

Investigation of the surface stress in SiC nanocrystals by in-situ high pressure powder diffraction technique

B. Palosz¹, S. Stel'makh¹, E. Grzanka^{1,2}, S. Gierlotka¹, Y. Zhao³, and W. Palosz⁴

¹High Pressure Research Center UNIPRESS, ul. Sokolowska 29/37, 01-142 Warsaw, Poland

²Institute of Experimental Physics, Warsaw University, ul. Hoza 69, 00-681 Warsaw, Poland

³Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

⁴USRA/NASA-Marshall Space Flight Center, Huntsville, Alabama 35812, USA

ABSTRACT

The properties of nanocrystals were studied by in-situ high-pressure powder diffraction technique using our methodology of the structural analysis, the "apparent lattice parameter" (*alp*) concept. The experiments were performed for nanocrystalline SiC and diamond powders using synchrotron and neutron sources and hydrostatic or isostatic pressure. Elastic properties of the samples were examined based on the measurements of the lattice parameters and of the reflection width, as well as of interatomic distances. The results show a dual nature of the properties (compressibilities) of the powders indicating a complex, core-shell structure of the grains.

INTRODUCTION

Key properties of nanocrystals are determined by their real atomic structure, therefore a reasonable understanding and meaningful interpretation of their properties requires a realistic picture of the structure. In this paper we show the evidence of a complex response of the lattice distances to pressure indicating a presence of a complex structure of SiC nanopowders.

EXPERIMENTAL DETAILS AND DATA EVALUATION METHODOLOGY

The diffraction measurements were done in HASYLAB at DESY using a Diamond Anvil Cell (DAC) in the energy dispersive geometry, the diffraction vector range up to $3.5 - 4 \text{ \AA}^{-1}$, and pressures up to 50 GPa at room temperature. Larger Q-range was obtained in the angular dispersive geometry using laboratory, MoK α_1 radiation and different pressure media. In-situ high-pressure neutron diffraction measurements were done using the HIPD diffractometer at LANSCE in Los Alamos National Laboratory with the Paris-Edinburgh cell under pressures up to 8 GPa ($Q_{\text{max}} = 26 \text{ \AA}^{-1}$). For measurements under room temperature and normal pressure we used Stations ID11 at ESRF and BW5 at HASYLAB (wavelength 0.1 - 0.2 \AA), and SNBL Station at ESRF (wavelength 0.5 - 0.7 \AA , $Q_{\text{max}} = 15 \text{ \AA}^{-1}$).

As discussed in our earlier publications [1 - 3], evaluation of Bragg-type scattering on nano-size crystals based on standard methodologies is inadequate and may lead to incorrect results. Our method of evaluation of diffractograms of nanocrystals is based on the *apparent lattice parameter* (*alp*) concept, where *alp*'s are the values of the lattice parameters obtained from the Bragg equation but calculated for individual reflections (or groups thereof) [1 - 3]. In this work the analysis of a change/compression of the lattice of SiC on pressure was based on the *alp* values of low index ((111), (220), and/or (311)) reflections. The changes in the grain structure based on Bragg scattering were analyzed by two methods. As illustrated in figure 1, the average

