

Thermal Diffusivity of Diamond/Si Composite Films Measured by an ac Calorimetric Method.

II. Characterization of Deposited Diamond Layers¹

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Thermal diffusivity of diamond Si composite films was measured in the direction parallel to the plane of the film by an ac calorimetric method. The effect of two-dimensional heat conduction on the measured results appears to be due to the difference in the thermal diffusivities of the layers. The thermal diffusivity measured by the thermocouple attached on the diamond side was higher than that on the silicon side. This might be due to the two-dimensional effects. As a result, the estimated thermal diffusivity of the diamond layer from the result of composite film detected on the diamond side is higher than that detected on the Si side. This gives rise to an error in the estimated thermal diffusivity of the diamond layer. A criterion for the deviation of the estimated thermal diffusivity is proposed.

KEY WORDS: ac calorimetric method; diamond Si composite film; thermal diffusivity.

1. INTRODUCTION

Composite film materials have applications in various fields, such as optics and electronics. Thermal properties are important because they are involved in the process design and system operations. For example, pulsed-laser-induced damage of optical thin films is initiated by the absorption of laser radiation at interfaces between the film layers. An analysis of this process points out that the thermal conductivity of a host thin film plays an important role in establishing the laser-induced damage threshold [1].

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For semiconductor superlattices, thermal properties are important in the design of the device structure [2]. Thermal conductivity affects the recording performance of magneto-optical thin films [3]. Thermal diffusivity of thin films has successfully been measured by an ac calorimetric method [4]. This method can also be applied to the measurement of the thermal diffusivity of a composite thin film, if the condition

$$k_1 d_1 + k_2 d_2 \ll 1 \quad (1)$$

is satisfied. Thermal diffusivity of a composite film may be expressed as [4]

$$D = \frac{D_1 c_1 d_1 + D_2 c_2 d_2}{c_1 d_1 + c_2 d_2} \quad (2)$$

where c is the heat capacity per unit volume, d is the thickness, D is the thermal diffusivity, f is the frequency, and k is the as temperature decay constant, $k = (\pi f / D)^{0.5}$. Subscripts 1 and 2 indicate the layer numbers; for example, 1st layer, diamond; 2nd layer, silicon. Using known thermophysical properties for one of the layers, for example, the second layer silicon, the thermal diffusivity of the other layer, the first layer diamond, can be estimated from the measured thermal diffusivity of the composite film using the relation

$$D_1 = \frac{D(c_1 d_1 + c_2 d_2) - D_2 c_2 d_2}{c_1 d_1} \quad (3)$$

Generally, two-dimensional (x and z directions) heat conduction should be taken into account in the measurements of such a composite film. It results in the difference of the measured values between the first and the second layer sides. This means that the measured thermal diffusivity using the thermocouple attached on the first layer side is different from the measured thermal diffusivity using the thermocouple attached on the second layer side. Therefore, the estimated thermal diffusivity of the first layer from Eq. (3) includes a deviation due to the difference of the measured thermal diffusivity of the composite film on both sides which is caused by the two-dimensional effects. In the present study, diamond(1st)/Si(2nd) composite films have been measured where the thermophysical properties of the silicon layer were known. Then, the thermal diffusivity of the diamond layer was estimated from Eq. (3) with the results of the composite film measured on both sides. The estimated values based on the results measured on both sides of the composite film are different. Finally, the thermal diffusivity of the diamond layer, which was estimated based on the thermal diffusivity of the composite film measured on either side

(the diamond side and the silicon side), was compared with the measured value of the free-standing diamond film which was obtained by removal of silicon substrate from the composite film in HF-HNO_3 solution. In another paper [6], the thermal diffusivity of diamond/Si composite films is presented, with special attention to the thermal diffusivity measurement of films with a high thermal diffusivity, in which edge effects should be taken into account. In the measurement of the thermal diffusivity of diamond/Si composite film and free-standing diamond film, the contribution of edge effects was also taken into account and corrected in the present paper. A criterion proposed in this paper indicates how the deviation of the estimated thermal diffusivity of the diamond layer is related to the deviation of the measured thermal diffusivity of the diamond/Si composite film. According to this criterion, one can choose proper thicknesses of the two layers (diamond and silicon) to make the deviation as small as possible.

