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Organometallic Molecules for Semiconductor Fabrication [and Discussion]

D. V. Shenai-Khatkhate, Marjory B. Parker, A. E. D. McQueen, J. B. Mullin, D. J. Cole-Hamilton and P. Day

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Organometallic molecules for semiconductor fabrication

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Adduct purification of metal alkyls for use in metal-organic vapour-phase epitaxy is described and shown to give high purity alkyls of Al, Ga, In, Cd, Zn and Te. In most cases involatile Lewis bases are used to form dissociable adducts, but for tellurium alkyls, halides of mercury or cadmium are used. Alternative source materials such as higher alkyls, volatile adducts and mixed alkyls are discussed and new results on the stability of mixed alkyls of tellurium are presented.

Introduction

Metal-organic vapour phase epitaxy (MOVPE) has become production technology for the growth of thin single crystalline films of, for example, gallium arsenide (Watanabe *et al.* 1988). Recent research has also brought the technique close to commercial exploitation for other 13/15 and 12/16 semiconductors, e.g. InP, InGaAsP, $Cd_xHg_{1-x}Te$, etc. The technique involves the decomposition of suitable volatile precursor materials over a single-crystal substrate and both the nature and the purity of the precursor materials have been shown to be crucial in determining the crystallographic and electrical quality of the grown layers. In this paper, we review methods for the purification of simple metal alkyls that have traditionally been used as source materials and then discuss the relative merits of different precursors. Finally, the use of alternative and new precursors is described together with new results concerning the synthesis and thermal stability of mixed alkyl compounds of tellurium.

Purification of main-group metal alkyls

(*a*) *General considerations*

Table 1 lists a series of impurities that are conceivably present in certain organometallic precursors together with the concentration in the gas phase that will give a doping level of 10^{15} atoms per cubic centimetre in the grown layer. For most modern electronic devices, doping levels in the as grown material need to be considerably less than 10^{15} atoms per cubic centimetre (10 p.p.b.†) and hence the purity of the precursor needs to be significantly better than indicated in the table. Clearly, in some cases, where there is a significant fractionation that keeps the impurity out of the layer (e.g. Si in GaAs), this criterion is not especially stringent, although much greater than is usual for organometallic compounds used, for example, as catalysts or polymerization agents. In other cases, impurities are substantially concentrated from the gas phase (e.g. Sn in GaAs) so that impurity levels even as low as 1 part in 10^{12} can

† p.p.b. is parts per thousand million.

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Table 1. Dopant incorporation from impurities in precursors

impurity	dopant type	semiconductor	maximum cylinder concentration[a] for 10^{15} cm^{-3}/p.p.b.
Si (SiH_4)	n	InP	16
Si (SiH_4)	n	GaAs	440
Sn (Et_4Sn)	n	GaAs	4×10^{-2}
Se (H_2Se)	n	InP	2
Mg (Cp_2Mg)	p	InP	440
Be (Et_2Be)	p	GaAs	20

[a] Flow rate ≈ 500 cm^3 min^{-1}.

be detrimental to the electrical properties of the grown layer. Organometallic compounds prepared by traditional methods typically contain up to about 0.1 % of unwanted impurities, and even using highly purified starting materials and clean procedures impurity levels of up to 50 p.p.m. are not uncommon. Clearly, even in the most favourable cases efficient purification methods need to be used for these precursor materials.

Main-group metal alkyls are generally volatile liquids or solids and, as such, traditional physical methods are available for their purification. These methods include fractional distillation, fractional crystallization from a suitable solvent, sublimation and zone refining. All of these methods have been used for the purification of metal alkyls, but in general, large amounts of the material have to be discarded to obtain highly pure products and the very high reactivity of these materials (most spontaneously inflame or explode on contact with air, others are highly noxious or toxic or both) means that some of these techniques can only be applied to organometallic compounds with great difficulty. This has led various research groups to explore a new chemical purification method: adduct purification.

