Effect of precursor's grain size on the conversion of microcrystalline gallium antimonide GaSb to nanocrystalline gallium nitride GaN

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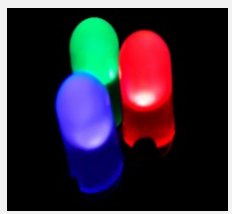
Gallium nitride GaN?

- wide bandgap semiconductor: 3.4 eV (ultraviolet)
- alloys with InN and AlN; alloy bandgap range: 1.8–6.2 eV (*blue* emitters)
- GaN bandgap is a function of particle size for R < 11 nm



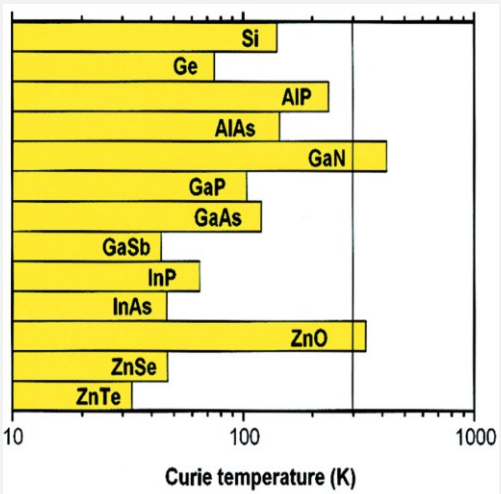
- two crystallographic forms at RT:

  stable ⟶ wurzite (hexagonal): a = 3.168 Å and c = 5.178 Å

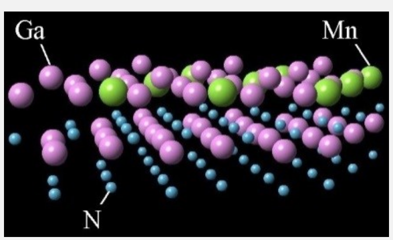
  metastable ⟶ zinc blende (cubic): a = 4.51 Å
- thermal stability up to 1000 °C
- high chemical stability

Also, current and upcoming applications…

- Spintronics
diluted magn. semiconductors



Computed values of the Curie temperature T_C for various p-type semiconductors containing 5 % of Mn and 3.5×10^{20} holes per cm^3.
(T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand; *Science* **2000**, vol. 287, No. 5455, 1019)



- Heterogeneous catalysis
- Adsorbents, nanosurfaces

⇧
Powders, ceramics
⇧

Porous GaN

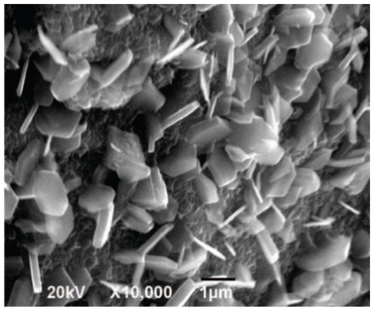
- HP-HT sintering of nano-GaN

Not to mention…

- Microwave power amplifiers with superior RF power performance
- MOSFET and MESFET transistors for high-power electronics
- Nanotubes in nanoscale electronics, optoelectronics and biochemical-sensing applications
- Military and space applications thanks to
stability in radiation environments

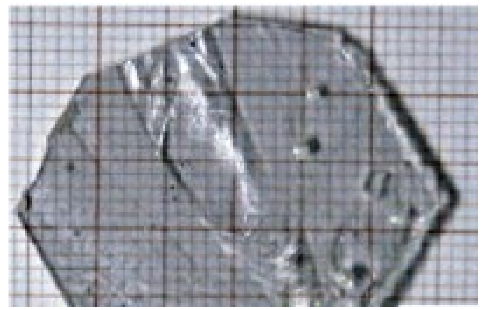
Materials forms of GaN

Microcrystals



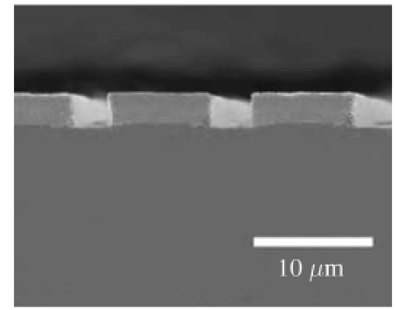
L. Lei, D. He; *Cryst. Growth Des.*, **2009**, *9*, 1263.

Bulk crystals



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

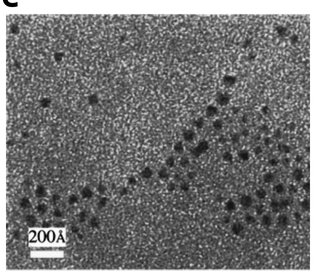
Thin films



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

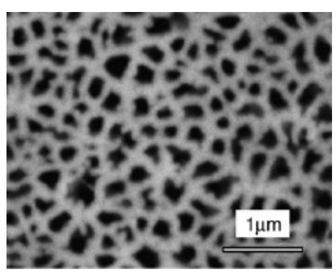
Gallium nitride
GaN

Quantum dots



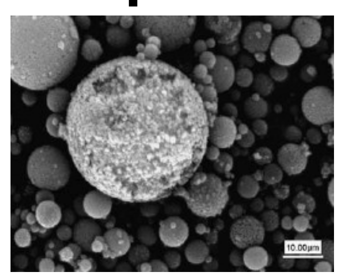
O. I. Micič *et al.*, *Appl. Phys. Lett.*, **1999**, *75*, 4.

Porous surface



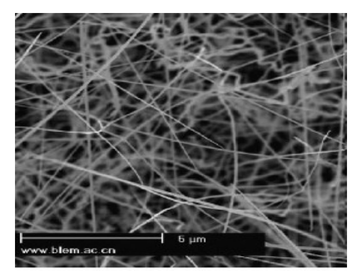
F. K. Yam, Z. Hassan, S. S. Ng; *Thin Solid Films*, **2007**, *515*, 3469.

