ESRF	**Experiment title:** **"Effect of the chemical state of the surface on the relaxation of the surface shell atoms of SiC nanoparticles"**	**Experiment number**: HS-1463
Beamline: BM01B	**Date of experiment**: from: 30/04/2001 to: 07/05/2001	**Date of report**: 26-February-2002
Shifts: 15	**Local contact(s)**: Hermann EMERICH	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Hans-Peter Weber* SNBL at ESRF

Bogdan Palosz* High Pressure Research Center UNIPRESS, Warsaw, Poland

Stanislaw Gierlotka* High Pressure Research Center UNIPRESS, Warsaw, Poland

Ulrich Bismayer* Mineralogisch-Petrographisches Institut, Uni Hamburg, Germany

Report:

Results expected

Determination of the strains in the surface shell layers in SiC nanocrystals as a function of grain size and chemical composition (environment) of the surface. Effect of size on the structure of grain cores.

Materials: For the purpose of making comparative studies 3 kinds of nanocrystalline powders were used: SiC (average crystallite size 10 and 20 nm), diamond (6 and 10 nm), GaN (6 and 30 nm).

Experiment: The diffraction data was collected in transmission geommetry with application of 4 scintillation counters and secondary beam monochromators, $\lambda \sim 0.5$ Å, room-temperature. Silicon standard was used to callibrate the instrument.

Method of data elaboration

We investigated the effect of the chemical state of the surface of the nanoparticles on the relaxation in the near-surface layer with application of a method of determination of apparent lattice parameter, *alp,* measured for different diffraction vectors Q [1,2]. Apparent lattice parameter is the lattice parameter determined taking into account a particular (limited) part of the diffraction pattern. It appears that at low diffraction vectors the Bragg peak positions are affected by the structure of the near-surface layer while at high Q only the interior of the nano-grain shows. Following the measurements on raw (as prepared) powders we investigated powders cleaned (annealed at 400^{o}C) under vacuum and those wetted by water. Subsequent *alp*-Q plots have shown that the structure of the surface layer changed with the of treatment of the sample. Semi quantitative analysis was based on the comparison of experimental and theoretical *alp*-Q plots. Theoretical *alp*-Q plots were obtained from diffraction patterns calculated for models of nanocrystals with strained surfaces.

Results

A strong dependence of experimental *alp*-Q plots on grain size was observed for all examined samples. Also dependence of *alp* values on purity of materials and its surrounding was observed.

Nanocrystalline silicon carbide SiC.

Raw nanocrystalline SiC powders show a strong increase of measured *alp* values at small Q-values, Fig.1. There is much stronger increase of *alp* values measured for 8 nm powder than for larger grains 20 nm.