(*b*) *Adduct purification alkyls of groups* 12 *and* 13

The first use of a dissociable adduct was described in 1962 for the removal of diethylether from dimethylcadmium, with which it forms a stable distillable adduct (Coates *et al.* 1962). Addition of 2,2′-bipyridyl to an ethereal solution of Me_2Cd produced a yellow crystalline precipitate from which Me_2Cd could be released on heating *in vacuo*. Although this process was not originally intended for the production of ultra-high purity Me_2Cd, but rather for its separation from diethylether, it does illustrate the generalities and the power of the adduct purification technique for group 12 or 13 metal alkyls.

Because these metal alkyls are Lewis acids, they readily form adducts with Lewis bases. These adducts vary in stability depending upon the nature of the metal, the nature of the alkyl groups, the nature of the donor atom in the Lewis base and the nature of the remaining segments of the Lewis base.

For use in adduct purification of a given metal alkyl, the Lewis base and the adduct must have certain well-defined properties. These include the following.

1. The Lewis base and the adduct must both be of very low volatility.
2. An adduct must form between the metal alkyl and the Lewis base and this should preferably be crystallizable in high yield.
3. The adduct must dissociate at an accessible temperature (preferably between 25 and 150 °C), well below the sublimation temperature of the adduct and the Lewis base.

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4. The dissociation should release as much of the alkyl as possible.
5. The Lewis base should be available in a pure form on a large scale, preferably at low cost.
6. The Lewis base should preferably contain group 15 donor atoms for group 13 metal alkyls or group 16 donor atoms for group 12 metal alkyls to prevent undesirable doping if traces of the Lewis base remain in the alkyl. In practice, efficient separation of the alkyl from the Lewis base generally means that this is not a severe problem.

The necessity for formation of the dissociable adduct between the metal alkyl and the Lewis base places certain limits on the strength of the donor–acceptor bond, which are largely determined by the fact that at the dissociation temperature the alkyls are generally gases and hence ΔS for dissociation is determined largely by the nature of the metal alkyl (Bradley *et al.* 1988*c*). For dissociation to occur within in an accessible temperature range, the value of $\Delta H^{\ominus}$, the bond dissociation energy for the 1:1 adduct must be *ca.* 50 KJ mol^{-1} (Jacobs *et al.* 1986; Bradley *et al.* 1988*a*). In most cases, the adducts are crystalline solids which can be purified by recrystallization. In some cases, however, it is more convenient for the adduct to be formed between the alkyl and a liquid Lewis base and if this is also the reaction solvent, it is possible to carry out the purification as an integral step in the synthetic procedure (Shenai-Khatkhate *et al.* 1986; Jones *et al.* 1984).

To illustrate the processes involved in the purification of a metal alkyl using a liquid Lewis base in which the adduct is soluble, table 2 shows the boiling points of various components in the Me_3Ga–Ph_2O system, together with the dissociation temperature of the adduct and the boiling point of MeI, the latter to illustrate the removal of volatile impurities.

Table 2. Boiling points and dissociation temperature for compounds in the Me_3Ga–Ph_2O–MeI system

compound	boiling point/°C
Me_3Ga	56
MeI	44
$Me_3Ga \cdot OPh_2$	140[a]
Ph_2O	258

[a] Dissociation temperature.

Thus the boiling points of Me_3Ga and MeI are such that their separation so as to give Me_3Ga in the required degree of purity by conventional means would require discarding a substantial proportion of the Me_3Ga. By contrast, on dissolving Me_3Ga in Ph_2O, an involatile adduct is formed, which is stable towards dissociation below *ca.* 140 °C. By pumping on the solution at temperatures up to *ca.* 80 °C all of the methyl iodide and any other volatile impurities will be removed. On heating to 160 °C at 1 atm ($\approx 10^5$ Pa), the adduct dissociates and releases Me_3Ga (b.p. 56 °C). This readily separates from the solvent, and from other impurities that were insufficiently volatile to be removed during the pumping phase, on passage through a short Vigreux column. In this way, Me_3Ga can be purified and high yields of product can be recovered. Even diethyl ether, which binds strongly to the Me_3Ga, can be removed in this way on account of its high volatility (Jones *et al.* 1984).

More generally, crystallizable adducts are formed between the metal alkyl and the Lewis base. These can be recrystallized and purified *in vacuo* to remove soluble and volatile impurities respectively. On heating they dissociate to give the metal alkyl free from impurities. The design of Lewis bases for these purposes is of some difficulty and is illustrated for Me_3In.

