

Molecular Precursors to Group 13 Nitrides, 14¹⁼¹Synthesis and Structures of (N₃)₂Ga[(CH₂)₃NMe₂], (N₃)Ga[(CH₂)₃NMe₂]₂ and (N₃)₃Ga(NR₃) (R = CH₃, C₂H₅)Anjana Devi,^[a] Harald Sussek,^[a] Hans Pritzkow,^[b] Manuela Winter,^[a] and Roland A. Fischer^{*[a]}**Keywords:** Gallium / Azides / Chemical vapour deposition / Gallium nitride / Single source precursors

The synthesis, properties and X-ray single crystal structure analysis of the intramolecularly adduct-stabilised organogallium bisazide (N₃)₂Ga[(CH₂)₃NMe₂] (**1**), the mono azide (N₃)Ga[(CH₂)₃NMe₂]₂ (**2**) and the trialkylamine adducts of triazidogallium of the type (N₃)₃Ga(NR₃) (**3a–d**; R = alkyl) are reported. An unusual isomer **1b** of compound **1** is described, which was obtained by slow cooling of the analytically pure neat liquid compound **1** to 0 °C. The new and unusual structure **1b** can be regarded as a weak associate of dimers linked together by head-to-tail azide

bridges. In contrast, compounds **2** and **3a–b** (R = CH₃, C₂H₅) are monomeric in the solid state. The suitability of the volatile compounds **1** and **2** as single source precursors to grow GaN thin films by chemical vapour deposition is compared, showing that preferentially oriented crystalline films can be obtained from compound **2** on sapphire substrates at 600–700 °C in vacuo (0.1 Pa). However the films have a grey rather than a transparent appearance, which is presumably due to N-deficiency owing to the lower N-content of the single molecule precursor **2** relative to **1**.

Introduction

The binary group 13 nitride GaN, and its ternary mixed phases with Al and In, are very promising materials for advanced microelectronic and optoelectronic devices such as light emitting diodes and lasers, high temperature and high power devices, as well as chemical sensors, acoustic surface-wave conductors and passivation layers (AlN) for GaAs^[1–4] Organometallic vapour phase epitaxy (OMVPE) of these materials is currently achieved by the co-pyrolysis of ER₃ (E = Al, Ga, In; R = alkyl) with a large excess of ammonia (> 1000:1) at very high temperatures (> 1000 °C).^[5–7] In order to avoid a large, background n-type carrier concentration due to nitrogen deficiencies, low temperature deposition techniques (< 850 °C) are interesting.^{[8][9]} However, in this situation, the crystal quality of the layers, especially the concentration of point, line and planar defects which are likely to be electrically active, may be a problem. Considerable effort is currently being directed to the development of alternative molecular routes for the synthesis of group 13 nitride materials in the form of thin epitaxial films, disperse powders or nanocrystals embedded into various matrices. Recent examples include the growth of GaN single crystals (2 mm) by a solid-state reaction from sodium azide and gallium metal, the pyrolysis of various gallium amides, hydrazides or gallium azides yielding nanodisperse GaN materi-

als.^[11–19] Novel *volatile* single source precursors for use in OMVPE have also increasingly been studied.^[17–19] Pre-formed E–N bonds in the precursor molecule lower the activation energies for the chemical vapour deposition (CVD) growth process. This could be advantageous even in the presence of ammonia as the typical (additional) nitrogen source. Azide derivatives of the group 13 metals are especially promising in this respect because the azide unit constitutes an almost ideal source for the N-component avoiding the nonselective formation of undesired side products upon fragmentation of the hydrocarbon ligands of the precursor during the growth process.^[20] We are currently studying a series of adduct-stabilised organo group 13 azides of the general formula (N₃)_{3–a}E(R)_a(L)_b (E = Al, Ga or In; a = 0, 1, 2; R = alkyl; L = py, b = 3; L = NR₃, b = 1), as single molecular sources for OMVPE of the group 13 nitride thin films in the absence of ammonia.^[14–16] Other related works deal with the compounds [R₂GaN₃]₃ (R = H, CH₃, C₂H₅), [(CH₃)₂N]₂GaN₃ and [X₂Ga(N₃)]_n (X = H, Cl.^[21–24] Here we wish to report in detail on the improved synthesis and structural properties of the compounds (N₃)₂Ga[(CH₂)₃NMe₂] (**1**), (N₃)Ga[(CH₂)₃NMe₂]₂ (**2**) and (N₃)₃Ga(NR₃) (**3a**: R = CH₃; **3b**: C₂H₅) all of which have been successfully used to produce GaN materials. The results of these studies have been published elsewhere, except for the new compound **2** discussed here.^[16,19,20]

Results and Discussion

Synthesis and Properties

Molecular precursors of the materials used in electronic devices need to be very pure therefore their chemical syn-

[¹⁼¹] Part 7: Ref.^[31][^a] Lehrstuhl für Anorganische Chemie II, Ruhr-Universität Bochum, D-44780 Bochum, Germany
E-mail: rfischer@aci.ruhr-uni-bochum.de[^b] Anorganisch-chemisches Institut der Ruprecht-Karls-Universität, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