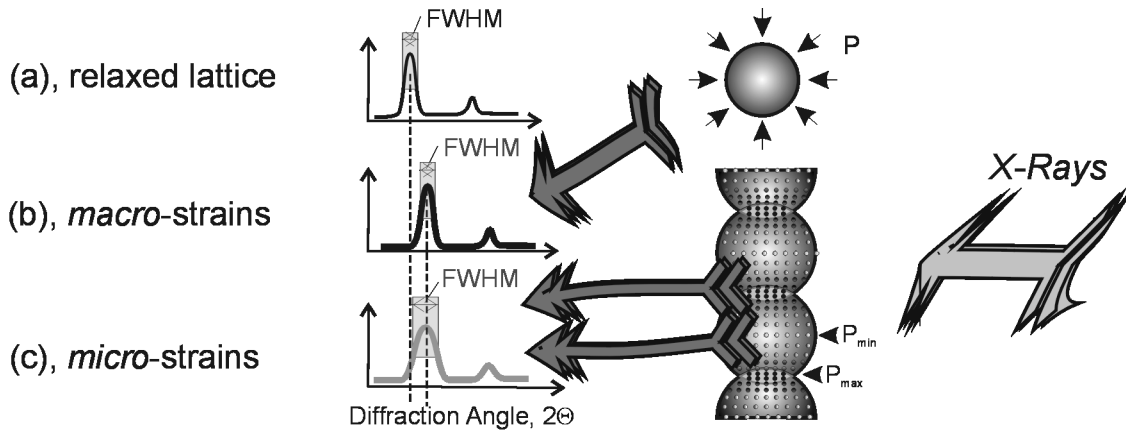


Figure 1. The effect of a presence of *macro-* and *micro-*strains on the Bragg reflections.

lattice parameter of the sample can be determined, in general, from the position of the diffraction peak and provide information about *macro*-strains. Any gradients of the lattice strains lead to broadening of the peaks what can be used to evaluate *micro*-strains in the grains. Figure 1b demonstrates the effect of *macro*-strains developed under hydrostatic pressure, figure 1c the combined effect of *macro-* and *micro*-strains under isostatic conditions. Alternate method is based on splitting the Bragg line into several components (e.g. Gaussian and Lorentzian) as illustrated in figure 2. The components correspond to two fractions of the material being under different stress, e.g. to the interior and the surface of the grain [4, 5]. Interatomic distances were obtained by PDF analysis using the PDFgetN program of Peterson et al. [6].

RESULTS AND DISCUSSION

Response of the samples to pressure based on the position and width of the (111) peak for 8 nm grains of SiC is shown in figures 3a and 3b. Figure 3a shows a relative change of the ap value (i.e. a measure of the average compression of the lattice, *macro* strain) with pressure. Figure 3b shows the accompanying change in the peak width. As can be seen, the changes in the grain structure under isostatic pressure conditions are complex, non-monotonic, and show several regions of different apparent compressibility. Even under hydrostatic pressure conditions both the change of the lattice parameter (*macro*-strain) and of the peak width (*micro*-strain) with pressure deviate from those expected for a uniform and uniformly compressed lattice.

A second indication of a complex structure of nanocrystals, based on splitting the Bragg reflection ((111)) into its Gaussian and Lorentzian components, is shown in figure 4. The results are given for three sizes of SiC grains and show a relative change of the lattice parameter

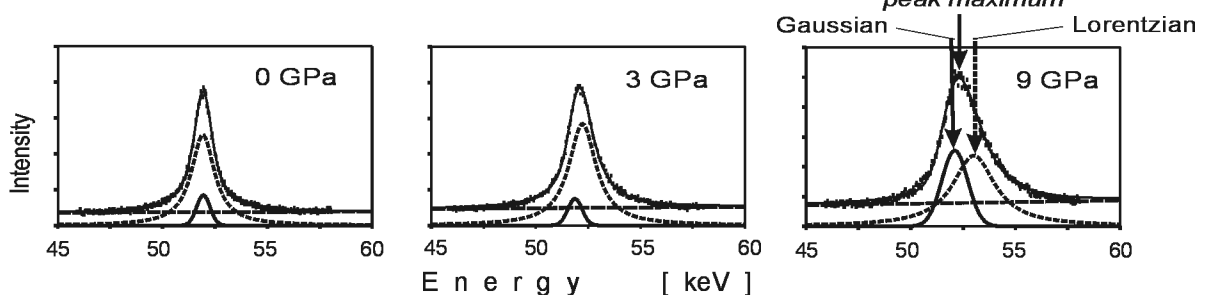


Figure 2. (111) reflection of 10 nm SiC crystal measured under different pressures.

