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Thermal Diffusivity Measurement of CVD Diamond Film Using a Step Heating Technique

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A step heating method for the measurement of the thermal diffusivity of diamond thin film is described. The step heating method is a transient heat flow method. Transient temperature profiles are generated in a strip-shaped sample by heating one end of the sample while the other end is clamped to a heat sink. Three thermocouples are used along the heat path. The results are compared with the literature values over the temperature range from −190 to 50°C.

KEY WORDS: diamond film; low temperatures; step heating technique; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

The synthesis of diamond films utilizing the chemical vapor deposition (CVD) technique has received worldwide attention in the recent years. Diamond films exhibit exceptionally high thermal conductivity ($2000\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$) and high electrical resistivity ($10^{14}\ \Omega \cdot \mathrm{m}$). These remarkable properties make the diamond film a highly desirable material for passive or active devices. One of the current critical issues in CVD diamond film is to find correlations between properties and fabrication processes. The characterization of thermal conductivity can be used to determine factors which affect the quality of the films and may lead to improvements in the manufacturing process to permit fabrication of better materials [1].

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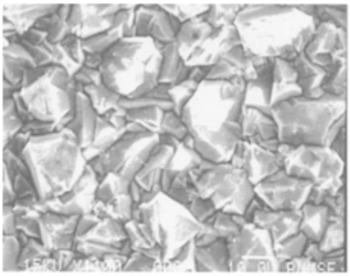
Thermal conductivity is difficult to measure compared to some of the other thermal properties. The measurements on diamond thin films are even more difficult due to the high thermal conductivity and limited geometrical dimensions. The standard steady-state four-probe technique [2] is difficult to apply to highly conductive thin films (e.g., thinner than 50 μm) or above room temperature because of the effect of radiation heat loss ($\sim 10\%$) [2, 3]. The thermal wave phenomenon (also called the "mirage effect") has also been applied to diamond thin films measurement. However, in this technique, the measurements can be performed only at room temperature and their accuracy strongly depends on the optical alignment and the complicated calibration procedure [4, 5]. An AC calorimetric method is another alternative which has been used to measure in-plane thermal diffusivity [6]. Some other techniques have also been proposed [7, 8].

In this paper, we demonstrate the use of a step heating technique to measure the in-plane thermal diffusivity of polycrystalline diamond films. This is a transient heat flow method which is a fast, simple, and inexpensive approach compared to other techniques. In determining the thermal diffusivity of the sample with this technique, prior knowledge of the sample's properties and those of a reference material is not necessary. The measurement is also independent of the sample thickness and is relatively insensitive to the intensity of the heat flux. Satisfactory results over a reasonably wide temperature range (-190 to 50°C) were obtained for both low-conductive and high-conductive thin samples as long as the length of the strip-shaped samples met certain requirements (e.g., longer than 25 mm for CVD diamond films). Once the product of density (ρ) and specific heat (C_p) for the material is known, the thermal conductivity (λ) may be determined from the thermal diffusivity (α) results using the relation $\lambda = \alpha C_p \rho$.

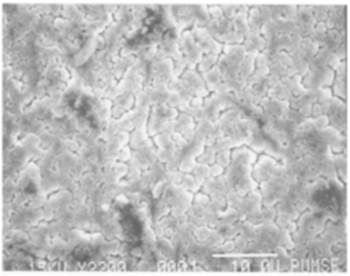
2. EXPERIMENTAL PROCEDURE

Two kinds of diamond films were investigated in this study. Sample A, a freestanding sample $50 \times 6 \times 0.4$ mm in size, was deposited in a DC arc-jet system; Sample B, a freestanding sample $25 \times 10 \times 0.1$ mm in size, was prepared in a microwave plasma CVD system. Scanning electron microscope (SEM) photographs of the samples are shown in Fig. 1 and the diamond crystallites are clearly visible.

The in-plane thermal conductivity of the two films was measured using a step heating technique. The principle of this method is shown in Fig. 2. A mask is mounted in front of the sample so that the two are not in contact. Both the sample and the mask are clamped to a heat sink. The



Sample A



Sample B

Fig. 1. Scanning electron microscope photographs of the samples. Sample A, grain size ≈ 2 μm; Sample B, grain size ≈ 20 μm.

