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Insights into the chemical vapor deposition of GaN using the single-source precursor $Me_2N(CH_2)_3Ga(N_3)_2$: matrix isolation of $Ga(N_3)$

Jens Müller* and Sabine Bendix

Organometallics & Materials Chemistry, Anorganische Chemie II, Ruhr-Universität, 44780 Bochum, Germany. E-mail: jens.mueller@aci.ruhr-uni-bochum.de

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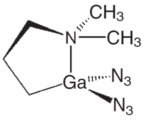
The investigation of the pyrolysis of the single-source precursor $Me_2N(CH_2)_3Ga(N_3)_2$ 1 by matrix-isolation FTIR spectroscopy revealed monomeric $Ga(N_3)$ as a reactive intermediate.

The group 13 nitrides of Al, Ga and In and their ternary alloys $Al_xGa_yIn_zN$ ($x + y + z = 1$) are wide direct band gap materials with promising applications as new microelectronic and optoelectronic devices.[1] For example, blue-light emitting diodes and lasers based on gallium nitride can be constructed.[2] Usually, thin films of the nitrides can be epitaxially grown by chemical vapor deposition (CVD) from the trialkyl compounds MR_3 with a large excess of ammonia.[1,2] These organometallics are toxic, pyrophoric, and very sensitive to air and moisture and several efforts have been made to synthesize alternative precursors. If the element is equipped with a ligand that is capable of intramolecular coordination, then non-pyrophoric organometallics are accessible. In particular, the 3-dimethylaminopropyl ligand, $Me_2N(CH_2)_3$, has been successfully applied to various precursors: for example, the diazide $Me_2N(CH_2)_3Ga(N_3)_2$ **1** is a single-source precursor for the MOCVD of GaN.[3]



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For a deeper understanding of a CVD process and a rational design of improved precursors, detailed knowledge of fragmentation mechanisms is needed. Recently, we started to investigate the fragmentation of intramolecularly coordinated alanes and gallanes of the type $Me_2N(CH_2)_3MX_2$ (X = Cl, Br, Me) using matrix isolation techniques.[4–7] In this procedure a carrier gas/precursor mixture is transported through a small pyrolysis tube and reactive intermediates produced by the fragmentation of the organometallic precursor are trapped on a CsI window at 15 K.

A series of high vacuum thermolysis experiments with the diazide **1** and argon as carrier gas was performed between ambient temperature and 800 °C.† Up to 450 °C compound **1** passes the thermolysis oven unchanged, but above this temperature new IR bands in the matrix IR spectra indicate the beginning of the fragmentation of **1**. Fig. 1 shows a typical IR spectrum of matrix-isolated products recorded after a thermolysis experiment at 520 °C (spectrum A). Under these conditions precursor **1** was completely fragmented; its typical IR absorptions could no longer be detected in argon matrices. In the common region of asymmetric stretching modes of azido groups two intense IR bands at 2135.4 and 2106.0 cm^{-1} were observed (Fig. 1A). The IR band at 2135.4 cm^{-1} unequivocally belongs to hydrazoic acid, HN_3, which has a well-known set of bands at 3316.7, 2286.2, 2135.4, 1264.1 and 1146.0.[8] That the second intense IR band, that at 2106.0 cm^{-1}, belongs to a second azide was revealed by photolysis experiments (Fig. 1B). Irradiation of the matrix-isolated thermolysis products with an Xe arc lamp for *ca.* 30 s selectively bleached the band at 2106.0 cm^{-1} plus an IR band at 1340.3 cm^{-1};‡ the frequencies, intensity pattern, and low half-band widths ($h_{\frac{1}{2}} < 2\ cm^{-1}$) of these bands are indicative of a small molecular azide and we assign these two bands to the symmetric and asymmetric N_3 stretching mode of $Ga(N_3)$. The calculated harmonic frequencies and intensities [B3LYP/6-311+G(d)][9] of the two modes $\nu_{as}(N_3)$ [2230.7 cm^{-1}; 1080 km mol^{-1}] and $\nu_s(N_3)$ [1408.2 cm^{-1}; 249 km mol^{-1}] are in good agreement with our measured values. Recently, gallium(I) azide was observed for the first time by co-deposition matrix experiments of laser-ablated Ga atoms with nitrogen.[9] Among other Ga–N species, Zhou and Andrews identified $Ga(N_3)$ in excess of solid N_2 by IR bands at 2103.6 / 2096.8 cm^{-1} [$\nu_{as}(N_3)$] and 1331.3 / 1328.3 cm^{-1} [$\nu_s(N_3)$]; both bands were split by matrix site effects.[9] This assignment was strongly supported by nitrogen isotopic substitutions and DFT calculations. According to B3LYP/6-311+G(d) calculations, $Ga(N_3)$ is a C_s symmetrical molecule with a linear N_3 group and a Ga–N–N angle of 149.5°.[9] From the six normal modes only the two azide stretching vibrations and the Ga–N stretching mode are expected to have a sufficiently high transition moment to be detectable. The harmonic frequency of the Ga–N stretch was predicted at 384.3 cm^{-1} with an intensity of 133 km mol^{-1}, but it could not be detected in the laser-ablation experiments.[9]

