MODELLING POROSITY OF HIGH SURFACE AREA NANOPOWDERS OF THE GALLIUM NITRIDE GaN SEMICONDUCTOR

Jerzy F. Janik,* Mariusz Drygas, L. Czepirski

AGH University of Science and Technology, Faculty of Energy and Fuels
Al. Mickiewicza 30, 30 059 Krakow, Poland

*E-mail: janikj@agh.edu.pl

IVC18/ICN+T2010/ICSS-14/VASSCAA-5, Beijing, China, 2010
Gallium nitride GaN

- two crystallographic forms at RT:
  - wurzite (hexagonal): $a = 3.168 \, \text{Å}$ and $c = 5.178 \, \text{Å}$
  - zinc blende (cubic): $a = 4.51 \, \text{Å}$
- thermal stability up to 1000 °C
- high chemical stability
- strong piezoelectric effect
- wide bandgap semiconductor: 3.4 eV (hexagonal)
- alloys with InN and AlN; alloy bandgap range: 1.8–6.2 eV
- GaN bandgap is a function of particle size for $R < 11 \, \text{nm}$
Materials forms of GaN

- Microcrystals
  - L. Lei, D. He; *Cryst. Growth Des.*, 2009, 9, 1263.

- Bulk crystals

- Thin films

Gallium nitride GaN

- Quantum dots

- Porous surface

- Nanopowders

- Nanotubes

- Nanofibers
Porous GaN

Heterogenous catalysis  Adsorbents, nanosurfaces

Powders, ceramics

Layers, supports

Porous GaN

Properties

Luminescent devices

Reduced dislocation density

Significant PL intensity enhancement and wavelength shifting

Sensing devices upon surface metallization

Reduction of cracks

Advantageous intermediate layers for overgrowth of GaN/InGaN/AlGaN films

Relaxation of compression stress

Applications
This work – anaerobic synthesis of GaN nanopowders

(CH₃)₂NH → Synthesis of lithium dimethylamide LiN(CH₃)₂

CH₃(CH₂)₃Li →

Lithium dimethylamide LiN(CH₃)₂

GaCl₃

Metathesis of LiN(CH₃)₂ and GaCl₃

Tris(dimethylamino)gallium Ga[N(CH₃)₂]₃

Reactions in liquid NH₃ (ammonolysis), −33 °C, 4 h

Pyrolysis: 350-800 °C, 4-16 h, NH₃ flow

Gallium imide [Ga(NH)₃/2]ₙ

[Ga(NH)₃/2]ₙ → nGaN + n / 2NH₃↑

Gallium nitride nanopowders

This work – aerosol synthesis of GaN nanopowders

![Diagram of the synthesis process](image)

\[ 2Ga(NO_3)_3 \xrightarrow{1050 \, ^\circ C} Ga_2O_3 + "3N_2O_5" \uparrow \to \cdots Ga_2O_3 + 2NH_3 \xrightarrow{950-975 \, ^\circ C} 2GaN + 3H_2O \uparrow \]

This work – synthesis of GaN nanopowders from Ga$_2$O$_3$

Reaction of bulk gallium oxide powder with ammonia

\[ Ga_2O_3 + 2NH_3 \xrightarrow{950 \degree C} 2GaN + 3H_2O \uparrow \]

High surface area GaN powders – to date


Max. BET surface area: 224 m²/g


Max. BET surface area: 320 m²/g


Max. BET surface area: 331 m²/g
Capillary condensation vs. pore size and spherical particle morphology

If a capillary's radius increases sharply, then capillary condensation (adsorption) will cease until an equilibrium vapor pressure is reached which satisfies the larger pore radius. However, during evaporation (desorption), liquid will remain filled to the larger pore radius until an equilibrium vapor pressure that satisfies the smaller pore radius is reached.


http://www.nippon-bel.co.jp/tech/seminar12_e.html
Assumptions of Langmuir theory

1. Fixed number of adsorption sites are available on the surface.
2. All the vacant sites are of equal size and shape on the surface.
3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.
4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

\[
A(g) + B(s) \xrightleftharpoons{\text{adsorption}}{\text{desorption}} AB
\]

5. Adsorption is monolayer.
Assumptions of BET theory

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses.