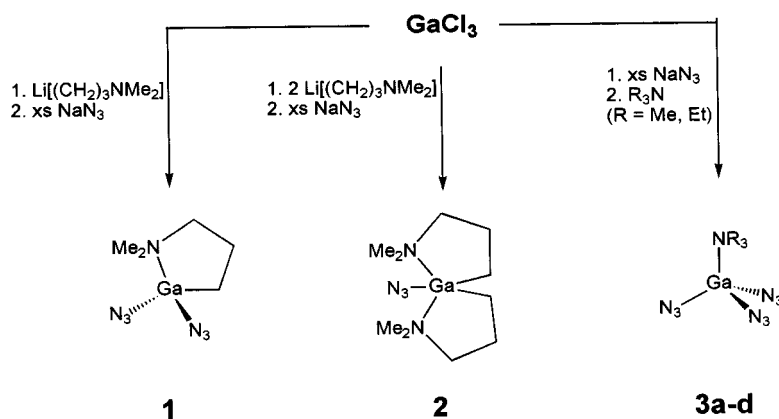
thesis needs to be optimised for ultra high purification; a straightforward and high yield synthesis, very pure starting materials, easy scaling-up for larger quantities (multi-gram to kilogram) and very clean, e. g. oxygen and moisture-free, conditions (dry-box) are required. In the case of azide-type precursors for GaN, the compounds GaCl_3 and NaN_3 are the natural starting materials and are easily available in very pure forms. Furthermore, traces of chloride impurities are not a serious problem since Cl is electronically inactive in GaN. Adduct formation at the group 13 centre has also been successfully employed to reduce the incorporation of O-impurities arising from the solvents used for synthesis (e.g. ethers) or traces of moisture.^{[25][26]} The title compounds (**1–3**) were thus synthesised from GaCl_3 , NaN_3 , $\text{Li}[(\text{CH}_2)_3\text{NMe}_2]$ and NR_3 ($\text{R} = \text{alkyl}$) according to Scheme 1. The previously reported synthesis of the bisazido derivative **1** has been significantly improved, indicated by a much higher melting point of $+36(\pm 0.1)^\circ\text{C}$ (by DSC) rather than -28°C obtained earlier.^[14] At temperatures above 40°C the pure compound **1** is a colourless liquid which can be repeatedly distilled in a dynamic vacuum without decomposition at 150°C (10^{-5} Torr base pressure of the turbo molecular pump system; equilibrium vapour pressure of **1** see below). Transparent single crystals suitable for X-ray crystallography were grown by slow cooling of the neat compound to 0°C . Total elemental analysis gave perfect results within the resolution of the method. NMR and mass spectrometry proved the chemical identity and the absence of any detectable trace impurities, such as $\text{Ga}-\text{O}$ or $\text{Ga}-\text{Cl}$ species (isotope pattern). The new monoazido compound **2** was synthesised in a similar manner (Scheme 1). Neither compound **1** nor compound **2** is pyrophoric or explosive when exposed to sudden heating (>10 K/min) or mechanical shock. Compound **2** is almost insensitive to hydrolysis, but prolonged exposure to moist air of **1** and **2** leads to decomposition and, eventually, traces of (explosive) HN_3 are formed. The synthesis of **3a–b** had been described previously starting from isolated $[\text{Ga}(\text{N}_3)_3]_\infty$.^[14] However this is dangerous, because of the explosive nature of the polymeric triazidogallium. A one-pot synthesis of **3a–b** was thus developed which avoids the isolation of explosive intermediates. The treatment of a toluene suspension of the intermediately

formed compound $\text{Na}[\text{Ga}(\text{N}_3)_4]$ with tertiary alkyl amines as donors is a safe way to yield the triazido congeners of type **3** (Scheme 1).^{[14][27]}

Crystal Structures

The X-ray crystallographic data of **1** revealed that a different isomer **1b** had been obtained. The previously reported crystal data for compound **1** were obtained by zone-melting/crystallisation of a sample in a sealed Lindemann capillary mounted on the goniometer of the diffractometer and the data collection were performed at 150 K.^[14] This was necessary because crystals of **1** could not be obtained by other techniques at that time, probably because of some unknown trace impurities lowering the melting point of the sample. This isomer **1a** crystallises in the triclinic space group $P1bar$ and consists of centrosymmetric dimers exhibiting two asymmetric head bridging azide groups and two terminal azide units (Figure 1a).

The structure of the new isomer **1b** is rather different (Figure 1b). It crystallises from the neat liquid or concentrated toluene solutions (ice cold conditions) in the monoclinic space group $P2(1)/n$ with four molecules attached together by loose head-to-tail azide bridges (Figure 1c). This tetramer can best be described as a dimer of dimers. Two molecules with the gallium centres Ga and Ga(A) are linked together by one single head-to-tail azide bridge $\{\text{Ga}(\text{A})-\text{N}(3\text{B}) = 2.814(5) \text{ \AA}\}$ and these dimers are attached to each other by rather long head-to-tail azide bridges of $3.069(6) \text{ \AA}$. Figure 1d shows the molecular packing of **1b** in the crystal lattice. No further Ga–N distances shorter than 4.11 \AA are present in the crystal lattice. The whole complex is centrosymmetric: for example, the positions of Ga and Ga(B) as well as Ga(A) and Ga(AA) are symmetrically related. All other $\text{N}_{\text{azide}}-\text{Ga}$ contacts are well above the van-der-Waals limit of about 3.50 \AA . The two (symmetry related) pairs of terminal azide groups at Ga(A) and Ga(AA), as well as the pairs of bridging azide units at Ga and Ga(B), show the typical features of covalently bonded azides: one longer $\text{N}_\alpha-\text{N}_\beta$ bond of about $1.16\text{--}1.18 \text{ \AA}$ and one shorter $\text{N}_\beta-\text{N}_\gamma$ bond of about