Nanopowders



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

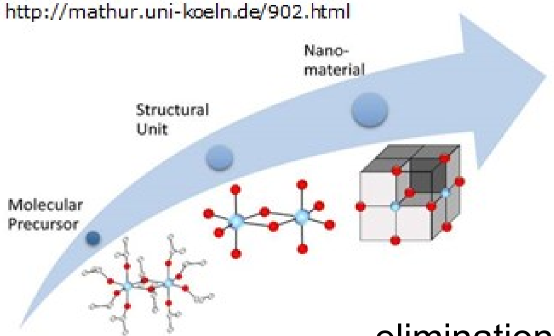
Nanotubes Nanofibers

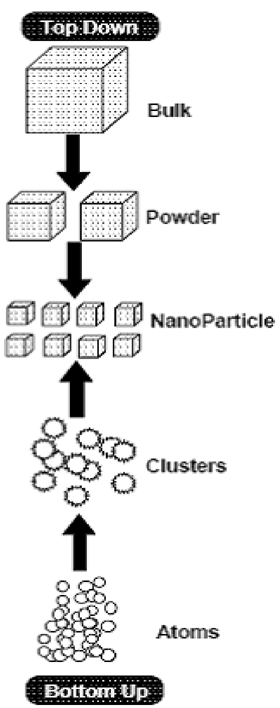


W. Lv *et al.*; *J. Cryst. Growth*, **2007**, *307*, 1.

Chemistry of materials precursors – <u>bottom-up</u> and <u>top-down</u> ways to nanomaterials

http://mathur.uni-koeln.de/902.html





1:1 stoichiometry of M (Group III) to E (Group V);
X, Y – ligands; XY – small, volatile molecule

$$MX_3 + EY_3 \longrightarrow X_3M \cdot EY_3; \quad \textbf{Lewis adduct}$$

elimination-condensation rxs

$$X_3M \cdot EY + EY_3 \xrightarrow{\Delta} 1/n[X_2M - EY_2]_n + XY$$

$$1/n[X_2M - EY_2]_n \xrightarrow{\Delta} 1/n[XM - EY]_n + XY$$

$$1/n[XM - EY]_n \xrightarrow{\Delta} ME + XY$$

Δ - temperature-driven reactions

For nanonitrides: excess of E = N; R = organic ligand

transamination rx

$$M(NR_2)_3 + 3NH_3 \longrightarrow M(NH_2)_3 + 3HNR_2$$

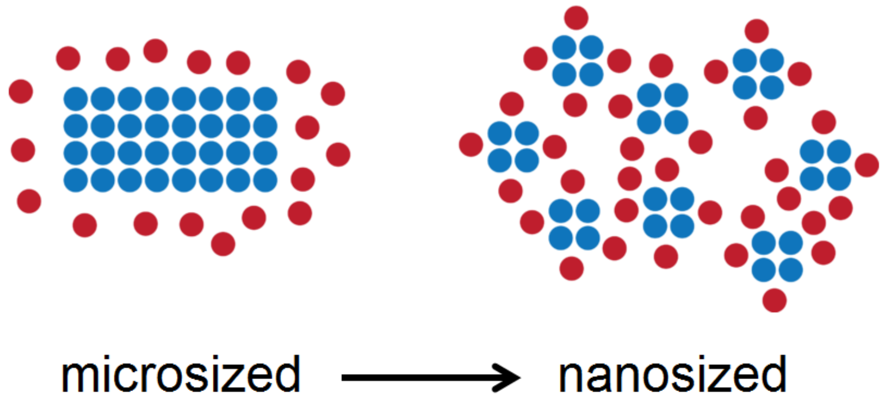
deamination rxs

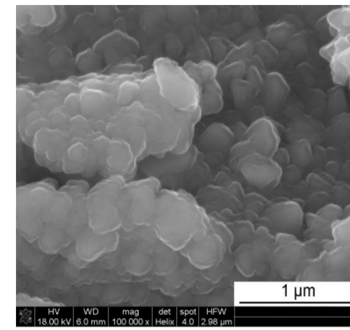
$$M(NH_2)_3 \xrightarrow{\Delta} 1/n[M(NH_2)(NH)]_n + NH_3$$

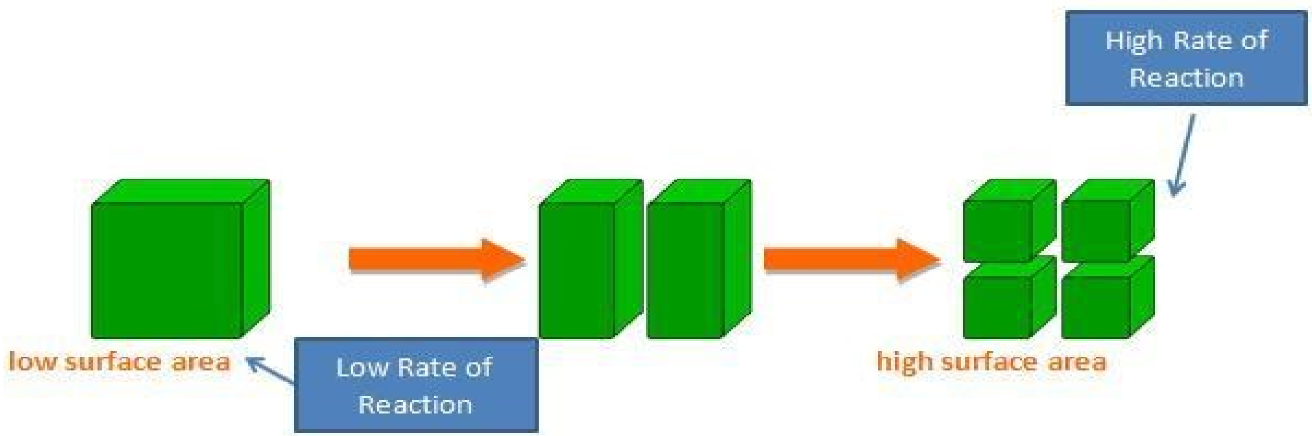
$$1/n[M(NH_2)(NH)]_n \xrightarrow{\Delta} 1/n[M(NH)_{3/2}]_n + 1/2NH_3$$

