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# GaN materials growth by MOVPE in a new-design reactor using DMHy and $NH_3$

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## Abstract

Thin films of GaN were grown on template substrates of 4-μm-thick GaN layers on sapphire substrates by low-pressure metal organic vapour-phase epitaxy (LP-MOVPE) in a new-design reactor with the shape T. Wide range of growth temperature from 520 to 1100 °C was explored. At low temperature growth between 550 and 690 °C, dimethylhydrazine (DMHy) was used as source of atomic nitrogen while ammonia ($NH_3$) was used at high temperature growth (1000–1100 °C). At low temperature micro-Raman spectroscopy revealed a significant relaxation of the selection rules for the scattering by the optical phonons in the films grown at lower temperatures. Variation of the intensity ratio for $E_2^H$ and $E_1$ phonon modes has been attributed to changes in the structural quality of the films grown at different temperatures. At high temperature, the quality of GaN layers were comparable to that of the substrate before growth.

*Keywords:* A1. Micro-Raman spectroscopy; A3. Low-temperature epitaxy; A3. Metal organic vapour-phase epitaxy; A3. New reactor design; B2. Gallium nitride

## 1. Introduction

In MOVPE technology, the growth chamber design plays an important role in the materials growth. The most common growth chamber design approaches in MOVPE are horizontal shape and vertical shape. A new design of reactor called T-shape reactor has been developed. It is a combination of horizontal and vertical reactors and, therefore, combines the advantages of both. From horizontal reactor, it is easy to obtain a laminar gas flow, and from the vertical, it is simple to implement a mechanical rotation of the susceptor in the clean and cold area of the system. State-of-the-art results in term of uniformity, quality and device performances with this reactor have been demonstrated on InP [1] and GaAs [2]-based materials. In this study, the T-shape reactor has been reconfigured in order to be used at low and high growth temperatures of GaN-based materials (Fig. 1).

## 2. Reactor design

The cross section of the growth system is shown in Fig. 2. The reactor is a quartz tube with geometry of T. The cylindrical-shape graphite susceptor is RF heated. The growth temperature is controlled by a thermocouple passing through the central axis of the susceptor and through a pin hole in the centre of the wafer carrier. As a result, the temperature is measured near the back side of the wafer. In order to prevent heat propagation by radiation and conduction next to the seals connection and rotation mechanic systems, specially designed "wings reflectors" and "water cooling parts" are placed around the sensitive areas. The quartz T-shape growth chamber is set inside a hermitically sealed metal box filled with nitrogen and cooled with water on the surface. This box

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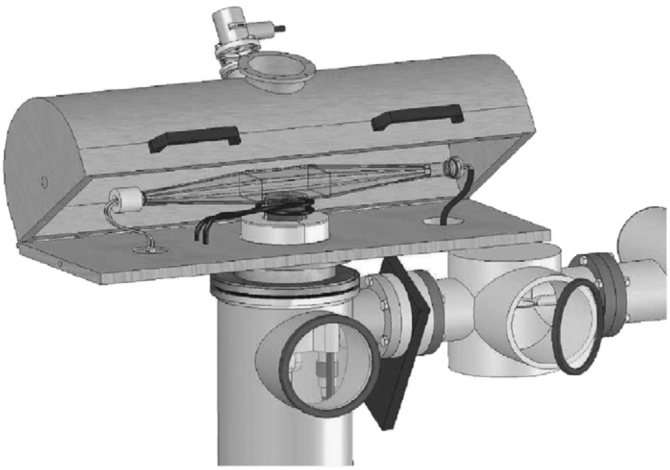

Fig. 1. Global view of the T-shape reactor.

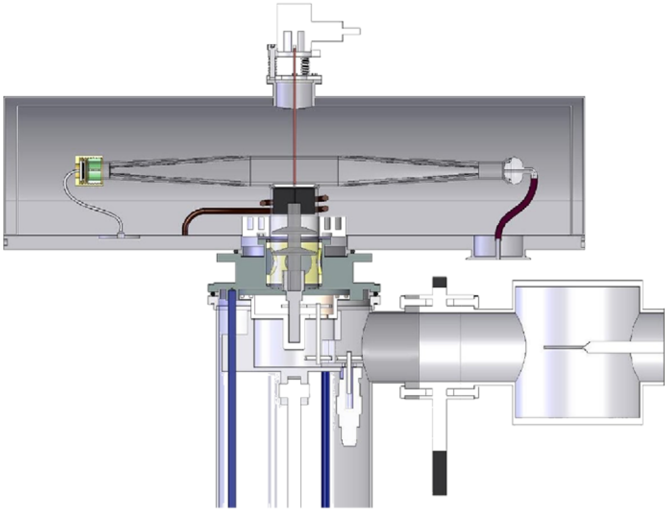

Fig. 2. Cross-section of the growth chamber and the rotation setup.

has two viewports that provide access for in-situ optical characterization. In this configuration no double walls cooling water of the growth chamber is needed to keep its upstream and ceiling clean of deposits. As a result the implementation of in-situ reflectometry is straightforward. Vertical in-situ reflectometry was installed and the flange window was tilted by a slight angle to prevent back reflection of laser source toward the detector.

