

Thermal Conductivity of CVD Diamond Films¹

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Diamond films 60 and 170 μm in thickness were grown by PACVD (plasma-assisted chemical vapor deposition) under similar conditions. The thermal diffusivity of these freestanding films was measured between 100 and 800 K using AC calorimetry. Radiation heat loss from the surface was estimated by analyzing both the amplitude and the phase shift of a lock-in amplifier signal. Thermal conductivity was calculated using the specific heat data of natural diamond. At room temperature, the thermal conductivity of the 60 and 170 μm films is 9 and 16 $\text{W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$ respectively, which is 40–70 % that of natural diamond. The temperature dependence of thermal conductivity of the CVD diamond films is similar to that of natural diamond. Phonon scattering processes are considered using the Debye model. The microsize of the grain boundary has a significant effect on the mean free path of phonons at low temperatures. The grain in CVD diamond film is grown as a columnar structure. Thus, the thicker film has the larger mean grain size and the higher thermal conductivity. Scanning electron microscopy (SEM) and Raman spectroscopy were used to study the microstructure of the CVD diamond films. In this experiment, we evaluated the quality of CVD diamond film of the whole sample by measuring the thermal conductivity.

KEY WORDS: AC calorimetry; CVD diamond film; Debye phonon model; grain boundary; thermal conductivity; thermal diffusivity; U-process.

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1. INTRODUCTION

Diamond is one of the most attractive materials among the solids of extreme physical properties. It is the hardest, has the highest Young's modulus, has the highest Debye temperature, and also has the highest thermal conductivity at room temperature of any material [1]. The thermal conductivity of diamond is about four to five times that of high-thermal conductivity metals such as Cu or Ag (thermal conductivity of Cu and Ag is 4 and 4.3 $\text{W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$, respectively). This is due to its low phonon density, i.e., lattice vibrations, near room temperature, in a solid with a high Debye temperature [2].

The thermal conductivity from early measurements of CVD diamond film was poor and the temperature dependence of thermal conductivity had a positive slope near room temperature [3-6]. These measurements showed that the quality of films was not good. Recently, Graebner and Herb [7] measured the thermal conductivity of their CVD diamond films between 10 and 400 K with the steady-state method. They reported that the thermal conductivity was 17 $\text{W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$ at room temperature and the temperature dependence also showed a negative slope [8].

We studied our CVD films between 100 and 800 K using AC calorimetry.

2. MEASUREMENTS

2.1. Specimen Preparation

Diamond films were synthesized using DC plasma-assisted chemical vapor deposition (DC PACVD). The substrate, a cylindrical tungsten plate, was placed on top of the water-cooled Cu anode. After evacuation of the synthesizing chamber, hydrogen gas was flowed and a voltage was applied between the two electrodes and slowly increased. When the pressure reached about 200 Torr, methane gas was added to the flow. The power density was approximately 2 $\text{kW} \cdot \text{cm}^{-2}$ during the film growth. The substrate was heated only by the plasma energy and its temperature was near 1573 ± 10 K. The mixed gases were of 3% methane, 1% oxygen, and the balance hydrogen. The growth rate was 10 $\mu\text{m}/\text{h}$.

2.2. Procedure

Thermal diffusivity of thin solid films can be measured by modified AC calorimetry [9,10]. A known frequency of chopped light is used to irradiate a portion of the film surface using a mask which can be moved

with micrometer accuracy. AC plane thermal waves are generated in the exposed region and they propagate through the masked region. The amplitude of the AC thermal waves decay exponentially as they propagate into the masked region. Measuring the decaying temperature profile with a thermocouple (K-type) and the distance between the thermocouple and the edge of the mask, the thermal diffusivity of the film can be deduced. In the experiments, instead of moving the thermometer (here, thermocouple), the mask is moved.

For a film, in the XY plane, of thickness d , the one-dimensional heat flow equation with linearized radiative loss is written [9] for temperature excursion T from ambient,

$$cd \frac{\partial T}{\partial t} + \delta T - \kappa d \left(\frac{\partial^2 T}{\partial x^2} \right) = Q(x, t) \tag{1}$$

Here c is the specific heat, κ is the thermal conductivity of the film, and Q is the light energy per unit area, which is written as follows:

$$Q(x, t) = \begin{cases} 0 & \text{for } x > 0 \\ Qe^{i\omega t} & \text{for } x \leq 0 \end{cases}$$

Here δ is the thermal conductance from the film to the surrounding environment, which is written $\delta = \delta_{\text{rad}} + \delta_{T/C} + \delta_{\text{convec}}$. In a vacuum, conduction through convection, δ_{convec} , can be neglected and conduction through the thermocouple wires, $\delta_{T/C}$, is also very small for the 0.005-cm-diameter wires used. The major loss is through radiation, δ_{rad} , given by the Stefan-Boltzmann law.