Scheme 1

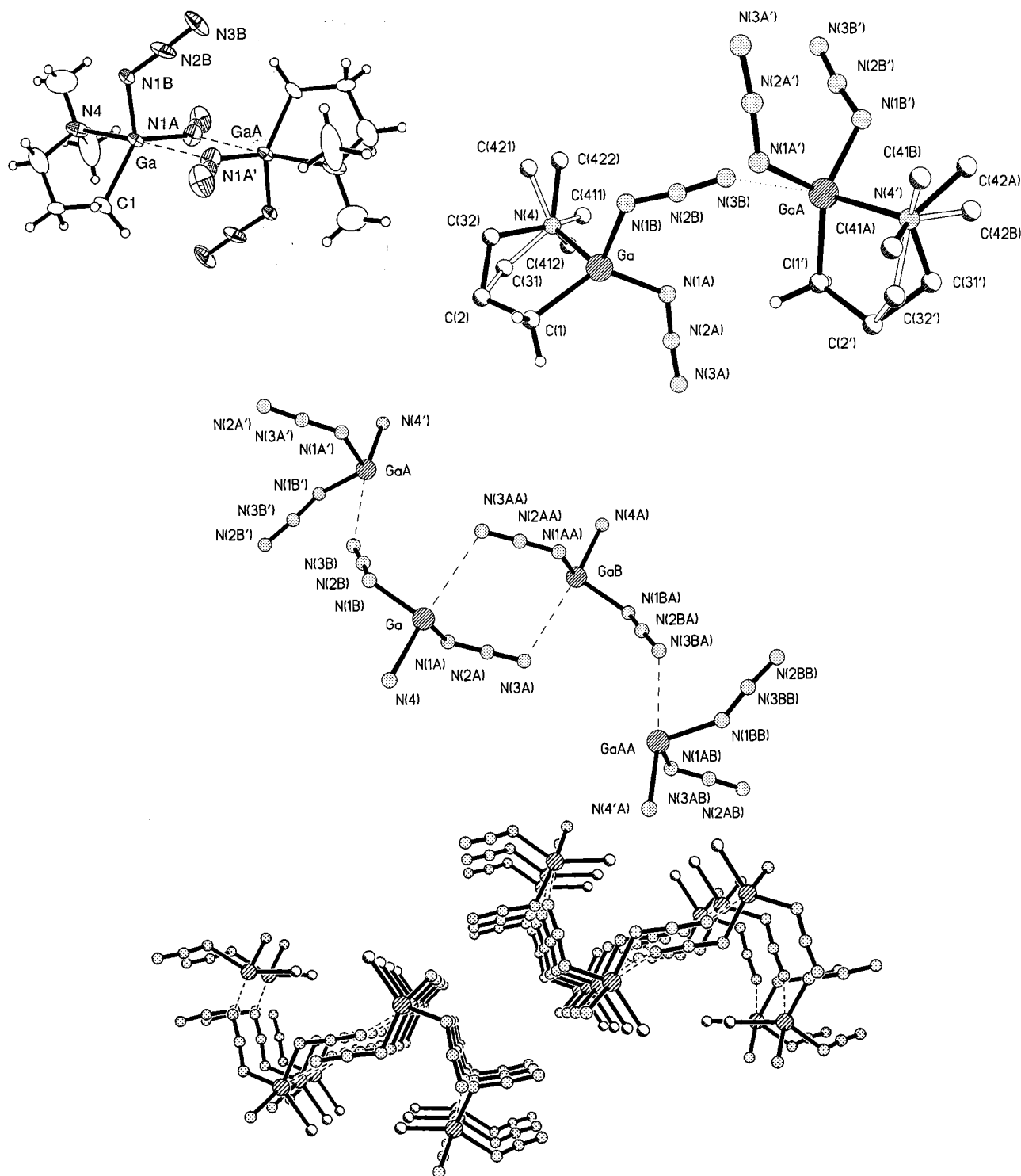


Figure 1. Molecular Structure of **1** in the solid state (ORTEP drawings, the thermal ellipsoids are at the 50% level): (a) compound **1a**;^[14] (b) the two crystallographically independent centres Ga and Ga(a) of compound **1b** showing the disordering of the five-membered heterocyclic chelate rings (view of the molecular packing in the cell); (c) the characteristic tetramer (centrosymmetric dimer of dimers); (d) molecular packing of **1b** in the crystal lattice; selected bond lengths [Å] and bond angles [deg] around the coordination centre Ga (the respective values for GaA are quite similar) for compound **1b**: Ga–N(1b) 188.5(4), Ga–N(1a) 190.5(4), Ga–N(4) 204.7(4), Ga–C(1) 193.8(4), N(1a)–N(2a) 116.2(5), N(2a)–N(3a) 113.9(5), N(1b)–N(2b) 118.0(5), N(2b)–N(3b) 113.8(5), N(3b)–GaA 281.4(5), Ga–N(3aa) 306.9(6); N(1b)–Ga–N(1a) 105.9(2), N(1b)–Ga–C(1) 123.2(2), N(1a)–Ga–C(1) 123.7(2), N(1b)–Ga–N(4) 101.7(2), N(1a)–Ga–N(4) 105.7(2), C(1)–Ga–N(4) 90.7, N(2a)–N(1a)–Ga 123.5(3), N(3a)–N(2a)–N(1a) 176.0(5), N(2b)–N(1b)–Ga 127.6(3), N(3b)–N(2b)–N(1b) 173.7(4)

1.14–1.15 Å; the angles Ga–N_α–N_β range around 126–129° as a consequence of the sp² hybridisation mode

at N_α; the angles N_α–N_β–N_γ are close to 180°. There is no significant difference in the structural characteristics be-

tween terminal and bridging azide groups, again indicating the very weak interaction. On including the longer distances of 3.069(6) Å of Ga–N(3AA) compared to 2.814(5) Å for Ga(A)–N(3b), the coordination spheres of Ga and Ga(A) can be described as distorted trigonal bipyramidal. The trigonal bipyramidal coordination sphere of Ga is more distorted than that of Ga(A) as can be judged by the respective sums of their equatorial angles (356.9° vs. 352.8°). The five-membered heterocyclic chelate rings show a typical disorder because of the facile envelope flip due to intramolecular adduct formation. The positions of the involved atoms, C(31), C(32) and C(31'), C(32') as well as the N–CH₃ groups are disordered (site occupation factor of 0.5). The dative Ga–N bonds, e. g. Ga–N(4) of 2.047(4) Å, are within the usual range.

Compound **2** (Figure 2a) crystallises in the monoclinic space group $P2_1$ with only one enantiomer in the asymmetric unit. In contrast to **1**, intermolecular contacts via azide bridges are absent. The structural parameters of monomeric **2** compare with the largely isostructural aluminium homologue.^{[20][28]} Interestingly the respective indium homologue crystallises as a coordination polymer with *symmetric* head-to-tail bridging azide groups and hexa coordinated indium centres.^[19] Compound **2** adopts a distorted trigonal bipyramidal structure with the two dimethylamino donor groups at the apical positions with an angle N(1)–Ga–N(2) of 178.0(8)°. The structural parameters of the equatorially coordinated azide are essentially similar to **1a** and **1b** exhibiting a somewhat more pronounced alternation of the N–N bond lengths and a longer Ga–N_α distance of 2.005(5) Å because of the larger covalent radius of the pentacoordinated Ga-centre. The conformational requirements of the chelating aminoalkyl groups cause an enlarged angle C1–Ga–C6 of 144.1(4)° and consequently smaller angles C6–Ga–N3 and C1–Ga–N3 of 107.6(4)° and 108.3(3)°, respectively. The Ga–C bonds are normal and the Ga–N1 and Ga–N2 dative bonds are within the usual range for related structures with penta-oordinated Ga centres, e.g. the chloro analogue of **2**.^[25] Figure 2b shows the packing of compound **2** in the elementary cell.

In contrast to **1**, the compounds **3a** and **3b** crystallise as monomeric units, with no short intramolecular contacts, in the triclinic space group $P1\bar{1}$ (**3a**) or in the monoclinic space group $P2_1/n$ (**3b**). Figure 3 shows the molecular structure of **3a**, which is essentially the same as for **3b** (see Experimental Section). The discussion therefore concentrates on **3a**. The only other structurally characterised compound with a triazido gallium unit is the hexacoordinated pyridine adduct py₃Ga(N₃)₃.^{[14][29]} Due to the increased steric bulk of the tertiary amines only one amine ligand binds to the Ga(N₃)₃ moiety, rather than three (flat) pyridine ligands, yielding a trigonal pyramidal structure. Consequently the Ga–N_{azide} bond lengths of **3a** and **3b** are somewhat shorter than the values obtained for the pyridine adduct (Figure 3). The short dative Ga–NR₃ bond of about 2.00 Å indicates a rather strong donor–acceptor bond to the Ga(N₃)₃ unit similar to **1** or R₃N–GaCl₃.^[14] The structural parameters of the azide groups for **3a** and **3b** are similar to **1** and **2**.