1. Gas molecules physically adsorb on the surface with random distribution of sites covered by one, two, three, etc. molecules.

2. There is no interaction between each adsorption layer.

3. The Langmuir theory can be applied to each layer.
Barrett, Joyner, Halenda (BJH) theory

Assumptions of BJH theory

1. The relative pressure $p/p_0$ at which decondensation (from capillary phase to multilayer adsorbed phase) occurs in a cylindrical pore is given by the Kelvin law,

$$kT \ln \left( \frac{p}{p_0} \right) = -2 \sigma v_1/(R-t)$$

$k$ - Boltzmann constant, $T$ - temperature, $p$ - equilibrium pressure, $p_0$ - saturation vapor pressure, $\sigma$ - surface tension, $v_1$ - liquid molecular volume, $R$ - pore radius, $t$ - multilayer thickness

2. The curvature of the solid surface has no influence on $t$. Thus, $t$ can be experimentally determined using non porous adsorbents.

$$kT \ln \left( \frac{p}{p_0} \right) = U(t)$$
## Samples and experimental results

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>$D_{\text{GaN}}$ (XRD) [nm]</th>
<th>$d_{\text{He}}$ [g/cm³]</th>
<th>$S_{\text{BET}}$ [m²/g]</th>
<th>$S_{\text{Lang}}$ [m²/g]</th>
<th>$S_{\text{meso}}$ (BJH/des) [m³/g]</th>
<th>$V_{\text{meso}}$ (BJH/des) [cm³/g]</th>
<th>Av. pore size (BJH/des) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Anaer 450 vac</td>
<td>1.0</td>
<td>3.6</td>
<td>179</td>
<td>265</td>
<td>30.2</td>
<td>0.021</td>
<td>2.7</td>
</tr>
<tr>
<td>2</td>
<td>Anaer 450 N₂</td>
<td>1.2</td>
<td>3.8</td>
<td>165</td>
<td>262</td>
<td>145</td>
<td>0.089</td>
<td>2.4</td>
</tr>
<tr>
<td>3</td>
<td>Anaer_350 NH₃</td>
<td>1.6</td>
<td>4.0</td>
<td>134</td>
<td>216</td>
<td>96</td>
<td>0.070</td>
<td>3.7</td>
</tr>
<tr>
<td>4</td>
<td>Anaer_450 NH₃</td>
<td>1.8</td>
<td>4.5</td>
<td><strong>222</strong></td>
<td><strong>357</strong></td>
<td><strong>216</strong></td>
<td>0.138</td>
<td>2.6</td>
</tr>
<tr>
<td>5</td>
<td>Anaer_600 NH₃</td>
<td>3.0</td>
<td>5.2</td>
<td>103</td>
<td>162</td>
<td>133</td>
<td>0.154</td>
<td>4.6</td>
</tr>
<tr>
<td>6</td>
<td>Anaer 700 NH₃</td>
<td>6.0</td>
<td>5.2</td>
<td>58</td>
<td>91</td>
<td>76</td>
<td>0.146</td>
<td>6.9</td>
</tr>
<tr>
<td>7</td>
<td>Anaer 800 NH₃</td>
<td>8.1</td>
<td>5.0</td>
<td>42</td>
<td>66</td>
<td>66</td>
<td>0.143</td>
<td>17.8</td>
</tr>
<tr>
<td>8</td>
<td>Aero DM 950</td>
<td>17.0</td>
<td>6.0</td>
<td>23.5</td>
<td>37.0</td>
<td>38.0</td>
<td>0.181</td>
<td>19.0</td>
</tr>
<tr>
<td>9</td>
<td>Aero_DM 950</td>
<td>18.0</td>
<td>6.0</td>
<td>24.0</td>
<td>37.5</td>
<td>42.0</td>
<td>0.213</td>
<td><strong>20.3</strong></td>
</tr>
<tr>
<td>10</td>
<td>Aero_MeOH 950</td>
<td>18.0</td>
<td>6.1</td>
<td>20.8</td>
<td>32.1</td>
<td>22.8</td>
<td>0.086</td>
<td>15.1</td>
</tr>
<tr>
<td>11</td>
<td>Aero_H₂O 975</td>
<td>30.0</td>
<td>6.0</td>
<td>6.3</td>
<td>9.7</td>
<td>5.2</td>
<td>0.015</td>
<td>11.5</td>
</tr>
<tr>
<td>12</td>
<td>Ga₂O₃ 950</td>
<td>39.0</td>
<td>6.1</td>
<td>8.0</td>
<td>12.2</td>
<td>6.7</td>
<td>0.019</td>
<td>11.6</td>
</tr>
</tbody>
</table>
Adsorption isotherms (N₂, 77.5 K) and mesopore distribution (BJH) - 1

