Preparation of nano-crystalline diamonds using pulsed laser induced reactive quenching

PII: S0953-8984(98)90347-2

Preparation of nano-crystalline diamonds using pulsed laser induced reactive quenching

Guo-Wei Yang†‡, Jin-Bin Wang† and Qui-Xiang Liu†

† Department of Physics, Xiangtan University, Xiangtan 411105, Hunan, People's Republic of China
‡ Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Abstract. Nano-crystalline diamond is prepared with a unique method in which a graphite target is etched by a high-power pulsed laser in water. Transmission electron microscopy (TEM) and high resolution electron microscopy (HREM) indicate nano-crystalline diamond is obtained, having a hexagonal lattice or cubic lattice.

The interest in preparation of diamond is motivated by its unique combinations of physical hardness, high thermal conductivity and optical transparency and others. Many methods have been developed to prepare diamond since the 1950s when diamond was synthesized first with a high temperature and high pressure method [1]. Owing to its unique structure, diamond is very difficult to prepare, while another material which is similar to diamond in character, namely diamond-like carbon (DLC) is relatively easy to synthesize. So synthesis of DLC in some methods have been reported gradually [2–12]. In the last few years, pulsed laser deposition (PLD) has been proved to be an efficient method for the preparation of a variety of thin films [3–15]. Particularly, the deposition of amorphous films with diamond-like character has been widely reported for laser ablation of graphite [6–20], in which some researchers reported the growth of crystalline particles, but the lack of a diamond peak in Raman spectra was a common result in all reports. It was not until in 1995 that Polo *et al* first showed the Raman spectroscopy analysis of the sample which is confirmed to have diamond cubic structure of the crystals by the presence of a sharp peak at 1332 cm^{-1} [21]. In addition, a method named pulsed-laser-induced reactive quenching (PLIRQ) was developed by Patil *et al* [22, 23] which is likely to synthesize a new metastable phase of compound films. Specifically, two main points are included: (i) the compound synthesized in PLIRQ is of metastable structure; (ii) it is through chemical reaction and in high temperature and high pressure that the compounds are obtained. Ogale *et al* obtained diamonds having cubic structure using PLIRQ [24]. In this report, we first successfully synthesize nano-crystalline hexagonal diamonds with metastable structure by using this method.

