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Thermal expansion of a high purity synthetic diamond single crystal at low temperatures

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Measurements of lattice parameters were made for a single crystal of a high-purity synthetic diamond using the x-ray-diffraction Bond method between 4.2 and 300 K. The key features of the present measurement are as follows: (1) The lattice parameter is determined with an accuracy of 10^{-6}. (2) A very small negative thermal expansion is detected between 30 and 90 K. (3) Thermal expansion shows a behavior of the T^4 law represented by the Debye theory within the measuring temperature range. By comparing the present results with the previously reported results for nitrogen-doped diamond and boron-doped diamond, it is found that diamond becomes harder following doping by nitrogen.

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I. Introduction. While most materials expand upon heating, many tetrahedral semiconductors exhibit negative thermal expansion below a certain temperature,[1] for example, 48 K for Ge,[2] 120 K for Si,[3] 55 K for GaP,[4] and 80 K for InP.[5] It is generally believed that this unusual negative thermal expansion behavior in semiconductor crystals can be attributed to the negative Grüneisen parameters of the transverse acoustic phonons near the Brillouin-zone boundary.[6–8] Xu *et al.*[9] calculated phonon-dispersion curves, Grüneisen parameters, and the coefficients of thermal expansion for silicon and diamond. Their theoretical results showed that the transverse acoustic-phonon modes of Si behaved anomalously. On the other hand, their results showed that such behavior was not expected in the corresponding phonon branches of diamond. In 1956, Thewlis and Davey[10] investigated the lattice parameters of two diamond samples, industrial and precious (gem-quality) diamonds, by x-ray analysis from 123 to 1223 K. They found that in the case of industrial diamond the thermal expansion coefficient passed through a sharp minimum of negative value at $T\approx 243$ K. In the case of the precious diamond the curve of the thermal-expansion coefficient had no minimum. They assumed that the anomaly could presumably arise from some intracrystalline impurity. In 1960 Novikova[11] measured a relative change of length of the two natural diamond crystals, and reported a small negative thermal expansion between 20 and 90 K. Parsons[12] pointed out that Novikova's result was within the experimental error, and therefore the confirmation of negative thermal expansion was incomplete. In 1992 Haruna *et al.*[13] measured the lattice parameter of nondoped synthetic diamond crystal in a temperature range between 4.2 and 320 K by using the x-ray Bond method. The nondoped specimen was a Ib type, in which nitrogen atoms of 100 ppm or less were included and it was colored yellow (hereafter we call this specimen nitrogen-doped diamond). The negative thermal expansion was not detected, even with the accuracy of 10^{-6} in their measurements. In 1998 Saotome *et al.*[14] measured the thermal expansion of boron-doped diamond single crystal in temperature range between 4.2 and 320 K by the x-ray-diffraction method. This specimen contains about 100-ppm boron (hereafter we call this specimen boron-doped diamond). They also did not detect a negative thermal expansion.

In the low-temperature range, where host crystal contributions are themselves small, defects can have relatively large effects on the thermal expansion. In order to detect the negative thermal expansion of diamond, which is expected to be very small, we should use a defect-free single crystal. So we have measured the lattice parameter of a high-purity synthetic single-crystal diamond, which contains nominally nitrogen atoms with concentrations of less than several ppm. This paper is organized as follows: the experimental procedures are described in Sec. II. Results of the experiments and the temperature dependence of the thermal expansion coefficient are presented in Sec. III.

II. Experimental procedure. A single crystal of synthetic high-purity diamond used in our experiment was provided by Sumitomo Denko. The specimen is type-IIa diamond. The nominal defect is nitrogen, whose concentration is less than several ppm (hereafter we call this specimen high-purity diamond). The specimen is transparent, and has a shape of a thin square plate with dimension $3.9\times 3.7\times 0.3\ \mathrm{mm}^3$. The surfaces are oriented parallel to the (100) planes. In general, nitrogen is the most common atomic impurity found in natural and as-grown synthetic diamond. Diamond is classified according to its infrared spectrum of the defect-induced one-phonon absorption in the region between 500 and 1500 cm^{-1}, which results from vibrations at different atomic arrangements of nitrogen.[15] We performed the infrared absorption measurements at room temperature by a Simazu IR-8200DC Fourier transform infrared spectrometer. The wavelength range was from 1.3 to 28.6 μm. The concentration of nitrogen in single-substitutional nitrogen atoms (C-form nitrogen) was determined from the strength of absorption of the peak at 1130 cm^{-1}.[16] The high-purity diamond did not show a peak at 1130 cm^{-1} in the spectrum. This result confirms that the nitrogen concentration of the high purity diamond is less than several ppm.

