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Transportation in MOCVD of traces of oxygenated aluminum and gallium organometallics

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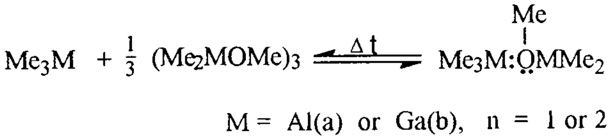
Abstract

Gas-phase transportation of dimethylmethoxy compounds of aluminum and gallium, which contaminate corresponding trimethyl metal compounds used in MOCVD, were investigated. It was found that larger amounts of oxygenated compounds were transported than can be calculated from the vapor pressure ratio of Me_2MOMe (**I**) to Me_3M (**II**). A decrease in the ratio (m/n) of the concentration of oxygenated compound (m) in the bubbler to the concentration of that transported to the reactor (n) was observed, especially at very low content of **I** in Me_3M. The ^{1}H-NMR and cryometric studies strongly suggest that an equilibrium between the system of trimeric dimethylmetal methoxy compound $(Me_3M)_n$ and mixed species $Me_3M{:}\overset{Me}{O}MMe_2$(III) exists in the mixture:



$$Me_3M + \frac{1}{3}(Me_2MOMe)_3 \overset{\Delta t}{\rightleftharpoons} Me_3M{:}\overset{Me}{\underset{\cdot\cdot}{O}}MMe_2$$
$$M = Al(a) \text{ or } Ga(b),\quad n = 1 \text{ or } 2 \qquad (1)$$

The presence of **III**, more volatile than $(Me_2MOMe)_3$, rationalizes the higher transportation ratio.

Keywords: Organogallium compounds; Oganoaluminum compounds; High purity; MOCVD; Synthesis

1. Introduction

Me_3Al and Me_3Ga are the most commonly used compounds of aluminum and gallium elements in epitaxial growth [1]. Both have convenient vapor pressure, 8.7 and 182.3 mmHg (29.7 mmHg at -15°C) at 20°C, respectively, for application in atmospheric and low-pressure MOCVD. Both, but especially the aluminum compound, have extremely high affinity to oxygen and oxygen-bearing compounds. They not only form adducts with, e.g. ethers, but they react violently with any trace of O_2, with insertion of oxygen into the M–C bond. With water they eliminate methane, forming a complex mixture of nonvolatile strongly associated species with many different M–O bonds.

Associates possessing R_2MOR units can be unintentionally introduced into the MOCVD system as trace contamination in supplied organometallics. They can also be formed during transportation by the in situ reaction of traces of oxygen from the transporting gas in the bubbler, from impurities of the Group 5 hydrides or from species adsorbed on the walls of the apparatus. But oxygen can also be intentionally introduced in order, e.g. to obtain high resistivity of epitaxial GaAs, suitable for buffer layers of concentration 5×10^{17}–5×10^{18} [2].

Independently of the origin of oxygen introduced into the reactor, the quality of epilayers formed is strongly affected by the presence of this contamination

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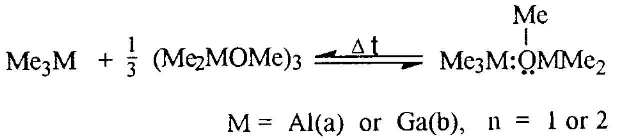
in the growth ambient in the reactor, especially at lower deposition temperatures. The oxygen incorporation has been invoked to explain virtually all the deleterious effects in the grown $Al_xGa_{1-x}As$ [3,4]. Though the Ga–O bond is much weaker than the Al–O bond (285 ± 17 and 500 ± 10.5 kJ mol^{-1}, respectively for isolated M–O molecule) [5] and the Ga_2O intermediate is easy to volatilize, we also investigated the organogallium compounds system because it can undergo transalkoxylation reaction when growing, e.g. $Al_xGa_{1-x}As$ structures.

