

X-ray powder diffraction study of atomic structure of nanocrystalline SiC and Diamond materials

E. Grzanka^{1,2}, B. Palosz¹, S. Gierlotka¹, S. Stel'makh¹, R. Pielaszek^{1,2},
U. Bismayer³, J. Neufeind⁴, P. Jovari⁴, W. Palosz⁵

¹High Pressure Research Center, Polish Academy of Sciences, Sokolowska 29/37, 01 142 Warsaw, Poland

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

³Mineral-Petrographisches Institut, Uni Hamburg, Grindelallee 48, D-20146 Hamburg, Germany

⁴HASYLAB at DESY, Notkestr. 85, D-22603 Hamburg, Germany

⁵USRA/NASA-Marshall Space Flight Center, Huntsville, Alabama 35812, USA

Keywords: nanocrystals, surface structure, diffraction

Abstract. A considerable fraction of atoms in nanosize particles is at the grain surface (due to the small size of the crystals). We assume that the surface atoms form a separate structural phase relative to the bulk of the grain (the core). Therefore, one set of the lattice parameters characterizing a nanocrystal may be inadequate for a unique description of its structure. An alternate evaluation of diffraction data of nanoparticles, based on the “apparent lattice parameter” is proposed. Based on this new methodology it is shown that real nano-crystals constitute a complex, more than a one-uniform-phase structure.

Introduction

Since the surface atoms have different surrounding and their interatomic distances may differ from those in the bulk material, one set of lattice parameters for a nanocrystal may be inadequate for a unique description of its structure. Accordingly, application of lattice parameters concept, when used for characterisation of the structure of nanocrystals, has to be modified [1,2]. We suggest a replacement of the lattice parameters, describing the dimensions of the unit cell, by a set of different values of the “lattice parameters” associated with (determined from) each individual Bragg reflection, each at its specific diffraction vector Q . In [1,2] we have shown that from the plots of the “*apparent lattice parameter*” (αp) vs. diffraction vector Q one can draw conclusions about the modification of the interatomic distances at the surfaces relative to the bulk. Preliminary experimental evidence shows that in GaN and SiC nanocrystals tensile surface strain exists [1,2].

Nanocrystals with non-uniform structure

The surface atoms of crystals are subjected to a highly asymmetrical interaction field as opposed to those in the bulk, so their spacings may be expected to be different than those in the interior of the crystallite. Usually those surface atoms constitute only a small fraction of the crystal and their effect on the overall properties of the material can be ignored. The situation is different in the small, nano-size particles where, due to their size, a considerable fraction of the atoms forms the surface of the grain. Assuming that the surface shell has the thickness of 1 nm, a 10 nm diameter grain contains 25% of its atoms in the surface layer, while a 4 nm grain has 60% of such atoms. That shows that, in very small objects the number of surface-related atoms can exceed the number of the “bulk” atoms. That leads to unique properties of these materials. Therefore, in a meaningful research on nanocrystals the surface layer (the shell) should be treated as a separate structural phase relative to the bulk of the grain (the

core). We believe that the grain surface is a real three-dimensional object that has its own characteristic atomic arrangement.

In this work we applied the model of a nanocrystal where the grain core has a uniform crystallographic structure and is unambiguously characterized by the lattice parameter a_0 . We assumed that the atomic structure of the surface is strongly correlated with the parent structure of the grain: it is basically the structure of the core but centro-symmetrically deformed, compressed (Fig. 1) or expanded due to a presence of the surface strain. The surface strain can extend over several interatomic distances in the direction normal to the surface [3-6].

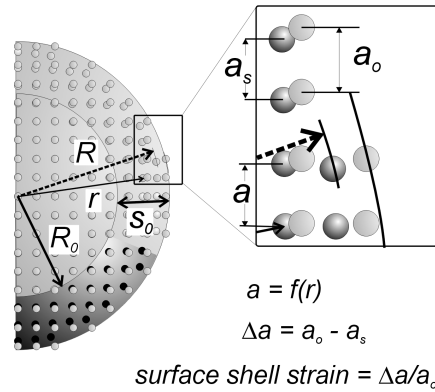


Fig 1. Tentative model of a nanocrystal with strained (compressed) surface layer. R_0 , radius of the core; R , radius of the grain; s_0 , thickness of the surface layer; r , distance from the center; a_0 , interatomic distance in the relaxed lattice; a_s , interatomic distance at the surface.

