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Pressure-Induced Transformation of Graphite and Diamond to Onions

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Abstract: In this study, we present a number of experiments on the transformation of graphite, diamond, and multiwalled carbon nanotubes under high pressure conditions. The analysis of our results testifies to the instability of diamond in the 55–115 GPa pressure range, at which onion-like structures are formed. The formation of interlayer sp^3-bonds in carbon nanostructures with a decrease in their volume has been studied theoretically. It has been found that depending on the structure, the bonds between the layers can be preserved or broken during unloading.

Keywords: onions; carbon; high pressure

1. Introduction

On the basis of experimental data, we have recently proposed a new phase diagram of carbon with a region of diamond instability in the 55–115 GPa pressure range [1,2]. In this range, the data on shock compression of single-crystal graphite [3] indicate formation of a phase denser (by 2%) than diamond. At pressures less than 55 GPa and above 115 GPa, graphite transforms to diamond. No diamond formation in the intermediate pressure range is observed, while graphite transforms to onion-like structures [4]. Multiwall carbon nanotubes (MWCNT) also transform into onions with layers cross-linked by sp^3-bonds at around 65 GPa [5]. For comparison, the outer shells of MWCNT form some sp^3-hybridized regions at pressures below 50 GPa [6]. In this case, the inner layers of the nanotubes are retained. In shock wave experiments, diamond formation from MWCNT was observed at a pressure of $\leq$50 GPa and temperature of 1500 °C [7,8]. According to the data on shock compression of graphite [3], formation of a phase denser than diamond is observed at 55–100 GPa (at a temperature of about 3000 K). However, the structure of this phase is underinvestigated.

The existence of denser phases should lead to a loss of stability in diamond [9,10], which was also observed in [1–3]. The loss of stability of diamond can be initiated by a critical shear stress at room temperature. In [11], a phase transformation from diamond to the intermediate carbon phase was observed [12], the latter being composed of graphene plates cross-linked by sp^3-bonds.

The transition was stimulated by additional stresses applied to the compressed diamond anvils with torque by rotation of the anvil around the anvil's axis; the maximal shear stress approached 55 GPa during rotation under a hydrostatic part of the stress tensor around 40 GPa [11].

The aim of this work is to study the onion-like structures that are formed in the diamond instability region in the 55–115 GPa pressure range.

2. Materials and Methods

We used a shear diamond anvil cell (SDAC) for our high-pressure study. In the SDAC, controlled shear deformation was applied to the compressed sample by rotation of one of the anvils around the anvil's symmetry axis [13]. Pressure was measured from the stress-induced shifts of the Raman spectra from the diamond anvil tip [14]. The sample (graphite or MWCNT) was placed in a hole of a pre-pressed tungsten gasket without any pressure-transmitting media. We used the samples made of synthetic single-crystal graphite. The MWCNT were synthesized using a chemical vapor deposition procedure [15]. To study the diamond stability, we used a diamond with a mean crystal size of 25 nm produced at the Microdiamant AG (Lengwil, Switzerland). The diamond grain size must be much bigger than 2–5 nm when quantum confinement effect is not significant. As a result of quantum confinement effect, a bandgap of nanodiamond increases in the 2–5 nm size interval, along with discrete energy levels arising at the band edges. In a case of covalently bonded solids, the bandgap growth means an increase in the chemical bond energy which means an increase in elastic moduli. Indeed, bulk modulus of the 2–5 nm nanodiamond is around 560 GPa, while bulk modulus of the 25 nm diamond being identical to bulk diamond (443 GPa) [16].

On the other hand, the smaller the grain size, the larger the specific surface area that is the source of structural instability. The mixture of 25 nm nanodiamond and 25 wt % of NaCl as a pressure-transmitting media was placed in the gasket hole. The mixture has been preliminary treated in a planetary mill. A Fritsch planetary mill with ceramic silicon nitride (Si_3N_4) bowls and balls of 10 mm in diameter was used. Treatment in a planetary mill provides preparation of homogeneous nanocomposites without contamination by material of the balls [16]. The Raman spectra were recorded with a Renishaw inVia Raman microscope, excitation wavelength 532 nm (Renishaw plc, New Mills, Wotton-under-Edge, Gloucestershire, UK), and a TRIAX 552 (Jobin Yvon Inc., Edison, NJ, USA) spectrometer, equipped with a CCD Spec-10, 2KBUV Princeton Instruments 2048 $\times$ 512 detector and razor edge filters (excitation wavelength 257 nm). The transmission electron microscope (TEM) studies were done by a JEM 2010 high-resolution microscope (JEOL Ltd., Tokyo, Japan).

Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential was used [17] to theoretically study the atomic structure and mechanical properties of the proposed models. Simulation was carried out using the LAMMPS software package for molecular dynamics (Sandia National Laboratories, Albuquerque, NM, USA), which allows calculating structures containing up to 10^6 atoms. An undoubted advantage of this method is the ability to simulate huge systems with a sufficiently high calculation speed and acceptable quality.

3. Results

3.1. Onion Formation from Graphite and MWCNT

The Raman spectra of the initial graphite and MWCNT samples are characterized by a G-band at 1581 cm^{-1}. A disorder-induced D-band in fact is absent in both samples (Figure 1a). The graphite or MWCNT samples were loaded into a shear diamond anvil cell (SDAC), and their Raman spectra (Figure 1b) were studied in situ.

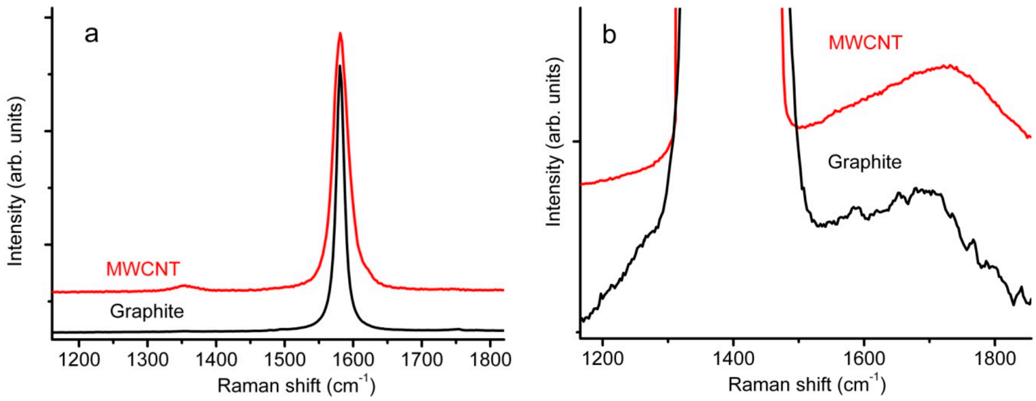

Figure 1. (**a**) Raman spectra of the initial samples of graphite and MWCNT; (**b**) Raman spectra of the samples of graphite and MWCNT under a 62 GPa pressure (note the Raman G band shifts to ~1700 cm^{-1}). A part of the spectra between 1310 cm^{-1} and ~1490 cm^{-1} is covered by the stressed diamond anvil.

Pressure dependences of the Raman G-band of graphite and MWCNT (Figure 2) are quite similar. Both dependences are linear below 25–30 GPa. With further increase in pressure, both dependences display the instability of sp^2-bonding [18] at a pressure above 30 GPa. Slowing in the change of Raman frequency indicates that the graphite and MWCNT structures become unstable at pressures above 30–35 GPa.

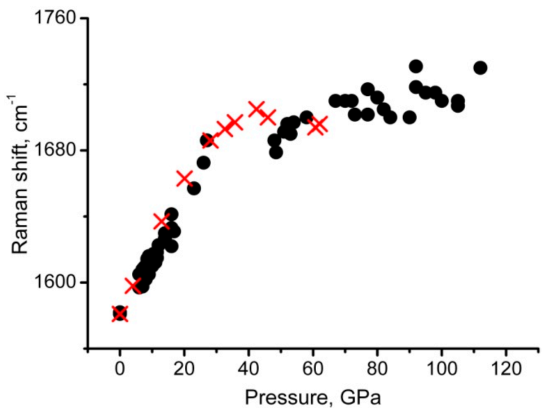

Figure 2. Pressure dependences of the Raman G-band of graphite (circles) and MWCNT (crosses).

