

## Distribution of Strain in GaN and SiC Nanocrystals under Extreme Pressures

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**ABSTRACT** Nanocrystalline powders of GaN and SiC with grain sizes ranging from 2 to 30 nm were examined under high external pressures by *in situ* diffraction techniques. The experiments, which simulated the process of densification of pure powders under high pressures, were performed without a pressure medium, under so-called isostatic conditions. Mechanism of generation of internal strains and their distribution in nanoparticles was deduced from the positions and broadenings of Bragg reflections measured *in situ* under high pressures at room temperature: (i) *macro*-strain was calculated from average compressibility of the crystal lattice, (ii) *micro*-strain - from FWHM of Bragg lines. Under external stress there are observed several pressure ranges in which *micro*- and *macro*-strains behave differently. Densification of nanopowders occurs in steps and it involves different mechanisms in relatively soft GaN (bulk modulus  $\approx 125$  [1];  $\approx 190$  GPa [2]) and very hard SiC ( $\approx 240$  GPa [3]). The shapes of plots presenting generation of *micro*- and *macro*-strains change with the size of nanograins. Here we discuss the effects of size and agglomeration of powders on mechanism of relaxation of local strains under increasing external stresses.

**EXPERIMENTAL** Nanocrystalline GaN with grain sizes 3, 8, 20, 30 nm, and several  $\mu\text{m}$ , also SiC powders with grain sizes 2, 4, 6, 10 and 30 nm were examined with use of Diamond Anvil Cell up to 40 GPa (Station F3, HASYLAB at DESY). The diffraction data were collected in energy dispersive geometry, gold was applied as a pressure marker, no pressure medium was used.

**MATERIALS** Nanocrystalline GaN powders were synthesized by pyrolysis of the gallium imide precursor [4], SiC nanopowders were synthesized by pyrolysis of chlorine-containing polysilane [5,6]. In both cases the materials of given grain sizes were obtained by annealing the precursors at well controlled temperatures: 900-1500°C for SiC and 500-1100°C for GaN. Microcrystalline GaN was obtained by grinding GaN single crystals grown under high pressure of nitrogen.

Stable crystallographic phase of bulk GaN at ambient p-T conditions is hexagonal wurtzite structure, 2H polytype. A high pressure modification of GaN above 50 GPa is rock salt structure [1]. Polycrystalline GaN shows a wurtzite structure but, with a decrease of the grain size below 20-30 nm, there is an increasing number of stacking faults present in the powder grains [7]. The density of stacking faults in the smallest GaN grains with 3-8 nm is very large and their structure becomes similar to cubic sphalerite-type, 3C polytype. There are neither theoretical predictions nor experimental data which would indicate that 3C cubic polytype is an alternative structure to 2H-type GaN. Appearance of cubic-like structure of GaN is apparently a result of generation of stacking faults in the wurtzite structure: implementation of a stacking fault in 2H polytype always leads to formation of cubic-type layer stackings.

SiC nanocrystals show a sphalerite cubic structure with one-dimensional disordering. Density of stacking faults depends on the grain size [8,9] but no changes of the disordering are observed in SiC nanocrystals during high pressure processing at room temperature. Appearance of

the disordering in nanocrystals, this is a common behaviour of isotypical structures like SiC, diamond or GaN, may result from relaxation of a strong internal strain present in very small crystallites [10]. Generation of stacking faults is obviously connected with dislocations, which, in very hard materials like SiC or diamond, are immobile at low temperatures. Creation of fresh dislocations or their rearrangement is possible only at elevated temperatures [11-13].

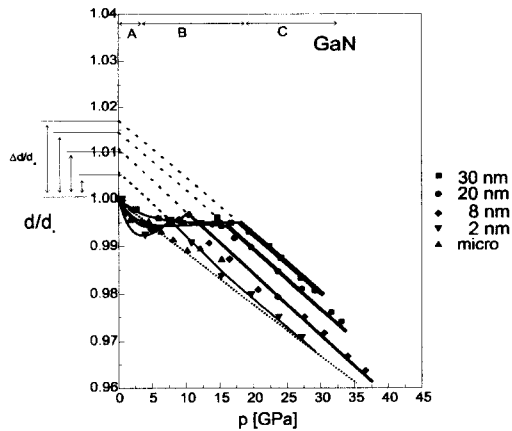


Fig.1 Relative changes of  $d/d_0$  values determined for GaN nanocrystals. The Bragg peak positions were taken as maxima of a split-Pearson function