According to the model, the term "lattice parameters" may not be applied to the whole nanocrystal nor to the surface layer. No common, specific interatomic distances can be assigned to the surface shell. However, to simplify the description of the model, we introduce the parameter a_s which corresponds to the interatomic distances at the outmost atomic layer of the particle (Fig. 1). Assuming that the arrangement of the atoms in the surface shell is similar to that in the grain core, the value of a_s can be expressed as a fraction (in %) of the lattice parameter a_0 . The actual values of the interatomic distances within the surface shell can be expressed as a function of the distance from the particle center and may vary between a_0 in the grain core (at distances $r < R_0$) and $a_s = a_0 \pm \Delta a$ (for $r = R$). The sign in front of Δa depends on whether the surface is compressed (–) or expanded (+) relative to the grain core. The ratio $\Delta a/a_0$ is quantifying the surface strain.

Based on new approach ($alp - Q$ plots) to the elaboration of powder diffraction data of nanocrystalline materials we performed a systematic theoretical study of diffraction by nanocrystalline materials using models with different thickness of the surface layer, various magnitudes of the surface strain, and diverse gradients of the strain in the shell [1,2]. Example of $alp-Q$ data determined from theoretical diffraction patterns calculated [7] for different models of SiC nanocrystals are shown in Fig. 2. The sensitivity of the alp values on the parameters of the model is quite high: differences as small as 1% in the lattice strain are clearly visible (Fig. 2). Although in all models the lattice parameter of the grain core is the same ($a_0 = 4.349 \text{ \AA}$ - relaxed lattice) the alp values practically never reach a_0 except for greater Q 's and larger surface strains. This shows that conventional diffraction experiments (low intensity laboratory sources, CuKa or MoKa, maximum Q range of 7 and 15 \AA^{-1} , respectively, elucidation of the common lattice parameters from the entire diffraction diagram) do not allow for a unique interpretation of the lattice parameters calculated from the Bragg reflections.

Determination of alp values for individual reflections which, for small crystallites, are broad and overlap, is not always unique and often impossible. Therefore, we suggest an alternate elaboration of powder diffraction patterns of nanocrystals based on a refinement of the lattice parameters for

selected ranges of the diffraction pattern, i.e. lattice parameters calculated not for individual but for groups of reflections.