$$1/n[M(NH)_{3/2}]_n \xrightarrow{\Delta} MN + 1/2NH_3$$

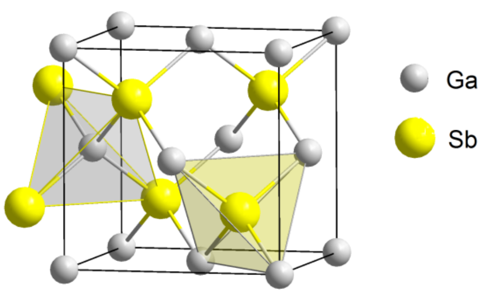
From micro-GaSb to nano-GaN…in one step







From c-GaSb to c-GaN…or h-GaN ?



GaSb
cubic, zinc-blende structure

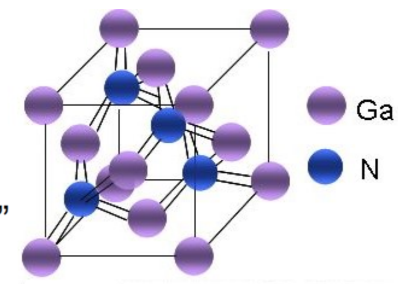
c-GaSb + NH_3

→ c-GaN (metastable) + "SbH_3"
via topochemical mechanism

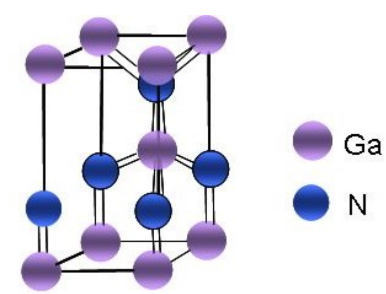
→ h-GaN (stable) + "SbH_3"
via thermodynamic stability

↓ *via* decomposition

Ga + Sb + NH_3 → h-GaN (stable) + "SbH_3"



GaN
cubic, zinc-blende-type



GaN
hexagonal, wurzite-type

Reactions of GaSb with ammonia NH_3

„Effect of precursor's grain size on the conversion of microcrystalline gallium antimonide GaSb to nanocrystalline gallium nitride GaN"

$$GaSb + NH_3 = GaN + „SbH_3" \ (Sb + 3/2H_2)$$

- Thermodynamics: O.K. GaN ⟶ $\Delta H^o_{298} = -157$ kJ/mol
  GaSb ⟶ $\Delta H^o_{298} = -42$ kJ/mol
- Melting point of GaSb: 710 ºC
- „SbH_3": stibine is not stable at ambient conditions
- Dissociation partial pressure of Sb at m.p.: 3×10^{-6} Torr
  (*during 10 h run, ca. 10^{-3} mol of Sb is lost*)
- Dissociation partial pressure of Ga at m.p.: $< 10^{-9}$ Torr

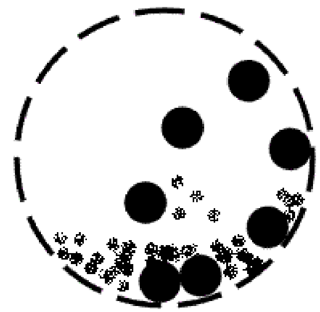
GRINDING (grain size distribution) is expected to crucially impact the rate of GaSb nitridation, h-GaN/c-GaN proportions, and GaN av. crystallite sizes.

Experimental details - grinding

GRINDING

Manual

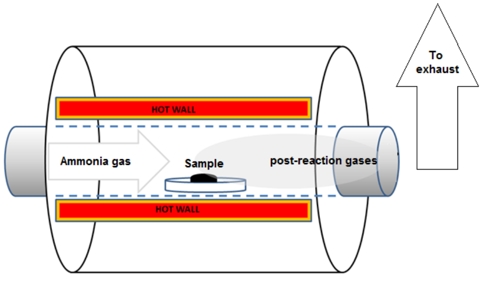
Ball milling



- Several grams of small GaSb chunks were placed in an agate mortar and ground with a pestle for 10 minutes to afford a gray powder.

- A few grams of GaSb chunks crashed below *ca.* 1 mm were placed in a FRITSCH Pulverisette 7 planetary ball mill onto which 10 ml of xylene were also added. Twenty 3-minute intermittent grinding periods were applied at 900 rpm, each separated with a 10-minute break. The resulting paste was evacuated for 1 hour to remove xylene.

Experimental details – nitridation with ammonia



Conditions:

- sample mass – 2 to 3 g
- heating rate – 5 $^{o}C/min$
- NH_3 flow rate – 0.05 L/min
- hold time – 36 to 170 h
- 1-hour product evacuation
- product – off-white yellowish, loosely agglomerated powder

Characterization methods

- Particle size distribution for the ball milled powder of GaSb was measured by dynamic light scattering on Nanosizer-ZS of Malvern Instruments.
- All final product were characterized by standard powder XRD analysis (X'Pert Pro Panalytical, Cu K_α source; 2Θ=10-110°). Average crystallite sizes were evaluated from Scherrer's equation applying the Rietveld refinement method.
- FT-IR spectra for KBr pellets were recorded with a Nicolet 380 (Thermo Electron Corp.).
- SEM/EDX data were acquired with a Hitachi Model S-4700 scanning electron microscope.
- Solid-state MAS NMR spectra of ^{71}Ga nuclei were measured on the APOLLO console (Tecmag) at the magnetic field of 7.05 T and at the spinning rate 10 kHz.