In measurements of the thermal expansion of lattice parameter, the x-ray Bond method was used to determine the temperature variation of the lattice parameter. With nearly perfect crystals the lattice parameters can be measured to a few parts in a million.[17] For the x-ray source, a fine-focus Fe target was used with a collimator of 0.2 mm in width, attached to make the x-ray beam thinner. To improve the ac-

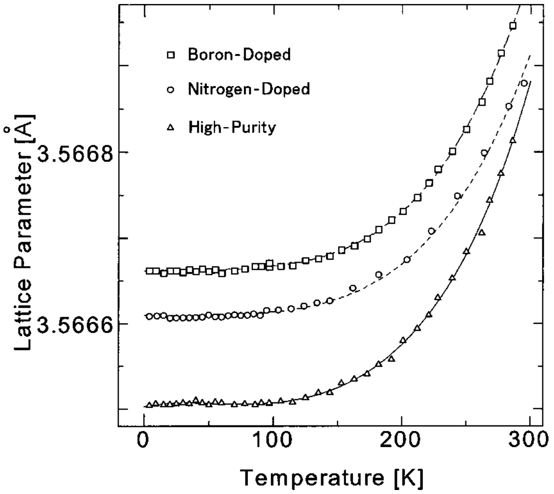

FIG. 1. Temperature dependence of the lattice parameter. The open triangle represents the experimental data of the lattice parameter of the high-purity diamond. The full line represents the fifth polynomial. The open circle represents the result of the nitrogen-doped diamond. The open square represents the result of the boron-doped diamond.

curacy, the highest possible diffraction line of the (400) reflection was used. For this plane, $2\theta = 160.01°$, where θ is the measured Bragg angle. The wavelength of the $K\beta$ line is taken as 1.756 53 Å. We must be sure that the atomic plane of the sample is sufficiently parallel to the axis of rotation. To this end the tilt angle of the specimen was carefully adjusted before each measurement. The temperature was varied in the range from 4.2 to 300 K. To perform the low-temperature measurements, a glass cryostat specially designed for the Bond method was used. The details of the cryostat were reported in Ref. 18. The temperature of the specimen during the measurement was controlled within an accuracy of 0.1 K by using an automatic temperature controller. Hence the relative accuracy of 10^{-6} was finally attained in determining the temperature variation of the lattice parameter.

III. Experimental results and discussions. Measurements of the lattice parameter were repeated twice, in the decreasing and increasing temperature cycles. In Fig. 1 we show the temperature dependence of the lattice parameter between 4.2 and 300 K. The values are corrected for refraction, absorption, and Lorentz factors. There is no obvious systematic variation of the lattice parameter. Figure 1 also shows, for comparisons, the results of the nitrogen-doped diamond obtained by Haruna *et al.*[13] and those of the boron-doped diamond obtained by Saotome *et al.*[14] In the high-purity diamond we do not observe an apparent minimum in the lattice parameter over a wide temperature range. However, the figure shows that the lattice parameter has a tendency to decrease faintly with increasing temperature between 30 and 90 K. This anomalous temperature region corresponds to a temperature region in which Novikova[11] already reported that a small negative thermal expansion appeared in natural diamonds. As mentioned in Sec. I, the theoretical result[9] does not predict the negative thermal expansion for diamond. However, it is our opinion that there is likely a very small negative thermal expansion, as suggested by Novikova. In the figure the solid line gives reasonable values of the lattice parameters that are fitted to the fifth-order polynominal