If we define the external relaxation time τ_e as $\tau_e = cd/\delta$, then the solution in $x > 0$ can be written as

$$T(x) = \frac{Q}{i2\omega cd(1 - i(1/\omega\tau_e))} \exp\left(-\sqrt{i\frac{\omega}{D}\left(1 - i\frac{1}{\omega\tau_e}\right)}x\right) \tag{2}$$

Here D is the thermal diffusivity of the film; $D = \kappa/c\rho$, where ρ is the density. Simultaneously measuring the amplitude and the phase shift of the lock-in amplifier signal as a vector, the thermal diffusivity and the external time constant can be estimated. Thermal wave number can be written as $k = k_r + ik_\theta$ and Eq. (2) can be rewritten as

$$T(x) = \frac{Q}{\omega cd(\sqrt{1 + \alpha^2})} \exp(-k_r x - i(k_\theta x - \theta)) \tag{3}$$

Here α , θ , k_r , and k_θ are $\alpha = 1/\omega\tau_e$, $\theta = \tan^{-1}(1/\alpha) = \tan^{-1}(\omega\tau_e)$,

$$k_r \equiv \sqrt{\frac{\omega}{2D_r}} = \sqrt{\frac{\omega}{2D}} (\sqrt{1 + \alpha^2} + \alpha) \quad (4)$$

and

$$k_\theta \equiv \sqrt{\frac{\omega}{2D_\theta}} = \sqrt{\frac{\omega}{2D}} (\sqrt{1 + \alpha^2} - \alpha) \quad (5)$$

Therefore, the true thermal diffusivity D of the film can be expressed by Eqs. (4) and (5) as the following formula:

$$D = \frac{\pi f}{k_r k_\theta} = \sqrt{D_r D_\theta} \quad (6)$$

where f is the chopping frequency in Hz. The external relaxation time can be determined from

$$\tau_e = \frac{1}{D(k_r^2 - k_\theta^2)} \quad (7)$$

In the vectorial method, the external relaxation time τ_e and thermal diffusivity D can be calculated from the above formula without any approximation. The AC calorimeter which we used was previously constructed in one of our laboratories, the Korean Research Institute of Science and Standards (KRISS), for the measurement of thermal diffusivity of thin foils [10]. Diamond films were coated with 2–3 μm of graphite (dry graphite fluid spray) to increase the absorption of light on the surface. The temperature of the furnace and cryostat was controlled within ± 0.1 K.

3. RESULTS

The wave number k_r from the amplitude and k_θ from the phase shift are plotted in Fig. 1a. Thermal diffusivities D_r , D_θ , and D are plotted in Fig. 1b. D_r and D_θ are very different, especially in the low-frequency region, but the true thermal diffusivity D varies only 2% from 1 to 65 Hz. In the low-frequency region, the big difference between D_r and D_θ may arise because the thermal diffusion wavelength ($\lambda_{\text{th}} = 2\pi/k$) is longer than the sample length. In this case, the decay of the thermal waves is not sufficient to measure the thermal diffusivity. For the thermal diffusion length to be shorter than the sample length, the chopping frequency for study of diamond should be higher than 30 Hz near room temperature. It is safe to choose a lower frequency than 30 Hz above room temperature and higher than 40 Hz below room temperature.

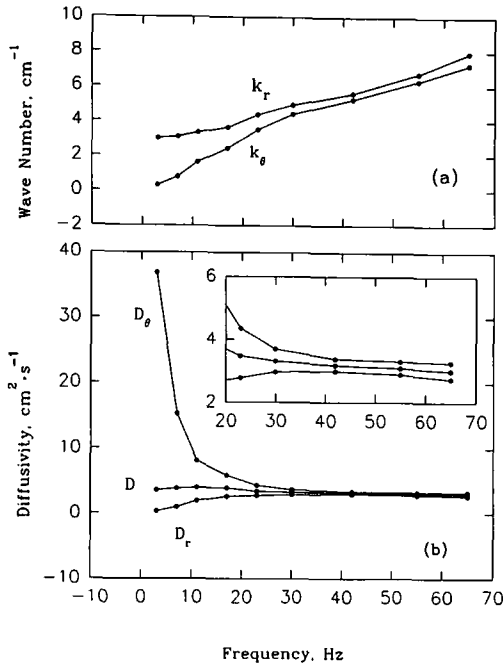


Fig. 1. (a) Thermal wave numbers; k_r and k_θ are given from the analysis of the amplitude and the phase shift of the temperature waves, respectively. (b) The thermal diffusivity from the thermal waves at each frequency. D_r and D_θ are given from the analysis of the amplitude and the phase shift of the temperature waves, respectively. D is the true thermal diffusivity. The inset is the magnified high-frequency region.

