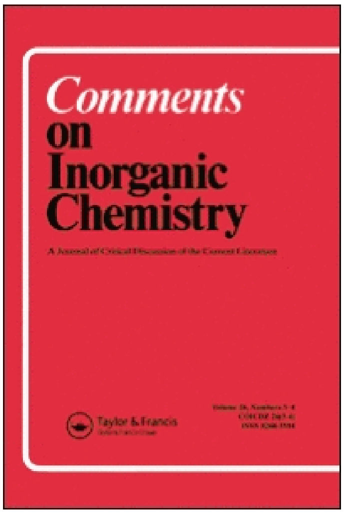
This article was downloaded by:
On: *15 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Organolanthanides in Materials Science

Yurii K. Gun'ko[a]; Frank T. Edelmann[a]
[a] Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, Magdeburg, Germany

To cite this Article Gun'ko, Yurii K. and Edelmann, Frank T.(1997) 'Organolanthanides in Materials Science', Comments on Inorganic Chemistry, 19: 3, 153 — 184

To link to this Article: DOI: 10.1080/02603599708032734

URL: http://dx.doi.org/10.1080/02603599708032734

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Organolanthanides in Materials Science

YURII K. GUN'KO and FRANK T. EDELMANN
Chemisches Institut der Otto-von-Guericke-Universität Magdeburg,
Universitätsplatz 2,
D-39106 Magdeburg, Germany

Received August 25, 1996

Various uses of organolanthanide complexes in materials science are reviewed. The most advanced application involves doping of III–V semiconductors using substituted tris(cyclopentadienyl)lanthanide complexes as precursors. Major efforts have been made to develop volatile liquid organolanthanides by introducing suitable substituents on the cyclopentadienyl rings. Lanthanide organometallics have also been demonstrated to be useful MOCVD precursors for the deposition of lanthanide oxide thin films.

Key Words: *organolanthanide complexes, materials science, III–V semiconductors, MOCVD precursors, sandwich complexes*

1. INTRODUCTION

In recent years, the importance of yttrium and the lanthanides in fabrication and modification of new materials has increased substantially. Rare earth elements are used in the creation of high-T_c superconductors, semiconductors, sensors, electrooptical ceramics, and optical materials. Different lanthanide precursors and their applications in materials science have recently been compiled in two review articles.[1,2] The purpose

---

Comments Inorg. Chem.
1997, Vol. 19, No. 3, pp. 153–184
Reprints available directly from the publisher
Photocopying permitted by license only

of the present work is to consider some properties and aspects of using organolanthanide complexes which contain metal–carbon bonds. This particular area is currently not well developed. However, recent investigations show that this is an area which offers a great potential for novel and useful applications.

2. ORGANOLANTHANIDES AS DOPING MATERIALS FOR III–V SEMICONDUCTORS

Lanthanide elements incorporated into semiconductor host materials have attracted high interest. As all lanthanides have a typical oxidation state +3, they should be suitable for doping III–V semiconductors. In fact, this is currently the most advanced application of organolanthanide complexes in materials science. Inneratomic optical transitions of lanthanides are well-defined and insensitive to temperature and influences of the host material, because they are screened by the outer electronic shells. Nevertheless, they can be excited optically and electrically via the semiconductor host materials.[3–6] Observation of strong infrared intra-4*f*-shell luminescence in rare-earth-doped III–V semiconductors has increased interest in the materials for their application in injection-type optical devices such as semiconductor lasers, optical amplifiers and light emitting diodes.[4,7–11]

2.1. Methods and Devices

The most important methods for obtaining doped semiconductor layers are Liquid Phase Epitaxy (LPE), Vapor Phase Epitaxy (VPE), Molecular Beam Epitaxy (MBE), and ion implantation. The use of lanthanides in elemental form for doping of semiconductors by liquid phase epitaxy led only to rather low doping concentrations.[12,13] High concentrations can be attained by employing the ion implantation method,[14–17] but only in locally defined small regions. New modern methods such as Molecular Beam Epitaxy (MBE),[18–20] Metal-Organic Chemical Vapor Deposition (MOCVD) or Metal-Organic Vapor Phase Epitaxy (MOVPE) allow the incorporation of high lanthanide concentrations in a wide range of semiconductor host materials.

The advantage of using organometallic sources can be either safety, improved thermal stability, better input control, improved decomposition characteristics or the reduction of unwanted side reactions before the reactants reach the susceptor. The surface quality of MOVPE samples is much better than that of LPE-grown layers with LPE typical defects, which result from inevitable rare earth precipitates in the melt.

Utilization of MOVPE requires a reactor constructed with considerable attention paid to various technical details. All MOVPE reactors[21] comprise several sections: a gas handling section for controlling the input gases; a reactor tube with a susceptor that is either heated with RF or by IR radiation; and some type of exhaust arrangement, which may include a vacuum pump system for low pressure operations (Fig. 1). The heart of the reactor is the reaction chamber tube, called an RF cell (Fig. 2). The cell can be orientated either vertically or horizontally relative to the gas flow direction. The susceptor shape can be a flat rectangular slab with some smoothing of its leading edge, a cylindrical disk, or a truncated polygon, which is called a barrel reactor and favored for larger capacity systems. The most common tubes are of the horizontal type with a simple susceptor placed parallel to the gas stream.

2.2. Requirements for Semiconductor Doping Precursors

The MOVPE method requires the simple control of most properties of the growing structure via the independent control of the gas flows of the different precursors. This requirement can easily be fulfilled for the Group V and VI elements of the periodic system with hydrides such as PH_3, AsH_3 or H_2S. Thus, when rare earth elements are to be used as dopants, the development of suitable precursors represents a major problem. Such compounds should fulfill many requirements such as an acceptable substantial vapor pressure, chemical stability, high purity, and release of the desired element (and only it) at normal MOVPE growth conditions. Liquids can be handled much more easily in MOVPE bubblers than solids; therefore rather low melting points are needed. Only very few classes of organometallic rare earth compounds are known which might meet at least some of these demands.[1,21,22] In general, organolanthanide complexes are known to be highly air-sensitive though thermally very robust high-melting materials. High melting points in the range of 150–350°C are common, and the design of volatile, low-melting precursors is a synthetic challenge.

2.3. Tris(cyclopentadienyl)lanthanide Complexes as Precursors for Doping of III–V Semiconductors

Synthesis, structure, volatility and application of tris(cyclopentadienyl)lanthanides have already been discussed in a review article by Deacon *et al.*[1]

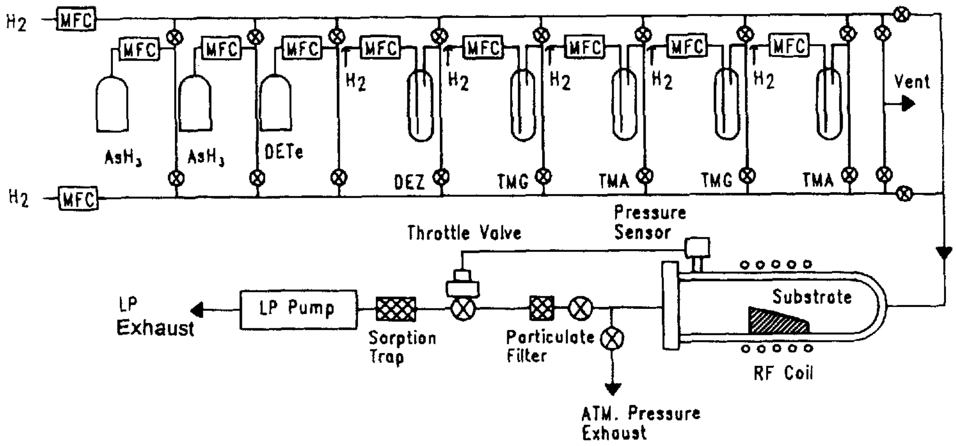


FIGURE 1 Scheme of a low pressure MOVPE reactor.

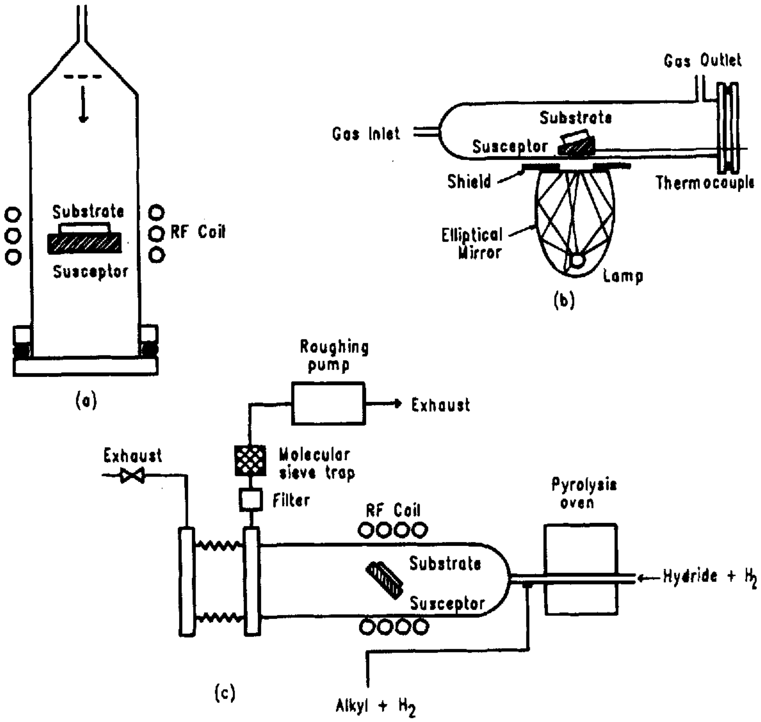


FIGURE 2 Various types of MOVPE reaction tubes (a–vertical, b–horizontal, c–horizontal low pressure cell).

However, a large amount of new information about the compounds has accumulated in recent years, and we would like to emphasize some new aspects.

