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REVIEW

CVD of metal organic and other rare-earth compounds

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Three major applications have been found for rare-earth compounds in Metal Organic Chemical Vapour Deposition (MOCVD) or Chemical Vapour Deposition (CVD). Yttrium 2,2,6,6-tetramethyl-3,5-heptanedionates and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionates have been used in conjunction with barium and copper(II) β-diketonates to deposit $YBa_2Cu_3O_{7-\delta}$ as superconducting thin films. Rare-earth fluorides and chlorides have been used for CFD doping of rare earths into MOCVD-deposited ZnS, whilst yttrium chloride has been used, with barium iodide and copper(I) chloride, to produce $YBa_2Cu_3O_{7-\delta}$ superconducting material by CVD. Lanthanoid (Ln) tris(cyclopentadienyl) compounds, $Ln(C_5H_5)_3$ or $Ln(C_5H_4Me)_3$, have been used for doping of rare earths into 13–15 (III–V) semiconductors. Their volatility, structure/volatility relationships, and preparations are discussed. Possible alternative reagents and problems to be faced in doping 12–16 (II–VI) semiconductors are also considered.

Keywords: MOCVD, CVD, rare-earths, lanthanoids, organometallics, β-diketonates, superconductors

1 INTRODUCTION

Metal Organic Chemical Vapour Deposition (MOCVD), alternatively termed OMCVD or MOVPE (Metal Organic Vapour Phase Epitaxy), has become a major route to formation of epitaxial layers of 13–15 (III–V), e.g. GaAs, InP, and 12–16 (II–VI), e.g. ZnSe, $Hg_{1-x}Cd_xTe$ semiconductors (see, for example, Refs 1, 2), and recently has attracted considerable attention as a route to thin films of warm superconductors (e.g. Ref. 3). The current considerable interest in modification and development of properties of 13–15 and 12–16 semiconductors by use of dopants also offers opportunities for use of MOCVD methods. Rare-earth doping is of particular importance since rare-earth ions can undergo electro- and photo-luminescence. Sharp, temperature-independent emission peaks are observed, based on $4f \leftarrow 4f$ transitions.[4,5] This property is useful in rare-earth-doped laser materials, e.g. neodymium in yttrium aluminium garnet (YAG).[6] Potentially, doped materials may provide temperature-stable light sources, such as semiconductor lasers for optical communications. Erbium-doped GaAs produced by MOCVD has been fabricated into light-emitting diodes.[7]

This review deals mainly with the synthesis of warm yttrium superconductors, $YBa_2Cu_3O_{7-\delta}$, by MOCVD and with the selection and use of organolanthanoids as feedstocks for doping of rare earths into 13–15 and 12–16 semiconductors. In the former case, complexes with organic ligands rather than organometallics are used, hence 'metal organic' is used in the literal (both present) rathern than structural (M–C bond present) sense. A short section on use of rare-earth salts in CVD, viz. in superconductor syntheses and doping into MOCVD-deposited ZnS, is also included.

2 SYNTHESIS OF RARE-EARTH SUPERCONDUCTORS BY MOCVD

MOCVD reagents and equipment are too expensive for routine bulk synthesis of $YBa_2Cu_3O_{7-\delta}$ superconductors. However, the method becomes competitive for the preparation of superconductor films, which are required for microelectronics

Table 1 Preparation of $YBa_2CuO_3O_{7-\delta}$ superconducting films by MOCVD[a]

				Deposition		Film treatment			
Volatile MOCVD reagent	Source temp (°C)	Deposition substrate	Reagent gas	Temp. (°C)	Press (mm)	Gas	temp. (°C)	Time h	Ref.
$Y(thd)_3$	100	MgO[100]	$H_2O_{(v)}$	700	5	O_2	600	1.0	9[b]
$Ba(fod)_2$	170						900	1.5	
$Cu(acac)_2$	150						960	0.17	
							Cool	Slow	
$Y(thd)_3$	160	MgO[100]	O_2	780	75		—	—	8,13[c]
$Ba(thd)_2$	260–300	$SrTiO_3$[110]							
$Cu(thd)_2$	140–180								
$Y(thd)_3$[d]	160	MgO	O_2	400	—	O_2	890–920	0.33	14[d]
$Ba(thd)_2$	230–240		$H_2O_{(v)}$				920	0.17	
$Cu(acac)_2$	170						930–650	Fast	
							650–RT	Slow	
$Y(fod)_3$	225[e]	$SrTiO_3$[100]	O_2	500	—	$Ar/H_2O_{(v)}$	825	0.5	15[e]
$Ba(fod)_2$	350		$H_2O_{(v)}$			Ar	900	0.17	
$Cu(acim)_2$	225	Al_2O_3[1102]				O_2	900–400	1.0	
						O_2	400	0.5	
$Y(thd)_3$	125	$SrTiO_3$[100]	O_2	900	5	O_2	Cool	15°C/min	16,17[f]
$Ba(thd)_2$	240								
$Cu(thd)_2$	120								
$Y(thd)_3$	134	$SrTiO_3$[100]	O_2	800	5	O_2	Cool	100°C/min	18[g]
$Ba(thd)_2$	234					or		or	
$Cu(thd)_2$	128	$SrTiO_3$[110]				Air	Cool	5s	
$Y(thd)_3$	110	$SrTiO_3$[100]	O_2	700	1.5	O_2	Cool	20°C/min	19[h]
$Ba(thd)_2$	240								
$Cu(thd)_2$	115								
$Y(thd)_3$	160	YSZ[100]	O_2	650	50	O_2	950	30	20[j]
$Ba(thd)_2$	300					O_2	Cool	4°/min	
$Cu(thd)_2$	170								
$Y(thd)_3$	160	YSZ	O_2	780	5	Ar/O_2	780–400	2	21[i]
$Ba(thd)_2$	260	BaF_2/YSZ				O_2	400–100		
$Cu(thd)_2$	160								

