

# MICROSTRUCTURE AND MECHANICAL PROPERTIES OF GaN NANOCERAMICS SINTERED UNDER HIGH-PRESSURE HIGH-TEMPERATURE CONDITIONS

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## Introduction

GaN-based blue optoelectronic devices are rapidly entering the market. There is, however, a lot to be done to improve the technology and lower manufacturing costs. *In this regard, we investigated the possibility of sintering GaN nanopowders into nanocrystalline GaN ceramics.* The use of such ceramics as heat sinks for high-power blue diodes/lasers and alternative substrates for GaN homoepitaxy can now be envisioned.

## Experimental methods

### 1. Starting materials

Nanocrystalline GaN powders used for sintering were prepared by three different methods:

- aerosol-assisted vapor phase synthesis (SEM, Figure 3)
- conversion of commercial Ga<sub>2</sub>O<sub>3</sub> with ammonia (SEM, Figure 4)
- anaerobic imide route (SEM, Figure 5).

### 2. Sintering equipment

The goal of the project was to prepare compact nanocrystalline bodies. In order to inhibit grain growth we sintered the nanocrystalline powders in a high pressure torroid cell (Figure 1a). Therein, an uniaxial force applied by the 400 Tonn hydraulic press (Figure 1b) generated a quasi-hydrostatic pressure. The samples were simultaneously heated by passing the current through the graphite heater.

### 3. Sintering conditions

The equipment is capable of producing pressures up to 8 GPa and temperatures up to 2000 °C. High pressures promote sintering and prevent the decomposition of GaN at elevated temperatures. In order to investigate the effectiveness of pressure, several sintering processes were performed at 4, 6, and 8 GPa. The sintering temperatures varied in the range 800-1200 °C. Higher than that temperatures were not used since they were found to cause anomalous grain growth and the loss of nanocrystallinity.

### 4. Ceramic compacts/pellets

The sintered samples were pellets 5 mm in diameter and 2-4 mm in height (Figure 2). Depending on the initial powder, the GaN ceramics were either yellow (original powder color) or black. The origin of the black color is not clear at this point. Its possible explanation could invoke traces of some metallic gallium present in the samples. Characterization of the compacts was performed by means of X-ray diffraction, SEM, TEM, as well as by determinations of density and hardness.

## Results and discussion

Microscopic images of selected GaN nanoceramic samples are presented in Figures 6-9 and 11.

- High pressure sintering produces compacts of nanosized GaN with 93-97 % theor. density (Table 1; density of single crystal GaN, 6.15 g/cm<sup>3</sup>).
- Quality of the ceramics, as measured by the Vickers microhardness, is good since the values of approx. 1600 HV<sub>02</sub> can be reached (Table 1) while the hardness of single crystals of GaN is in the range 1200-1700 HV<sub>02</sub> depending on the crystallographic direction.
- The best results are obtained with sintering temperatures in the range 900-1100 °C. The exact value of the optimum temperature for sintering without grain growth depends on the kind of used powder. In all cases, grain growth becomes considerable above 1100 °C.
- Grain growth results in, relatively, less hard nanoceramics (Table 1).
- Higher sintering pressures cause the grain growth to begin at lower temperatures (Figures 7 and 8).
- Although chemical and X-ray analyses suggest that the initial powders are low in oxygen, the ceramic samples contain between 4 and 12 wt% of gallium oxide which corresponds to 1-3 wt% of oxygen contents (Figures 10 and 12). The most O-contaminated samples were those obtained from the imide route powders. This correlates well with the high reactivity and lowest sintering temperatures of these powders.

## Conclusions

- High pressure sintering of nanocrystalline powders of GaN produces dense and mechanically robust GaN ceramics with grain sizes in the nanosized range.
- Controlling the size of the crystallites is possible by adjusting selected parameters of the sintering process, *i.e.*, pressure and temperature.
- The sintered bodies are well suited for GaN homoepitaxy (Fig. 12).