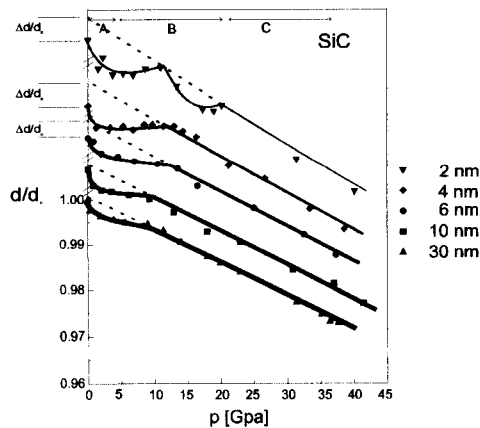


Fig.2 Relative changes of  $d/d_0$  values of (111) Bragg reflections determined for SiC nanocrystals. The starting  $d/d_0$  values measured for all samples are the same; the plots for different samples are shifted for clarity

(B) is only from 3 to 10 GPa for the smallest 2 nm grains but it extends from 3 up to 20 GPa for 30 nm grain powders.

*in SiC, Fig.2:* The width of the pressure range (B) increases with a decrease of the size of SiC grains: it extends from 3 to 8 GPa for 30 nm material and from 3 to 20 GPa for the smallest 2 nm grain size powder.

## RESULTS

### Macro-strain – Figs.1&2

*Note:* The plots in Figs.1 and 2 we call "compressibility-like" but not "compressibility" because they show changes of the lattice parameters under isostatic pressure conditions and thus reflect interactions between individual grains under external load. A proper meaning of compressibility is "compression of lattice parameters under hydrostatic pressure" where there are no micro-strains neither at the surface not in the volume of the grains. In our experiments, the external load is transferred to the material through point contacts between individual grains (necks) where, there is locally very strong gradient of lattice parameters demonstrated as micro-strain. The lattice parameters, which are measured from the positions of Bragg reflections, are the values averaged over the whole volume of the material. Hydrostatic pressure conditions are reached in a polycrystalline compact only when the material is fully dense.

The dependencies of lattice parameters on the applied external stresses measured for both GaN and SiC, Figs. 1 & 2, show some apparent similarities but also clear differences:

**Similarities:** At the initial stage of densification (A), under relatively low pressures 1-3 GPa, there is observed a strong decrease of lattice parameters for both SiC and GaN. In the pressure range (B) there is a tendency for less-than-lattice-compressibility decrease of the crystal lattice parameters. In the pressure range (C) the plots "stabilize" and look like compressibility plots.

**Differences:** The width of pressure range (B), where compressibility is much less than expected for bulk materials, depends on the grain size but it shows opposite tendencies in GaN and SiC:

*in GaN, Fig.1:* The width of the pressure range

### Micro-strain – Figs.3&4

A typical shape of plot presenting generation of *micro*-strains in a porous material under increasing stress is a quadratic type function, as marked by broken lines in Figs.3 and 4. During increase of the external stress applied to GaN and SiC, different mechanisms of relaxation of the internal strains are being activated, depending of the actual stress and specific materials properties. There are

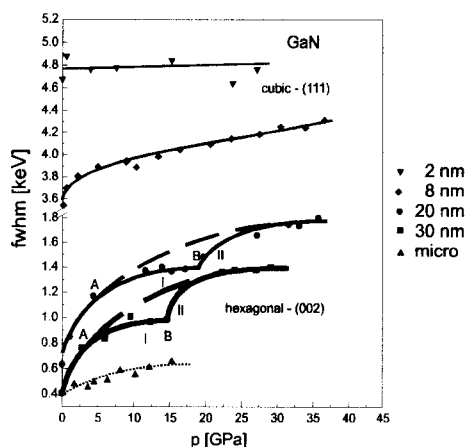


Fig.3 Generation of *micro*-strain in GaN nanocrystals showed as variation of FWHM of Bragg reflections.

