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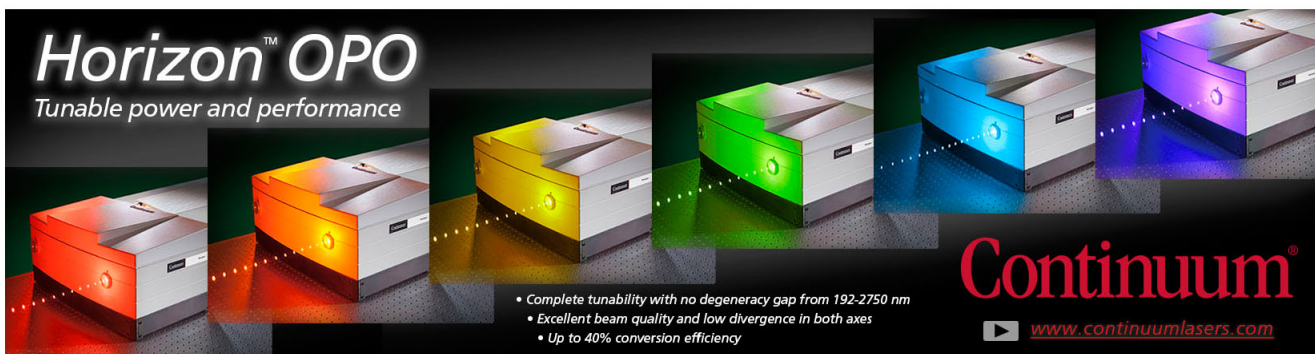J. Appl. Phys. **108**, 073503 (2010); 10.1063/1.3471818

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Elastic properties of nanopolycrystalline diamond: The nature of ultrahigh stiffness

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Recent experimental reports on the production of nanopolycrystalline diamond with outstanding mechanical stiffness highlight the importance of theoretical investigation of this unusual effect. Here, we provide the comprehensive theoretical investigation of such material. We traced the evolution of the nanopolycrystalline diamond stiffness characterized by bulk modulus with the grain size increasing up to 10 nm and found samples with bulk modulus higher than that of diamond. We studied nature of such specific behavior and proposed a mechanism of stiffening in nanopolycrystalline diamond which could explain reference experimental results. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4931493]

Superhard materials (diamond, c-BN, etc.) attract a special interest in the modern material science. The possible fabrication of material harder than diamond (ultrahard materials) can create a new branch in science and technology due to a high potential to extend the boundaries of applicability of devices and tools based on them and to effectively process superhard materials. There are generally two branches in this field of research: amorphous carbon materials based on graphite or fullerite[1–4] and nanopolycrystalline diamond (NPD) with its hardness depending on the grain size. Most likely, only NPDs with a grain size of ∼10 nm can display hardness higher than that of diamond.[5,6] Unlike hardness, elastic stiffness of an NPD has always been reported to be lower than that of bulk diamond, but in the experimental work,[7] an NPD with superior mechanical rigidity was observed. This result was related to the appearance of a hexagonal diamond in the NPD structure.[7,8] While not neglecting the fact that twin boundary and lonsdeilite-type interface can significantly increase the hardness and stiffness of the structure,[5] it should be noted that usually nanopolycrystalline diamonds with an amorphous grain boundary are fabricated.[9,10] The question about the possible ultrahigh stiffness in such kind of NPD still remains under debate.

Here, we theoretically investigated in details the elastic properties of nanopolycrystalline diamond with crystallite sizes up to 10 nm. By analyzing the contributions from grains with the diamond structure and amorphous interface, we obtained the dependence of the NPD bulk modulus on the average size of crystallites which was fully supported by atomistic simulation of a few NPD models. Despite of a very good correspondence between the analytical and computational data, several structures with ultrahigh stiffness were found that did not fit the predicted trend. We investigated the nature of such specific behavior and proposed a mechanism of ultrahigh stiffening which could explain the reference experimental results.

For a theoretical study of the atomic structure and mechanical properties of the proposed models of nanopolycrystalline diamond, the empirical many-body Brenner potential[11,12] was used. The simulations were performed using a LAMMPS molecular dynamics software which allows the consideration of systems consisting from thousands to millions of atoms. The undoubted advantage of this method is the possibility of modeling a large system with sufficiently high calculating speed. The bulk modulus (B_0) was calculated by applying hydrostatic deformations to the investigated structure. The B_0 was obtained by fitting a parabola to the thus obtained energy versus strain data. To evaluate the accuracy of the chosen approach, the corresponding characteristics of bulk diamond were calculated. The bulk modulus of diamond was determined as $B_0 = 457$ GPa, which corresponds well with the experimental values of 445 GPa (Ref. 13) and 442 GPa.[14]

The bulk modulus of nanopolycrystalline diamond depends on the grain and interface sizes. We consider the bulk modulus of NPD (B_0^{NPD}) with volume V, as an average of grain B_0^{grain} and interface $B_0^{interface}$ bulk moduli contributions with volumes V_{grain} and $V_{interface}$, respectively,

$$B_0^{NPD} = \frac{B_0^{grain}V_{grain} + B_0^{interface}V_{interface}}{V}. \quad (1)$$

The eligibility of this approach for the considered case is justified by localized character of C-C bonds. Its reliability is also validated by the study of local rigidity in silicon nanocrystals[15] where separate contributions from grains and interface were taken into account.