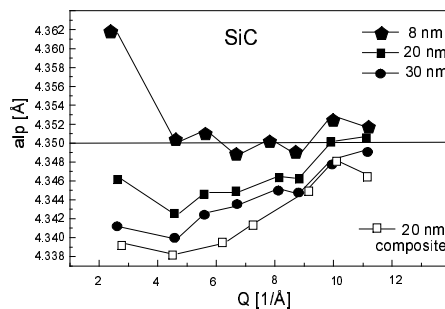
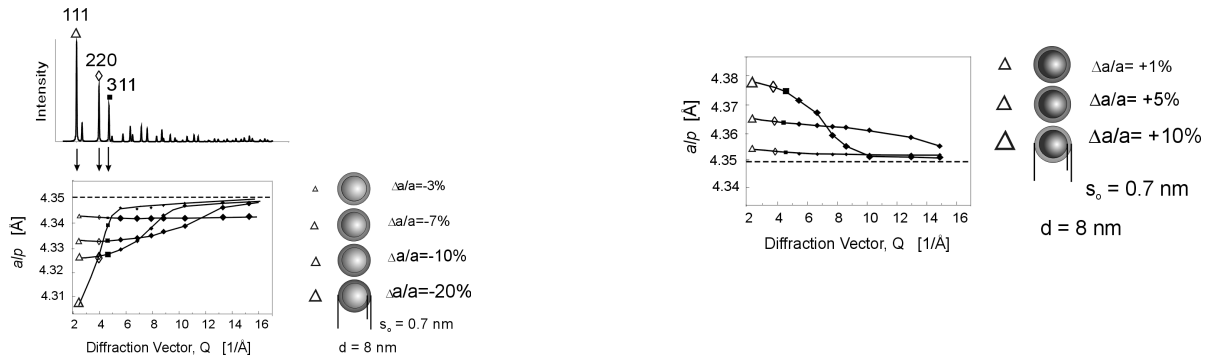
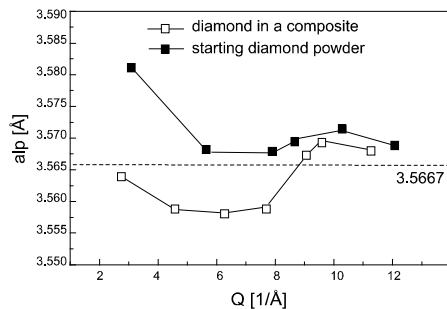
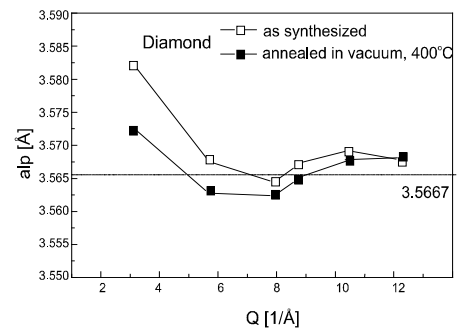


Fig. 2. Alp - Q plots calculated theoretically for spherical 8 nm diameter SiC nanocrystals for different strain values in the surface shell.

Fig. 3: Alp plots of SiC nanopowders with different grain sizes compared to that of SiC grains in nanocomposite SiC-Diamond



(a)



(b)

Fig. 4: (a) Comparison alp plots of nanocrystalline diamond powders to the alp plot of nanocrystalline diamond in a composite material: the average crystallite diameter of both materials is 12 – 15 nm. (b) Comparison alp plots of nanocrystalline diamond powders as synthesized to the alp plot of nanocrystalline diamond annealed in vacuum in 400°C; grain size of this diamond powder is 5 nm.

Experiment

We applied our methodology for evaluation of the experimental diffraction data of different nanocrystalline powders. The powder diffraction patterns in the range up to $Q = 16 \text{ \AA}^{-1}$ were obtained using a short wavelength synchrotron radiation sources (at BW5 Station at HASYLAB). At the present

stage of our studies we can claim a qualitative agreement between the *alp*-Q plots determined from the experimental powder diffraction data of nanocrystalline SiC and diamond, and our theoretical calculations. For example, we deduced that a tensile strain exists in the surface shell of nanocrystalline SiC (compare Figs. 2 and 3). Similar strain is present in diamond nanoparticles.

The surface of a nanoparticle is in a metastable state and, thus, is strongly dependent on its surrounding. The surface exposed to a gas, liquid or solid medium can adsorb foreign atoms or even undergo a chemical reaction. When that happens the properties of the surface change accordingly, what is widely used in catalytic reactions and sorption processes. Interaction of the surface with foreign atoms must affect the atomic structure of the surface. We have examined this problem in a series of experiments performed for nanocrystalline powders of diamond and SiC. The powders were annealed at elevated temperature under vacuum used as components of ceramic composites. Representative plots of the *alp* values vs. the Q vector are given in Figs. 3 – 4b.

Desorption of foreign atoms from the powders apparently leads to a considerable contraction of the surface shell (relative to the raw material, aged in the air) as indicated by the reduction (in the *alp* values) in the low Q range (Fig. 4b). Similar effect is observed when the environment of the grains changes to a dense matrix of the composite (Fig. 4a).

