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Isotopic Effect on Thermal Conductivity of Diamond Thin Films

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The thermal conductivities of 99.95%^{12}C and natural diamond films at temperatures from 1.5 to 300 K were studied. The thermal conductivity was measured by a steady heat-flow method. The thermal conductivity of ^{12}C enriched diamond was increased compared to that of natural isotope abundant diamond. Its maximum value was about 1.4 times higher than that of the natural isotope-abundant diamond at around 180 K. The increase in thermal conductivity for the isotope diamond can be explained by Callaway's model, that is, by lowering the isotope-scattering effect.

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1. Introduction

Isotopes are generally used to label elements by their difference in atomic mass, or they are utilized as nuclear fuels. Recently, isotope materials have been reported to improve the thermal properties of ceramics and semiconductor materials in which phonon excitation controls the thermal flows.[1–3] Among isotopic materials, the purified ^{12}C single crystal diamond has been reported to have 2 orders higher thermal conductivity than natural isotope-abundant diamond.[3] The isotope effect has also been observed on the polycrystalline diamond film.[4] The diamond film with ^{12}C of 50% showed the lower thermal conductivity than natural isotope-abundant diamond.[4]

In the present study, the thermal conductivities of diamond films with natural isotope abundance (^{12}C: 99% and ^{13}C: 1%) and ^{12}C of 99.95% prepared with a plasma CVD were examined at temperatures from 1.5 to 300 K.

2. Experimental Procedures

2.1 Materials preparation

Diamond films were grown from the natural abundant CH_4 and isotopic CH_4 using a plasma CVD at the Tokyo Gas Co. The films were formed on a molybdenum substrate at 1213–1333 K at a total pressure of 26.6 kPa. The reactant mixture gas was composed of Ar of 500 cc/s, H_2 of 187 cc/s, and CH_4 of 2.83 cc/s. The applied power of the RF was 45 kW. The films formed are columnar polycrystalline diamond films, of which the main growth direction perpendicular to the substrate was ⟨111⟩. After growing the film to a thickness of 0.1 mm, rectangular specimens, 3 mm × 20 mm × 0.1 mm, were cut from the disk for thermal conductivity measurements. The isotopic abundances were 98.89%^{12}C for natural diamond and 99.95%^{12}C for ^{12}C diamond.

2.2 Thermal conductivity measurements

The thermal conductivity was measured by the steady heat-flow method, as shown in Fig. 1. The measurements were made at 1–300 K. The heat flow was parallel to the crystal growth. In the case of diamond films, a graphite support with a horseshoe shape was used so that the film would not break as the specimens were set and the measurements taken.

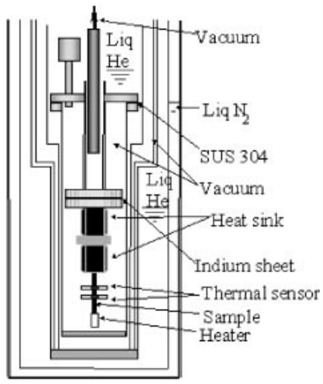


Fig. 1 Apparatus for thermal conductivity measurements at low temperatures.

The thermal conductivity, k, was determined from the experimental data using eq. (1).

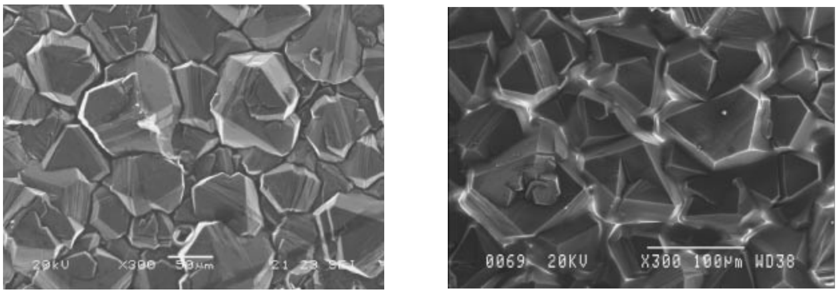
$$k = \frac{P}{\Delta T} \cdot \frac{L}{S}, \tag{1}$$

where P is an input heat power and ΔT and L are the temperature difference and the distance between measured points, respectively. S is the cross sectional surface area of the sample.

3. Results

Figure 2 shows the microstructures of the ^{12}C diamond and natural abundant diamond films. The grain size of both specimens is in the range of 10–65 μm, and the average size is 50 μm. The thermal conductivity measurements were made in the longitudinal direction.

Figure 3 shows the thermal conductivities of ^{12}C diamond and natural isotope-abundant diamond and the graphite support results as a function of temperature. As seen in this figure, the contribution of the graphite support to the thermal conductivity of diamond films is negligibly small. Although the diamond films are not single crystals but polycrystallines with a grain of around 50 μm in diameter, the high thermal



(a) (b)

Fig. 2 Microstructures of ^{12}C diamond (a) and natural abundant diamond (b) films.

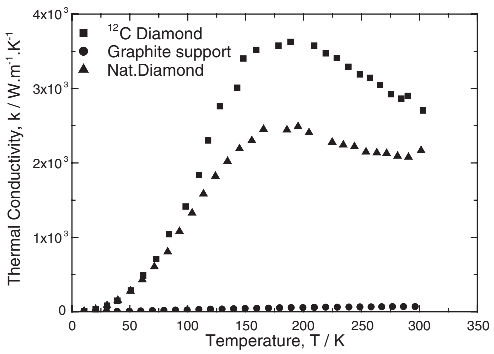


Fig. 3 Thermal conductivities of natural and ^{12}C diamond films.