Anaero_450_vac

Anaero_450_N₂

Anaero_350_NH₃
Adsorption isotherms ($N_2$, 77.5 K) and mesopore distribution (BJH) - 2

Aero_DMF/MeOH_950

Aero_DMF_950

Aero_MeOH_950

IVC18/ICN+T2010/ICSS-14/VASSCAA-5, Beijing, China, 2010
**Scherrer's equation:**

\[
\text{Av. crystallite size} = \frac{K \cdot \lambda}{B \cdot \cos \Theta}
\]

- **K** (crystallite shape factor) = 0.9 (usually)
- **\(\lambda\)** (X-ray wavelength) = 1.540598 Å (Cu K\(_\alpha\))
- **B** (line broadening at half the maximum) = \(\sqrt{\text{sq. root}(B_{\text{obs}}^2 - B_{\text{std}}^2)}\)
- **\(\Theta\)** (Bragg angle)

- possible superimposed peaks for the hexagonal and cubic polytypes
- potentially defected hexagonal polytype
- vaguely addressed problem of lattice strain contribution to line broadening in nanograins
- equivocal interpretation of X-ray diffraction outcome for small nanocrystallites due to significant contribution of surface layers

**Increased uncertainty in average size determinations for** \(D < \text{ca. 10 nm}\)
TEM pictures of GaN powders

Anaero - 900 °C, 4 h; $D_{av} = 15$ nm

Aero - 975 °C, 6 h; $D_{av} = 20$ nm
SEM pictures of GaN powders

Aerosol-assisted synthesis, 950-975 °C, 6 h
Can pore system and pore surface area for gallium nitride GaN nanopowders be adequately modelled by interparticle spaces and surface area, respectively, of closely packed equiradial spherical particles as the simplest model case?

**Model validation** by testing correlation between the experimental standard "porosity" parameters, i.e., BET, Langmuir, and BJH-derived specific surface areas and the experimental "particle size" parameter, i.e., average crystallite diameter from XRD determinations with respect to predictions of the model.
Helium density aspect

\[ d_{agg} \ [g/cm^3] = \frac{m_{agg}}{V_{agg}} = 6.1 \cdot \frac{n \cdot \frac{4}{3} \pi \left( \frac{D_{GaN}}{2} \right)^3}{n \cdot \frac{4}{3} \pi \left( \frac{D_{GaN} + D_{He}}{2} \right)^3} = 6.1 \cdot \frac{D_{GaN}^3}{(D_{GaN} + D_{He})^3} = 6.1 \cdot \frac{D_{GaN}}{(D_{GaN} + 0.26)^3} \]

\[ d_{agg} \ vs \ D \ [\mu m] \]

- \( d_{theor} = f(D) \)
- \( d_{He(exp)} = f(D_xrd) \)
Model 1 – double adsorbate layer particle bridging

\[ n / \text{cm}^3 = \frac{0.7405}{4 \pi \left( \frac{D + 2D_{N_2}}{2} \right)^3 \cdot 10^{-21}}; \quad n \text{- number of particles per } 1 \text{ cm}^3 \]

\[ S_p [m^2] = 4 \pi \left( \frac{D}{2} \right)^2 \cdot 10^{-18}, \quad S_p \text{- particle surface area} \]

\[ S [m^2 / cm^3] = n \cdot S_p = \frac{0.7405}{4 \pi \left( \frac{D + 2D_{N_2}}{2} \right)^3 \cdot 10^{-21}} \cdot 4 \pi \left( \frac{D}{2} \right)^2 \cdot 10^{-18} = \frac{4443 \cdot D^2}{(D + 2D_{N_2})^3} \]

\[ S_{corr} [m^2 / g] = S [m^2 / g] \cdot k = \frac{728.36 \cdot (D + D_{N_2})^2}{(D + 2D_{N_2})^3} \cdot \frac{(D + D_{He})^3}{D^3} \]