uses. Other methods for films include electron beam and laser evaporation, sputtering, molecular beam epitaxy, spray deposition, and thermal decomposition of 'spun on' coatings.[8,9] Use of metal complexes with organic ligands has not been restricted to MOCVD methods. Thus, metal alkoxides (2-ethylhexanoates and neodecanoates) have been used in 'spun on' coatings to give superconducting films,[10,11] whilst alkoxides and amides have been used in other procedures.[12] MOCVD is claimed to offer the advantages of simplified apparatus, excellent film uniformity, compositional control, high deposition rates and convertibility to large scale, and it is not limited to line-of-sight deposition.[9]

Within a short period, there have been numerous reports of the deposition of films of $YBa_2Cu_3O_{7-\delta}$ by MOCVD.[8,9,13-23] Details of these studies are summarized in Table 1. In each case, an unreactive gas, usually argon, was passed over or through yttrium, barium and copper complexes (generally β-diketonates—Table 1) heated in bubblers to temperatures (Table 1) at which the complexes are sufficiently volatile for transport. The metal complex vapours were mixed and then a gaseous reagent, usually oxygen, admitted just before entry into the reactor chamber. Chemical vapour deposition onto a heated substrate, e.g. $SrTiO_3$[100], Mg[100], yttria-stabilized zirconia (YSZ), was effected at reduced pressure. Either

Table 1 Continued[a]

Volatile MOCVD reagent	Source temp (°C)	Deposition substrate	Reagent gas	Deposition		Film treatment			Ref.
				Temp. (°C)	Press (mm)	Gas	temp. (°C)	Time h	
$Y(thd)_3$	122	$SrTiO_3$[100]	N_2O	650	40	O_2	650–400	0.1	22[k]
$Ba(thd)_2$	256	MgO[100]					400		
$Cu(thd)_2$	136	Si[100]					400–150		
$Y(thd)_3$	150–165	$SrTiO_3$	O_2	900		O_2	550	2	23[l]
$Ba(thd)_2$	280–300								
$Cu(thd)_2$	150–155								
Hthd	100								

[a] Carrier gas Ar unless indicated otherwise. Where alternative deposition substrates are listed, they were generally not equally satisfactory: see specific footnotes.

[b] No detectable CuO, $BaCuO_2$, or $Ba_3Y_4O_9$ impurities. A little BaF_2 detected. Onset superconductivity 90 K, zero resistivity 66 K.

[c] On MgO, onset superconducting 85 K, zero resistivity 65 K. With a deposition temperature of 600°C, no superconductivity phase was obtained. On $SrTiO_3$[110], CuO impurities detected; superconducting film highly oriented, zero resistivity 20 K.

[d] Nitrogen carrier gas used. CuO and possible mixed oxide ($BaCuO_2$, $Ba_3Y_4O_9$) impurities detected. Onset superconductivity 80–36 K, zero resistance 20 K.

[e] Source temperature not given, only delivery line temperature. On $SrTiO_3$[100], CuO impurities detected. Onset superconductivity 90 K, zero resistance 70 K. On Al_2O_3[1102], zero resistance 65 K.

[f] Highly oriented film, *c*-axis perpendicular to plane of substrate. Zero resistivity 84 K, critical current density 2×10^4 A/cm^2.[16] Similar films, T_c 89 K, had critical current densities 4.1×10^5, 1.9×10^5, and 6.5×10^4 A/cm^2 at 2, 10 and 27T respectively.[17]

[g] On $SrTiO_3$[100] with cooling at 100°C/min, T_c 88 K, and transient temperature 5 K; 001 surface parallel to the substrate surface. Quenched (5 s in air) sample, T_c 60 K, orientation similar. On $SrTiO_3$[110], T_c 84 K, 110 surface parallel to the 110 surface of substrate. Quenched sample, onset temperature 75 K, T_c 60 K, similar orientation.

[h] Onset superconductivity 86 K, zero resistivity 83 K; samples grown at higher pressure (3 mm, 10 mm) had superconductivity onset and zero resistivity at lower temperatures.

[i] At 650°C, Y_2O_3, CuO, $BaCO_3$ deposited as a homogeneous mixture. Annealing at 900°C produced $YBa_2Cu_3O_{7-\delta}$. Some $BaZrO_3$ formed at the film/substrate interface. Onset superconductivity 93 K, zero resistance 84 K.

[j] On YSZ, onset temperature *ca* 80 K, zero resistance 50 K. On YSZ/BaF_2, onset temperature *ca* 90 K, zero resistance 80 K (BaF_2 layer deposited by MOCVD on YSZ). CuO impurities in both samples, less on YSZ/BaF_2.

[k] On $SrTiO_3$[100], onset superconductivity *ca* 90 K, zero resistivity 79 K. Higher deposition temperatures gave zero resistivity >79 K. On MgO[100] zero resistivity 65 K. On Si[100], onset superconductivity 30 K, zero resistivity ≤20 K. On $SrTiO_3$[100] with O_2 as the reactant gas, T_c 88 K for growth at 800°C, T_c 68 K for growth at 750°C. Y/Ba and Cu/Ba higher using N_2O than O_2.