Application of shear deformations in the beginning of the instability region (around 30–35 GPa) activates the phase transition. In the case of graphite we observe a phase transition to diamond [19]. If we use MWCNT, the outer shells of the nanotubes form some sp^3-hybridized regions [6]. In this situation, the inner layers of the nanotubes are retained.

According to the results of our simulation, the onion-like structures containing sp^3-bonds have a density higher than that of diamond in the 50–100 GPa pressure region. Consequently, their formation is preferable in comparison to diamond in this pressure range [9,10].

The results of the simulation are confirmed by the TEM studies. Figure 3 illustrates the onions obtained from graphite and MWCNT. The resulting structures have some common features: an onion with radial disorders (linear defects) responsible for the formation of sp^3-bonds.

The defects indicated by arrows in Figure 3 are formed inside the sp^2 network and are bound by sp^3-bonds. This was first reported in Refereces [20,21]. The relative content of these defects in the onion structure (carbon onion) is small compared to sp^2-hybridized carbon, so the presence of these defects with sp^3-bonds does not lead to appreciable changes in the EELS spectra obtained by us.

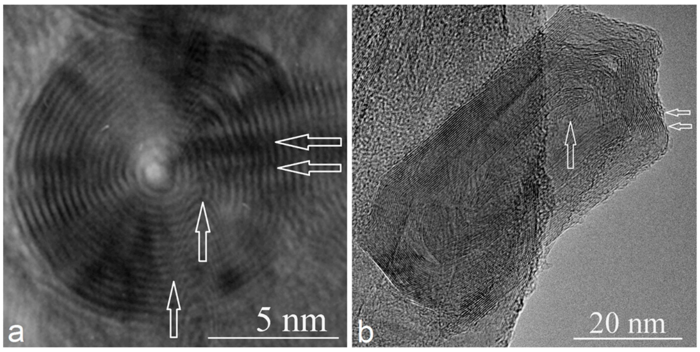

Figure 3. Onions formed from different precursors. (**a**) An onion obtained from graphite at 70 GPa. The arrows denote linear and point defects. There is a splitting of some graphene layers in multi-layered onions. According to [20,21] in the places of splits, the atoms of adjacent layers join and form sp^3-bonds; (**b**) An onion obtained from MWCNT. The horizontal arrows indicate the radial disorders (linear defects) responsible for the formation of sp^3-bonds, the vertical arrow points to the fragments of nanotubes inside the onion.

3.2. Onion Formation from Diamond

The presence of a 55–115 GPa diamond instability region in the phase diagram of carbon indicates the possibility of phase transformations of diamond into onion-like structures. However, in view of the large hysteresis of the phase transitions in carbon [9] and the high strength of diamond, activation of the phase transition by application of shear strains in a SDAC is a technically challenging problem [11]. The transition of diamond to onion-like structures can be facilitated if the size of the diamond particle is close to the ~20 nm size of the onions formed in this pressure range. The choice of diamond grain sizes is discussed in more detail in the Materials and Methods section.

The mixture of 25 nm nanodiamond and 25 wt % of NaCl as a pressure-transmitting media was placed in the gasket hole. The Raman band of the diamond loaded in a NaCl medium to 52 GPa is located at 1483 cm^{-1}, which is appropriate to the known data [22]. The Raman band of diamond shifts from 1333 cm^{-1} to 1483 cm^{-1} under a 52 GPa pressure. The stress tensor conditions in the diamond sample differ from the ones in the diamond anvils, so the Raman band of the diamond loaded between the anvils is separated from the Raman band of the diamond anvil [22]. An increase in pressure from 52 GPa to 57 GPa leads to the disappearance of the diamond Raman band (Figure 4) under the influence of laser radiation (the Raman spectra were registered when excited by a 1 mW laser beam with a 532 nm wavelength focused to a 1–2 µm spot). The G-band does not appear in the spectra (according to Figure 2, one could be expected around 1700 cm^{-1} at pressure ~60 GPa). Under ambient conditions, the same irradiation does not lead to degradation of diamond powder with a 25 nm grain size.