D – particle (crystallite/agglomerate) diameter [nm]
\( D_{He} = 0.260 \text{ nm} \) – helium atom kinetic diameter
\( D_{N_2} = 0.455 \text{ nm} \) – nitrogen molecule diameter
Model 1 - double adsorbate layer
particle bridging

Model 1 - theoretical relationships between the specific surface and sphere diameter

\[ S = f(D_{the or}) \]

\[ S (c \; or) = f(D_{the or}) \times k \]

\[ k = \frac{S_m}{S} = \frac{(D + D_m)}{D} \]

Specific surface, \( [m^2/g] \)

Diameter, \( [nm] \)
Model 2 – single adsorbate layer particle bridging

\[ S \left[ m^2 / g \right] = \left( D^2 - \frac{3 \cdot D^2 \cdot D_{N_2}}{D + 2D_{N_2}} \right) \cdot \frac{728.36}{(D + D_{N_2})^3} \cdot \frac{(D + D_{He})^3}{D^3} \]

\[ S_{corr} \left[ m^2 / g \right] = S \left[ m^2 / g \right] \cdot k = \left( 1 - \frac{3 \cdot D_{N_2}}{D + 2D_{N_2}} \right) \cdot \frac{728.36}{(D + D_{N_2})} \cdot \frac{(D + D_{He})^3}{D^3} \]

D – particle (crystallite/agglomerate) diameter [nm]
\[ D_{He} = 0.260 \text{ nm} \] – helium kinetic diameter
\[ D_{N_2} = 0.455 \text{ nm} \] – nitrogen molecule diameter
Model 2 – single adsorbate layer particle bridging

Model 2 - theoretical relationships between the specific surface and sphere diameter
Model 3 – no adsorbate layer particle bridging

\[ S \left[ \frac{m^2}{g} \right] = \left(1 - \frac{6D_{N_2}}{D + 2D_{N_2}}\right) \cdot \frac{728.36 \cdot (D + D_{He})^3}{D^3} \]

\[ S_{corr} \left[ \frac{m^2}{g} \right] = S \left[ \frac{m^2}{g} \right] \cdot k = \left(1 - \frac{6D_{N_2}}{D + 2D_{N_2}}\right) \cdot \frac{728.36 \cdot (D + D_{N_2})^2}{D^3} \cdot \frac{(D + D_{He})^3}{D^3} \]

\[ k = \frac{S}{S_c} = \frac{(D + D_{He})}{D} \]

\[ D \] – particle (crystallite/agglomerate) diameter [nm]
\[ D_{He} = 0.260 \text{ nm} \] – helium kinetic diameter
\[ D_{N_2} = 0.455 \text{ nm} \] – nitrogen molecule diameter

IVC18/ICN+T2010/ICSS-14/VASSCAA-5, Beijing, China, 2010
Model 3 – no adsorbate layer particle bridging

Model 3 - theoretical relationships between the specific surface and sphere diameter

\[ S = f(D_{\text{theor}}) \]

\[ S (\text{corr}) = f(D_{\text{theor}}) \times k \]

\[ k = \frac{S}{S'} = \frac{(D + D_c)}{D} \]

Where:
- \( S \) is the specific surface area (m²/g)
- \( D \) is the diameter (μm)
- \( D_{\text{theor}} \) is the theoretical diameter
- \( D_c \) is the critical diameter
- \( k \) is the correction factor

Graph showing the relationship between specific surface area and diameter, with equations and a correction factor formula.
Model 1 – correlation equations

(i) No correction for the cross-sectional area of \(N_2\)

\[ S[m^2 / g] = \frac{728.36 \cdot D^2 \cdot (D + D_{\text{le}})^3}{(D + 2D_{N_2})^3 \cdot D^3} \]

