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The vapour-phase ultraviolet spectra of metallo-organic precursors to III–V compounds

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Vapour-phase UV (ultraviolet) spectra are reported for the trimethyls and triethyls of gallium and indium, aluminium triethyl and indium cyclopentadienyl. Strong absorptions are observed between 200 and 300 nm; these are adequate for efficient energy coupling in photolysis.

1. Introduction

The pyrolysis of metallo-organic vapours is attracting increasing attention as a method of depositing metallic, semiconducting and insulating layers. Photolysis of these vapours has recently been proposed for the same purpose [1, 2]. When used as an alternative to pyrolysis, or in conjunction with it, photolysis offers several potential advantages. Firstly, if the radiation is spatially confined, the deposition can be restricted to small well-defined regions of the substrate [1]. Secondly, since a particular molecular species can be photolysed only by radiation of a wavelength lying within an absorption band of the species, the possibility exists of selectively photolysing one species in the presence of others, under circumstances where pyrolysis would produce a general decomposition of all the species. Applications of this selectivity can be foreseen in the deposition of solid solutions as, for example, optoelectronic materials.

To date, two types of photolytic process have been used for deposition. IR (infrared) multiphotonic excitation [3] decomposes the molecules by successive promotion through vibrational levels without taking them out of their electronic ground state. Visible/UV electronic or vibronic excitation takes the molecules from this electronic ground state into excited electronic states. In these states, bonds are often sufficiently weakened to have a high probability of breaking thermally. It may even be that in some cases the excited state is non-bonding or repulsive. In these cases the absorption appears as a continuum (without high energy limit), and a bond breaks spontaneously.

In investigating the possible modes of photolysing a given species it is necessary to examine the vibrational and electronic spectra, both to look for the appropriate absorption frequencies where radiative energy may be coupled into the molecule, and, by examining the absorption bands, to deduce the nature of those excited states which may be produced. Finally it is necessary to establish whether these states will be of a type to generate the required molecular dissociation.

In this paper we present the UV spectra of some metallo-organic species in the vapour phase, obtained with a view to the use of the compounds as precursors for III–V semiconductor epitaxy. The spectra are discussed with reference to the criteria for the choice of precursors, and to the choice of wavelengths for photolysis.

2. Experimental details

Gallium and indium trimethyl and indium and aluminium triethyl were electronic-grade samples supplied by Alfa-Ventron. Gallium triethyl was electronic grade and supplied by Labolac. Indium cyclopentadienyl was prepared by the method of Fischer and Hofmann [4] and supplied by Queen Mary College, University of London.

Spectra were obtained with either a Perkin Elmer 137 or a Pye Unicam SP8-400 visible/UV spectrophotometer. Some of the compounds were entrained in a carrier gas stream of pure (Pd-diffused) hydrogen at a pressure of one atmosphere, from a bubbler whose temperature was chosen to give a suitable vapour pressure. Others were measured at low pressures. The latter method