The oxygenated organometallics have dramatically lower vapor pressure than corresponding trialkyl metal compounds due to their trimeric structure and intermolecular oxygen–metal interactions ($[Me_2AlOMe]_3$ — 20^{87} mmHg and $[Me_2GaOMe]_3$ — 20^{97} mmHg). The ratio of vapor pressures of $[Me_2MOMe]_3$ to $[Me_3M]_n$ is much lower than 1/10 for both aluminum and especially for gallium compounds, but in the gas transported volume the ratio of oxygenated compounds is visibly higher. The aim of the investigations was to monitor the gas-phase transportation of dimethylmetal methoxy compounds from the solutions in corresponding trimethylmetal compounds, and to determine the difference between the change of the ratio of concentration in the receiver and bubbler. Finally, it was important to find some proof of the existence in the mixtures of other reasonably volatile species, which increase the population of Me_2MOMe component in the vapor phase (Eq. (1)).



$$\mathrm{Me_3M} + \tfrac{1}{3}\,(\mathrm{Me_2MOMe})_3 \overset{\Delta t}{\rightleftharpoons} \mathrm{Me_3M{:}\overset{Me}{\underset{\cdot\cdot}{O}}MMe_2}$$

M = Al(a) or Ga(b), n = 1 or 2

2. Experimental

2.1. ^{1}H-NMR measurements

Gas-phase transportation of the Me_3M–Me_2MOMe mixture from a bubbler was performed on an atmospheric pressure MOCVD apparatus using its source part (Fig. 1). Hydrogen purified by a palladium diffuser (less than 10 ppb of oxygen-possessing impurities) was used as carrier gas. The gas-phase mixture was trapped in a container cooled with liquid N_2 connected directly to an NMR tube. Neither a small change of bubbler temperature nor change of H_2 flow rate influenced visibly the concentration of alkoxy compounds in the receiver. The Me_2MOMe concentration in the bubbler was determined on the basis of the amount of methanol introduced to pure Me_3M. The concentrations in the receiver, and also in the bubbler, were detected using ^{1}H-NMR spectra in which the ratio of CH_3–O to CH_3–M signals was determined. At low concentration of oxygenated compounds the detection of their amount was realized using the residual CH_3 signal of perdeuterated toluene, which was calibrated by cyclohexane, quantitatively added to this solvent.

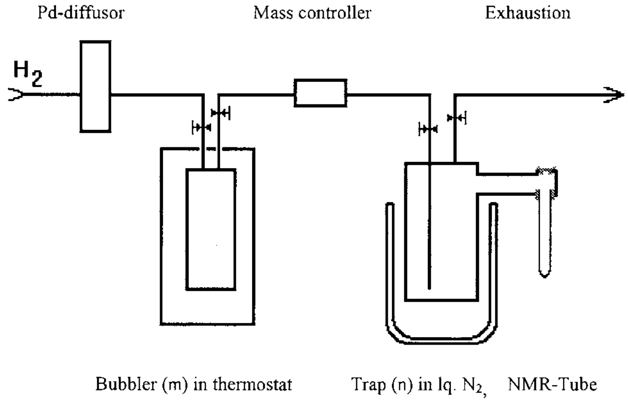


Fig. 1. Source part of the MOCVD apparatus with a trapping system.

The low-temperature ^{1}H-NMR spectra of 10% toluene-d_8 solutions of about 1:1 mixtures of Me_3M–Me_2MOMe were recorded after heating the samples for 1 h (Al — 110°C, Ga — 50°C) and cooling immediately to −78°C. The spectra were then obtained at −60, −30, 0 and 20°C.

2.2. Cryometric measurements

The cryometric measurements were recorded in benzene applying a Beckmann thermometer and a vessel that could be vacuum evacuated and heated to at least 100°C. The cryometric constant was measured to be $k = 5.265$.

A mixture (m_1) of 16.60 mmol (2.390 g) of $(Me_3Al)_2$ (**IIa**) with 6.8 mmol (1795 g) of $(Me_2AlOMe)_3$ (**Ia**) was prepared. The molar ratio of $Al_{(\mathbf{IIa})}/Al_{(\mathbf{Ia})}$ was 1.63. The calculated molecular weight of such an unreacted mixture should be 179 (Table 1).

A mixture (m_1) of 10.00 mmol (1.147 g) of Me_3Ga (**IIb**) and 3.3 mmol (1.307 g) $1/3(Me_2GaOMe)_3$ (**Ia**) was prepared. The molar ratio of $Ga_{(\mathbf{IIb})}/Ga_{(\mathbf{Ib})}$ was 1.00. The calculated molecular weight of such an unreacted mixture should be 184.