$$a = \sum_{n=0}^{5} a_n T^n. \tag{1}$$

These coefficients, determined by the method of least squares, for the high-purity diamond, are as follows: $a_0 = 3.566503$, $a_1 = 2.99\times 10^{-7}$, $a_2 = -6.98\times 10^{-9}$, $a_3 = 5.79\times 10^{-11}$, $a_4 = -1.62\times 10^{-13}$, and $a_5 = 2.74\times 10^{-16}$. As shown in Fig. 1 the effects of boron and nitrogen impurities are likely to be appreciable in the low-temperature range. According to Mainwood[19] the relaxation sets the boron in an equilibrium position with a 10% elongation of the C-B bonds over the normal C-C distance. This elongation causes an impurity-dependent difference in the lattice parameter of boron-doped diamond. Lang *et al.*[20] measured the increase of the lattice parameter of a diamond containing 88-ppm nitrogen at room temperature to be $\Delta a/a = 1.18\times 10^{-5}$. When the fractional atomic concentration of substitutional nitrogen is denoted by $c(N)$ in atomic ppm, the dilatation is given by $\Delta a/a = 0.14c(N)$, which indicates that the effective volume of a single substitutional nitrogen atom in diamond is $1+3\times(0.14) = 1.42$ times that of the carbon atom it replaces at room temperature. This result is consistent with the fact that the stable relaxation makes a 5–10 % increase of the length of the C-N bond.[19] In the case of the nitrogen-doped diamond which is type Ib, the lattice dilatation caused by the substitutional nitrogen can be given at 300 K by

$$\begin{aligned}\Delta a/a &= [a_{\text{nitrogen-doped}}(300\text{ K}) \\ &\quad - a_{\text{high-purity}}(300\text{ K})]/a_{\text{high-purity}}(300\text{ K}) \\ &= 1.11\times 10^{-5}.\end{aligned}$$

After combining this dilatation with Lang's relation $\Delta a/a = 0.14c(N_s)$, we can estimate the nitrogen concentration to be 78 ppm, which is consistent with the data published by the Sumitomo Denko Company.

In the above equation we assume that the high-purity diamond is defect free. In accepting the lattice parameter value quoted for defect-free (type-II) diamond, caution is needed for two aspects. First, the absence of a nitrogen impurity should be confirmed by the infrared-absorption spectra. In our high-purity specimen infrared spectroscopy verified that the nitrogen concentration was below the level of a few ppm. The second caution stems from the fact that specimens have crystal dislocations. The population of such a dislocation may increase the mean lattice parameter by a measurable amount. Our high-purity diamond is a synthetic single crystal, so that the dislocation concentration may be negligible. Hence, we may conclude that the lattice parameter of our high-purity diamond represents the lattice parameter of defect-free diamond. Our value of the lattice parameter of the high-purity diamond at 300 K is $3.56689\,_6$Å. In 1951 Straumanis and Aka[21] carried out a lattice parameter determination of four diamond samples from the Belgian Congo. The three clear white diamond samples showed the same lattice parameter: 3.56679 Å at 293 K. The lattice parameter of the gray board was 3.56687 Å at 293 K. Furthermore, they revealed the presence of 15 elements in the sample by means of spectrographic analysis, and reported the possibility of a very small amount of silicon or other elements in gray board diamond to increase the lattice parameter by 0.000 080 Å. Until 1957 a number of investigators already determined the lattice parameters of diamond. However, a considerable variation of data existed. The knowledge at that time did not support the thesis of compositional variation sufficiently well to explain the differences among references. Skinner[22] also doubted if the large variation in the lattice parameter was due as much to compositional variation as to experimental errors in the different methods of measurement. At that time too diamonds studied were not chemically analyzed, and, even when analyses were made, investigators generally did not state whether the impurities were present as inclusions or in solid solution. Skinner studied a single colorless fragment of diamond from southwest Africa, and further performed spectrographic analysis of the sample. The major impurity was silicon, whose concentration was smaller than 40 ppm. Silicon is a common component of the minerals frequently found as inclusions in diamond. The silicon atom is about 50% larger than the carbon atom, and a large isotropic (totally symmetric) distortion of 25% is necessary to accommodate it in diamond. The lattice parameter of natural diamond, which contained Si less than 40 ppm was 3.566 88 Å at 298.16 K. The lattice parameter obtained by Kaiser and Bond[23] for natural diamonds, which did not show nitrogen-dependent infrared absorption, was 3.56682 Å. In Ref. 24, infrared-absorption spectroscopy verified that nitrogen concentration was down to the level of a few ppm. That determination of the lattice parameter of natural diamond was 3.566 89 Å. Holloway *et al.*[25] reported measurements of the lattice parameter of single-crystal synthetic diamonds and obtained 3.56714 Å at 298 K. The literature values ranges from 3.566 82 to 3.567 14 Å. Our value for the high-purity diamond is between two values.

