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Thermal Diffusivity of Diamond/Si Composite Films Measured by an ac Calorimetric Method.
I. Edge Effects[1]

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In measurements of thermal diffusivity, by an ac calorimetry method, on films of materials of high thermal diffusivity, attention should be paid to the effects of the sample length, i.e., the reflection of ac temperature waves at the sample edge. For such a case, the apparent thermal diffusivity of the sample having a finite length is given analytically as a function of frequency. Measurements were performed on diamond/Si composite films. The overall behavior of the frequency dependence of the apparent thermal diffusivity obtained is satisfactorily explained by the analytical expression. The true thermal diffusivity is obtained by fitting a theoretical curve to the experimental results. Especially when the apparent thermal diffusivity saturates in a high-frequency region, the saturated value gives the true thermal diffusivity.

KEY WORDS: ac calorimetry; composites; diamond; films; silicon; thermal diffusivity.

1. INTRODUCTION

The ac calorimetric method has been used extensively for the measurement of thermal diffusivity of thin-film samples in the direction parallel to the plane surface [1]. In this method, chopped radiation is applied to the surface of the sample partly shadowed by a mask and the mask is moved along the surface (Fig. 1). Figure 1 shows periodically modulated uniform thermal energy $Qe^{i\omega t}$ applied to the surface of a film sample. In practice, a fine thermocouple with a diameter smaller than the thermal diffusion

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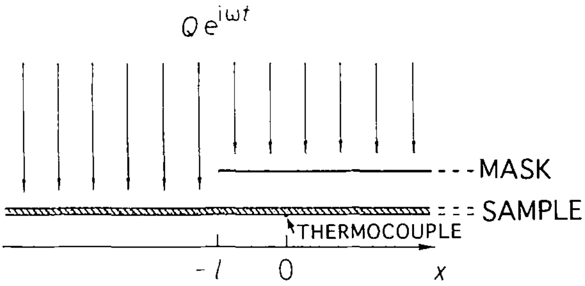

Fig. 1. The principle of an ac thermal diffusivity measuring method. The sample and the mask constitute an infinite plate and a half-plane, respectively. The ac thermal energy is supplied uniformly on their surface by chopped radiation. The ac temperature is detected at $x = 0$ by a thermocouple. The mask can be moved along the x-axis.

length is attached to a part of the film lying under the mask with silver paste (at $x = 0$ in Fig. 1). The ac temperature at the thermocouple is measured as a function of the relative distance between the thermocouple and the boundary of the mask (for instance, l in Fig. 1). Both the decay constant and the wave number of the ac temperature are given by the same expression:

$$k = (\pi f/D)^{1/2} \tag{1}$$

where $f (= \omega/2\pi)$ is the measuring frequency and D is the thermal diffusivity. Then, from the measurement of either the decay or the phase shift as a function of the relative distance, we can obtain the thermal diffusivity D of a thin film sample.

The ac calorimetric thermal diffusivity measurement can be applied to a variety of materials with low and high thermal diffusivities, i.e., from a polymer film to a diamond plate. For convenience, in this paper materials are classified into the following three classes.

L (low):	$D > 0.02\ \mathrm{cm^2 \cdot s^{-1}}$
M (medium):	$0.02 < D < 0.2\ \mathrm{cm^2 \cdot s^{-1}}$
H (High):	$0.2 < D\ \mathrm{cm^2 \cdot s^{-1}}$

In class L glass and polymer, in class M rock salt, stainless steel, and antimony, and in class H iron, silicon, gold, and diamond are included. The experimental conditions required and/or the experimental procedures to be taken should be according to the above classification.

Special attention should be paid to the measurement of films in classes L and H. During the propagation of ac temperature waves in a thin-film sample, the dissipation of heat takes place, for instance, by the emitted radiant heat. The effects of such a heat loss are dominant in the measurement of a film sample in class L. By solving the one-dimensional ac temperature wave propagation equation in the sample, the contribution of the heat loss can be expressed in terms of the relaxation time due to the heat exchange between the sample and the surroundings [2]. On the other hand, in the measurement of a film sample in class H the edge effects that are created by the reflection of the ac temperature waves at the edge of the film sample should be taken into account.

In the present study (paper I), we examine the edge effects in composite films of diamond and silicon.

