PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 1, 01NDLCN02(3pp) (2012)

Influence of Shear Deformation on Carbon Onions Stability under High Pressure

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(Received 22 May 2012; published online 17 August 2012)

The influence of shear deformation on carbon onions stability under high pressure up to 45 GPa was investigated in a Shear Diamond Anvil Cell (SDAC) by the Raman spectroscopy and the Transmission Electron Microscopy (TEM). At shear less then 40 degrees the carbon onions are stable up to 30 GPa. Bigger shear deformation leads to increasing of size and destruction of the onions and to formation of sp^3 C-C bonds. At pressure exceeded 45 GPa shear deformation leads to diamond-like carbon (DLC) formation.

Keywords: Transmission electron spectroscopy, Carbon onions, Diamond like carbon, Spectroscopy.

PACS numbers: 78.30. – j, 68.37.Lp, 64.70.Nd, 62.23.St, 61.48. – c, 61.48. – c

1. INTRODUCTION

There are several stable forms of structural organization of carbon atoms can exist on the nanoscale. Fullerenes, nanotubes, and carbon onions are among them. Carbon onions are spherical 5–10 nm particles consisting of concentric shells of graphitic carbon. Since the first synthesis and observation of carbon onions by Ugarte [1] some large-scale production methods, which make use of either high temperature annealing of carbon soot and diamond nanoparticles or energetic carbon ion implantation in metal substrates has been reported [1-7].

Carbon onions are a promising material for the lubricant purposes. Used as lubricant additives, carbon onions lead to a strong reduction of both friction and wear, even at low temperature [8-11].

The stability of polyhedral onions obtained from nanodiamonds up to 20 GPa has been previously shown [12]. But there is no information about the carbon onions stability at a higher pressure.

The goal of this work is to study stability of polyhedral onions under shear deformation at pressure higher 20 GPa and nanostructured carbon material obtained at these conditions by means of transmission electron microscopy (TEM) and Raman scattering.

2. EXPERIMENT

High-pressure experiments were performed using a shear diamond anvil cell. A controlled shear deformation is applied to a specimen under pressure by rotation of one of the anvils around the load axis of SDAC.

TEM investigations was performed with JEM-2000 FX11 (JEOL) transmission electron microscope.

The Raman spectra were measured in backscattering geometry using TRIAX 552, Jobin Yvon spectrometer equipped with CCD Spec-10, 2KBUV, Princeton Instruments 2048x512 detector and razor edge filters. The Raman spectra were excited with the line at 514.5 nm and 257 nm. The spectral resolution was about 1-3 cm^{-1}. We have used the micro-Raman attachment to collect scattered light of sample studied in SDAC with spatial resolution 1 μm.

3. DISCUSSION

Figure 1 shows TEM images of the as-prepared carbon onions and onions treated in the SDAC. Initial onions have a polyhedral shape with an average particle size of about 5 nm and concentric non-defect layer structure. The interlayer distance in the polyhedrals is 0.345 nm, close to that of the graphite (002) plane, and the onions are fully filled by the graphite sheets (see Fig. 1a). TEM image of recovered after treatment in SDAC sample shows appearance of onions with 7 – 25 layers. Their particle size reached 20-40 nm exceeded those in as prepared onions. These onions are surrounded with amorphous carbon and particles of destroyed onions (see Fig. 1b). Presence of some sp^3–bonded carbon atoms in material treated in SDAC at 45 GPa and 180 degrees shear confirmed by EELS. The EELS spectra of this recovered sample has a single loss feature with an onset at about 290 eV owing to its σ* electronic states, while the graphite has an additional absorption starting at around 285 eV due to its lower lying antibonding π* states. An amorphous or disordered carbon has a peak at about 285 eV, similar to the graphite, but with different intensity. A peak close to 307 eV is common for a diamond. Figure 2 shows the Raman spectrum of as-prepared carbon onions as well as spectra of treated carbon onions exited with laser line 514 nm and 257 nm.

The visible Raman spectrum of starting material (see Fig. 2a) is similar to that of carbon onions which have been previously described in the literature [12-15]. It has two characteristic Raman bands at 1356 cm^{-1} and 1585 cm^{-1} corresponding to the D- and G-modes of the graphite carbon.

It is obviously that shear deformation magnitude has a great influence on the onions stability. So at 40 degrees shear onions are stable up to 30 GPa(see curves 1-3 in Fig. 2a). Increasing of the shear deformation magnitude at pressure above 25 GPa leads to a drastic change of spectra. There is a noticeable increase in FWHM of the D- and G-modes which associated with

