First Volatile Alkylgallyl Manganese Complexes; Structure of [(CO5)Mn]2Ga[(CH2)3NMe2]. Molecular Control of the Stoichiometry of Mn–Ga Thin Films Grown by Low-pressure MOCVD

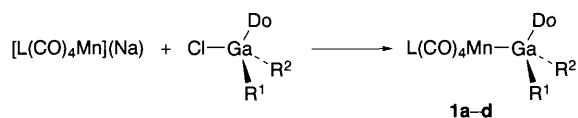**Roland A. Fischer,* Alexander Miehr, Markus M. Schulte and Eberhardt Herdtweck**

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The Mn–Ga complexes of the general formula {L(CO)$_4$Mn}$_a$[GaR$_{3-a}$(Do)] (L = CO, R = alkyl; Do = N-Lewis-donor) are obtained in yields $\geq$90% and used as volatile single source precursors for the gas-phase deposition of thin Mn–Ga alloy films.

Intermetallic phases such as β-CoGa and ε-NiIn, which are of interest as novel contact metallizations for III/V-semiconductor devices, have been grown by low-pressure MOCVD from volatile transition metal/group 13 organometallic complexes.[1] Besides the related work of Aylett *et al.* on the deposition of transition metal silicides,[2] little is known about the growth of metal alloy thin films from organometallic single sources.[3] The progress in this area of potential applications is limited by the availability of appropriate precursors. This is particularly true for the combination Mn–Ga. The few known compounds featuring this linkage are either non-volatile clusters or contain very bulky aryl substituents and also Ga–Cl or Ga–O bonds, properties that rule out these systems as useful for MOCVD. We have synthesized the first volatile and largely heteroatom free Mn–Ga compounds 1a–d, Scheme 1† with almost quantitative yields. The strongly polarized Mn$^{\delta-}$–Ga$^{\delta+}$ bonds of 1b–d are instantaneously cleaved by electrophilic/nucleophilic attack with Me$_3$SnCl or by oxidation with iodine giving (CO)$_5$Mn-SnMe$_3$ and (CO)$_5$MnJ, respectively, beside the corresponding alkylgalliumhalide. Interestingly, the bond polarization of 1a is considerably lower, since it reacts slower and is more stable against moist air than 1b–d.

The formation of a Lewis acid–base adduct stabilizes 1a–d against alkyl exchange equilibria, which are usually very rapid for the base free alkylgallium complexes R$_{3-a}$Ga[ML$_n$]$_a$ (a = 1, 2). Such compounds with threefold coordinated gallium atoms could be isolated in a few cases only.[4] An X-ray diffraction study was undertaken on compound 1c (Fig. 1),‡ which revealed an average σ(Mn–Ga) bond length of 265.3 pm. Other σ(Mn–Ga) bonds range between 245 pm[5] and 253 pm[6] for threefold coordinated gallium and 269.1(4) pm for the cluster ion [Mn$_3$(CO)$_{12}$(μ-GaCl$_2$)]$^{2-}$[7] with a fourfold coordinated gallium atom. The comparably long Mn–Ga bond of 1c thus agrees with the sp^3 bonding type of the gallium centre. In the solid state the molecular structure of 1c is chiral, owing to the envelope conformation of the five-membered metallacycle including the gallium atom. The two different Mn–Ga distances are most likely due to packing effects. The geometry around the gallium atom of 1c is quite similar to the respective properties of [(CO)$_4$Co]$_2$Ga[(CH$_2$)$_3$NEt$_2$], which is the only close congener of 1c so far.[8] There are no noticably short intra- or intermolecular contacts for 1c.

Compounds 1b–d sublime unchanged at 45–80 °C, 1–10 Pa with practical rates of about 1 g h^{-1}. The EI-, FI- and CI-MS of 1c–d do not show the molecular ions due to the preferred Mn–Ga bond splitting of the ionized species.[9] The MOCVD experiments were performed using 1b–d without carrier gases in an isothermal horizontal hot-walled quartz tube reactor *in vacuo* (1–10 Pa) at substrate temperatures of 250–300 °C

[typical growth rates of 0.3(±1) nm s^{-1}]. The compositions of the obtained polycrystalline films§ were uniform over the plated areas of 3–4 cm^2 and depths of 1–6 μm [profilometry; relative roughness of 5(±2)‰]. The films were rather pure and essentially free of N (Fig. 2). They exhibit a metal ratio Mn : Ga of 2.0(±0.05) for 1c and 1.08(±0.05) for 1d and conductivities of 10–45 mΩ cm (four-point probe). The MnGa films grown
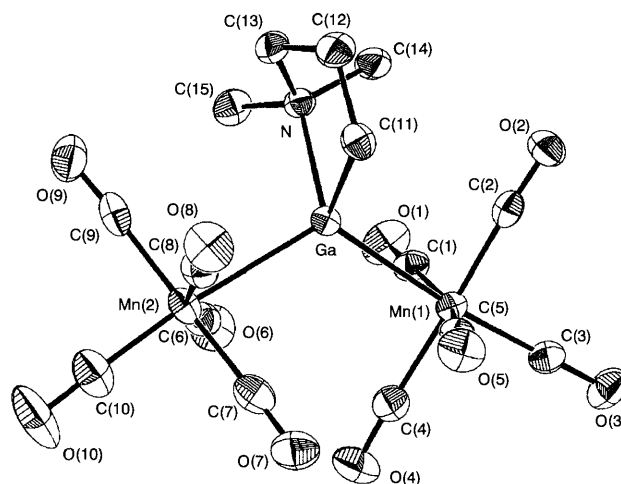