2.3.1. Synthesis of tris(cyclopentadienyl)lanthanides

The first tris(cyclopentadienyl)lanthanide complexes[23] were obtained by the reaction of anhydrous $LnCl_3$ with three equivalents of NaC_5H_5 in THF followed by sublimation of the compounds from the dry reaction mixture at 200–250°C (10^{-4} torr):

$$\mathrm{LnCl_3 + 3NaC_5H_5 \xrightarrow{THF} Ln(C_5H_5)_3 + NaCl} \qquad (1)$$

$Ln(C_5H_5)_3$ (Ln = Tb, Ho, Tm, Lu) compounds have been synthesized in a similar manner from the $LnCl_3$ and NaC_5H_5 or KC_5H_5 but in Et_2O or benzene.[24,25] $Ln(C_5H_5)_3$ can also be obtained by the reaction of $Mg(C_5H_5)_2$ (or $Be(C_5H_5)_2$ [26]) with $LnCl_3$,[26] LnI_3 [27] or LnF_3.[27,28] $Ln(C_5H_5)_3$ derivatives have been prepared starting from lanthanide metals by transmetalation reactions with $Hg(C_5H_5)_2$ or with TlC_5H_5 in THF solution:[29–32]

$$2Ln + 3Hg(C_5H_5)_2 \longrightarrow Ln(C_5H_5)_3 + 3Hg \qquad (2)$$

Various substituted tris(cyclopentadienyl)lanthanide complexes can be prepared in a similar manner from the appropriate lanthanide trichlorides and alkali-metal cyclopentadienides in THF solution. However, this traditional route is often not applicable for the synthesis of tris-Cp-lanthanide complexes with bulky Cp ligands which contain two or more substituents in the rings. In this case, tris(cyclopentadienyl)lanthanide complexes can be obtained by using a Bronsted acid-base reaction in diethyl ether:[33]

$$\begin{aligned} &Ce\left[N(SiMe_3)_2\right]_3 + 3(Me_3Si)_2C_5H_4 \longrightarrow \\ &\qquad Ce\left[(Me_3Si)_2C_5H_3\right]_3 + 3(Me_3Si)_2NH \end{aligned} \qquad (3)$$

Tris(neopentylcyclopentadienyl) neodymium has been prepared analogously through the reaction of the neodymium silylamide $Nd[N(SiMe_3)_2]_3$ with the appropriate cyclopentadiene derivative.[34]

$Sm[(Me_3Si)_2C_5H_3]_3$ has been synthesized from $SmCl_3$ and $KC_5H_3(SiMe_3)_2$ by refluxing the mixture in toluene for 24 hrs.[35] $Sm(C_5Me_5)_3$ was obtained from the reaction between $Sm(C_5Me_5)_2$ and cyclooctatetraene in toluene:[36]

$$2Sm(C_5Me_5)_2 + C_8H_8 \longrightarrow Sm(C_5Me_5)_3 + (C_5Me_5)Sm(C_8H_8) \qquad (4)$$

Another way of preparing lanthanide complexes with three bulky Cp ligands has recently been proposed by Chadwick and Andersen:[37]

$$\begin{aligned} &2Ce(OSO_2CF_3)_3 + 3Mg(R_2C_5H_3)_2 \longrightarrow \\ &2Ce(R_2C_5H_3)_3 + 3Mg(OSO_2CF_3)_2 \\ &R = SiMe_3, Bu^t \end{aligned} \qquad (5)$$

All these tris(cyclopentadienyl)lanthanide complexes can be easily purified by sublimation under vacuum.

2.3.2. Thermal behavior of tris(cyclopentadienyl) lanthanides

Tris (cyclopentadienyl)lanthanides are volatile compounds. As was already shown,[1] the volatility of tris (cyclopentadienyl) lanthanides largely depends on the structures of the compounds. Most volatile complexes have monomeric structures (or very long intermolecular contacts); less volatile species are of polymeric nature. The volatility of $Ln(C_5H_5)_3$ has been found to increase when going from lanthanum to ytterbium. Vapor pressures of $Ln(C_5H_5)_3$, $Yb(C_5H_4Me)_3$ and $Ln(C_5H_4Pr^i)_3$ (Ln = La, Nd) have been reported in the literature.[1,38–41] Volatility also varies greatly depending on the Cp-ligand type. The dependence of volatility from the substituents on the cyclopentadienyl rings is shown in Fig. 3 for different tris(cyclopentadienyl)neodymium complexes.[34] Complexes with isobutyl- and tert-butyl-substituents in the rings exhibit the highest volatility. High volatility has also been reported for lanthanide complexes containing the $Me_3SiC_5H_4$

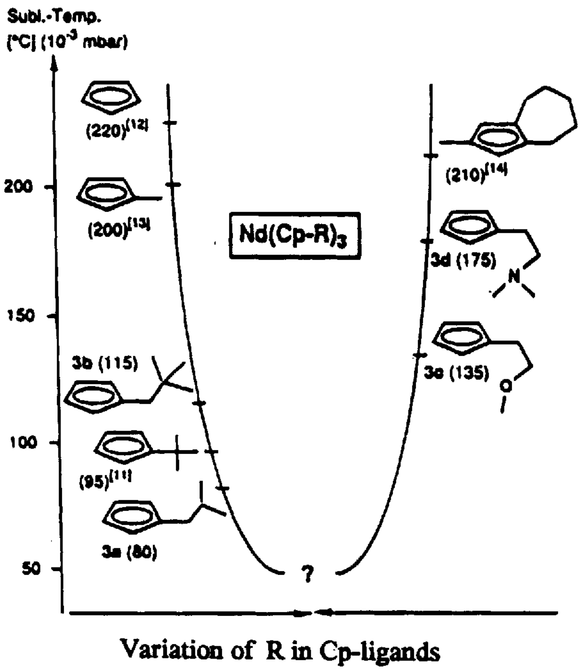


FIGURE 3 Dependence of volatility from the nature of substituents in the cyclopentadienyl rings for $Nd(Cp\text{-}R)_3$.

ligand; for example, $Ce(Me_3SiC_5H_4)_3$ sublimes at 60°C/10^{-3} torr.[33] $Ln(Bu^tC_5H_4)_3$ (Ln = Nd, Dy, Tm) have sublimation temperatures lower than 110°C/10^{-3} torr.[42] Concerning Cp ligands with functional substituents such as OMe and NMe_2, for optimal volatility all donor groups should be coordinated to the central lanthanide ion.[34]

From thermogravimetric and mass-spectroscopic investigations of the tris(*tert*-butylcyclopentadienyl) lanthanides $Ln(Bu^tC_5H_4)_3$ (Ln = Nd, Dy, Tm),[42] competitive processes between volatility and the tendency to form non-volatile derivatives in the residue were proposed (Fig. 4). MOCVD experiments with the compounds (substrate temperature 120–200°C, 0.36 torr, bubbler temperature 400°C, argon flow) yielded a metallic mirror in the reactor besides gaseous and liquid products such as *tert*-butylcyclopentadiene, isobutane, isobutene and methane as determined by GC.[42]

2.3.3. $Ln(C_5H_5)_3$ sources for doping of III–V semiconductors

The first MOCVD and MOVPE experiments designed for growing rare-earth-doped III–V semiconductors were carried out using $Yb(C_5H_5)_3$

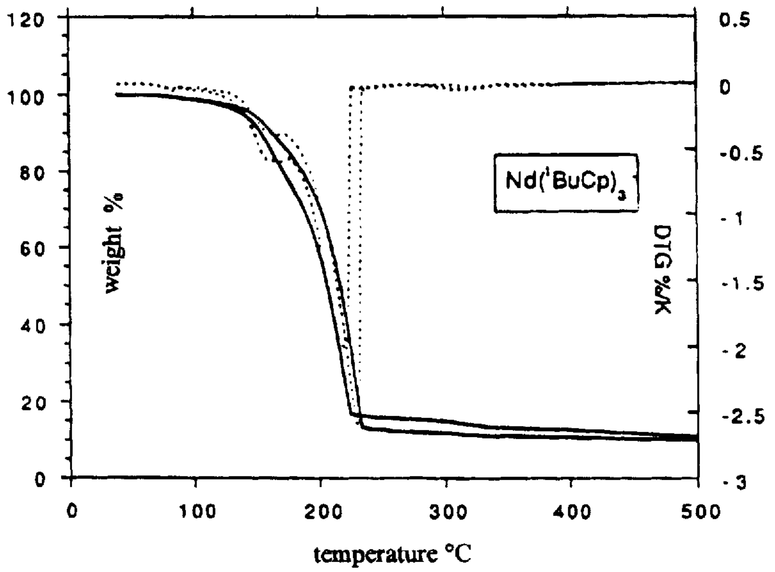


FIGURE 4 Thermogravimetry- and DTG-curves of the $Nd(^tBuCp)_3$ complex.

and $Er(C_5H_5)_3$ as precursors.[43–48] Most of the experiments were focused on the system InP:Yb because it was thought to play the role of a characteristic model for rare earth metals in III–V semiconductors. Ytterbium occupies an indium lattice site[49–52] because of its similar ionic radius. Moreover, the electronic transitions of Yb can be easily described, as only one electron is missing in the 4f shell. Er-doped III–V semiconductors are also very interesting for applications in optoelectronic communication due to a characteristic inneratomic transition ($^4I_{1\,3/2} \rightarrow {}^4I_{1\,5/2}$) at 1.54 μm (0.805 eV), which is close to an optical window of the glass fibers.[7]

Ytterbium-doped InP (InP:Yb) samples were obtained by using $Yb(C_5H_5)_3$ as lanthanide source.[43,46,48] The InP:Yb epitaxial layers have been grown by low-pressure (0.1 atm) MOCVD in a horizontal quartz reactor using trimethylindium or triethylindium, phosphine and $Yb(C_5H_5)_3$ as doping material. Ytterbium-doping was achieved by subliming and transporting $Yb(C_5H_5)_3$ in a H_2 flow. Growth temperatures were in the range of 550–650°C. SIMS (Secondary Ion Mass Spectroscopy) measurements revealed that Yb was doped uniformly throughout the entire depth of the epitaxial layers. The Yb concentration has a flat profile except for the surface and the epitaxial layer/substrate interface (Fig. 5).[43]

In contrast to ion-implanted InP:Yb layers, photoluminescence spectra of the MOCVD-Yb-doped samples have shown the absence of Yb ions associated with other impurities or defects. The InP:Yb layer have n-type conductivity even for Yb concentrations above 10^{19} cm^{-3}, while LPE doped InP:Yb samples always exhibit p-type conductivity.[12,13] A significant decrease of the carrier concentration was observed for layers with Yb concentrations about 10^{15} cm^{-3} when the temperature was lowered from 300 to 77 K (Fig. 6).[46] The results of Hall effect measurements and deep level transient spectroscopy have revealed the presence of an acceptor-like level. The level lies about 0.03 eV below the condition-band edge. The dependence between trap concentration of the 0.03 eV acceptor-like level and Yb concentration is almost linear (Fig. 7). The latter indicates that the level is related to isolated Yb ions.[46]

Some electrical characteristics of InP:Yb epitaxial layers, which were obtained by MOCVD on (100)-oriented Fe-doped InP substrates by use of $Yb(C_5H_5)_3$ as doping source or by LPE using metallic Yb as source, are presented in Table I.[48]