Results - 1

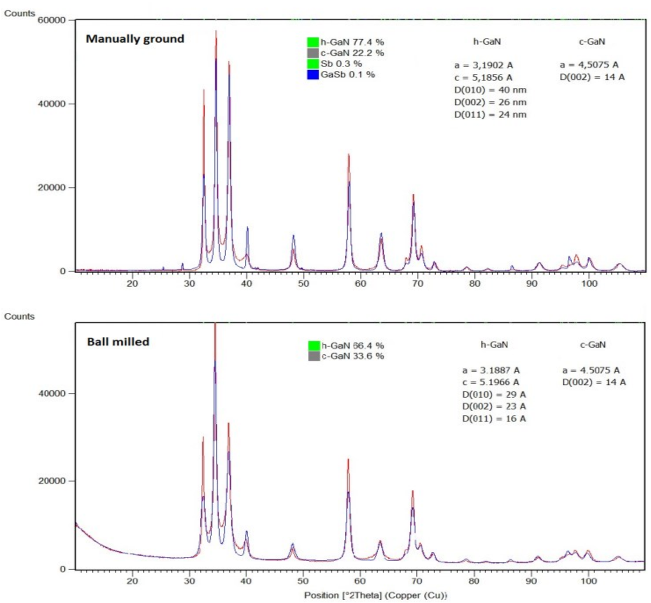


Fig. 1. XRD diffraction patterns for the products from nitridation with NH_3 *at* ***900 °C, 90 h***, of powdered GaSb; *top* – manually ground, *bottom* – ball milled

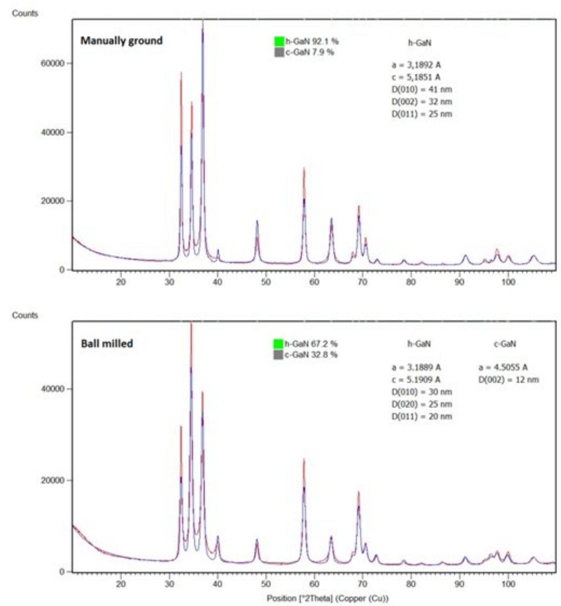


Fig. 2. XRD diffraction patterns for the products from nitridation with NH_3 at ***900 °C, 170 h***, of powdered GaSb; *top* – manually ground, *bottom* – ball milled

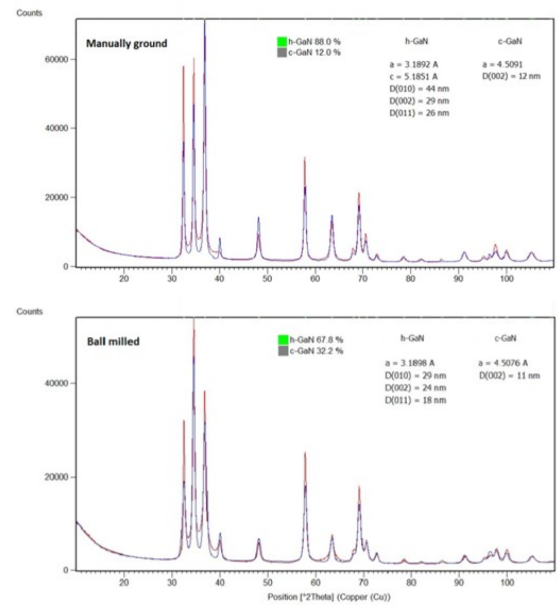


Fig. 3. XRD diffraction patterns for the products from nitridation with NH_3 at ***1000 °C, 36 h***, of powdered GaSb; *top* – manually ground, *bottom* – ball milled