[l] Onset temperature, 90 K, zero resistance 68 K. Co-deposition of $BaCuO_2$ occurred with a deposition temperature of 800 K. At <800 K or with deposition on Al_2O_3, superconducting films were not obtained.

Abbreviations: thd, 2,2,6,6-tetramethyl-3,5-heptanedionate; fod, 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate; acac, acetylacetonate; acim, acetylacetoniminate.

superconducting $YBa_2Cu_3O_{7-\delta}$ layers or precursors of the superconductor were deposited, the former being favoured by high deposition temperatures (Table 1). In the latter case, annealing procedures were employed (Table 1) during which the precursors were converted into $YBa_2Cu_3O_{7-\delta}$.

With one exception, β-diketonate complexes have been used as feedstocks for MOCVD. The bulky 2,2,6,6-tetramethyl-3,5-heptanedionate ligand (thd) (also termed dipivaloylmethanate) has had a dominant role (27 out of 33 feedstock complexes in Table 1 are thd derivatives), because the bulky ligands are expected to inhibit association and promote volatility. The readily prepared[24] $Y(thd)_3$ is monomeric[25] and volatile,[26] and functions as an effective feedstock with bubbler temperatures of 100–170°C. 6,6,7,7,8,8,8-Heptafluoro-2,2-dimethyl-3,5-octadionate (fod) complexes are also volatile and the easily prepared[27] $Y(fod)_3$ has been used in one study.[15] Bis(2,2,6,6-tetramethyl-3,5-hepta nedionato)barium(II) is much less volatile than the yttrium analogue,[9] and two groups have preferred $Ba(fod)_2$ as the barium source.[9,15] A source temperature of 170°C was used[9] by contrast with 230–300°C for $Ba(thd)_2$ (Table 1). The lack of volatility of $Ba(thd)_2$ is attributable to an associated structure, and dimeric, trimeric and tetrameric species are detectable in the vapour phase by mass spectrometry.[23] Although the higher volatilization temperatures used for $Ba(thd)_2$ lead to adverse decomposition,[9,15,23] it has been widely and successfully used as the barium source (Table 1). Besides use of the alternative reagent $Ba(fod)_2$,[9,15] there have been two other approaches to the problem of low volatility of $Ba(thd)_2$. Passage of the carrier gas through an Hthd source and then through $Ba(thd)_2$ led to steady evaporative behaviour by contrast with that of $Ba(thd)_2$ alone.[23] However, the sublimation temperature was not lowered. Possibly, a monomeric complex, $[Ba(thd)_2(Hthd)_2]$, is formed. Alternatively, conversion of $Ba(thd)_2$ into eight-coordinate monomeric $Ba(thd)_2(dme)_2$ (dme = 1,2-dimethoxyethane) leads to enhanced volatility,[28] with sublimation at 85–150°C/0.005–0.5 mm and sublimation rates reaching 95%. In addition, co-evaporation of $Ba(thd)_2$ and dme has been achieved at room temperature.[28] Three different copper complexes have been used, with $Cu(thd)_2$ and $Cu(acac)_2$ (acac = acetylacetonate) being sufficiently volatile at 110–180°C and $Cu(acim)_2$ (acim = acetylacetoniminate) requiring a bubbler temperature of 225°C.

Little has been reported on the chemistry of deposition. With $Y(thd)_3$, $Ba(thd)_2$, and $Cu(thd)_2$ or $Cu(acac)_2$ as volatile reagents, high-temperature decomposition in the presence of oxygen[8,13,16–21,23] or nitric oxide[22] presumably involves both pyrolysis and oxidation, whilst use of $H_2O_{(v)}/O_2$ is considered to involve hydrolysis as well.[14] Minimization of the deposition temperature is of considerable interest, but $YBa_2Cu_3O_{7-\delta}$ is not formed if the temperature is too low. Thus, deposition on MgO at 400°C (the lowest temperature used) gave amorphous films. These required annealing at high temperature to give the superconductor, which contained CuO and mixed oxides, possibly $BaCuO_2$ and $Ba_3Y_4O_9$, and had a low zero resistance temperature.[14] Deposition on YSZ at 650°C gave Y_2O_3, CuO, and $BaCO_3$ as a homogeneous mixture, which was converted into $YBa_2Cu_3O_{7-\delta}$ by annealing at 900°C.[20] Use of a relatively low deposition pressure (1.5 mm) enabled high-quality $YBa_2Cu_3O_{7-\delta}$ to be prepared on $SrTiO_3[100]$ at 700°C without need for annealing.[19] Higher pressures gave less satisfactory (lower zero resistivity temperature) film. The deposition temperature can be lowered to 650°C with either $SrTiO_3[100]$ or MgO[100] as substrate by using N_2O rather than oxygen (cf. use of O_2 at 650°C[20]) as the reactant gas.[22] To achieve equivalent film with O_2, a deposition temperature of 800°C was needed.[22] A recent study on pyrolysis of copper(II) hexafluoroacetylacetonate has shown the importance of the oxidant gas in removing carbon. Pyrolysis under argon gave pure copper at 340–390°C, attributed to cleavage of copper–ligand bonds, whereas at higher temperatures carbon incorporation was observed, presumably due to ligand decomposition.[29]