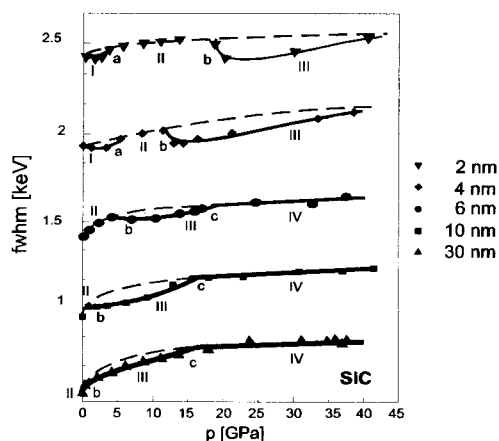


Fig.4 Generation of *micro*-strain in SiC nanocrystals showed as variation of FWHM of (111) Bragg reflections.

obviously different mechanisms which operate in SiC and GaN what is reflected by different shapes of the plots presented in Figs. 3 and 4. Tentative mechanisms of relaxation of strains in these materials are given in Figs.3a and 4a.

**DISCUSSION** An external stress applied to a porous powder compact (with typically 30 to 70% porosity) leads to a very strong deformation of individual grains. In a diffraction experiment the deformation can be observed as elastic compression of the crystal lattices, Figs.1&2. In presence of pores, the external load is transferred through a number of relatively small contact points between grains. In general, development of *micro*-strains which are generated in a powder follows changes of total surface of the contact points which link the individual grains. The applied external stress leads to concentration of strain in the vicinity of the contact points between individual grains. In a powder polycrystal, the grains are bonded together (they are agglomerated in chains, clusters etc.) and form a network which exhibits its hardness and elasticity and which tends to resist changes of the initial arrangement of the particles in the starting powder compact. Under relatively low stress the network of the grains does not change - it behaves like an elastic material. The local stresses can be very high and accordingly the lattices of individual crystallites in the vicinity of contact points compress more than it would occur under similar external stresses applied to a denser (less porous) material. Nanocrystals of GaN and SiC behave similarly at the beginning of densification (pressure range A) where they show very strong lattice compressions. Different behaviour of these materials is observed under larger stresses.

The decrease of lattice parameters measured experimentally at the beginning of densification, is much larger in small than in large grains materials, Figs.1,2. To explain this, one has to consider that Bragg peaks bring information on average values of lattice parameters, which correspond to whole volume of the material. As stated above, there are strong variations of lattice parameters within a powder compact, which occur between relaxed and strained parts of crystallites. In fact, this information is contained in Bragg peaks, in their positions and widths. The

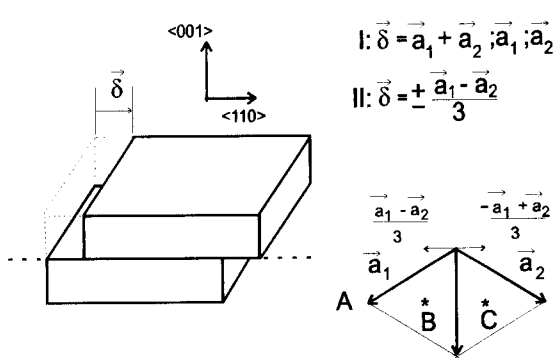


Fig.3a Tentative model of two mechanisms of relaxation of *micro*-strain induced in GaN nanocrystals under high pressures - see text.

problem is to withdraw information on specific distribution of strains in a powder from Bragg reflections. This is particularly difficult in case of in situ high pressure diffraction experiment which gives rather poor counting statistics and resolution and permits for recording only few reflections. The purpose of this work is evaluation of the actual lattice parameters which vary within the sample. Here we consider this problem in connection with changes of relative volumes of these parts of the sample which have different lattice parameters.

Local gradients of lattice parameters are larger in larger grains. This follows from a simple model of a porous material where, for

same density of a powder compact exposed to given external stress:

(i) the number of contact points (CP) between the individual grains increases with a decrease of grain dimensions as:  $N_{CP} \sim 1/r^2$ ,

(ii) local stresses at contact points between two grains,  $P_{CP}$ , are inversely proportional to the number of the points through which the external stress is transferred to/through the material:

$P_{CP} \cong F_p / (S_{CP} \times N_{CP}) = (F_p / S_{CP}) \times r^2$ , where  $F_p$  is external load,  $S_{CP}$  - area of a single contact point.

