We synthesized an ultrapure nano-polycrystalline diamond (NPD) containing very few chemical impurities (<1 ppm). The $^{13}$C concentration of the carbon source was reduced to less than 0.01% by using $^{13}$C-enriched high-purity carbon. The ultrapure NPD was synthesized by direct conversion from graphite under high-pressure and high-temperature (HPHT) conditions. We measured the optical properties of the ultrapure NPD, which appeared yellowish, attributed to the structural features of the specimen. Also, the one-phonon absorption peak at 1220 cm$^{-1}$ is attributed to the broken symmetry of the diamond lattice. Moreover, a defect-related PL peak was found at 730 nm. © 2016 The Japan Society of Applied Physics

Optical properties of ultrapure nano-polycrystalline diamond

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Diamond is a representative covalent crystal material. The physical properties of diamond reflect its chemical and/or isotopic impurities.1–3 Among diamonds, nano-polycrystalline diamond (NPD) can be synthesized by the direct conversion method at ultra high pressure and temperatures. It consists of fine diamond grains of 50–70 nm binding directly and strongly to one another without any binding metals; therefore, the hardness and strength of NPD surpass those of single-crystal diamonds.4–5

Although nanocrystalline diamond (NCD) films have similar or smaller crystal grains because they are synthesized by chemical vapor deposition (CVD), they have thus far been proved inadequate for synthesizing bulk bodies and to contain graphic components.6 Moreover, the mechanism of the synthesis of these novel hard materials through conversion from precursors such as graphite is also becoming a new focus of research.7 The color of NPDs has attracted great interest, because colorless and transparent NPDs can be used in a variety of applications. However, although existing NPDs are transparent, they appear yellowish, which make them inapplicable for high-pressure-proof windows or high-pressure anvils. By analogy with single-crystal diamonds,8,9 it is believed possible to remove the color from the NPD by decreasing the concentration of impurities, such as nitrogen, to 0.1 ppm.

In this study, we have decreased the concentration of such impurities to a practical lower limit in an attempt to synthesize colorless transparent NPDs. In addition, we have performed $^{13}$C enrichment up to 99.995% to remove isotopic impurities.

High-purity isotopically enriched graphite phase carbon was annealed at 2000 K in vacuo to remove chemical impurities. The graphite tablet (chemical impurities <0.1 ppm, isotopic purity >99.99%, refined by annealing at 2000 °C and $9 \times 10^5$ Pa) was used as the starting material. Then, the graphite which is the starting material of NPD, was put into a capsule in an Ar-filled glove box. Prior to the direct conversion, the capsule was evacuated to a pressure below 0.1 Pa and exchanged with Ar (99.99% pure) gas three times to remove any residual molecules from the air. Then, the capsule was put into a multianvil cell.

Chemically and isotopically pure NPD specimens of 3 mm diameter and 1 mm thickness were synthesized by direct conversion from high-purity graphite at pressures of 15–18 GPa and a temperature of ~2300 °C for 20 min. The surfaces of both sides of the obtained NPD specimens were finely polished to a mirror finish using a high-speed polishing machine with a metal-bonded diamond wheel. The Knoop hardness measured for the ultrapure NPD at several arbitrarily selected areas was equal to 130 GPa in any direction, which was higher than that for the widely used polycrystalline diamond containing a binder (60 GPa).

Secondary-ion mass spectroscopy (SIMS) measurements were performed using a CAMECA IMS-7f instrument to measure the chemical and isotopic impurities in the ultrapure NPD. The first ion species was Cs+, the acceleration voltage was 15.0 kV, the measured area was 30 µm in diameter, and the accuracy of the measurement was ±40% ($2\sigma$).

The optical properties were measured using a UV–vis measurement system. Fourier-transform infrared (FT-IR) spectroscopy measurements were performed to distinguish between the absorption originating from chemical impurities and that from the structure, i.e., the isotope effect. In these experiments, specimen thickness and transparency can directly affect the measurements; thus, we prepared specimens with identical thicknesses of 0.7 mm. For detailed analysis, we also polished the specimens to 0.2 mm thickness.

Grain size and crystallinity were determined by X-ray diffraction (XRD; PANalytical X’Pert) analysis in the 2θ range from 20 to 100° with a resolution of 0.1°. Scanning electron microscopy (SEM) was also performed on both ultrapure and conventional NPD specimens to investigate their microstructures. In-plane Raman spectra were measured using a Raman measurement system (Horiba LabRam) in standard configuration at room temperature by observing the first-order Raman spectrum and evaluating its FWHM. The calibration was implemented using a standard single-crystal sample containing the natural abundances of carbon isotopes and less than 0.1 ppm chemical impurities. Because of the isotope enrichment, any observed broadening of the spectral line width could be attributed to only the grain size. Photoluminescence (PL) spectra were measured by excitation with a 532 nm laser.