MOCVD with $Ba(fod)_2$[9] or with $Y(fod)_3$ and $Ba(fod)_2$[15] is considered to involve initial deposition of BaF_2 or BaF_2 and YF_3, which are converted into the oxides by reaction with water vapour at high temperatures. When O_2 was used instead of H_2O vapour as the gaseous reactant, large amounts of BaF_2 were deposited.[9] Thermogravimetric experiments have shown that YF_3 but not BaF_2 is converted into the appropriate oxide on treatment with $H_2O_{(v)}$ or $O_2/H_2O_{(v)}$ at 1000°C.[15] Since both deposition and annealing temperatures are below this value, the formation of $YBa_2Cu_3O_{7-\delta}$ must provide a driving force for the reaction. A mixture of YF_3, BaF_2 and CuO underwent hydrolysis with an onset temperature of 550°C in $Ar/H_2O_{(v)}$ and $O_2/H_2O_{(v)}$, but was complete only in the former.

In most preparations, highly oriented films were obtained. $SrTiO_3[100]$, MgO[100], and YSZ were the most commonly used substrates, and in several cases considerable variation in properties was observed with change of substrate (Table 1). Thin films grown on MgO[100] by MOCVD show an ideal ac Josephson effect,[30] and have been used to construct a dc SQUID.[31] A patent describing deposition of $YBa_2Cu_3O_{7-\delta}$ by MOCVD has recently appeared,[32] and plasma-assisted MOCVD of the superconductor has been effected.[33]

3 CVD WITH RARE EARTH SALTS

3.1 Superconductor synthesis

Use of simple metal salts in CVD has the disadvantage that very high temperatures are needed both for the bubblers and for the lines. Yttrium trichloride, barium di-iodide, and cuprous chloride have been carried by argon from sources at 820, 950, and 340°C respectively and react with oxygen/water vapour to deposit $YBa_2Cu_3O_{7-\delta}$ on calcium-stabilized zirconia plates at 740–950°C over 2–4 h.[34] The onset of superconductivity was at 80 K with zero resistivity at 40 K, and, after annealing under oxygen for 48 h at 475°C, zero resistivity was observed at 70 K. A patent has been lodged describing use of chlorine as a carrier gas to transport yttrium, barium and copper for reaction with oxygen to give $YBa_2Cu_3O_{7-\delta}$.[35] Similarly, yttrium oxide has been deposited on silicon or sapphire after transport as YCl_3 by an inert gas or hydrogen and reaction with O_2/water vapour.[36]

3.2 Doping with rare-earth salts

AC-thin film electroluminescent (EL) devices made from manganese-doped ZnS have been widely studied because of the brightness of their yellow–orange colour.[37] Recent reports that rare-earth doped ZnS prepared by electron-beam evaporation or RF sputtering can give different colours with high brightness (e.g. Ref. 38) led to an investigation of the MOCVD route to these new materials.[37] This technique provides an inexpensive preparation for large-area films. Into a standard ZnS deposition system using $ZnMe_2$ and H_2S[39] was introduced LnF_3 (Ln = Tb, Sm or Tm) or $SmCl_3$ vapour.[37] The high melting points of the dopants (Table 2) are a major disadvantage in their use as vapour sources. High brightness was obtained with TbF_3 and $SmCl_3$ (Table 2). The results for the last compound, especially by contrast with SmF_3, contradict a commonly held view that maximum brightness in lanthanoid-doped ZnS requires a fluoride co-activator. Interestingly, the F/Tb ratio for TbF_3-doped ZnS of maximum brightness is considerably less than 3. Annealing at 450–550°C did not change the F/Tb ratio or the brightness. This behaviour contrasts with that of $ZnS(TbF_x)$ devices prepared by sputtering where maximum brightness was obtained with F/Tb = 1. Moreover, annealing at 600°C produced the F/Tb = 1 composition.[40]

Photoluminescence (PL) and electroluminescence (EL) characteristics of MOCVD-prepared $ZnS{:}TbF_x$ have been studied as a function of x.[41] The intensity of PL excitation of 330 nm, which is indirect excitation from the ZnS host to the Tb centre, increases markedly with decrease in x from *ca* 2.0 to *ca* 1.2. By contrast, the intensity of the excitation at 377 nm, which is a direct PL excitation of the Tb centre, is independent of x. Devices prepared from these films have an EL intensity which is independent of x. The difference in x dependence between films prepared by MOCVD and by sputtering has been attributed to differences in sites occupied by fluoride ions.[41]

4 DOPING OF RARE EARTHS INTO SEMICONDUCTORS BY MOCVD

This section is primarily concerned with doping into the 13–15 (III–V) semiconductors InP and GaAs, but the problems to be faced in doping 12–16 (II–VI) semiconductors are also considered. Doping into 13–15 semiconductors should be favoured by the isovalent relationship between the main lanthanoid oxidation state and those of Group 13 and 15 elements. However, size differences, e.g. between Ln^{3+} and Ga^{3+}, and differences in ionic character between lanthanoid and Group 13 compounds are likely to affect structural features. At this stage, work in this area has been dominted by the NTT Electrical Communications and Basic Research Laboratories, Tokyo.