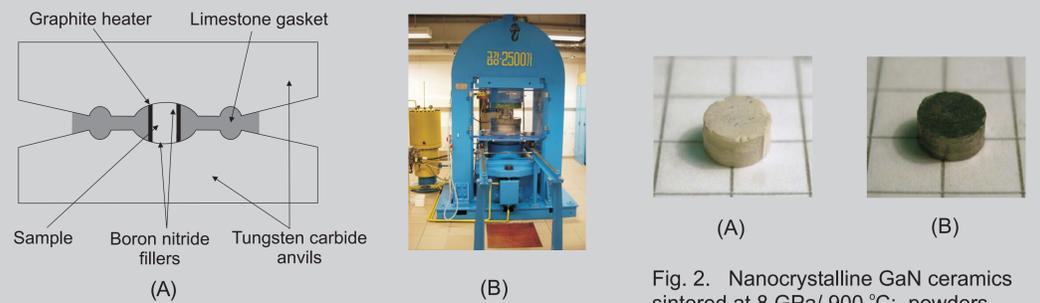


Fig. 1. High pressure sintering equipment: (A) scheme of a toroid HP-HT cell; (B) 400 Tonn hydraulic press.

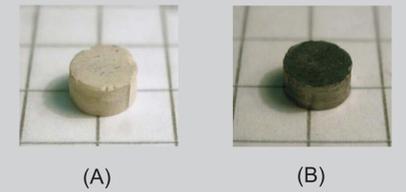


Fig. 2. Nanocrystalline GaN ceramics sintered at 8 GPa/ 900 °C; powders prepared by: (A) imide route, (B) Ga<sub>2</sub>O<sub>3</sub> conversion.

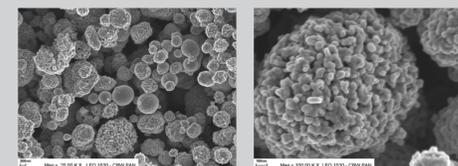


Fig. 3. SEM images of GaN powder obtained by the aerosol-assisted method at 975 °C, 6 h.

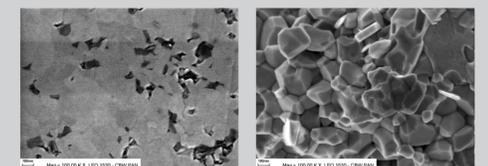


Fig. 6. SEM images of sintered powder from the aerosol-assisted method; 6 GPa/1200 °C; polished (L) and fractured (R) surfaces.

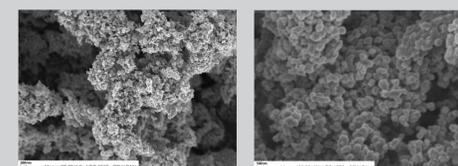


Fig. 4. SEM images of GaN powder obtained by Ga<sub>2</sub>O<sub>3</sub> conversion at 900 °C, 12h.

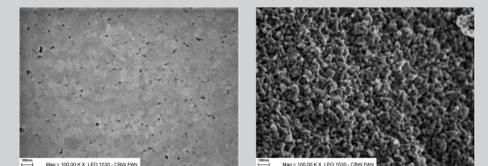


Fig. 7. SEM images of sintered powder from the Ga<sub>2</sub>O<sub>3</sub> conversion method; 4 GPa/1100 °C; polished (L) and fractured (R) surfaces.

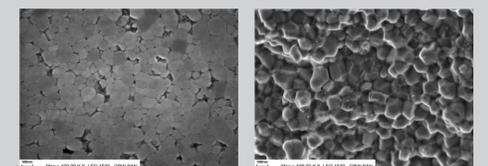


Fig. 8. SEM images of sintered powder from the Ga<sub>2</sub>O<sub>3</sub> conversion method; 6 GPa/1100 °C; polished (L) and fractured (R) surfaces.