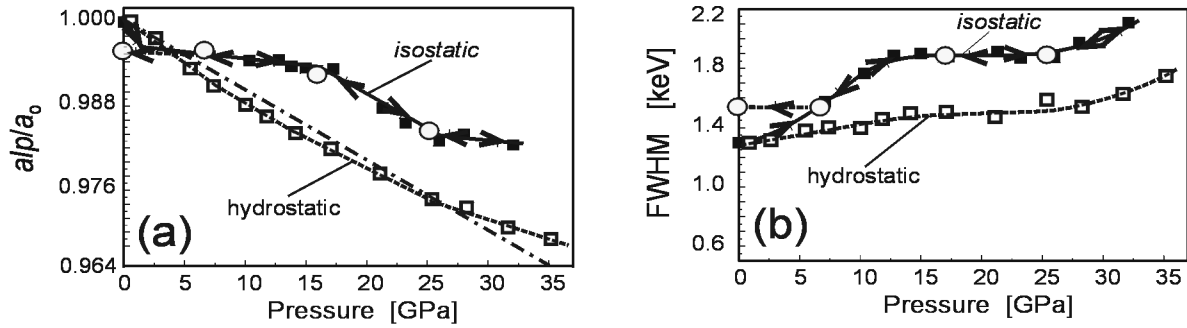


Figure 3. Effect of pressure on strains in 8 nm SiC crystals. (a), *macro*-strains (change of the lattice parameter); (b), *micro*-strains (change of the peak width).

(reflected by the ratio of alp value for (111) reflection to that of the lattice parameter of a relaxed (without pressure) lattice of microcrystalline SiC, alp/a_0) with pressure. The top figures are based on the weighted average positions of the (111) reflection. The bottom figures show the relative change of the alp/a_0 values with pressure separately for each component of the peak. As can be seen, the combined peak is composed of two peaks reflecting two different (apparent) compressibilities. The initial compressibility of the Lorentzian component is similar to that of gold, while that of the Gaussian component resembles compressibility of a diamond or even harder material. The apparent compressibility of each component depends on the pressure range and, as suggested in the figure, it may be expected that at sufficiently high pressure these two components will merge and further compression will become uniform. The split of the compression curve into two components may be interpreted as due to the presence of two phases in the grain. The Gaussian component may be expected to reflect the behavior of the grain core having a uniform crystal structure. The Lorentzian component apparently comes from the part of the crystal subjected to strong stresses from interaction with other grains and resulting in non-uniform strain field in the surface layer.

Another support of a two-phase structure concept of nanocrystals comes from the results presented in figure 5. The figure shows the experimentally determined alp values for three reflections ((111), (220), and (311)) for different pressure conditions. Figure 5a shows the