\(a\) – relaxed variable (relaxed \(D\))

\[ S_{\text{corr}}[m^2 / g] = \frac{728.36 \cdot (a \cdot D + D_{N_2})^2 \cdot (D + D_{\text{le}})^3}{(a \cdot D + 2D_{N_2})^3 \cdot D^3} \]

\(a, b\) – relaxed variables (relaxed \(D\) and "constant")

(ii) Corrected for the cross-sectional area of \(N_2\)

\[ S[m^2 / g] = \frac{b \cdot (a \cdot D)^2 \cdot (D + D_{\text{le}})^3}{(a \cdot D + 2D_{N_2})^3 \cdot D^3} \]

\(a, b\) – relaxed variables (relaxed \(D\) and "constant")

\[ S_{\text{corr}}[m^2 / g] = \frac{b \cdot (a \cdot D + D_{N_2})^2 \cdot (D + D_{\text{le}})^3}{(a \cdot D + 2D_{N_2})^3 \cdot D^3} \]
Model 2 – correlation equations

(i) No correction for the cross-sectional area of $N_2$

\[
S \text{ [m}^2 \text{/g]} = (D^3 - \frac{3 \cdot D^2 \cdot D_{N_2}}{D + 2D_{N_2}}) \cdot \frac{728.36}{(D + D_{N_2})^3} \cdot \frac{(D + D_{He})^3}{D^3}
\]

- $a$ – relaxed variable (relaxed D)
- $a, b$ – relaxed variables (relaxed D and one "constant")
- $a, b, c$ – relaxed variables (relaxed D and two "constants")

\[
S \text{ [m}^2 \text{/g]} = \left( (a \cdot D)^2 - \frac{3 \cdot D^2 \cdot D_{N_2}}{a \cdot D + 2D_{N_2}} \right) \cdot \frac{728.36}{(a \cdot D + D_{N_2})^3} \cdot \frac{(D + D_{He})^3}{D^3}
\]

\[
S \text{ [m}^2 \text{/g]} = \left( (a \cdot D)^2 - \frac{c \cdot D^2 \cdot D_{N_2}}{a \cdot D + 2D_{N_2}} \right) \cdot \frac{b}{(a \cdot D + D_{N_2})^3} \cdot \frac{(D + D_{He})^3}{D^3}
\]
Model 2 – correlation equations, cntd.

(i) Corrected for the cross-sectional area of $N_2$

\[
S \left[ \frac{m^2}{g} \right] = \left(1 - \frac{3 \cdot D_{N_2}}{a \cdot D + D_{N_2}} \right) \cdot \frac{728.36 \cdot (D + D'_{le})^3}{a \cdot D + D_{N_2}} \cdot \frac{D + D'_{le}}{D^3}
\]

- **$a$** – relaxed variable (relaxed $D$)
- **$a$, $b$** – relaxed variables (relaxed $D$ and one ”constant”)
- **$a$, $b$, $c$** – relaxed variables (relaxed $D$ and two ”constants”)

\[
S \left[ \frac{m^2}{g} \right] = \left(1 - \frac{3 \cdot D_{N_2}}{a \cdot D + 2D_{N_2}} \right) \cdot \frac{728.36}{a \cdot D + D_{N_2}} \cdot \frac{(D + D'_{le})^3}{D^3}
\]

\[
S \left[ \frac{m^2}{g} \right] = \left(1 - \frac{3 \cdot D_{N_2}}{a \cdot D + 2D_{N_2}} \right) \cdot \frac{b}{a \cdot D + D_{N_2}} \cdot \frac{(D + D'_{le})^3}{D^3}
\]

\[
S \left[ \frac{m^2}{g} \right] = \left(1 - \frac{c \cdot D_{N_2}}{a \cdot D + 2D_{N_2}} \right) \cdot \frac{b}{a \cdot D + D_{N_2}} \cdot \frac{(D + D'_{le})^3}{D^3}
\]
Model 3 – correlation equations

(i) No correction for the cross-sectional area of $N_2$

\[
S[m^2 / g] = \left(1 - \frac{6 \cdot D_{N_2}}{a \cdot D + 2D_{N_2}}\right) \cdot \frac{728.36 \cdot (D + D_{\text{tie}})^3}{D^3}
\]