To investigate the thermal expansion, it is necessary to estimate the usual effect of the anharmonic contribution of the thermal vibration of atoms of the lattice. The low-temperature expansion can be expressed as

$$\Delta a/a=(3\pi^4\kappa N\gamma k_B T^4/15V_0\Theta_D^3),$$

where $\kappa=1/B$ is the compressibility and B is the bulk modulus. γ is the Grüneisen constant. V_0 is the volume of a crystal of N atoms. Θ_D is the Debye temperature and k_B is the Boltzmann constant, respectively. In Fig. 2 we plot the lattice parameter against T^4. The thermal expansion curves can be expressed as

$$\Delta a/a(\text{high-purty})=[(a(T)-a(0))/a(0)]=1.30\times10^{-14}T^4,$$

$$\Delta a/a(\text{nitrogen-doped})=1.05\times10^{-14}T^4$$

and

$$\Delta a/a(\text{boron-doped})=1.19\times10^{-14}T^4,$$

respectively. Theoretically Saotome *et al.*[14] obtained the expression $\Delta a/a=0.95\times10^{-14}T^4$. The slope in the $\Delta a/a-T^4$ line is inversely proportional to the bulk modulus. If we can neglect change of the Grüneisen parameter by doping impurities, we obtain the following ratios of the bulk modulus of the doped diamonds to that of the high-purity diamond: $B(\text{nitrogen-doped})/B(\text{high-purity})=1.23$ and $B(\text{boron-doped})/B(\text{high-purity})=1.09$. Hence, we come to the conclusion that by doping nitrogen the bulk modulus of diamond becomes greater. Han and Ihm[26] investigated the structure and electronic properties of diamond with vacancies in order to understand the behavior of hard materials in the presence of vacancies and impurities. After replacing carbon atoms surrounding the vacancy by nitrogen or boron atoms, the bulk modulus of the material with nitrogen substitution is greater than that without substitution, although it is still smaller than that of vacancy-free diamond. On the other hand, boron substitution has the opposite effect. Han and Ihm's results is qualitatively consistent with our experimental results. So we may expect that it is possible to make a "superhard diamond" by doping nitrogen impurity.

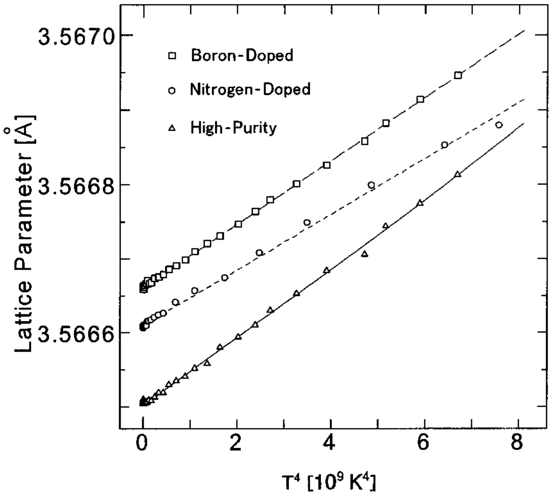

FIG. 2. T^4 plots of the lattice parameter a. Notations are the same as in Fig. 1.

The thermal expansion coefficients are calculated from the observed lattice parameter values. The linear thermal expansion coefficient is defined by $\alpha=[1/a(\text{He})(da/dT)]$, where $a(\text{He})$ is the lattice parameter at liquid-He temperature. The calculated results are plotted in Fig. 3. In this figure the solid circles α are calculated by taking the difference in the lattice constant Δa and the temperature ΔT, respectively, between successive data values and by using the relation $\alpha=[1/a(\text{He})](\Delta a/\Delta T)$. The solid line traces reasonable values of the thermal expansion coefficients, that are fitted to the fourth-order polynominal

$$\alpha=\sum_{n=0}^{4}\alpha_n T^n. \tag{2}$$

The coefficients, determined by the method of least squares, are as follows: $\alpha_0=0.00$, $\alpha_1=4.10\times10^{-10}$, $\alpha_2=-1.42\times10^{-11}$, $\alpha_3=1.46\times10^{-13}$, and $\alpha_4=-1.55\times10^{-16}$. The