4.1 Deposition methods and conditions

Successful dopants are currently restricted to tris(cyclopentadienyl)lanthanoids, $Ln(C_5H_5)_3$ (Ln = Yb[4,5,42,43] or Er[7,44,45]) and $Ln(C_5H_4Me)_3$ (Ln = Yb[46], Er[45,47] or Nd[48]), but this should change

Table 2 Doping in ZnS using LnF_3 and $LnCl_3$[a]

Dopant	M.p. (°C)	Emission colour	Brightness (Cd/m^2)	Ln[b] (%, w/w)	F/Ln
TbF_3	1172	Green	5000	4–6	1.5–2.2
SmF_3	1306	Red	*ca* 200	—[c]	—[c]
TmF_3	1158	Blue	10	—[c]	—[c]
$SmCl_3$	678	Red	10000	0.3	[c]

[a] Data from Ref. 37. [b] For maximum brightness. [c] Not reported.

as the field develops. In general, the volatile organolanthanoid was carried by hydrogen from sources at *ca* 200°C ($Ln(C_5H_5)_3$) or *ca* 100°C ($Ln(C_5H_4Me)_3$) into a MOCVD reaction chamber in which InP or GaAs was deposited from Et_3In,[5] Me_3In[45] or Me_3InPEt_3[46] and PH_3 or Et_3Ga and AsH_3.[45,47] The lowest source temperature used was 70–90°C for $Yb(C_5H_4Me)_3$.[46] Growth temperatures were 460–700°C,[4,5,44–47] and the substrates used included Fe- or S-doped InP, and undoped or Si- or Cr-doped GaAs.[44,45] In one case, the mole fraction of ytterbium in the reaction chamber was monitored and found to be 10^{-9}–10^{-7}.[46] Dopant levels were in the range 10^{15}–$10^{19}\,cm^{-3}$, doping was uniform except at the surface or the interface with the substrate, and high-quality layers were obtained.[4,5,44–46,48] Ytterbium-doped InP showed n-type conduction[5,46] by contrast with layers grown by liquid-phase epitaxy.[49] It has been suggested that the p-type conductivity associated with the latter may be due to unintentionally incorporated impurities.[5] Variation in the ytterbium content had little effect on conduction; hence doped Yb^{3+} appears electrically inactive.[46] Carrier concentrations were adjusted up to $7 \times 10^{17}\,cm^{-3}$ by doping with sulphur to levels of $7 \times 10^{16}\,cm^{-3}$. Sulphur and ytterbium doping was effected concurrently, the former by introduction of an H_2S flow similar to that used for doping InP with S alone.[46] Electrical properties were similar for samples doped with either $Yb(C_5H_5)_3$[5] or $Yb(C_5H_4Me)_3$.[46]

Similar photoluminescence (PL) spectra were observed between samples doped with $Ln(C_5H_5)_3$[5,45] or $Ln(C_5H_4Me)_3$.[45,46] Sharp lines attributable to $f \leftarrow f$ transitions were generally observed[5,43–48] and the intensity has been related both to the dopant concentration (e.g. Refs 5, 45) and to the gas-phase mole fraction.[46] However, the intensity of $f \leftarrow f$ emissions for Nd-doped GaAs are nearly concentration-independent.[48] For a constant AsH_3/Et_3Ga mole ratio (30:1) in the feedstock, considerable sharpening of the photoluminescence spectra was achieved by lowering the deposition temperature progressively from 550 to 500 to 460°C.[47] A similar sharpening was observed on lowering the AsH_3/Et_3Ga ratio from 30:1 to 3:1. Similar deposition temperature-dependence of PL spectra has been found for GaAs:Er grown by molecular-beam epitaxy.[50] These observations are relevant to the preparation of materials suitable for devices. Indeed, erbium-doped GaAs has been fabricated into light emitting diodes. The wavelength of the $f \leftarrow f$ maximum is shifted by <1 nm from 180 K to 296 K, indicating that the materials are suitable for temperature-stable light sources.[7]

4.2 Selection of organolanthanoids for MOCVD doping into 13–15 semiconductors

4.2.1 Volatility of feedstocks

Tris(cyclopentadienyl)lanthanoids are air- and moisture-sensitive but this is not a specific disadvantage of these compounds, since all organolanthanoids display similar behaviour.[51–53] All simple $Ln(C_5H_5)_3$ compounds are volatile. Their vapour pressures (including Ln = Sc) have been determined,[54–58] except for Ln = Pm or Eu, and the equations for the vapour pressures are also listed in *Gmelin's Handbook*.[53] For the more volatile $Ln(C_5H_4Me)_3$ compounds, quantitative vapour pressure data are available only for Ln = Yb.[46] Vapour pressures have also been determined for the tris(isopropylcyclopentadienyl)lanthanoids, $Ln(C_5H_4Pr^i)_3$ (Ln = La, Pr or Nd),[59] and these are markedly more volatile than $Ln(C_5H_4R)_3$ (R = Me or H). The cerium complex $Ce(C_5H_4Pr^i)_3$ has been recently prepared and is also volatile.[60]

In Table 3 are listed vapour pressures of representative cyclopentadienyl- and monosubstituted cyclopentadienyl–lanthanoid complexes. Values are given for 27°C (near storage temperature), 100°C (a temperature suitable for MOCVD of $Ln(C_5H_4Me)_3$ complexes[45–47]), and 227°C (a temperature near those used for $Ln(C_5H_5)_3$ complexes[45,47]). At room temperature and 100°C, the most volatile compound is clearly $Nd(C_5H_4Pr^i)_3$, but $Yb(C_5H_4Me)_3$ is most volatile at 227°C (Table 3). The vapour pressure of $Yb(C_5H_4Me)_3$ is low at 90–100°C and it is surprising that an MOCVD bubbler at these temperatures[46] generates sufficient vapour for effective doping.