2. ANALYSIS

In the ac calorimetric method, the thermal diffusivity is determined from the decay of the temperature waves propagating in a thin film sample under the condition of one-dimensional heat conduction. The decay coefficient and the thermal diffusivity are given by the following equations

$$k = -\frac{d \ln |T(x)|}{dx} \quad (4)$$

$$D = \frac{\pi f}{k^2} \quad (5)$$

where T is the temperature and x is the coordinate in the direction of the temperature wave propagation. In the ac calorimetric method, the isoamplitude lines of temperature waves are parallel to each other and normal to the plane of the surface of the sample shown in Fig. 1, based on the condition that the temperature waves propagate in one dimension along the surface of the composite film sample. However, for a composite film made of

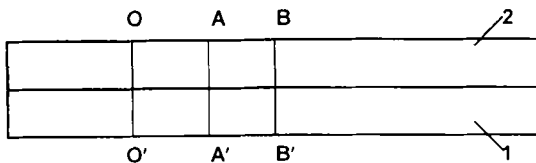


Fig. 1. Isoamplitude lines of temperature waves under one-dimensional propagation.

two layers where the thermophysical properties of each layer are different, as in a composite film of diamond and silicon layers, two-dimensional effects take place.

2.1. Effect of the Difference in Thermal Diffusivity of Layer Materials

Because of the difference in the thermal diffusivity of the two layers, that is, the first layer has a higher thermal diffusivity and the second layer has a lower one [diamond(1st) and silicon(2nd) composite film], the temperature wave in the first layer propagates faster than that in the second one. Thus, the isoamplitude lines become more inclined and sparser in the first layer than in the second layer as shown by $OO'-AA'-BB'$ in Fig. 2. As a result, the measured thermal diffusivity on the side of the first layer is higher than that on the side of the second layer.

The heat conduction in both x and z directions causes an inclined and sparse tendency in isoamplitude lines along x and they become constant in both layers, such as CC', DD' , as shown in Fig. 2. Then the thermal diffusivity obtained from both sides is the same. However, the length of the sample is limited, and furthermore, the signal level becomes significantly low in such a case, which creates practical difficulties. Therefore, the thermal diffusivities of both sides obtained under the limited conditions are usually different, that is, the value obtained on the diamond side is higher and the value obtained on the silicon side is lower in comparison to that derived from Eq. (2).

2.2. Effect of the Thermal Contact Resistance Between Two Layers

The heat conduction along the z direction should be considered when there are differences in the thermophysical properties of layer materials. Furthermore, the interface with thermal contact resistance gives rise to additional two-dimensional effects.

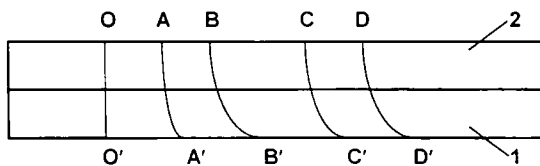


Fig. 2. Isoamplitude lines with a two-dimensional effect due to the difference of layer materials.

2.3. Deviation of the Estimated Thermal Diffusivity of a Diamond Layer in the Diamond/Si Composite Film Measurement

The relation among deviations is given as

$$\delta_1 = (1 + \eta) \delta + \eta \delta_2 \quad (6)$$

where δ is the relative deviation of the measured thermal diffusivities of the composite film from different sides; δ_1 is the deviation of the estimated thermal diffusivity of the first diamond layer; and δ_2 is the deviation of the thermal diffusivity of the second silicon layer, which is considered as zero because of its known value. The deviation of the estimated thermal diffusivity for the diamond layer depends not only on the deviation caused by the composite film measurement but also on the parameter η ,

$$\eta = \frac{D_2 c_2 d_2}{D_1 c_1 d_1} = \frac{\lambda_2 d_2}{\lambda_1 d_1} \quad (7)$$

where λ is the thermal conductivity. The quantity η can be used as a criterion for the deviation of the estimated thermal diffusivity of the first diamond layer. If η is much bigger than 1, the estimation of the thermal diffusivity of the first layer can not be successful. According to this criterion, we can also choose proper thicknesses, d_1 , and d_2 , of the layers, to obtain a more accurate estimate of the thermal diffusivity of the first diamond layer in the measurement of a diamond/Si composite film.

