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Mastering high surface area materials forms of nanosized gallium nitride GaN

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Gallium nitride GaN

- two crystallographic forms at RT:
  - wurzite (hexagonal): a = 3.168 Å and c = 5.178 Å
  - zinc blende (cubic): a = 4.51 Å
- thermal stability up to 1000–1100 °C
- high chemical stability
- strong piezoelectric effect
- wide bandgap semiconductor: 3.4 eV
- alloys with InN and AlN; alloy bandgap range: 1.9–6.2 eV
- GaN bandgap is a function of particle size for $R < 11$nm

Materials forms of GaN

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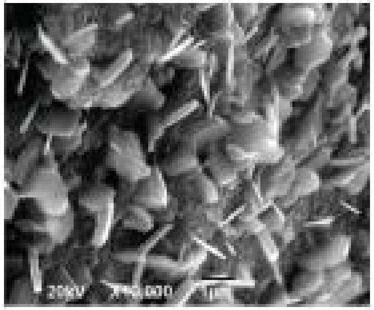
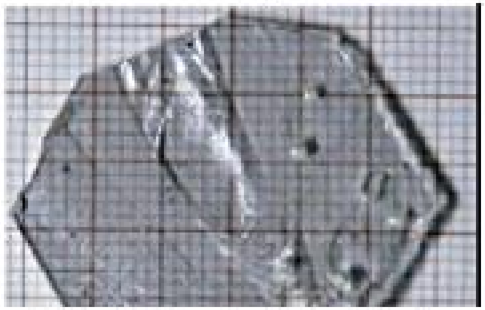
Microcrystals



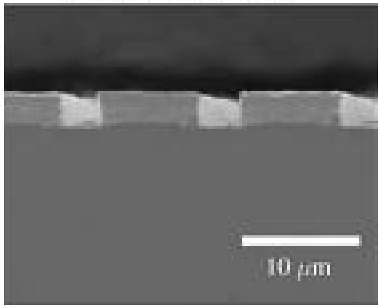
L. Lei, D. He; *Cryst. Growth Des.*, 2009, *9*, 1263.

Bulk crystals



T. Fukuda, D. Ehrentraut; *J. Cryst. Growth*, 2007, *305*, 304.

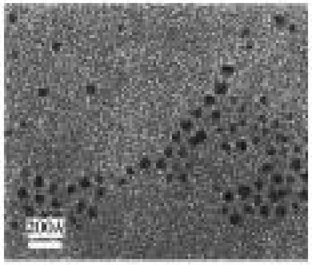
Thin films



H. K. Cho *et al.*; *Superlattices and Microstruct.*, 2004, *36*, 385.

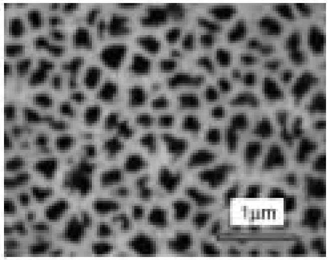
Gallium nitride
GaN

Quantum dots



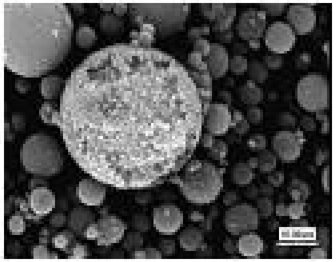
O. I. Micic *et al.*, *Appl. Phys. Lett.*, 1999, *75*, 4.

Porous surface



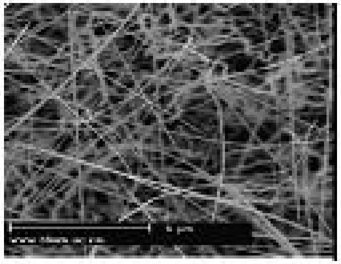
F. K. Yam, Z. Hassan, S. S. Ng; *Thin Solid Films*, 2007, *515*, 3469.