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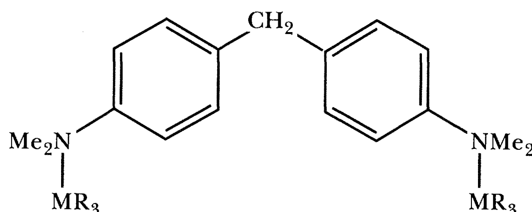
The properties of a range of adducts of Me_3In with Lewis bases are shown in table 3 (Foster *et al.* 1988*a*). Careful examination of this table suggests that stable or dissociable adducts can be formed with Lewis bases in which there are two nitrogen atoms arranged so as to be able to form an adduct with two different Me_3In molecules. Pyridine nitrogen atoms appear to bind strongly so that the adduct sublimes without dissociation (4,4′-bipy) or with dissociation of one Me_3In molecule (3,3′-bipy), whereas Me_2N groups appear to dissociate more readily. This information led to the design of an adduct using Arnold's base (bis(4-dimethylamino-phenyl)methane):



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which is involatile but which can be formed in high yield and dissociated quantitatively to give high purity Me_3In. The same Lewis base can be successfully used for purification of R_3M, R=Me, Et, M=Al, Ga or In (see table 4) (Foster *et al.* 1988*b*).

Table 3. Adducts of trimethylindium with nitrogen containing Lewis bases

(Abbreviations: dman, 1,8-bis(dimethylamino)naphthalene; bipy, bipyridyl; tmpd, 1,4-bis(dimethylamino)-benzene; tmeda, 1,2-bis(dimethylamino)ethane; dmap, 4-dimethylamino pyridine; s, sublimes; d, dissociates.)

base	solvent	base: In	stability
Ph_3N	—	—	—
dman	—	—	—
2,2′-bipy		non-stoichiometric adduct	
3,3′-bipy	Et_2O	1:1	100 s
	petroleum/toluene	1:2	150 d[a]
4,4′-bipy	Et_2O	1:1	70 s
	petroleum/toluene	1:2	80 s
tmpd	Et_2O	1:1	70 s
	petroleum	1:2	100 d[a]
tmeda	Et_2O	1:2	60 s
	petroleum	1:2	60 s
dmap	Et_2O	1:1	80 s
	petroleum	1:1	80 s

[a] Dissociates to give 1:1 adduct.

Table 4. Purification of group 13 trialkyls using Arnold's base (4,4′-methylene bis(N,N'-dimethylaniline))

alkyl	yield of adduct (%)	dissociation temperature/°C	yield of liberated alkyl (%)	overall alkyl recovery (%)
Me_3Al	97	170–220	64	62
Me_3Ga	98	80–130	88	86
Me_3In	89	80–130	97	86
Et_3In	93	120–150	91	85

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Similar arguments have been used in the successful purification of group 13 metal alkyls using 1,2-bis(diphenylphosphino)ethane (diphos) (Bradley *et al.* 1988*c*) as well as in the purification of group 12 metal alkyls using *N*-donor ligands (Jacobs 1986; Shenai-Khatkhate 1986). In the last case, the possibility of polymer formation by bridging Lewis acids is present and this has been utilized successfully because it greatly reduces the volatility of the adducts.

These adduct purification techniques have been of enormous importance in the development of device quality MOVPE grown semiconductors and table 5 shows typical Hall effect results obtained routinely for various semiconductors. Electron mobilities as high as 400000 at 50 K have been obtained in InP grown from Me_3In purified using the 'diphos' route (Thrush *et al.* 1988).

TABLE 5. TYPICAL ELECTRICAL PROPERTIES AT 77 K OF SEMICONDUCTORS GROWN WITH CURRENT PURITY ALKYLS

semiconductor	mobility/($cm^2\ V^{-1}\ s^{-1}$)	carrier concentration/cm^{-3}
GaAs	130000	10^{14}
InP	120000	2×10^{14}
$Cd_xHg_{1-x}Te$ (p-type as grown)	700	$1\text{–}5 \times 10^{16}$
(n-type annealed)	200000	10^{15} ($x = 0.21$)
ZnSe	700	10^{16}

