Investigations of high temperature conversion of microcrystalline gallium antimonide GaSb to nanocrystalline gallium nitride GaN

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Described is a new simple route to nanocrystalline powders of gallium nitride GaN by ammonolysis of ground monocrystalline gallium antimonide GaSb. The microcrystalline powders of the latter were pyrolyzed under a flow of NH_3 for up to 150 hours at temperatures in the range of 750-1000 ºC. The fine products were characterized by powder XRD supplemented with SEM/EDX.

EXPERIMENTAL SECTION

Monocrystalline platelets of gallium antimonide GaSb (zinc blende structure, electronic grade) with a defined growth direction (100) were placed in an agate mortar and ground for 30 min. After grinding, the resulting microcrystalline powder (0.5 g) was loaded in an end-opened alumina crucible. The crucible was inserted into a ceramic tube reactor and, following a purge of the system with nitrogen, high purity ammonia was introduced at 1 cm^3/s. After reaching a selected furnance temperature (range 750-1000 ˚C) the GaSb powders were nitridated for 6 to 150 hours. The fine yellow product powders were analyzed using the powder XRD and SEM/EDX examination.

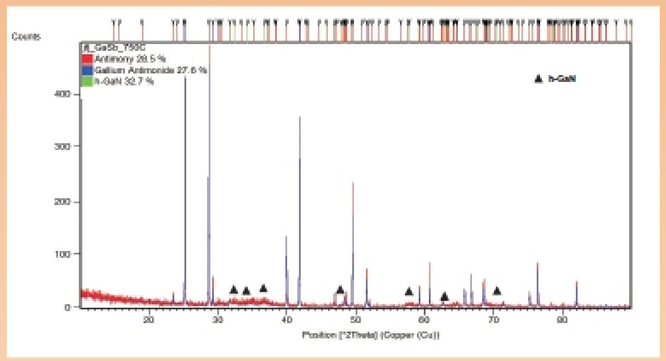
RESULTS

Powder X-ray diffraction

Sample ID	Temperature and time of conversion [ºC/hours]	Content of the GaN polytype [%]		h-GaN average crystallite size [nm]
		h-GaN	c-GaN	
Sample 1 (incomplete conversion)	750/6	33	-	N/A
Sample 2	900/90	94	6	38
Sample 3	900/150	100	-	47
Sample 4	1000/36	70	30	49
Sample 5	1000/90	74	26	53

The XRD data point out to complex products prepared under various conditions.

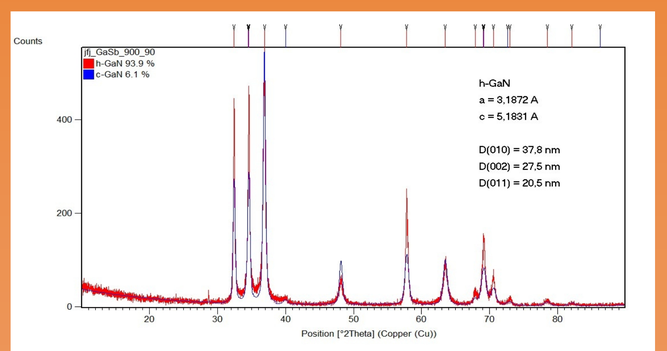
Sample 1



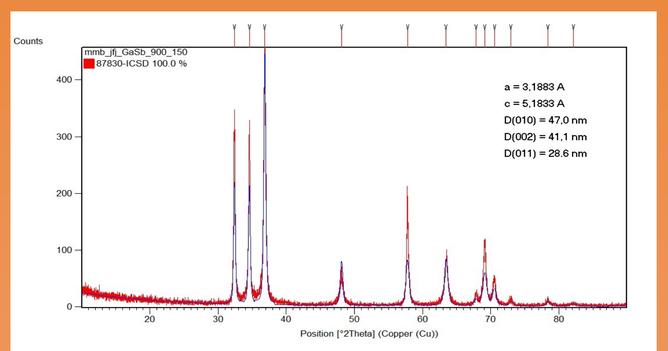
The product powder from the lowest temperature of 750 ºC and short reaction timeof 6 h (Sample 1, XRD pattern above) contains some GaN but, also, a proportion of unreacted gallium antimonide GaSb and elemental antimony Sb, a transient by-product. The proportion of nanocrystalline h-GaN in this powder was estimated at *ca.* 33 %.