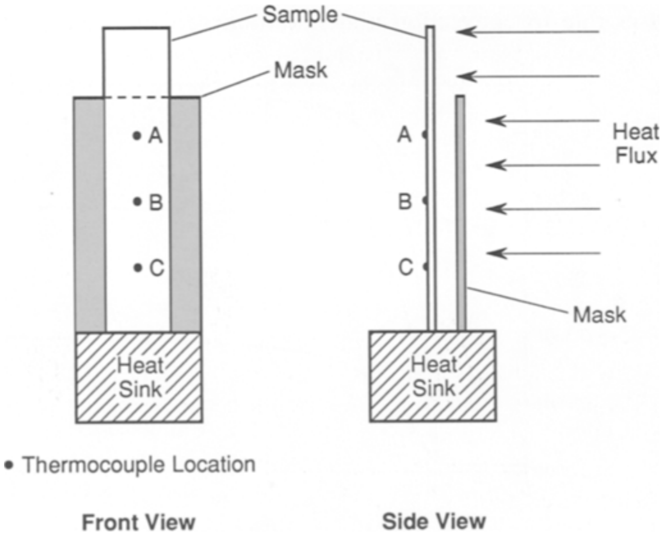


Fig. 2. Schematics of the step heating method.

sample temperature is controlled by a cooling block as shown in Fig. 2. Liquid nitrogen, cool water, and warm water are sequentially used to control the temperature of the heat sink from −190 to 50°C.

The sample initially is at a uniform temperature and the unmasked portion is then subjected to a homogeneous heat flux from an IR lamp (~200 W). Temperature gradients are generated from the irradiated area to the other end connected to the heat sink. Transient temperature responses at three locations in the masked area are recorded. In Fig. 2, temperatures at locations A and C served as boundary conditions. Thermal diffusivity values are estimated by fitting the temperature at B, which is located halfway between A and C, to the analytical model using a nonlinear least-squares regression. Figure 3 illustrates the temperature history from transient state to steady state. Only the transient time domain is useful for the estimation.

The time response of the temperature probe, a major uncertainty source, is very critical in the experiment. Three K-type thermocouples are bonded on the sample surface using high-conductive epoxy (OB-CY20-2 Omega). This bond configuration can give almost the same time response as that obtained using thermocouples spot-welded to thin metal strips. This conclusion is applicable to diamond samples [9]. A data acquisition system with signal conditioners which are designed for direct connection to thermocouples is used. The experiment is controlled by software and a PC.

Since the experiment is performed in a vacuum chamber and the sample was surrounded by aluminum foil thermally connected to the heat sink, heat losses due to convection and radiation can be neglected during the

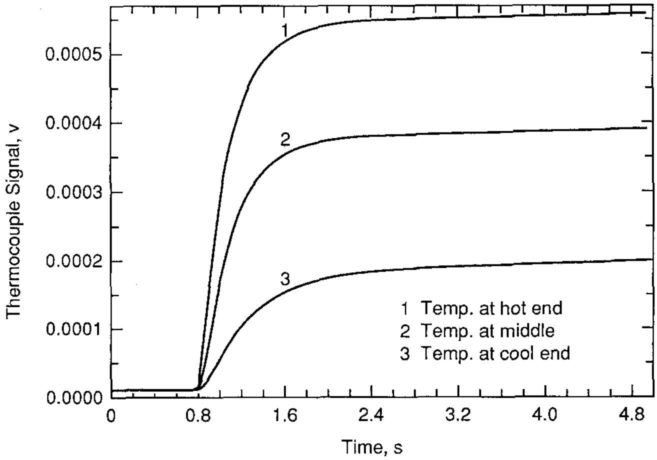


Fig. 3. Transient temperature distribution in the sample.

process. Heat conduction through the thickness can also be neglected compared with the in-plane heat conduction. Therefore, the one-dimensional heat conduction equation can be written as

$$\frac{\partial U}{\partial t} = \alpha \frac{\partial^2 U}{\partial^2 x} \tag{1}$$

where $U = T(t, x) - T(0, x) =$ temperature excursion. A three-node scheme is used by a finite-difference method. Equation (1) can be discretized into

$$\frac{U_2^n - U_2^{n-1}}{\Delta t} = \alpha \frac{U_1^n - 2U_2^n + U_3^n}{(L/2)^2} \tag{2}$$

or

$$U_2^n = \frac{U_2^{n-1}}{1+2r} + \frac{r(U_1^n + U_3^n)}{1+2r} \tag{3}$$

where $r = \alpha \Delta t/(L/2)^2$, Δt is the sampling interval, and L is the space between thermocouple A and thermocouple C.