Table 1
Calculated and measured molecular weights of about 1:1 mixtures of $Me_3M + Me_2MOMe$ in benzene

	Aluminum compounds	Gallium compounds
Calculated values of unreacted mixture	179 (2.34 mmol)	184.1
Measured values	156	220
Calculated values of mixtures with only mixed dimers (structure **I** and **II**)	156 (2.68 mmol)	245.4

The samples were similarly heated like for ^{1}H-NMR experiments followed by fast cooling to room temperature, dissolving in a known amount of benzene (m_0) and quantitative introduction into the cryometric vessel. The temperature of crystallization ($\Delta t = 0$ for a longer period of time) was measured three times and molecular weights (M) were calculated from the known equation,

$$M = \frac{km_1 1000}{m_0(t_0 - t_1)} \qquad (2)$$

where t_0 is the temperature of crystallization of benzene and t_1 is the temperature of crystallization of the investigated solutions.

3. Results and discussion

3.1. ^{1}H-NMR investigations

3.1.1. Transportation of oxygenated organometallics

The ^{1}H-NMR studies were carried out to determine the ratio of the concentration of oxygenated compounds in the source (m) to that in the receiver after transportation (n).

Fig. 2 shows that the concentration of R_2MOMe is clearly smaller in the receiver. There is also presented the higher transport rate of oxygenated compounds of aluminum, compared with corresponding gallium compounds, in agreement with the lower vapor pressure of Me_3Al and higher of R_2AlOMe compared with corresponding gallium compounds.

In Fig. 3 the change in the transportation ratio (m/n) with the concentration change of Me_2MOMe in the bubbler is shown. For both systems the ratio of concentrations of the oxygenated compounds in the source to that in the receiver decreased with a decrease in their concentration in the source. This indicates a low effectiveness of purification using distillation or the vapor transport technique, especially for the final stages of the preparation of puratronic compounds. Also in MOCVD one cannot expect a straight-line relation between the concentration of oxygenated compounds in the source and oxygen in the deposited layer.

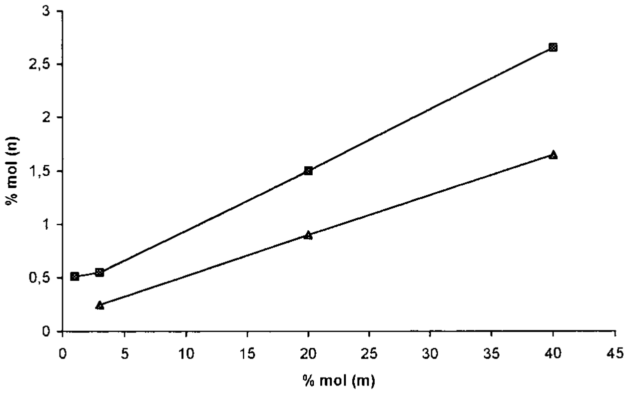


Fig. 2. The decrease of concentration of Me_2MOMe in Me_3M after transportation from the bubbler (m) to the receiver (n): ■, $Me_3Al + Me_2AlOMe$; ▲, $Me_3Ga + Me_2GaOMe$.

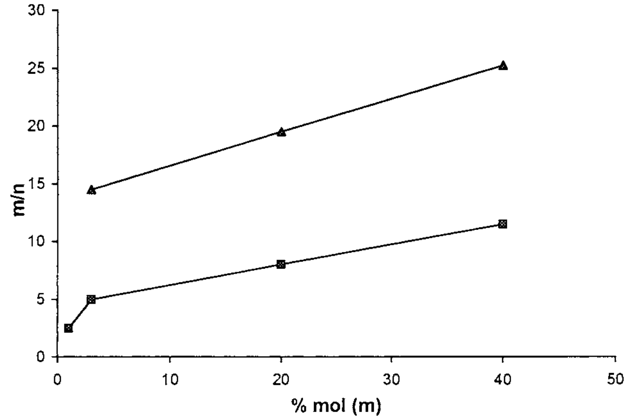


Fig. 3. The concentration dependance m/n ratio of the presence of Me_2MOMe in Me_3M in the bubbler (m) to its presence after transportation into the trap (n): ■, $Me_3Al + Me_2AlOMe$; ▲, $Me_3Ga + Me_2GaOMe$.