The ultrapure NPD obtained in this research has a light yellowish color and a high transparency. The XRD pattern in Fig. 1 shows that only the cubic diamond structure is present in the specimen. No graphitic components are observed, which could deteriorate the transparency (Fig. 1).
SIMS analysis revealed that the conventional NPD contains 100–200 ppm hydrogen, 10–30 ppm oxygen, and 50–100 ppm nitrogen as impurities. In a previous study on the optical properties of NPDs, electron spin resonance (ESR) measurements revealed that the concentration of isolated substitutional nitrogen impurities (P1 centers) in NPDs was less than 0.5 ppm and the boron concentration was less than 1 ppm. On the other hand, an ultrapure NPD does not contain hydrogen, oxygen, nitrogen, boron, or silicon as impurities within their detection limits of 1, 0.1, 0.1, 0.1, and 0.2 ppm, respectively. These concentrations of chemical impurities were measured by SIMS. The isotopic composition was also confirmed to be 99.995% $^{12}$C by SIMS.

The Raman spectra shown in Fig. 2 clearly exhibit peak shifts of $^{12}$C and $^{13}$C in the NPD. The starting graphite materials used in this study were ultrapure. Usually, the hydrogen (100–200 ppm) and oxygen (10–30 ppm) impurities in the conventional NPD detected by SIMS are thought to originate from air in the open pores in the starting graphite, which is exposed to air before sample preparation. These impurities seem to be included as contaminants (absorbed atmospheric water molecules) at grain boundaries in the NPD. Nitrogen can also be absorbed in atmospheric water. Here, however, we not only used ultrapure graphite, but also exchanged the water-contaminated gas in the cell with argon. This facilitated the synthesis of an ultrapure NPD.

The nanostructures of the polished NPDs are shown in SEM images in Fig. 3. The grains in the ultrapure NPD are obviously smaller than those in the NPD containing chemical impurities. SIMS measurements have shown that, among the common impurities in the conventional NPD, hydrogen is the most abundant. Here, we also note that, during chemical vapor deposition (CVD) in particular, hydrogen is involved in the formation of diamond. After considering all the evidence, we assume that hydrogen catalyzes the direct conversion to NPDs.

Figures 4 and 5 show the IR transmission spectra of NPDs. The optical absorption bands seen above 2000 cm$^{-1}$ are due to multiphonon absorption, which is intrinsic to diamond. The shape of the multiphonon absorption peak of NPDs is similar to that of single-crystal diamonds, indicating that NPDs do not have a strong lattice strain within each grain. In the single-phonon region, NPDs have an absorption band with a peak at 1220 cm$^{-1}$ attributed to the distortion of the diamond lattice by inclusions of hexagonal diamond. In the $^{13}$C (99.99%) NPD, we observe a –50 cm$^{-1}$ shift, which corresponds to the shift of the one-phonon absorption for $^{13}$C NPD, as calculated using the obtained peak at 1220 cm$^{-1}$ for the $^{12}$C-enriched NPD and the mass difference between $^{12}$C and $^{13}$C as follows:
where $\omega_{12C}$ and $\omega_{13C}$ denote the vibrational energies of $^{12}$C and $^{13}$C, respectively. $m_{12C}$ and $m_{13C}$ denote the masses of the species.

We assume that this phonon absorption is the single-photon absorption that occurs when substitutional nitrogen occupies a carbon site and forms a dipole moment. According to this hypothesis, asymmetry in the carbon sites caused by distortion and strain from the substituting species is also probable. Thus, our data suggest that nitrogen does not contribute to the band at approximately 1220 cm$^{-1}$ and that this peak is attributable to only structural features such as distortion, lattice mismatching, strain, and dangling bonds. In fact, the multiphonon peaks are similar to those of a single-crystal diamond, and the single-phonon absorption is attributable to grain boundaries where lattice mismatches occur.

Figure 6 shows the UV–vis transmission spectra of the ultrapure NPD, along with the spectra of a typical NPD. The NPD has a continuous absorption shoulder starting at 700 nm. This broad absorption confers the characteristic coloration of NPDs. The shoulder is probably attributable to lattice defects generated in each particle by plastic deformation during the 20 min of direct conversion, similar to the defects observed in natural brown type-IIa diamonds. The weak absorption peaks observed at 611 and 667 nm correspond to the luminescence peaks observed in the PL spectrum, as discussed below. Because these peaks are also observed for the ultrapure NPD, we assume that they are not related to impurities.

Figure 6 shows another absorption component beginning at 450–500 nm. To investigate this absorption feature below 500 nm, we measured the UV transmission spectra using a 0.20-mm-thick specimen. The result is shown in Fig. 6(b). The conventional NPD exhibits continuous absorption below 320 nm, which is thought to correspond to the secondary absorption edge attributed to electron transitions from A-aggregates of nitrogen to the conduction band. These transitions are also observed in natural type-Ia diamond crystals. However, this absorption trend also exists in the optical spectrum of the ultrapure NPD, even though the concentrations of impurities are below the detection limits in this specimen. In addition, no absorption peaks from dispersed nitrogen impurities at 270 nm were observed.