Nanopowders



J. F. Janik *et al.*; *J. Phys. Chem. Solids*, 2004, *65*, 639.

Nanotubes Nanofibers



W. Lu *et al.*; *J. Cryst. Growth*, 2007, *307*, 1.

Porous GaN

Heterogenous catalysis

⇧ Powders, ceramics ⇧

Porous GaN

⇩ Layers, supports ⇩

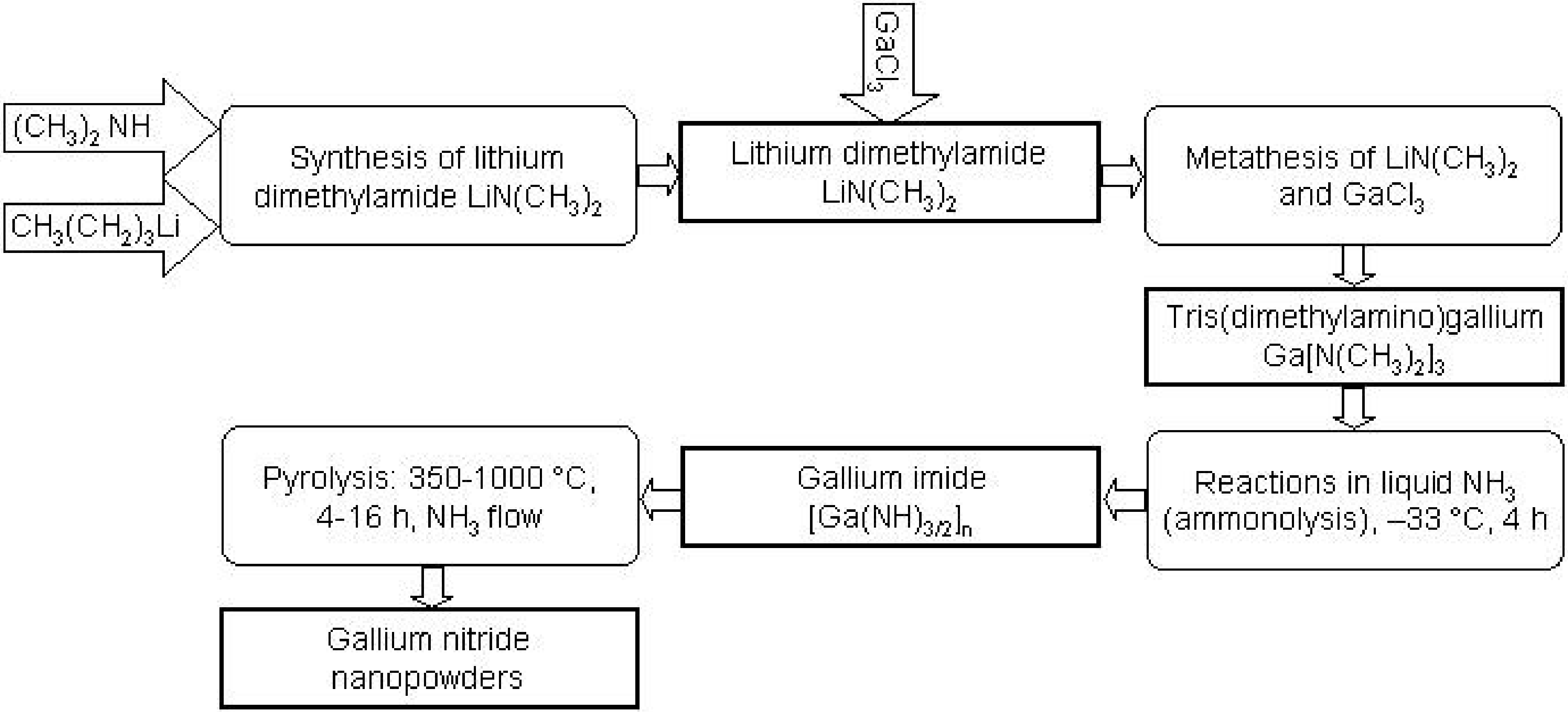
Applications

- Luminescent devices
- Sensing devices upon surface metallization
- Advantageous intermediate layers for overgrowth of GaN/InGaN/AlGaN films

Properties

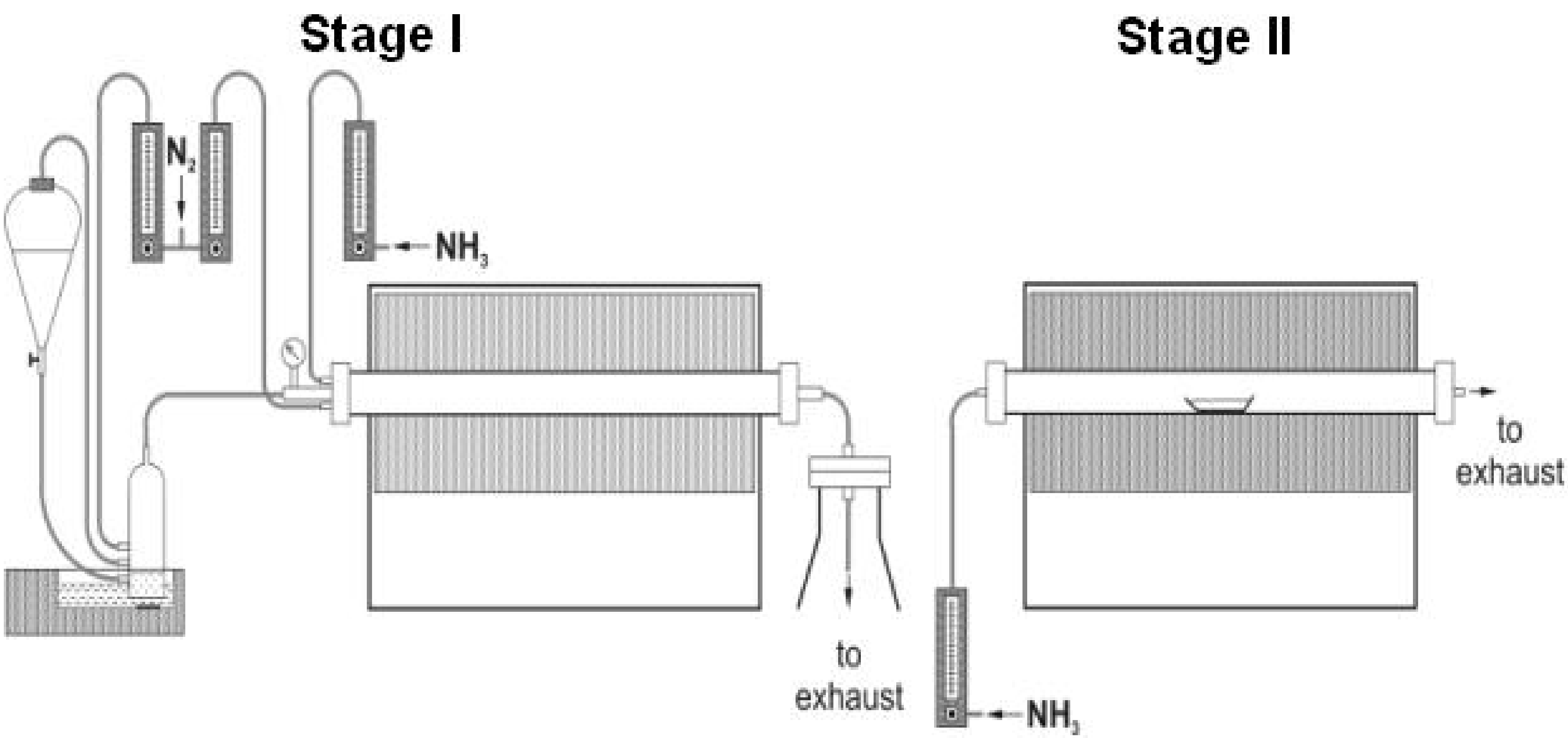
- Reduced dislocation density
- Significant PL intensity enhancement and wavelength shifting
- Reduction of cracks
- Relaxation of compression stress

Anaerobic synthesis of GaN nanopowders



[1] J. F. Janik, R. L. Wells; *Chem. Mater.* **1996,** *8*, 2708.
[2] J. F. Janik, R. L. Wells, J. L. Coffer, J. V. St. John, W. T. Pennington, G. L. Schimek; *Chem. Mater.* **1998,** *10*, 1613

Aerosol synthesis of GaN nanopowders



[1] E. A. Pruss, G. L. Wood, W. J. Kroenke, R. T. Paine; *Chem. Mater.* **2000**, *12*, 19.
[2] J. F. Janik, M. Drygas, S. Stelmakh, E. Grzanka, B. Palosz, R. T. Paine; *phys. stat. sol. a* **2006**, *203*, 1301.