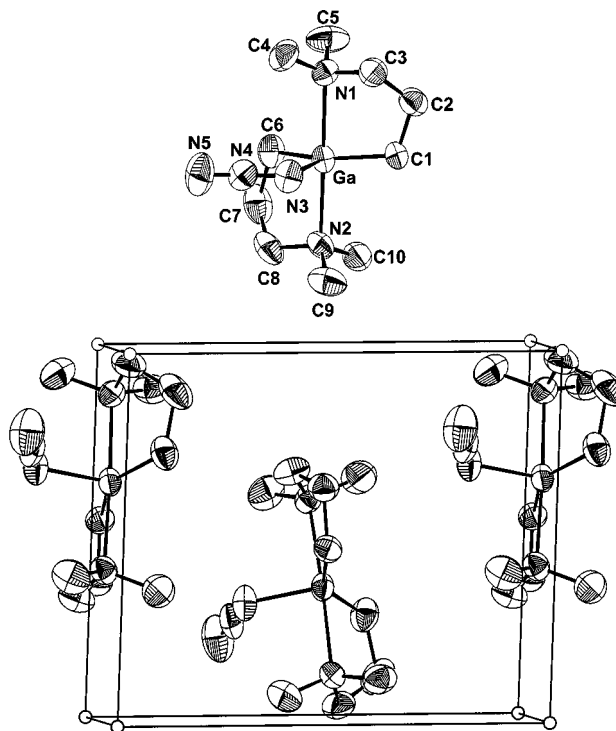


Figure 2. Molecular Structure of **2** in the solid state (ORTEP drawings, the thermal ellipsoids are at the 50% level); (a) the monomeric unit of **2**; (b) the packing in the elementary cell; selected bond lengths [Å] and bond angles [deg]: Ga–N1 234.5(5), Ga–N2 231.1(5), Ga–N3 200.5(5), Ga–C3 197.3(5), Ga–C8 197.7(7), N3–N4 120.7(8), N4–N5 132.2(9); C3–Ga–C8 144.1(4), C3–Ga–N3 107.6(4), C8–Ga–N3 108.3, C3–Ga–N2 96.8(2), C8–Ga–N2 84.3(3), N3–Ga–N2 89.3(3), C3–Ga–N1 83.4(2), C8–Ga–N1 97.1(2), N3–Ga–N1 88.3(2), N2–Ga–N1 177.5(3), N3–N4–N5 178.0(8), N4–N3–Ga 118.7(5)

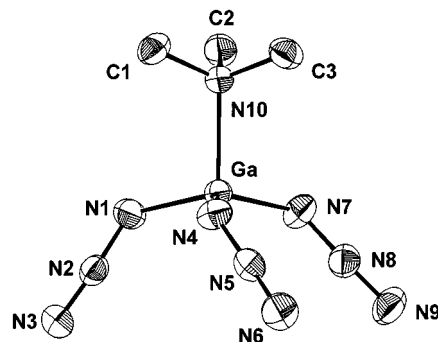


Figure 3. Molecular Structure of **3a** in the solid state (ORTEP drawings, the thermal ellipsoids are at the 50% level); selected bond lengths [Å] and bond angles [deg]: Ga–N1 188.8(2), Ga–N4 188.7(3), Ga–N7 189.2(2), Ga–N10 200.5(2), N1–N2 121.5(3), N2–N3 114.0(3); N1–Ga–N4 124.3(1), N1–Ga–N7 113.0(19), N1–Ga–N10 101.2(1), N4–Ga–N7 112.5(1), N4–Ga–N10 99.5(1), N7–Ga–N10 101.7(1), Ga–N1–N2 122.7(2), N1–N2–N3 175.5(3)

Materials Chemistry

Transparent, smooth (rms of 16 nm by AFM), epitaxial [full width at half maximum (FWHM) of the GaN(002) reflection of 0.72°] and stoichiometric films of GaN were grown by OMCVD on sapphire (0001) substrates at tem-

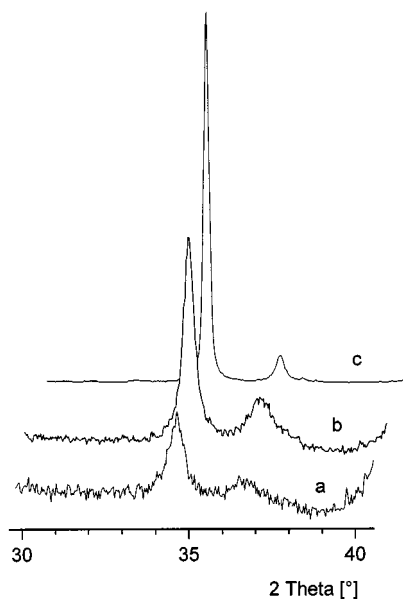


Figure 4. XRD patterns of GaN layers grown on $\text{Al}_2\text{O}_3(0001)$ using compound **2** in an isothermal horizontal hot wall tube reactor in vacuo (10^{-3} Torr) in the absence of carrier gases and additional sources of nitrogen (i.e. in the absence of ammonia) at substrate temperatures of (a) $T = 600^\circ\text{C}$; (b) $T = 650^\circ\text{C}$; (c) $T = 750^\circ\text{C}$

peratures as low as 1070 K with growth rates up to 3–4 $\mu\text{m/hr}$ from **1** with no additional source of nitrogen (ammonia) either employing an isothermal hot walled or a non-isothermal cold wall reactor system.^[16] The vapour pressure of **1** between 25 (2.5 mPa) and 160°C (16 Pa) was determined by standard methods employing a Netzsch VP433 vapour pressure balance by the condensation or the impulse method.^[16b] Thus, the vapour pressure of **1** can be calculated according to Equation 1. Compound **2** exhibits a vapour pressure which is an order of magnitude lower. These

results show that increasing the coordinative shielding of the Ga centre by sacrificing one azide group does not improve the volatility as one might have expected on the basis of the *monomeric* structure of **2** when contrasted with the *associated* structure of **1**.

$$\ln[p(T)] = 23.7 - 8840/T [\text{Pa}] \quad (1)$$

With a special reactor design the concentration of the fragments HGaN_x and GaN_x ($x = 1-6$) in the boundary layer above the substrate were measured as a function of the substrate temperature showing a correlation with the growth rate of GaN.^[30] We were interested in comparing the properties of the bisazido gallium compound **1** with a closely related compound with only one azide group and thus a lower nitrogen content. Compound **2** proved suitable to grow GaN films by CVD techniques employing similar hot wall conditions as for precursor **1**. The XRD pattern (Figure 4) of the films grown from **2** reveals a small shoulder for the (101) peak besides the dominant (002) reflection. The identity of the bulk material as GaN was independently established by RAMAN spectroscopy (Figure 5). The GaN thin film obtained from **2**, is only preferentially oriented on the sapphire substrate. Due to the lower nitrogen content of the monoazido precursor **2** the quality of the deposited GaN material was poor as judged by the grey appearance of the layers (Ga droplets were not detected by XRD). Also, because of the lower vapour pressure of **2** the growth rates of less than 1 $\mu\text{m/hr}$ obtained were significantly lower than the growth rates obtained from precursor **1** at the same settings of the vaporiser (temperature of $80-100^\circ\text{C}$). The idea to have fewer Ga–C bonds and as many Ga– N_3 moieties as possible in the precursor is nicely underlined by the comparison of the films grown from **1** and **2**. Thus compound **1** seems still to be the best choice