4.2.2 Structure/volatility relationships

The vapour pressures of $Ln(C_5H_5)_3$ increase from Ln = La to a maximum at Ln = Yb with a reduction at Ln = Lu[61] (Table 2), whilst the value for Ln = Y is similar to that for Ln = Tm or Er, consistent with the similar sizes of Tm^{3+}, Er^{3+} and Y^{3+}.[62] The variation in vapour pressure with atomic number can be correlated with the structures of the tris(cyclopentadienyl)lanthanoids.[61] Representative structures are shown in Fig. 1. The least volatile complex (Table 3), $La(C_5H_5)_3$, has a

Table 3 Vapour pressures of lanthanoid cyclopentadienyls[a]

Compound $Ln(C_5H_4R)_3$	Pressure, *P* (mm) 27°C	100°C	227°C
$Y(C_5H_5)_3$	9.6×10^{-7}	2.3×10^{-3}	7.6
$La(C_5H_5)_3$	1.3×10^{-8}	3.7×10^{-5}	0.16
$Nd(C_5H_5)_3$	4.7×10^{-10}	1.9×10^{-5}	1.2
	1.2×10^{-8}	6.2×10^{-5}	0.46[b]
$Sm(C_5H_5)_3$	3.0×10^{-8}	1.6×10^{-4}	1.3
$Er(C_5H_5)_3$	1.3×10^{-6}	2.7×10^{-3}	7.8
$Tm(C_5H_5)_3$	9.7×10^{-7}	5.0×10^{-3}	38
	1.2×10^{-6}	2.7×10^{-3}	9.0
$Yb(C_5H_5)_3$	2.1×10^{-6}	3.9×10^{-3}	10
$Lu(C_5H_5)_3$	2.1×10^{-8}	3.3×10^{-4}	7.7
$Yb(C_5H_4Me)_3$	1.2×10^{-6}[c]	9.5×10^{-3}[c]	108[c]
$La(C_5H_4Pr^i)_3$	0.12[d]	1.4[d]	19[d]
$Nd(C_5H_4Pr^i)_3$	0.75[d]	5.1[d]	37[d]

[a] Interpolated and extrapolated from log *P* (mm) = *A* − *B*/*T*(K) data in Ref. 53, compiled from Refs 54–58, unless indicated otherwise. Where two values are given, the first is from Ref. 55 and the second from Ref. 57 (Ln = Nd) or Ref. 56 (Ln = Tm). The vapour pressure equations were derived from measurements in quite different temperature ranges, hence some variation in extrapolated values is not surprising.

[b] The value for *B* (5961)[53] is incorrect and should be 5691.[57]

[c] From data in Ref. 46.

[d] From data in Ref. 59.

polymeric structure (Fig. 1a), in which each lanthanum has two non-bridging η^5-C_5H_5 ligands, one bridging μ-η^5:η^2 ligand, and one bridging μ-η^2:η^5 ligand and the formal coordination number is 10 or 11.[63] Longer bonds are observed to the bridging ligands than the terminal ligands. A related but more disordered structure is observed for $Pr(C_5H_5)_3$.[64] With the decline in ionic radius to thulium,[62] a different structure is observed (Fig. 1b).[65] Each thulium is surrounded by two terminal η^5-C_5H_5 ligands, one μ-η^5:η^1-C_5H_5 ligand, and one μ-η^1:η^5-C_5H_5 group. The intermolecular Tm · · · C bonds are particularly long, the shortest[65] being *ca* 0.2 Å (0.02 mm) longer than the longest for $La(C_5H_5)_3$.[63] Thus, although the coordination number is 10, intermolecular forces are weak. With the slightly smaller ytterbium, a monomeric nine-coordinate structure with pseudotrigonal stereochemistry is observed.[66] The shortest intermolecular Yb · · · C contacts (Fig. 1c) are extremely long (>4.0 Å) and are clearly non-bonding. A similar structure is observed for $Yb(C_5H_4Me)_3$[61] (Fig. 1e). The further decrease in size with lutetium leads to a lower coordination number, which is obtained by adoption of a polymeric structure (Fig. 1d). Each lutetium has two η^5-C_5H_5 terminal ligands and two μ-η^1:η^1 bridging groups giving overall eight-coordination.[67] In an alternative representation of the structural data,[61] it has been shown that the bond length difference between Ln–C_{br} (or the shortest intermolecular contact) and Ln–C_{ter} increase from $La(C_5H_5)_3$ to $Tm(C_5H_5)_3$ and then dramatically to monomeric $Yb(C_5H_5)_3$. Thus, the decrease in ionic radius from La to Lu leads to a decrease in coordination number from $La(C_5H_5)_3$ to $Lu(C_5H_5)_3$ and a change from polymeric structures to monomeric (Ln = Yb) and then to a lower-coordinate polymeric structure (Ln = Lu). This accounts for an increase in vapour pressure from $La(C_5H_5)_3$ to a maximum with $Yb(C_5H_5)_3$, followed by a decline with $Lu(C_5H_5)_3$ (Table 3).