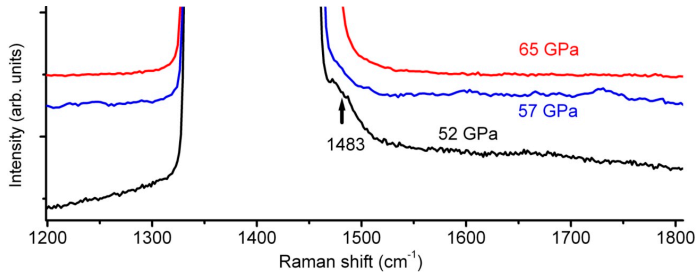

Figure 4. Raman spectra of the 25 nm diamond under a 52 GPa pressure, and the disappearance of the Raman band under 57 GPa. A part of the spectra between 1330 cm^{-1} and $\geq$1460 cm^{-1} is covered by the stressed diamond anvil.

For a more detailed study of the observed effect, four samples of the 25 nm diamond in a NaCl medium were loaded to pressures of 57, 60, 70, and 120 GPa, respectively. The samples were irradiated under pressure by a 15 mW laser beam with a 532 nm wavelength focused to a 1–2 μm spot in steps of 2 μm for 100 s in each position. The grain temperature of the 25 nm diamond in NaCl could reach 2000–3000 K.

The diamonds irradiated at a pressure of 120 GPa are preserved without any noticeable changes in the phase composition. The diamonds irradiated at 57, 60, and 70 GPa are transformed into onions. Figure 5 depicts two types of onions created from diamond under 57 and 60 GPa, and the onion-like structures with nuclei of 5 nm nanodiamonds in the center obtained under laser radiation at a 70 GPa pressure (Figure 6a). The latter structure could be also considered as 5 nm nanodiamonds covered by a few graphitized layers of carbon created from a 25 nm nanodiamond. Nevertheless, comparison of Figures 5 and 6 prompts consideration of the structures presented in Figure 6a as onion-like structures with nuclei of 5 nm nanodiamonds in the center. The images of the initial 25 nm diamonds are provided for comparison (Figure 6b). No graphitized layers of carbon can be seen on the surface of the initial diamonds.

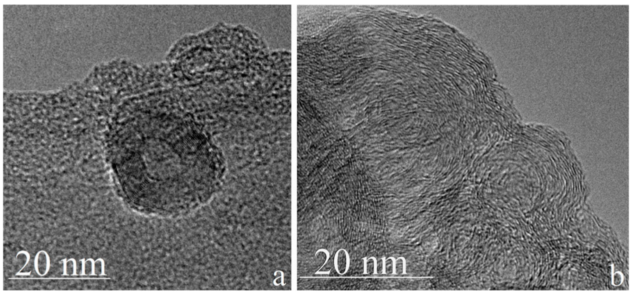

Figure 5. Onions, formed from diamond: (**a**) onion created from diamond under 57 GPa; (**b**) onion-like structure created from diamond under 60 GPa. This onion type corresponds to the simulation results.

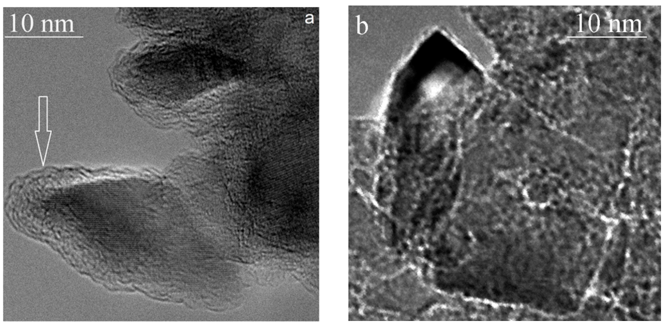

Figure 6. (**a**) onion-like structures with nanodiamond nuclei (of around 5 nm) created from 25 nm diamond under a 70 GPa pressure (the onion-like structure is marked with an arrow); (**b**) initial 25 nm diamonds.

4. Discussion

There are various traditional methods for producing carbon onions. For example, carbon onions are synthesized using the high-energy electron irradiation of carbon particles [23], annealing of nanodiamonds [24], an arc discharge between two graphite electrodes submerged in water [25], the carbon-ion implantation of silver [26] or copper [27] substrates, etc. In recent years, the onions have been obtained under high-pressure conditions. For example, carbon onions made by four different methods, three of them using high-pressure techniques, have been investigated in [28]. In the present work, we continue investigations of the onions obtained using high pressures.