Total amount of the material which is strained is larger in smaller grains powders. Assuming, for simplicity, that the strain field generated around a single contact points has a constant volume,  $V_{CP}$ , total amount of the material which is strained is proportional to the number of grains,  $V_{strained} = V_{CP} \times (N = V/V_0) \sim 1/r^3$ ; where  $V$  is total volume of the material,  $V_0$  is volume of a single particle.

With an increase of the external stress the distribution of internal strains becomes more and more homogenous because total area of the contacts between powder particles increases with density. In a dense polycrystal, a solid, *micro*-strains are nor generated but, the strain arising during early stages of densification remains in the compressed material. However, it can be relaxed through diffusion at elevated temperatures and/or redistributed among the powder particles during subsequent stages of densification.

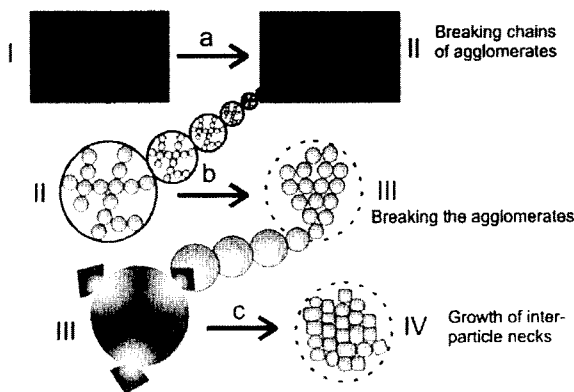


Fig.4a Three stages of subsequent relaxations of *micro*-strains in SiC compacts correlated with changes of the material microstructure

stacking. At higher pressures, at stage II above (B), there is observed an increasing number of

#### Models of densification of nanocrystals

The individual particles of relatively soft materials like GaN, can change their shape plastically under sufficiently strong stress due to movement of dislocations. Analysis of the diffraction patterns registered with increasing external stress shows that the initial wurtzite structure of GaN remains unchanged up to the pressure (B), above which there is an increasing amount of cubic phase in the compressed GaN compact. A tentative corresponding mechanism of plastic deformation of GaN particles is presented in Fig.3a: during stage I, which begins at pressure (A) and extends to (B), Fig.3, the dislocations move along the layer planes without changing the hexagonal layer

stacking faults which are generated in the initial hexagonal GaN and cause transforms of hexagonal to cubic layer stacking. We suggest that this occurs due to dislocations which move across the hexagonal layers and change locally the structure from hexagonal to cubic.

A tentative model of subsequent stages of densification of agglomerated powders of a non-plastic material like SiC, is presented in Fig.4a. Under increasing external stress the microstructure of a powder compact remains unchanged for as long as the framework of the grains resists breaking bonds between the particles. The initial decrease of the lattice parameters under low pressures results from elastic deformation of individual crystallites incorporated into the framework. This stage of densification ends when the stress reaches a "critical value" determined by strength of the interparticle bonds. At this "critical stress" the bonds between individual grains break and the agglomerates of particles split into smaller pieces - this begins at the end of the range (A), Fig.2. A sudden increase of the number of particles leads to their rearrangement such that the local strains at the contacts between the particles get minimized. To fulfill this condition the number of contact points increases and the particles tend to pack themselves as dense as possible, i.e. with formation of possibly large areas of contact points between them. The process of rearrangement of the powder particles extends over the whole range (B), Figs.1,2, until the powder compact reaches nearly full physical density. Beginning from a certain applied external stress, above range (B), the density reaches value close to that of a solid. In the pressure range (C) both GaN and SiC show behaviour similar to ordinary compression observed under hydrostatic pressure conditions.

#### Different mechanisms of densification of small and large grain polycrystals

Development of *micro*-strain in polycrystalline GaN and SiC shows distinct deviations from a "smooth" quadratic type function.