We also studied the films by Raman spectroscopy and SEM. In the Raman spectra, there is no indication of graphite, located in 1581 cm^{-1} , and amorphous carbon, located at 1360 and 1590 cm^{-1} . Films of 170 and $60\text{ }\mu\text{m}$ have Raman peaks at 1332.7 and 1333.6 cm^{-1} , respectively, with the resolution of the spectrometer $\pm 0.5\text{ cm}^{-1}$. Hass et al. [13] studied the relationship between the isotope ^{13}C contents and the Raman peaks. From this, each of our samples has 1% ^{13}C because the natural content of ^{13}C in the earth is 1%. FWHM of the Raman peaks of the 170 - and $60\text{-}\mu\text{m}$ films are 3.0 and 5.5 cm^{-1} , respectively. This indicates larger grains in the thicker film—consistent with SEM studies showing increasing grain width moving up through the thickness of the film.

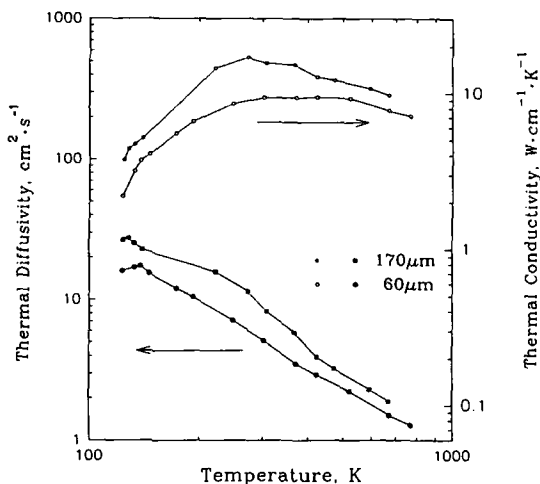


Fig. 2. Experimentally determined thermal diffusivity and calculated thermal conductivity of CVD diamond films.

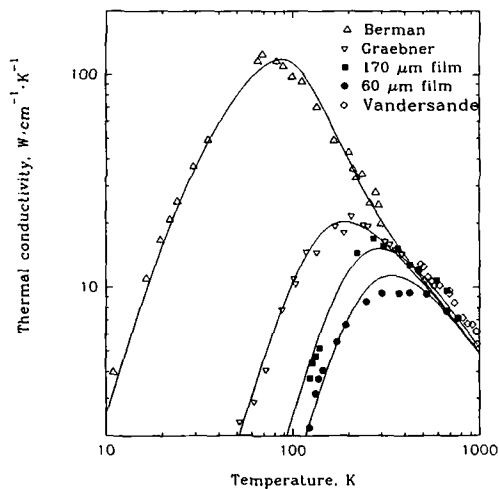


Fig. 3. Thermal conductivity of various diamond samples. Data from Berman et al. [14] and Vandersande et al. [15] are for natural diamond type IIa, data from Graebner and Herb [7] are for 350- μm -thick CVD diamond film, and our results are for 170- and 60- μm -thick CVD diamond films.

The temperature dependence of the thermal diffusivity of 170- and 60- μm diamond film is shown in Fig. 2. The thermal conductivity shown in this figure is calculated using the specific heat data of natural diamond [12]. The results are compared with other reported results in Fig. 3. The specific heats of CVD diamond and natural diamond are similar, since the specific heat is related to the phonon mode only if the number of defects is small.