- $a$ – relaxed variable (relaxed D)
- $a, b$ – relaxed variables (relaxed D and one "constant")
- $a, b, c$ – relaxed variables (relaxed D and two "constants")

\[
S[m^2 / g] = \left(1 - \frac{6 \cdot D_{N_2}}{a \cdot D + 2D_{N_2}}\right) \cdot \frac{b}{a \cdot D} \cdot \frac{(D + D_{\text{tie}})^3}{D^3}
\]

\[
S[m^2 / g] = \left(1 - \frac{c \cdot D_{N_2}}{a \cdot D + 2D_{N_2}}\right) \cdot \frac{b}{a \cdot D} \cdot \frac{(D + D_{\text{tie}})^3}{D^3}
\]
Model 3 – correlation equations, cntd.

(i) Corrected for the cross-sectional area of $N_2$

$$S \left[ m^3 / g \right] = (1 - \frac{6 \cdot D_{N_2}}{D + 2D_{N_2}}) \cdot \frac{728.36 \cdot (a \cdot D + D_{N_2})^2 \cdot (D + D_{ile})^3}{(a \cdot D)^3 \cdot D^3}$$

- $a$ – relaxed variable (relaxed $D$)
- $a, b$ – relaxed variables (relaxed $D$ and one "constant")
- $a, b, c$ – relaxed variables (relaxed $D$ and two "constants")

$$S \left[ m^3 / g \right] = (1 - \frac{6 \cdot D_{N_2}}{a \cdot D + 2D_{N_2}}) \cdot \frac{728.36 \cdot (a \cdot D + D_{N_2})^2 \cdot (D + D_{ile})^3}{(a \cdot D)^3 \cdot D^3}$$

$$S \left[ m^3 / g \right] = (1 - \frac{c \cdot D_{N_2}}{a \cdot D + 2D_{N_2}}) \cdot \frac{b(a \cdot D + D_{N_2})^2 \cdot (D + D_{ile})^3}{(a \cdot D)^3 \cdot D^3}$$
### Correlation Coefficients

**Model 1 (double adsorbate layer particle bridging)**

<table>
<thead>
<tr>
<th>Correction for cross-sectional area of ( N_e )</th>
<th>BET</th>
<th>LANGMUIR</th>
<th>BJH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>0.84</td>
<td>0.94</td>
<td>n/a</td>
</tr>
<tr>
<td>No</td>
<td>0.91</td>
<td>0.95</td>
<td>n/a</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Correction for cross-sectional area of ( N_e )</th>
<th>BET</th>
<th>LANGMUIR</th>
<th>BJH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>0.87</td>
<td>0.92</td>
<td>n/a</td>
</tr>
<tr>
<td>No</td>
<td>0.87</td>
<td>0.94</td>
<td>n/a</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Correction for cross-sectional area of ( N_e )</th>
<th>BET</th>
<th>LANGMUIR</th>
<th>BJH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>0</td>
<td>0.64</td>
<td>n/a</td>
</tr>
<tr>
<td>No</td>
<td>0.64</td>
<td>0.76</td>
<td>n/a</td>
</tr>
</tbody>
</table>

**Model 2 (single adsorbate layer particle bridging)**

<table>
<thead>
<tr>
<th>Correction for cross-sectional area of ( N_e )</th>
<th>BET</th>
<th>LANGMUIR</th>
<th>BJH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>0.65</td>
<td>0.95</td>
<td>0.93</td>
</tr>
<tr>
<td>No</td>
<td>0.95</td>
<td>0.95</td>
<td>0.95</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Correction for cross-sectional area of ( N_e )</th>
<th>BET</th>
<th>LANGMUIR</th>
<th>BJH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>0.95</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>No</td>
<td>0.80</td>
<td>0.95</td>
<td>0.95</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Correction for cross-sectional area of ( N_e )</th>
<th>BET</th>
<th>LANGMUIR</th>
<th>BJH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>0.82</td>
<td>0.82</td>
<td>0.80</td>
</tr>
<tr>
<td>No</td>
<td>0.82</td>
<td>0.82</td>
<td>0.80</td>
</tr>
</tbody>
</table>