The preparation system is described as follows. The second harmonic was produced by a Q-switched Nd:YAG laser with wavelength $\lambda = 532$ nm, pulse width $\tau = 10$ ns, repetition frequency $\nu = 5$ Hz, power density $P = 10^{10}$ W cm^{-2}. The targets were spectroscopically pure polycrystalline graphite. During the experiment, the target is first fixed in the bottom of the glass chamber, then the twice distilled water is poured slowly into the chamber until
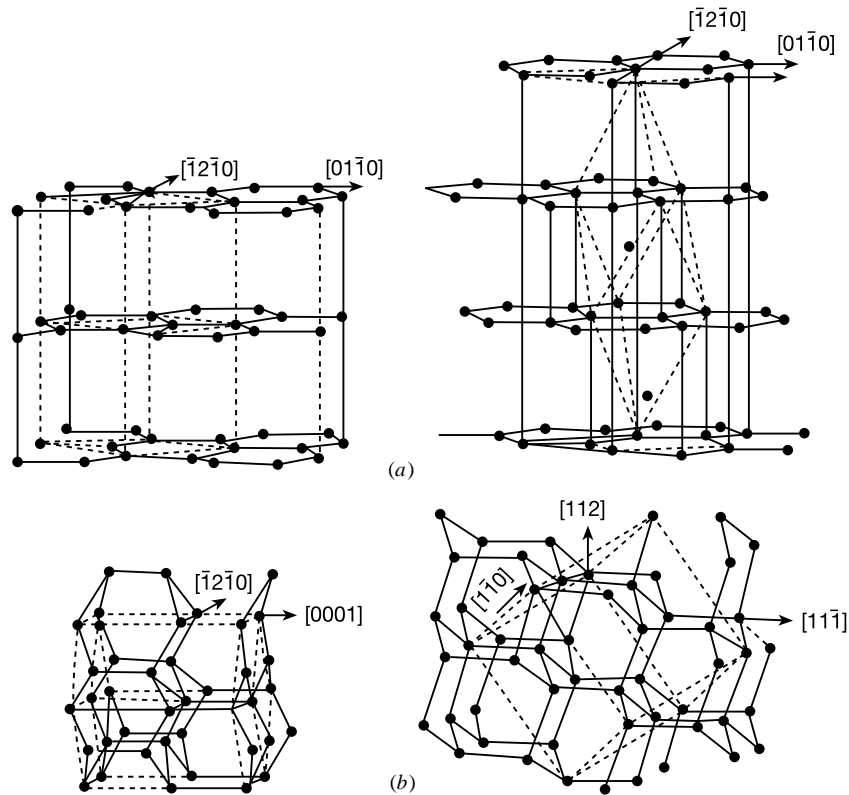
the target is covered by 1–2 mm liquid. The laser beam is focused by a quartz lens and finally guided by a reflection mirror onto the graphite target. The target and liquid are all at room temperature. When the experiment has been running for 30 minutes, the powders in the liquid are collected to be analysed. The samples analysed are prepared in the same conditions. The samples are analysed under H800 transmission electron microscopy (TEM), and some nano-crystalline diamonds with good crystalline morphology are observed, which is shown in figure 1. Owing to the fact that the grains are up to 300–400 nm, we can see the crystalline planes and very regular morphology clearly; this is a common morphology in diamond. The electron diffraction pattern in figure 2(a) suggests indexing in terms of a mixture of a cubic and hexagonal diamond phase, as shown in figure 2(b). Assuming these two crystal structures, a lattice content can be estimated. For the lattice parameter of the cubic phase, we obtain value of $a = 3.56 \pm 0.01$ Å, which is in good agreement with values found in the literature [26]; for the lattice parameters of the hexagonal phase, we obtain values of $a = 2.53 \pm 0.01$ Å and $c = 4.11 \pm 0.01$ Å, which is in excellent agreement with values found in the literature for the Wurzite-like hexagonal diamond structure often referred to as Lonsdaleite [27]. The cubic and hexagonal phases of diamond are intermixed in the crystallites investigated here. The oriented relationship between these two phases is $[110]_c//[1\bar{2}10]_h$, $[1\bar{1}1]_c//[0001]_h$ and $[1\bar{1}2]_c//[10\bar{1}0]_h$. In the obtained powders, the ratio of nano-crystalline diamonds to the whole powder is small, and the ratio of graphite to the whole powder is large. However, based on our experiments it is found that the graphite in the synthesized powders displays sheet and sphere shapes, so it is easy to distinguish graphite from crystalline diamonds. The nano-crystals are polycrystal mostly and single crystals are very few.

(a)   (b)
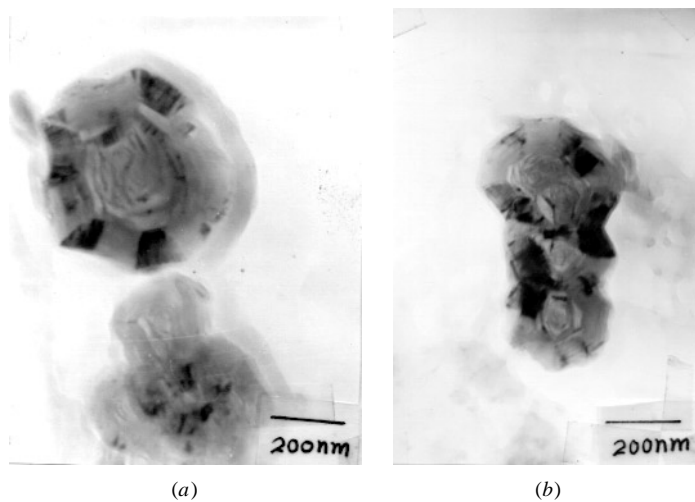
Figure 1. The morphologies of nano-crystalline diamonds. (*a*) A single grain whose size is about 300 nm; (*b*) three connected grains whose size is about 200 nm.