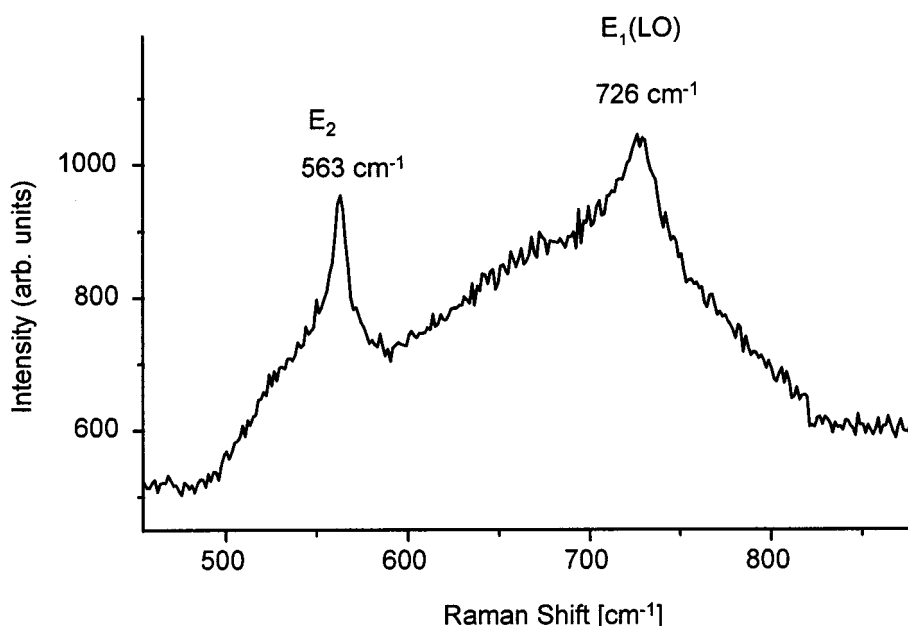


Figure 5. Raman data obtained from the GaN layer of Figure 4c; the characteristic E_2 and E_1 modes at 563 cm^{-1} and 726 cm^{-1} respectively of the GaN lattice vibrations are detected

to derive a nitrogen rich organometallic GaN precursor with an acceptable volatility for technical applications.

In contrast to **1** and **2** the triazido compounds of type **3** cannot be sublimed or volatilised at reasonable rates without the severe danger of explosion of the sample. This is probably because of the gradual loss of the volatile protecting donor ligand NR_3 and the formation of the parent compound $\text{Ga}(\text{N}_3)_3$ which is highly explosive. TG/DTA measurements were undertaken but have not yet given good quality data because of the detonation of the samples (1–2 mg). However, by taking advantage of this particular property, nanocrystalline GaN was obtained by controlled detonation of **3a** and **3b** contained in a suitable sealed stainless steel autoclave.^[27,31,32] Other related adducts of long chain amines, e.g. **3c–e** were also pyrolysed under similar conditions to yield nanocrystalline GaN samples. However, it proved difficult to obtain very pure nano-GaN samples from **3a–b** due to the much higher hydrocarbon content of these precursors.^[32]

Conclusions

Molecular precursors of the type $(\text{N}_3)_2\text{Ga}[(\text{CH}_2)_3\text{NMe}_2]$ and $(\text{N}_3)\text{Ga}[(\text{CH}_2)_3\text{NMe}_2]_2$ are single source precursors suitable for the growth of crystalline GaN films by CVD. Compound **2** is monomeric in the solid state while compound **1b** is basically a tetramer (dimer of dimers) with four molecules attached together by loose head to tail azide bridges. The testing of these compounds by CVD has demonstrated the feasibility of depositing GaN films at low temperatures (600–750°C) without any additional source of nitrogen. With respect to the accessible growth rate and thin film properties, films grown from compound **1** were of higher quality than those obtained from compound **2**.

Experimental Section

General procedures: All manipulations were performed utilising carefully oven-dried reaction vessels and Schlenk techniques under an inert atmosphere of purified argon or in a glove box. Solvents were dried under N_2 by standard methods and stored over 4 Å molecular sieves (residual water < 3 ppm, Karl-Fischer). Starting materials not available from commercial sources were synthesised according to the literature or by modified procedures, i. e. $\text{Cl}_a\text{-Ga}[(\text{CH}_2)_3\text{NMe}_2]_{3-a}$ ($a = 1, 2$).^[25] The ^1H and ^{13}C NMR spectra were recorded on a Bruker EM 200 spectrometer and were referenced to residual protic impurities of the internal solvent and corrected to tetramethylsilane. The IR spectra were obtained in solution (toluene, pyridine) using 0.1 mm CaF_2 and NaCl cells on a Perkin–Elmer 1650 FT IR or a Bruker IFS 66. Elemental analysis were provided by the Microanalytic Laboratory of the Chemical Institute of the University of Heidelberg and the Service centre of the Faculty of Chemistry at the Ruhr-University of Bochum.

Bisazido[3-(dimethylamino)propyl]gallium (1): $\text{Li}[(\text{CH}_2)_3\text{NMe}_2]$ ^[33] (4.2 g, 45.4 mmol) was suspended in dry ether (75 mL) and was added dropwise to a Schlenk vessel containing GaCl_3 (8 g, 45.4 mmol) in dry diethyl ether (75 mL) placed in a dry ice bath. After the addition was completed, the reaction mixture was allowed

to stir at room temperature for 15 hours and the bis chloro[3-(dimethylamino propyl)] gallium formed was sublimed at 100°C to separate it from LiCl . The sublimed product (9.16 g, 40.38 mmol) was then treated with excess NaN_3 (9.72 g, 120 mmol) in toluene and refluxed at 115°C for another 15 hours. After filtration from the white residue, the solvent was removed by vacuum distillation. The product was purified by flask to flask distillation at reduced pressure using a turbomolecular pump (150°C, 10^{-5} mbar). Yield: 5.75 g (90%). – ^1H NMR (C_6D_6 , 20°C): $\delta = 0.38$ (t, 2 H, $\text{Ga}-\text{CH}_2$), 1.08 (m, 2 H, CH_2), 1.49 (t, 2 H, $\text{N}-\text{CH}_2$), 1.71 {s, 6 H, $\text{N}(\text{CH}_3)_2$ }. – ^{13}C NMR (C_6D_6 , 20°C): $\delta = 3.29$ ($\text{Ga}-\text{CH}_2$), 21.10 (CH_2), 44.57 { $\text{N}(\text{CH}_3)_2$ }, 61.70 ($\text{N}-\text{CH}_2$). – MS (EI, 70 eV) $m/z = 239$ [$(\text{N}_3)_2\text{Ga}\{(\text{CH}_2)_3\text{NMe}_2\}$]. – IR (toluene): $\tilde{\nu} = 2103$ vs (N_3) cm^{-1} . – $\text{C}_5\text{H}_{12}\text{GaN}_7$: calcd. C 25.03, H 5.04, N 40.87, Ga 29.06; found C 24.76, H 5.09, N 40.15, Ga 29.07.