The dimension of T-shape reactor, in particular its conic entrance, was designed in such way that the growth can be carried out at the pressure from 50 Torr to near atmospheric and the temperature from 500 to 1100 °C with only two parameters of adjustment the total gas flow in the reactor and the ratio between alkyl and hydride carrier gases.

## 3. Experimental procedure

Growth conditions were optimized to grow GaN at high and low temperatures using 100% nitrogen as carrier gas. The growth pressures were 100 and 450 Torr. For both pressures the total nitrogen carrier gas that allowed laminar gas flow and relatively cold entrance wall of the growth chamber was around 7 slm $N_2$. At low-temperature growth between 550 and 690 °C dimethylhydrazine (DMHy) was used as source of atomic nitrogen while ammonia ($NH_3$) was used at high-temperature growth (1000–1100 °C). For all the growths the typical thickness layer was 350 nm. The growth was carried out on the template substrates of 4-μm-thick GaN layers on sapphire. The growth rate was estimated in-situ by reflectometry using a semiconductor laser operating at a wavelength of 670 nm. The laser beam was focused on the sample surface through a quartz reactor window and the spot size on the sample was 1 mm.

The surface morphology of the layers was examined by atomic force microscopy. The Raman spectra were measured with a Dilor confocal micro-Raman spectrometer using the excitation laser wavelength of 514.5 nm and the optical power at about 10 mW on the sample. The laser beam was focused through a × 100 numerical aperture objective lens. The confocal aperture was fixed to analyse approximately 1 $\mu m^3$ of the sampling volume. Polarization of the Raman spectra was analysed in backscattering geometries.

## 4. Results and discussion

At low temperature the growth rate was investigated as function of growth temperature. The V/III ratio that gave good surface morphology was around 30. Fig. 3 shows the growth rate versus reciprocal growth temperature at V/III ratio of 10. In the temperature range from approximately 550 to 610 °C, the growth rate increases with the temperature, characteristic of the process limited by surface kinetics. In other words, variation of the growth rate was related to the pyrolysis process of TMGa. The data points

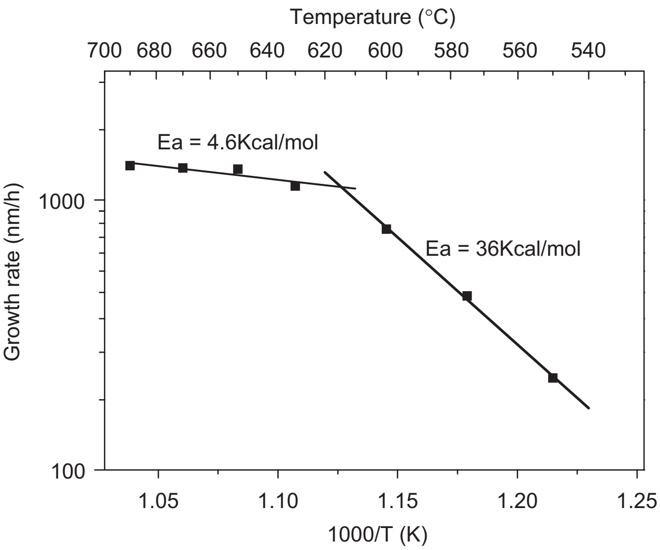

Fig. 3. Growth rate versus $1/T$ with the Arrhenius line fit.

