Atomic force microscopy studies of cubic BC_2N, a new superhard phase

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New nanocrystalline materials recently synthesized under high pressure and temperature [1–3], exhibit extremely high hardness. Nanocrystalline BC_2N (c-BC_2N) phase was found to be the second hardest material (76 GPa [4]) after diamond (115 GPa [5]). The nature of the high hardness of c-BC_2N is not understood yet. Hardness of hard materials is mainly determined by atomic structure (bond density, bond length, and degree of covalent bonding) of the materials [6–9], leading to a correlation between hardness and value of shear modulus [6]. Brillouin scattering (BS) measurements of the elastic properties of a millimeter-size c-BC_2N sample revealed that it had moderate elastic moduli [10] and demonstrated that the high hardness of BC_2N was not determined only by its elastic properties. The shear modulus of the new phase measured by BS (238 GPa) is lower than that predicted from hardness measurements (447 GPa, [4]) using the correlation between hardness and shear moduli characteristic for hard materials [6]. The other factor that can significantly increase hardness may be related to the granular structure [11, 12]. For metal, the hardness increases with decreasing grain size as $1/\sqrt{a}$ (where a is the grain size). This phenomena is called the Hall–Petch effect [11, 12]. The granular structure of the c-BC_2N phase has not been investigated yet, and here we report the results of atomic force microscopy studies of the nanostructure of the new of cBC_2N phase.

A transmission electron microscopy (TEM) study [4] indicated that the size of the c-BC_2N crystallites ranges from 10 to 30 nm; but the TEM images do not show sharp contrast at grain boundaries, and grains are overlapped. Because c-BC_2N is an insulator, the sample requires coating for imaging by scanning electron microscopy (SEM). Atomic force microscopy (AFM) allows one to study nanostructure of solids [13, 14] without coating.

The polycrystalline bulk cBC_2N sample was synthesized according to Solozhenko *et al.* [1, 15] by direct conversion of graphite-like $(BN)_{0.48}C_{0.52}$ solid solution at 25 GPa and 2100 K using a large-volume multianvil system and the Sumitomo 1200-ton press at the Bayerisches GeoInstitut. Detailed information on the synthesis of the cBC_2N can be found elsewhere [1, 15, 16].

The surface morphology was visualized by AFM in the flat area of the specimen. The AFM (Nanoscope III) was used in contact imaging mode to obtain constant-force topographic images. Both silicon and silicon nitride cantilevers were used, with approximately 10-nm and 20-nm tip curvature radius, respectively (Digital Instruments, USA).

AFM images of the surface of the c-BC_2N phase were taken in contact mode using a silicon nitride cantilever. As illustrated in Fig. 1, grains of approximately 200 nm are clearly seen in the images. The average grain size was measured to be 189 ± 66 nm and 225 ± 87 nm in the 2-μm size image (Fig. 1b) and in the 5.2-μm image (Fig. 1a) respectively. To make the appearance of the grain boundary sharper in the 5.2-μm image, we used a high-pass filter. Fig. 2 shows the effect of applying a high-pass filter to the original topographic image (Fig. 1a). A filter generally applies a matrix of multiplying coefficients to alter the value of each pixel in relation to its nearest neighbors. In the case of a high-pass filter, this gives more weight to fine, sharp details on the surface at the expense of the underlying larger scale topography. As illustrated in Fig. 2, this operation is partially successful in showing the grain boundaries. The average grain size in 5.2-μm size image (Fig. 1a) agrees reasonably well with that shown in the 2-μm size image: however it is nearly 10 times higher than the value of the grain size obtained from TEM measurements.

To explain the grain-size discrepancy with TEM results, we have imaged the surface of the c-BC_2N phase using a silicon cantilever with a small tip curvature radius (∼10 nm). The AFM images obtained in the

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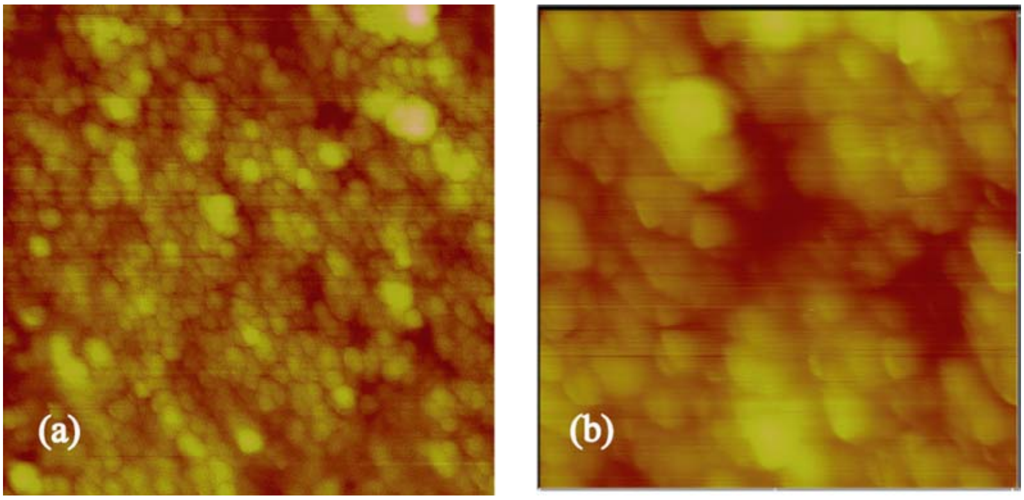