Azidobis[3-(dimethylamino)propyl]gallium (2): Chlorobis[3-(dimethylamino)propyl]gallium^[25] (2 g, 7.20 mmol) was dissolved in toluene (10 mL), added to a suspension of sodium azide (2.50 g, 38.45 mmol) in toluene and cooled to -78°C . The mixture was allowed to warm to room temperature after the addition and was subsequently heated to reflux for 15 h. After filtration from the white residue the solvent was removed by vacuum distillation at 25°C. The product was recrystallised from concentrated toluene solution at 5°C. Yield 1.98 g (6.99 mmol, 97.1%) as colourless needles, m.p. 40.3°C. – ^1H NMR (C_6D_6 , 20°C): $\delta = 0.38$ (m, 4 H, $\text{Ga}-\text{CH}_2$), 1.54 (m, 4 H, CH_2), 1.88 {s, 6 H, $\text{N}(\text{CH}_3)_2$ }, 1.98 (t, 4 H, NCH_2). – ^{13}C NMR (C_6D_6 , 20°C): $\delta = 4.86$ ($\text{Ga}-\text{CH}_2$), 22.53 (CH_2), 44.58 { $\text{N}(\text{CH}_3)_2$ }, 61.35 (NCH_2). – MS (EI, 70 eV) m/z (%) = 282 (20) [$\text{M} - \text{H}^+$], 241 (100) [$\text{Ga}\{(\text{CH}_2)_3\text{N}(\text{CH}_3)_2\}_2^+$], 197 (8) [$(\text{N}_3)\text{Ga}\{(\text{CH}_2)_3\text{N}(\text{CH}_3)_2\}^+$]. – IR (toluene): $\tilde{\nu} = 2080$ vs (N_3) cm^{-1} . – $\text{C}_{10}\text{H}_{24}\text{GaN}_5$ (284.05): calcd. C 42.28, H 8.51, N 24.65, Ga 24.54; found C 42.41, H 8.45, N 24.44, Ga 25.28.

General One-Pot Synthesis for Alkylamine Adducts of $\text{Ga}(\text{N}_3)_3$ of the Formula $(\text{R}_3\text{N})\text{Ga}(\text{N}_3)_3$ (3a–d): A sample of freshly sublimed GaCl_3 (5.00 g, 28.40 mmol) was treated with a sample of sodium azide (9.23 g, 142.00 mmol) in 20 mL of toluene at -78°C . To this mixture 100 mL of THF was added with stirring. The suspension was allowed to warm to room temperature and was stirred for an additional 24 h. After filtration from the white residue the solution was concentrated by vacuum distillation at 25°C (removal of most of the THF) and 100 mL of toluene was added. At -78°C a sample of the respective alkylamine (113.6 mmol) was added and the mixture warmed to room temperature whilst stirring for 12 h. The reaction mixture was filtered and the solvent removed by vacuum distillation at 25°C. Compounds **3a–b** were recrystallised from concentrated toluene solutions at -30°C . The long chain alkylamine adducts **3a–d** were obtained as viscous, slightly yellow oils, which were thoroughly washed with *n*-pentane to remove excess alkylamine.

$\{(\text{CH}_3)_3\text{N}\}\text{Ga}(\text{N}_3)_3$ (3a): yield 6.88 g (27 mmol, 95%) m.p. 42.5°C. – ^1H NMR ($[\text{D}_8]\text{THF}$, 20°C) $\delta = 2.49$ (s, CH_3). – ^{13}C NMR ($[\text{D}_8]\text{THF}$, 20°C) $\delta = 47.30$ (CH_3). – IR (toluene) $\tilde{\nu} = 2132$ (vs), 2104 (vs), 1351 (s), 1293 (s) (N_3) cm^{-1} . – $\text{C}_3\text{H}_9\text{GaN}_{10}$ (254.86): calcd. C 14.14, H 3.56, N 54.96, Ga 27.36; found C 14.35, H 3.45, N 54.72, Ga 27.12.

$\{(\text{C}_2\text{H}_5)_3\text{N}\}\text{Ga}(\text{N}_3)_3$ (3b): yield 8.21 g (27.63 mmol, 97.3%) m.p. 47.5°C. – ^1H NMR (C_6D_6 , 20°C) $\delta = 2.98$ (q, 2 H, NCH_2), 1.15 (t, 3 H, CH_3). – ^{13}C NMR (C_6D_6 , 20°C) $\delta = 49.1$ (NCH_2), 10.1 (CH_3). – IR (toluene) $\tilde{\nu} = 2131$ (vs), 2105 (vs), 1344 (s), 1291 (s) (N_3) cm^{-1} . – $\text{C}_6\text{H}_{15}\text{GaN}_{10}$ (296.97): calcd. C 24.27, H 5.09, N 47.17, Ga 23.48; found C 24.60, H 5.02, N 47.53, Ga 24.12.