(*c*) *Purification of tellurium alkyls*

Although in general the group 15 or 16 sources used in MOVPE are hydrides (e.g. AsH_3, PH_3, H_2S, H_2Se), H_2Te is insufficiently stable to be useful as a source of tellurium in the growth of, for example, cadmium telluride, mercury telluride or cadmium mercury telluride. However, alkyl tellurium compounds have proved to be suitable with metallic mercury and Me_2Cd generally being the other source materials (see Irvine *et al.* (1988) and references therein). New synthetic techniques have been developed (Shenai-Khatkhate *et al.* 1986, 1988) for these alkyls which give very high quality material; metallic impurities are all below the 50 p.p.b. level (Shenai-Khatkhate *et al.* 1988). This high purity has been attributed to the synthesis being carried out in an aqueous medium because this removes all alkyls of electropositive metals by hydrolysis to the involatile hydroxides. Dialkyltellurium compounds prepared in this way have been used (Thompson *et al.* 1988) to grow very high quality cadmium mercury telluride by the interdiffused multilayer process and these have been used to fabricate devices that are better than those available from any other source of cadmium mercury telluride (Irvine *et al.* (1988) and references therein).

Nevertheless, further improvements in quality would be highly desirable so adduct purification methods have been developed. Here a different strategy is required because tellurium alkyls are Lewis bases and hence the adducting molecule must be a Lewis acid. Dimethyltellurium was quantitatively released from $[AgI(TeMe_2)_2]$ and used for analysis of this complex (Coates 1951). Table 6 shows the properties of a range of Lewis acid adducts with tellurium alkyls which are suitable for purification of the tellurium compounds (Shenai-Khatkhate *et al.* 1988). In general, yields of recovered alkyl are lower than for the acidic metal alkyls and they have not yet been assessed by growth testing. The adducting metal atoms are generally Cd or Hg because contamination with small traces of these will not prove deleterious

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TABLE 6. ADDUCTS FOR THE PURIFICATION OF DIALKYLTELLURIUM COMPOUNDS

adduct used	thermal behaviour/°C melts	thermal behaviour/°C dissociates	yield of dialkyltellurium (%)
$(Et_2Te)_2 \cdot CdI_2$	≈40	90	37
$Et_2Te \cdot (CdBr_2)_2$	—	⩽80	67
$Et_2Te \cdot HgCl_2$	≈100	≈100–120	65
$(Et_2Te \cdot CuI)_n$	—	⩽120	47
$Et_2Te \cdot HgI_2$	45	⩽140	50
$^iPr_2Te \cdot CdI_2$	≈40	⩽130	51
$(^iPr_2Te)_2 \cdot CdBr_2$	—	<125	66

to the grown semiconductor; however, the presence of halide (n-type dopants) could potentially cause a serious problem if any of the adduct or Lewis acid is transported with the released alkyl.

ALTERNATIVE PRECURSORS

(a) *Simple homoleptic metal alkyls*

Methyl compounds of group 13 metals are generally used for atmospheric MOVPE growth of 13/15 semiconductors as higher alkyls tend to decompose at too low temperatures or give problems with pre-reactions or both (Smeets *et al.* (1986) and references therein). By contrast, low-pressure growth is generally carried out using ethyl compounds because methyl compounds lead to increased carbon incorporation in the grown layer (M. D. Scott, personal communication). Clearly, the growth mechanisms must differ in the two different pressure régimes.

For tellurium alkyls, the growth temperature decreases in the order $Me_2Te > Et_2Te > {^iPr_2Te} > {^tBu_2Te}$ (Irvine *et al.* (1988) and references therein). Because higher quality materials are obtained at lower growth temperatures, the best quality material has been grown using $^iPr_2Te$. $^tBu_2Te$ has not been extensively used because its low volatility leads to low growth rates.

(b) *Adducts*

Although the use of adducts for the purification of metal alkyls has already been described, volatile adducts have been successfully used for the growth of semiconductors. Much of the impetus for this work arose from original attempts to grow InP, which were of limited success on account of a pre-reaction that occurred in the gas phase between Me_3In and PH_3 to give a product believed to be polymeric $[MeInPH]_n$ (Didchenko *et al.* 1960). This problem was overcome by using volatile adducts of the form Me_3InER_3 (E=N or P, R=Me or Et) (Moss *et al.* 1981). The Lewis base (ER_3) simply blocked the vacant site on the indium preventing the pre-reaction, but was released intact at some point during the growth process so that, for example, when using NR_3, no nitrogen was incorporated into the layers. More recent evidence suggests that the pre-reaction was catalysed by impurities in the Me_3In because it does not occur when using highly purified Me_3In. The impetus for growth from adducts has therefore subsided.