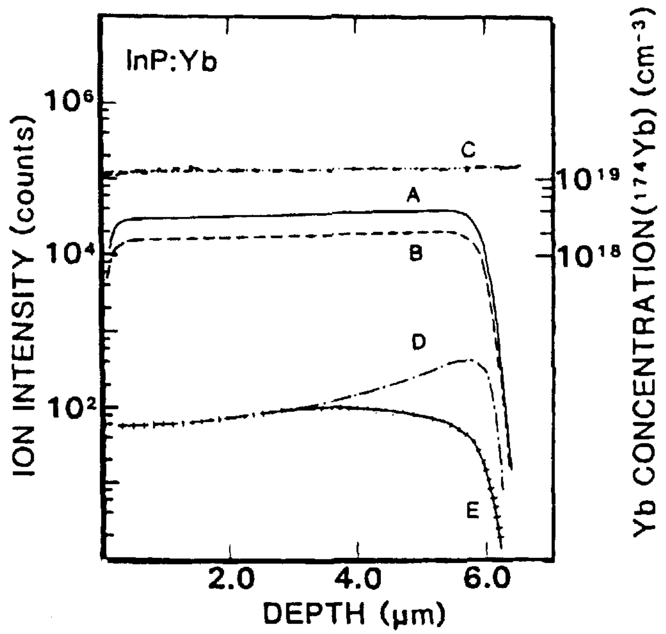


FIGURE 5 SIMS profile for an InP:Yb sample. Secondary ion intensities of ^{174}Yb (curve A), ^{173}Yb (curve B), ^{31}P (curve C), ^{56}Fe (curve D), ^{55}Mn (curve E) are shown as functions of the depth from the surface.

The first successful growth of erbium-doped InP (InP:Er) and GaAs (GaAs:Er) by MOCVD has been carried out using $Er(C_5H_5)_3$ as doping source.[44] Uniform Er doping up to concentrations of 1.5×10^{19} cm^{-3} have been achieved (SIMS profiles of the InP:Er epitaxial layers is shown in Fig. 8). Yb and Er show pile-up at the epitaxial layer/substrate interface. In contrast to ion-implanted layers, which show complicated photoluminescence spectra varying from sample to sample, MOCVD-grown Er-doped layers give simple and reproducible spectra. Er and Yb-ion related photoluminescence intensities of intra-4*f*-shell were observed to increase only sublinearly as a function of excitation photon density.[47]

2.3.4. $Ln(MeC_5H_4)_3$ *sources for doping of III–V semiconductors*

As $Ln(C_5H_5)_3$ derivatives have a relatively low vapor pressure and high melting points (for example $Yb(C_5H_5)_3$ m.p. 273°C [23]), they require extremely high bubbler temperatures of about 200°C.[45] In this case, the

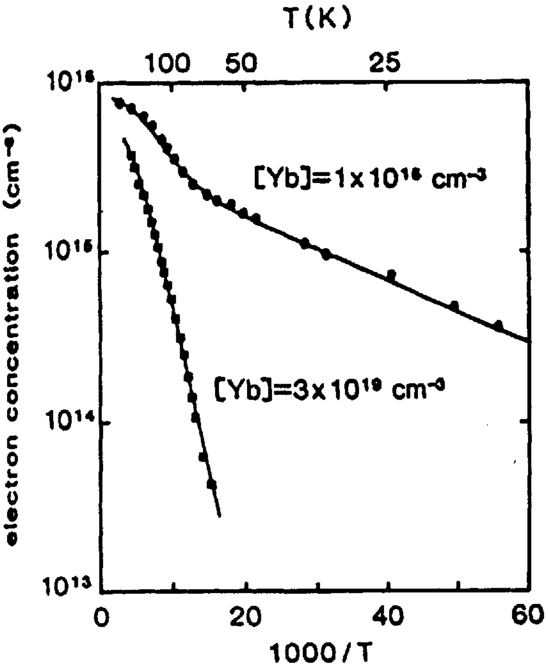


FIGURE 6 Temperature dependence of the free-electron concentration for an InP:Yb epitaxial layer.

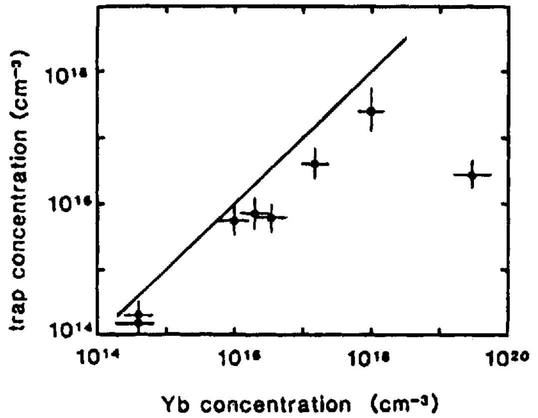


FIGURE 7 Dependence between trap concentration of the 0.03 eV acceptor-like level and Yb concentration in InP:Yb epitaxial layers.

TABLE I

Electrical characteristics of InP:Yb epitaxial layers, doped by using $Yb(C_5H_5)_3$.[48]

Samples	Conductivity Type	Carrier Concentration at 77 K (10^{14} cm^{-3})	Carrier Concentration at 300 K (10^{14} cm^{-3})	Yb Concentration (10^{14} cm^{-3})
heavily doped InP:Yb	n	40	200	2000
medium doped InP:Yb	n	60	200	200
lightly doped InP:Yb	n	20	20	1
LPE doped InP:Yb	p	~1000	~1000	<1

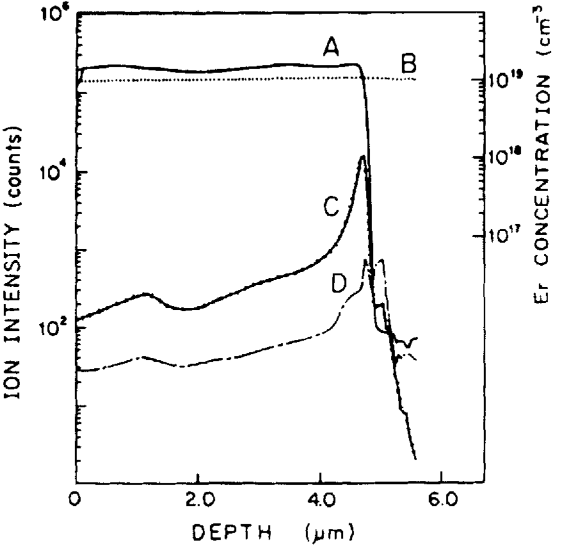


FIGURE 8 SIMS profile for an InP:Er layer. Secondary ion intensities of ^{166}Er (curve A), ^{31}P (curve B), ^{55}Mn (curve C), ^{56}Fe (curve D) are shown as functions of the depth from the surface.

MOVPE system has to be specially designed with gas lines and valves heated up to more than 200°C, and the doping reproducibility is limited.[45] By replacing one hydrogen atom in the Cp ring by a methyl group, the intermolecular attractive forces can be reduced, and at the same time the vapor pressure increased and the melting point lowered. With a melting point of 117°C and a vapor pressure of 0.15 Pa at 80°C, $Yb(MeC_5H_4)_3$ was found to be a much more suitable precursor than $Yb(C_5H_5)_3$.[22,53] The dependence of the vapor pressure of $(MeC_5H_4)_3Yb$ on temperature is shown in Fig. 9.[53] The use of $Yb(MeC_5H_4)_3$ allowed the growth of high quality InP:Yb layers by adduct MOVPE at low bubbler temperatures (70–90°C). The $Yb(MeC_5H_4)_3$ could be transferred into the bubbler by sublimation (80°C, 10^{-2} Pa), which could then be fitted to the MOVPE system. The InP:Yb layers were grown at atmospheric pressure in a horizontal MOVPE reaction chamber with rectangular cross section. The Yb incorporation from $Yb(MeC_5H_4)_3$ could be stimulated by raising the growth temperature from 560°C to 670°C. The Yb concentrations could be varied by the Yb source temperature (70–90°C) and H_2 flow over the Yb compound (9–90 sccm). Yb mole fractions in the reaction chamber ranged from 1.4×10^{-9} to 1.3×10^{-7}, and ytterbium concentrations of about 2×10^{19} cm^{-3} have been achieved.[22,53]

The MOVPE Yb-doped samples exhibited n-type conduction (in contrast to LPE grown layers). The carrier concentrations n ranged

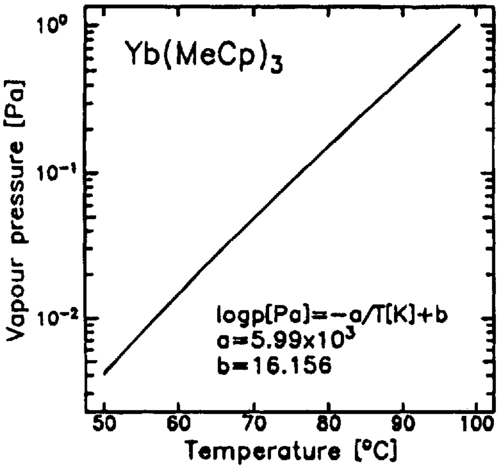


FIGURE 9 Dependence of the vapor pressure of $(MeC_5H_4)_3Yb$ on temperature.

from 9×10^{14} cm^{-3} to 2×10^{16} cm^{-3} at 300 K. For higher doping levels an extremely strong 4*f* luminescence signal in comparison to LPE layers was detected.[53]

$Er(MeC_5H_4)_3$ was also used as Er source for growing of GaAs:Er[54,55] and InP:Er[56] epitaxial layers by MOCVD. The photoluminescence spectra dependence on MOCVD conditions was studied. When the growth temperature and III/V ratio for GaAs:Er were reduced, the intensity of a few lines increased (Fig. 10).[54]

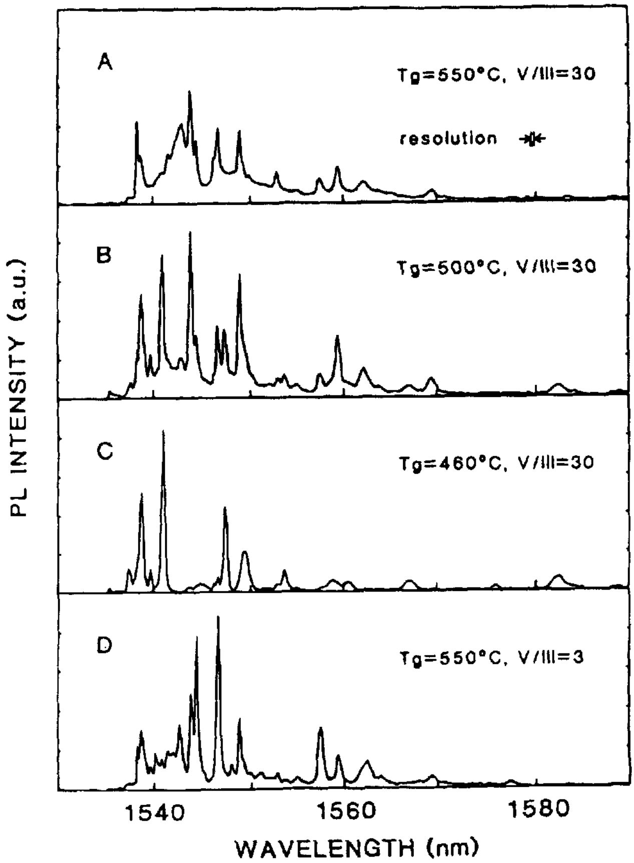


FIGURE 10 Er-related photoluminescence for GaAs:Er grown with various growth temperatures (*Tg*) and V/III ratios.