3.1.2. Structural justification of transportation rate

High transportation rates of oxygenated compounds that contaminate Me_3M can be explained by the formation of more volatile species due to transassociation of the components. It could be expected that the temperature-dependent ^{1}H-NMR spectra can bring some evidence for this assumption. The results for both close to stoichiometric mixtures are presented in Tables 2 and 3,

Table 2
Variable-temperature ^{1}H-NMR spectra of about 1:1 mixture of $Me_3Al + Me_2AlOMe$ (excess of Me_2AlOMe)

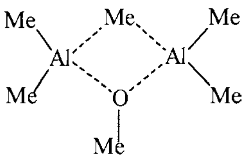
Temperature (°C)	Position of proton peaks and relative intensity ($OCH_3 = 1$)			
	$(CH_3)_3Al$ (τ)	$(CH_3)_2AlOMe$ (τ)	$(Me)_2AlOCH_3$ (τ)	Relative intensity of the sum of CH_3–Al peaks
−60	0.03 (Bridging)	−0.71 (Terminal)	2.92	0.64+3.09
−30	−0.66		3.04	3.58
0	−0.37	−0.69	3.10	1.50+2.08
20	−0.38	−0.70	3.12	1.51+1.92
Pure Me_3Al	−0.37	–		–
Pure Me_2AlOMe	–	−0.71	3.15	2

Table 3
Variable-temperature ^{1}H-NMR spectra of about 1:1 mixture of $Me_3Ga + Me_2GaOMe$ (excess of Me_3Ga)

Temperature (°C)	Position of proton peaks and relative intensity ($OCH_3 = 1$)			
	$(CH_3)_3Ga$ (τ)	$(CH_3)_2GaOMe$ (τ)	Me_2GaOCH_3 (τ)	Relative intensity of the sum of CH_3–Ga peaks
−60		−0.22	3.11	6.93
−30		−0.21	3.12	6.69
0		−0.20 shoulder upfield	3.15	6.77
20	−0.17	−0.22	3.17	6.25
Pure Me_3Ga	−0.19	–	–	–
Pure Me_2GaOMe	–	−0.25	3.16	2

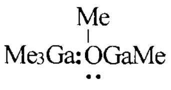
complemented with the room-temperature spectra of pure Me_3M and Me_2MOMe compounds.

The most important feature visible in the spectra of a nearly equimolar mixture of $1/2(Me_3Al)_2$ with $1/3(Me_2AlOMe)_3$ is the growth of the $(CH_3)_2AlOMe$ peak with a decrease of temperature. At −30°C both CH_3–Al peaks collapse, forming a new one, of an intermediate position, which suggests the formation of new species. It splits again at −60°C into two rather broad signals forming a different pattern of positions and intensities of peaks [6]. These can be explained by the slowing down of the terminal-bridging methyl group's exchange to extend that they can be seen in the spectra. The intensity ratio and their positions agree with a cyclic, dimeric structure with mixed bridges.



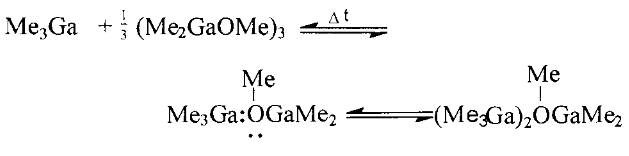
A mixture of a small molar excess of Me_3Ga with $1/3(Me_2GaOMe)_3$ gives two CH_3–Ga sharp signals at 20°C in agreement with the existence of the two compounds. At temperature ca. 0°C the signals collapse, forming one broader peak of intermediate position, with scarcely visible shoulder upfield. At −30 and −60°C the peak is a little better resolved but it does not split again. The formation of one peak at lower temperatures with an intermediate value of shift can be rationalized by one or both mechanisms of exchange:

1. The lower-temperature-formed



$$Me_3Ga{:}\underset{\bullet\bullet}{\overset{\overset{\textstyle Me}{|}}{O}}GaMe$$