4.2.3 Synthesis of feedstock organometallics

A further attractive feature of lanthanoid cyclopentadienyls as MOCVD dopant feedstocks is the availability of comparatively simple (for air-sensitive compounds) syntheses. For $Ln(C_5H_4R)_3$ (R = H, Me, or Pr^i), the classical metathesis reaction with an alkali-metal cyclopentadienide in tetrahydrofuran is satisfactory.[59,68,69]

$$LnCl_3 + 3MC_5H_4R \rightarrow 3MCl\downarrow + Ln(C_5H_4R)_3 \qquad [1]$$

$$M = Na \text{ or } K$$

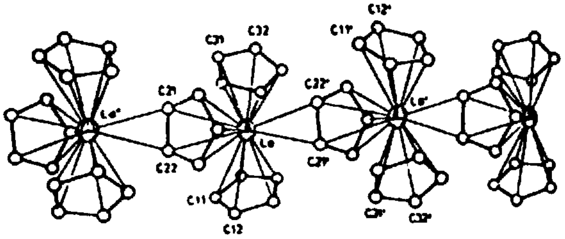
Sublimation under vacuum is a satisfactory purification method and removes coordinated tetrahydrofuran. Use of air- and water-sensitive reagents (reaction [1]) can be avoided by use of two redox transmetallation reactions in tetrahydrofuran.[70–73]

$$2Ln + 3Hg(C_5H_5)_2 \rightarrow 2Ln(C_5H_5)_3 + 3Hg\downarrow \qquad [2]$$

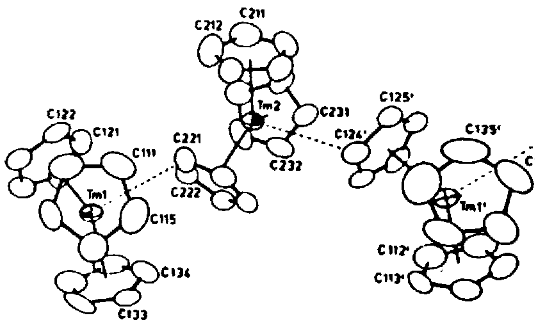
$$Ln + 3Tl(C_5H_4R) \rightarrow Ln(C_5H_4R)_3 + 3Tl\downarrow \qquad [3]$$

$$(R = H \text{ or } Me)$$

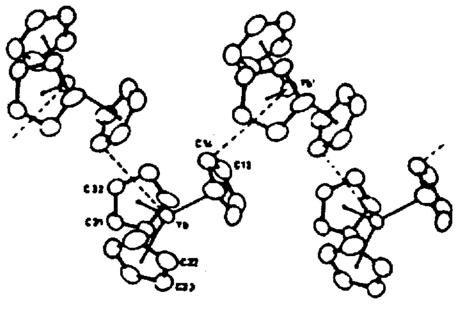
Reaction [3] has an advantage over [2] for $Ln(C_5H_5)_3$ because thallous cyclopentadienide is easier to prepare and has better storage characteristics than bis(cyclopentadienyl)mercury.[74,75] Although europium fails to react with $Tl(C_5H_5)$ in tetrahydrofuran, reaction can be achieved in pyridine.[73] A still more recent method[76] enables $Ln(C_5H_5)_3$ derivatives to be prepared at room temperature from the lanthanoid metal, the easily prepared bis(pentafluorophenyl)mercury,[77] and



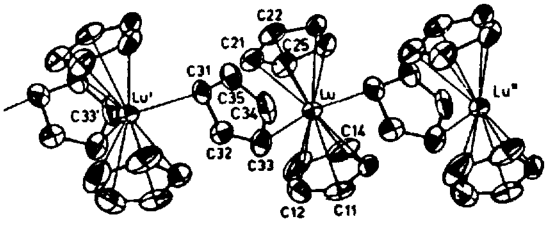
a. $La(C_5H_5)_3$[63]



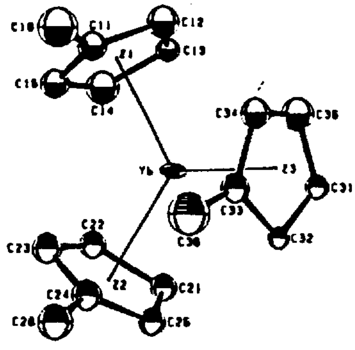
b. $Tm(C_5H_5)_3$[65]



c. $Yb(C_5H_5)_3$[66]



d. $Lu(C_5H_5)_3$[67]



e. $Yb(C_5H_4Me)_3$[61]

Figure 1 Structures of some tris(cyclopentadienyl)lanthanoids. Reproduced with permission from (a) Ref. 63, *Organometallics* Copyright (1986) American Chemical Society (b) *J. Organomet. Chem.*, Elsevier Sequoia S.A., Lausanne (c) Ref. 66, *Acta Crysta C.*, International Union of Chemistry (d) Ref. 67, *Angew. Chem., Int. Ed.*, VCH (e) *J. Organomet. Chem.*, Elsevier Sequoia S.A., Lausanne.

cyclopentadiene.

$$2Ln + 3(C_6F_5)_2Hg + 6C_5H_6 \rightarrow 2Ln(C_5H_5)_3 + 6C_6F_5H + 3Hg\downarrow \qquad [4]$$