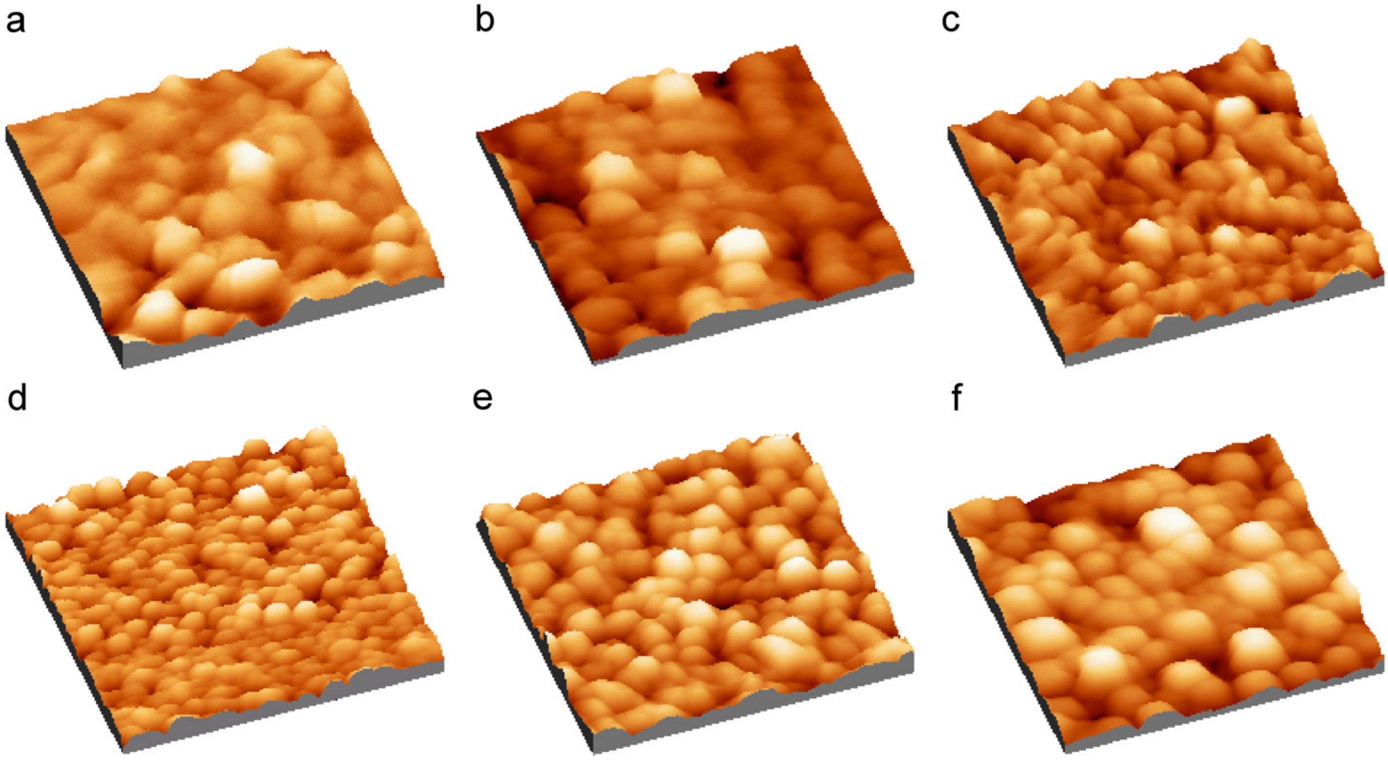

Fig. 4. AFM scans (1 μm × 1 μm) taken on the layers obtained at 550 °C (a), 575 °C (b), 600 °C (c), 650 °C (d), 670 °C (e) and 690 °C (f).

fit well using Arrhenius plot with the slope corresponding to the activation energy of approximately 36 kcal/mol. This value is slightly higher than the activation energy of 28.5 kcal/mol reported by Hsu et al. [3]. This difference in the activation energies is probably caused by the difference in the growth conditions such as growth pressure, and TMGa and DMHy flows. Between 620 and 690 °C, the growth rate has a much smaller slope corresponding to the activation energy of approximately 4.6 kcal/mol. This growth temperature regime is indicative of a mass transport-limited growth.

Surface roughness has been characterized by the AFM (Fig. 4). At low-temperature growth, a few islands appear on the surface of the layers. Above 600 °C, these islands are more numerous and more regular. The roughness and the $z$-average of the layers increase with growth temperature (Table 1).

Raman characterizations: Gallium nitride on sapphire substrate crystallizes in hexagonal (wurtzite; space group $C_{6v}^4$) structure and the group theory predicts eight sets of phonon normal modes at the $\Gamma$ point: $2A_1+2E_1+2B_1+2E_2$. The $A_1$ and $E_1$ modes are acoustic, while the other six modes, $A_1+E_1+2B_1$ (silent) $+2E_2$ are optical [4]. Table 2 summarizes the Raman-active modes for gallium nitride in the backscattering $x(-,-)\bar{x}$ geometries [5]. The $A_1$ mode can be observed when the incident and scattered light have parallel polarization (e.g. $x(y,y)\bar{x}$ geometry), while the $E_1$ mode is observed only in crossed polarization geometry (e.g. $x(y,z)\bar{x}$). The $E_2^H$ mode is allowed only in the $x(y,y)\bar{x}$ geometry.