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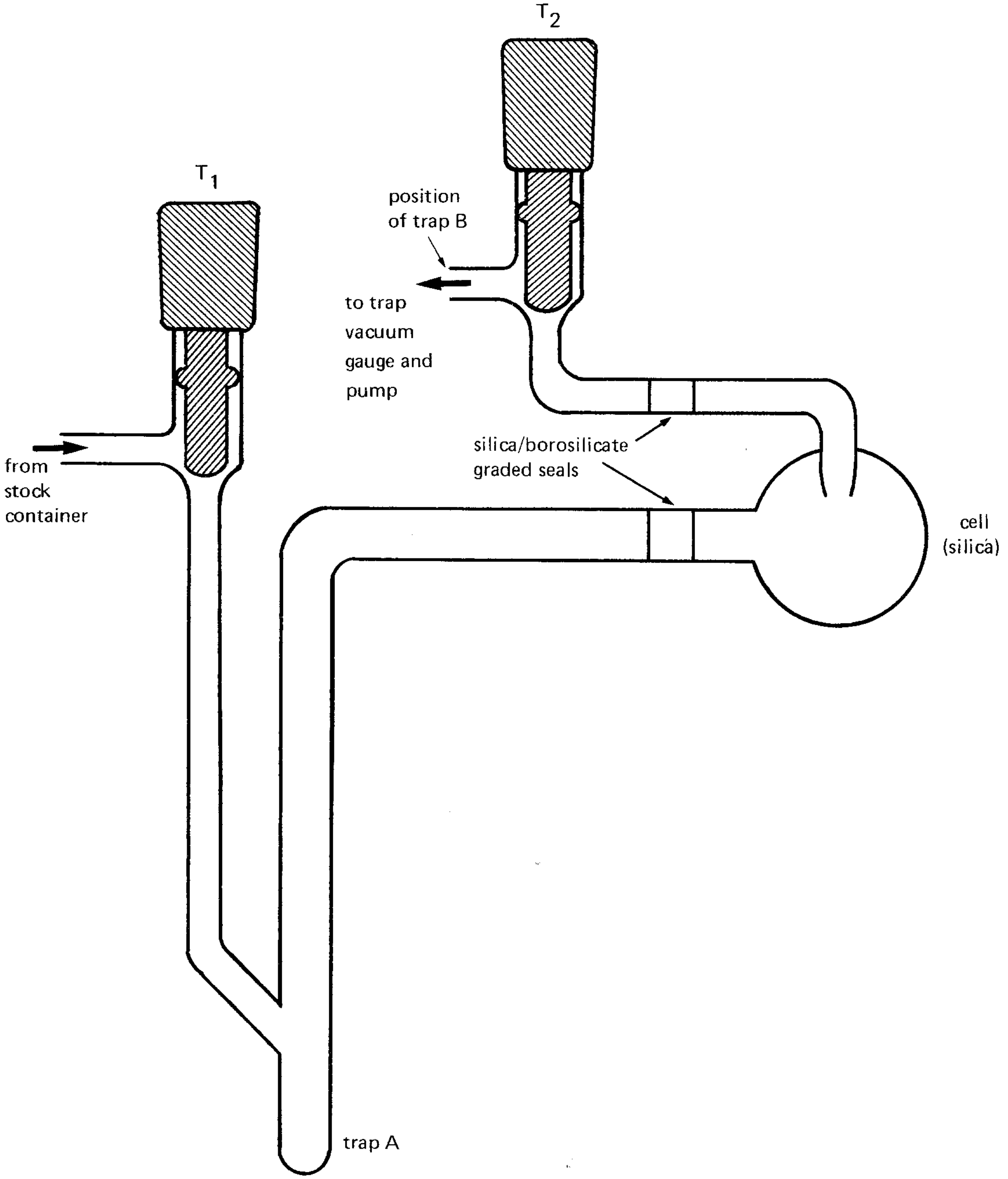

Figure 1 Apparatus used for recording the vapour spectra of metallo-organic compounds under vacuum.

has the advantage of requiring smaller amounts of the frequently expensive and air-sensitive compounds. In passing it is noted that although the two types of measurement were made at roughly equal partial pressures of the compounds, the presence of the inert carrier gas can cause broadening effects in some UV spectra, and this possibility must be borne in mind (see below).

The low-pressure apparatus is shown in Fig. 1. The spectra are shown in Figs. 2 to 4. It was designed so that the whole internal surface which came into contact with the vapour could be dried in vacuum by heating. This was necessary because all the compounds used were moisture-sensitive and, in the case of indium cyclopentadienyl (InCp) the hydrolysis product, cyclopentadiene, has an intense UV absorption spectrum (see below). After drying the cell, about 0.5 cc of the compound was distilled or sublimed from the stock container into the trap A, held at liquid