Results - 2

Table 1. Amounts and average crystallite sizes of GaN polytypes

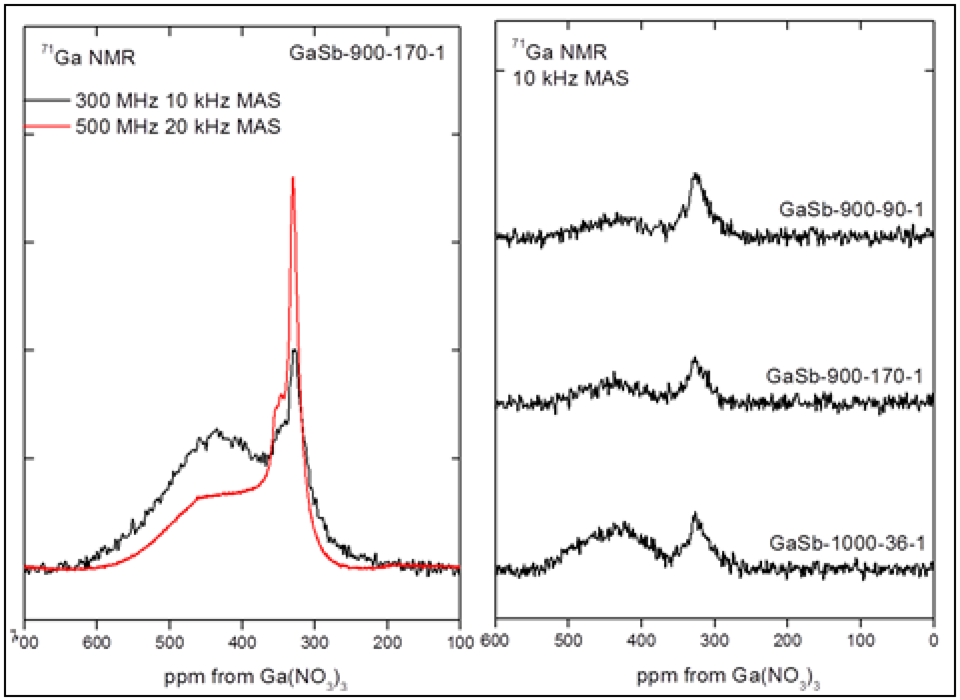
	Grinding	h-GaN amount / av. size	c-GaN amount / av. size	Other amount
900 °C, 90 h	manual	77.4 % / 30 nm	22.2 % / 14 nm	GaSb, 0.1 % Sb, 0.3 %
	ball milling	66.4 % / 23 nm	33.6 % / 14 nm	-
900 °C, 170 h	manual	92.1 % / 33 nm	7.9 % / nd	-
	ball milling	67.2 % / 25 nm	32.8 % / 12 nm	-
1000 °C, 36 h	manual	88.0 % / 33 nm	12.0 % / 12 nm	-
	ball milling	67.8 % / 24 nm	32.2 % / 11 nm	-

Results - 3

- For reaction temperatures < 900 ^{o}C, some unreacted GaSb and by-product Sb are seen.
- At 900 ^{o}C and higher, total conversion is achieved with the relatively shorter reaction times for the ball milled GaSb precursor.
- The proportion of the polytypes h-GaN/c-GaN depends on the conversion temperature and precursor’s grain size:
  - the higher is the temperature, the higher is the ratio,
  - the finer are the particles (*e.g.*, ball milling *vs.* manual grinding), the higher is the ratio.
- The average crystallite size of h-GaN depends mostly on the precursor’s grain size/grinding in the range of 900-1000 ^{o}C and hold times of 36-170 h whereas that of c-GaN is independent on this factor.

	manual	ball milling
h-GaN	30-33 nm	23-25 nm
c-GaN	12-14 nm	11-14 nm

Results - 4



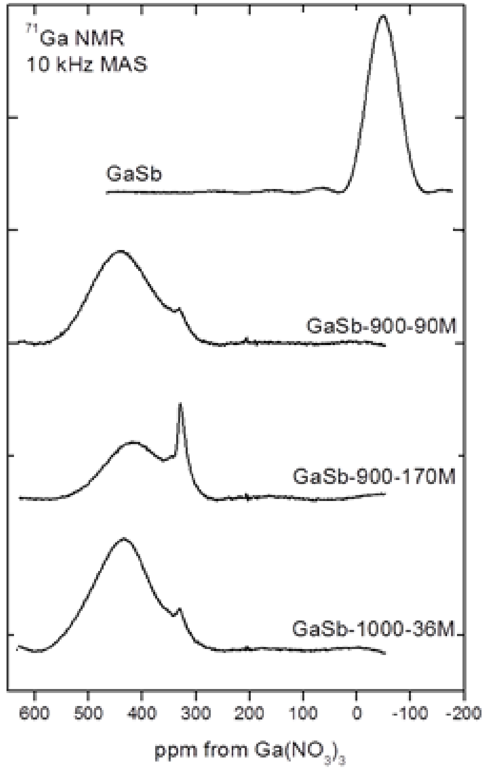


Fig. 4. ^{71}Ga MAS NMR spectra for the products from nitridation with NH_3 of powdered GaSb; *left* – manually ground, *right* – ball milled

NMR spectra consistent with the mixtures of h-GaN and c-GaN, each polytype made of (i) stoichiometric and (ii) defected varieties.

Results - 5

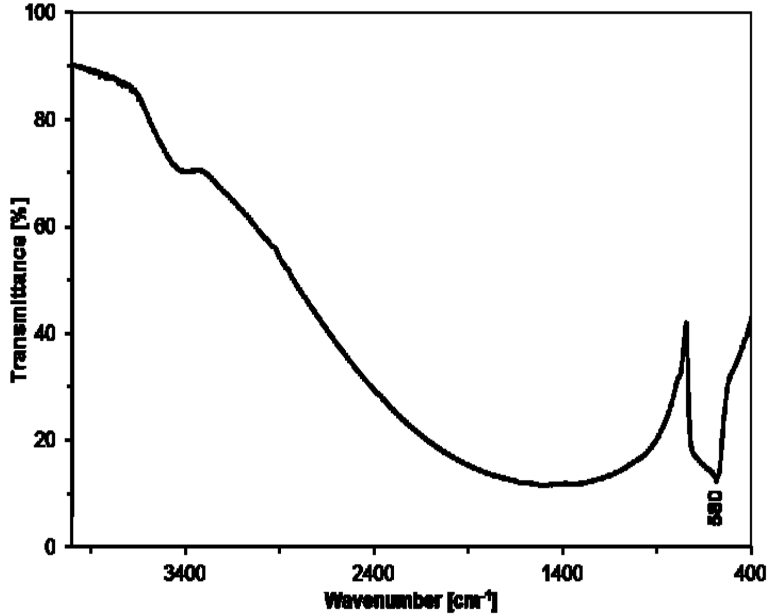


Fig. 5. FT-IR spectrum of the product from nitridation with NH_3 at ***1000 °C, 36 h***, of balled milled GaSb

The band at 580 cm^{-1} is in the region typical for Ga-N stretches in GaN.

Bending of the baseline is an artifact of an opaque KBr pellet.