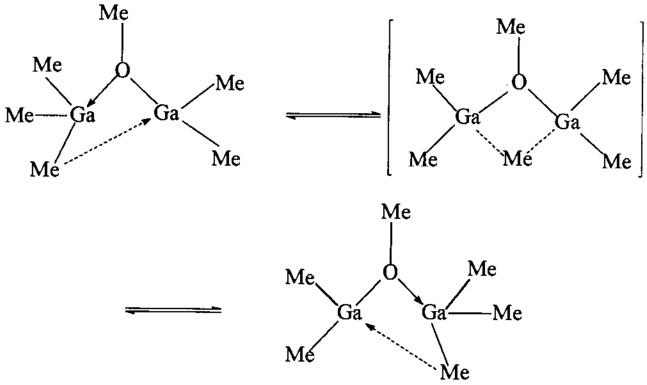
undergoes fast exchange with monomeric Me_3Ga.



$$Me_3Ga + \tfrac{1}{3}(Me_2GaOMe)_3 \xrightleftharpoons{\Delta t} Me_3Ga{:}\underset{\bullet\bullet}{\overset{\overset{\textstyle Me}{|}}{O}}GaMe_2 \rightleftharpoons (Me_3Ga)_2\overset{\overset{\textstyle Me}{|}}{O}GaMe_2$$

The exchange is able to proceed easily with very low activation energy due to the presence of the empty low energy orbital p_z of gallium of Me_3Ga and the free electron pair of oxygen.

2. The methyl groups exchange in **IIIb**, which is expected to proceed in the mixed dimmer through the cyclic four-centre ring (Eq. (3)). The three-center–two-electron bridging by methyl group (if formed not only as a transition state) is weak because its donor ability is small. The negatively charged $-\delta$ on methyl carbon is calculated [7] to be only −0.031 compared with −0.16 on Al atom in Me_3Al. As a consequence, even at −60°C, the exchange can be too rapid to split the signals into bridging and terminal groups or, alternatively, to resolve CH_3–Ga of **Ib** and **IIb** in the complex **IIIb**.



(3)

3.2. Cryometric measurements

The calculated molecular weight for a not fully stoichiometric mixture of $(Me_3Al)_2$ (excess) with $(Me_2AlOMe)_3$ used for cryometric measurement is 179, whereas the measured value was found to be lower — 156. This is exactly the predicted value 156, calculated for a mixture of $Me_2Al(Me)(OMe)AlMe_2$ + existing excess of $(Me_3Al)_2$.

In the case of the stoichiometric Me_3Ga–$1/3(Me_2GaOMe)_3$ system, the molecular weight obtained at 5°C was much higher — 220, than calculated for an unreacted mixture (182.9) and a little lower than that of mixed dimer (245.4). This corresponds to the formation of about 90% of

$$\mathrm{Me_3Ga{:}\overset{Me}{O}GaMe_2}$$

Both results indicate the proceeding of reactions of **I** and **II** with the formation of **III**. It can be suggested that the mixture of organoaluminum compounds is practically in the form of a mixed cyclic dimer (Eq. (1)), but the mixed dimeric associates of organogallium compounds are in equilibrium with smaller amounts of substrates. With much smaller probability the change of molecular weight can result from reassociation of $(Me_2AlOMe)_3$ to dimer, due to the presence of trimethylaluminum, because high temperature favors the dimer → trimer reaction [8].

4. Conclusions

The cryometrically measured molecular weight of a mixture of investigated aluminium compounds is in agreement with the presence of only **IIIa** at lower temperature. Also ^{1}H-NMR measurements present the ratio and position of two Me–Al peaks at $-60°C$, which confirms the presence of such a mixed cyclic dimer. Such a structure bridged through methyl and methoxy groups was proposed before, for some other organoaluminum compounds [9,10]. The molecular-weight measurements of the $(Me_2GaOMe)_3–Me_3Ga$ mixture confirm the equilibrium (Eq. (1)) with the equilibrium strongly shifted to the right at temperature around 5°C. The collapsing of two Me–Ga signals without further changes below 0°C can be rationalized by: (1) fast exchange of the free Me_3Ga with the **IIIb**; (2) an intramolecular very fast exchange of methyl groups in the complex **IIIb**, through cyclic dimer.

The presence of proposed structures (**III**), of lower molecular weight than trimeric (**I**), in a mixture with Me_3M explains the increased supply of oxygenated compounds during transportation of the investigated organometallics to the MOCVD chamber.

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