High Nitrogen Pressure Solution (HNPS) growth of GaN in Multi Feed Seed (MFS) configuration. Highly conductive and semi-insulating crystals. Role of impurities: oxygen, magnesium and beryllium.

by M. Boćkowski

Institute of High Pressure Physics PAS, ul. Sokołowska 29/37, 01-142 Warsaw, Poland

TopGaN Ltd. ul. Sokołowska 29/37, 01-142 Warsaw, Poland
Outline

1. HNPS method
2. Multi-Feed-Seed (MFS) configuration
3. HNPS-MFS-GaN crystals without an intentional doping
4. HNPS-MFS-GaN crystals grown from Ga:In:N solution
5. HNPS-MFS-GaN:Mg crystals
6. HNPS-MFS-GaN:Be crystals
7. Summary
High Nitrogen Pressure Solution (HNPS) growth of GaN

- N₂ molecules under pressure
- Dissociative adsorption of N₂ on liquid metal surface
- Dissolution and transport to the crystallization zone
- Spontaneous crystallization

Perfect crystallographic quality but...too small!

MFS HNPS growth configuration

gallium between seeds

\[ \frac{dT}{dz} = 5-20^\circ C/cm \]

\[ t \approx 500 \text{ h} \]

\[ p = 1 \text{ GPa} \]

\[ T \in \{1300, 1500\}^\circ C \]
MFS configuration. How it works?
Seeds by HVPE growth

1. Growth on MOVPE GaN/sapphire
2. Me mask is used
3. Self lift-off procedure
4. 2 inch 1 mm thick free standing HVPE-GaN
5. $n=5\times10^{16}$ cm$^{-3}$ - $2\times10^{17}$ cm$^{-3}$
6. TDD=$5\times10^6$ - $10^7$ cm$^{-2}$
7. $R=1 - 5$ m
Seeds by HVPE growth

HVPE-GaN with R=1-5 m

-polished mechanically and mechano-chemically to the epi-ready state

-cut by a drill pipe to smaller objects
HVPE-GaN multistep regrowth
Semipolar and nonpolar substrates

MFS configuration.

Pure gallium between seeds.

(0001) oriented HVPE-GaN seeds

feed

T
Why the gallium side is grown?

Stable growth is observed on the Ga side!

Macroscopically flat growth
(as grown crystals-Ga side up)
Nitrogen side

Pinholes have flat bottoms!
Gallium side
Mixed growth mode
Growth mode depends on supersaturation

Supersaturation depends on:
- the growth temperatures,
- gallium heights between seeds,
- the temperature gradient applied.

Hillocks

\[ R = 0.5 - 1 \, \mu m/h \]

Macrosteps and hillocks

\[ R = 1 - 2 \, \mu m/h \]

Macrosteps

\[ R = 2 - 5 \, \mu m/h \]
Growth modes

Hillocks-low supersaturation-diffusional transport in the solution

Hillocks-corelated with screw and mixed dislocations

Etching performed in the liquid eutectic of KOH and NaOH at temperatures ranging from 673 to 723 K.
Growth modes

Mixed mode-average supersaturation-convection starts in the solution

Macrosteps appear
Growth modes

Macrosteps mode-high supersaturation-strong convection flow
Macrosteps mode-step bunching-formation of gallium inclusions
Macrosteps

Voids and gallium inclusions

Hillocks and mixed growth mode

No voids, no gallium inclusions

Hillocks or mixed growth modes are preferred!
HNPS-MFS-GaN substrates
Substrates for laser diodes

1. Laser diodes based on HNPS-MFS-GaN have been already demonstrated.

\[ U_{th} = 4.5 - 4.8 \text{ V} \]
\[ j_{th} = 2.5 \text{ kA/cm}^2 \]
2. HNPS-MFS-GaN crystals are used for preparing undulated substrates (locally controlled miscut).
Substrates for laser diodes

P-type electric contact pad
Plateau
Slope

Laser diode epitaxial structure

A - 0.35 deg
B - 0.85 deg

Optical power, mW
Electric current, mA

I_{th} = 4-6 \text{ kA/cm}^2
U_{th} = 5.5 \text{ V}

Chips B
Chips A

Intensity, arb. unit
Wavelength, nm

M. Sarzynski et al. APPLIED PHYSICS EXPRESS Volume: 5 Issue: 2 : FEB 2012
Free carrier concentration.
Van der Pauw/Hall measurements

Oxygen concentration by SIMS measurements

growth temperature °C

E. Litwin-Staszewska, SIMS by R. Jakieła (IF PAN)
SIMS measurements

GaN grown at 1380°C

GaN grown at 1430°C

SIMS by R. Jakieła (IF PAN)
Free carrier concentration.
Van der Pauw/Hall measurements

growth from Ga:In:N solution

E. Litwin-Staszewska
Indium in the solution. SIMS analysis

No standard for indium-relative measurements

GaN grown without In in the solution @1480°C

GaN grown with In in the solution @1480°C

The same oxygen level!!!
Indium in the solution. CL analysis

CL by A. Reszka and G. Teisseyre (IF PAN)
Oxygen and... nitrogen vacancies?