Table 1
Evolution of RMS roughness and $Z$ average versus the growth temperature

| Growth temperature (°C) | RMS roughness (nm) | $z_{\text{average}}$ (nm) | $Z_{\text{range}}$(nm) |
|---|---|---|---|
| 550 | 1.47 | 5.75 | 11 |
| 575 | 2.05 | 6.5 | 15 |
| 600 | 2.25 | 7.5 | 17 |
| 650 | 2.9 | 11.4 | 24 |
| 670 | 4.3 | 14.5 | 28 |
| 690 | 4.4 | 13.6 | 28 |

Table 2
Raman-active modes in the x(-,-)$x$ geometries [5]

| Geometry | Raman allowed modes | Raman Shift (cm$^{-1}$) |
|---|---|---|
| $x(y,y)x$ | $A_1$(TO), $E_2^H$ | 533, 570 |
| $x(y,z)x$ | $E_1$(TO) | 562 |
| $x(z,z)x$ | $A_1$(TO) | 533 |

Fig. 5 shows evolution of the Raman spectra measured in $x(y,z)\bar{x}$ geometry for several samples grown at different temperatures. Raman selection rules allow only $E_1$(TO) modes in this configuration. However, we observed the $E_2^H$ peak with a relative intensity (with respect to the $E_1$(TO) allowed peak) increasing with decreasing growth temperature. Fig. 6 shows the $E_2^H/E_1$(TO) intensity ratio as a function of the sample growth temperature. We note also

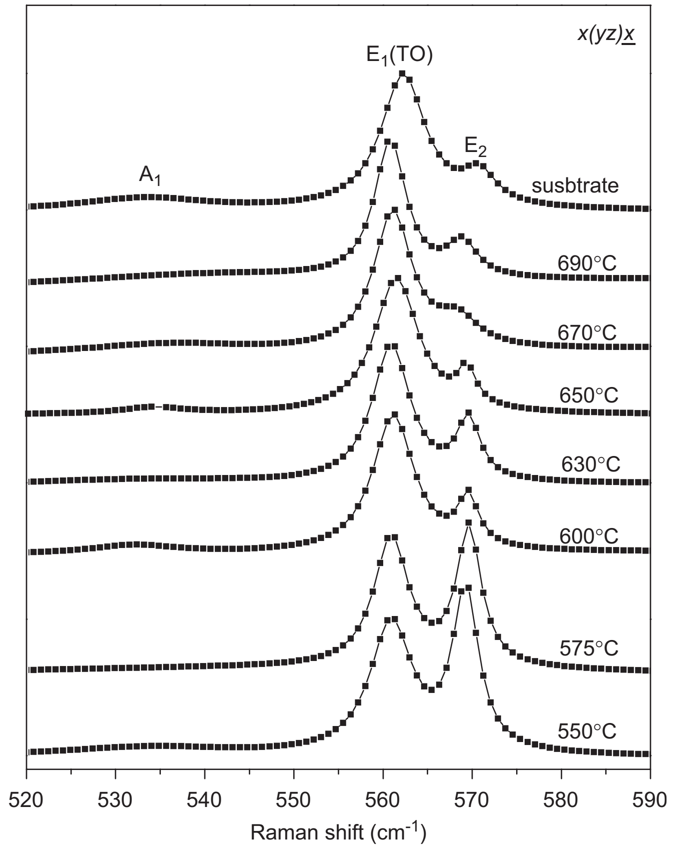

Fig. 5. The growth-temperature dependence of Raman spectra in the $x(y,z)\bar{x}$ geometry. All spectra are normalized to the $E_1$(TO) peak intensity.

