N coordination chemistry in diluted InGaAs nitride layers

M. Gabás, M.C. López-Escalante, J.R. Ramos-Barrado
The Nanotech Unit-Depto. Física Aplicada I
University of Málaga
Málaga, Spain

B. Ściana, W. Dawidowski, D. Radziewicz
Faculty of Microsystem Electronics and Photonics,
Wrocław University of Technology,
Wrocław, Poland

P. Dłużewski
Institute of Physics
Polish Academy of Science
Warsaw, Poland
Motivation

Lattice matched to GaAs
Band gap tunability

Unusual properties:
- Huge band gap bowing coefficient
- Band gap reduction with small amount of N
- Large conduction band offset ($\Delta E_c > 300$ meV)

Applications:
- promising material for IR lasers and HBT
- VCSELs and RCE devices
- high efficiency multi-junction solar cells - $\text{In}_{0.09}\text{Ga}_{0.91}\text{As}_{0.97}\text{N}_{0.03}$ lattice-matched to GaAs and Ge substrate $\rightarrow E_g \approx 1$ eV

Technological problems:
- Large miscibility gap between GaAs and GaN
- Large amounts of point defects: vacances, antisites, interstitials
- High concentration of impurities: oxygen, carbon, hydrogen (MOVPE)
- Large amounts of examination methods are needed for proper characterisation

Courtesy of Prof. M. Tłaczała
## Sample description

### Growth method
- AP MOVPE
- AIX200 R&D Aixtron horizontal reactor
- Organic sources: $\text{AsH}_3$ (10% in $\text{H}_2$), $\text{TMGa}$, $\text{TMIn}$, $\text{TBHy}$
- $\text{H}_2$ as a carrier gas
- (100)-oriented n-doped GaAs substrate

### Growth parameters
- Organic source temperatures: $T_{\text{TMGa}} = -10^\circ\text{C}$, $T_{\text{TMIn}} = 20^\circ\text{C}$, $T_{\text{TBHy}} = 30^\circ\text{C}$
- $V_{\text{AsH}_3} = 50 \text{ ml/ min (InGaAsN)}$
- Growth temperature: $T_g = 575^\circ\text{C}, 585^\circ\text{C}$
- Growth time: $t_g = 30 \text{ min, 10 min}$
- Annealing temperature and time: $T_g = 700^\circ\text{C}, t_g = 5 \text{ min}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>In$<em>y$Ga$</em>{1-y}$As$_{1-x}$N$_x$ thickness</th>
<th>Buffer GaAs thickness</th>
<th>n-GaAs:Sic substrate thickness</th>
<th>RTA process</th>
</tr>
</thead>
<tbody>
<tr>
<td>NI52n</td>
<td>$\sim 110$ nm</td>
<td>$\sim 0.3, 0.4 \mu$m</td>
<td>$350 \pm 25 \mu$m</td>
<td>$T_g = 575^\circ\text{C}, t_g = 30 \text{ min}$</td>
</tr>
<tr>
<td>NI52nA</td>
<td>$\sim 110$ nm</td>
<td>$\sim 0.3, 0.4 \mu$m</td>
<td>$350 \pm 25 \mu$m</td>
<td>RTA process</td>
</tr>
<tr>
<td>NI74n</td>
<td>$\sim 85$ nm</td>
<td>$\sim 0.3 \mu$m</td>
<td>$350 \pm 25 \mu$m</td>
<td>$T_g = 585^\circ\text{C}, t_g = 10 \text{ min}$</td>
</tr>
</tbody>
</table>

*Sciana, et. al., Crystal Research and Technology, 47, 313 - 320 (2012)*
**HRXRD**

NI52n, NI52nA

Diffraction curves for the 004 reflection

NI74n

Reciprocal space maps for the 224 reflection

- **Fully relaxed**
  - 20% In, 0.1% N, ~80 nm
  - 10% In, 0.48% N, ~30 nm
  - 7% In, 0.72% N

- **Fully strained**
  - 24% In, 0.2% N, ~20 nm
  - 13% In, 0.3% N, ~85 nm
  - 7% In, 0.5% N

In N

~80 nm

~30 nm

~85 nm
Spectral range of the N-related local vibrational modes: visible modes connected with different N atoms configurations - \( \text{NGa}_3\text{In} \), \( \text{NGa}_2\text{In}_2 \), \( \text{NGa}_4 \)
- elongated bulges on the surface of NI52n samples (smaller on NI74n)
- white nanometric spots on layer surfaces
InAs segregations

STEM + HRTEM
ARXPS

\[ \text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y \]

N content very low

\[ y = 0.002-0.004 \]

Survey spectra

XPS (a.u.)

BE (eV)

NI52n

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ARXPS

N 1s core level spectra

**NI52n**

- N – Ga bonds at surface
- In content decreases as depth increases

**NI52nA**

- \([N-In]/[N-Ga]\) increases after annealing, 1.3 → 1.5
ARXPS

In 3d core level spectra

**NI52n**

\[
\frac{[\text{In-N}]}{[\text{In-As}]} \sim 1\%
\]

**NI52nA**

\[
\frac{[\text{In-N}]}{[\text{In-As}]} \sim 1.3\%
\]

**NI74n**

\[
\frac{[\text{In-N}]}{[\text{In-As}]} \sim 4.5\%
\]
Summary

- InGaAsN layers characteristics are very much dependent on growth temperature.
- Regarding the structural quality of the samples:
  - no improvement has been observed after RTA,
  - better structural quality achieved with high growth temperature.
- More residues and contaminants in the surface of the samples prepared at lower temperature, even after annealing.
- Layer growth at higher temperature is a better option for increasing the number of In-N bonds in the layer.
- The combination of several experimental techniques is crucial to achieve reliable conclusions.
Acknowledgments

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