using GaMe₃.PEt₃ in addition to InMe₃.PEt₃ indicate that the method described is suitable for the growth of solid solutions.

In order to assess the suitability of adducts as source materials, it is necessary to state the ideal requirements for an MOCVD precursor. They may be listed as follows:

- i. The material should be stable at room temperature without spontaneous decomposition.
- ii. It should be sufficiently unreactive to allow simple handling and storage.
- iii. It should be volatile, without decomposition, at a conveniently low temperature (e.g. $< 100^\circ\text{C}$).
- iv. The rate of homogeneous pyrolysis should be low compared with heterogeneous decomposition (approx 1:1000).
- v. The rate of heterogeneous reaction on a substrate should be greater than on other hot surfaces (such as silica confining walls or susceptor); i.e. the reaction should be catalysed by the substrate.
- vi. The precursors must be adsorbed on the substrate; at least one of the reactants should be chemisorbed

To some extent these requirements may be incompatible, e.g. for strong adsorption, the properties leading to high interaction energies with a surface will be those which are responsible for intermolecular interactions and hence may cause low volatility. It is thus likely that some compromise must be made to achieve the most useful precursor materials. The fact that the use of the adduct precursors described here has been so successful is encouraging and $\text{InMe}_3\cdot\text{PEt}_3$ obviously meets many of the criteria listed above.

$\text{InMe}_3\cdot\text{PEt}_3$ and several other related adducts are dimeric, the association of two molecules satisfying the co-ordination requirement of the indium atoms:



Because of the stability and shielding effect of the organic groups in the dimer, molecular interactions between dimers are reduced and therefore volatility is enhanced.

This shielding effect of the dimer might be expected to reduce the reactivity and adsorption of the molecule onto the substrate but for the fact that dissociation of the dimer occurs on heating and is probably complete at the growth temperature (17). This dimerisation (or for $\text{GaMe}_3\cdot\text{PEt}_3$, trimerisation), which is also characteristic of the amido materials mentioned earlier, may well be a significant factor in the success achieved with these precursors. It would also imply that a sharp thermal gradient in the vicinity of the susceptor or substrate heater is a desirable feature of a reactor.

The design features of the small scale MOCVD apparatus described here are clearly not specific for the use of adducts. It incorporates a number of features and has a degree of simplicity, which makes it of interest for various research applications where the high cost of a conventional MOCVD system would not be justified. The degree of success achieved also clearly indicates that adducts are not exclusive to this small scale system, but could be incorporated into a conventional system

with the minimum of alterations being necessary.

The chemical problems encountered in MOCVD of indium containing compounds are also overcome by using adducts and this, coupled with the supply problems of trimethyl indium, make them particularly attractive for the growth of materials in the Ga-In-As-P system. If the expectation of obtaining adducts of higher purity than can be achieved for the metal alkyls is realised, then extension of the use of adducts for the Ga-Al-As system and for other III-V and II-VI compounds will be advantageous. Preliminary results certainly support this suggestion.

5 CONCLUSIONS

The work reported here leads to the following conclusions:

- i. adducts are suitable precursors for the growth of III-V compounds;
- ii. the use of adducts overcomes the chemical problems encountered in the MOCVD by indium compounds;
- iii. adducts have considerable advantages over alkyls in terms of safety, ease of preparation and transportation;
- iv. adducts offer the possibility of purer starting materials for MOCVD;
- v. the advantageous properties of the adducts helped considerably in achieving a simple, inexpensive growth apparatus;
- vi. adducts may be used in larger conventional systems with only slight modification of the equipment;
- vii. the basic design features of the reactor tube are good and make it suitable for a wider range of applications.

6 ACKNOWLEDGEMENTS

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