Tertiarybutylhydrazine: a new precursor for the MOVPE of Group III-nitrides

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Abstract

Tertiarybutylhydrazine (tBuHy), generated from tBuHy hydrochloride, was found to have a convenient vapor pressure (6.7 mbar at 20°C) for MOVPE applications. Thermolysis of tBuHy, studied by quadrupole mass spectroscopy (QMS), starts at about 220°C by homolytic cleavage into reactive tBuNH and NH₂ radicals. Almost complete decomposition under QMS conditions is observed above 350°C. Mirror-like GaN epilayers with mixed cubic/hexagonal and hexagonal structure were grown on GaAs and Al₂O₃ substrates, respectively, at 670°C using tBuHy and Me₃Ga or Et₃Ga with a V/III ratio of 70. Low carbon incorporation was found in tBuHy-grown layers with respect to layers grown with Me₂Hy under the same conditions. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The high stability of ammonia, which requires high growth temperatures in standard group III nitride MOVPE, stimulates the search for alternative nitrogen precursors. GaN epitaxy at decreased temperatures was achieved using methylized hydrazine derivatives Me₂NNH₂ [1–4] and Me(H)NNH₂ [5]. However, incorporation of carbon into the epilayers resulting from incomplete precursor pyrolysis was reported [4]. Tertiarybutyl-ligands as replacements of hydrogen in novel precursors are highly interesting due to a weaker carbon–metal bond strength with respect to methyl-ligands [6] and formation of stable fragments, favoring a low decomposition temperature and a reduced carbon incorporation. We therefore studied the pyrolysis of tertiarybutylhydrazine (tBuHy, (CH₃)₃C(H)NNH₂) which was found to have a convenient vapor pressure, and grew GaN epilayers using standard Ga sources and tBuHy as nitrogen precursor.

2. Experimental procedure

Tertiarybutylhydrazine was generated as a colorless liquid from tertiarybutylhydrazine hydrochloride, and repeatedly dried and purified by distillation. A vapor pressure of 6.7 mbar was measured at 17°C. Quadru-pole mass spectrometry (QMS) was used to study the thermolysis of tBuHy and, for comparison, also of 1,1-dimethylhydrazine (Me₂Hy). The studied compounds were introduced into an isothermal reaction tube at 0.1 mbar gas pressure with a fixed flow rate, heated at a constant rate of 15 °C min⁻¹ and analyzed at a sampling pressure of 10⁻⁶ mbar using 70 eV ionization energy. GaN layers were grown on GaAs(001), GaAs(111) возраст on Al₂O₃(001) by MOVPE under hydrogen carrier gas at 100 mbar total pressure, using tBuHy, Me₂Hy, Me₃Ga and Et₃Ga precursors.

3. Thermolysis study

The thermolysis of tBuHy under QMS conditions is shown in Fig. 1. Thermal decomposition starts at about
220°C as read from the signal of the undecomposed molecule (mol peak) at mass 88. Detected decomposition products are essentially (CH₃)₂CNH₂ (m/z 58), NH₃ and NH₂. The assignment of mass 16 to NH₂ (which could not be separated from CH₄) is based on the similar evolution of the NH₃ signal and the drop of the signal of H₂NNH₂ (hydrazine, H₂N) accompanying the increase of NH₃ and NH₂. The generation of (CH₃)₂CNH₂ and NH₂ results from a N–N bond cleavage according to

\[(CH₃)₂C(H)NNH₂ \rightarrow (CH₃)₂C(H)N⁺ + \cdot NH₂ \]  \(\text{(1)}\)

The (CH₃)₂C(H)N⁺ radical is transformed in the QMS under CH₄ production to the (CH₃)₂CNH₂ ion detected at mass 58. The \cdot NH radical is detected in the QMS either as NH₂ or ammonia NH₃. The signals of H₂N (m/z 32) and molecule mass reduced by a methyl mass (Mol/CH₃) at mass 73 show the same temperature dependence as the mol peak. They originate from decomposition of tBuHy by fragmentation in the QMS and are thus detected already at RT. The high signal strength of H₂N results from an efficient Onium reaction [7] which besets a hydrogen from the tertiarybutyl-ligand to nitrogen, analogous to a \(\beta\)-H elimination. The observed decomposition of tBuHy according to Eq. (1) agrees qualitatively with recently reported data [8]. The decomposition temperatures found in our study are, however, distinctly lower; the reason may be the low constant flow used in our setup.

