High-Quality Synthetic Diamond Crystals

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High-quality synthetic type IIa diamond crystals of several carats, containing less than 0.1 ppm chemical impurities and few inclusions, have been successfully synthesized by the temperature gradient method under high pressure and high temperature. The crystals are transparent over a wide range of wavelengths from ultraviolet to far infrared regions, showing no absorptions due to impurities. They also have high crystalline quality with fewer crystal defects, less internal strain, and less variation in defects among crystals than those of natural diamonds or conventional synthetic type Ib diamond. The outstanding characteristics of the synthetic type IIa diamond permit application to a considerably wide range of industrial and scientific uses such as optical parts, monochromators, high-pressure anvils, and so on. [synthetic diamond, high pressure, crystal growth, impurity, dislocation]

1. Introduction

Diamond is a typical covalent crystal in which carbon atoms are joined together with very strong bonds. This structural property gives rise to the extremely high hardness and high strength, as well as the excellent thermal conductivity, chemical stability, transparency, and so on. Owing to these intriguing properties, diamond has been employed to a wide range of industrial applications.

In 1985, we have successfully produced synthetic diamond crystals weighing about 1 carat (~5 mm across) by developing a peculiar mass-production process based on the temperature-gradient method under high pressure and high temperature. The synthetic diamond crystals are now being applied into heat sinks, cutting tools for high-precision machining, wire drawing dies, and other products [1]. Later in 1990, it became possible to reproducibly synthesize larger single crystal diamonds weighing 5 to 9 carats (10 to 12 mm on one side) and, further, to apply them to TAB (Tape Automated Bonding) tools, large heat sinks, and other large-size products [2,3].

However, these conventional commercialized synthetic diamond crystals include nitrogen impurity in a dispersed form (isolated substitutional impurity) in concentrations of several tens or hundreds ppm (type Ib diamond). Because the nitrogen impurity affects the

optical properties and deteriorate the crystalline quality to some extent, these synthetic type Ib diamonds cannot be applied to optical parts or functional materials that require high crystalline perfection.

Recently, we have developed a method for purifying synthetic diamond crystals [4]. This study allowed us to consistently synthesize high-purity type IIa diamond containing less than 0.1 ppm chemical impurities and few inclusions. Figure 1 shows the grown crystal of 1-2 carats (5-6 mm across). The crystal is transparent over a wide range of wavelengths from ultraviolet to far infrared regions, showing no absorptions due to impurities.

Fig. 1. Synthetic type IIa diamond crystals (1-2 carats).

We have also shown that such high-purity synthetic diamond has high crystalline quality with fewer crystal defects, less internal strain, and less variation in defects among crystals than those of natural diamonds or synthetic type Ib diamond [5]. The high crystalline quality improves the mechanical and physical properties of the diamond [6,7]. These salient characteristics permits us to employ the crystals to hitherto-unexplored fields of industrial and scientific applications.

In this paper, we summarize the characteristics of the synthetic type IIa diamond and present some of the particularly useful and noticeable applications originating from the distinctive features of the diamond.

2. Characteristics

2-1. Optical properties

The infrared and ultraviolet-visible transmission spectra of the synthetic type IIa diamond are respectively shown in Fig. 2 and Fig. 3, together with spectra of natural type Ia, natural type IIa, and synthetic type Ib diamond for reference. The synthetic IIa has no absorption bands arising from impurities of nitrogen, boron, nickel, etc. The absorption bands seen near 2000 cm^{-1} in the infrared region were due to multiphonon absorption, which is intrinsic to diamond. In both spectra, natural Ia and synthetic Ib diamonds have absorption bands due to nitrogen impurities in aggregated forms and dispersed form, respectively. In the ultraviolet-visible spectrum of natural IIa diamond, a tail or shoulder is observed at the absorption edge of 225 nm. The tail is ascribed to strains or defects in the crystal. The synthetic IIa diamond does not have such a tail at the absorption edge.

Fig. 2. Infrared transmission spectra of diamonds.

Fig. 3. Ultraviolet and visible transmission spectra of diamonds.

2-2. Crystalline quality

Natural diamonds have a number of defects and much strain in the crystals because of the complicated and various growth processes occurring in the earth's interior. On the other hand, synthetic diamonds, grown under controlled conditions of high pressure and high temperature in a thermodynamically stable region, have invariable quality. Especially, synthetic type IIa diamonds, in the absence of any crystal defects caused by impurities, are expected to have much higher crystalline quality.