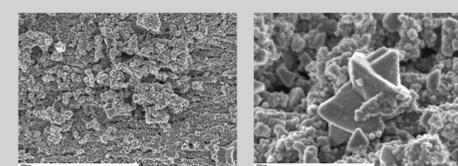


Fig. 5. SEM images of GaN powder obtained by the imide route method at 800 °C, 4 h.

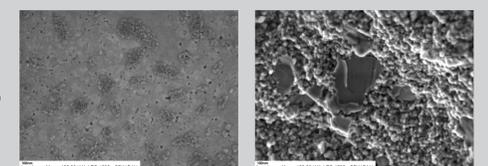


Fig. 9. SEM images of sintered powder from the imide route method; 4 GPa/1000 °C; polished (L) and fractured (R) surfaces.

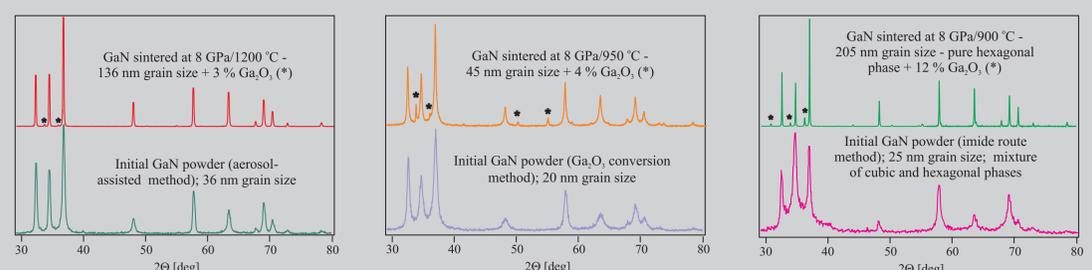


Fig. 10. X-ray diffraction patterns of GaN powders and corresponding sintered GaN nanoceramics.

Table 1. Properties of selected GaN ceramic samples prepared of powders of various origin at different sintering conditions.

Initial powder/source and average crystallite size	Sintering conditions	Density [g/cm <sup>3</sup> ]	Vickers hardness [HV <sub>02</sub> ]	Crystallite size [nm]
Aerosol- assisted method 36 nm	4 GPa/1000 °C	5.69(3)	900(30)	32
	6 GPa/1200 °C	5.91(4)	1100(90)	190
	8 GPa/900 °C	5.73(4)	1550(120)	45
	8 GPa/1200 °C	5.96(2)	1150(100)	136
Ga <sub>2</sub> O <sub>3</sub> conversion method 20 nm	4 GPa/1000 °C	5.62(2)	1500(60)	38
	6 GPa/1100 °C	5.69(2)	1250(70)	125
	8 GPa/950 °C	5.82(2)	1600(140)	45
Imide route method 25 nm	4 GPa/1000 °C	5.58(4)	1600(70)	43
	8 GPa/900 °C	5.71(3)	1000(110)	205

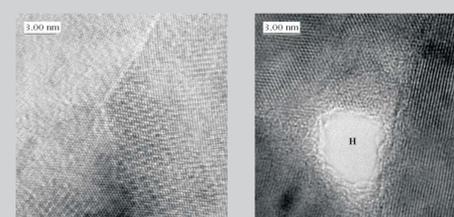


Fig. 11. HRTEM images of GaN nanoceramics showing a perfect tripple-junction and an inclusion (possibly Ga<sub>2</sub>O<sub>3</sub>).

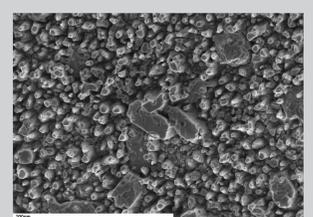


Fig. 12. Selective etching of GaN ceramics exposes (111) surfaces of nanocrystallites. On such surfaces, an epitaxial growth of highly textured GaN layers is feasible.