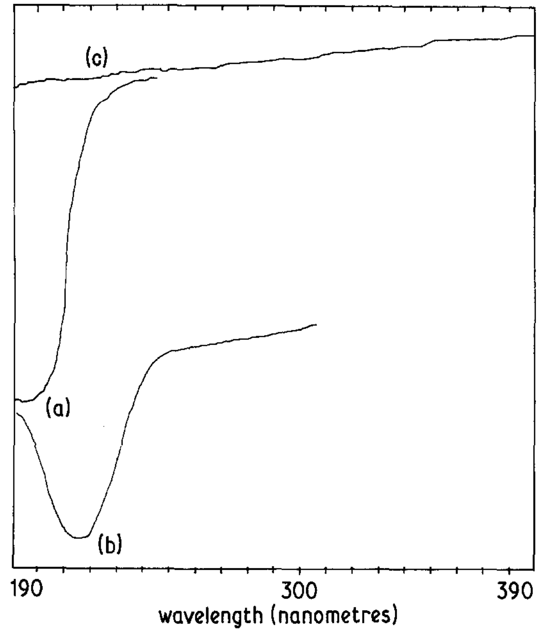

Figure 2 Spectra of (a) gallium trimethyl, (b) indium trimethyl, and (c) background (silica cell absorptions). Transmittance is plotted vertically, on an arbitrary scale, with the curves displaced arbitrarily. Peak absorption coefficients are given in Table I.

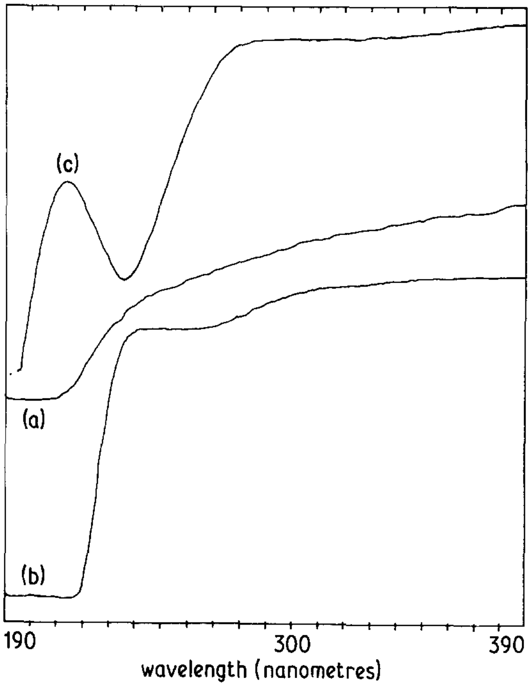

Figure 3 Spectra of (a) aluminium triethyl, (b) gallium triethyl, and (c) indium triethyl. Plotted as Fig. 2.

nitrogen temperature. The borosilicate/PTFE taps T_1 and T_2 were then closed and the apparatus transferred to the spectrometer. The absorption cell was warmed to 50 to 80° C for the measurements on the triethyls, since these adsorb on silica and give rise to unwanted strong spectral bands when the temperature is lower. The trap was warmed to the appropriate temperature (see Table I) and the vapour spectrum recorded. To check for decomposition the trap was re-cooled and then warmed with the tap T_2 open to the vacuum line so that any volatile decomposition products might distil away. The tap was then closed and the spectrum examined for changes. This procedure was particularly necessary with InCp, where traces of moisture rapidly caused the spectrum of cyclopentadiene [7] to appear. In fact with this compound it was found necessary to employ a guard trap added at B and fused to the cell assembly to prevent traces of moisture diffusing back from the PTFE pumping line.

3. Discussion

Table I lists the conditions under which the spectra were obtained. Vapour pressures, where available, are taken from the literature. (Often where there is more than one source of vapour pressure data these disagree significantly. Hence the values reproduced in Table I, and the molar absorption coefficients determined in part from them, should be taken only as a rough guide.) In