The thermolysis of Me₂Hy is shown in Fig. 1b for comparison. The onset of decomposition occurs at an increased temperature of 370°C under production of (CH₃)₂N (m/z 44) and NH₂. Me₂Hy is thus also decomposed by N–N bond cleavage. H₂CN (m/z 28) and CH are detected as further decomposition products. Such small carbon-containing fragments are not detected in mass spectra of tBuHy with a comparable significance. These products may be a reason for the high carbon incorporation observed in GaN layers grown with Me₂Hy. From the thermolysis study, tBuHy appears to be very suitable as precursor for group III-nitride growth.

4. Gallium nitride layer growth

GaN growth on GaAs substrates requires an in-situ surface preparation at temperatures well below usual growth temperatures, if no As stabilization is applied as in most of our runs. Oxide desorption at 510°C results in an As- and Ga-terminated (4×6) reconstruction of the GaAs surface, and a subsequent nitridation with tBuHy induces a change to a stable surface signature observed in reflection anisotropy spectroscopy [9]. At 570°C, a Ga-terminated (4×2) reconstruction is found, and surface roughening by the formation of Ga-droplets is observed during nitridation. This leads to subsequently grown GaN film with poor crystallinity. We therefore performed nitridation at a temperature well below 600°C or started GaN buffer or layer growth directly after oxide desorption. Most layers were grown with Me₃Ga and a V/III ratio kept at 70 using 4.2 mmol min⁻¹ tBuHy flow. GaN layers with mirror-like surfaces were grown in a temperature range from 500 to 720°C. Using the precursor supply specified above, the growth rate was found to be very low at low temperatures, e.g. 120 nm h⁻¹ at 520°C, while growth rates near 300 nm h⁻¹ were obtained at 670°C under the same conditions on all investigated substrates.

The surface morphology of GaN grown on GaAs(001) is shown in the scanning electron microscopy (SEM) images of Fig. 2. The faceted polycrystalline structure indicates a three-dimensional growth start and a subsequent coalescence of small single crystals. The observed ridges are aligned along a \(\langle 110 \rangle\) direction of the GaAs substrate. The surface
morphology is similar to that of GaN layers grown with Me$_2$Hy as nitrogen precursor.

X-ray diffraction spectra show a broad reflection of GaN near $2\Theta = 40^\circ$, see Fig. 3. Texture measurements and spacemaps reveal that the reflection originates from a wide-spread cubic (002) texture and an additional superimposed hexagonal (10.1) texture [10].

Growth on GaAs(111)$_B$ substrates results in a very smooth, wavy surface. No granular morphology could be resolved in SEM images. A triangular-shaped morphology was observed at the very edge of a wafer. The strong GaN reflection near $2\Theta = 34.5^\circ$ proves the highly textured growth of the layers.

On Al$_2$O$_3$(00.1) substrates, specular GaN layers were grown with a surface morphology as shown in Fig. 4. Crystallites with a triangular arrangement and a size comparable to that of the crystallites of layers grown on GaAs(001) are observed in plane view. The highly oriented growth is confirmed by X-ray diffraction spectra showing a strong GaN(002) reflection, see Fig. 3. Growth of the wurtzite modification was confirmed by texture measurements [10].

The purity of the GaN layers was checked by electron microprobe analysis. Significant oxygen contamination was observed, when only singly distilled nitrogen sources were used. After repeatedly drying and distilling, the oxygen content was below the detection limit of the analysis setup. A sometimes observed carbon signal was not related to the purity of the nitrogen source. GaN layers grown with Me$_2$Hy as nitrogen source under similar conditions showed a significant carbon content. This finding was confirmed by SIMS measurements.

5. Conclusion

Tertiarybutylhydrazine (tBuHy) was proved to be a promising nitrogen source for low temperature MOVPE of III-nitrides. Decomposition of tBuHy starts at temperatures as low as 250°C by N–N bond cleavage, producing reactive NH$_2$ and tBuNH radicals. Highly oriented, mirror-like GaN layers were grown on GaAs and Al$_2$O$_3$ substrates at temperatures above 500°C, a growth rate of 0.3 μm h$^{-1}$ is obtained at 670°C using a V/III ratio of 70 and 4.2 mmol min$^{-1}$.
tBuHy flow. Incorporation of carbon impurities was found to be very low with respect to Me₂Hy-grown layers produced under the same conditions.

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References