Fig. 1 Molecular structure of 1c in the crystal (ORTEP representation; the thermal ellipsoids are drawn at the 50% level; hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and angles (°): Ga–Mn(1) 262.63(5), Ga–Mn(2) 267.92(4), Ga–N 220.0(2), Ga–C(11) 202.1(2), Mn(1)–Ga–Mn(2) 116.5(1), Mn(1)–Ga–N 111.6(1), Mn(2)–Ga–N 110.0(1), Mn(1)–Ga–C(11) 115.9(1), Mn(2)–Ga–C(11) 114.0(1), N–Ga–C(11) 85.6(1), Ga–Mn(1)–C(5) 77.0(1), Ga–Mn(2)–C(6) 76.7(1).
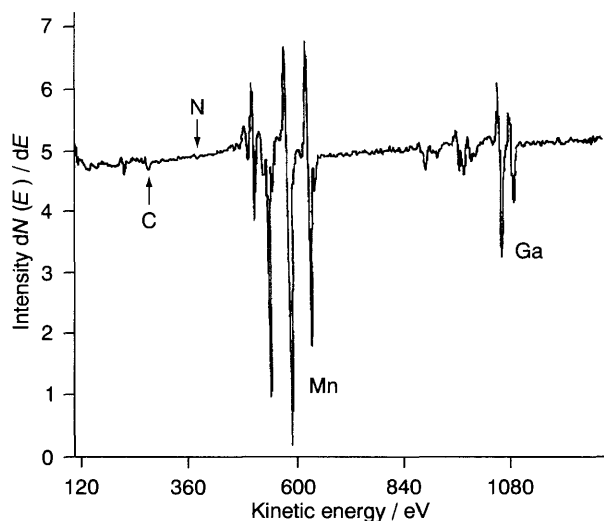

Fig. 2 Auger electron spectrum of the thin film Mn$_{0.52}$Ga$_{0.48}$ obtained from precursor 1d at 300(±10) °C and 10(±5) Pa (surface contaminations were removed by 2 min of Argon ion sputtering)

Scheme 1 Synthesis of 1a–d. 1a: L = PPh$_3$, R^1 = Cl, R^2 = (CH$_2$)$_3$NMe$_2$; 1b: L = CO, R^1 = [(CO)$_5$Mn], R^2 = (CH$_2$)$_3$NMe$_2$; 1d: L = CO, R^1 = R^2 = Et; Do = NMe$_3$.

from **1b** were expectedly contaminated with Cl. Compound **1d** proved to be suitable for the direct laser writing of MnGa microstructures. It was conjectured[6] that precursors with a stoichiometry of 2 : 1 rather than 1 : 1 may also be employed to deposit Mn_1Ga_1 thin films, because of a possible loss of volatile manganese species during the deposition process. It was argued also that base free Mn–Ga compounds might be favourable since the fragmentation of the Lewis-base will lead to incorporation of impurities into the growing films. Our results, however, show that given our isothermal low pressure MOCVD conditions, the metal ratio of the precursor is prefectly retained in the thin film. The films do not necessarily contain significant amounts of impurities arising from the Lewis base ligand.

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Footnotes

† Satisfactory microanalyses and spectra were obtained for compounds **1a–d**.

‡ *Crystal data* for **1c**: orthorhombic space group *Pbca*, a = 13.779(1), b = 15.537(2), c = 18.879(2) Å, U = 4042(1) Å^3, Z = 8, D_c = 1.794 g cm^{-3}, Stoe&Cie IPDS image plate diffractometer, λ(Mo-Kα) = 0.71073 Å, μ = 2.61 mm^{-1}, T = 193 K, F(000) = 2160, crystal dimensions 0.50 × 0.50 × 0.64 mm, 3507 unique reflections with no restrictions. R_1 = 0.031, wR_2 = 0.056. For general details concerning the data collection see ref. 10. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The X-ray powder diffraction patterns of the film obtained from **1d** (Fig. 2) revealed the presence of the two intermetallic phases η-MnGa and γ-MnGa according to the MnGa phase diagram[11] in the region of 48–58 atom% Mn.

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