Results - 6

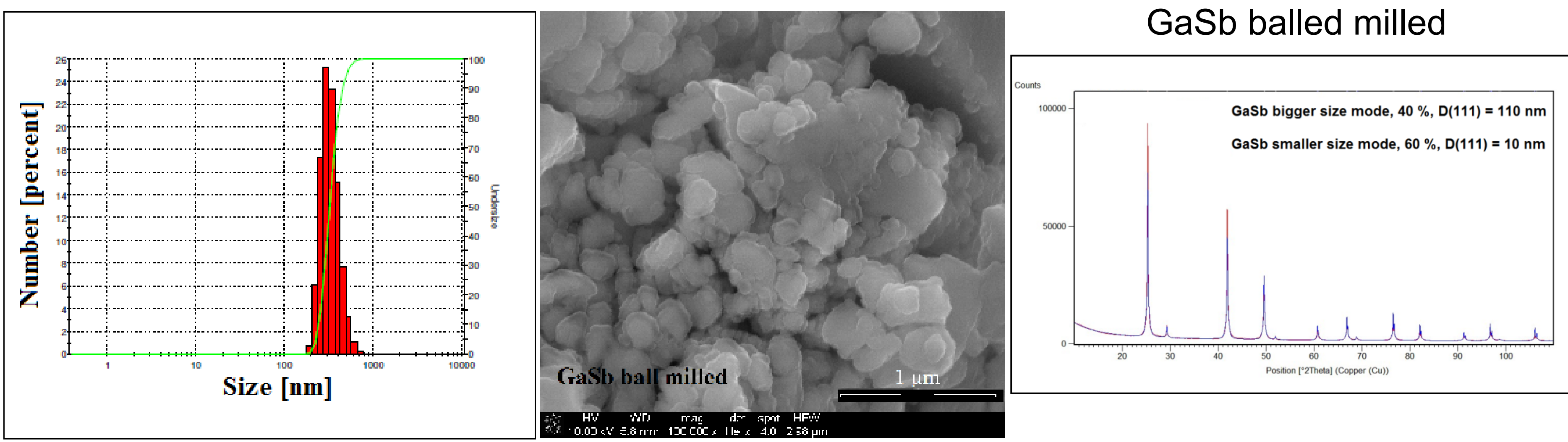


Fig. 6. Ball milled GaSb: *left* – particle size distribution by number, *middle* – SEM image, *right* – XRD spectrum

- Some 50 % of particles had diameters d < 400 nm and 95 % had d < 600 nm; the particle sizes covered a relatively narrow range of 200-700 nm.
- The particle sizes evaluated from the SEM image are consistent with these results.
- From XRD data, ball milling results in particles with bimodal size distribution.

Results - 7

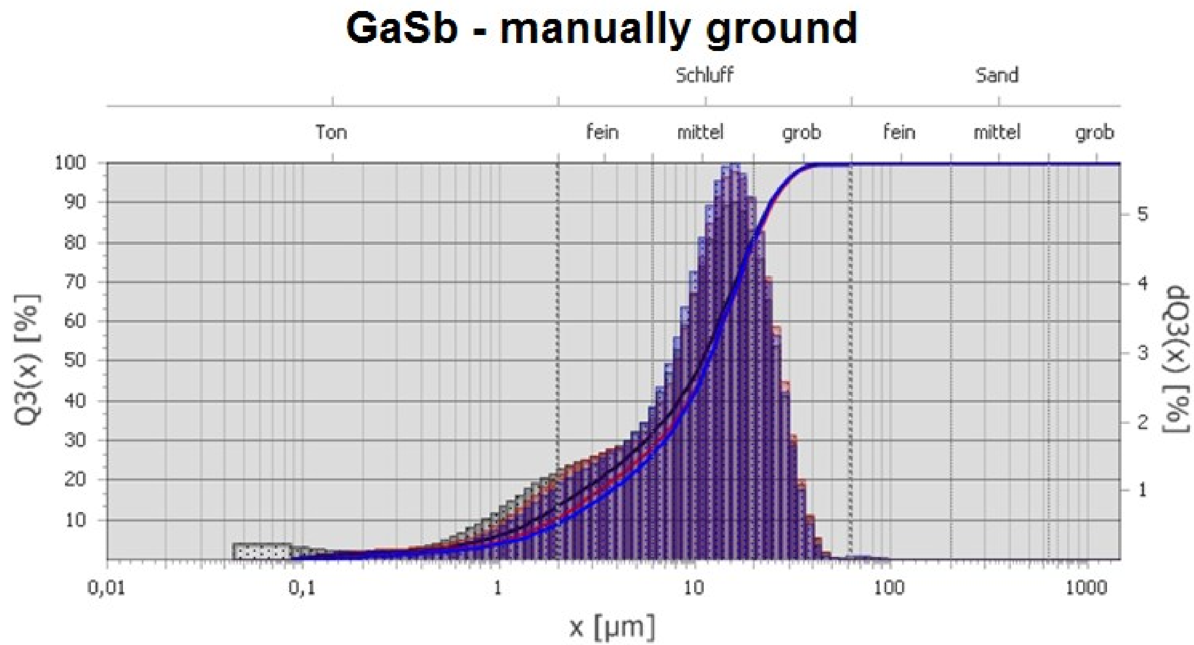
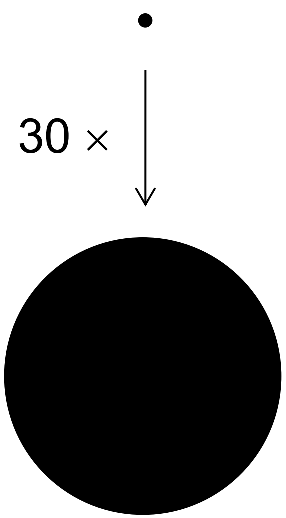


Fig. 7. Particle size distribution by number for manually ground GaSb

Some 50 % of particles had diameters d < 12 000 nm and 95 % had d < 30 000 nm; the particle sizes covered a relatively wide range of 500-50 000 nm.