We evaluated the crystalline quality of our synthetic type IIa diamonds by double-crystal X-ray rocking-curve measurement, polarizing microscopy, X-ray topography, and Raman spectroscopy [5]. Table 1 summarizes the results of evaluations. It is obvious that the synthetic IIa diamond has high crystalline quality with considerably fewer crystal defects and less residual strain than those of natural diamonds or conventional synthetic Ib diamond.

Some line (dislocation bundles) and plane defects were observed in the synthetic type IIa diamonds. The origin of the line defects is attributed to the crystal imperfections in seed crystals, and the plane defects are ascribed to heat stress developed during the high-pressure and high-temperature treatment. The line defects were found to be removed by using strain-free, low-defect diamond as the seed crystal, thereby improving the crystalline quality of the synthetic type IIa diamond crystals [5]. The largest size of the such

high quality diamond we obtained so far by this method is about 7 carats, 8-9 mm across. The X-ray topographs of (001) polished slabs of the large high-quality diamond crystals are shown in Fig. 4 [8].

Table 1 crystalline imperfections of various diamonds.

	Synthetic IIa	Synthetic Ib	Natural Ia	Natural IIa
Nitrogen content (ppm)	<0.1	~100	~1000	<1
Internal strain by polarizing microscopy	little~none	much	much	much
Defects by X-ray topograph	some (line,plane)	many (line,stripe)	many (line,stripe)	so many (tatami)
FWHM of rocking curves (CuK α_1 , arcsec)	4~6	6~20	7~60	200~2500
FWHM of Raman spectra (cm ⁻¹)	1.6~1.8	1.8~2.6	3.2~3.8	2.0~2.5

Fig. 4. X-ray topographs of (001) polished slabs of large high quality synthetic type IIa diamond crystals. MoK α_1 , (220) reflection.

2-3. Mechanical properties

We have investigated the mechanical properties of the synthetic type IIa diamond by Knoop hardness measurement and by observation of the cleavage surfaces [7]. Figure 5 shows the Knoop hardness in the <100> directions on the (001) planes of the synthetic diamond plotted against the concentration of nitrogen impurity. The hardness increases with the decrease in the concentration of nitrogen impurity. The hardness of synthetic type IIa diamond with little nitrogen impurity is the highest among synthetic diamonds. This is ascribed to the decrease in the amount of dispersed isolated nitrogen impurity that is responsible for the plastic flow. In addition, it was found that the Knoop

hardness in (001)<110> of synthetic type IIa diamond is extremely high, as evidenced by occurrence of no plastic deformation, and that the anisotropy in Knoop hardness of synthetic type IIa diamond is quite different from those of natural diamonds as well as synthetic type Ib diamond. The cleavage surface of synthetic type IIa diamond exhibits a very smooth and remarkably regular pattern. These results indicate that there are very few impurities and crystal defects in the synthetic type IIa diamond, also suggests that the diamond has the high resistance to plastic flow.

Fig. 5. Knoop hardness of synthetic diamond crystals in the <100> directions on the (001) surfaces.

3. Applications

3-1. Optical parts

As shown in Figs. 2 and 3, the synthetic type IIa diamond produced in this work is transparent over a wide range of wavelengths from ultraviolet to far infrared regions. Because of the rather exceptional optical transmission property, coupled with the high strength, abrasion resistance, and excellent chemical stability, synthetic type IIa diamond can be most useful for optical parts for infrared rays or laser lights. Figure 6 shows some examples of application to optical parts for FT-IR spectroscopy. To date, materials such as KBr, ZnSe, KRS-5, etc. have been employed for the pertinent parts. However, these conventional materials have disadvantages as exemplified by the low strength, vulnerability to scratching, deliquescence, toxicity, and poor resistance to chemical environments. Natural type IIa diamond has been used in compression cells which require high strength, but they have serious

problems such as high price and diversity of quality. In these respects, synthetic type IIa diamond is the most suitable material for such applications. We have developed some optical parts by using our synthetic type IIa diamond. These are shown in Fig. 7; (a) sample plate, (b) compression cell, and (c) ATR (attenuated total reflection) prism.

It is also expected that our synthetic type IIa diamond can be used for optical windows exposed to special harsh or hostile environments, for example, a window for high-pressure vessels for chemical investigations, a window for planetary probe, and so on.

Fig. 6. Schematic drawing of optical parts for FT-IR spectroscopy.

Fig. 7. Optical parts for FT-IR spectroscopy manipulated from synthetic type IIa diamond crystals: (a) sample plate, (b) compression cell, and (c) ATR prism.