Additional syntheses of GaN

- **from gallium oxide precursor [1]:**

$$Ga_2O_3 + 2NH_3 \rightarrow 2GaN + 3H_2O$$

- **from gallium arsenide precursor [2]:**

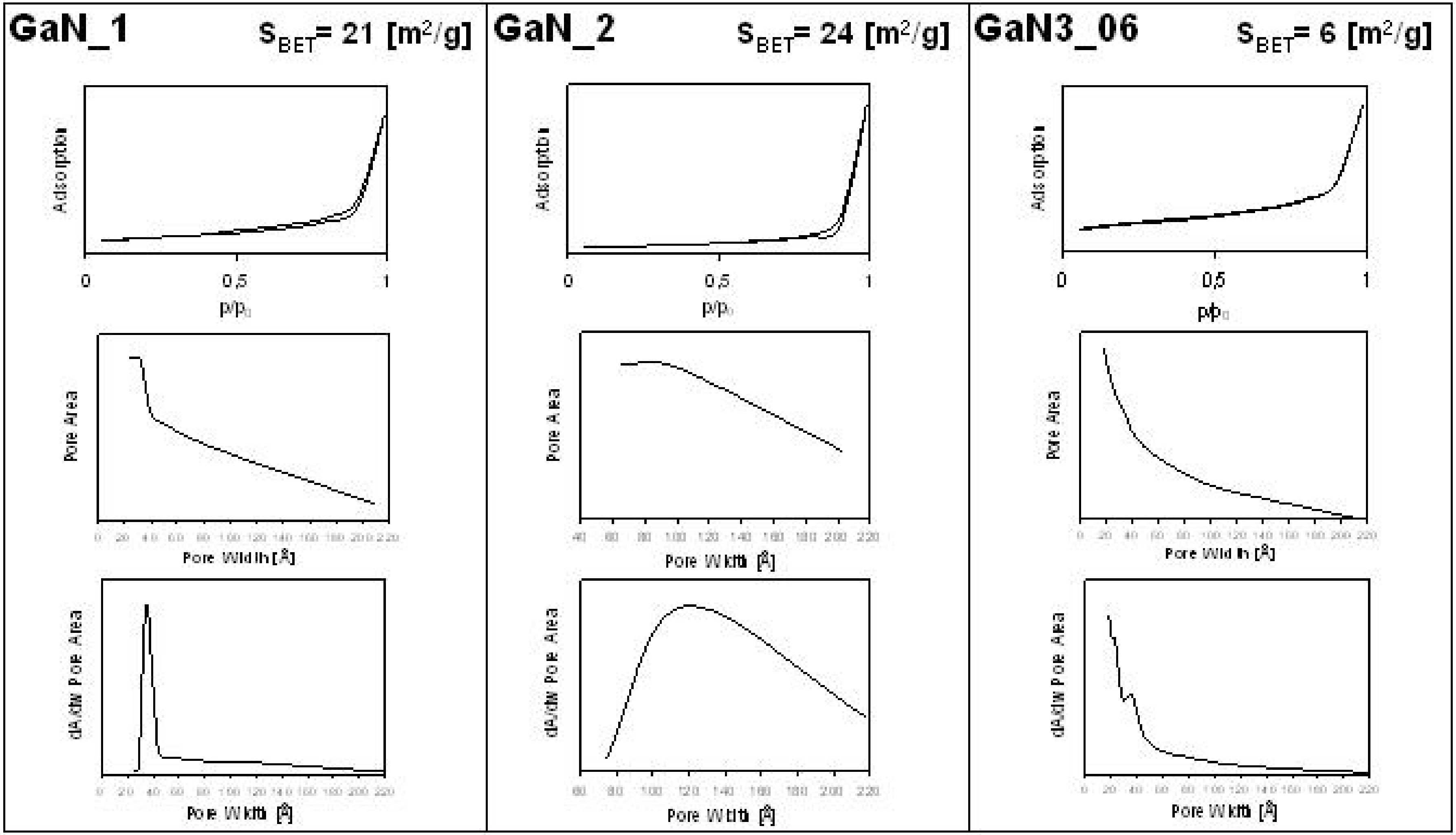
$$GaAs + NH_3 \rightarrow GaN + As + \frac{3}{2}H_2$$

[1] J. F. Janik, M. Drygaś, S. Stelmakh, E. Grzanka, B. Palosz, R. T. Paine; *phys. stat. sol. a* **2006**, *203*, 1301.
[2] M. Drygas, Z. Olejniczak, E. Grzanka, M. M. Bucko, R. T. Paine, J. F. Janik; *Chem. Mater*. **2008**, 20, 6816.

Sample organization

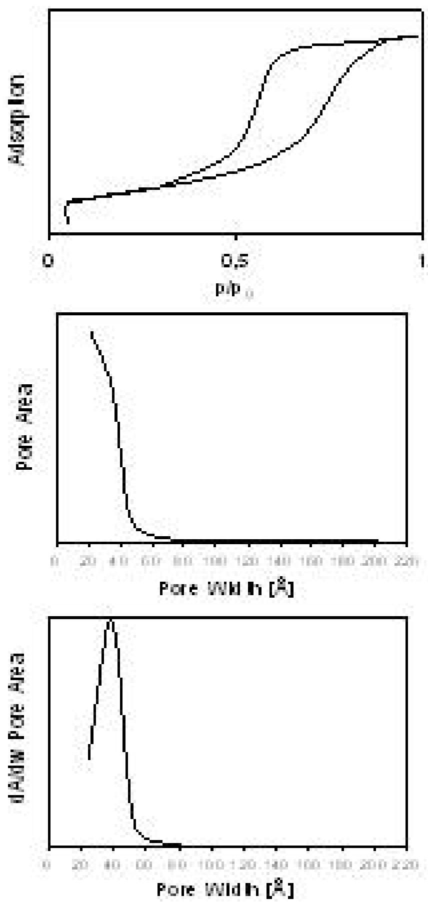
Sample ID – synthesis method
GaN_1 – aerosol synthesis, 1050 °C, MeOH, 950 °C, 12h, NH_3
GaN_2 – aerosol synthesis, 1050 °C, DMF; 950 °C, 12h, NH_3
GaN_3 – aerosol synthesis, 1050 °C, MeOH/DMF, 950 °C, 12h, NH_3
GaN3_06 – aerosol synthesis, 1050 °C, H_2O, 975 °C, 6h, NH_3
JFJ7_04 – Ga_2O_3 nitridation; 950 °C, 12h, NH_3
GaN_350 – anaerobic synthesis, 350 °C, 4h, NH_3
GaN_450 – anaerobic synthesis, 450 °C, 4h, NH_3
GaN_600 – anaerobic synthesis, 600 °C, 4h, NH_3