The general behavior of Eq. (1) can be estimated assuming the spherical shape of the grains with a radius R.[10] In this case, the volumes of the grain and interface in the NPD may be estimated as $V_{grain} = \frac{4}{3}\pi R^3$ and $V_{interface} = 4\pi R^2 d$ (here d is thickness of the interface). The bulk modulus of the grain B_0^{grain} can be taken with the specified degree of accuracy as bulk moduli of a diamond single crystal B_0^D, whereas

$B_0^{interface}$ can be considered as the bulk modulus of diamond-like carbon B_0^{DLC} assuming the amorphous nature of the interface between the neighbored grains in NPD.[16] Therefore, Eq. (1) can be rewritten as

$$B_0^{NPD} = \frac{B_0^D R + 3dB_0^{DLC}}{R + 3d}. \qquad (2)$$

This model predicts that the NPD stiffness monotonously tends to the bulk diamond value and cannot overcome it at any crystallite size, the same as in previously developed theories.[16] To see this, we present the atomistic calculations and compare them with the prediction of Eq. (2).

We create an atomistic model of an NPD supercell containing grains of random sizes and orientations separated by grain boundaries with atomic-size thickness (see Fig. 1). This method, although considerably demanding computationally, allows to reach a good statistical accuracy.

At the initial stage of model construction, the central points were randomly distributed in a cubic supercell. These points were used for building the Voronoi cells which were filled by a randomly oriented diamond structure. After that, the system was annealed at 700 K, which led to redistribution of the bonds at the edges of the cells and formation of the grain boundary. Finally, the structure was relaxed by a conjugate gradient method.

The computed bulk modulus dependence is shown in Fig. 2. According to Eq. (2), B_0^{NPD} monotonically tends to the bulk modulus of a diamond single crystal. The predicted trend can be directly compared with the results of atomistic simulations. We choose the following parameters for the equation: B_0^D is taken as 457 GPa from Ref. 17, thickness of the grain boundary is taken as a minimal possible value of a single diamond unit cell 0.356 nm, which is justified by our computations and reference experimental data.[9,10] B_0^{DLC} is dependent on the fraction of sp^3 bonds in the structure,[18,19] and to avoid this ambiguity, we assume the absence of graphitization in the interface (100% of sp^3 bonds), which
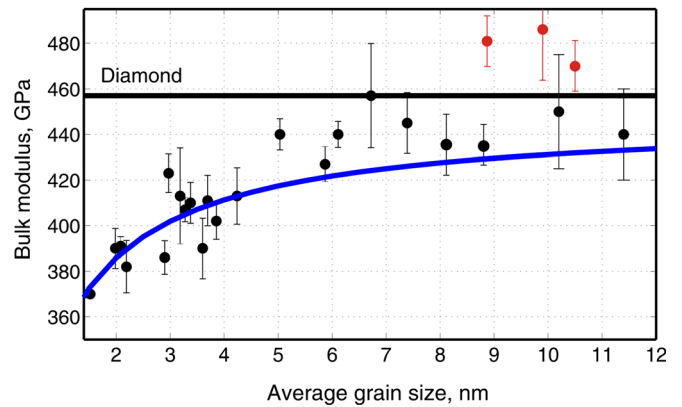
FIG. 2. Dependence of bulk modulus of polycrystalline diamond on the average crystallite size; the solid line is obtained from Eq. (2). The bulk modulus of the single crystal diamond is marked by horizontal black line.

allows us to set the value of B_0^{DLC} as 350 GPa from Ref. 19. The obtained dependence is presented in Fig. 2 as a solid line.

A good correspondence between the analytical and computational data validates the main contribution of the grain and interface volume fraction ratios to the bulk modulus-grain size dependence. Nevertheless, several points (marked by red in Fig. 2) locate outside of the predicted dependence and display stiffness surprisingly higher than that of bulk diamond by ~5%.