Powder X-ray diffraction, *cntd.*

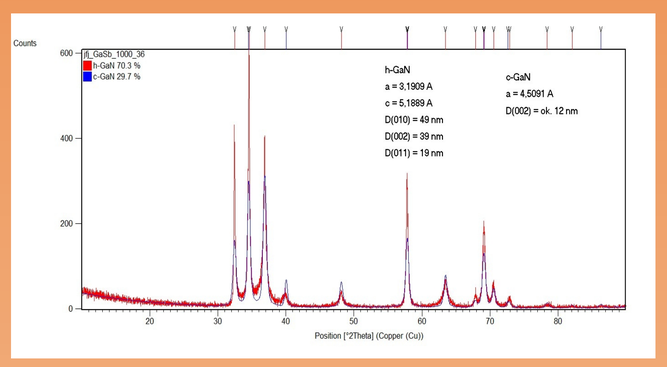
Sample 2



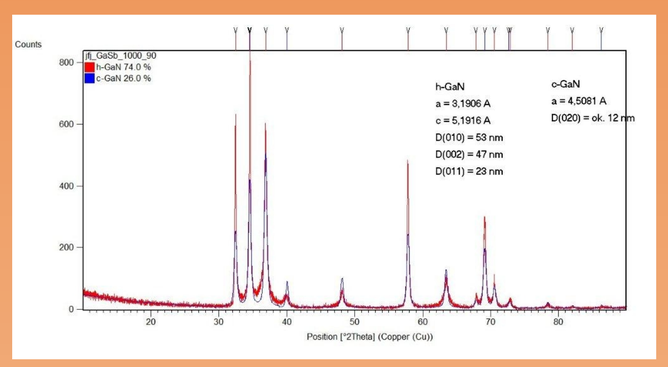
Sample 3



Sample 4

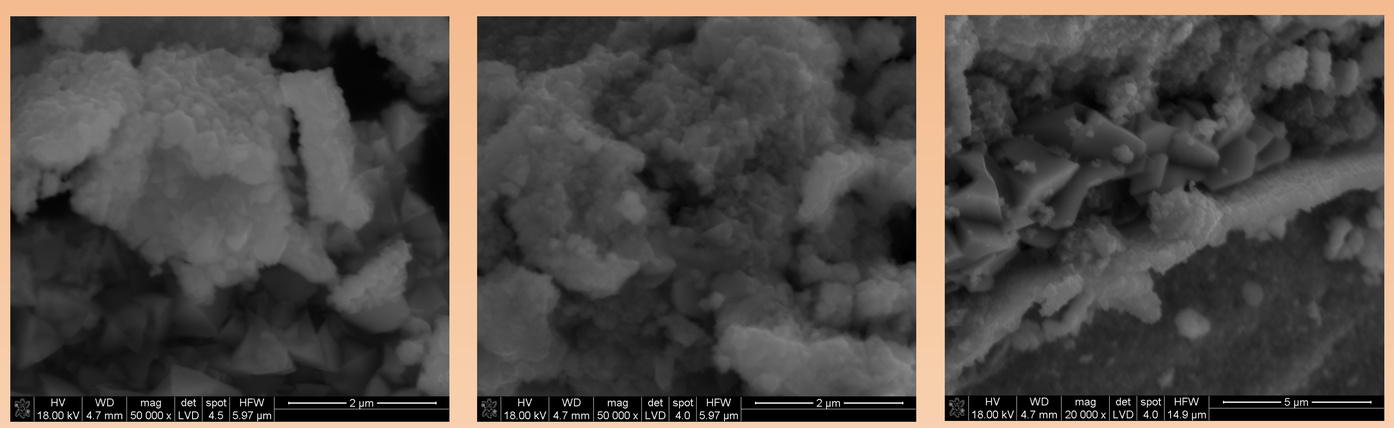


Sample 5



The application of the higher temperatures/longer reaction times was found beneficial for complete nitridation of GaSb and “removal” of the elemental Sb by-product. In the 900-1000 ºC pyrolyzed samples (Samples 2-5, above), GaN was exclusively detected by XRD either in a hexagonal form or as a mixture of the hexagonal and cubic forms. The average crystallite sizes of GaN, calculated using Scherer’s formula, clearly indicated that the microcrystalline powders of GaSb were eventually converted to nanosized GaN. The average crystallite size of GaN depends on the temperature and time of nitridation, *i.e.*, the higher the temperature and longer the time, the bigger GaN crystallites are formed still in the nanosized range for both polytypes .

SEM morphology



The fully reacted powders (Samples 2-5) were represented by two dominant morphologies. The pyramidal blocky nanocrystallites were observed in Sample 3 containing exclusively the h-GaN polytype. For Samples 2, 4, and 5 consisting of both polytypes, the pyramids were accompanied by particles with an ill-defined morphology.

CONCLUSIONS

In this study, we describe a new simple method of synthesis of nano-GaN by ammonolysis of ground monocrystalline gallium antimonide GaSb – a readily available and affordable precursor. The XRD investigations show that the microcrystalline precursor can be completely nitridated by using the appropriate reaction conditions (ammonia flow, temperature, time). Moreover, an average crystallite size of GaN can be controlled to some extent in the nanosized range. The mixtures of the hexagonal and cubic GaN polytypes or pure hexagonal polytype can easily be prepared. The phase composition of the GaN powders is reflected in their morphology – the pyramidal blocky nanocrystallites are characteristic for h-GaN while the ill-defined particles are likely associated with c-GaN in the polytype mixtures. Further studies on similar nitriding conversion to nanocrystalline GaN of other Group III-V compounds are in progress.

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