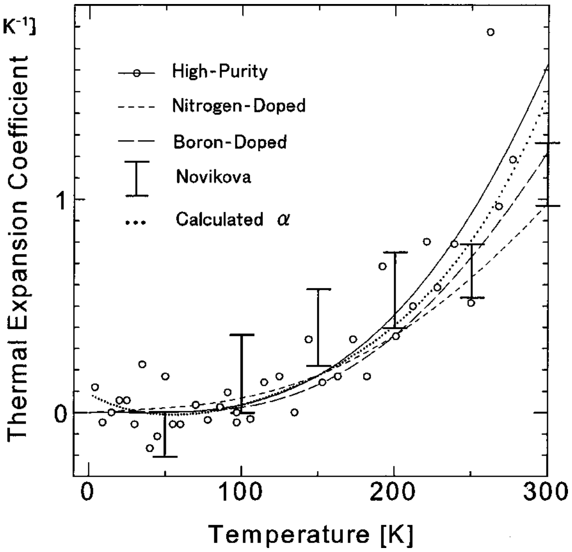

FIG. 3. The temperature dependence of the thermal-expansion coefficient. The open circle represents the experimental data of the lattice parameter of the high purity diamond. The full line represents the fifth polynomial. The dashed line represents the result of the nitrogen-doped diamond. The bold dashed line represents the result of the boron-doped diamond. In Novikova's results, data plotted show the spread of results obtained. Black dots show the results using $\alpha = (1/a(\mathrm{He}))\Sigma_{i=1}^{5} n a_n T^{n-1}$.

values of α obtained from this point-by-point determination are susceptible to random errors. In order to reduce the random error as much as possible, we first take the least-squares fitting of the lattice parameter a to polynominal in T that is $a(T) = \Sigma_{i=0}^{5} a_n T^n$, from which $\alpha = [1/a(\mathrm{He})](da/dT) = [1/a(\mathrm{He})]\Sigma_{i=1}^{5} n a_n T^{n-1}$ can be calculated directly.[27] The values of α are less susceptible to random errors in $a(T)$ than those obtained by a point-by-point determination. The thermal-expansion coefficient calculated by this method is close to that obtained by the point-by-point determination method excluding about $T = 0$ K (see black dots in Fig. 3). Hence we conclude that the polynominal equation (2) represents the experimental thermal expansion very well.

From Fig. 3 we find that high-purity diamond tends to possess larger thermal expansion coefficients compared with other doped diamonds in the high-temperature region. This tendency arises from the fact that the compressibility of the high-purity diamond is larger than the those of other doped diamonds. Straumanis and Aka[21] reported a thermal-expansion coefficient of $(1.38 \pm 0.12) \times 10^{-6}\ \mathrm{K}^{-1}$ between 283 and 323 K. Skinner[22] reported $1.011 \times 10^{-6}\ \mathrm{K}^{-1}$ at 298.16 K. The values obtained in our work are 1.60 $\times 10^{-6}\ \mathrm{K}^{-1}$ at 300 K for high-purity diamond. Furthermore, in Fig. 3 the results of Novikova's observation of the thermal-expansion coefficient of diamond are shown. Novikova's results show the same tendency as our results for the high-purity diamond.

In summary, we have shown that a precise x-ray Bond method provides an accurate determination of the lattice parameter of high-purity diamond as a function of temperature. From the results for high-purity diamond and those for boron-doped and nitrogen-doped diamond previously obtained, the following conclusions are obtained.

(1) The lattice parameter of the high-purity diamond has a tendency to decreasing faintly with increasing temperature between 30 and 90 K. This temperature range is consistent with the temperature range proposed by Novikova, in which the extremely small negative thermal expansion appears.

(2) For nitrogen-doped diamond Lang's relation may provide the relation between the dilatation and impurity concentration at room temperature.

(3) In the range of observed temperature, the $a - T^4$ law holds.

(4) Via doping nitrogen, diamond becomes harder, so that it is possible to make a "superhard diamond" by doping nitrogen.

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