The temperature dependencies of the spectral linewidth and the peak wavelength for Er-related infra-4*f*-shell photoluminescence and electroluminescence have also been investigated.[55] Results of the study have shown that the parameters of photo- and electroluminescence spectra are comparable to those for rare-earth-doped insulators such as neodymium-doped yttrium aluminum garnets. The magnitude of the linewidth and the peak wavelength shift rate are about two orders of magnitude smaller than those of the luminescence line for a typical III–V semiconductor, InGaAs. The properties could enable us to use these GaAs:Er layers as materials for optical devices requiring temperature-stable operating wavelengths and sharp luminescence linewidths.

Neodymium doped III–V semiconductors are also attracting a great deal of attention. The Nd^{3+} ion is an interesting emitting center because of its four-level lasing scheme of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition that may allow low-threshold lasing near 1.1 μm as the $^4I_{11/2}$ level is separated from the ground level, $^4I_{9/2}$.[57] Energy levels of the neodymium 4*f* shell and band gap energies of some III–V semiconductor hosts are presented in Fig. 11.[58]

Neodymium doped GaAs[59] and GaP[58,60] epitaxial layers have been grown by MOCVD using $Nd(Me_3C_5H_4)_3$ as doping source. The growth conditions and Nd concentrations of typical samples are presented in

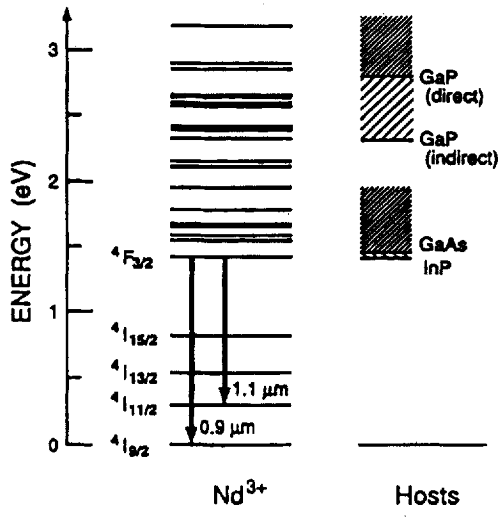


FIGURE 11 Energy levels of the neodymium 4*f* shell and band gap energies of some III–V semiconductor hosts.

Table II.[58] Photoluminescence spectra of the samples due to infra-4*f*-shell transitions of Nd^{3+} have been studied.[58–60] The photoluminescence intensity decreases by about two orders of magnitude from 3 K to 300 K. Sharply structured Nd-related luminescence[60] is distinctly observed at 300 K, and its peak intensity is stronger than Er-related luminescence at 1540 nm for MOCVD-grown InP:Er and GaAs:Er.[44,55] Photoluminescence spectra of GaP:Nd samples depend on growth conditions and excitation photon energy and reflect the formation of various mid-gap states in the GaP host. Luminescence from some Nd centers disappears as temperature increases, but that from some other Nd centers is observed up to room temperature. A comparative study of luminescence characteristics of GaP:Nd and GaAs:Nd has shown that only three kinds of Nd-related luminescence centers are observed in GaAs while many kinds of centers are observed in GaP.[58]

2.3.5. $Ln(iPrC_5H_4)_3$ *and* $Ln(nBuC_5H_4)_3$ *sources for doping of III–V semiconductors*

Further increasing the size of the Cp ligands in tris(cyclopentadienyl)lanthanides by introducing isopropyl or *n*-butyl substituents into the Cp ring leads to a reduction of the precursor's melting points to as low as 46–48°C and also allows a lowering of the bubbler temperatures (60–90°C).[22,56,61–63] $Ln(iPrC_5H_4)_3$ and $Ln(nBuC_5H_4)_3$ can be used as liquid precursors for MOCVD and MOVPE processes. Such liquid precursors of rare-earth metals are preferable to solid ones because of their high vapor pressures and good doping controllability.

The use of $Yb(iPrC_5H_4)_3$ (melting point 47°C) as liquid Yb precursor has enabled us to essentially improve the surface morphology of epitaxial layers. Thus $Yb(iPrC_5H_4)_3$ is a much better source for doping in terms of reproducibility, crystal quality and reduced memory effect than $Yb(MeC_5H_4)_3$. Moreover, samples doped by $Yb(iPrC_5H_4)_3$ have shown higher ytterbium photoluminescence intensities even at low growth tem-

TABLE II

Growth conditions and Nd concentrations of some GaP:Nd and GaAs:Nd samples.

Host	GaP	GaP	GaP	GaP	GaAs
Growth temperature (°C)	650	650	650	750	650
V/III ratio	17	17	170	17	40
Nd concentration (10^{17} cm^{-3})	3	60	30	30	3

peratures (580°C). The Yb(iPrC$_5$H$_4$)$_3$ liquid precursor disturbs the InP crystal growth less than Yb(MeC$_5$H$_4$)$_3$, and a higher fraction of Yb can contribute radiatively to the photoluminescence signal. This result was explained by the lower chemical bonding strength between Yb and the Cp rings in the case of the larger iPrC$_5$H$_4$-ligands.[22]

A comparison of typical growth parameters of InP:Yb layers for Yb(iPrC$_5$H$_4$)$_3$ with those for Yb(C$_5$H$_5$)$_3$ and Yb(MeC$_5$H$_4$)$_3$ is presented in Table III. The Yb(iPrC$_5$H$_4$)$_3$-doped InP:Yb layers exhibited higher Yb^{3+} emission intensities at 100 times lower Yb concentrations than Yb(MeC$_5$H$_4$)$_3$-doped samples.[61] Low temperature ($T = 2$ K) photoluminescence of the Yb(iPrC$_5$H$_4$)$_3$-doped InP:Yb layers revealed the typical ytterbium related spectra around 1μm. In many layers, one or more phonon replicas at lower energies have been observed. The latter fact demonstrated the good quality of the samples.[22] InP:Er[22,56] and GaAs:Er[62] layers, which were obtained using Er(iPrC$_5$H$_4$)$_3$, also displayed higher crystal quality and photoluminescence intensities than those obtained with the Er(MeC$_5$H$_4$)$_3$ precursor. Er concentrations in InP up to 5×10^{18} cm^{-3} could be reached.[22] Reproducibility of the growth of InP:Er layers in the case of Er(iPrC$_5$H$_4$)$_3$ was better than for Er(MeC$_5$H$_4$)$_3$.[56]

An investigation of the Er(iPrC$_5$H$_4$)$_3$-doped GaAs:Er by the Rutherford backscattering channelling method has shown that Er ions occupy a tetrahedral interstitial site in the GaAs.[62] It was also revealed that the atomic transitions of Er in InP:Er samples are much less influenced by the semiconductor host than those of Yb in InP:Yb. Ytterbium was found on a substitutional lattice site in InP, while Er was incorporated via different defects and clusters which gave rise to complex optical spectra.[22]

Tm(iPrC$_5$H$_4$)$_3$ was also successfully used as precursor for doping of GaAs, GaP, GaInP and InP by MOVPE.[22,64] The thulium-doped layers have been grown at 600°C in the case of InP and GaAs, whereas some GaAs, GaP and GaInP samples have been grown at 700–750°C. Tm(iPrC$_5$H$_4$)$_3$ could be used as a liquid source due to its low melting point (45–50°C).[64] The bubbler temperature was in the range of 50 to 95°C. According to SIMS data the concentration of Tm varied from 10^{16} to 10^{19} cm^{-3}. The surface morphology for all samples was only slightly influenced by the doping, even for high doping levels. Electrical measurements revealed no significant influence of the Tm doping on carrier concentrations and mobilities of the semiconductor host.

TABLE III

Growth parameters of InP:Yb layers for different Yb precursors.

Host Semic.	Dopant	Source	T_{growth} (°C)	T_{bubbler} (°C)	Yb (SIMS) (cm^{-3})	n_{300K} (cm^{-3})	Reference
InP	Yb	$Yb(C_5H_5)_3$	650	190	1×10^{19}	1×10^{15}	46
InP:Fe	Yb	$Yb(C_5H_5)_3$	650	200	2×10^{17}	2×10^{16}	48
InP	Yb	$Yb(MeC_5H_4)_3$	670	90	1.5×10^{19}	5×10^{15}	61
InP	Yb, S	$Yb(MeC_5H_4)_3$	670	90	2×10^{19}	2×10^{17}	61
InP	Yb	$Yb(iPrC_5H_4)_3$	580	70	3×10^{17}	5×10^{15}	61
InP	Yb, S	$Yb(iPrC_5H_4)_3$	580	70	3.5×10^{17}	3.6×10^{18}	61

(SIMS = secondary ion mass spectroscopy)

Thulium has optical transitions in the accessible range between 1 and 2 μm for the two oxidation states Tm^{+3} and Tm^{+2}.[65] The typical Tm^{+3} photoluminescence spectrum at 1.2 and 1.9 μm has been observed only in Tm-doped GaAs, GaInP and very weakly in InP.[64] The strongest emission was detected in GaInP:Tm hosts. In low temperature photoluminescence spectra of the Tm(*i*$PrC_5H_4)_3$-doped GaAs:Tm samples, two optical transitions ($^3H_5 \rightarrow {}^3H_6$ and $^3H_4 \rightarrow {}^3H_6$) could be resolved for rather high concentrations of thulium (> 10^{18} cm^{-3}). Ion implanted samples showed similar spectra at least for the 1.2 μm transition (Fig. 12). Thulium doped into GaAs formed one specific defect with the [001] axis (D_{2d}-symmetry) in MOVPE grown and in ion implanted samples.[22]