Earlier: …Some 50 % of particles had diameters d < 400 nm and 95 % had d < 600 nm; practically, the particle sizes covered a relatively narrow range of 200-700 nm.

Results - 8



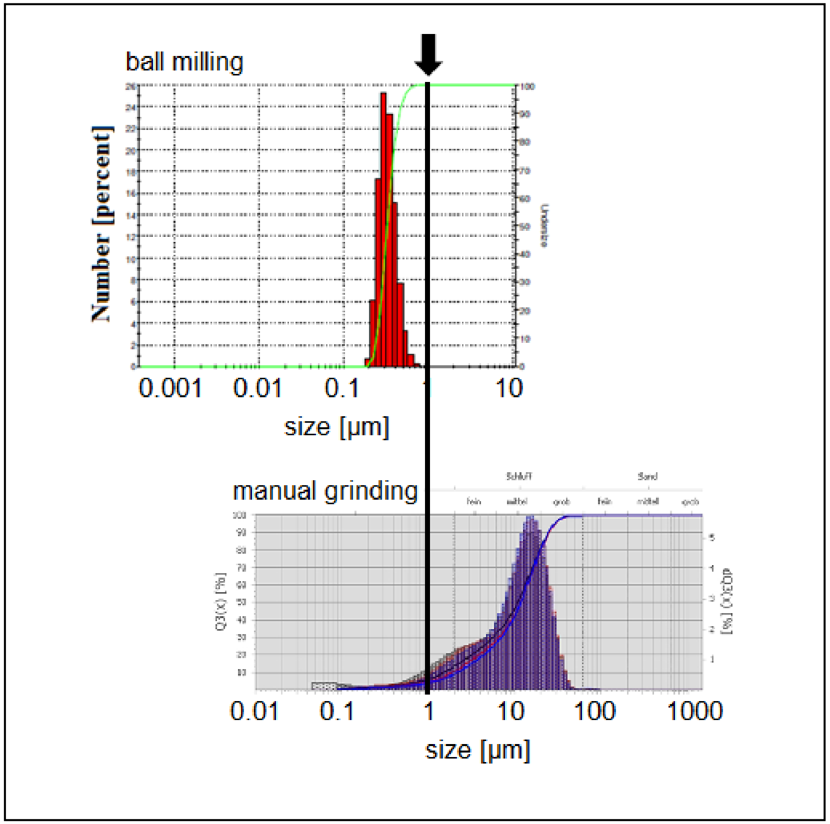


Fig. 8. Comparison of the particle size distributions for GaSb: *top* – ball milled, *bottom* – manually ground

Manual grinding results, relatively, in much wider particle size distribution and significantly bigger particles, on average, some 30 times bigger.

Results - 9

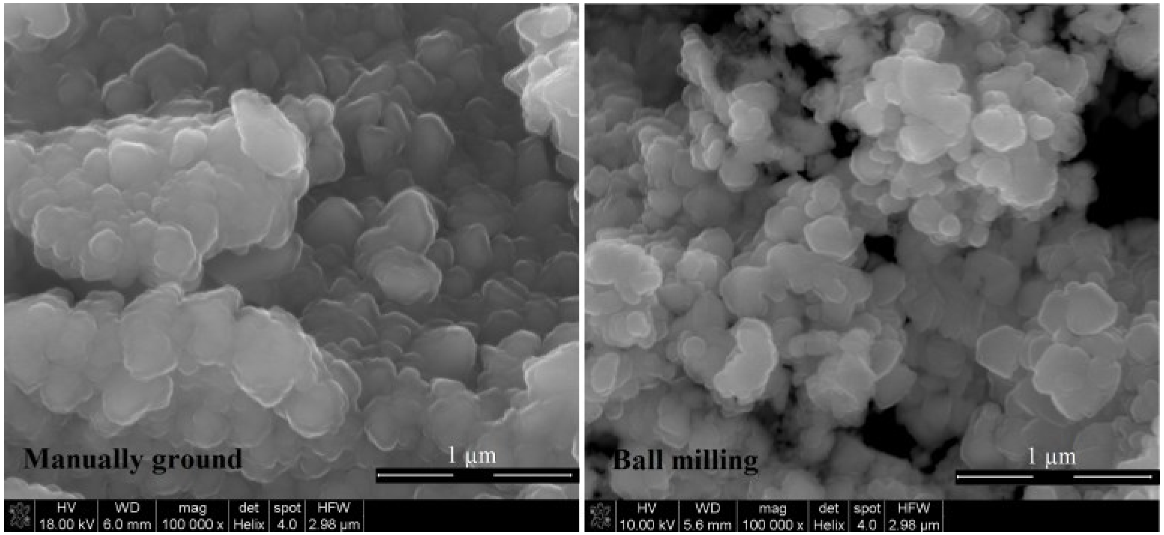


Fig. 9. SEM images of GaN powders prepared at ***900 °C, 170 h*** from: *left* – manually ground precursor, *right* – ball milled precursor. *Note the identical scale bars in both images.*

Powder particle sizes from the manually ground precursor (*left*) are on average bigger than the ones from the ball milled precursor (*right*).