We have studied two types of onion structures that demonstrate different behavior under the stress. We designed onions containing interlayer sp^3-bonds built on C_{20} and C_{36} fullerenes. We investigated stability of the four-layered structures C_{36}@C_{144}@C_{324}@C_{576} and C_{20}@C_{80}@C_{180}@C_{320}.

Figure 7 shows the energy dependence on the volume of intermediate structures during the onion–nanodiamond transition. We observe that the behavior of the two nanostructures under investigation is fundamentally different. In particular, the onions containing the chemically active C_{20} fullerene in their center (orange curve) tend to retain the energy-favorable sp^3-hybridized interlayer bonds. Consequently, these onions remain in a compressed state even after unloading. This is due to the fact that such a sequence of fullerene shells is obtained with a ~2.5 Å distance between the layers, which is much less than the interlayer distance in graphite (3.4 Å). While in the structure containing some interlayer sp^3-bonds their lengths are ~1.6 Å, with an increase in the number of layers this value tends more and more toward the characteristic bond length in cubic diamond (1.54 Å). The appearance of a local minimum of the dependence near 0.92 V/V_{onion} in the figure is explained by the fact that the fourth layer of the transition structure at this point is already at a distance significantly exceeding the characteristic length of the carbon sp^3-bond, while the three-layer nucleus still contains some interlayer bonds.

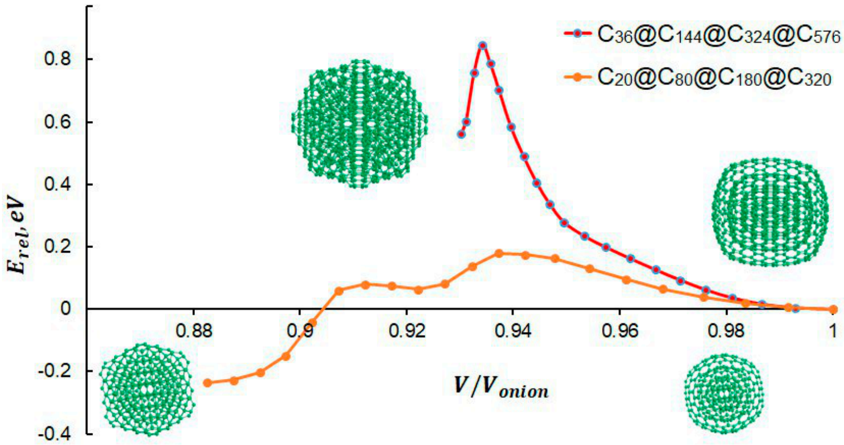

Figure 7. Behavior of the onion structures under pressure. The *x*-axis represents the volume of structures constructed with respect to the volume of the onion sp^2-hybridized structure. Along the *y*-axis, we plot the energy (per atom) given with respect to the energy of the onion sp^2-hybridized structure.

In the case of C_{36}-based structures, the dependence character changes to the opposite, that is, the structure containing interlayer sp^3-bonds becomes less energetically favorable than the corresponding onion in the absence of loading. The distance between the layers of fullerenes in this case is ~3 Å. Due to this, increasing number of layers in the structure is accompanied by quick accumulation of mechanical stresses by the interlayer bonds, which leads to structure destabilization and stratification into sp^2-hybridized onions when the load is removed.

5. Conclusions

It has been shown experimentally that diamond is unstable in the pressure range of 55–115 GPa. At these pressures, graphite, diamond, and multi-walled carbon nanotubes transform into onion-like structures. According to the results of our simulation, when the volume of the onion decreases, some sp^3-bonds can form between its layers, which can be retained when the load is removed from the material (depending on the structure of the onion).

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Author Contributions: Mikhail Yu. Popov, Valentin D. Churkin, and Alexey N. Kirichenko, prepared the samples and performed high-pressure and Raman studies. Boris A. Kulnitskiy, Igor A. Perezhogin, and Vladimir D. Blank carried out TEM studies. Pavel B. Sorokin, Sergey V. Erohin, and Vladimir D. Blank performed modeling. All the authors have taken part in discussions and in the interpretation of the results; and have read and approved the final manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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