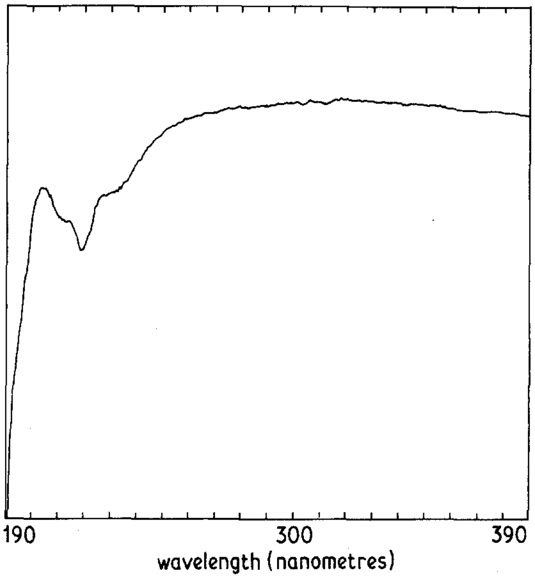

Figure 4 Spectrum of indium cyclopentadienyl. Plotted as Fig. 2.

TABLE I Experimental conditions, vapour pressures, and spectral data

	Measurement conditions	Vapour pressure (mm Hg)*	Molar absorption coefficient at peak max ($cm^{-1}\,l\,mol^{-1}$)	Wavelength at peak max (nm)
$GaMe_3$	H_2–1 atm	4 (– 45° C)	~ 2500	195
$GaEt_3$	H_2–1 atm	3 (15° C)	~ 4000	213
$InMe_3$	H_2–1 atm	3 (15° C)	~ 2500	213
$InEt_3$	vacuum	6 (70° C)	~ 3000	230
InCp	vacuum	–	–	220
$AlEt_3$	vacuum	4 (80° C)	~ 2000	200

*Data from [5] and [6]. The molar absorption coefficients are calculated as $\alpha = -[\log_e(I/I_0)]/[(\text{cell length}) \times (\text{molar vapour density})]$.

the case of indium trimethyl ($InMe_3$), InCp and probably gallium trimethyl ($GaMe_3$) it can be seen that the single band observed in the 200 to 250 nm region is not part of a continuum since both sides of the maximum are delineated. It should be noted that the spectrum of $AlMe_3$, reported by Deutsch and co-workers [1], is similar in this respect. This is not so clearly the case however with the triethyls; the gallium and aluminium compounds show rather broader maxima stretching to the short wavelength limit of the spectrometer, and the indium compound shows two bands, one peaking below 190 nm. The breadth of the bands makes it impossible to say whether there are underlying continuum absorptions, even in $GaMe_3$, $InMe_3$ and InCp where more of the band is observed.

Because of the relatively low resolution used in this work, we must consider the possibility that we are observing unresolved groups of sharp lines rather than truly broad bands. Thompson and Linnett [8] obtained spectra from low-pressure vapours of alkyl compounds of groups II and IV, using a high-resolution spectrograph. For many of these compounds they observed continuum absorptions in the region 200 to 300 nm. In the group IV alkyls these were the only spectral features, but in some of the group II alkyls there were sharp lines apparently of the order of 0.1 nm in width superimposed on the continua. It is not possible to say which pattern the group III alkyls would be expected to follow. When using highly monochromatic radiation sources for the photolysis, therefore, it is possible that the amount of radiation coupled into the compound may be greater or less than would be indicated by these absorption coefficients.

Table I contains calculated peak molar absorption coefficients together with the peak wavelengths. These absorption coefficients are large enough to allow efficient coupling of radiation into the vapour molecules. Looking at the group of spectra as a whole it is seen that the bands are broad enough to overlap appreciably with each other in a mixture of vapours. Thus in such mixtures it may not be possible to locate a wavelength where one compound absorbs to the total exclusion of others. However because a range of vibrational levels are excited as a band is scanned, and these levels may have different propensities to lead to dissociation, the quantum yield for photolysis may well vary across the band. This may in turn improve the possibilities for selective photolysis of one species in the presence of another with an overlapping band. Clearly there is a need for elucidation of these points by quantitative photolytic work.

4. Conclusion

Vapour spectra of a number of possible photolysis precursors to III–V compounds have been obtained. In all cases there are absorption peaks in the accessible spectral region above 190 nm, and these are strong enough for efficient energy coupling. The peaks, however, are wide enough for substantial overlapping to occur in mixtures, so that examination of further metallo-organic compounds will be necessary to attempt to provide a wider-ranging choice for selective photolysis.

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