To explain the origin of ultrahigh stiffness, the behavior of the grain atomic structure at isotropic deformation during calculation of the bulk modulus was investigated. It was obtained that the grains of ultrastiff NPD display an anisotropic response to hydrostatic stress with a ratio between the lowest and the highest strain rates from 1% to 1.5%. As an example, Fig. 3(a) presents a slice of NPD in which such ratio for the central grain is about 1%. Therefore, it can be concluded that the contribution to the bulk modulus of the whole structure made elastic constant of the grain differ from isotropic bulk modulus with value larger than B_0^D, which leads to the higher total NPD bulk modulus. To check how the anisotropic deformation affects the value of elastic constant of the grains, we calculated the elastic constant of bulk diamond with the same kind of strain (see Fig. 3(b)). We found out that the values of the elastic constant of diamond agree well with the corresponding values of the grains.

The increase of mechanical stiffness is characterized not by a specific atomic structure of the grains, but by their distinct shape and environment leading to the above-described anisotropic response to isotropic strain which can be considered as a unique property of nanopolycrystalline materials. It should be noted that in the reference experiment[7] it was observed that an NPD containing grains with similar size displayed the elastic constant growing by the same order of 5% as in our proposed theory. We can speculate that the main contribution to ultrahigh stiffness of such nanopolycrystals is also made by the unusual response of the individual grains to the applied deformation.

The results we obtained show that the bulk modulus of nanopolycrystalline diamond monotonously increased with increasing the average grain size (at least up to 10 nm).
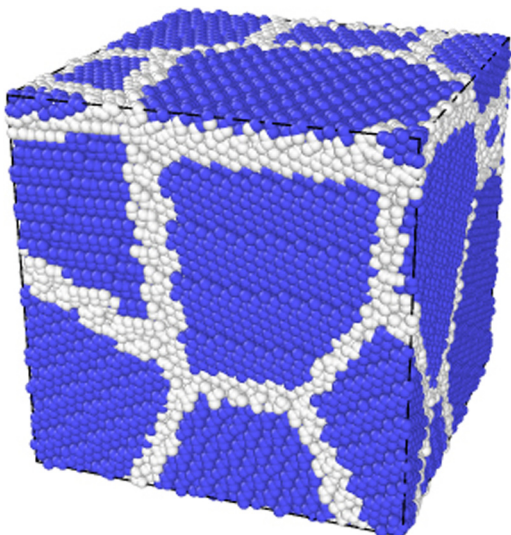

FIG. 1. An example of an NPD structure used in the simulation. The presented supercell contained 4 grains with an average size of 50 Å. The grains and interface are colored by blue and white colors, respectively.
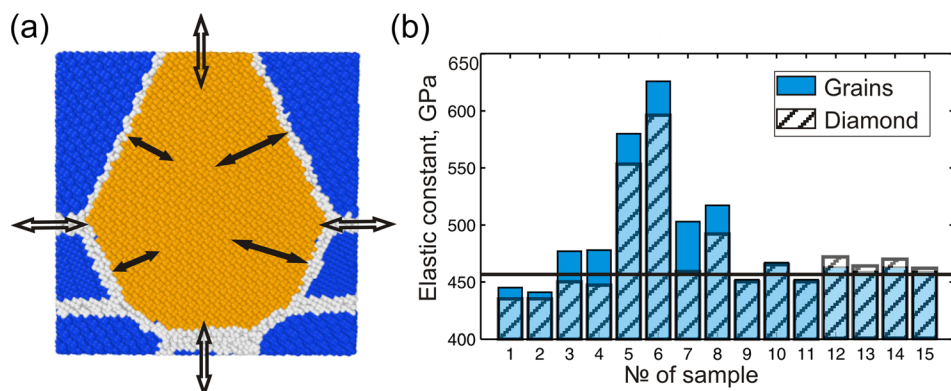
FIG. 3. (a) An example of anisotropic response of the grain atomic structure to hydrostatic stress. The external deformation and deformation of individual grains are depicted by transparent and black arrows, respectively. The arrows length represents the strain rate; (b) elastic constant of different grains (solid bars) and the corresponding value of elastic constant for diamond (crosshatched bars) for the same anisotropic deformation. The bulk modulus of the single crystal diamond is marked by horizontal black line.

Such kind of dependence can be decomposed on dependencies of bulk moduli of grains and interface on their particular size, which in turn can be equated to bulk moduli of single-crystal diamond and amorphous diamond-like carbon, respectively. If we simplify the problem to the grains with a spherical shape, the resulted equation can be well fitted to the atomistic simulation using the reference experimental and theoretical data. A good correspondence between the analytical and computational data validates that changes in the volume fraction of interface and grains in a nanopolycrystal make the dominant contribution to the total bulk modulus-grain size dependence. Nevertheless, several points locate outside the predicted dependence and display stiffness surprisingly higher than that of bulk diamond. Such a behavior of NPD mechanical properties was explained as anisotropic response of the particular grains to the hydrostatic stress which can be considered as a mechanism of stiffening in nanopolycrystalline diamond, whereas the correspondence with the reference experimental data holds out a hope that the predicted effect could be realized in nature.

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