Adsorption isotherms (N_2, 77.5 K) and mesopore distribution (BJH) - 1

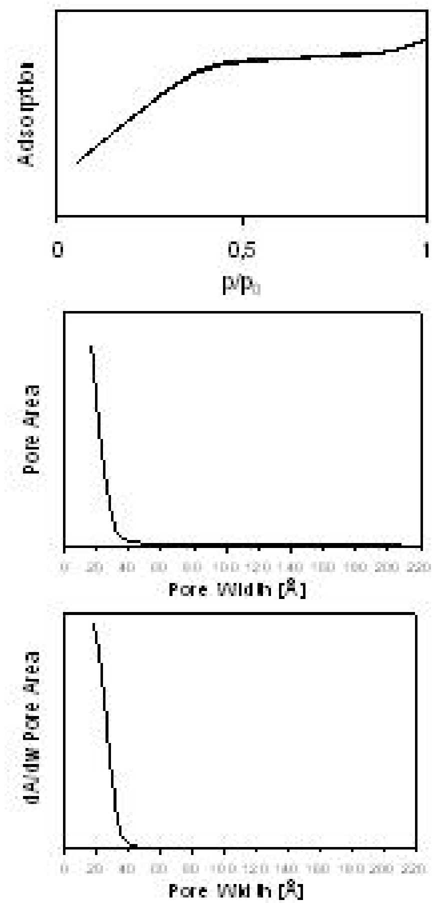


Adsorption isotherms (N_2, 77.5 K) and mesopore distribution (BJH) - 2

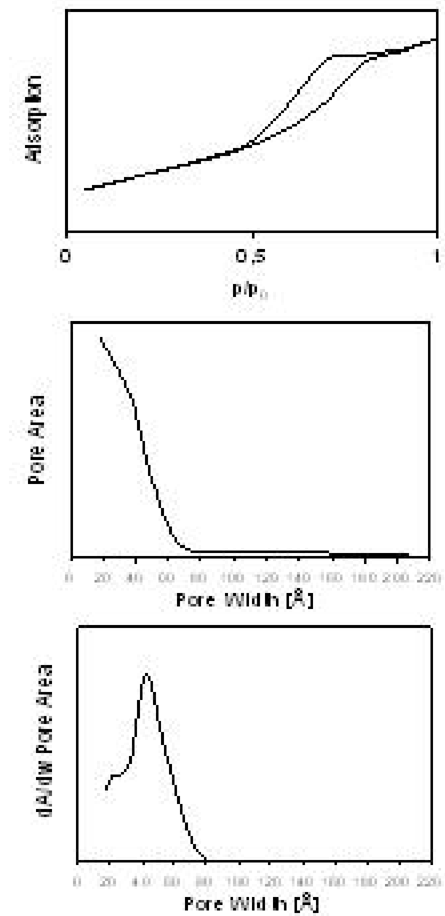
GaN_350 S_{BET}= 145 [m^2/g]



GaN_450 S_{BET}= 222 [m^2/g]



GaN_600 S_{BET}= 103 [m^2/g]



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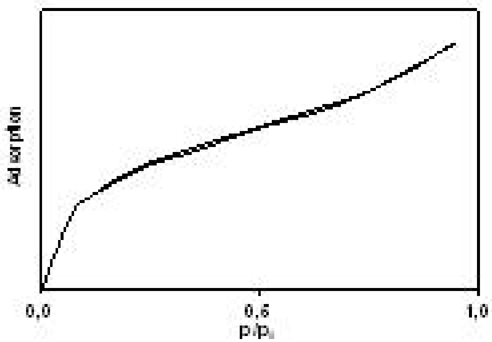
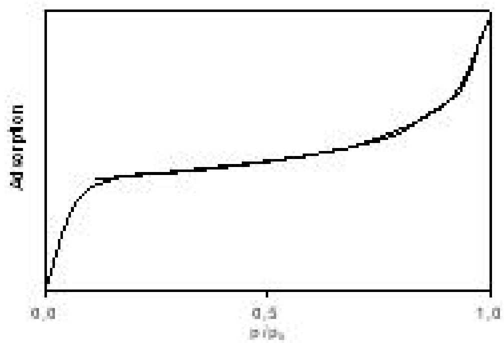
Adsorption isotherms (H_2O, 298 K)

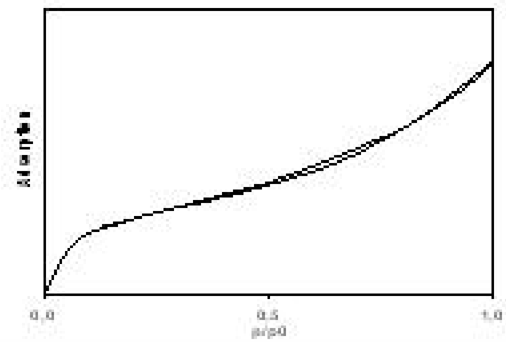
GaN_1 S_{BET}= 34 [m²/g]



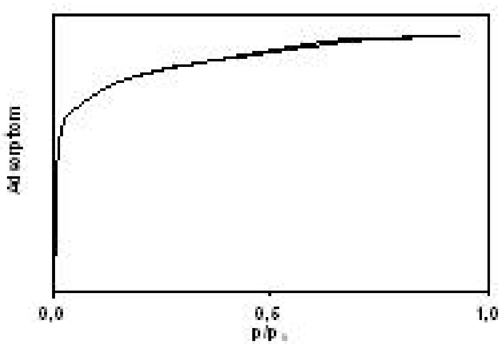
GaN_2 S_{BET}= 9 [m²/g]



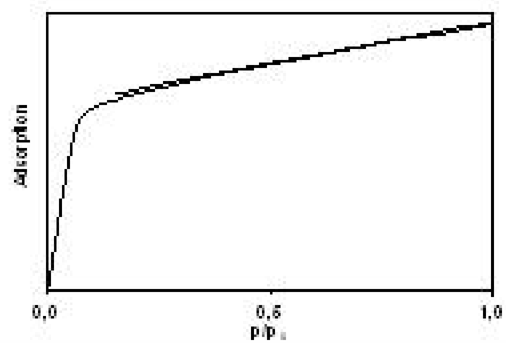
GaN3_06 S_{BET}= 4 [m²/g]