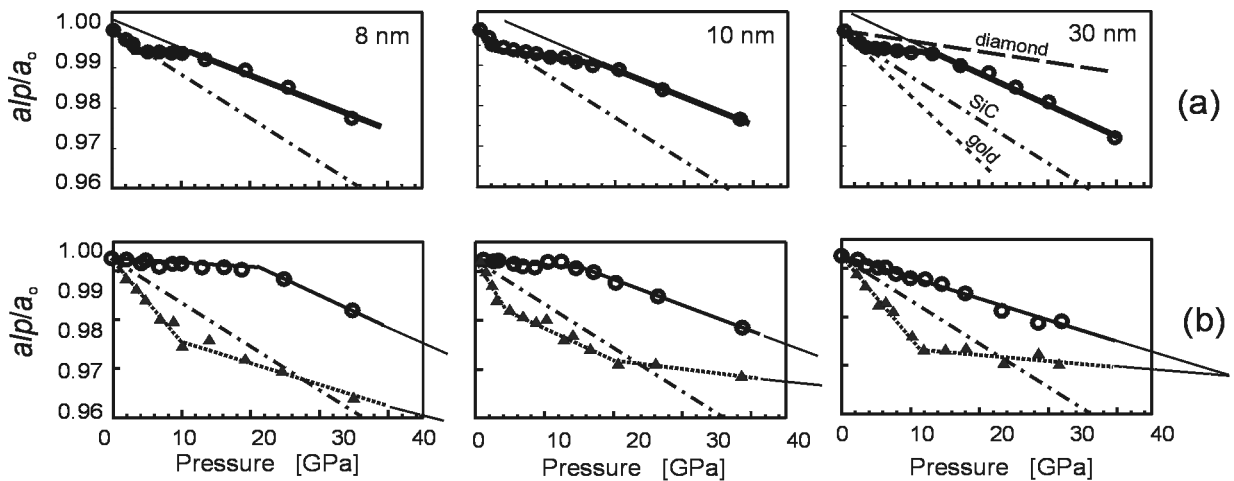


Figure 4. Change of the relative lattice parameter as a function of isostatic pressure for different grain sizes based on (111) reflection. (a), based on weighted average position; (b), based on the positions of the Gaussian (solid line) and Lorentzian (dotted line) components.

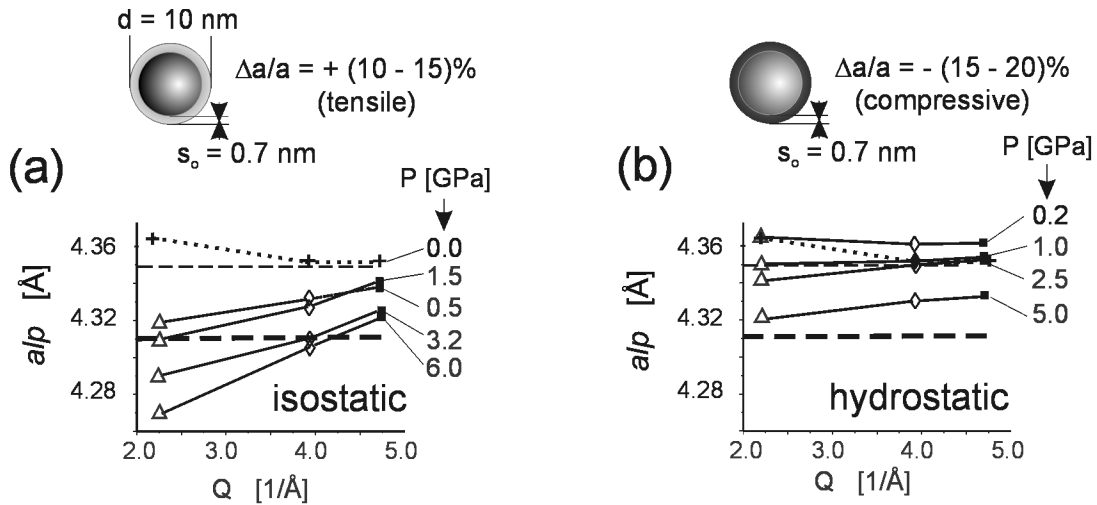


Figure 5. alp - Q plots of 10 nm grain nanocrystalline SiC powder measured under (a), isostatic, and (b), hydrostatic pressure. Dashed lines, lattice parameter of the core of the model (fine lines - for relaxed lattice, thick lines - those calculated from the bulk compressibility of SiC for 5 GPa).