Table 1. Crystal data and structure refinement for **1b**, **2** and **3a**

	1b	2	3a
Empirical Formula	C ₅ H ₁₂ GaN ₇	C ₁₀ H ₂₄ GaN ₅	C ₃ H ₉ GaN ₁₀
Formula weight	239.94	284.06	254.92
Crystal size [mm]	0.58 × 0.52 × 0.40	0.50 × 0.40 × 0.20	0.5 × 0.3 × 0.2
T, K	203(2)	203(2)	203(2)
Crystal system	Monoclinic	monoclinic	triclinic
Space group (#)	<i>P</i> 2 ₁ / <i>n</i> (14)	<i>P</i> 2 ₁ (4)	<i>P</i> (-1) (2)
<i>a</i> , Å	6.974(4)	7.275(4)	6.076(3)
<i>b</i> , Å	11.964(4)	10.821(5)	7.546(4)
<i>c</i> , Å	23.916(7)	9.622(5)	11.182(6)
α , °	90	90	79.57(2)
β , °	92.92(4)	106.93(3)	82.76(2)
γ , °	90	90	81.95(2)
<i>V</i> , Å ³	1992.9(14)	724.6(6)	496.6(4)
<i>Z</i>	8	2	2
Calcd. density [Mg/m ³]	1.599	1.302	1.705
<i>m</i> (Mo- <i>K</i> _α)mm ⁻¹	2.731	1.885	2.753
<i>F</i> (000)	976	300	256
θ_{\min} – θ_{\max} [°]	2.41–27.49	27	28
Index range	0 ≤ <i>h</i> ≤ 9, 0 ≤ <i>k</i> ≤ 15, –31 ≤ <i>l</i> ≤ 30	–10 ≤ <i>h</i> ≤ 9, –10 ≤ <i>k</i> ≤ 13, –11 ≤ <i>l</i> ≤ 13	–7 ≤ <i>h</i> ≤ 8, –9 ≤ <i>k</i> ≤ 9, 0 ≤ <i>l</i> ≤ 14
No. of reflection	4856	2966	2387
Unique	4527	2816	2387
Observed [<i>I</i> > 2σ(<i>I</i>)]	2992	2359	2387
Transmission min/max	0.245/1.000	0.802/0.996	0.653/1.000
No. of Parameters	229	251	164
Largest diff. peak/hole [eÅ ⁻³]	0.908/–0.625	0.984/–0.900	0.569/–0.516
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0454/0.1409	0.0506/0.1216	0.0313/0.0779
Goodness of fit	0.904	1.069	1.052

$$R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|; wR2 = [\Sigma_w(F_o^2 - F_c^2)^2/\Sigma_w(F_o^2)^2]^{1/2}; GOF = [\Sigma_w(F_o^2 - F_c^2)/(\text{NO} - \text{NV})]^{1/2}.$$

[(CH₃)₂N(C₈H₁₇)]Ga(N₃)₃ (3c**):** yield 9.01 g(25.53 mmol, 93.4%) m.p. 57°C. – ¹H NMR (C₆D₆, 20°C) δ = 1.86 (t, 2 H, NCH₂), 1.56 (s, 6 H, NCH₂), 1.26–0.80 (m, 12 H, CH₂), 0.9 (t, 3 H, CH₂CH₃) – ¹³C NMR (C₆D₆, 20°C) δ = 60.12 (NCH₂), 44.31 (NCH₃), 31.99, 29.22, 26.85, 24.10, 23.00 (5 × CH₂), 14.29 (CH₂CH₃). – IR (toluene) $\tilde{\nu}$ = 2130 (vs), 2100 (vs), 1344 (s), 1290 (s) (N₃) cm⁻¹. – C₁₀H₂₃GaN₁₀ (353.08): calcd. C 34.02, H 6.47, N 39.67, Ga 19.75; found C 34.27, H 6.84, N 39.17, Ga 19.51.

[(CH₃)₂N(C₁₀H₂₁)]Ga(N₃)₃ (3d**):** yield 9.95 g(26.13 mmol, 92%). – ¹H NMR (C₆D₆, 20°C) δ = 2.00 (t, 2 H, NCH₂), 1.80 (s, 6 H, NCH₂), 1.30–1.00 (m, 16 H, CH₂), 0.9 (t, 3 H, CH₃). – ¹³C NMR (C₆D₆, 20°C) δ = 59.0 (NCH₂), 43.5 (NCH₃), 31.8–24.6 (8 × CH₂), 13.8 (CH₂CH₃). – IR (toluene) $\tilde{\nu}$ = 2130 (vs), 2105 (vs), 1348 (s), 1300 (s) (N₃) cm⁻¹. – C₁₂H₂₇GaN₁₀ (381.13): calcd. C 37.79, H 7.09, N 36.74, Ga 18.38; found C 37.91, H 7.50, N 36.82, Ga 17.54.

X-ray Crystal Structure Determination: Crystal data and details of the structure determination of **1**, **2** and **3a** are compiled in Table 1. The data of compound **3b** are available as supplementary publication (see below). Unique sets of intensity data were collected with a four-circle diffractometer (Mo-*K*_α radiation, λ = 0.71073 Å), graphite monochromator, ω-scan). Empirical absorption corrections (ψ-scans) were applied. The structures were solved by direct methods^[34a] and refined by least squares methods based on *F*² with all observed reflections.^[34b] All non-hydrogen atoms were refined anisotropically. Crystals of **1**, **2** and **3a,b** were mounted on the goniometer using the perfluoro ether technique with cooling. Data collection was performed with a STOE-AED2 four circle instrument (University of Heidelberg, Mo-*K*_α radiation λ = 0.71073 Å, graphite monochromator, ω-scan). Empirical absorption correction (ψ-scans) were applied. Correction for absorption was done on the basis of ψ-scans. The structure solution was done with direct methods^[34a] and the structure refinement (full matrix least squares

against *F*²) was undertaken with anisotropic structural parameters for all nonhydrogen atoms employing the program.^[34c] The absolute structure of **2** was assigned on the basis of its Flack parameter × of –0.003(29).^[36] The structure **1b** shows a disorder at the position C(31), C(32) and C(31') and C(32') respectively due to the facile envelope-flip of the five-membered heterocycle defined by the atoms Ga, C(1), C(2), C(3), N(4). This disorder was fully resolved (Figure 1b). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre: CCDC-119479 (**1b**), 119673 (**2**), 119672 (**3a**) and 119671 (**3b**). Copies of the data can be obtained free of charge by application to CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK [Fax: (internat.) + 44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk].

MOCVD of GaN Thin Films With Compound 2 as Precursor: The MOCVD experiments were conducted employing a simple horizontal hot wall reactor (heated quartz tube) described elsewhere.^[35] The system was loaded with degreased single crystalline sapphire substrates (0001) heated to 450°C and evacuated to 10⁻⁶ mbar for several hours. After filling the reactor with argon the precursor vessel containing a sample of 0.5 g of compound **2** was attached to the quartz tube of the reactor and cooled to –30°C. The system was again evacuated down to a base pressure of 10⁻⁵ mbar and the oven was set to the desired temperature (600–750°C). Then the precursor reservoir was heated to vaporise the precursor. The pressure during the deposition was about 10⁻³ mbar. No carrier gas was used for the deposition. The obtained films (almost transparent to grey in appearance) were characterised by XRD using a Bruker AXS D8 ADVANCE diffractometer. RAMAN spectra of the films were recorded using a DILOR SPECTRALAB instrument equipped with a microscope using an argon ion laser operating at 514 nm.

Acknowledgments

The authors wish to thank the Deutsche Forschungsgemeinschaft for generous support and Prof. Dr. W. S. Sheldrick for his generous help rendered in solving the crystal structure of compound **1b**. A. D. is grateful to the Alexander von Humboldt Foundation for a fellowship.