2. THEORETICAL CONSIDERATIONS

Let us consider a plate-like sample with uniform width and thickness. Furthermore, the thickness is less than the thermal diffusion length given by $1/k$, i.e., this is the condition for one-dimensional ac temperature wave propagation. The ac temperature at a position ($x = 0$) of the sample lying under the mask is detected by a fine thermocouple attached to the sample. The coordinates of the sample edge in the irradiated part, at the position of the boundary of the mask, and of the sample edge in the masked part are given by $x = -n$, $-l$, and m, respectively (Fig. 1; but limit the sample to a finite length given by $x = -n$ and $x = m$). By moving the mask, i.e., by changing l, the decay or the phase shift of ac temperature is observed. When the edge effects are taken into account, the apparent thermal diffusivity D' is given by [3]

$$\frac{D'}{D} = \left[1 - \frac{\begin{array}{c} 2\exp[-2k(n, -l)]\{\cos[2k(n-l)] \\ +\sin[2k(n-l)] + \exp[-2k(n-l)]\} \end{array}}{1 + 2\exp[-2k(n-l)]\cos[2k(n-l)] + \exp[-4k(n-l)]} \right]^{-2} \qquad (2)$$

Then, we can obtain the true thermal diffusivity D of the sample from the analysis of the data using Eq. (2). It should be emphasized that in Eq. (2) we can no longer find m explicitly, i.e., the value m has nothing to do with the edge effects. In Fig. 2, a typical plot of Eq. (2) is shown for the case where $D = 1\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$, $n = 2$ cm, and $l \ll n$. As expected, at high frequencies D'/D tends to 1. With decreasing frequency, initially D'/D increases slightly, then begins to decrease, reaches a minimum and then increases

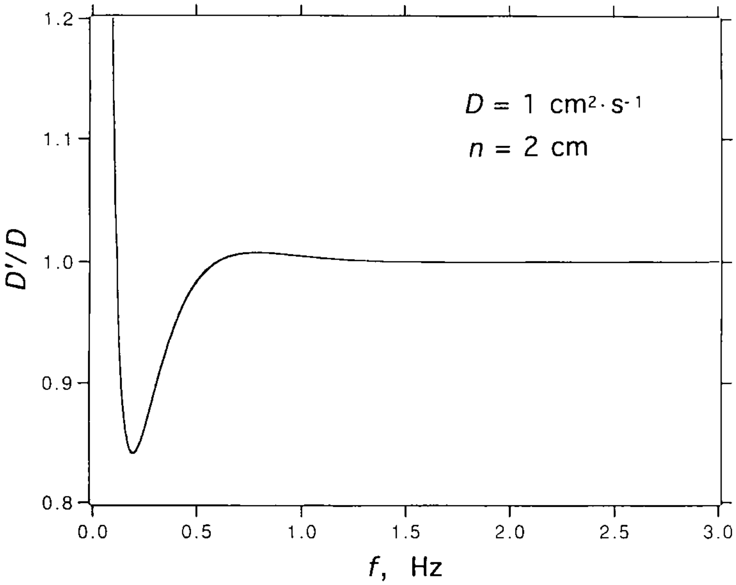

Fig. 2. Typical plot of apparent thermal diffusivity versus frequency according to Eq. (2).

sharply. Therefore, the measurements should be performed at a high frequency, where the apparent thermal diffusivity is nearly constant. Otherwise, the data obtained as a function of frequency should be analyzed by Eq. (2).

3. EXPERIMENTS AND ANALYSES

In the diamond/Si composite films used, the polycrystalline diamond layer was nucleated and grown on a (111) silicon crystal substrate by microwave-enhanced plasma chemical vapor deposition. The characteristics of the composite films used are listed in Table I. The last column indicates the volume percentage of methane in a methane and hydrogen mixture during nucleation and deposition. It has been shown by the radiation-bar technique that the polycrystalline diamond film deposited at a lower methane concentration has a higher thermal conductivity [4]. To show the quality of the diamond films, the growth surface as imaged in a scanning electron microscope is presented in Fig. 3. Consistent with the results on the thermal conductivity [4], the grain size of the diamond crystal was bigger for those grown at lower methane concentration. Furthermore, as may be seen in Figs. 3a–3c, even at the same methane concentration, the grain size at the surface is larger for thicker diamond layers.