The experiments performed on differently processed nanocrystalline SiC and diamond show very clearly that the structure of the surface shell in nanocrystals depends strongly on the amount and type of foreign atoms adsorbed on the grain surface. This observation is not surprising: our DTA and mass spectroscopy measurements showed that during annealing of raw powders of SiC and diamond in a vacuum and/or inert gas atmosphere the materials lose up to 10% of their initial weight. Apparent changes of the grain surface environment during densification and sintering into dense ceramics leads to changes in the atomic structure of the surface shell (Figs. 3 – 4b).

In this work we did not attempt to achieve a quantitative evaluation of the observed changes of *alp* values with Q; additional measurements of specific physical properties of our materials are necessary to examine what kind of changes occur at the surface and how much they affect the structure of the grain core. The *alp* concept provides sensitive tool for investigation of the structural features of very small, nano-sized crystallites. From our preliminary calculations based on the models of nanocrystals with different surface strain and thickness we conclude that annealing of diamond powders leads to a significant reduction in the strain present in the surface shell without much change of the structure of the grain core. This is indicated by the strongest changes of the *alp* occurring in the low Q range (which is very sensitive to the structure of the surface shell) and a convergence of the *alps* of raw and processed powders at larger Q values (Fig. 3). The *alp*-Q dependence for nanocrystals of SiC in the form of a powder and in the composite with diamond show very similar shapes but the *alp* values measured for the composite environment are lower than those for the powder even at the wide Q range (Fig. 4).

Summary and conclusions

For very small, several nm in diameter crystallites the number of atoms at the surface can exceed the number of atoms in the grain core. The structural and other properties of the surface atoms can dominate over the effects imposed by the bulk atoms. This effect is clearly observed in our diffraction experiments.

The results of our experimental work presented in this paper are only preliminary. A more definite description of the structure of nanosize particles requires both additional examination of the physical properties and structure of the materials (using techniques sensitive to the local atomic configuration, like Raman or IR spectroscopy) and more extensive modeling efforts that would include different strain fields both in terms of strength and distribution in the surface and core of the grain. That includes the non-monotonic nature of the *alp*-Q relations observed in Figs. 3 – 4 which may be

due to the anisotropic shape of the real grains and/or the grain size distribution. The work on these issues is in progress.

We have demonstrated a qualitative agreement between the experimental results and those obtained by numerical modeling using our *alp* concept methodology.

Acknowledgements

This work was supported by the Polish Committee for Scientific Research - grant PBZ/KBN-013/T08/30, the Polish-German Project POL-00/009 and in part by the EC Grant "Support for Centers of Excellence" No. ICA1-CT-2000-70005, DESY - HASYLAB Project II-99-053.

References

- [1] B. Palosz, E. Grzanka, S. Gierlotka, S. Stel'makh, R. Pielaszek, W. Lojkowski, U. Bismayer, J. Neufeind, H.P. Weber, W. Palosz, Phase Transitions, in press
- [2] B. Palosz, E. Grzanka, S. Gierlotka, S. Stel'makh, R. Pielaszek, U. Bismayer, J. Neufeind, J.F. Janik, HASYLAB Annual Report, 605, (2000)
- [3] Lennard-Jones, J.E.; Dent, B.M.: The change in Lattice Spacing at a crystal boundary, Proc. Royal. Soc. A **121** (1928) 247-259.
- [4] Molière, K.; Rathje, W.; Stranski, I.N.: Surface structure of ionic crystals. Discuss. Faraday Soc. **5** (1949) 21-32.
- [5] Alder, B.J.; Vaisnys, J.R.; Jura, G.: Penetration depth of surface effects in molecular crystals. J. Phys. Chem. Solids **11** (1959) 182-189.
- [6] Sanders, P.G.; Withey, A.B.; Weertman, J.R.; Valiev, R.Z.; Siegel, R.W.: Residual stress, strain and faults in nanocrystalline palladium and copper. Materials Sci. Eng. **A204** (1995) 7-11.
- [7] Pielaszek, R.; Gierlotka, S.; Stel'makh, S.; Grzanka, E.; Palosz, B.: X-Ray Characterization of Nanostructured Materials. Diffusion and Defect Forum **208-209** (2002), in press.