However, the much lower sensitivity to air, which leads to much safer handling of the adducts compared with the free alkyls and problems of pre-reaction between Me_2Zn and H_2X (X=S or Se), which have recently been reduced using adducts with dioxan or thioxan (Jones *et al.* 1988) may mean that growth from volatile adducts may again become an attractive proposition.

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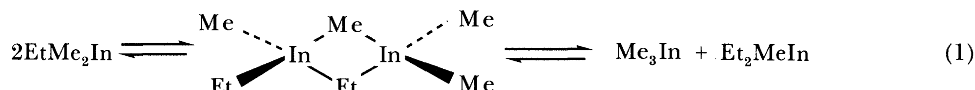
Involatile adducts can be used for the delivery of metal alkyls by the modified entrainment method (MEM) (Battat *et al.* 1974) or by Knudsen dosimetry (Bradley *et al.* 1988*a*), particularly if they release the metal alkyl at temperatures below their melting point. For example, this has been shown to be possible for the adduct between Arnold's base and Me_3In (Foster *et al.* 1988*b*) or between Me_2Cd and 4,4′-bipyridyl (Jacobs *et al.* 1986). However, the rates of evolution of metal alkyl by this method are generally rather low so that growth rates are low. MEM delivery may therefore be more useful for delivery of dopant alkyls.

(*c*) *Mixed alkyl compounds*

All of the preceding discussion has been concerned with homoleptic metal alkyls, that is alkyl compounds in which all the alkyl groups are the same. However, there are certain cases where it may be advantageous to use compounds where the alkyl groups are not all the same. For example, Me_3In is a solid and, as such, can lead to uneven volatilization and delivery. Et_3In is a liquid but is not suitable for MOVPE growth at one atmosphere because it breaks down too readily to indium metal and undergoes severe pre-reactions with phosphine (Smeets *et al.* 1986). It was reasoned, therefore, that a compound such as $EtMe_2In$ should be an ideal precursor because it is a liquid but should have decomposition properties more similar to those of Me_3In. Recent growth studies (Knaut *et al.* 1988) have shown that growth of indium-based materials can be achieved using this precursor. Very recently, however, it has been conclusively shown that $EtMe_2In$ is not a discrete molecule but rather a mixture of compounds undergoing rapid exchange of alkyls by mechanisms similar to that shown in equation (1),



which relies on the formation and cleavage of alkyl-bridged dimers (Bradley *et al.* 1988*b*). This kind of intermediate is well recognized in group 13 alkyls and indeed Me_3Al has a bridged structure in the liquid state, although rapid exchange of bridged and terminal alkyl groups occurs at room temperature.

The consequence of this facile exchange reaction is that, when $EtMe_2In$ is used as a source material for MOVPE, the most volatile component, Me_3In, is removed preferentially from the mixture and, although this means that reasonable growth occurs initially, the rate of transport of indium varies with time and it is very difficult to control the growth process.

Mixed alkyls of tellurium have also been shown to be of interest because, in some cases, lower growth temperatures are possible, without experiencing severe losses in volatility (see table 7) (Irvine *et al.* 1988). Because of the facile alkyl exchange that occurs for group 13 metal alkyls, we have studied the behaviour of mixtures of tellurium alkyls. Table 8 indicates our preliminary results obtained using ^{125}Te nuclear magnetic resonance (NMR) spectroscopy. In some cases alkyl exchange does not occur after the alkyls have been mixed for several weeks,

TABLE 7. GROWTH TEMPERATURES FOR HgTe FROM DIFFERENT ALKYL-TELLURIUMS

alkyl	growth, T/°C
Me_2Te	500
$(allyl)_2Te$	180
MeTe allyl	325[a]

[a] Hg source is Me_2Hg, which controls the reaction.