results for isostatic, figure 5b for hydrostatic conditions. As seen from the figures, the character of the alp - Q relation changes with pressure and shows, that a more complete description of the structure of the grains shouldn't be based on changes of a single reflection only. Our interpretation of the changes in the structure was based on comparison of the experimental alp - Q results with those calculated theoretically with the Debye equation for different models of the nanocrystal [4, 5]. Assuming the simplest, centro-symmetric geometry of the grain structure, the alp - Q dependence for the starting material ($P = 0$, crosses and dotted lines in figures 5a and 5b) corresponds to that of the model shown above figure 5a. The grain contains a core with a uniform lattice parameter corresponding to that of a macrosized SiC powder (a_0 , fine dashed lines in figures 5a and 5b). The grain core is surrounded by the surface layer 0.7 nm thick with its lattice expanded by 10 - 15% relative to that in the core. Our modeling showed, that the effect of the surface layer structure on alp is strongest at low Q -values. That is reflected in the figures by the value of alp for the lowest Q ((111) reflection) deviating the most from that of a_0 . As the pressure increases the lattice apparently contracts, again with the largest decrease for alp of the (111) reflection. That indicates that the surface compresses more than the bulk. This is confirmed by the model of the grain under pressure shown above figure 5b; that model yields alp - Q relation corresponding to that under 0.5 GPa of isostatic and 5 GPa hydrostatic pressure.

A similar type of behavior of identical SiC samples under both isostatic (figure 5a) and hydrostatic (figure 5b) conditions provides a clear indication that the origins of changes of alp values with Q have common roots. The change of the shape of alp - Q plot for isostatic compression is much stronger than that under corresponding hydrostatic pressure. That is understandable because stronger stress gradients between core and the surface develop when individual grains are in direct contact. From that we conclude, that the observed difference between alp - Q plots obtained under hydrostatic and isostatic pressures results from a difference in the elastic properties of the grain surface and its core; the surface shell with the initial tensile strain has apparently a larger compressibility (smaller bulk modulus) than the grain core.

A significant role of the surface and its effect on the grain structure is demonstrated also in figure 6. The figure shows the experimentally determined alp values for the first three peaks of

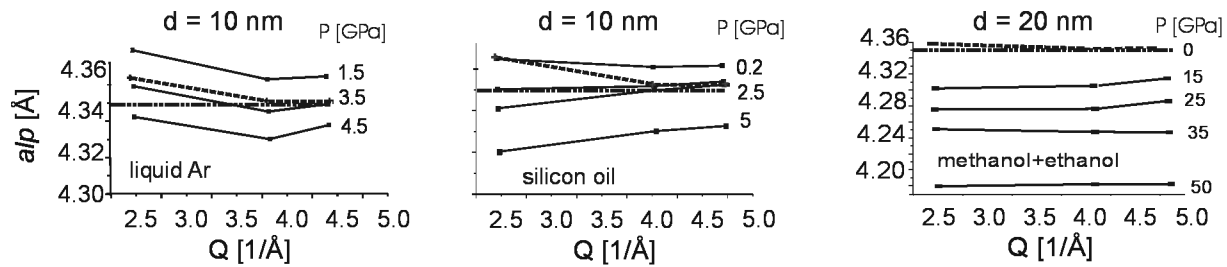


Figure 6. alp - Q relations for SiC under different hydrostatic pressures for various liquid media. Dashed lines, in the air, dashed-dotted lines, the lattice parameter of microcrystalline powder.

SiC diffractograms under different pressures. All pressure experiments were performed under hydrostatic conditions but using different liquid media (liquid argon and silicon oil for 10 nm grains, and methanol-ethanol mixture for 20 nm sample, figure 6). As seen in the figures, the environment of the powder has a profound effect on the structure of the grains, different for different media and reflected in different and variable changes of alp with pressure for different peaks. Even under some pressure (1.5 GPa for liquid Ar, 0.2 GPa for silicon oil) the grain lattice is under tensile strain relative to a regular, micron-size SiC powder. That tensile strain is apparently not confined to the surface layer only (as is obviously the case in the air), but extends to the grain bulk as well. At very high pressures (50 GPa for methanol+ethanol medium) the material apparently homogenizes structurally and the resulting alp values for different peaks become similar, as expected (compare with figure 4).