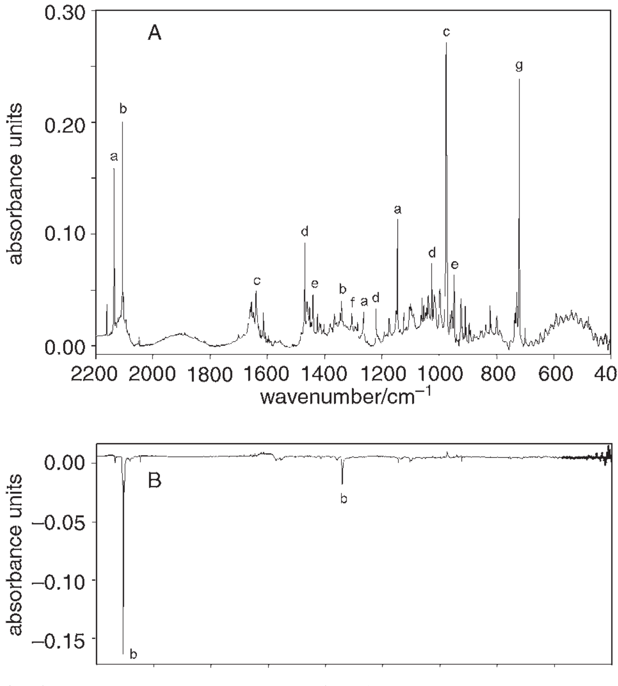

Fig. 1 A, products of thermolysis of **1** at 520 °C trapped in an excess of argon at 15 K; a: HN_3, b: $Ga(N_3)$, c: NH_3, d: $H_2C{=}NCH_3$, e: $H_2C{=}CH_2$, f: CH_4, g: HCN. B, difference IR spectrum obtained by photolysis of the product matrix A; negative IR bands indicate disappearing species.

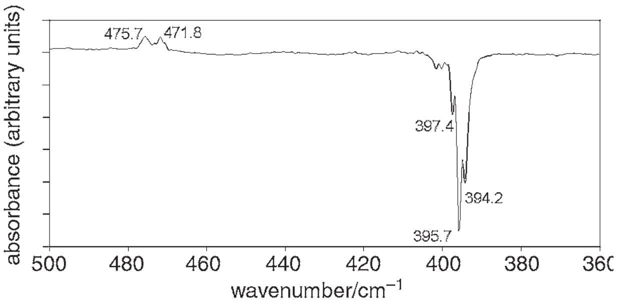

Fig. 2 Low-frequency region of the photolysis of the thermolysis products of **1** (see text for details).

We investigated the photolysis reaction of the thermolysis products of **1** in the frequency region 200–700 cm^{-1}. As depicted in Fig. 2 a set of three IR bands at 397.4, 395.7 and 394.2 cm^{-1}, disappears on irradiation. We assign this set to the missing ν(GaN) of Ga(N_3). The experimental frequencies fit quite well to the predicted frequency of 384.3 cm^{-1}; the B3LYP method is known to underestimate low frequency modes.[10] Because of the natural abundance of the two isotopes, ^{69}Ga (60%) and ^{71}Ga (40%), two IR bands are expected for this vibrational mode. If we assign the most intense IR band at 395.7 cm^{-1} to ν(^{69}GaN) then the same mode for the ^{71}Ga isotope should occur at 393.9 cm^{-1} [B3LYP/6-311+G(d)], which is in good agreement with the measured band at 394.2 cm^{-1}. The appearance of three IR bands could be caused by an overlap of resonances of Ga(N_3) in at least two different matrix sites: one site with 397.4 (^{69}Ga) and 395.7 cm^{-1} (^{71}Ga), and the other site with 395.7 (^{69}Ga) and 394.2 cm^{-1} (^{71}Ga). This interpretation is in accordance with the expected isotopic shifts, but the expected intensity pattern would be a little different from the observed one; the IR band at 395.7 cm^{-1} is expected to have a higher intensity. Furthermore, the IR band at 394.2 cm^{-1} shows a shoulder to its low frequency side indicating another overlap of IR bands.