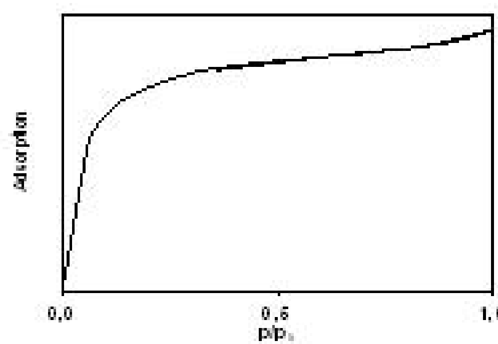
GaN_350 S_{BET}= 341 [m²/g]



GaN_450 S_{BET}= 83 [m²/g]



GaN_600 S_{BET}= 64 [m²/g]



BET theory

Classical form of the BET equation:

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

where:

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

$$C \approx \exp[-(E_1 - E_L)/RT]$$

E_1 - 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:

$$E_1 - E_L = RT\ln(C)$$

where: E_1 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 water molecule is 0.105 nm^2.

BET-2 theory

According to BET theory it is assumed that water is adsorbed as:

- primary molecules (adsorption sites with high binding energy, such as hydroxyl groups),
- secondary molecules (sites with lower binding energy, such as previously occupied primary and other secondary sites).

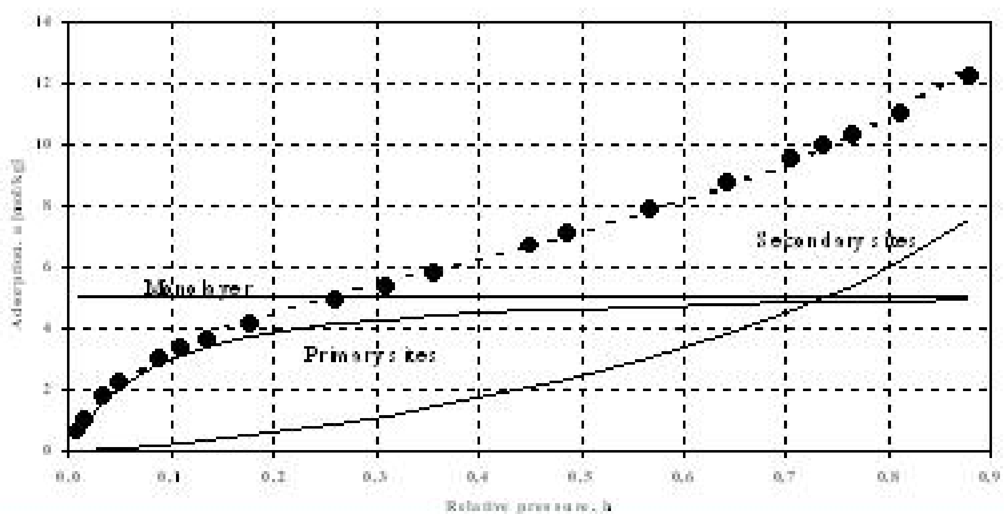
The following equations were used to represent the total (a), primary (a_p), and secondary (a_s) adsorption sites:

$$a = a_p + a_s \qquad a_p = \frac{a_m b_1 h}{(1 - b_2 h + b_1 h)} \qquad a_s = \frac{a_m b_1 b_2 h^2}{(1 - b_2 h)(1 - b_2 h + b_1 h)}$$

$$a = \frac{a_m b_1 h}{(1 - b_2 h)(1 - b_2 h + b_1 h)}$$

where: b_1, b_2 – parameters (kinetic constants related to sorption on primary and secondary centers) $C = b_1 / b_2$

Example of the water vapor adsorption isotherm and modeled BET-2 plots.



Adsorption data for GaN nanopowders

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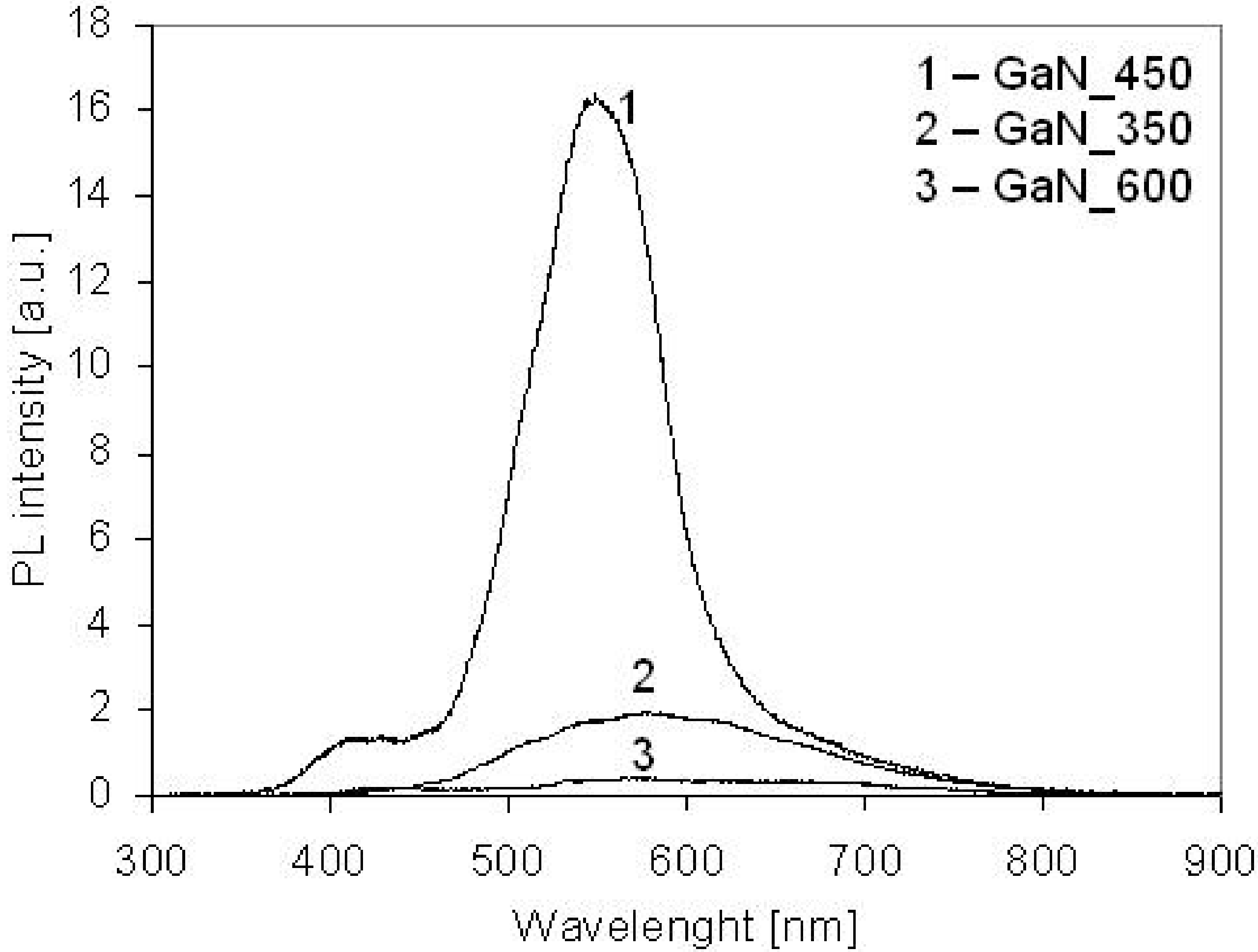
Sample ID	N_2 adsorption				H_2O adsorption		N_2 adsorption following H_2O adsorption
	S_{BET} [m^2/g]	Micropore area (t-method) [m^2/g]	Mesopore area (1.7-300 nm, BJH) [m^2/g]	Average pore width (BJH) [nm]	S_{BET} [m^2/g]	1-st layer adsorption heat, E_1 [kJ/mol]	S_{BET} [m^2/g]
GaN_1	21	4	23	15	34	53	18
GaN_2	24	2	42	20	9	58	25
GaN_3	24	2	38	19	26	57	26
GaN3_06	6	2	5	12	4	53	5
JFJ7_04	8	2	7	12	6	57	6
GaN_350	145	1	74	4	341	60	57
GaN_450	222	*n/a*	216	3	83	57	180
GaN_600	103	*n/a*	133	5	64	58	68

