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On twinning in ultrahard nanocrystalline cubic boron nitride

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Microstructure of bulk nanocrystalline cubic boron nitride synthesized at 20 GPa and 1770 K has been studied by scanning and high-resolution transmission electron microscopy. The material is characterized by high density of twins with average size of 5.5 nm, and multiple stacking faults within the twin domains that results in the exceptional material hardness.

Keywords: cubic boron nitride, transmission electron microscopy, nanotwinning

Cubic boron nitride (cBN) is a superhard phase that is half as hard as diamond [1] but with much higher chemical and thermal stability [2] that makes it a material of choice for a wide range of industrial applications [3].

Creation of nanostructures by extreme pressure–temperature conditions leads to significant increase of hardness of superhard materials [4-6], mainly due to the Hall–Petch effect [7,8]. The first synthesis of single-phase nanocrystalline cBN was performed in 2012 by direct solid-state phase transformation of graphite-like BN with "ideal random layer" (turbostratic) structure at 20 GPa and 1770 K [9]. The material showed very high Vickers ($H_V = 85(3)$ GPa [9]) and Knoop ($H_K = 63(2)$ GPa [10]) hardness and fracture toughness ($K_{Ic} = 10.5$ MPa·m^{1/2} [9]). Later synthesis of ultrahard cBN-based nanostructured material ("nanotwinned" cBN) has been reported [11], however, extremely high Vickers hardness (up to 108 GPa) claimed by the authors is obviously overestimated [12,13]. In the present Letter we report the microstructure of ultrahard nanocrystalline cubic boron nitride from transmission electron microscopy (TEM) studies.

Single-phase nanocrystalline bulks of cubic boron nitride have been synthesized in a LPR 1000-400/50 Voggenreiter press with Walker-type module at 20 GPa and 1770 K by direct phase transformation of turbostratic graphite-like BN according to the method described elsewhere [9].

High-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) studies were performed using a JEOL 3000F microscope. Sample lamella was

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prepared by focused ion beam lift-out procedure [14] using a FEI Nova NanoLab 600 dual beam scanning electron microscope. After lifting out, the lamella was thinned to electron transparency (50-100 nm).

A characteristic STEM image recorded in low angle annular dark field (LAADF) mode is presented in Fig. 1. STEM LAADF images provide crystal orientation contrast, thus highlighting individual grains and crystal twins. An average grain size of 41 nm was measured using dark field TEM.

HRTEM images showing the twin structure are displayed in Fig. 2 as exemplified for a single cBN grain. Crystal orientations in each twin segment are identified and labeled in Fourier transform images. All twin interfaces are found on the $\{111\}$ planes. Twins are formed in all grains, and the observations revealed no apparent change in the twin density from grain to grain, with high density of stacking faults within the twin domains. Thicknesses of 60 twin segments in 5 different grains measured by HRTEM were below 12 nm, with a mean twin thickness of 5.5 nm.

The nanotwins formed in the course of the solid-state turbostratic-to-cubic phase transformation in boron nitride significantly improve the material strength and hardness by formation of twin boundaries that are much more stable against dislocation migration than conventional grain boundaries [15], and by generation of multiple stacking faults. Thus, creation of nanotwinned structures of superhard phases can be considered as a prospective route to design novel ultrahard materials.

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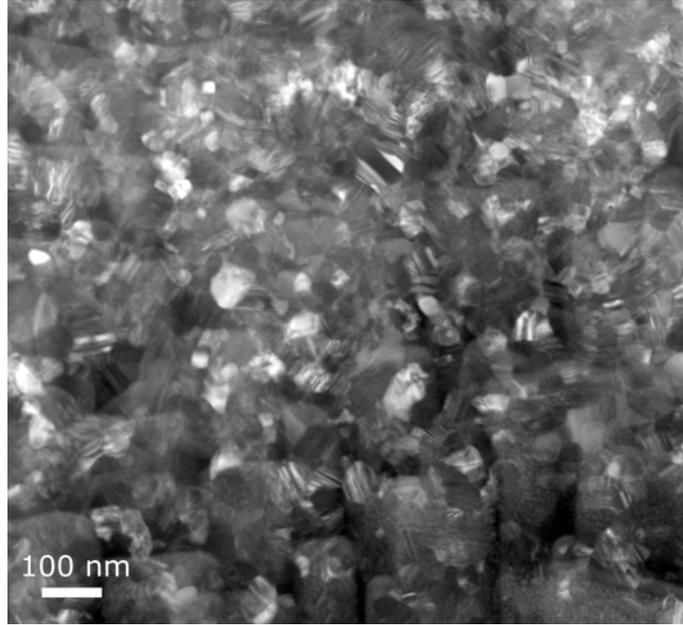


Fig. 1. Scanning transmission electron microscopy (STEM) low angle annular dark field (LAADF) image of bulk nanocrystalline cBN. Image contrast relates to crystal lattice orientation, thus highlighting grain and twin structure.

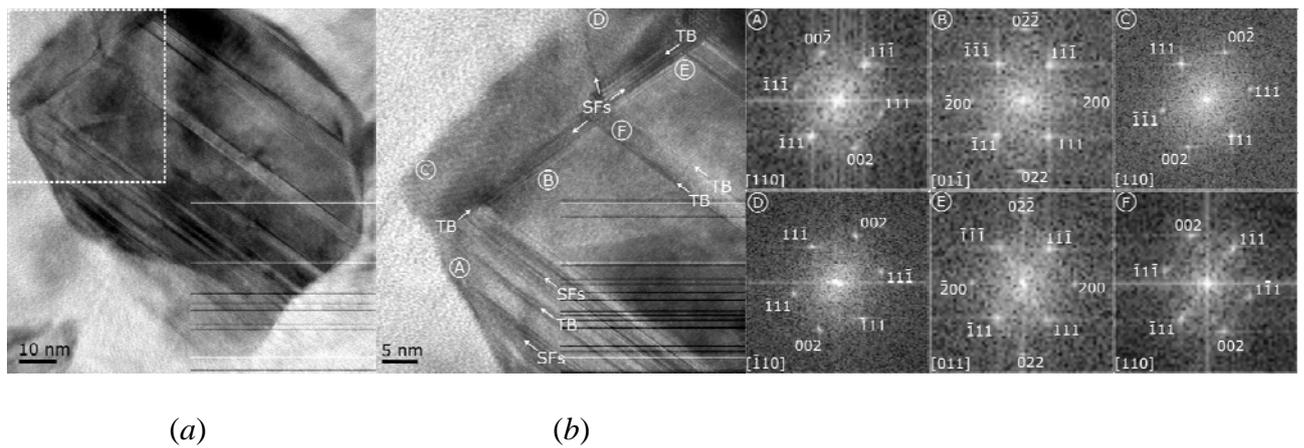


Fig. 2. High resolution transmission electron microscopy (HRTEM) image of a single nano-cBN grain with multiple twin segments: (a) overview of the grain and (b) atomic resolution image of a portion of the grain where six of twin segments are labeled A through F. Stacking faults (SFs) and twin boundaries (TB) are marked. Lattice orientations (relative to the electron beam) of the twin segments are shown in the Fast Fourier Transforms (FFT) images. The horizontal lines in the lower right quadrant of the two HRTEM images are artifacts from the microscope camera.