In Fig. 3, the lines are fitted with the Debye phonon model, which works well for nonconducting solids. In this model, thermal conductivity κ is written as follows:

$$\kappa = \frac{1}{3}v \int_0^{\Theta/T} l(x) c(x) dx \quad (8)$$

here v is the sound velocity in solid, l is the mean free path of phonon, Θ is the Debye temperature, which is related to the maximum phonon frequency ω_{\max} , $\omega_{\max} = \Theta(k_B/\hbar)$, $x = \hbar\omega/k_B T$, and c is the specific heat of solid and can be written as

$$c(x) dx = \frac{3k_B}{2\pi^2v^3} \left(\frac{k_B}{\hbar}\right) T^3 \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (9)$$

The relaxation time method expresses the relaxation time $\tau(x)$ with the mean free path as $\tau(x) = v/l(x)$. At low temperatures, phonons are scattered from the boundary of the sample surface or the grain boundaries. At medium temperatures, the major scattering centers are defects or impurities at the atomic scale, thus the isotope ^{13}C concentration is the main concern in natural diamond. At high temperatures, phonon-phonon scattering through the Umklapp process (U-process) is dominant and the major contribution to thermal resistance. These processes are independent of each other so that the relaxation time for each process is additive,

$$\tau^{-1}(x) = \sum_i \tau_i^{-1}(x) \quad (10)$$

and the thermal conductivity κ of Eq. (8) can be rewritten as

$$\kappa = \frac{1}{3}v^2 \int_0^{\Theta/T} \left(\sum_i \tau_i^{-1}(x) \right)^{-1} c(x) dx \quad (11)$$

The relaxation time of the boundary scattering, τ_g , can be written as

$$\tau_g^{-1} = \frac{v}{\alpha d} \quad (12)$$

Table I. Constants and Fitting Parameters (A_U , B_U , A_p , d) Used in Fitting the Data

	Natural diamond type IIa	CVD diamond films		
		AT&T	KIST	KIST
Thickness (μm)	4000	350	170	60
Debye temperature (K)	2030	— ^a	—	—
Sound velocity ($\text{cm} \cdot \text{s}^{-1}$)	1.32×10^6	—	—	—
A_U ($\text{s}^{-1} \cdot \text{K}^{-1}$)	640	—	—	—
B_U (K)	470	—	600	600
A_p ($\text{s}^{-1} \cdot \text{K}^{-4}$)	0.035	0.015	0.005	0.005
d (μm)	1000	6	1	0.5

^a Indicates no change from the natural diamond values.

Here the constant α is 1.12 and d is the mean size of the grain boundary. Scattering by the point defect is represented by a ω^4 term of Rayleigh scattering as

$$\tau_p^{-1} = A_p \chi^4 T^4 \quad (13)$$

here A_p is the scattering constant. At high temperatures, the Umklapp scattering is written as

$$\tau_U^{-1} = A_U \chi^2 T^3 \exp(-B_U/T) \quad (14)$$

where A_U and B_U are constants. Using the Debye temperature of diamond $\Theta = 2030$ K, the values of the four parameters, d , A_p , A_U , and B_U , giving the best fit to experimental thermal conductivity data are tabulated in Table I.

Data of natural diamond type IIa are taken from Berman et al. [14]. The two parameters for U-processes in natural diamond have values of $A_U = 640 \text{ s}^{-1} \cdot \text{K}^{-1}$ and $B_U = 470$ K. Applying the same values in U-processes of AT&T film gives reasonable fitting, but for our films a better fit is obtained with the same A_U but $B_U = 600$ K. This may come from the high-temperature data; we measured up to 800 K rather than 400 K as did AT&T [7, 8]. However, there is still a discrepancy between our high-temperature data and the calculated curve. But the high thermal conductivity we observed at high temperatures agrees well with the data of Vandersande et al. [15], who studied natural diamond type IIa up to 1200 K. The fit with their high-temperature data is under study now.

The fit is best for the type IIa natural diamond when A_p is $0.035 \text{ s}^{-1} \cdot \text{K}^{-4}$, but theoretical calculation by Turk and Klemens [16]

gives $A_p = 0.0044 \text{ s}^{-1} \cdot \text{K}^{-4}$. In this natural diamond, the only defect considered is the 1.03% ^{13}C . This means that there must be other kinds of impurities, such as vacancy, dislocation, etc. However, these also scatter phonons via the Rayleigh scattering mechanism with a ω^4 dependence, thus it can be included in A_p . For our films $A_p = 0.005 \text{ s}^{-1} \cdot \text{K}^{-4}$.

In natural diamond type IIa, for the boundary scattering, $d = 1 \text{ mm}$ is used. For AT&T film, we used $d = 6 \mu\text{m}$ for a best fit. In our films, $d = 1$ and $0.5 \mu\text{m}$ for the 170- and $60\text{-}\mu\text{m}$ films, respectively.

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