Further evidence of the complex structure and structural changes of the lattice with pressure was obtained by PDF analysis of neutron diffractograms of SiC samples. Figure 7 shows the experimentally determined dependence of several interatomic distances on (isostatic) pressure. R_1 and r_7 are distances between unlike atoms (C-Si), r_2 and r_6 between same atoms (C-C, Si-Si), as shown schematically to the left of the graphs. The arrows in the graphs mark the value of a given distance in the relaxed lattice (micrograin crystals). As seen in the graphs, the interatomic distances undergo complex, non-monotonic changes with a change in pressure. R_1 and r_2 exhibit an initial increase with a maximum at 0.3 - 0.4 GPa. That maximum seems to correspond to the pressure at which the SiC chains start to break. (That interpretation is consistent with the results of our Low Angle Neutron Scattering experiments where an apparent breaking of the SiC chains was observed about 0.5 GPa [7].) It is interesting, that even at substantial pressures a considerable relaxation of the lattice may take place. That behavior is not that surprising given

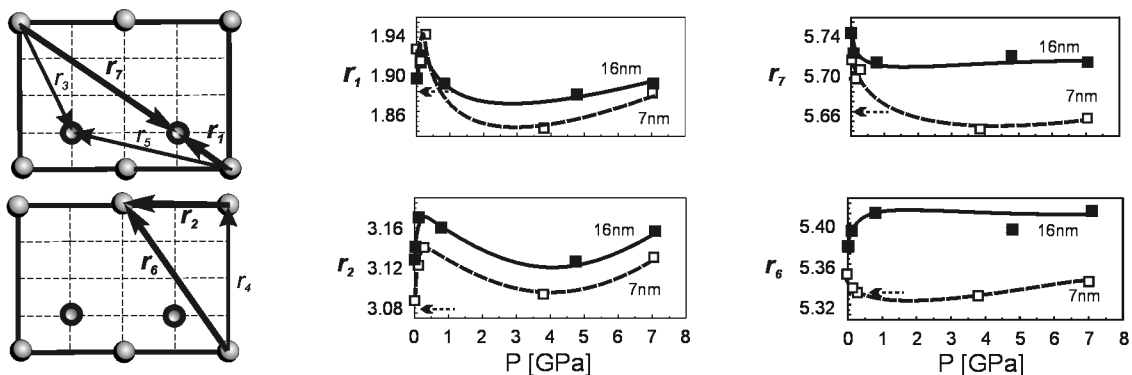


Figure 7. Dependence of interatomic distances on pressure in SiC nanocrystals. The arrows mark the interatomic distances in the relaxed lattice.

the fact that even under the pressure of a few GPa the relative density of the sample is only about 60%. As expected, the changes in the distances with pressure are more pronounced for smaller grains. For r_6 even the character of change with pressure for smaller grains (7 nm) is different than for the larger ones (16 nm). The difference in the effect of pressure on r between smaller and larger grain powders can be explained using a two-phase, core and shell model of a nanograin. It is reasonable to assume that the thickness of the surface layer is little dependent on the size of grains. Therefore, as the diameter of the grain goes down, the relative weight of the surface layer in the overall (average) structure and related properties of the material increase.

CONCLUSIONS

The results presented in the paper show, that the structure and related properties (compressibility) of nano-size crystallites are rather complex and cannot be realistically described using simple parameters adequate for larger (micro-size) crystals. Based on our results for silicon carbide nanopowders (and similar results for nanodiamond) the materials have the features of two phases, each with its distinct elastic properties. These complex structures are present both under ambient as well as under high pressure (isostatic, hydrostatic) conditions and require non-standard methodology of the materials characterization and description.

ACKNOWLEDGEMENTS

This work was supported by the Polish Committee for Scientific Research, the Polish-German Project POL-00/009, and in part by the EC Grant "Support for Centers of Excellence". Experimental assistance from the staff of the Swiss-Norwegian Beam Lines at ESRF is gratefully acknowledged. Support of the Office of Biological and Physical Research of NASA and of the US Department of Energy/LANL-LANSCE (project # 2002060) is greatly appreciated.

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