Equation (2) indicates that the current temperature at location B can be expressed in terms of the current boundary U_1^n and U_3^n as well as the previous temperature U_2^{n-1} at B. This model has only one unknown parameter (r) which contains the thermal diffusivity value. This model, expressed by Eq. (2), is fitted to the NL2SOL software routine [10] to perform one-parameter estimation analysis.

3. RESULTS

Although no standards are needed for the calibration of this technique, several materials with well-established properties were used to verify the reliability of the method. Copper, tantalum, and molybdenum foils (purity of 99.8%) of 250-μm thickness were used. The metal foils were blackened with graphite near the irradiated end. The space between each thermocouple (TC) was 15 mm. In order to minimize the effect of inhomogeneous heating, the edge of the mask was 4 mm away from thermocouple A. A 100-Hz sampling rate was maintained. Figure 4 shows comparisons of the experimental results with the generally accepted values [11]. Maximum of 8% deviations were obtained near room temperature, but deviations greater than 10% were found at temperatures below 120 K. A possible explanation for these low-temperature deviations would be impurity effects and problems with the measurement system.

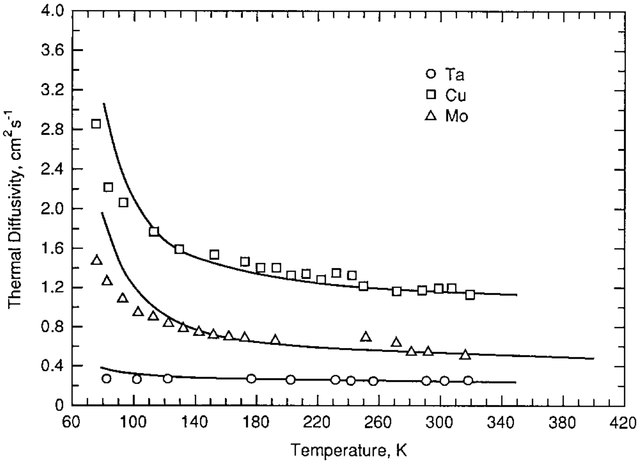


Fig. 4. Thermal diffusivity of some pure metal foils. The solid lines correspond to curves fitted to the experimental data.

4. ERRORS

Step heating experiment is subjected to two general types of errors: measurement errors and nonmeasurement errors. Measurement errors are associated with uncertainties that exist in measured quantities contained in the equation used to compute the diffusivity from experimental data. Nonmeasurement errors are associated with deviations of actual experimental conditions from the boundary conditions assumed in the mathematical model used to derive the equation for computing the diffusivity [12].

The relative error of α can be approximated from Eq. (2) as

$$\frac{\delta\alpha}{\alpha}=\frac{\delta U_i}{U_i}+\frac{2\delta L}{L}+\frac{\delta t}{\Delta t} \tag{4}$$

In Eq. (4), there exist three major measuremental errors. The first one is associated with determining the temperature on the sample, the second one is associated with determining the distance between the thermocouples, and the third one is associated with determining the resolution of the data acquisition system and the sampling rate. Since the uncertainty of L is limited by the flatness of the sample surface and the diameter of the thermocouple beads (~ 0.2 mm), or $2\delta L/L \sim 2\times 0.2/15=3\%$. The errors of temperature reading include the determination of the response time of the data acquisition system (DAS) and the thermocouple. In the step heating experiment, the latter one is dominant [9]. The time response from thermocouples can be understood through the analysis of intrinsic thermocouples where the thermocouple wires are independently spot-welded on the sample. The response time (the time to reach 95% of the steady-state value) could be defined as [13]

$$t_{95} = \frac{25}{\pi} \frac{d_\mathrm{T}^2}{\alpha_\mathrm{s}} \frac{k_\mathrm{T}}{k_\mathrm{s}} \tag{5}$$