Two tris (*t*-butylcyclopentadienyl)lanthanoids, $Ln(C_5H_4Bu^t)_3$ (Ln = La or Sm), which may also be of interest as MOCVD feedstocks, have been prepared by reaction [1] ($R = Bu^t$).[78] No indication of the volatility was given. The derivative of the largest lanthanoid was isolated as a THF complex, $La(C_5H_4Bu^t)_3(THF)$, samarium gave the unsolvated $Sm(C_5H_4Bu^t)_3$, whilst $[Lu(C_5H_4Bu^t)_2Cl]_2$ was obtained from an attempted preparation of $Lu(C_5H_4Bu^t)_3$. Thus, the change in lanthanoid ion size has a major effect on the preparative chemistry with the bulky *t*-butylcyclopentadienyl ligand.[78]†

4.2.4 Thermal decomposition of feedstock organometallics

The successful use of $Ln(C_5H_5)_3$ and $Ln(C_5H_4Me)_3$ as MOCVD dopants indicates that the complexes decompose smoothly at 460–700°C (the deposition temperature range) under hydrogen with no significant carbon retention. There do not appear to have been independent studies of decomposition of the feedstocks in a hydrogen atmosphere. However *gas-phase* pyrolysis of $Ln(C_5H_5)_3$ ($Ln = Y$, La, or Nd) has been carried out at *ca* 520–570°C.[79] The thermal stability is between that of ferrocene and other 3*d* metal cyclopentadienyls. Decomposition in the gas phase under static conditions follows first-order kinetics for 70–80% conversion ($Ln = Y$ or La) or 40–50% conversion ($Ln = Nd$). The rate of reaction for $Ln = La$ is increased by the presence of solid pyrolysis products on the walls, but there is no effect for $Ln = Nd$. Hydrogen is the major gaseous product and is the primary decomposition product. As the reaction proceeds, there is an increase in the gaseous concentration of methane, ethane, and ethylene, possibly due to reaction of hydrogen with solid pyrolysis products. The solid products are rich in hydrogen, and yield hydrogen and methane (7:3) at 650°C. Heating the solid film in hydrogen yields methane. This is consistent with the view that hydrocarbons result from secondary processes,[79] and is highly relevant to successful doping without carbon retention by $Ln(C_5H_5)_3$ in hydrogen. There has been a detailed study of electron-impact-induced breakdown of $Ln(C_5H_4Me)_3$ complexes (Paolucci, G, Fischer, R D, Breitbach, H, Pelli, B and Traldi, P *Organomet.*, 1988, 1918).

4.3 Selection of organolanthanoids for doping into 12–16 semiconductors

Although CVD of rare-earth salts into ZnS has been carried out (see above), MOCVD doping into CdTe or $Hg_{1-x}Cd_xTe$ has not been achieved. Tris(cyclopentadienyl)lanthanoid(II) compounds do not have an isovalent relationship with Hg, Cd, and Te. More importantly, multilayer deposition of $Hg_xCd_{1-x}Yb$, as required in material for some devices, is effected at 300–400°C, which is well below the decomposition temperatures of $Ln(C_5H_4R)_3$. Higher temperatures lead to interdiffusion, the production of homogeneous materials (which may be desirable in some applications), and loss of mercury from $Hg_{1-x}Cd_xTe$. These strictures do not apply to doping of CdTe.

Isovalent doping has to be restricted to Sm, Eu, and Yb, the only elements with a stable Ln(II) state. No quantitative volatility data appear available for organolanthanoid(II) complexes. Of Ln $(C_5H_5)_2$ complexes, only $Yb(C_5H_5)_2$ has been reported to sublime, viz. at 360°C under high vacuum with substantial decomposition,[80] and this is unsatisfactory for MOCVD. Monomeric $Ln(C_5Me_5)_2$ ($Ln = Sm$,[81,82] Eu[82] or Yb[83]) complexes are volatile at *ca* 100°C, but a vacuum of 10^{-4}–10^{-5} mm is required. Clearly there is a fruitful field of synthetic endeavour to attempt to obtain LnR_2 complexes of suitable volatility and thermal stability.

Zerovalent compounds, e.g. bis(diazadiene)-lanthanoid(0)[84] and bis(arene)lanthanoid(0)[85–87] complexes, may be of interest. The compounds are prepared by metal-atom vapour methods.

$$Ln_{(v)} + 2L_{(v)} \xrightarrow{\text{condense}} LnL_2 \qquad [5]$$

Although this is not a simple laboratory procedure, it could probably be adapted for large-scale use. Sublimation at *ca* 100–130°C/7 × 10^{-5} mm has been achieved for the diazadiene complexes ($Ln = Y$, Nd, Sm, Yb)[84] and some bis(arene) complexes ($Ln = Y$, Gd, Nd, Tb, Dy, Ho, Er or Lu).[84] The latter compounds have been decomposed in the gas at *ca* 130°C to deposit a metal film and some impurities.[84] Better transport and decomposition may be possible in a hydrogen stream.

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† Note added in proof: The highly volatile $Yb(C_5H_4Pr^i)_3$ (m.p. 47°C, b.p. 160°C/0.75 × 10^{-5} mm) has been prepared from $KC_5H_4Pr^i$ by reaction [1] and doped into InP by MOCVD with hydrogen as the carrier gas, a bubbler temperature of 50–80°C and a growth temperature of 580–670°C. Better surface morphology and high photoluminescence intensities were observed for the InP:Yb layers than when $Yb(C_5H_4Me)_3$ was used. (Weber, J, Moser, M, Stapor, A, Scholz, F, Hörcher, G, Forchel, A, Bohnert, G, Hangleitor, A, Hammel, A, and Weidlein, J *J. Cryst. Growth*, 1990, 100: 467.

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