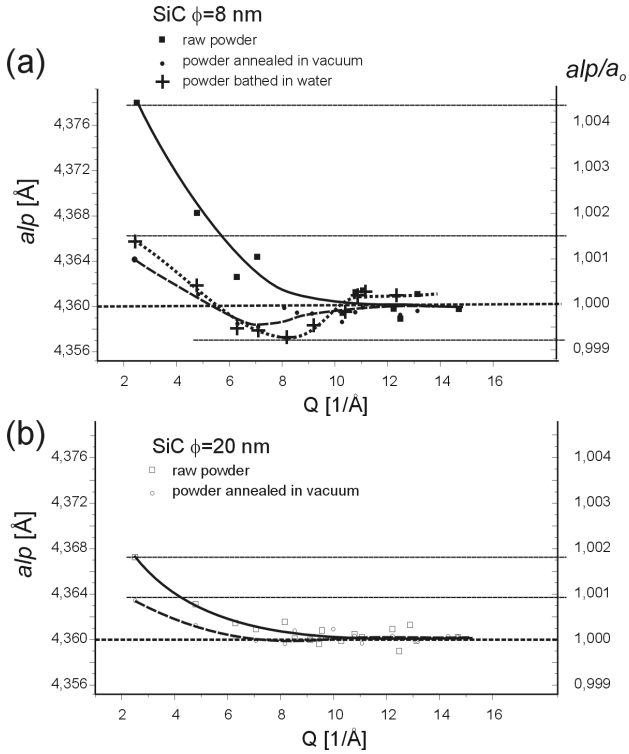

Fig.1 Experimental *alp*-Q plots of nanocrystalline SiC powders

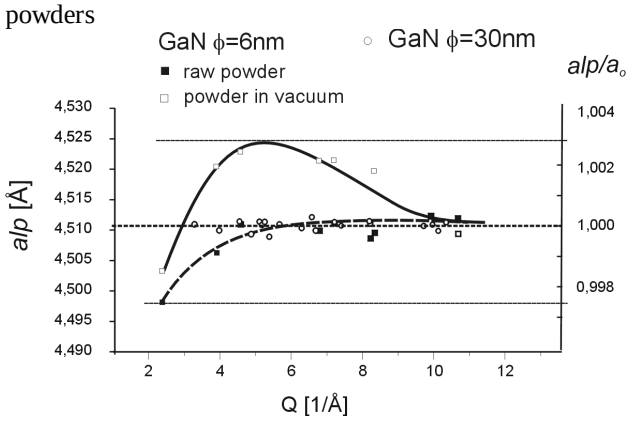

Fig.2 Experimental *alp*-Q plots of 6 nm nanocrystalline GaN

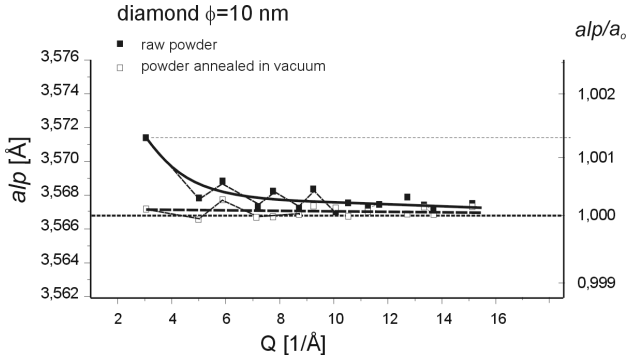

Fig.3 Experimental alp-Q plots of nanocrystalline diamond.

According to theoretical calculations, this shape of *alp*-Q plots corresponds to a core-shell model of nanocrystals where the atomic structure of the surface shell is similar to that in the grain core but it is expanded - its under tension. The estimated thickness of the shell is 4-6 Å, the strain is around 10%. Annealing of powders at 400^{o}C in vacuum leads to a strong decrease of the surface strain: theoretical calculations show that the initial tensile strain in the surface becomes significantly smaller and shows a tendency to convert in compressive strain (note that the measured alp values are smaller than the lattice parameter of a relaxed SiC lattice). The shape of *alp*-Q plot changes again when the powder is wetted by water. This is obviously the effect of changes of surface energy (surface tension) of SiC due to interaction with strongly polar water molecules.

Nanocrystalline GaN

Raw powder of 6 nm nanocrystalline GaN shows a decrease of *alp* values measured at low Q. This shape of the plot corresponds to a core-shell model of nanocrystal with a compressed surface shell. The estimated thickness of the shell is around 7Å, the strain is 10-15%. Annealing of the powder leads to a very strong change of measured *alp* values suggesting complete reconstruction of the atomic structure of the surface. The increase of *alp* above the lattice parameter of the relaxed lattice suggests that in the surface shell, there is a combination of tensile and compressive strains.

Nanocrystalline diamond

Raw powder of 10 nm nanocrystalline diamond shows an increase of *alp* values al low Q, what demontrates presence of tensile strain in the surface shell. Evaluated thickness of the shell is 4-5Å, the strain is around 5%. After annealing of the powder the strain disappears.

Summary and conclusion

The *alp*-Q plots demonstrate a strong dependence of the structure of the surface shells of all examined materials. At large Q, above 10-12 [1/Å] the measured *alp* values correspond to lattice parameters of relaxed lattices (that measured for bulk crystals). This is a clear indication that there is no internal pressure generated in the interior of the grains, although there are very strong strains present in the surface of nanocrystals.

Rerefences

[1] B.Palosz, E.Grzanka, S.Gierlotka, S.Stel'makh, R.Pielaszek, W.Lojkowski, U.Bismayer, J.Neuefeind, H.-P.Weber, & W.Palosz, "Application of X-ray powder diffraction to nano-materials; determination of the atomic structure of nanocrystals with relaxed and strained surfaces", *Paper presented at: "Recent research activities in light scattering techniques", 22-24 September 2001, Hamburg, Germany, Phase Transitions - in press*

[2] B.Palosz, E.Grzanka, S.Gierlotka, S.Stel'makh, R.Pielaszek, U.Bismayer, J.Neuefeind, H.-P.Weber, & W.Palosz, "Diffraction studies of nanocrystals: theory and experiment", *(ISSPMS, Ustron-Jaszowiec, 22-29 September 2001), Acta Physica Polonica A, 2002, in press*