where d_T is the diameter of the thermocouple wires and α_s is the thermal diffusivity of the sample. The subscripts T and s refer to the thermocouple and the sample, respectively. Equation (5) shows that a small-diameter thermocouple of low-conducting material attached to a highly conducting sample yields the fastest response time. For instance, if a 25-μm-thick K-type thermocouple was bonded to a thin diamond sample, it should take less than 0.2 μs for it to reach 95% of its steady-state value. If the sampling rate is approximately 100 Hz, then the time response of the intrinsic thermocouple is much faster so that the relative error associated with the DAS $[(\delta U_i/U_i) \sim (t_{95}/\Delta t) \sim (10^{-6}/10^{-2}) \sim 10^{-4}]$. However, in most cases, the TC bead is bonded on the sample with epoxy. The effective response time can be much longer, depending upon the thermal diffusivity of the epoxy and the adhesion qualities. The latter is also affected by the operating temperature. It can be shown that the time response for the bond τ_b is proportional to $l_\mathrm{b}/\alpha_\mathrm{b}$, where l_b and α_b are the bond thickness and thermal diffusivity, respectively. Similarly the time response of the sample temperature is L^2/α_b, where L is the thermocouple location. If the bond effective thickness is 0.05 mm and α_b is 0.01 $\mathrm{cm^2\,s^{-1}}$, then τ_b is proportional to 2 ms. The fastest temperature response of the sample (and hence the lowest case) is at lower temperatures (higher α values) at the 10-mm location of the first thermocouple. For copper, τ_s is proportional to 50 ms, or 25 times larger then τ_b. However, for diamond at 100 K, τ_s is much shorter than for copper. Thus the effective time response for bonded thermocouples could have a significant effect on the accuracy of values obtained on diamonds at low temperatures. The uncertainty contributed by this effect is still being investigated. The last term in Eq. (4) is determined by the resolution of DAS. In our case, $\delta t \sim 10\,\mu$s and $(\delta t/\Delta t) \sim 0.1\%$, which is negligible.

The major sources of nonmeasurement errors are the following: (i) geometry effect, (ii) heat losses and gains, (iii) nonuniform temperature distribution at the initial state, and (iv) nonuniform heating. The geometry effect is associated with any heat transfer other than along longitudinal direction (such as in-depth heating). This effect in the irradiated area can be approximated by the relation used in the flash technique [12]: $t_{1/2} = 0.1388(L^2/\alpha)$. For molybdenum foil 0.2 mm in thickness, the time lag of the heat conduction in the thickness direction is $t_{1/2} = 0.2$ ms, while the time lag along the 2-cm length is $t_{1/2} = 2$ s. The time lag of the through thickness direction is four orders of magnitude smaller than the in-plane direction because $(d/L)^2 \ll 1$.

The heat loss effects include radiation and convection. Convection heat loss is minimized by placing the sample in a vacuum environment. The sample is surrounded by a black-painted, thin aluminum foil which is thermally connected to a heat sink. A temperature rise in the sample is limited to less than 20°C above the temperature of the heat sink, which is about the same as the surrounding foil (T_0). In this situation, the contribution of the radiation heat loss to the in-plane conduction problem can be calculated through the following approximation: $Q_{\text{loss}} \sim 4\sigma\varepsilon_0 T_0^3(T - T_0)A$, where A is the surface area of the sample, σ is the Stefan–Boltzmann constant, and ε_0 is the emissivity of the sample. For a 2-cm-long molybdenum foil 0.2 mm in thickness, the estimation of $(Q_{\text{loss}}/Q_{\text{cond}}) \sim 0.04$ at $T_0 = 300$ K, and $(Q_{\text{loss}}/Q_{\text{cond}}) = 0.01$ at $T_0 = 200$ K. This estimation shows that radiation heat loss could cause a 4% error at room temperature but less than a 1% error at low temperatures for molybdenum. Fortunately, the relative error from the neglection of radiation heat loss at room temperature is below 1% for diamond samples because of their high thermal conductivity. The error sources from nonuniform initial temperature distribution and heating can be minimized by adjusting the mask and the lens in the system so that these errors can be neglected compared with geometry effects and heat losses [9].

In summary, the error sources in the experiment arise mainly from the uncertainty of the distance between thermocouples, the temperature response time, and radiation heat losses. The overall uncertainty of the experiment is about 5% at room temperature and 8% at the low-temperature range of 100 K.

