Preparation of nanodiamonds by laser irradiation of graphite

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Graphite powders were irradiated by pulsed laser at room temperature and normal pressure and then boiled in perchloric acid. Samples were characterized by high-resolution transmission electron microscopy (HRTEM), electron diffraction pattern (EDP), X-ray diffraction (XRD) pattern, and Raman spectroscopy. The analyses on the HRTEM images, EDP, and XRD show that the diamond particles with a size of about 5 nm are obtained. The shifting and broadening of the diamond peak in Raman spectrum indicate that there are high defect density and residual internal stress in synthetic diamond.

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Nanometer-sized diamond has recently attracted intense interest because of its outstanding properties different from those of bulk diamond. It is expected to be used for a wide range of applications, such as abrasives for semiconductors, reinforcer for polymers and rubber, and additive of lubricating oil.

Many methods of diamond synthesis have been developed since diamond was firstly synthesized in the 1950s. Nanometer-sized diamonds were prepared by the trinitrotoluene (TNT) detonation method[1]. Polycrystalline diamond films were synthesized by a variety of chemical vapor deposition (CVD) techniques[2−4]. Recently, nanometer-sized diamond particles or films were also acquired by laser irradiation of a bulk graphite target or aromatics[5,6].

In this work, the loose graphite powders were irradiated by Nd-YAG pulsed laser flux coaxially at room temperature and normal pressure, so that the powders could react with pulsed laser beam fully. The laser beam could be focused to provide a spot of 0.2-mm diameter, with power density of 10^6 W/cm^2, pulse width $\tau = 1.2$ ms, and repetition frequency $\nu = 20$ Hz. The size of graphite powders was about 2 μm with the purity of 99.9%. This method of diamond synthesis is simpler and more efficient than other previous laser induced technique, and there are fewer impurities in the produced diamond than that obtained by detonation of TNT explosive.

A schematic diagram of the experiment is shown in Fig. 1. The system consists of a Nd-YAG laser and a set of powder feeder.

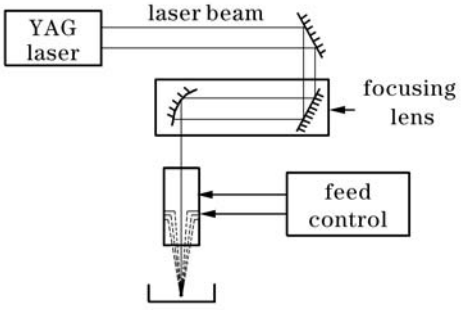

Fig. 1. The scheme of equipment configuration for pulsed laser synthesis.

The laser-treated graphite powders were recycled several times to ensure laser-particle interaction and then collected and boiled in perchloric acid for 4 hours at 200 °C to separate the transformed high-pressure phase from the untransformed graphite.

Raman spectroscopy is a comparatively simple, nondestructive analysis technique, which can precisely characterize various carbon phases[6]. The Raman spectra obtained by using a Renishaw MKI-2000 con-focal micro-Raman spectrometer with the 632.8-nm line from a He-Ne laser for different samples in the frequency range from 100 to 2000 cm^{-1} were shown in Fig. 2. Spectrum (Fig. 2(a)) is obtained from raw graphite and obvious bands assigned to graphite at around 570 and 1580 cm^{-1} are observed.

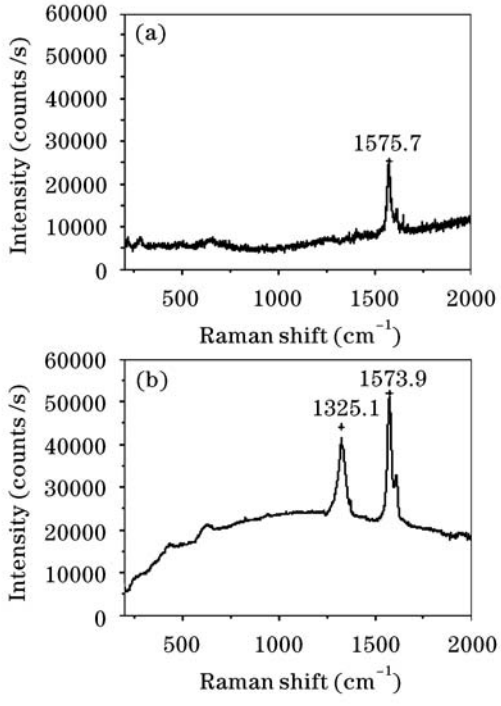

Fig. 2. Micro-Raman spectra of raw graphite (a) and laser treated graphite (b).

The sharp, intense peak at about 1330 cm^{-1} in Fig. 2(b) corresponding to Raman band of bulk diamond (1332.79 cm^{-1})[7] indicates the existence of diamond in the laser treated graphite. The Raman band shifts to the low frequency by about 3 cm^{-1}, relative to that of the bulk diamond crystal. Knight and White reported Raman frequency of synthetic diamond ranging from 1328 to 1345 cm^{-1} and attributed the peak-shift to internal stress in diamond particles[8].