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TABLE 8. MIXED ALKYL TELLURIUMS FROM SYMMETRICAL DIALKYLS

(*, exchange occurs; ×, exchange does not occur at a measurable rate.)

R/R′	Me	Et	^{i}Pr	^{n}Bu	^{s}Bu	^{i}Bu	^{t}Bu	all	vin
Me	·	×	×	·	·	·	×	×	·
Et	×	·	*	·	×	·	*	·	·
^{i}Pr	×	*	·	·	*	*	·	×	·
^{n}Bu	·	·	·	·	·	·	×	·	·
^{s}Bu	·	×	*	·	·	×	*	·	·
^{i}Bu	·	·	*	·	×	·	·	·	·
^{t}Bu	×	*	·	×	*	·	·	·	×
all	×	·	×	·	·	·	·	·	×
vin	·	·	·	·	·	·	×	·	×

even at 60 °C, whereas in other cases mixed alkyl products can be observed after a few hours and grow until they reach their equilibrium concentration. In general this corresponds to an equilibrium constant for reaction (2) of *ca.* 4†.

$$R_2Te + R'_2Te \rightleftharpoons 2RTeR'. \quad (2)$$

Although these results are preliminary, certain trends are apparent. Firstly, the reactions are under kinetic rather than thermodynamic control. Even in the case of exchange reactions that have not been observed it is possible to make this claim because, for example, MeTe(allyl) can be prepared by another route and is stable towards disproportionation. If the reaction between Me_2Te and $(allyl)_2Te$ did not occur for thermodynamic reasons, MeTe(allyl) would disproportionate to the homoleptic alkyls; secondly, under the stated conditions, Me_2Te, $(allyl)_2Te$ and $(vinyl)_2Te$ do not exchange alkyl groups with any of the tellurium alkyls that we have studied; and thirdly, alkyl exchange appears to be more facile when the alkyls are of similar steric size, although there are certain exceptions to this rule. For example, $^{t}Bu_2Te$ exchanges with Et_2Te whereas $^{i}Bu_2Te$ and $^{s}Bu_2Te$, where the alkyls are of similar steric bulk, do not exchange. Further studies of these exchange reactions are in progress, but their mechanism is unclear. Presumably, it involves the formation of bridging groups using vacant d-orbitals as the acceptor orbitals on tellurium. A possible explanation of the dependence of the exchange reaction might be as follows.

If a small group forms the first bridge, there is insufficient space between the two tellurium atoms for a large group to form the second bridge, whereas if a larger group is present, steric interaction will hold the two tellurium atoms further apart and hence give sufficient space between the two tellurium atoms for another large group to enter and form the second bridge.

Further experimental and theoretical studies are in progress to explain more fully the exchange reactions observed.

EXPERIMENTAL

Homoleptic tellurium alkyls were mixed in approximately 1:1 molar ratios. Their ^{125}Te NMR spectra were recorded on a Bruker Associates AM 300 Fourier Transform NMR spectrometer at intervals over a period of several weeks. In some cases the samples were heated at 60 °C for several days. All quantitative data were obtained by using integrated areas of undecoupled ^{125}Te spectra.

† We thank Dr P. O'Brien (Queen Mary College) for pointing out the correct value of this equilibrium constant.

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Discussion

P. Day, F.R.S. (*Institut Laue Langevin, Grenoble, France*). How is the very high degree of purity measured?

D. J. Cole-Hamilton. Table 9 shows detection limits for a range of different analytical techniques. We currently use inductively coupled plasma optical emission spectroscopy at

Table 9. Possible analytical methods

method	detection limit/p.p.b.
flame atomic absorption	1–100
furnace atomic absorption	0.01–0.1
inductively coupled plasma emission spectroscopy[a]	1–20
inductively coupled plasma mass spectrometry	0.01–0.1
growth + SIMS analysis of layers	(0.001–0.1)

[a] Sample preparation by direct injection.

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Epichem and frequently can see no metallic impurities at all by this technique. We would very much like to use inductively coupled mass spectrometry, but this is not currently available to us. In collaboration with growers, we have grown layers and carried out secondary ion mass spectrometry analysis; this perhaps gives our best indication to date of the possible impurities, but not of their level in the gas phase (see table 1).

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