Er(*n*$BuC_5H_4)_3$ was used as a new liquid source for doping of GaAs grown by MOCVD.[63] The GaAs:Er layers were grown at atmospheric pressure in a horizontal quartz reactor from trimethylgallium and *tert*-butylarsine sources. The growth rate was 1–2 μm/h. The Er(*n*$BuC_5H_4)_3$ sample used for doping has a boiling point in the range of 230–240°C at 0.1 torr, and the vapor pressure is about 1.0 torr at 200°C. The Er-

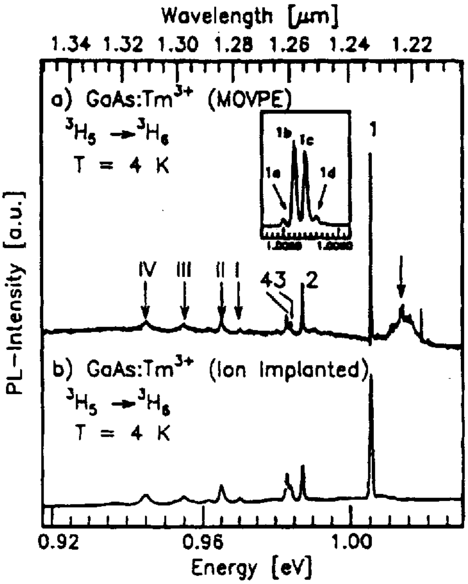


FIGURE 12 Low temperature photoluminescence spectra of GaAs:Tm grown by MOVPE (a) and ion implanted (b) transition at 1eV.

source temperature was in the range 175–225°C. The growth temperature was varied from 620 to 680°C. The optimal surface morphology has been obtained at 620°C. Degradation of morphology could be related to the incorporation of erbium into the GaAs crystal lattice. A maximal Er-concentration of 10^{19} cm^{-3} has been achieved. The obtained samples were characterized by SIMS and photoluminescence spectra. Erbium related photoluminescence spectra were found to be independent of growth conditions.[63]

2.3.6 Comparison of tris(cyclopentadienyl)lanthanides with other precursors for doping of semiconductors

As we have seen, tris(cyclopentadienyl)lanthanides are quite suitable precursors for doping of semiconductors by MOCVD or MOVPE. However, there are some other lanthanide precursors such as the tris (heptafluorodimethyloctanedionate) complex Yb(fod)_3,[66] tris(tetramethylheptanedionato) lanthanides Ln(thd)_3 (Ln = Er, Yb, Tm)[67–70] and tris(amido)erbium complexes Er[N(R)(R')]_3 ($\text{R} = \text{R}' = \text{SiMe}_3$; $\text{R} = \text{CMe}_3$, $\text{R}' = \text{SiMe}_3$; $\text{R} = \text{R}' = \text{SiHMe}_2$; $\text{N(R)(R')} = \overline{\text{NSiMe}_2\text{CH}_2\text{CH}_2\text{Si}}\text{Me}_2$, which have also been successfully employed.[71,72]

The diketonates Yb(fod)_3 and Ln(thd)_3 are commercially available and not air sensitive like the tris(cyclopentadienyl)lanthanides. In addition, they have sufficiently high vapor pressures at ambient temperature. However, the solid state nature of these compounds requires high source temperatures of 120–160°C and the use of special source arrangements.[66–70] A comparative study of $\text{Er(C}_5\text{H}_5)_3$ and $\text{Er[N(SiMe}_3)_2]_3$ as sources for doping of AlGaAs and germanium by MOCVD has shown that $\text{Er(C}_5\text{H}_5)_3$ left a significantly larger amount of carbon in the films.[71] The amide compounds decomposed with a trace of silicon, nitrogen or carbon contamination. Thus $\text{Er[N(SiMe}_3)_2]_3$ appears to be a more suitable precursor for MOCVD than $\text{Er(C}_5\text{H}_5)_3$. Some characteristics of $\text{Er(C}_5\text{H}_5)_3$ and $\text{Er[N(SiMe}_3)_2]_3$ as doping sources are presented in Table IV.[71]

3. PERSPECTIVE ORGANOLANTHANIDE PRECURSORS FOR MAGNETIC SEMICONDUCTORS

Rare earth monochalcogenides LnE (Ln = Yb, Eu, Sm; E = S, Se, Te) display very interesting magnetic properties. The compounds could be very promising materials for diluted magnetic semiconductors such as

TABLE IV

Characteristics of $Er(C_5H_5)_3$ and $Er[N(SiMe_3)_2]_3$ as doping sources for MOCVD (the metal film composition was measured by Rutherford Backscattering Spectroscopy).

Characteristics	$Er(C_5H_5)_3$	$Er[N(SiMe_3)_2]_3$
Melting point (°C)	285	162
Sublimation temperature at 10^{-4} torr (°C)	200	175
Vapor pressure (torr/°C)	0.01/200	0.1/120
Source temperature (°C)	200	150–175
Deposition temperature (°C)	600	400–600
Erbium content (atomic %)	4.7	17.9
Oxygen content (atomic %)	2.4	57.9
Carbon content (atomic %)	42.3	4.7

$Hg_{1-x}Sm_xTe$.[73] These materials are normally obtained by high-temperature syntheses from the correspondent elements, but in this case the materials often contain impurities which are readily incorporated due to the high oxophilicity of the rare earth centers.[74,75]

Chalcogenide-containing organolanthanides are very promising precursors for convenient syntheses of the rare earth monochalcogenides. The use of organolanthanides could enable us to obtain the LnE materials with required purity by a relative low temperature synthesis.

Investigations of chalcogenide-containing inorganic (without Ln–C bond) lanthanide(II) complexes as precursors to lanthanide(II)-based semiconductors have been reported by Bianconi *et al.*[76,77] The compounds containing aryl chalcogenolate ligands have been prepared by treatment of a lanthanide(II) halide with the appropriate alkali metal aryl selenolates or tellurolates according to Eq. (6).[76,77] $Yb(SeMes)_2(DME)x$ can also be obtained from the amide complex $Yb[N(SiMe_3)_2]$ and MesSeH in DME.[77]

$$\begin{gathered}\mathrm{LnX_2(THF)_{2\text{-}3} + 2KEMes \xrightarrow[DME]{THF} Ln(EMes)_2(THF)_{2\text{-}3} + 2KX}\\ \mathrm{Ln = Yb, Sm, Eu;\ X = I, Br;}\\ \mathrm{E = Se, Te;\ Mes = 2,4,6-trimethylphenyl} \qquad (6)\end{gathered}$$

The obtained lanthanide–halcogenide complexes are soluble in toluene, DME and THF and can be easily purified by recrystallization from these solvents. Thermal decomposition of the complexes leads to the corresponding monochalcogenide LnE and to the organochalcogenide byproducts $EMes_2$, which are volatile and can be easily removed from the mixture. For example, pyrolysis of $Yb(TeMes)_2 \cdot THF_{2-3}$ at 900°C for 24 h yielded a crystalline powder of YbTe.[76]

$$Ln(TeMes)_2(THF)_{2-3} \xrightarrow{\Delta} LnTe + TeMes_2 \qquad (7)$$

Solid-state thermolyses of other lanthanide(II) chalcogenolates such as $Yb[ESi(SiMe_3)_3]_2(TMEDA)_2$ (E = Se, Te)[78] also gave the corresponding YbE.

According to these investigations the above-mentioned compounds appear to be promising precursors for rare earth monochalcogenides LnE and for magnetic semiconductors based on them.

Organolanthanide chalcogenide complexes such as $[(Me_5C_5)_2Yb]_2[\mu\text{-}E]$ (E = S, Se, Te),[79] $[(Me_5C_5)_2Yb]_2Te_2$,[80] $(Me_5C_5)_2Yb(ER)(L)$ (E = S, Se, Te; R = Ph or PhMe; L = OEt_2 or NH_3),[81] $[(Me_5C_5)_2Sm(THF)]_2(E)$ and $[(Me_5C_5)_2Sm]_2(E_3)(THF)$ (E = S, Se, Te),[82] $[Sm(\mu\text{-}SAr)(C_8H_8)(THF)_n]_2$ (Ar = Ph, $C_6H_2Me_3$ or $C_6H_2(i\text{Pr})_3$; $n = 1, 2$)[83] are well known. However, these substances are still not studied as precursors to lanthanide(II)-based semiconductors. It can be anticipated that these compounds might also be useful as precursors for the corresponding lanthanide chalcogenide materials if it would be possible to find appropriate conditions for their thermal decomposition in reductive (for instance, H_2) atmosphere.

4. MIXED-SANDWICH CYCLOOCTATETRAENYL – CYCLOPENTADIENYL LANTHANIDE COMPLEXES AS PRECURSORS FOR CVD PROCESSES

The discovery of high T_c superconductors (type $YBa_2Cu_3O_{7-\delta}$) involving lanthanides has stimulated the development of the chemistry of potential lanthanide precursor compounds. The preparation of $YBa_2Cu_3O_{7-\delta}$ films by MOCVD using 2,2,6,6-tetramethyl-3,5-heptanedionate (thd) and heptafluoro-2,2-dimethyl-3,5-octanedionate (fod) yttrium derivatives was already considered.[1] More recently some organolanthanides have been used as precursors for rare earth oxides. For example, high purity Gd_2O_3 has been obtained by thermal decomposition of tris(isopropylcyclopentadienyl)dysprosium, $Dy(Pr^iC_5H_4)_3$.[84] However, facts about the use of organolanthanides as precursors for superconductors are still very limited.