- [1] S. Fujieda, M. Mitzuta, Y. Matsumoto, *Adv. Mater. Opt. Elec.* **1996**, 6, 127–134.
- [2] H. Morkoc, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, M. Burns, *J. Appl. Phys.* **1994**, 76, 1363–1398.
- [3] H. Okano, N. Tanaka, Y. Takahashi, T. Tanaka, K. Shibata, S. Nakano, *Appl. Phys. Lett.* **1994**, 64, 166–168.
- [4] J. I. Pankove, *Mater. Res. Soc. Symp. Proc.* **1990**, 162, 515–522.
- [5] M. A. Khan, J. N. Kuznia, J. M. V. Hovea, D. T. Olson, *Appl. Phys. Lett.* **1991**, 58, 526–527.
- [6] T. Detchprohm, K. Hiramatsu, N. Sawaki, I. Akasaki, *J. Cryst. Growth* **1994**, 137, 171–174.
- [7] S. Nakamura, N. Iwasa, T. Mukai, *Jpn. J. Appl. Phys.* **1992**, 31, 1258–1266.
- [8] S. D. Lester, F. A. Ponce, M. G. Crawford, D. A. Steigerwald, *Appl. Phys. Lett.* **1995**, 66, 1249–1251.
- [9] D. J. Smith, D. Chandrasakher, B. Sverdlov, A. Botchkarev, A. Salvador, H. Morcok, *Appl. Phys. Lett.* **1995**, 67, 1830–1832.
- [10] H. Yamane, M. Shimada, S. J. Clarke, F. J. DiSalvo, *Chem. Mater.* **1997**, 9, 413–416.
- [11] M. I. Baraton, X. Chen, K. E. Gonsalves, *J. Mater. Chem.* **1996**, 6, 1407–1412.
- [12] [12a] O. T. Beachley, Jr., J. C. Pazik, M. J. Noble, *Organometallics*, **1998**, 17, 2121. — [12b] D. K. Gaskill, N. Bottka, M. C. Lin, *Appl. Phys. Lett.*, **1986**, 48, 1449. — [12c] S. Miyoshi, K. Onabe, N. Ohkouchi, H. Yaguchi, R. Ito, S. Fukatsu, Shirak, S. Yoshida, *J. Cryst. Growth*, **1992**, 124, 439.
- [13] A. C. Jones, C. R. Whitehouse, J. S. Roberts, *Chem. Vap. Dep.* **1995**, 1, 63–78.
- [14] R. A. Fischer, A. Miehr, E. Herdtweck, M. R. Mattner, O. Ambacher, T. Metzger, E. Born, S. Weinkauff, C. R. Pulham, S. Parsons, *Chem. Eur. J.* **1996**, 2, 1353–1358.
- [15] R. A. Fischer, A. Miehr, O. Ambacher, T. Metzger, E. Born, *J. Cryst. Growth* **1997**, 170, 139–143.
- [16] [16a] A. Miehr, O. Ambacher, T. Metzger, E. Born, R. A. Fischer, *Chem. Vap. Dep.* **1996**, 2, 51–55. — [16b] A. Devi, W. Rogge, A. Wohlfart, G. Becker, R. A. Fischer, *Chem. Vap. Dep.* **1999** to be submitted.
- [17] J. Kouvetakis, D. Beach, *Chem. Mater.* **1989**, 1, 476–478.
- [18] J. Kouvetakis, J. McMurrin, P. Matsunaga, M. O’Keeffe, J. L. Hubbard, *Inorg. Chem.* **1997**, 36, 1792–1797.
- [19] R. A. Fischer, H. Sussek, A. Miehr, H. Pritzkow, E. Herdtweck, *J. Organomet. Chem.* **1997**, 548, 73–82.
- [20] R. A. Fischer, A. Miehr, H. Sussek, H. Pritzkow, E. Herdtweck, J. Müller, O. Ambacher, T. Metzger, *J. Chem. Soc., Chem. Commun.* **1996**, 2685–2686.
- [21] H. S. Park, S. D. Waezsada, A. H. Cowley, H. W. Roesky, *Chem. Mater.*, **1998**, 10, 2251–2257.
- [22] V. Lakhotaia, D. A. Neumayer, A. H. Cowley, R. A. Jones, J. G. Eckerdt, *Chem. Mater.*, **1995**, 7, 546–552.
- [23] K. –L. Ho, K. F. Jensen, J. W. Hwang, W. L. Gladfelter, J. F. Evans, *J. Cryst. Growth*, **1991**, 107, 376–380.
- [24] J. McMurrin, D. Dai, K. Balasubramanian, C. Steffek, J. Kouvetakis, J. L. Hubbard, *Inorg. Chem.* **1998**, 37, 6638–6644.
- [25] H. Schuhmann, T. D. Seuss, O. Just, R. Weimann, H. Hemling, F. H. Goerlitz, *J. Organomet. Chem.*, **1994**, 479, 171–186.
- [26] A. C. Jones, *Chem. Soc. Rev.*, **1997**, 101–110.
- [27] A. C. Frank, F. Stowasser, H. Sussek, H. Pritzkow, C. R. Mis-kys, O. Ambacher, M. Giersig, R. A. Fischer, *J. Am. Chem. Soc.*, **1998**, 120, 3512–3513.
- [28] J. Mueller, R. A. Fischer, H. Sussek, P. Pilgram, R. Wang, H. Pritzkow, E. Herdtweck, *Organometallics*, **1998**, 17, 161–166.
- [29] D. A. Neumayer, A. H. Cowley, A. H. Decken, R. A. Jones, L. Lakhotaia, J. G. Eckerdt, *J. Am. Chem. Soc.* **1995**, 117, 5893–5895.
- [30] J. Schaefer, J. Wolfrum, R. A. Fischer, H. Sussek, *Chem. Phys. Lett.* **1999**, 300, 152–156.
- [31] R. A. Fischer, A. C. Frank, F. Stowasser, O. Stark, H. T. Kwak, H. Sussek, A. Rupp, H. Pritzkow, O. Ambacher, M. Geirsig, *Adv. Mater. Opt. Electron.* **1998**, 8, 135–146.
- [32] A. Rupp, Dipl. Thesis, Heidelberg, **1997**.
- [33] K. H. Thiele, E. Langguth, G. E. Mueller, *Z. Anorg. Allg. Chem.* **1980**, 462, 152.
- [34] [34a] G. M. Sheldrick, *SHELX86*, Univ. Göttingen, 1986. — [34b] G. M. Sheldrick, *SHELXL97*, Univ. Göttingen, 1997. — [34c] G. M. Sheldrick, *SHELXL93*, Univ. Göttingen, 1993.
- [35] R. A. Fischer, A. Miehr, *Chem. Mater.* **1996**, 8, 1356–1359.
- [36] G. Bernardinelli, H. D. Flack, *Acta Crystallogr.* **1982**, B38, 907.

Received May 25, 1999
[199188]