3. EXPERIMENTS

The experiments were performed using an apparatus for the thermal diffusivity measurement of thin films (SINKU-RIKO Inc., type PIT-1). A fine thermocouple was attached to a sample of diamond/Si composite film with a width of 4 mm and a length of 10–20 mm. Each sample was measured twice, with the thermocouple attached on the diamond side one time and on the silicon side another time, and the thermocouple was attached at the same distance from the edge of heated region of the sample (i.e., the light-irradiated spot) for twice measurements, and then, from two measured thermal diffusivities for a composite film, two estimates of the thermal diffusivities for the first diamond layer were obtained. In this measurement, a suitable frequency region was selected so as to satisfy the conditions that heat loss could be negligible [5]. The details of the measurements on diamond/Si composite films are discussed in another

Table I. Characteristics of the Samples

Sample	d_1 (μm)	d_2 (μm)	CH_4/H_2 (vol %)
1	6.6	79.5	0.2
2	28.1	102.8	0.2
3	4.2	89.1	0.2
4	13.5	91.8	0.5
5	11.5	75.4	1.0

paper [6]. The correction for the edge effects was performed according to the following equation [7, 8]:

$$\frac{D}{D^*} = \left\{ 1 - \frac{e^{-2k(n-1)} [\cos 2k(n-1) + \sin 2k(n-1) + e^{2k(n-1)}]}{1 + 2e^{-2k(n-1)} \cos 2k(n-1) + e^{-4k(n-1)}} \right\}^2 \quad (8)$$

where D^* is the measured apparent thermal diffusivity considering the edge effect; $(n-1)$ is the distance between the end of the sample and the center of the heated region (i.e., the light-irradiated spot) in the sample [7]. In this paper, the results for the five composite film samples are discussed. The characteristics of the samples with the different concentrations of reaction gas, methane CH_4/H_2 (vol%), are given in Table I and the results are given in Table II. In Table II, we focus our attention to the estimated thermal diffusivity of a diamond film. After the measurement on composite films, by removing the silicon substrate from composite film in HF-HNO_3 solution, the free-standing diamond films were obtained. Thermal diffusivity of the four free-standing diamond films from samples 1, 2, 4, and 5 were measured using the same apparatus. We corrected the measured

Table II. Results on Composite Film^a

Sample	$D(1)$ ($\text{cm}^2 \cdot \text{s}^{-1}$)	$D(2)$ ($\text{cm}^2 \cdot \text{s}^{-1}$)	$D_1(1)$ ($\text{cm}^2 \cdot \text{s}^{-1}$)	$D_1(2)$ ($\text{cm}^2 \cdot \text{s}^{-1}$)	δ (%)	δ_1 (%)	η
1	1.092	1.029	3.786	3.047	5.9	21.6	2.6
2	1.721	1.488	4.803	3.754	14.5	24.5	0.7
3	0.926	0.899	2.652	2.077	3.0	24.3	7.2
4	0.984	0.826	1.915	0.728	17.5	89.8	4.1
5	0.845	0.738	0.870	0.092	13.5	161.7	10.9

^a $D(1)$ and $D(2)$ are the thermal diffusivities measured on the first layer and second layer, respectively, at 21°C. $D_1(1)$ and $D_1(2)$ are the estimated thermal diffusivities of the first layer from $D(1)$ and $D(2)$.