4.1. General Features of Cyclooctatetraenyl–Cyclopentadienyl Lanthanide Mixed-Sandwich Complexes

Organolanthanide mixed-sandwich complexes containing a cyclooctatetraenyl and a cyclopentadienyl ligand are of significant interest as precursors for MOCVD processes. The first examples of such mixed-sandwich complexes to appear in the literature were compounds of the type $(C_8H_8)Ln(C_5H_5)(THF)$.[85] These complexes have been obtained by treatment of mono(cyclopentadienyl)lanthanide dichlorides with equimolar amounts of $K_2C_8H_8$ (Scheme 1a) or alternatively by the reaction of $[(C_8H_8)Ln(\mu\text{-}Cl)(THF)_2]_2$ with sodium cyclopentadienide (Scheme 1b).[85]

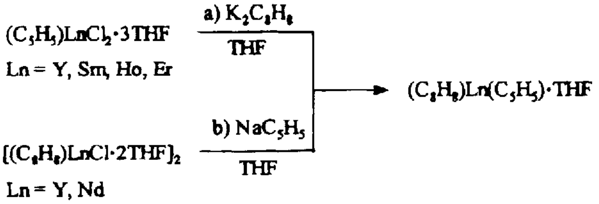
More recently it was found that the complexes $(C_8H_8)Ln(C_5H_5)(THF)_n$ (Ln = Pr,Nd, $n = 2$; Ln = Gd, $n = 1$) could also be synthesized by simultaneous treatment of anhydrous $LnCl_3$ with equimolar amounts of NaC_5H_5 and $K_2C_8H_8$:[86]

$$\begin{aligned} LnCl_3 + NaC_5H_5 + K_2C_8H_8 \xrightarrow{\text{THF}} {} & (C_8H_8)Ln(C_5H_5)(THF)_n \\ & +NaCl + 2KCl \\ Ln = Pr,\ Nd,\ n = 2;\ Ln = Gd,\ n = 1 & \qquad (8) \end{aligned}$$

A mixed cyclooctatetraenyl–pentamethylcyclopentadienyl complex of samarium has been obtained by the reaction of bis(pentamethylcyclopentadienyl)samarium(II) with cyclooctatetraene:[36,87]

$$\begin{aligned} (C_5Me_5)_2Sm(THF)_2 + C_8H_8 \longrightarrow {} & (C_8H_8)Sm(C_5Me_5)(THF) \\ & + \tfrac{1}{2}(C_5Me_5)_2 \qquad (9) \end{aligned}$$

A large number of related organolanthanide mixed-sandwich complexes has been prepared by using cyclooctatetraenyl and cyclopentadi-



SCHEME 1 Preparation of $(C_8H_8)Ln(C_5H_5)(THF)$ complexes.

enyl ligands with various substitutents in the rings. Well-characterized examples include the pentamethylcyclopentadienyl derivatives $(C_8H_8)Ln\ (C_5Me_5)(THF)$ and $(C_8H_8)Ln(C_5Me_5)$ (Ln = Sc, Y, La, Pr, Nd, Sm, Gd, Tb, Dy, Er, Lu),[87–90] the methylcyclopentadienyl derivative $(C_8H_8)\ Y(MeC_5H_4)(THF)$,[91] tetramethylcyclopentadienyl complexes $(C_8H_8)\ Ln(C_5Me_4H)(THF)_n$ and $(C_8H_8)Ln(C_5Me_4H)$ (Ln = Y, La, Pr, Sm, Gd, Dy, Er, Lu),[92] the pentabenzylcyclopentadienyl derivative $(C_8H_8)\ Lu[C_5(CH_2Ph)_5]$,[93] as well as the di(*tert*-butylcyclopentadienyl) complex $(C_8H_8)Y(Bu^t{}_2C_5H_3)$[94] and phosphino-substituted mixed-sandwich complexes of the type $(C_8H_8)Sm(C_5R_4PR'_2)(THF)_n$ (R = H or Me; R′ = Ph or Me; $n = 0$ or 2).[95] A series of closely related indenyl–cyclooctatetraenyl mixed-sandwich complexes have been prepared by the simultaneous reaction between $LnCl_3$, $K_2C_8H_8$ and $K_2C_9H_7$ in THF solution.[86,96,97] Even (azacyclopentadienyl)(cyclooctatetraenyl)lanthanide complexes $[(\eta^8\text{-}C_8H_8)Ln(\eta^5\text{-}NC_4H_2Bu^t_2\text{-}2,5)(THF)_n]$ (Ln = Sm, $n = 1$; Ln = Tm, Lu, $n = 0$) have been synthesised recently from $[(\eta^8\text{-}C_8H_8)Ln(\mu\text{-}Cl)(THF)_2]_2$ and $Na(NC_4H_2Bu^t_2\text{-}2,5)$:[98]

$$\begin{gathered}\left[(\eta^8\text{–}C_8H_8)Ln(\mu\text{–}Cl)(THF)_2\right]_2 + 2Na\left(NC_4H_2Bu^t_2\text{–}2,5\right)\\ \rightarrow 2\left[(\eta^8\text{–}C_8H_8)Ln\left(\eta^8\text{–}NC_4H_2Bu^t_2\text{–}2,5\right)(THF)_n\right]\\ +2NaCl\\ Ln{=}Sm, n{=}1; Ln{=}Tm, Lu, n{=}0\end{gathered} \tag{10}$$

Mixed-sandwich complexes with trimethylsilyl substitutents at the cyclooctatetraenyl ligand, $[\{(Me_3Si)_2C_8H_6\}Ln\{(Me_3Si)_2C_5H_3\}]$, have also been obtained recently.[99] Sublimation of the THF-solvated mixed-sandwich complexes generally leads to the unsolvated derivatives which are thermally stable. Some examples of the compounds are presented in Table V.

The main structural types of mixed cyclooctatetraenyl–cylopentadienyl lanthanide complexes are shown in Figs. 13–15. In bis(THF)-solvated $(C_8H_8)La(C_5Me_4H)(THF)_2$ (Fig. 13),[92] the La atom adopts a distorted tetrahedral coordination arrangement, which is described by the cyclooctatetraenyl and tetramethycyclopentadienyl ring centroids and two THF molecules. Mono-solvated $(C_8H_8)Y(MeC_5H_4)(THF)$ is a wedge-sandwich compound with one coordinated THF molecule (Fig. 14).[91] Finally, unsolvated $(C_8H_8)Lu(C_5Me_5)$ is a sandwich compound with the lutetium atom η^8- and η^5-bonded to the planar

TABLE V

Synthetic routes and sublimation temperature of some unsolvated lanthanide mixed-sandwich complexes.

Compound	Synthetic route	Sublimation temp. (°C/torr)	Reference
$(C_8H_8)Sc(C_5Me_5)$	Eq. (8)	160/0.1	89
$(C_8H_8)Y(C_5Me_5)$	Eq. (8)	150/0.1	89
$(C_8H_8)La(C_5Me_5)$	Eq. (8)	$200–225/10^{-3}$	89
$(C_8H_8)Ce(C_5Me_5)$	Eq. (8)	$160/10^{-3}$	90
$(C_8H_8)Sm(C_5Me_5)$	Eq. (4) or (9)	$70/10^{-4}$	36
$(C_8H_8)Y(C_5Me_4H)$	Scheme 1b	120/0.1	92
$(C_8H_8)La(C_5Me_4H)$	Scheme 1b	189/0.1	92
$(C_8H_8)Pr(C_5Me_4H)$	Scheme 1b	225/0.1	92
$(C_8H_8)Sm(C_5Me_4H)$	Scheme 1b	147/0.1	92
$(C_8H_8)Gd(C_5Me_4H)$	Scheme 1b	145/0.1	92
$(C_8H_8)Dy(C_5Me_4H)$	Scheme 1b	138/0.1	92
$(C_8H_8)Er(C_5Me_4H)$	Scheme 1b	118/0.1	92
$(C_8H_8)Lu(C_5Me_4H)$	Scheme 1b	145/0.1	92

cyclooctatetraenyl and pentamethylcyclopentadienyl rings, respectively (Fig. 15).[88]

The pentamethylcyclopentadienyl and tetramethylcyclopentadienyl derivatives are quite volatile. Sublimation temperatures of $(C_8H_8)Ln$

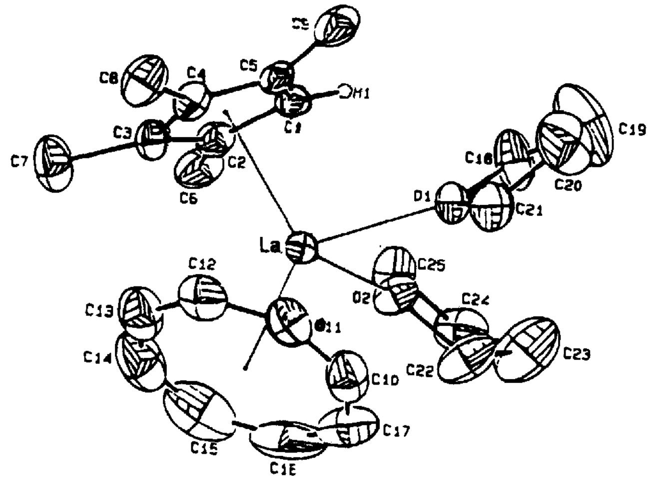


FIGURE 13 ORTEP drawing of $(C_8H_8)La(C_5Me_4H)(THF)_2$.

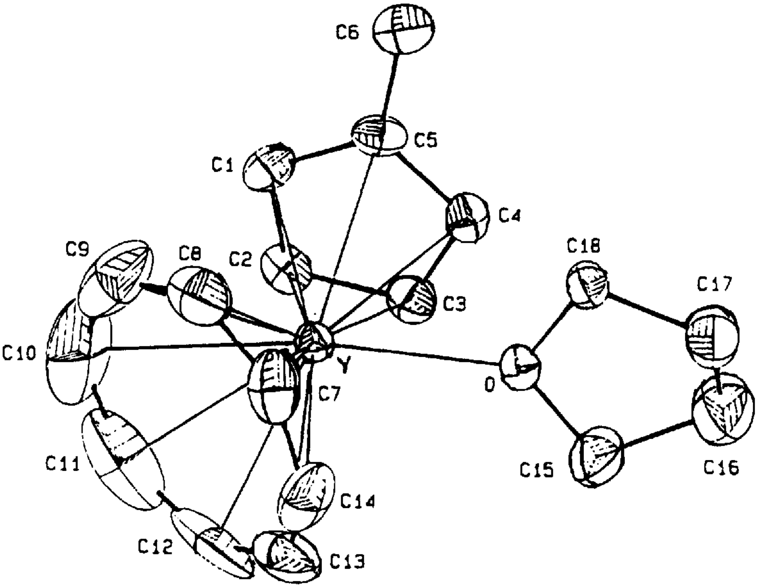


FIGURE 14 ORTEP drawing of $(C_8H_8)Y(MeC_5H_4)(THF)$.

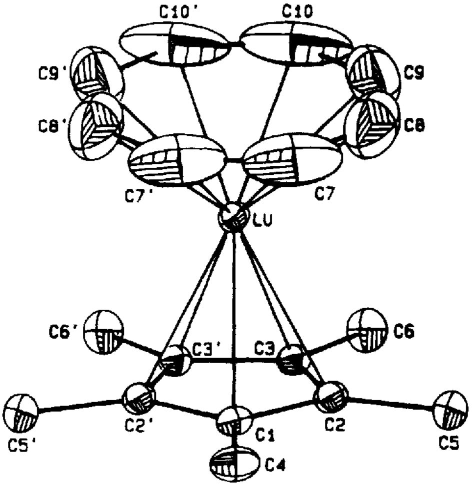


FIGURE 15 ORTEP drawing of $(C_8H_8)Lu(C_5Me_5)$.