3-2. Monochromators

Recently new synchrotron radiation facilities started in France (European Synchrotron Radiation Facility, ESRF), USA (Advanced Photon Source, APS), and Japan (Super Photon Ring, SPring-8). The synchrotron beams in these facilities are so powerful that heat flux intercepted by the monochromator crystal would develop serious problems. For instance, Si which has been used as an X-ray monochromator cannot be feasible in these facilities, because of the thermal problem [9,10].

Diamond crystal has excellent thermal properties (high thermal conductivity and small thermal expansivity) and a smaller structure factor than Si.

Therefore, diamond crystals have been planned for use as the monochromators for high power X-ray beams. Actually some natural diamonds and synthetic diamonds have been tested, showing feasibility of diamond as the monochromators [9-13]. However, the high-quality natural diamonds suitable to the monochromator are extremely rare, and it has been very difficult to supply high-quality synthetic diamonds constantly. Our synthetic type IIa diamonds have very high crystalline quality, and the quality from crystal to crystal changes very little (Table 1, [5]).

In order to test the feasibility of our diamond as a synchrotron X-ray monochromator, experiments were carried out by the SPring-8 project team at the Photon Factory of the National Laboratory for High Energy Physics [14]. Rocking curves of several type IIa diamond crystals were measured by using a synchrotron beam. A typical result is shown in Fig. 8. The crystal had been grown on a high-quality seed [5]. The width in the rocking curve of the synthetic type IIa diamond crystal (FWHM = 1.2 arcsec) is very close to the calculated one (1.0 arcsec for intrinsic width), demonstrating that our crystals are very useful for monochromators. Along this line, plans are under way to use the synthetic type IIa diamond for the monochromator of high power synchrotron radiation beams at the new synchrotron facilities [14].

Fig. 8. Rocking curve and topographs of synthetic type IIa diamond grown on a high-quality seed, for (004) reflection under synchrotron radiation with an incident wavelength of 0.76 Å.

3-3. High-pressure anvils

Diamond crystals have been used as anvils for generation of ultra-high pressure as shown in Fig. 9 [15]. The diamond anvils have been mainly utilized for studying material science, condensed matter physics, geophysics, geochemistry, medical science, and so on. Natural diamond crystals have been employed for the anvils but there are limitations pertinent to stability, attainable pressure, and lifetime because of the crystal defects and the diversity of quality.

Fig. 9. A example of high-pressure diamond anvil [15].

In 1986, synthetic type Ib crystals were tested as diamond anvils by Onodera et al [16], and the feasibility of synthetic diamonds for high-pressure anvils was shown. Subsequently, Ruoff et al. also tried to generate high pressure by using synthetic diamond anvils [17,18], and succeeded in generating pressures up to about 300 GPa. They suggested that synthetic diamonds have a great potential for ultra-high pressure research using diamond-anvil cell. Sumitomo Electric Industries applied synthetic type Ib diamond crystals to the diamond anvils, but they have been still inadequate for optical measurements under high pressure because of the absorption arising from nitrogen impurity.

The synthetic type IIa diamond crystals show no absorption due to the impurities (Figs. 2 and 3). Furthermore, they have few crystal defects and little internal strain which may be the origins of destruction or deformation (Table 1, [5]). Actually the synthetic diamond has higher resistance for plastic deformation, having high hardness and showing very smooth cleavage surface [7]. Therefore, synthetic type IIa diamond crystals are expected to be very useful as diamond anvils. In Fig. 10, diamond anvils prepared from our synthetic

type IIa diamond crystals are shown. These are already in use by some high-pressure researchers.

Fig. 10. Diamond anvils prepared from the synthetic type IIa diamond crystals.

3-4. Others

Since the synthetic type IIa diamond has very few impurities and few crystal defects that cause inhomogeneous formations of internal stress and phonon scattering, the mechanical and physical properties are very much improved compared with those of natural diamond or conventional synthetic type Ib diamond. For example, the hardness of synthetic type IIa diamond is higher than that of synthetic type Ib diamond (Fig. 5, [7]). Also, the thermal conductivity of synthetic type IIa diamond is 10~20 % higher than that of natural or synthetic type Ib diamond [6]. Therefore, use of synthetic type IIa diamond may lead to improving the performance characteristics and the reliability of conventional diamond products such as heat sinks, high precision cutting tools, and wire drawing dies.

Besides, synthetic type IIa diamond is also very useful for scientific purposes; i.e., specimens for the determination of essential diamond properties, raw materials for the studies of crystallography, reference materials for various kinds of analysis, etc. They have already been used as a reference material for Raman spectroscopic analysis, a raw material for doping tests [19], substrata for CVD diamond epitaxial growth tests, a specimen for positron annihilation experiments [20], a detector for neutron radiation [21], and so on.

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