#### *Generation of micro-strains in powders with grains larger than 10 nm*

**GaN:** In relatively large 20 and 30 nm grains GaN powders the *micro*-strain develops in two stages as described in Fig.3a. At each stage, the increase of *micro*-strain follows an "ordinary" behaviour, i.e it follows a quadratic type function, Fig.3. This obviously results from the increase of total area of contacts between individual grains. The points (A) and (B) in Fig.3 for 20 nm material are shifted towards larger pressures relative to the material with 30 nm grains. This is understandable because under similar external load, the local stresses in a compressed powder compact are larger in larger grains, see above. To generate or move dislocations comparatively smaller external stress is required to reach the critical local stress in 30 nm than in 20 nm grains material. A two step relaxation of strain is observed neither in very small nor very large crystallites.

**SiC:** This material is much harder than GaN and dislocations, even if they are present in the initial powder grains, do not take part in relaxation of strain because they are very little mobile below 1000°C [11-13]. For same reasons, no fresh dislocations are generated during high pressure densification at room temperature. Therefore in SiC the relaxation of *micro*-strains at the contact points can occur only through rearrangement of the particles, by turning, gliding, breaking bonds between individual particles etc, as presented schematically in Fig.4a.

#### *Development of micro-strains in powders with 10 nm grains and smaller*

**GaN:** In 2 nm GaN crystallites there is practically no *micro*-strain observed in the whole pressure range. This suggests that the powder easily changes its microstructure and relaxes the local strains immediately under increasing external stress. This can also mean that the strain field around the point contacts between the grains has size comparable to the particle diameter. A gradient of the lattice parameters, which probably occurs within single crystallites, is so little that it is not detected within the experimental error of the diffraction experiment.

The *micro*-strain generated in 8 nm GaN powders is much smaller than that observed in large grains: FWHM of Bragg lines of 8 nm sample increases by 0.6 keV from 0 to 45 GPa but it is nearly twice as much in 20 nm grains, 1.1 keV. Moreover, there is no step-like relaxation of strain such, that we observe in 20 and 30 nm samples. Explanation of this behaviour can be two-fold: (i) in the grains as small as 8 nm there are no dislocations and thus there is no way to relax the strain through movement of dislocation and/or (ii) in 8 nm samples the stress is distributed evenly and the

strain at the contact points is too little to activate movement or generate fresh dislocations.

**SiC:** The grains with 2 and 4 nm average diameter show a very characteristic behaviour of the *micro*-strain: there is no strain generated up to 2-3 GPa (range I) and then there is a "fast" increase of strain at (a) and a little increase of strain in the pressure range (II), up to 10 and 15 GPa for 4 and 2 nm materials, respectively. When the external stress reaches value (b) there is a sudden decrease (drop) of the *micro*-strain (the FWHM reaches it's starting value) what looks-like that there are no *micro*-strains present in SiC powder. A model explaining this behaviour is presented in Fig.4a.

**SUMMARY** Interpretation of the high-pressure diffraction experiments which we present here is based only on determination of positions and broadening of Bragg reflections. With use of these data we examined changes of geometry of the crystal lattice, in fact geometry of "an average" crystal lattice. A diffraction technique in general and in situ high pressure experiments in particular have some "weak points" which make unique interpretation of the experimental data just impossible. This follows from the fact that only this part of the material contributes to the Bragg reflections, which scatters coherently. Therefore, we are unable to estimate what fraction of the materials under examination contributes to Bragg scattering. In general, stress energy can be accumulated in the material in various forms and elastic energy of the crystal lattice is only one of them. The stress energy is accumulated in non-crystalline or other disordered phases present in the material, e.g. in grain boundaries, what is not registered by Bragg reflections. Based on the present diffraction data we were able to evaluate only the elastic energy stored in this fraction of the material which contributes to Bragg scattering. The "offset" of the compressibility-like lines relative to the reference bulk compressibility line, ( $\Delta d/d_0$ ), showed in Figs. 1&2, is an indication that the stress energy is distributed among different structural fractions, i.e. in the "Bragg fraction" but also it is stored in disordered phases, which are probably associated with grain boundaries. There are distinct differences between "offset" of lattice compressibility-like lines measured for GaN and SiC powders: this offset increases for GaN but it decreases for SiC with an increase of the grain size. We suggest that this results from the fact that the non-crystal lattice elastic energy is located in grain boundaries in SiC but it concentrates around lattice defects in the volume of GaN crystallites. Discussion of this problem is outside scope of this paper.

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