Results - 10

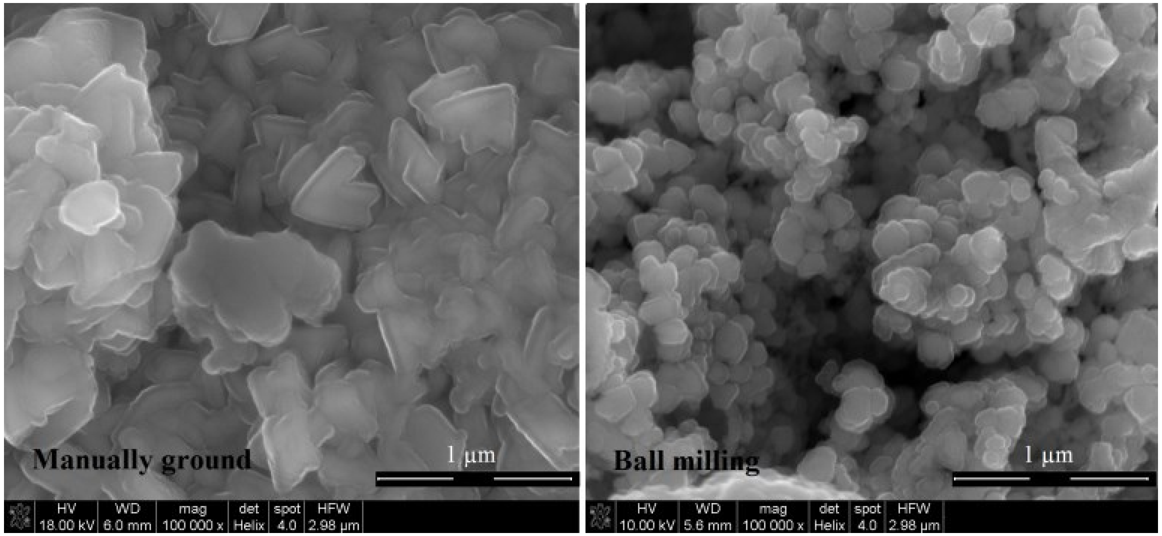
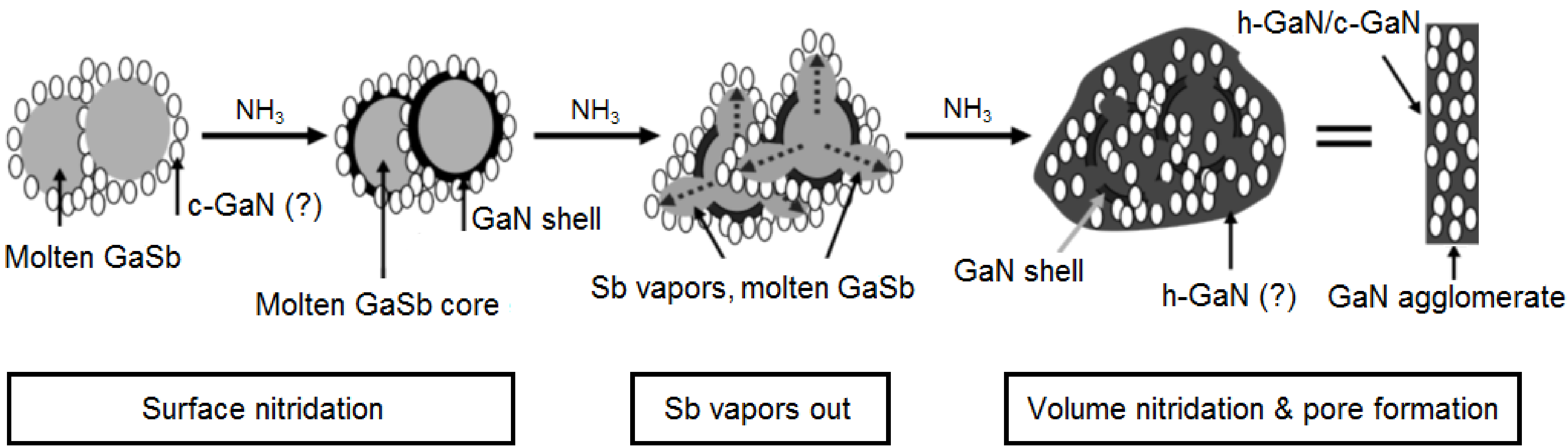


Fig. 10. SEM images of GaN powders prepared at ***1000 °C, 36 h*** from: *left* – manually ground precursor, *right* – ball milled precursor. *Note the identical scale bars in both images.*

- Powder particle sizes from the manually ground precursor (*left*) are on average bigger than the ones from the ball milled precursor (*right*); the latter particles are more homogeneous.
- These sizes are not crystallite sizes but they rather represent particle agglomerates.

Nitridation mechanism - impact of particle size/grinding



- Primary nitridation on particle surfaces yields c-GaN (topochemistry).
- Secondary nitridation of the molten bulk results in h-GaN (thermodynamics).

Conclusions - 1

- Nitridation with ammonia of the readily available microcrystalline gallium antimonide GaSb yields nanocrystalline powders of the gallium nitride GaN semiconductor in a convenient one-step synthesis process.

- The completion of the nitridation reactions requires temperatures above 900 °C and, relatively, long reaction times of the order of several tens to more than a hundred hours. For instance, increasing the temperature from 900 to 1000 °C results in reducing this time from 170 to 36 hours.

Conclusions - 2

- Grinding the GaSb precursor has a pronouced effect on the reaction time, average crystallite size of GaN, and the h-GaN/c-GaN polytype ratio in the product and, specifically:
  - ball milled precursor, relatively, shortens this time and yields the GaN nanopowders with a quite stable h-GaN/c-GaN ratio of *ca.* 2:1, independent on reaction temperature and time,
  - manually ground precursor is characteristic of the temperature and time dependent h-gaN/c-GaN ratio and, relatively, much higher amounts of h-GaN,
  - the average crystallite size of c-GaN, 11-14 nm, is very much independent on reaction conditions and GaSb grinding method whereas for h-GaN it mainly depends on grinding:
    30-33 nm (manual grinding) and 23-25 nm (ball milling).

Could we make pure c-GaN?

Thank You For Your Attention!

ACKNOWLEDGMENT

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