(C_5Me_5) complexes are in the range from 150°C/0.1 torr for yttrium to 200–225°C/0.1 torr for the lanthanum compound. For tetramethylcyclopentadienyl derivatives the sublimation temperatures fall in the range between 118°C/0.1 torr for $(C_8H_8)Er(C_5Me_4H)$ and 225°C/0.1 torr for $(C_8H_8)Pr(C_5Me_4H)$ (Table VI). Thus the complexes were supposed to be suitable for MOCVD processes.

4.2. Cyclooctatetraenyl–Pentamethylcyclopentadienyl Lanthanide Complexes as Precursors for Rare Earth Oxide Films

The cyclooctatetraenyl–pentamethylcyclopentadienyl lanthanide mixed-sandwich complexes have been studied as precursors for depositing oxide films via plasma enhanced chemical vapor deposition (PECVD).[100] The experiments have been done by decomposition of $(C_8H_8)Ln(C_5Me_5)$ (Ln = Y, Dy, Er) in argon/oxygen, in argon/water vapor, nitrous oxide (N_2O), and carbon dioxide (CO_2) plasmas. Important results of the experiments are presented in Table VI. The films obtained by these methods have been analyzed by elemental analyses, SEM micrographs, XPS, CTEM electron diffraction and FTIR spectra. In the case of argon/oxygen plasma, only $(C_8H_8)Y(C_5Me_5)$ produced an oxide film. The corresponding Dy and Er derivatives decomposed before reaching the substrate electrode. The results have shown that an increase of substrate temperature (T_{sub}) and rf-power (P_{rf}) leads to lower carbon and higher metal contents. The best film characteristics have been obtained with water vapor plasma. The use of $(C_8H_8)Ln(C_5Me_5)$ complexes allows us to obtain purer carbon-free oxide films at rates 5–6 times higher than with the corresponding β-diketonates.[101] Thus the cyclooctatetraenyl–pentamethylcyclopentadienyl lanthanide mixed-sandwich complexes are good precursors for depositing oxide films. It can be anticipated that other volatile mixed-sandwich complexes of the lanthanides such as the tetramethylcyclopentadienyl derivatives $(C_8H_8)Ln(C_5Me_4H)$ will be suitable precursors as well.

5. CONCLUSIONS AND SOME PERSPECTIVES ON USING ORGANOLANTHANIDES IN MATERIALS SCIENCE

The results highlighted above show that the application of organolanthanides in materials sciences is still limited. Thus far, organolanthanides have found wide application only as doping sources for III–V semiconductors. Data about the use of these compounds as precursors

TABLE VI

Results of $(C_8H_8)Ln(C_5Me_5)$ PECVD experiments (Ref. 100).

Compound	Plasma	$T_{sub.}$	P_{rf} W/cm^2	R_{dep} μg/min cm^2	C-cont. %	Ln-cont. %
$(C_8H_8)Y(C_5Me_5)$	Ar/O_2 20/20	300	1.0	2.8	14.4	63.8
		350	1.0	3.1–6.2	5.7–11.3	66.7
		400	1.0	1.9–4.2	<1–8.4	70.1
		400	1.5	1.1–2.2	<1–3.1	75.5
$(C_8H_8)Y(C_5Me_5)$	Ar/water vapor	350	1.0	2.8–7.5	<1–5.5	74.8
		350	1.5	0.6–3.8	<1–3.1	78.3
		400	1.0	1.7–5.2	<1–2.1	77.8
		400	1.5	4.1–5.5	<1	78.5
$(C_8H_8)Dy(C_5Me_5)$	Ar/water vapor	350	0.75	4.5	7.0	–
		400	0.75	2.9–5.2	3.6–3.8	80.3
		400	1.5	2.6–5.4	<1	85.1
$(C_8H_8)Er(C_5Me_5)$	Ar/water vapor	400	1.5	3.2 ± 1.3	<1	84.9
$(C_8H_8)Y(C_5Me_5)$	N_2O	350	1.0	3.5–4.0	5.3 ± 0.6	70.3
		350	1.5	3.1–3.5	<1	76.5
		400	1.0	2.9–3.1	2.3 ± 1.0	72.1
		400	1.5	3.2–3.8	<1	75.9
$(C_8H_8)Dy(C_5Me_5)$	N_2O	350	1.5	3.0–5.1	<1–6.8	82.4
		400	1.5	3.5	<1	85.8
$(C_8H_8)Er(C_5Me_5)$	N_2O	350	1.5	3.1–3.6	2.8 ± 0.8	81.3
		400	1.5	3.9–5.7	<1–5.6	86.0
$(C_8H_8)Y(C_5Me_5)$	CO_2	400	1.5	1.5–2.0	11.3 ± 0.9	68.5
$(C_8H_8)Dy(C_5Me_5)$	CO_2	400	1.5	2.9–3.8	1.6–4.1	82.8
$(C_8H_8)Er(C_5Me_5)$	CO_2	400	1.5	1.7–6.5	<1–6.0	83.5

for magnetic semiconductors and for rare earth oxide films are still limited.

In the future, tris(cyclopentadienyl) lanthanide complexes with *iso*-butyl, *tert*-butyl and $SiMe_3$ substituents on the Cp rings, as well as volatile cyclooctatetraenyl–cyclopentadienyl lanthanide mixed-sandwich complexes should be also investigated as doping sources for various semiconductors. All these compounds are expected to be good precursors for deposition of rare earth metal and oxide films as well.

Organolanthanide chalcogenolate complexes such as $[(Me_5C_5)_2Yb]_2[\mu\text{-E}]$ (E = S, Se, Te),[79] $[(Me_5C_5)_2Yb]_2Te_2$,[80] $(Me_5C_5)_2Yb(ER)(L)$ (E = S, Se, Te; R = Ph or PhMe; L = OEt_2 or NH_3),[81] $[(Me_5C_5)_2Sm(THF)]_2(E)$ and $[(Me_5C_5)_2Sm]_2(E_3)(THF)$ (E = S, Se, Te),[82] $[Sm(\mu\text{-SAr})(C_8H_8)(THF)_n]_2$ (Ar = Ph, $PhMe_3$ or $Ph(i\text{Pr})_3$; $n = 1, 2$)[83] should be investigated as precursors for the corresponding lanthanide chalcogenides, which offer interesting applications for new magnetic semiconductor materials.

Thus far, no efforts have been made to extend any of the above-mentioned procedures to the preparation of lanthanide borides, carbides, nitrides, or phosphides. This is a largely unexplored field which should lead to interesting discoveries in the future.

References

1. G. B. Deacon, P. MacKinnon, R. S. Dickson, G. N. Pain and B. O. West, Appl. Organomet. Chem. **4**, 439 (1990).
2. L. G. Hubert-Pfalzgraf, New J. Chem. **19**, 727 (1995).
3. W. H. Haydl, H. D. Müller, H. Ennen, W. Körber and K. W. Benz, Appl. Phys. Lett. **46**, 870 (1985).
4. H. Ennen, Extended Abstracts of 19th Conference on Solid State Devices and Materials, Tokyo, 83 (1987).
5. A. Rolland, A. Le Corre, P. N. Favennec, M. Gauneau, B. Lambert, D. Lecrosnier, H. L'Haridon, D. Moutonnet and C. Rochaix, Electron. Lett. **24**, 956 (1988).
6. P. S. Whitney, K. Uwai, H. Nakagome and K. Takahei, Electron. Lett. **24**, 740 (1988).
7. J. P. van der Ziel, M. G. Oberg and R. A. Logan, Appl. Phys. Lett. **50**, 1313 (1987).
8. G. S. Pomrenke, R. L. Hengehold and Y. K. Yeo, *Proceedings of the International Symposium on GaAs and Related Compounds, Karuizawa, Japan, 1989* (Inst. Phys. Conf. Ser. No. 106, 1989), Chapter 5, 339.
9. K. Takahei and A. Taguchi, Mater. Sci. Forum **83–87**, 641 (1992).
10. T. Beyattou, D. Seghier, G. Guillot, R. Moncorge, P. Galtier and M. N. Charasse, Appl. Phys. Lett. **60**, 350 (1992).
11. *Rare Earth Doped Semiconductors*, edited by G. S. Pomrenke, P. B. Klein and D. W. Langer (Mater. Res. Soc. Proc. No. 301, Pittsburgh, PA, 1993).
12. W. Korber, J. Weber, A. Hangleiter, K. W. Benz, H. Ennen and H. D. Müller, J. Cryst. Growth **79**, 741 (1986).