Figure 1 Contact mode AFM images of the c-BC_2N sample. The scan areas and data scales (heights) for images are: (a) 5.2 × 5.2 μm, and 195 nm; (b) 2.0 × 2.0 μm, and 106 nm, respectively.

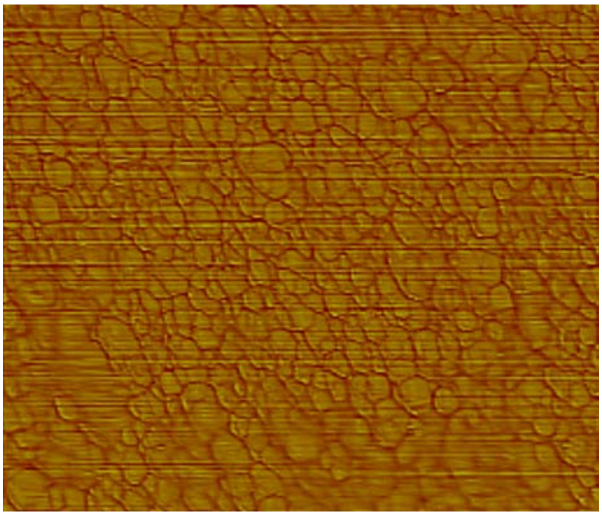

Figure 2 AFM images with enhanced boundaries between grains after application of the high-pass filter to the image (a) in Fig. 1.

tapping mode are shown in Fig. 3. Grains seen in the tapping mode images are approximately the same size (200 nm) as those seen in the contact mode images (Fig. 1). It is also apparent (Fig. 3b) that grains have the fine structures observed elsewhere [15]. It is possible that the fine structure seen inside the grain can be attributed to small crystallites of 20–30 nm, which are combined into larger aggregates (∼200 nm).

Recently, Musil and Regent [17] found that the hardness of NiCr-N films increased with a decreasing grain size down to 7 nm (Hall–Petch effect). It was further demonstrated that when it reaches a maximum for smaller grains, the film hardness decreases [18]. Schiotz *et al*. also showed that a relatively large grain size (200 nm) enhanced the hardness of the nanocrystalline metals [19]. It might be of interest to carry out a comparative study of the hardness of the new phase with different grain sizes and to measure hardness of the single c-BC_2N grain using AFM with a diamond tip [20].

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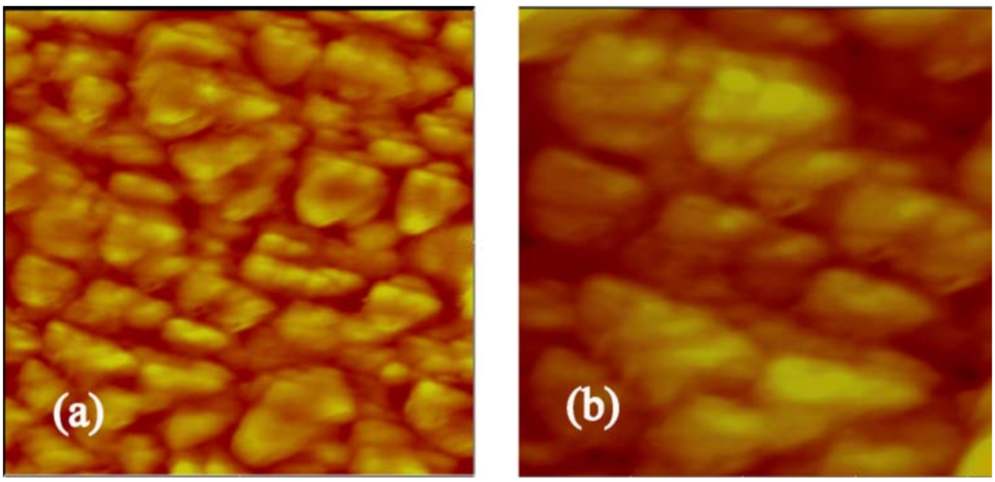

Figure 3 Tapping mode AFM images (amplitude) of the c-BC_2N sample. The scan areas for images are: (a) 2 × 2 μm and (b) 1 × 1 μm.

bulk cBC_2N samples. Multianvil experiments were performed at the Bayerisches Geoinstitut under the EU "IHP—Access to Research Infrastructures" Program.

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