PL data for GaN nanopowders (anaerobic synthesis)



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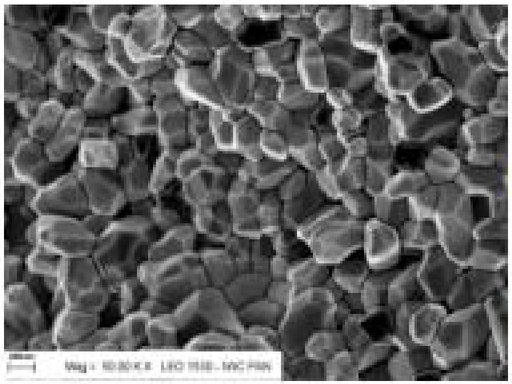
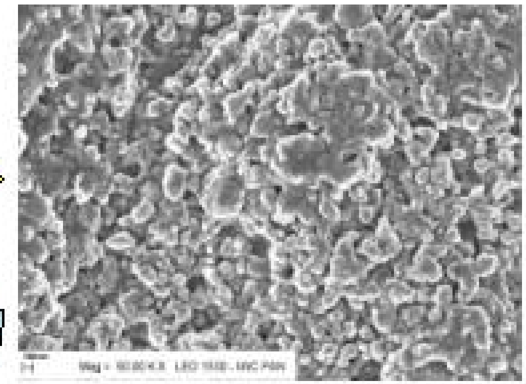
Bulk GaN ceramics – examples