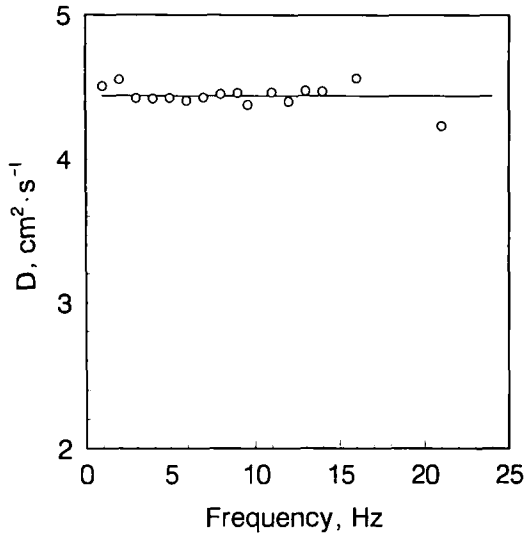


Fig. 3. Edge effect-corrected thermal diffusivity versus frequency. Open circles are the corrected thermal diffusivity for sample 2. The horizontal line indicates the average value of corrected value at various frequencies.

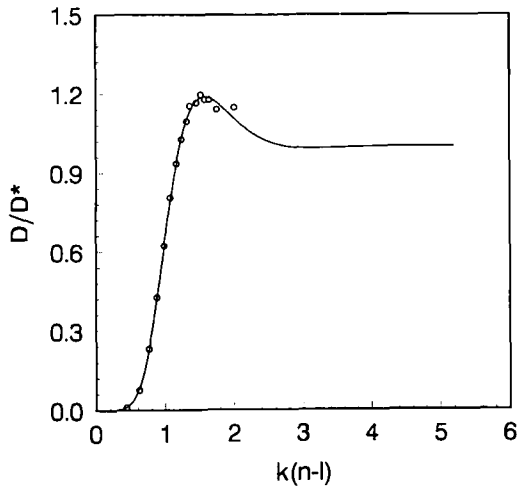


Fig. 4. Edge effect. Open circles are the ratio of the average value of corrected thermal diffusivity to the apparent thermal diffusivity. The solid curve is calculated by Eq. (8).

Table III. Results on Free-Standing Diamond Films^a

Sample	$D_1(1)$ ($\text{cm}^2 \cdot \text{s}^{-1}$)	$D_1(2)$ ($\text{cm}^2 \cdot \text{s}^{-1}$)	D_1 ($\text{cm}^2 \cdot \text{s}^{-1}$)
1	3.786	3.047	2.976
2	4.803	3.754	4.442
4	1.915	0.728	1.181
5	0.870	0.092	0.277

^a D_1 is the measured thermal diffusivity of the free-standing diamond film.

values of D^* according to Eq. (8) and then the corrected value D no longer depend on frequency as expected. For example, for free-standing diamond film sample 2, the thermal diffusivity, D , with the edge effect correction by Eq. (8) is shown in Fig. 3 and the ratio of its average value to the measured apparent thermal diffusivity, D^* , at various frequencies is shown in Fig. 4. These figures indicate that the corrected D at various frequencies is almost constant and D/D^* is in good agreement with Eq. (8). The results of the free-standing films are shown in Table III. Except for sample 1, the measured thermal diffusivity of free-standing diamonds lies between the range of the two estimated values from the results of the composite film measurement. The exception of sample 1 might be due to the high heat loss caused by the sample holding.

4. SUMMARY

The thermal diffusivity measurements of diamond/Si composite films using an ac calorimetric method indicated that heat conduction exists in the direction perpendicular to the plane surface of the film caused by the different thermophysical properties of diamond and silicon. However, detailed theoretical analysis on this two-dimensional effects is required. The present study draws experimental evidence and qualitative theoretical consideration as follows.

- a. In the thermal diffusivity measurement of a composite film with two layers using an ac calorimetric method, the thermal diffusivity of one of the layers can be estimated if the thermophysical properties of the other layer are known.
- b. The difference in thermophysical properties between the two layers usually causes temperature wave propagation in the z direction. This results in a systematic error, that is, the measured value of

thermal diffusivity on the diamond side is higher, and on the silicon side is lower in comparison with the value expressed by Eq. (2).

- c. A criterion concerned with η was proposed. η is a useful parameter to compare the deviations between the true thermal diffusivity and the estimated thermal diffusivity.
- d. Choosing proper thicknesses of layers d_1 , and d_2 is important in the successful estimation of thermal diffusivity of a layer from the composite film measurement.

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