**Model 3 (no adsorbate layer particle bridging)**

<table>
<thead>
<tr>
<th>Correction for cross-sectional area of ( N_e )</th>
<th>BET</th>
<th>LANGMUIR</th>
<th>BJH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>0.94</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>No</td>
<td>0.88</td>
<td>0.95</td>
<td>0.95</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Correction for cross-sectional area of ( N_e )</th>
<th>BET</th>
<th>LANGMUIR</th>
<th>BJH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>0.94</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>No</td>
<td>0.88</td>
<td>0.95</td>
<td>0.95</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Correction for cross-sectional area of ( N_e )</th>
<th>BET</th>
<th>LANGMUIR</th>
<th>BJH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>0.88</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>No</td>
<td>0.81</td>
<td>0.90</td>
<td>0.90</td>
</tr>
</tbody>
</table>
Model 1 – selected best fits for BET, Langmuir, and BJH data

(i) very good overall fits for the BET and Langmuir data, a rather bad fit for the BJH data

(ii) distinct characteristics of the $S_{BJH} = f(D)$ relationship for $D < ca. 5$ nm
- not compatible with Model 1

(iii) uncertainty in the trend for $D < ca. 2-3$ nm
- what are nano-GaN low size limits?
Model 2 – selected best fits for BET, Langmuir, and BJH data

(i) very good overall fits for the BET and Langmuir data, and a good fit for the BJH data
(ii) similar relationship characteristics suggested for all data (local maxima in the smallest D range)
(iii) correction for the cross-sectional area of N₂ beneficial for the BJH data fit
(iv) small spread between the model curves (red or green) and the best fit curves (black)
Model 3 – selected best fits for BET, Langmuir, and BJH data

(i) very good overall fits for the BET and Langmuir data, and a good fit for the BJH data

(ii) similar relationship characteristics suggested for all data (local maxima in the smallest D range)

(iii) relatively large spread between the model curves (red) and the best fit curves (black)
Conclusions

1. A pool of twelve GaN nanopowders with crystallite sizes spanning the 1 to 40 nm range (from powder XRD scans) was shown each to consist of **tight agglomerates of regularly shaped crystallites forming larger loose aggregates** as supported by characteristic size dependent helium densities and SEM/TEM examinations.

2. A general model of porosity of such nanopowders was proposed wherein the **pore system and pore surface area could be represented by the interparticle spaces and surface area**, respectively, of **closely packed equiradial spherical agglomerates of particles**:

   (i) three cases of the model were investigated, namely, Model 1 – with double adsorbate layer particle bridging, Model 2 – with single adsorbate layer particle bridging, and Model 3 – with no adsorbate layer particle bridging; all model equations for \( S = f(D) \) were derived with the option to include corrections for the sphere curvature adjusted cross-sectional area of the adsorbate molecule,

   (ii) within the limits of the smallest particle sizes going from ca. 5 to 1 nm, Model 1 predicted steeply increased surface areas with values reaching a few hundred \( \text{m}^2/\text{g} \) while Model 2 and Model 3 suggested local maxima of lower magnitude for the diameters of ca. 1-2 nm and 3-4 nm, respectively.
Conclusions, cntd.

3. The model-based relationships of the surface area as function of sphere diameter, now with some relaxed variables, were statistically fitted for the cases of the BET, Langmuir, and BJH surface areas (from low temperature nitrogen adsorption experiments) being a function of the average crystallite size (from powder XRD scans):

(i) the best fits for the BET and Langmuir surface areas vs. $D_{\text{XRD}}$ yielded for both the correlation coefficients $R$ equal to 0.95 while for the BJH data $R$ reached 0.90, supporting the overall very good relevance of the applied models,

(ii) it appeared that the circumstances somewhat between Model 1 and Model 2 are the closest to best describe the experimental data as far as the magnitude of the particular surface area is concerned,

(iii) it is our opinion that the observed discrepancies between the model and the experimental data in each case are, at least, partly due to the unknown degree of agglomeration of the GaN crystallites and its likely dependence on $D_{\text{XRD}}$; a mismatch between the $D_{\text{aggl}}$ and $D_{\text{XRD}}$ causes the displacement of the experimental and model curves.