JFJ71, 6 GPa, 1150 °C, 10 min

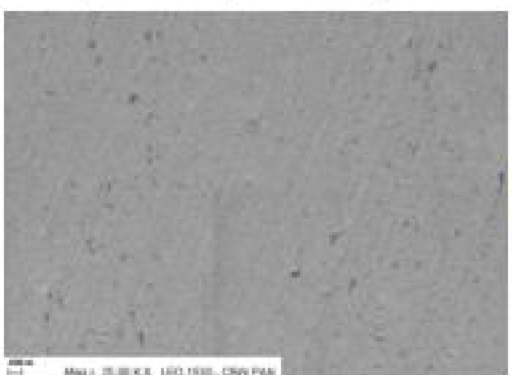


JFJ71_HF, 6 GPa, 1200 °C, 10 min

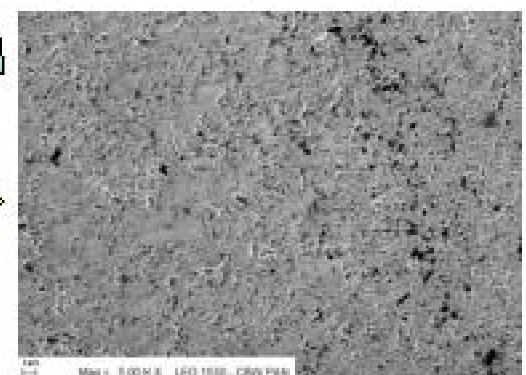


Cross-sections

JFJ28, 6 GPa, 900 °C, 10 min



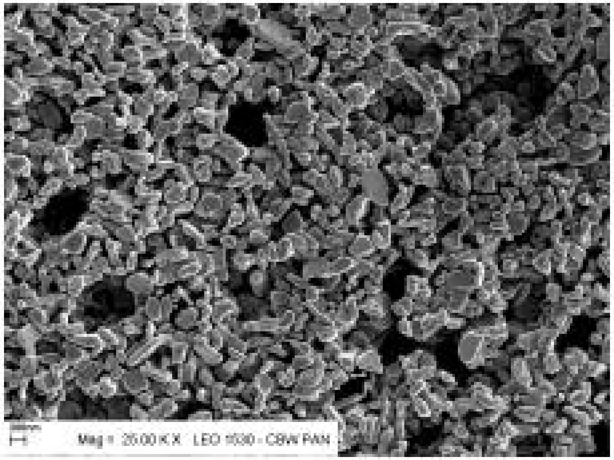
JFJ4, 7.8 GPa, 900 °C, 100 min



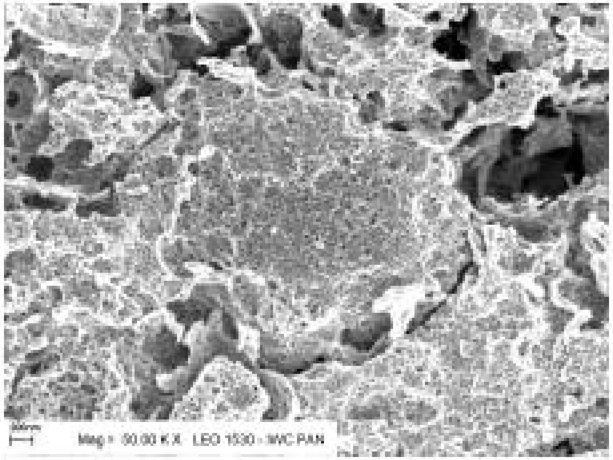
Mechanically polished surfaces

Porous GaN ceramics surfaces – examples

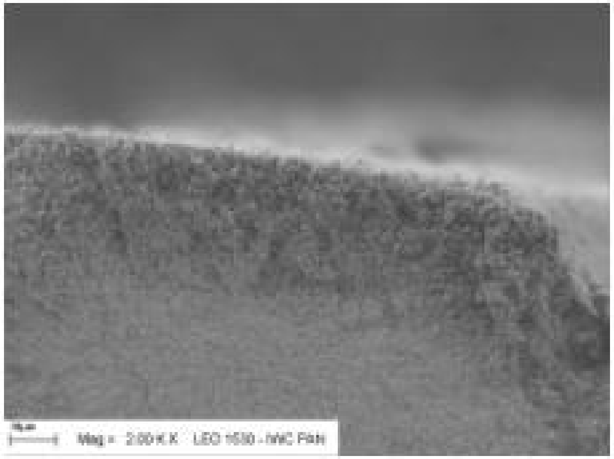
JFJ47, chem.



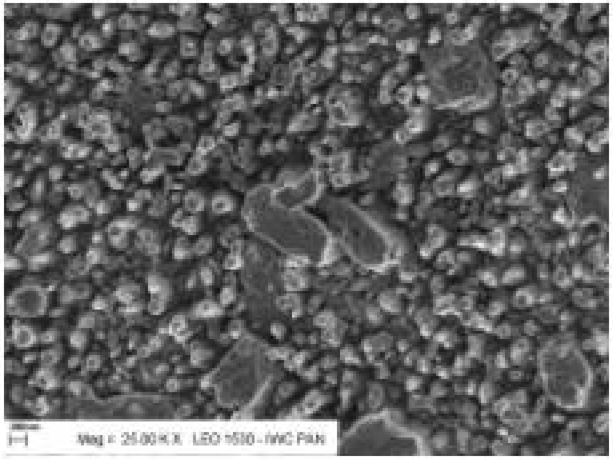
JFJ72, chem.



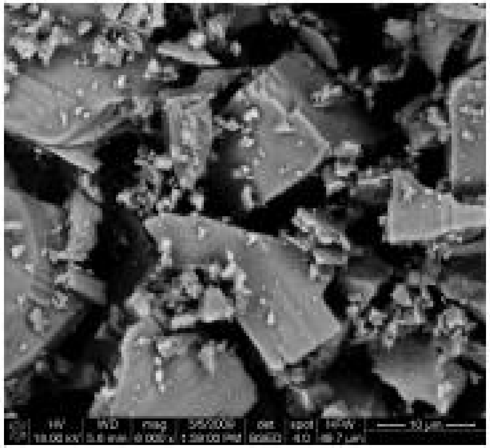
JFJ72, chem., RIE

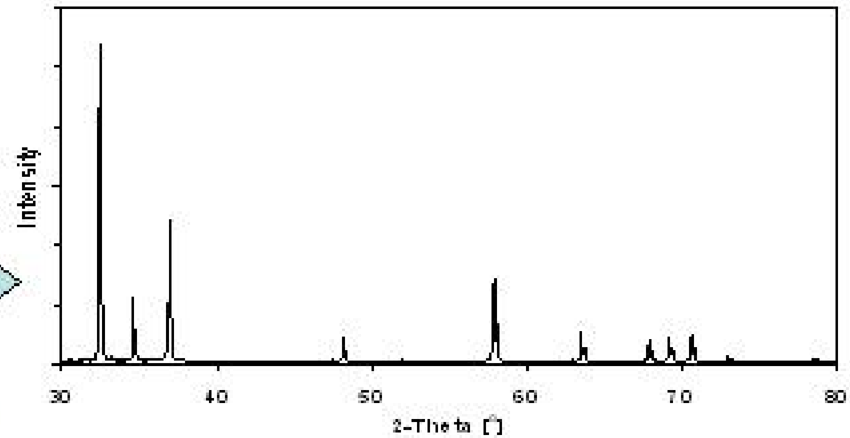


JFJ72, chem., RIE

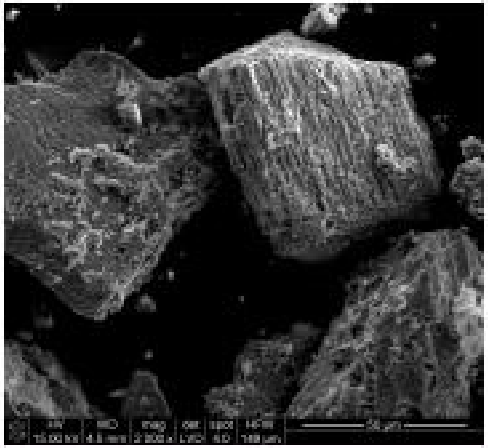


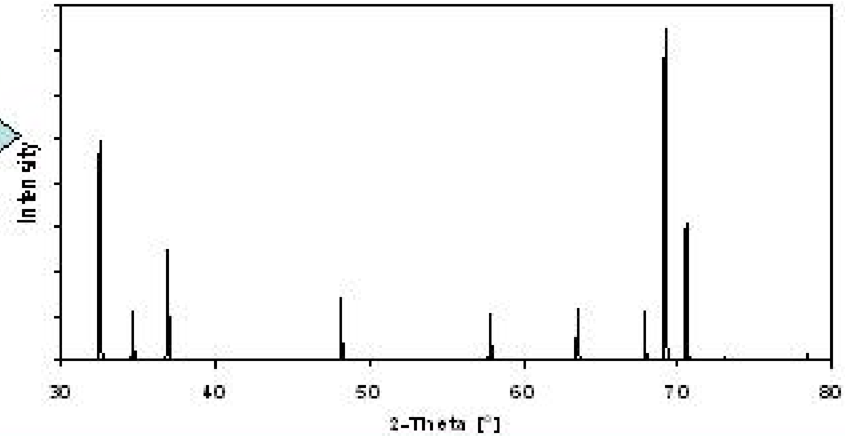
HVPE epitaxial GaN-controlled decomposition