GaN is the expected product of the photolysis of Ga(N_3) in matrices. As a result of the photolysis reaction only two unresolved IR bands of low intensity at 475.7 and 471.8 cm^{-1} evolved (Fig. 2). Zhou and Andrews assigned an unresolved IR band at 484.9 cm^{-1} to GaN in N_2 matrices.[9] Because of a large mismatch between the calculated frequency (580.9 cm^{-1}) and the measured value, the authors interpreted the IR band at 484.9 cm^{-1} as being due to a GaN$\cdots N_2$ complex. We tentatively assign the two IR bands at 475.7 and 471.8 cm^{-1} to GaN, which might be perturbed by the N_2 molecule produced photochemically in the same matrix cage.

In addition to HN_3 and Ga(N_3) the matrix containing the thermolysis products of **1** at 520 °C (Fig. 1) contained the well-known molecules NH_3, $H_2C{=}NCH_3$, $H_2C{=}CH_2$, CH_4 and HCN, which were identified by comparison with published data. With the exception of ammonia, all fragments have been found previously in similar thermolysis experiments with alanes and gallanes of the type $Me_2N(CH_2)_3MX_2$ (X = Cl, Br).[4,5]

Prior to our work, compound **1** was investigated by mass spectrometry[11] which is commonly used for *in situ* analysis of gas-phase species in CVD processes. Within this work $HGaN_6$, GaN_6, $HGaN_2$ and GaN_2 were identified close to the substrate surface. On the basis of the experimental data, however, the authors could not explain the formation of these species. Furthermore, it was not possible to distinguish between β-hydrogen elimination and homolysis of the Ga–C bond of **1**. The main aim of our investigation was to understand the fragmentation of the single-source precursor **1**. A β-hydrogen elimination of **1** would result in $HGa(N_3)_2$ and allyldimethylamine; this amine was not detected in any of our experiments. We checked independently that allyldimethylamine is stable under our applied thermolysis conditions.[4] This means that a β-hydrogen elimination can be excluded unequivocally for **1**.

We identified the monomeric hydrides HMX_2 in thermolysis reactions with alanes and gallanes of the type $Me_2N(CH_2)_3MX_2$ (X = Cl, Br).[4,5] Even though allyldimethylamine was not obtained in any of these experiments, the results were explained by β-hydrogen eliminations. We proposed that the temperatures needed for fragmentation reactions (> 800 °C) were so high that allyldimethylamine, formed as an intermediate, fragmented further to the obtained carbon-containing species. In order to prove this interpretation, we synthesized selectively deuterated starting compounds $Me_2NCH_2CD_2CH_2MBr_2$ (M = Al, Ga) and investigated them by matrix isolation techniques.[12] In none of the thermolysis experiments did we find the expected deuterates $DMBr_2$; only hydrides $HMBr_2$ were formed. That β-hydrogen elimination can occur for intramolecularly coordinated gallanes with high efficiency had been shown for the dimethyl derivative $Me_2NCH_2CD_2CH_2GaMe_2$.[7]

In summary, the following picture for the fragmentation of $Me_2N(CH_2)_3MX_2$ (X = Cl, Br, N_3) is in accordance with all experimental results. Homolysis of the M–C bond results in radicals of the type MX_2. These radicals presumably trap H atoms on their way to the matrix window. In the case of X = Cl or Br, the respective hydrides HMX_2 are stable enough to be detectable in an excess of solid argon. In the case of the azide **1** the proposed intermediate $HGa(N_3)_2$ eliminates HN_3 to give Ga(N_3), an interpretation in accordance with the detected mixtures of HN_3 and Ga(N_3).§ In terms of the CVD process with **1** as a single-source precursor, it is feasible that gallium(I) azide is a key intermediate in the GaN deposition.

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Notes and references

† The matrix isolation apparatus is described in ref. 7. For the photolysis experiments a 150 W Xe arc lamp (XBO 150 W/4 in an Oriel arc lamp housing 66055-M) equipped with a cut-off filter for λ = 225 nm (Schott WG 225) was used.

‡ Because of matrix site effects, the intense band at 2106.0 cm^{-1} is accompanied by a low intensity band at 2102.7 cm^{-1}.

§ According to DFT type calculations at the BP/DZVP level of theory (R. Schmid, TU Munich, Germany) the free energy of activation (including zero point vibrational energy) at 600 K, for the elimination of $HGa(N_3)_2$ to HN_3 and Ga(N_3) is 42.1 kcal mol^{-1}. This fragmentation is energetically preferred over an N_2 loss reaction.

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