Synthesis of BN Nanotubes in a Laser Heated DAC

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BN nanotubes were found in laser heated cBN and hBN at nitrogen pressures up to 10.1 GPa in a diamond anvil cell. The BN nanotubes were recrystallized from the BN-melts in a super critical nitrogen fluid. Their shape, bonding nature and stoichiometry were examined by high resolution electron microscopy and electron energy loss spectroscopy. The BN nanotubes did not contain any additional inclusion. The nanotubes typically exhibit 3-8 shells and stoichiometry of B/N ~1.

[nanotube, boron nitride, diamond anvil cell, laser heating, electron microscopy]

1. Introduction

Laser heating experiment using diamond anvil cell (DAC) is one of the most suitable tools to generate high temperature under high pressure. Up until now, we carried out the experiments which are a direct transformation of graphite to diamond [1], and a melting of boron nitride [2, 3]. During the latter experiments, we found nanotubes as a new form of BN in the laser-heated products [4,5]. The nanotubes have similar structure to carbon nanotubes [6]. Their structure, bonding character, and chemical composition were surveyed by high resolution analytical electron microscopy, electron energy loss spectroscopy (EELS), and Raman spectroscopy.

2. Experimental

A thin platelet of single crystal cBN ($< 10 \mu\text{m}$) synthesized in BN-LiH system under high P, T conditions [7] or highly grain-oriented pyrolytical hBN were used as starting samples. A stainless steel (T301) gasket (0.3 mm diam.) was prepared for a sample chamber. Nitrogen was chosen as a pressure medium, which was inserted into the DAC with liquid state at low temperature. BN samples were located in the middle of the gasket hole to avoid contact with anvil surfaces (Fig.1). The samples were heated by a CO_2 laser, after increasing pressure up to 10.1 GPa.

Fig. 1 Sample assembly of the laser-heated DAC.

Fig. 2 (a)

Photomicrograph of cubic boron nitride at 8.4 GPa in a DAC with a transmitted light before laser heating.

(b)

The sample irradiated by CO_2 laser.

(c)

The sample after laser heating. The heated areas change into fine particles.

A continuous CO_2 laser (Synrad, 240 W at max.) was focused on to the sample in a DAC with $80 \mu\text{m}$ diameter for several seconds. The sample can be readily heated as shown in Fig. 2(b), since the TO phonon of the cBN located around $9.5 \mu\text{m}$, which is close to the wavelength of the CO_2 laser ($10.6 \mu\text{m}$). At higher temperature above $4000 \sim 5000 \text{ K}$, the heated

area of the sample changed to a dark rounded shape (Fig. 2(c)). Judging from the change of a shape, and the phase diagram of BN [8], the cBN could be melted. A fluidal motion of nitrogen surrounding the sample was able to be observed during heating. Therefore, the sample was melted in a supercritical fluid of nitrogen. It is not sure that the BN sample can be soluble in nitrogen or not. The sample was quenched rapidly by shutting off the laser.

Fig. 3 SEM micrograph of the recovered sample.

After releasing the pressure, the products were carefully taken from the DAC. Firstly, the products were checked with an optical microscope and a scanning electron microscope (JSM-5410). Fig. 3 shows that the heated area consists of fine flakes, which are optically white. Raman spectra show that the flakes consist of a mixture of hexagonal and cubic phase. The flakes were picked up with a needle and deposited onto holey carbon grids, and characterized by high resolution lattice images and nanodiffractions with the use of a field emission type transmission electron microscope (JEM-3000F), operating at 300 keV. Parallel detection electron energy loss spectroscopy experiments were performed by means of a Gatan spectrometer. A stationary focused 0.8 nm electron probe was used for nanodiffraction and EELS experiments.

3. Results and discussion

Fig. 4(a) shows a representative nanotube of a polygonal cross section that was found in the product after laser irradiation at nitrogen pressure of 10.1 GPa. The nanotube has 6 shells and a outer dimension cross section of about 10 nm.

We found a number of nanotubes which have 3 - 8 shells in recovered samples. A typical EELS spectrum from a nanotube

exhibits a π^* -type peak which is typical for hexagonal B-N bonding, as shown in Fig. 4(b). The EELS spectrum shows ionization edges at approximately 188 and 401 eV, corresponding to the characteristic *K*-shell ionization edges of boron and nitrogen, respectively. The stoichiometry of the nanotube can be calculated from the intensity of peaks. The B/N ratio of this spectrum was determined to be B/N $\sim$ 1. It is emphasized that the BN nanotube does not contain carbon and any other elements.

Fig. 4 High resolution transmission electron microscopy image of representative polygonal nanotube in the laser-heated BN at a nitrogen pressure of 10.1 GPa and typical core electron *K*-shell EELS spectra from the nanotube area (b) and the base of nanotube (c).

The base of the nanotubes was also examined. The EELS spectrum taken at the base of the nanotube exhibits cubic phase (Fig. 4(c)). In more details, a small amount of amorphous BN exists at the bottom of the nanotube. It is interesting to think about a growth mechanism of the nanotubes. The cBN can be melted under such high P-T conditions. If the cooling process is sluggish and the sample is held at high temperature for a long time under subliquidus, the recrystallized melts should be converted to hBN and cBN. However, the laser heating

experiments using DAC provide the rapid cooling condition, when the laser is shutting off. The fluid can be quenched at a very rapid cooling rate, because the diamond anvils work as a heat sink. Subsequently, as shown in Fig. 5, the nanotubes grow on the surface of the cBN crystal, which is colder than fluid. Hence, the nanotube is thought to be formed during the recrystallization of BN from the fluid phase by rapid quenching process. This mechanism is quite different from that which is effective under use of an arc-discharge technique, conventionally applied for C and BN nanotube formation [9, 10].

We carried out the laser heating of BN in argon pressure medium at the same pressure conditions. The recovered product exhibits a mixture of hexagonal and cubic phases, however, no nanotubes were found. The result indicates that the high nitrogen pressure plays an important role to synthesize the nanotubes.

Fig. 5 High resolution transmission electron micrograph of BN nanotube, which grows on a cBN crystal.

4. Conclusion

BN nanotubes were produced from cBN or hBN in a laser heated DAC under high pressure. High temperature, a rapid quenching, and high nitrogen pressure were found to be necessary to synthesize the BN nanotubes. The nanotubes are chemically pure BN compound with a stoichiometry of B/N ~ 1 . The laser heating technique using DAC is a competitive way with an arc-discharge method to produce nanotubes.

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