The hexagonal phase is a metastable phase of diamond. Natural hexagonal diamond has been found in aerolite [25]. Bundy and Kasper synthesized it by using a high temperature and high pressure method [26], in which the hexagonal graphite is pressed along the *c*-axis. It has also been synthesized by Trueb with an explosive method [28]. The advantage of the PLIRQ method is that it can prepare metastable compounds which are generally

Figure 2. An intergrowth crystal which has both hexagonal and cubic diamonds. (*a*) Electron diffraction pattern; (*b*) indexing, $B = [1\bar{1}2]$, $B = [10\bar{1}0]$.

prepared at high pressure, high temperature and high density. This paper demonstrates that the compounds only prepared at extreme conditions generally can be synthesized at normal temperature and pressure by using the PLIRQ method. Two parts are included in the synthesis mechanism of nano-crystal diamonds: (i) In the plasma plume at high temperature, high pressure and high density [22], two kinds of graphite lattice are transformed into two kinds of diamond lattice in a solid state diffusionless transformation manner, which is followed by the formation of diamond crystal nuclei and the growth of nuclei [29]. Specifically, only graphite atoms in the (000l) basic plane have compression displacement without diffusion, in which the distances between neighbour atoms adjust their displacement by an average of 8% during phase transformation. In this way, the hexagonal graphite lattice is changed into a hexagonal diamond lattice, and the rhombohedral graphite lattice is changed into a cubic diamond lattice, which are shown in figure 3. (ii) Through simulating the conversion of carbon from graphite to diamond under high pressure, Scandolo *et al* found that the transformation path proceeds through sliding of graphite planes into an unusual orthorhombic stacking [30], from which an abrupt collapse and bulking of the planes leads to both cubic and hexagonal forms of diamond in comparable proportions. Although hexagonal diamond is metastable, it could be kept when it is prepared in development methods such as the shock-wave method or explosive method. The plasma plume containing synthesized metastable and stable diamond crystals will quench in the liquid when the laser pulse is complete. By heat exchange from the target to the liquid on top of it, the liquid is super-heated and forms a high-temperature, high-pressure vapour, which expands only slowly compared to the duration of the laser pulse and melt (~10 ns) [23]. Because of this high-density vapour, there is a sufficient supply of OH^- and H^+ to keep the incorporation and diffusion mechanism going, and these ions OH^- and H^+ can promote the growth of the diamond by suppressing graphite sp^2 bondings [31]. From our experiment and discussion, we can predict that nano-crystalline B–C–N compounds could be synthesized from laser ablation of BN in acetone or alcohol, and so could cubic BN nano-crystallines when the hexagonal BN target is covered by water. Furthermore, the method can be widely used also to prepare various kinds of nano-crystal with metastable phase at normal conditions.

Figure 3. Diagrammatic sketch of transformation from graphite lattice to diamond lattice. (*a*) The transformation from hexagonal graphite to hexagonal diamond; (*b*) the transformation from rhombohedral graphite to cubic diamond.

From the above we conclude: nano-crystalline diamond with a hexagonal lattice or cubic lattice is synthesized for the first time in a method called high-power pulsed-laser-induced reactive quenching at a solid–liquid interface. TEM and HREM indicate its hexagonal structure or cubic structure. Based on our work, we predict that some other crystals such as C–N and cubic BN could be synthesized.