5. DISCUSSION

Two freestanding CVD diamond films were measured following the tests on metal foils. The in-plane diffusivity along with the literature values of ρC_p [11] was used to calculate thermal conductivity values. The diffusivity and conductivity results are presented in Table I and the conductivity values are shown in Fig. 5. Data obtained with the four-probe method [14] and the data from GE [4] are also included in Fig. 5. Several remarks can be made about the plot. First, the measured thermal conductivity values increase in the temperature range from 100 to 200 K and then tend to decrease above 200 K. The peak values of sample A and sample B occur near 200 and 250 K, respectively. The thermal conductivity of both samples roughly follows the T^3 rule in the low-temperature region (below 200 K) where boundary phonon scattering is dominant. However, at relatively high temperatures, the thermal conductivity is relatively less sensitive to T and the boundary phonon scattering is less important. One observation in Fig. 5 is that the thermal conductivity data at low temperatures follow the following sequence: GE sample > Sample A > Sample B. The peak values of each sample follow the reverse sequence. The grain scattering effect could be one explanation for this phenomenon. The SEM of samples A and B in Fig. 1 shows that the grain sizes of sample A and sample B are about 20 and 2 μm, respectively, and the grain size of GE sample was reported to be 175 μm. Phonon theory indicates that the

Table I. Calculated Thermal Conductivity (λ) of CVD Diamond Films from the Measured Values of Thermal Diffusivity (α) and the Known Values [11] of Density (ρ) and Specific Heat (C_p)

Sample	T (K)	α ($\mathrm{cm^2 \cdot s^{-1}}$)	$C_p\rho$ ($\mathrm{J \cdot cm^{-3} \cdot K^{-1}}$)	λ ($\mathrm{W \cdot cm^{-1} \cdot K^{-1}}$)
Sample A	101	74	0.072	5.3
	113	53	0.1171	6.2
	123	50	0.1482	7.4
	133	41	0.2014	8.2
	153	37	0.3130	11.5
	173	29	0.4537	13.2
	183	26	0.5363	13.8
	193	22	0.6220	13.9
	205	19	0.7324	14.2
	225	16	0.9340	15.3
	243	13	1.1310	14.7
	250	12	1.2070	14.5
	273	9.9	1.4810	14.7
	295	8.2	1.7480	14.3
	305	7.0	1.8690	14.0
	320	6.6	2.0450	13.7
Sample B	100	26.5	0.072	1.91
	125	19.1	0.1588	3.03
	150	15.3	0.2919	4.46
	175	13.5	0.4678	6.32
	200	12.5	0.682	8.55
	225	11.6	0.934	10.83
	250	10.4	1.207	12.5
	275	8.8	1.505	13.3
	298	7.4	1.786	13.2
	320	6.3	2.045	12.9

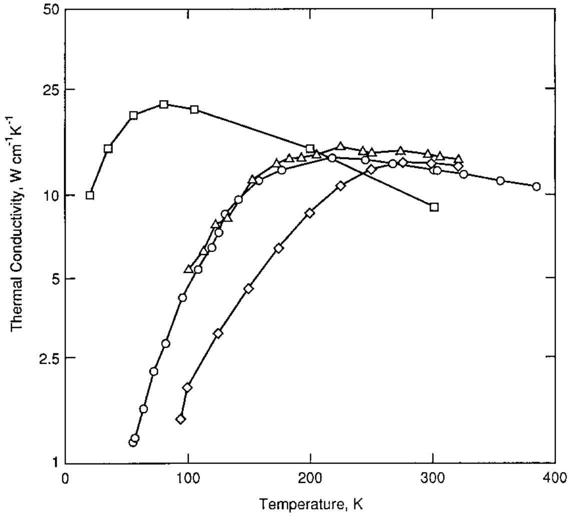


Fig. 5. Thermal conductivity of CVD diamond films. (△) Step heating (Sample A); (◇) step heating (Sample B); (□) GE data [4]; (○) four-probe technique [15].

effect of the smaller grain size will depress the conductivity at very low temperatures and shift the peak value to higher temperatures.

Our final observation in Fig. 5 is that the measured data of polycrystalline films approach the value for single crystal diamond [14] near room temperature, which indicates that boundary phonon scattering is not the dominant phenomenon in CVD diamond near room temperature. Umklapp processes dominate the phonon scattering in this temperature region.

In conclusion, the step heating method was used to measure the thermal conductivity of diamond films. The technique was shown to be a simple, fast method with reasonable resolution in the application to high-conductive thin film measurements. Further studies to improve the resolution and uncertainty of the system have been proposed [9].

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