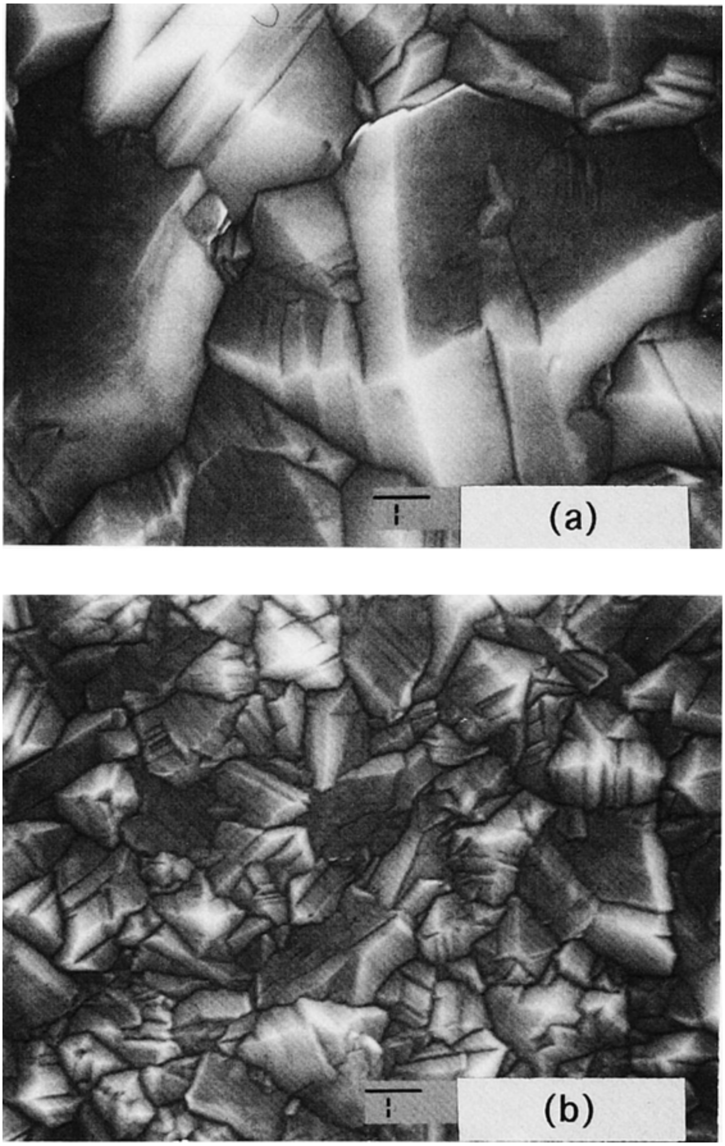

Fig. 3. Scanning electron micrographs of the diamond layer growth surface. a to e correspond to samples 1 to 5 denoted in Table I, respectively. Bar = 0.7 μm.