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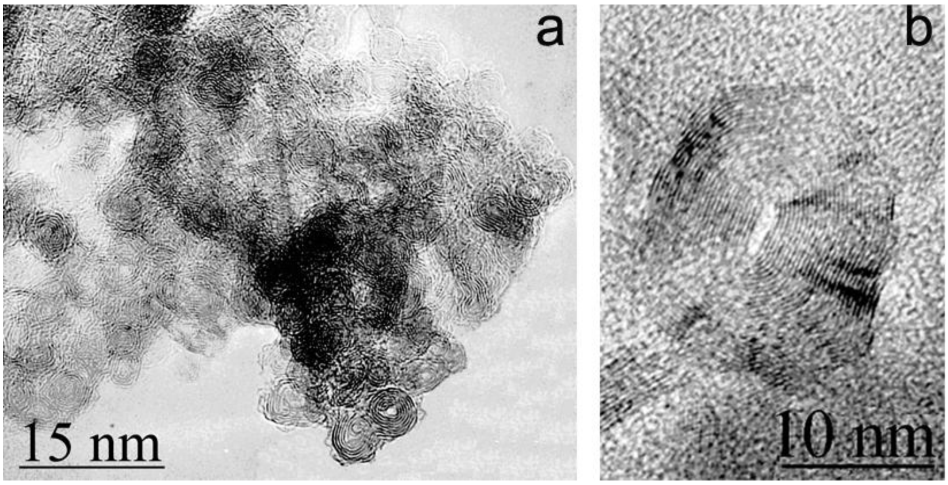

Fig. 1 – TEM image of the initial carbon onions (a) and a big-sized onion from a sample recovered under a 30 GPa loading and a 40-degree shear deformation (b)

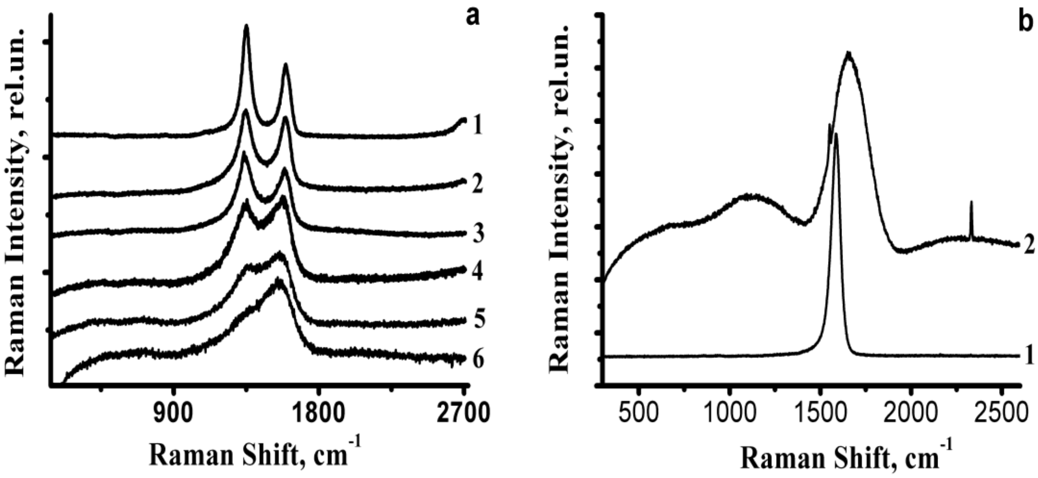

Fig. 2 – a) The Raman spectra exited with 514 nm laser line for the carbon onions and onions treated with shear deformation at various pressures.:
1 – Initial OLC, 2 – 17GPa and shear 40°, 3 – 30 GPa and shear 40°, 4 - 27GPa and shear 200°, 5 – 35GPa and shear 300°, 6 – 45 GPa and shear 180°.
b) The UV Raman spectra exited with 257 nm laser line of carbon onions (1) and onions treated at 45 GPa and shear 180° (2).

formation of amorphous phase of carbon. Also there is a drop of G-mode from 1580 cm^{-1} to 1550 cm^{-1} (see curve 6 in Fig. 2a) which indicates formation of sp^3-bonds [16, 17]. The G-mode intensity also increased compared to that of a D-mode. The Raman spectra of the the onions treated at 45 GPa and 180 degrees shift becomes similar to those of diamond-like carbon (DLC).

The UV Raman spectrum of onions after pressure 45 GPa and shear 180° (see curve 2 in Fig. 2b) is also similar to that of DLC and consist of wide band centered at about 1050 cm^{-1} (T- band) and 1670 cm^{-1} (G-band). T- band corresponds to sp^3- bonded carbon atoms vibration density of states (VDOS) [16]. Narrow lines belong to O_2 (line at 1550 cm^{-1}) and N_2 (2330 cm^{-1}) from air. In materials with only sp^2 rings, the G peak dispersion saturates at a maximum of ca. 1600 cm^{-1}) [16]. Up shift of the G- band indicates presence of ~50% sp^3- bonded carbon atoms [16, 17]. So formation of sp^3 bonded carbon atoms was confirmed with EELS and Raman.

4. CONCLUSIONS

Carbon onions are stable up to 30 GPa if shear deformation did not exceed 40^0. Increasing of the shear deformation up to 180^0 at pressures from 25 to 35 GPa leads to a deformation of the initial onion shapes and their destruction. Meanwhile bigger polyhedral onions are formed with the number of layers up to 25 which exceeded those of the initial material. At pressure 45 GPa and 180° shear onions transformed to DLC material. UV and Visible Raman and EELS confirmed presence of 50% sp^3- bonded carbon in the treated sample.

AKNOWLEDGEMENTS

The present work was supported through a research grant from Russian ministry of Education and Science (Contract Nos. 16.552.11.7014/16.523.11.3002/16.523.12.3003).

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