Ultrasmall diamond nanoparticles with unusual uncompressibility

Mikhail Popov[1,2,3,*], Valentin Churkin[1,3], Danila Ovsyannikov[1], Almaz Khabibrakhmanov[1,3], Alexey Kirichenko[1], Elena Skryleva[2], Yury Parkhomenko[2], Mikhail Kuznetsov[1], Sergei Nosukhin[1], Pavel Sorokin[1,2,3], Sergey Terentiev[1], Vladimir Blank[1,3]

[1]*Technological Institute for Superhard and Novel Carbon Materials, 108840, 7a Tsentralnaya, Troitsk, Moscow, Russian Federation*

[2]*National University of Science and Technology MISiS, 119049, Leninskiy prospekt 4, Moscow, Russian Federation*

[3]*Moscow Institute of Physics and Technology State University, 141700, Institutskiy per. 9, Dolgoprudny, Moscow Region, Russian Federation*

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*e-mail: mikhail.popov@tisnum.ru

Based on experimental and theoretical studies, the 607 GPa bulk modulus of nanodiamond 2-5 nm was determined, which significantly exceeds the bulk modulus of diamond crystals (443 GPa) and approaches the values typical of ultrahard fullerite (600-1000 GPa). Bulk modulus of nanodiamond 2-5 nm was experimentally measured by piezospectroscopy using a diamond anvil cell with anvils made of synthetic diamond with a high (~ 60%) ^{13}C isotope content. The Raman frequency in such diamond is at 1306 cm^{-1} and does not interfere with the recording of a peak at 1325 cm^{-1} of nanodiamond 2-5 nm. The bulk compression modulus was calculated from the dependence (Fig. 1) of the displacement of two Raman bands at 1325 cm^{-1} and 1600 cm^{-1} (the latter does not apply to sp^2 bonds) [1] of nanodiamond 2-5 nm on pressure up to 68 GPa. Simulation of nanodiamond 2-5 nm (diamond quantum dots) confirms experimental results and also predicts rise of bulk modulus with decrease of dots size. Analysis of simulated structures suggest possible explanation of observed effect due to increasing contribution of surficial compressed bonds when dots size reduces.

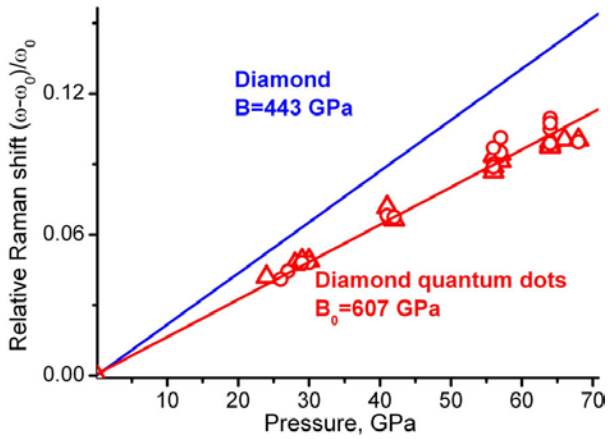

Fig. 3. Experimental data on the relative Raman shift $(\omega-\omega_0)/\omega_0$ (relative frequency) dependence on pressure for diamond quantum dots with ω_0=1325 cm^{-1} (marked with triangles) and with ω_0=1600 cm^{-1} (marked with circles; one as shown in [1] does not apply to sp2 bonds), and their least-squares fit line. For comparison, there is a straight line corresponding to the relative frequency dependence on pressure for a diamond single crystal with ω0=1333 cm-1.

In order to elucidate reasons of nanodiamonds stiffening we investigated the mechanical properties of nanodiamonds theoretically in the wide size region. Obtained dependence of bulk modulus upon the nanodiamonds size is presented in the Fig. 2. The pronounced increasing of the B_0 with the structure size reduction coincides well with the experimental observation whereas with clusters enlarging B_0 approaches to the corresponding value for bulk diamond. Both AIREBO and Tersoff potentials give similar dependencies that verifies obtained results. the surface and near-surface bonds are shorter than in bulk diamond (1.46 – 1.53 Å) and as soon as shorter bonds are stronger, they mainly contribute to the stiffening of the diamond dot. On the other hand, minor presence of elongated bonds (1.56 – 1.62 Å) cannot significantly affect the resulting nanostructure stiffness.

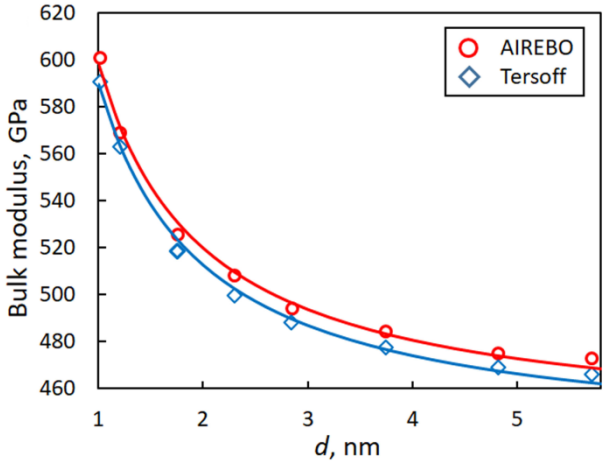

Fig. 2. Results of the theoretical investigation. Size-dependence of diamond nanoclusters bulk modulus calculated using AIREBO and Tersoff potentials (marked by circles and diamonds, respectively). Obtained data was fitted by hyperbolic curves.

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[1] M. Popov, V. Churkin, A. Kirichenko, V. Denisov, D. Ovsyannikov, B. Kulnitskiy, I. Perezhogin, V. Aksenenkov,V. Blank, *Nanoscale Research Letters* 2017, **12**, 561.