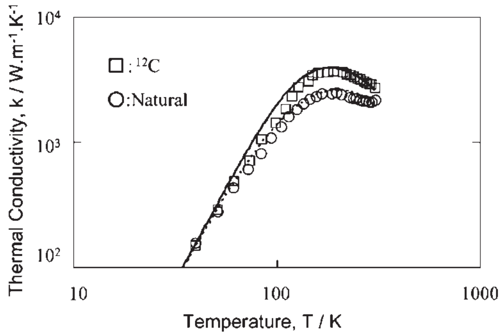


Fig. 4 Curve fittings of thermal conductivities using the Callaway model.

conductivity of ^{12}C was clearly observed. The maximum value taken at around 180 K was about 1.4 times higher than that of the natural abundant diamond film. Moreover, the ^{12}C films showed higher thermal conductivity than the natural diamond even at room temperature.

4. Discussion

The thermal conductivity, k, for dielectric materials is given as

$$k(T) = \frac{1}{3} Cv \cdot (v\tau), \tag{2}$$

where C is the specific heat, v is the phonon velocity, and τ is the relaxation time. Equation (2) is given by Callaway[5] as

$$k(T) = \frac{k_B}{2\pi^2 v}\left(\frac{k_B T}{h}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} \cdot \tau(x)dx. \tag{3}$$

k_B is the Boltzman constant, h is the Planck's constant, and $x = h\omega/k_B T$. ω is a phonon frequency. The total relaxation time, τ, is given as

$$\tau^{-1} = \tau_i^{-1} + \tau_B^{-1} + \tau_U^{-1} + \tau_N^{-1}, \tag{4}$$

where τ_i, τ_B, τ_U, and τ_N are contributions from the isotope scattering, boundary scattering, Umklapp effect, and normal phonon scattering, respectively. Each relaxation time is further given as: $\tau_i = P_I\omega^4$, $\tau_B = v/P_L$, $\tau_U = P_U T^3\omega^2 \exp(-\Theta_D/2T)$, and $\tau_N = P_N T^3\omega^2$. Θ_D is the Debye temperature. P_I, P_U, and P_N are the parameters for the isotope scattering, Umklapp effect, and normal scattering process, respectively. P_L is the grain size. In the present study, we assumed the Debye temperature and phonon velocity for diamond to be 1860 K and 12800 m/s, respectively.[6] The grain size was assumed to be around 10 µm, which is the minimum size in the present study.

Table 1 Parameters for relaxation times in the Callaway model.

Materials	P_I	P_L	P_U	P_N
Natural Diamond	6.5×10^{-47}	1.0×10^{-5}	1.03×10^{-26}	7.0×10^{-26}
^{12}C Diamond	1.0×10^{-48}	1.0×10^{-5}	1.03×10^{-26}	7.0×10^{-26}

The least-squares method was applied to fit eq. (3) to the experimental data. Figure 4 shows the results for ^{12}C and natural abundant diamond films. Fairly good fittings are observed. From the curve fittings, the parameters P_I, P_U, and P_N are obtainable. The results are shown in Table 1. There is no clear difference in the P_L, P_U, and P_N for natural materials and ^{12}C diamond. However, the P_I values are reduced by increasing the isotopic concentration. The isotopic scattering parameter, P_I, is given as a function of the isotope concentration as,

$$P_I = \frac{3a^3}{4\pi v^3} \sum_j f_j \cdot (1 - M_j/M_a)^2, \tag{5}$$

where a is the lattice space, ν is the phonon velocity, f_j is the isotope concentration, M_j is the isotope mass for j isotope, and M_a is the average mass of the diamond films. The calculated P_I values from eq. (5) are 2.54×10^{-47} and 1.42×10^{-48} for natural abundant diamond and 99.95%^{12}C diamond, respectively. These data are close to the data obtained by the curve fittings, as seen in Table 1. The Callaway model can then be used to explain the increase in thermal conductivity in isotopic diamond films. That is, the isotopic scattering effect on the thermal conductivity was reduced by the isotopic purification. Olson *et al.*[6] reported that the maximum thermal conductivity of 1.1×10^4 $\mathrm{W\,m^{-1}\,K^{-1}}$ at around 100 K for 99.93% ^{12}C single crystalline diamond. This value is about 3 times higher than that of the present result in spite of the similar ^{12}C concentration. The Callaway model predicts that the thermal conductivity increases and the peak position shifts to lower temperature with increasing the grain size. If our sample is a single crystalline, the P_L value will be 0.1 mm corresponding to the film thickness. Equation (3) then gives a maximum thermal conductivity of $1 \times 10^4\,\mathrm{W\,m^{-1}\,K^{-1}}$ at around 100 K. This value agrees with that by Oson *et al.* The difference in thermal conductivity between the present result and the reported value is therefore considered to be due to the difference in grain size.

5. Conclusions

The thermal conductivities of ^{12}C and natural isotope-abundant diamond polycrystalline films at 1–300 K were examined. The following conclusions were reached:

(1) The thermal conductivity of ^{12}C with 99.5% abundance was 1.4 times higher than that of natural isotope-abundant diamond at around 180 K and 1.3 times higher at room temperature.

(2) The temperature dependence of the thermal conductivities of isotopic diamond films can be approximated by the Callaway model.

(3) The increase in thermal conductivity was explained by the increase in isotopic concentration, leading to lowering the isotope-scattering effect for thermal flows.

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