13. H. Nakagome, K. Takahei and Y. Homma, J. Cryst. Growth **85**, 345 (1987).
14. C. Rochaix, A. Rolland, P. N. Favennec, B. Lambert, A. Le Corre, H. L'Haridon and M. Salvi, J. Electron. Mat. **17**, 351 (1988).
15. C. Rochaix, A. Rolland, P. N. Favennec, B. Lambert, A. Le Corre, H. L'Haridon and M. Salvi, Jap. J. Appl. Phys. **27**, L2348 (1988).
16. H. Isshiki, H. Kobayashi, S. Yugo, T. Kimura and T. Ikoma, Appl. Phys. Lett. **58**, 484 (1991).
17. P. B. Klein, F. G. Moore and H. B. Dietrich, Appl. Phys. Lett. **58**, 502 (1991).
18. H. Ennen, J. Wagner, H. D. Müller and R. S. Smith, J. Appl. Phys. **61**, 4877 (1987).
19. A. Rolland, A. Le Corre, P. N. Favennec, M. Gauneau, B. Lambert, D. Lecrosnier, H. L'Haridon, D. Moutonnet and C. Rochaix, Electron. Lett. **24**, 956 (1988).
20. M. N. Charasse, P. Galtier, A. M. Huber, C. Grattepain, J. Chazelas and J. P. Hirtz, Electron. Lett. **24**, 1458 (1988).
21. R. L. Moon and Y. Houng, in *Chemical Vapor Deposition, Principles and Applications*, edited by M. L. Hitchman and K. F. Jensen (Academic Press, 1993), p. 252.
22. F. Scholz, J. Weber, K. Pressel and A. Doernen, Mater. Res. Soc. Symp. Proc. **301**, 3 (1993).
23. J. M. Birmingham and G. Wilkinson, J. Am. Chem. Soc. **78**, 42 (1956).
24. S. G. Krasnova, G. K. Borisov and G. G. Devyatykh, Zh. Neorg. Khim. **16**, 1733 (1971).
25. E. O. Fischer and H. Fischer, J. Organomet. Chem. **3**, 181 (1965).
26. P. G. Laubereau and J. H. Burns, Inorg. Chem. **9**, 1091 (1970).
27. A. F. Reid and P. C. Wailes, Inorg. Chem. **5**, 1213 (1966).
28. F. Bottomley, D. E. Paez and P. S. White, J. Organomet. Chem. **291**, 35 (1985).
29. G. Z. Suleimanov, T. Kh. Kurbanov, Ya. A. Nuriev, L. F. Rubakova and I. P. Beletskaya, Dokl. Chem. (Engl. Transl.) **265**, 254 (1982).
30. G. B. Deacon, A. J. Koplick and T. D. Tuong, Aust. J. Chem. **37**, 517 (1984).
31. G. B. Deacon, G. N. Pain and T. D. Tuong, Inorg. Synth. **26**, 17 (1989).
32. G. B. Deacon, C. M. Forsythe, R. H. Newnham and T. D. Tuong, Aust. J. Chem. **40**, 895 (1987).
33. S. D. Stults, R. A. Andersen and A. Zalkin, Organometallics **9**, 115 (1990).
34. W. A. Herrmann, R. Anwander, F. C. Munck and W. Scherer, Chem. Ber. **126**, 331 (1993).
35. W. J. Evans, R. A. Keyer and J. W. Ziller, J. Organomet. Chem. **394**, 87 (1990).
36. W. J. Evans, S. L. Gonzales and J. W. Ziller, J. Am. Chem. Soc. **113**, 7423 (1991).
37. D. C. Chadwick and R. A. Andersen, J. Organomet. Chem. **501**, 271 (1995).
38. J. F. Duncan and F. G. Thomas, J. Chem. Soc. 360 (1964).
39. H. O. Haug, J. Organomet. Chem. **30**, 53 (1971).
40. G. G. Devyatykh, G. K. Borisov and S. G. Krasnova, Dokl. Akad. Nauk SSSR. **203**, 110 (1972).
41. G. G. Devyatykh, N. P. Chernyaev, Yu. B. Zverev, E. M. Gavrishchuk, I. V. Runovskaya, E. F. Krupnova and S. G. Chesnokova, Russ. J. Inorg. Chem. **25**, 1168 (1980).
42. W. A. Herrmann, R. Anwander, M. Kleine, K. Öfele, J. Riede and W. Scherer, Chem. Ber. **125**, 2391 (1992).
43. K. Uwai, H. Nakagome and K. Takahei, Appl. Phys. Lett. **50**, 977 (1987).
44. K. Uwai, H. Nakagome and K. Takahei, Appl. Phys. Lett. **51**, 1010 (1987).
45. K. Uwai, H. Nakagome and K. Takahei, J. Cryst. Growth **93**, 583 (1988).
46. P. S. Whitney, K. Uwai, H. Nakagome and K. Takahei, Appl. Phys. Lett. **53**, 2074 (1988).
47. K. Takahei, K. Uwai and H. Nakagome, J. Lumin. **40 & 41**, 901 (1988).
48. K. Takahei, H. Nakagome, K. Uwai and P. S. Whitney, J. Appl. Phys. **66**, 4941 (1989).

49. G. Aszodi, J. Weber, Ch. Uihlein, L. Pu-lin, H. Ennen, U. Kaufmann, J. Schneider and J. Windscheif, Phys. Rev. **B31**, 7767 (1985).
50. V. F. Masterov, V. P. Savel'ev, K. F. Shtel'makh and L. F. Zakharenkov, Sov. Phys. Sem. **23**, 1381 (1989).
51. A. Kozanecki, Phys. Stat. Solidi. **A 112**, 777 (1989).
52. A. Kozanecki and R. Grötschel, J. Appl. Phys. **68**, 517 (1990).
53. J. Weber, A. Molassioti, M. Moser, A. Stapor, F. Scholz and G. Hörcher, Appl. Phys. Lett. **53**, 2525 (1988).
54. H. Nakagome, K. Uwai and K. Takahei, Appl. Phys. Lett. **53**, 1726 (1988).
55. K. Takahei, P. S. Whitney, H. Nakagome and K. Uwai, J. Appl. Phys. **65**, 1257 (1989).
56. J. Weber, M. Moser, A. Stapor, F. Scholz, G. Bohnert and G. Hörcher, J. Cryst. Growth **104**, 815 (1990).
57. R. B. Chesler and J. E. Geusic, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-Dubois (North Holland, Amsterdam, 1972), Chap. B2.
58. K. Takahei and H. Nakagome, J. Appl. Phys. **72**, 3674 (1992).
59. H. Nakagome and K. Takahei, Jap. J. Appl. Phys. **28**, L2098 (1989).
60. K. Takahei and H. Nakagome, "Gallium arsenide and related compounds 1989," in Inst. Phys. Conf. Ser. No. 106, Chapter 12, 913 (1989).
61. J. Weber, M. Moser, A. Stapor, F. Scholz, G. Hörcher, A. Forchel, G. Bohnert and A. Hangleiter, J. Cryst. Growth **100**, 467 (1990).
62. J. Nakata, M. Taniguchi and K. Takahei, Appl. Phys. Lett. **61**, 2665 (1992).
63. X. M. Fang, Y. Li and D. W. Langer, J. Appl. Phys. **74**, 6990 (1993).
64. F. Scholz, J. Weber, D. Ottenwälder, K. Pressel, C. Hiller, A. Dörnen, F. Cordeddu, K. Locke and D. Wiedmann, J. Cryst. Growth **124**, 470 (1992).
65. Z. K. Kiss and P. N. Yocom, J. Chem. Phys. **41**, 1511 (1964).
66. D. M. Williams and B. W. Wessels, Appl. Phys. Lett. **56**, 566 (1990).
67. A. J. Neuhalfen and B. W. Wessels, Appl. Phys. Lett. **59**, 2317 (1991).
68. A. J. Neuhalfen and B. W. Wessels, Mat. Res. Soc. Symp. Proc. **240**, 195 (1992).
69. A. J. Neuhalfen and B. W. Wessels, Appl. Phys. Lett. **60**, 2657 (1992).
70. X. Z. Wang, A. J. Neuhalfen and B. W. Wessels, Appl. Phys. Lett. **64**, 466 (1994).
71. A. C. Greenwald, W. S. Rees Jr. and U. W. Lay, Mater. Res. Soc. Symp. Proc. **301**, 21 (1993).
72. W. S. Rees, Jr., U. W. Lay and A. C. Greenwald, Mater. Res. Soc. Symp. Proc. **334**, 207 (1994).
73. *Handbook of the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner and L. R. Eyring (North-Holland, Amsterdam, 1979), Vol. 2, Chapter 19; Vol. 4, Chapter 31.
74. C. F. Hickey and U. J. Gibson, J. Appl. Phys. **62**, 3912 (1987).
75. J. F. Nakahara, T. Takeshita, M. J. Tschetta, B. J. Beardry and K. A. Gschneidner, J. Appl. Phys. **63**, 2331 (1988).
76. A. R. Strzelecki, P. A. Timinski, B. A. Helsel and P. A. Bianconi, J. Am. Chem. Soc. **114**, 3159 (1992).
77. A. R. Strzelecki, C. Likar, B. A. Hesel, T. Utz, M. C. Lin and P. A. Bianconi, Inorg. Chem. **33**, 5188 (1994).
78. D. R. Cary and J. Arnold, Inorg. Chem. **33**, 1791 (1994).
79. D. J. Berg, C. J. Burns, R. A. Andersen and A. Zalkin. Organometallics **8**, 1865 (1989).
80. A. Zalkin and D. J. Berg, Acta Crystallogr. **44c**, 1488 (1988).
81. D. J. Berg, C. J. Burns, R. A. Andersen and A. Zalkin. Organometallics **7**, 1858 (1988).
82. W. J. Evans, G. W. Rabe, J. W. Ziller and R. J. Doedens. Inorg. Chem. **33**, 2719 (1994).

83. K. Mashima, Y. Nakayama, N. Kanehisa, Y. Kai and A. Nakamura, J. Chem. Soc. Chem. Commun. 1847 (1993).
84. V. D. Makhaev, Y. B. Zvedov, N. G. Chernorukov and V. I. Berestenko, Vysokchist. Veshchestva 210 (1990).
85. J. D. Jamerson, A. P. Masino und J. Takats, J. Organomet. Chem. **65**, C33 (1974).
86. W. Ke, J. Zhongsheng and C. Wenqi, J. Chem. Soc. Chem. Commun. 680 (1991).
87. A. Recknagel, M. Noltemeyer and F. T. Edelmann, J. Organomet. Chem. **410**, 53 (1991).
88. H. Schumann, R. D. Köhn, F. W. Reier, A. Dietrich and J. Pickardt, Organometallics **8**, 1388 (1989).
89. P. Bruin, M. Booij, J. H. Teuben und Oskam, J. Organomet. Chem. **350**, 17 (1988).
90. M. Booij, N. H. Kiers, H. J. Heeres and J. H. Teuben, J. Organomet. Chem. **364**, 79 (1989).
91. H. Schumann, J. Sun und A. Dietrich, Monatsh. Chem. **121**, 747 (1990).
92. H. Schumann, M. Glanz, J. Winterfeld and H. Hemling, J. Organomet. Chem. **456**, 77 (1993).
93. H. Schumann, C. Janiak, R. D. Köhn, J. Loebel and A. Dietrich, J. Organomet. Chem. **365**, 137 (1989).
94. H. Schumann, J. Winterfeld, R. D. Köhn, L. Esser, J. Sun and A. Dietrich, Chem. Ber. **126**, 907 (1993).
95. A. Visseaux, A. Dormond, M. M. Kubicki, C. Moise, D. Baudry and M. Ephritikhine, J. Organomet. Chem. **433**, 95 (1992).
96. W. Ke, J. Zhongsheng and C. Wenqi, J. Chem. Soc. Chem. Commun. 693 (1991).
97. W. Ke, J. Zhongsheng, G. Wei and C. Wenqi, Chin. J. Chem. **10**, 331 (1992).
98. H. Schumann, E. C. E. Rosenthal, W. Jörn, R. Weimann and J. Demtschuk, J. Organomet. Chem. **507**, 287 (1996).
99. F. T. Edelmann, New J. Chem. **19**, 535 (1995).
100. A. Weber, H. Suhr, H. Schumann and R. D. Köhn. Appl. Phys. **A51**, 520 (1990).
101. A. Weber and H. Suhr, Mod. Phys. Lett. **B 3**, 1001 (1989).