Acknowledgments

References

[1] Wagal S S, Juengerman E M and Collins C B 1988 *Appl. Phys. Lett.* **53** 187
[2] Aisenberg S and Chabot R 1971 *J. Appl. Phys.* **42** 2953
[3] Spencer E G, Schmidt P H, Joy D C and Sansalone F J 1976 *Appl. Phys. Lett.* **29** 118

[4] Mori T and Namba Y 1983 *J. Vac. Sci. Technol.* A **1** 23
[5] Kashi S, Kang H and Wayne Rabalias J 1987 *Phys. Rev. Lett.* **59** 75
[6] Sawabe A and Inzuka T 1985 *Appl. Phys. Lett.* **46** 2
[7] Holland L and Ojha S M 1979 *Thin Solid Films* **58** 107
[8] Vora J and Moravec T J 1981 *J. Appl. Phys.* **52** 6151
[9] Kurihara K, Sasaki K, Motonobu M and Koshino N 1988 *Appl. Phys. Lett.* **52** 437
[10] Weissmantel C, Bewilogua K, Dietrich D, Erler H J, Hinnen H J, Klose S, Nowich W and Rcisse G 1980 *Thin Solid Films* **72** 19
[11] Miyasato T, Kawano Y and Miraki A 1984 *Japan. J. Appl. Phys.* **23** L234
[12] Kitabataske M and Wasa K 1985 *J. Appl. Phys.* **58** 1693
[13] Dijkkamp D, Venkatesan T, Wu X D, Shaheen S, Jisrawi N, Min-Lee Y H, Mclean W L and Croft M 1987 *Appl. Phys. Lett.* **51** 619
[14] Horwitz J S, Grabowski K S, Chrisey D B and Lenchter R E 1991 *Appl. Phys. Lett.* **59** 1565
[15] Sarchez F, Varela M, Queralt X, Aguiar R and Morenza J L 1988 *Appl. Phys. Lett.* **61** 2228
[16] Sato T, Furuno S, Iguchi S and Hanabuso M 1988 *Appl. Phys.* A **45** 355
[17] Collins C B, Davanloo F, Lee T J, Park H and You J H 1993 *J. Vac. Sci. Technol.* B **11** 1936
[18] Rengan A, Biuhno N and Narayan J 1990 *Mater. Res. Soc. Symp. Proc.* vol 162 (Pittsburgh, PA: Materials Research Society) p 162
[19] Bourdon E B D, Kovarik P and Prince R H 1993 *Diamond Relat. Mater.* **2** 425
[20] Seth J, Padiyath R, Rasmussen D H and Babu S V 1993 *Appl. Phys. Lett.* **63** 473
[21] Polo M C, Cifre J, Sanchez G, Aguiar R, Varela M and Esteve J 1995 *Appl. Phys. Lett.* **67** 485
[22] Patil P P, Phase D M, Kulkarni S A, Ghaisas S V, Kulkarni S K, Kanetkar S M and Ogale S B 1987 *Phys. Rev. Lett.* **58** 238
[23] Ogale S B, Patil P P, Phase D M, Bhandarkar Y V, Kulkarni S K, Kulkarni S, Ghaisas S V and Kanetkar S M 1987 *Phys. Rev.* B **36** 8237
[24] Ogale S B, Malshe A P, Kanetkar S M and Kshirsayar S T 1992 *Solid State Commun.* **84** 371
[25] Hanneman R E *et al* 1967 *Science* **155** 995
[26] Bundy F P and Kasper J S 1967 *J. Chem. Phys.* **46** 3437
[27] DeCarli P S and Jameson J C 1961 *Science* **133** 1821
[28] Trueb L F 1971 *J. Appl. Phys.* **42** 503
[29] Wang C Z and Ho K M 1993 *Phys. Rev. Lett.* **71** 1184
[30] Scandolo S, Bermasconi M, Chiarotti G L, Focher P and Tosatti E 1995 *Phys. Rev. Lett.* **74** 4015
[31] Xiao R F 1995 *Appl. Phys. Lett.* **67** 3117