The PL spectra of the NPD excited by a 532 nm laser are shown in Fig. 7. A broad optical absorption over 420–460 nm is observed; this is an essential absorption for NPDs. In addition, the known peaks appearing at 611, 626, and 653 nm for the conventional NPD show much lower intensities or are absent. Thus, we presume that these peaks are related to impurities. The broad band appearing at 500–800 nm with a peak at approximately 690 nm is attributed to the B band observed in natural brown type-IIa diamonds containing dislocations.

Intriguingly, PL appears at 730 nm in the ultrapure NPD. First, from the viewpoint of impurities, we assumed that this peak arose from silicon-related defects such as the SiV center speculated to appear along with nitrogen. However, SIMS showed that no silicon was detected in the specimen, whereas
it was present in the conventional NPD. Note that in CVD-grown synthetic diamonds, silicon is commonly unintentionally introduced during the growth process through the plasma etching of parts of the quartz reactor chamber or from the substrate.\textsuperscript{12–14} This silicon concentration was reported to approach 100 ppm for microwave-assisted CVD-grown diamond.\textsuperscript{15} This diamond exhibits a 737 nm PL peak, which appears for Ia and IIa crystals with low nitrogen concentrations.\textsuperscript{16}

Because the center of the peak for the ultrapure NPD in this study was not exactly the same as that of the SiV center appearing at 737 nm, we considered the possibility of a stress-induced peak shift. However, since nitrogen and silicon are absent, the concentration of SiV, if such sites even form, is much lower than 0.1 ppm. Therefore, we could not reasonably attribute this peak to SiV or related defects.

From the structural viewpoint, we considered that the mechanism for this 730 nm peak may be related to an obtuse triple junction, such as those found in CVD-grown polycrystalline diamonds.\textsuperscript{17} This mechanism also implies crystal twinning. Mora et al. reported the observation of a peak at 732 nm near the obtuse triple junctions of [111], [221], and [111], which are characteristic of CVD diamonds and typically sites of local stress concentration. This structure produces a very high stress. As a result, nanosized twins are found to exist parallel to {111} or, alternatively, a highly stressed structure is formed by two different types of extended defects located on either side of the plane boundary.\textsuperscript{18} These results suggest the possible presence of dense twin structures producing the PL peak at ∼730 nm. However, in general, this peak appears along with the GR1 center. In the GR1 spectrum, the peak intensity tends to increase near the grain boundaries and other defects; in addition, the peak position is still somewhat different from that obtained in our experiment. It is possible to increase the intensity of this NPD peak and compare it with those of CVD films, since the NPD has more grain boundaries where dislocations such as twins or misfits form. If this particular peak arises from a structural optical electronic transition caused by disordered structures, such as twins and misfits induced by stress at the grain boundaries, it might be possible to better understand it by performing high-temperature annealing with and without a high pressure.

The properties of nano-polycrystalline materials are generally affected by their surface area per unit volume. This quantity is significantly greater for nano-polycrystalline materials than for polycrystalline diamonds with micrometer-sized grains. At a mean diameter of 100 nm, the surface ratio is generally higher than 1%. Therefore, the optical properties of the bulk could reflect the surface components in this material.

In conclusion, we synthesized an ultrapure NPD with extremely high chemical and isotopic purities and focused mainly on a pure $^{12}$C-enriched NPD. Although the concentrations of typical impurities such as hydrogen, nitrogen, oxygen, boron, and silicon were below the SIMS detection limit, the NPD still appeared yellowish. We need to perform a detailed study on defects near the boundary at which a specific photoluminescence occurs. We found unusual absorption in the FT-IR spectra and evaluated two possible origins: chemical impurities causing the aggregation of nitrogen impurities and structural effects. Because we observed one-phonon absorption even without nitrogen impurities, we consider that the peak at 1220 cm$^{-1}$ is attributed to the broken symmetry of the diamond lattice with hexagonal diamond. Although the concentrations of impurities were greatly reduced to below the detection limit, we observed a new photoluminescence. This might originate from twin grain boundaries and defects. Further investigations, such as the analysis of the temperature and grain size dependences of PL spectra, and ESR measurement to clarify structure in detail are required. In addition, we observed the suppressed crystal grain growth of the ultrapure NPD. This might indicate that hydrogen works as a catalyst during the direct conversion of graphite to diamond. Hydrogen incorporation may support the direct conversion of graphite to diamond as in the case of CVD diamond. These essential properties, including the isotope effect in NPDs, will provide a key to utilizing NPDs’ optical properties, improving NPDs’ mechanical properties, and understanding the basic properties of diamond and therefore covalently bonded materials.

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