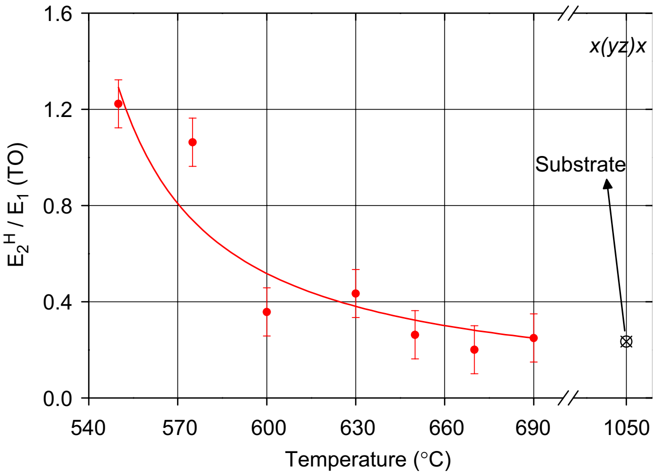

Fig. 6. Evolution of the Raman $E_2^H/E_1$(TO) peak intensity ratio on the growth temperature. For comparison the ratio for the high-temperature growth gallium nitride is shown (for this reference sample, used as substrate, the growth temperature is about 1050 °C).

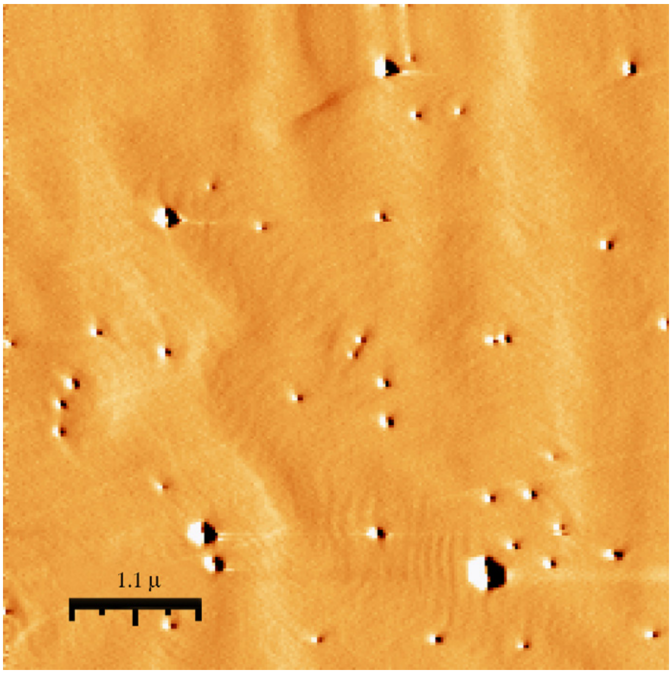

Fig. 7. AFM scan of GaN grown at high temperature.

the weak appearance of the $A_1$(TO) mode, which is forbidden in this configuration, with much lower relative intensity than the $E_2^H$ one. The $E_2^H/E_1$(TO) peak intensity ratio measured for high-temperature-grown gallium nitride substrate is shown as a reference. The observed relaxation of the Raman selection rules can have two origins: (a) large solid angle of the objective lens of our Raman microscope [5] and (b) disorder in epitaxial layers. For our reference sample—high temperature grown GaN on sapphire—the first reason is dominant for observation of the forbidden modes in $x(y,z)\bar{x}$ geometry with the $E_2^H/E_1$(TO) peak intensity ratio of about 0.2. For the low temperature grown GaN samples relaxation of the Raman selection rules is significantly enhanced (Fig. 6) bringing the $E_2^H/E_1$(TO) peak intensity ratio above 1. It can be only explained by the crystalline properties of the grown material, namely by the growth temperature-related disorder in the epitaxial layers. Low-temperature samples exhibit the maximum degree of disorder, while for the samples grown at $T \geqslant 650\,^{\circ}\mathrm{C}$ $E_2^H/E_1$(TO) peak intensity ratio became comparable to the reference GaN substrate, thus showing an increase in the layer quality. We can correlate this evolution to the morphology showed in the AFM images (Fig. 4): appearance of islands, probably crystallites at low growth temperature, which coalesce at higher temperature.

At high temperature around 1100 °C, the growth was performed using $NH_3$ as source of nitrogen. The growth rate of GaN was around 1.4 μm/h at 450 Torr and decreased slightly to 1.2 μm/h at 100 Torr. The surface morphology was good and the GaN layers were smooth and transparent in both pressures and comparable to that of the substrate before growth. The RMS roughness measured by AFM (Fig. 7) is less than 2 nm.

## 5. Conclusion

New reconfiguration of T-shape reactor was developed for high temperature GaN-based materials. Good quality of GaN materials growth at low and high temperatures was demonstrated in this reactor. AFM and micro-Raman measurements clearly revealed the dependence of crystalline quality of GaN layers on growth temperature. In this reconfiguration of the growth system no hardware modifications are needed to swap from the standard III–V to III–N semiconductors growth.

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