In Fig. 2(b), the full-width at half-maximum of diamond band (45 cm^{-1}) is much larger than that for the bulk diamond crystal (2.45 cm^{-1}) and the spectrum is asymmetric with tail at low-frequency side. Richter *et al.* have developed a phonon-confinement model to explain the asymmetric broadening of the Raman bands[9,10]. According to the model, they assumed the relationship between Lorentzian line width and the particle size as

$$\Gamma = 2.990 + 0.185/L, \quad (1)$$

where Γ is the bandwidth of the spectrum and L is the crystalline size. According to Eq. (1), we can deduce that the size of diamond particles is about 5 nm.

Figure 3 shows the X-ray diffraction (XRD) spectrum of the laser treated graphite powders by using Rigaku D/MAX 2500 X-ray diffractometer. In Fig. 3, one can see that the diffraction peaks belonging to the graphite are found and the broadening peaks corresponding to diamond indicate that the diamond particles are obtained during the laser treating process and the size of the particles is very small.

High-resolution images of the laser treated graphite taken by DFEI Technai G^2 field-emission-gun transmission electron microscopy (TEM) indicate the randomly distributed diamond particles with size of about 5 nm which agrees with the result obtained from Raman spectrum. The clear crystalline planes, very regular morphology, and many twins are observed even in these nanometer-sized crystallites (Fig. 4(a)). The electron diffraction pattern (EDP) taken from an area of 150 nm in diameter reveals that the cluster does consist of small diamond crystals with different orientations with respect to the electron beam (Fig. 4(b)). This ring pattern was analyzed and three inner rings corresponded well to the {1 1 1}, {2 2 0}, and {3 1 1} planes of diamond.

Few works have made on the transformation from graphite powder to nanometer-sized diamond particles

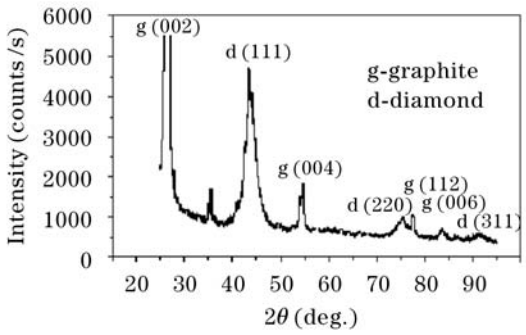

Fig. 3. XRD spectrum of laser treated graphite.

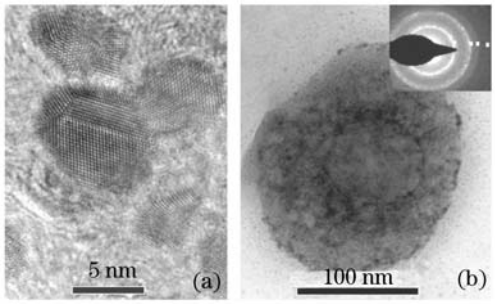

Fig. 4. HRTEM images and EDP of laser treated graphite.

by pulsed laser irradiation, and the mechanism keeps unclear. We propose that the pulsed laser provides energy and heats the raw powders to a high temperature, and then the surface layers of powders cool down at a high rate which causes high pressure on the core of powders after the laser pulse. So there is a high temperature and high-pressure circumstance in favor of the formation of nanometer-sized diamond. In short, the transformation mechanism is different from traditional theories, and further researches are needed to discover the root cause.

From the above, we can conclude that nanometer-sized diamond crystals were synthesized by the pulsed laser at room temperature and normal pressure. Calculation on the Raman data, the results of high-resolution transmission electron microscopy (HRTEM) and XRD show that the diamond particles have a size of about 5 nm, with high defect density and residual internal stress.

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References

1. Q. Chen and S. Yun, Materials Research Bulletin **35,** 1915 (2000).
2. H.-K. Chung and J. C. Sung, Diamond and Related Materials **10,** 1584 (2001).
3. Y. Chakk, R. Kalish, and A. Hoffman, Diamond and Related Materials **5,** 1047 (1996).
4. N. M. Hwang, J. Crystal Growth **198/199,** 945 (1999).
5. J. B. Wang, C. Y. Zhang, X. L. Zhong, and G. W. Yang, Chem. Phys. Lett. **361,** 86 (2002).
6. M. Yoshikawa, Y. Mori, H. Obata, M. Maegawa, G. Katagira, and H. Ishida, Appl. Phys. Lett. **67,** 694 (1995).
7. M. Yoshikawa, Y. Mori, M. Maegawa, G. Katagiri, H. Ishida, and A. Ishaitani, Appl. Phys. Lett. **62,** 3114 (1993).
8. P. S. Knight and W. B. White, J. Mater. Res. **4,** 385 (1989).
9. H. Richter, Z. P. Wang, and L. Ley, Solid State Commun. **39,** 625 (1981).
10. J. W. Ager III, D. Kirk Veirs, and G. M. Rosenblatt, Phys. B **43,** 6491 (1991).