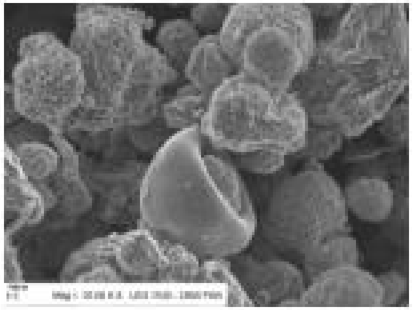


Decomposition: 1300 °C, 10 h, NH_3 flow

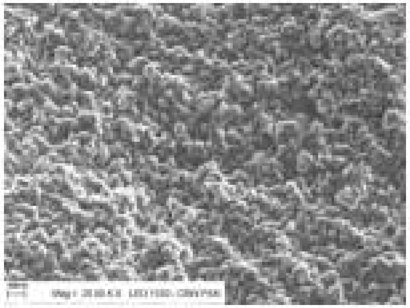




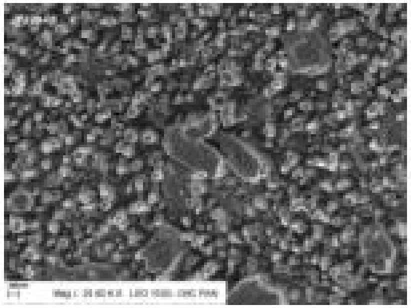
Towards GaN ceramic supports



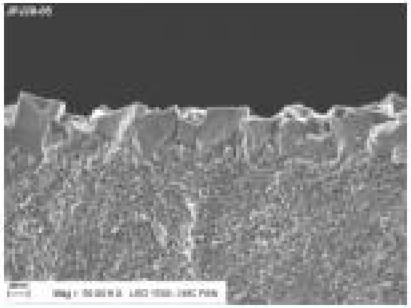
Aerosol synthesis:
975 °C, 6 h, NH_3 flow



Sintering: 6 GPa, 900 °C

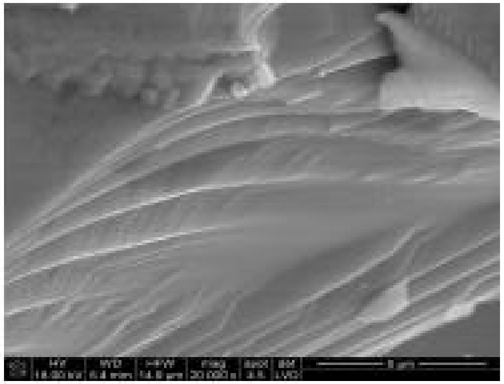


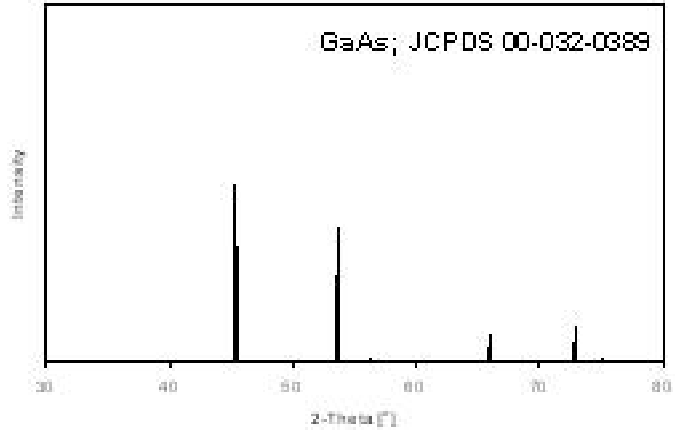
Etching:
- Piranha solution, 5 min
- NH_3 treatment, 975 °C, 5 min



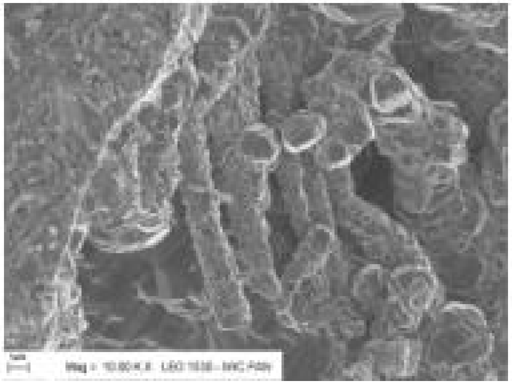
MOCVD deposition:
50 min, p=100 mbar,
rate=0.4 μm/h

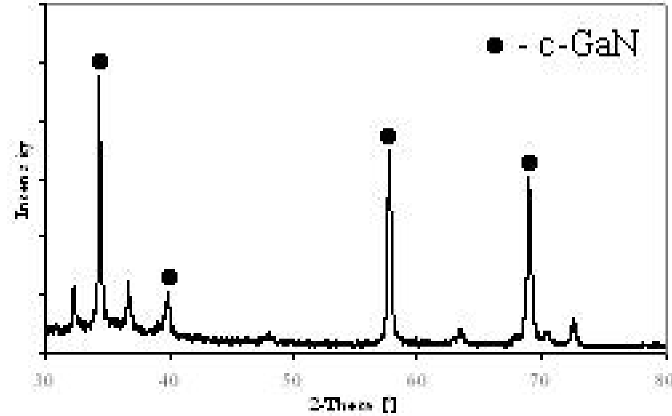
GaAs bulk crystal nitridation





Nitridation: 800 °C, 90 h, NH_3 flow





Conclusions

GaN nanopowders

- Powders of up to 300 m^2/g BET surface area; mostly mesopores.
- H_2O adsorption implicates strong interactions of H_2O molecules with surface centers.

GaN nanoceramics

- No-additive HT/HP sintering of GaN powders can produce ceramic bodies with significant porosities.
- Chemical etching of GaN ceramic supports leads to increased surface porosity.

Conclusions, cntd.

GaN polycrystals

- Thermal decomposition of large single crystallites results in an enhanced textured grain porosity.

GaAs bulk supports

- Preliminary results on GaAs nitridation with NH_3 indicate porous characteristics of the nitrided surfaces.

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Thank You For Your Attention !