1. Indium atoms are in the solution;
2. Indium atoms are in the crystals;
3. No InN or InGaN phases in the crystals
4. Oxygen concentration does not change;
5. Free carrier concentration increases.
X-ray diffraction

reflexion 002; beam dimension: 3x10 mm²

<table>
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<th>FWHM</th>
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<td>[arcsec]</td>
<td>HNPS</td>
<td>(after regrowth)</td>
<td>HNPS-GaN</td>
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<td>X</td>
<td>3</td>
<td>4.0</td>
<td>X</td>
<td>20</td>
</tr>
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Time evolution of the growing crystal

\[ \Delta \varepsilon = \frac{a_{\text{HNPS}} - a_{\text{HVPE}}}{a_{\text{HVPE}}} \]

- **HNPS compressive strain**
- **HVPE tensile strain**

B. Lucznik/T.W Clayne „Encyclopedia of Material Science and Technology”; Elsevier 2001
Seeds quality requirements

If a seed (HVPE-GaN) is strained elastically it can be used for further successful growth.

FWHM,002 = 0.037
beam dimension: 3x10 mm^2

Intensity vs. w (deg)
Seeds quality requirements

If a seed (HVPE-GaN) is composed by grains or it is plastically strained, it cannot be used for further successful growth.
Dislocation densities

Etching performed in the liquid eutectic of KOH and NaOH at temperatures ranging from 673 to 723 K.

\[ TDD = 10^6 \text{ cm}^{-2} \]
Multi feed seed GaN:Mg

(000-1) oriented
HVPE-GaN
or
HNPS-GaN

Ga:Mg between seeds

Ga:Mg

Polarity of the GaN seed surface for stable growth is determined and controlled by the Ga solution and its impurities!
HNPS-MFS-GaN:Mg

SIMS by R. Jakieła (IF PAN)
HNPS-MFS-GaN:Mg

ρ(Ωcm) vs. 1/T (K⁻¹)

room temperature

Ea=757meV

E. Litwin-Staszewska
Near interface region is decorated by MgO.

TEM by J.Smalc-Koziorowska
The MgO crystallites are epitaxially overgrown by GaN.

TEM by J.Smalc-Koziorowska
HNPS-MFS-GaN:Mg

\[ a_{\text{hnps}} = 3.1885 \, \text{Å} \]
\[ a_{\text{hvpe}} = 3.1885 \, \text{Å} \]

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<th>R</th>
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<td>HVPE</td>
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</tr>
<tr>
<td>-1.2 m</td>
<td>+1.5 m</td>
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<td>-1.5 m</td>
<td>+2 m</td>
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<tr>
<td>-4 m</td>
<td>+5 m</td>
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TDD: \(5 \times 10^6 - 10^7\) cm\(^{-2}\)
HNPS-MFS-GaN:Mg
Surface preparation
HNPS-MFS-GaN:Mg
2D GaN/AlGaN structures on HNPS-MFS-GaN:Mg

Mobility @ 295K
2100 cm$^2$/Vs
$n_{2DEG}=5\times10^{12}$ cm$^{-2}$

GaN/AlGaN on GaN bulk crystals

Temperature (K)

Mobility (cm$^2$/Vs)
n$_{2DEG}$ (cm$^{-2}$)

3 nm GaN
21 nm AlGaN
1 um GaN
MBE-222 (Mg) na TG-1296 (M115)

P1708 HEMT

C. Skierbiszewski
GaN:Be
What for?

GaN:Be
What for?

Emission intensity is only slightly lower than that of the Lumileds conversion cap!

Measurements: Michael Kunzer @ Fraunhofer IAF

GaN:Be

How to prepare Ga:Be solution?

Homogeneization of Ga:Be solution in Ar

Films on the Ga surface

\[ 2 \text{Be} + \text{O}_2 \rightarrow 2 \text{BeO} \]
\[ 3 \text{Be} + \text{N}_2 \rightarrow \text{Be}_3\text{N}_2 \]
GaN:Be

Spontaneously grown GaN crystals verify if the solution was well prepared
GaN:Be

N-side; Ga-side

Polarity of the GaN seed surface for stable growth is determined and controlled by the Ga solution and its impurities!
GaN:Be?

Problems:

1. Back etching (wetting)
2. Surface passivation
3. Polarity ?
4. ???
Summary

1. HNPS-MFS configuration involves the conversion of free-standing HVPE-grown GaN crystals to free-standing HNPS-GaN, which has with a much higher quality than the seed material;

2. HNPS-MFS configuration allows obtaining stable and macroscopically flat growth of the HNPS-GaN; hillocks or mixed growth modes are preferred;

3. Polarity of the HVPE-GaN seed surface is determined and controlled by the Ga solution and its impurities;

4. Free standing HNPS-GaN crystals can be strongly n-type (GaN:0 or $V_N$) or semi-insulating (GaN:Mg; GaN:Be);

5. faster growth rate is needed thus some changes of Ga solution properties should be carried out.
People

IHHP PAS:

TopGaN Ltd.:

IF PAN:
A. Reszka, H. Teisseyre, R. Jakieła,
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