Acknowledgement. Research supported by the Polish Ministry of Science and Higher Education/MNiSW, Grant No. NN 507 443534.
Thank You For Your Attention
Appendix
Adsorption isotherms ($N_2$, 77.5 K) and mesopore distribution (BJH) - 1
Appendix

Adsorption isotherms ($N_2$, 77.5 K) and mesopore distribution (BJH) - 2
Appendix

Adsorption isotherms ($N_2$, 77.5 K) and mesopore distribution (BJH) - 3
Appendix
Adsorption isotherms ($N_2$, 77.5 K) and mesopore distribution (BJH) - 4
Appendix
Adsorption isotherms ($N_2$, 77.5 K) and mesopore distribution (BJH) - 5
Assumptions of Langmuir theory

1. Fixed number of adsorption sites are available on the surface.
2. All the vacant sites are of equal size and shape on the surface.
3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.
4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.
   \[
   A(g) + B(s) \overset{adsorption}{\rightarrow} AB \overset{desorption}{\rightarrow} A(g) + B(s)
   \]
5. Adsorption is monolayer.
Langmuir adsorption equation in terms of pressure $P$:

$$\frac{P}{V} = \frac{P}{V_{\text{mono}}} + \frac{1}{KV_{\text{mono}}}$$

If we plot a graph between $P/V$ vs. $P$, we will obtain a straight line with

- slope $= \frac{1}{V_{\text{mono}}}$  
- intercept $= \frac{1}{KV_{\text{mono}}}$

$V_{\text{mono}}$ - adsorbed volume of gas covering the surface with a monolayer

$K$ - constant;  
$K = \frac{K_a}{K_d}$ ; $K_a$ – rate of adsorption,  
$K_d$ – rate of desorption
Assumptions of BET theory

http://upload.wikimedia.org/wikipedia/commons/8/83/BET_Multilayer_Adsorption.jpg

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses.

1. Gas molecules physically adsorb on the surface with random distribution of sites covered by one, two, three, etc. molecules.

2. There is no interaction between each adsorption layer.

3. The Langmuir theory can be applied to each layer.
Classical form of the BET equation:

\[ a = a_m \cdot \frac{C h}{(1-h)[1+(C-1)h]} \]

where:

- $a$ - the adsorption capacity equilibrium humidity $h$
- $h$ - the relative pressure ($h = \rho/\rho_s$)
- $\rho$ - the equilibrium partial pressure of the adsorbate vapor
- $\rho_s$ - the saturated vapor pressure of the adsorbate at absolute temperature $T$
- $a_m$ - monolayer capacity
- $C$ - energy constant:

\[ C \approx \exp \left[ -(E_f - E_L)/RT \right] \]

- $E_f$ - heat effect of adsorption in the first layer
- $E_L$ - latent heat of condensation
- $R$ - the gas constant

- the coordinates of the points of monolayer $h_m$ calculated according to the known formula:

\[ h_m = 1/(\sqrt{C}+1) \]

- the first layer heat of adsorption calculated from the equation:

\[ E_f - E_L = RT \ln(C) \]

where:

- $E_f$ is the first layer heat of adsorption, $E_L$ is the heat of condensation, $R$ is the gas constant, and $T$ is the absolute temperature,
- surface area of samples calculated from $a_m$ values assuming that cross-sectional area of adsorbed nitrogen molecule is 0.162 nm$^2$. 
Assumptions of BJH theory

1. The relative pressure $p/p_0$ at which decondensation (from capillary phase to multilayer adsorbed phase) occurs in a cylindrical pore is given by the Kelvin law,

$$kT \ln \left( \frac{p}{p_0} \right) = -2 \sigma \frac{v_1}{(R-t)}$$

- $k$ – Boltzmann constant, $T$ – temperature, $p$ – equilibrium pressure,
- $p_0$ – saturation vapor pressure, $\sigma$ – surface tension, $v_1$ – liquid molecular volume,
- $R$ – pore radius, $t$ – multilayer thickness

2. The curvature of the solid surface has no influence on $t$. Thus, $t$ can be experimentally determined using non porous adsorbents.

$$kT \ln \left( \frac{p}{p_0} \right) = U(t)$$