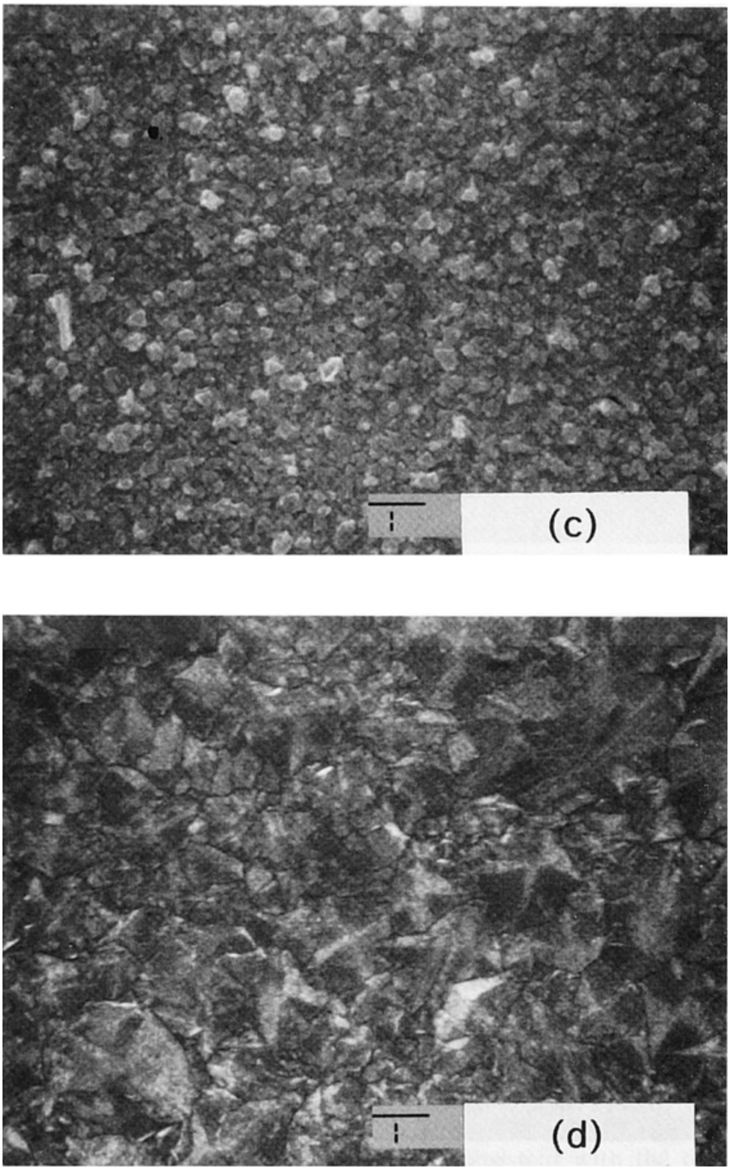

Fig. 3. *(Continued)*

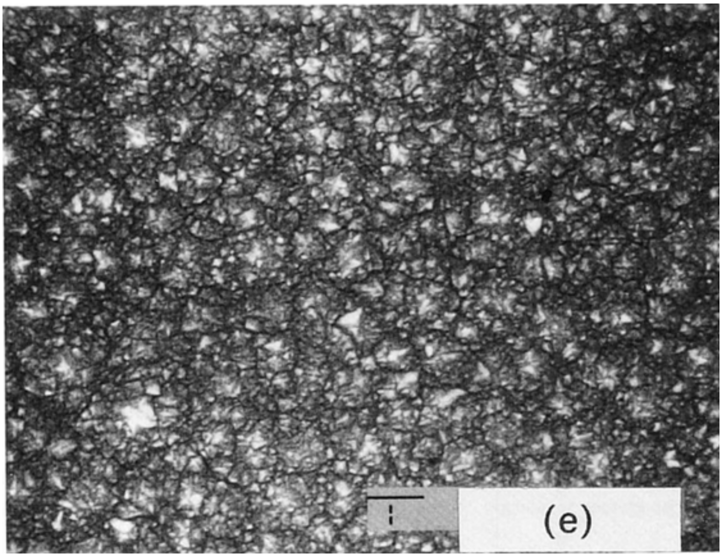

Fig. 3. (*Continued*)

The samples are plate-like; the length is 20 mm and the width is 4 mm. To convert thermal radiation to heat efficiently, a bismuth film (0.1 μm thick) was deposited on the silicon side of the composite films. In the present study, chopped radiation was applied to the silicon side. A fine thermocouple, with a diameter of 12.5 μm for detecting ac temperature, was glued on the silicon surface (at a position approximately $n = 19$ mm and $m = 1$ mm). The position of the boundary of the mask was moved from approximately $l = 2$ to 5 mm.

Table I. Diamong/Si Composite Films Used for the Measurements

Sample	Thickness Diamond (μm)	 Si (μm)	CH_4/H_2 concentration during diamond deposition (%)
1	28.1	102.8	0.2
2	6.6	79.5	0.2
3	4.2	89.1	0.2
4	13.5	91.8	0.5
5	11.5	75.4	1.0

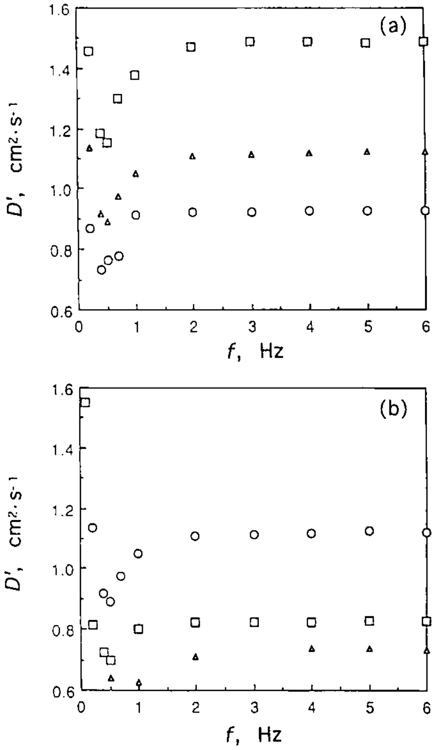

Fig. 4. Apparent thermal diffusivity versus frequency of diamond/Si composite films. (a) For sample 1 (squares), for sample 2 (triangles), and for sample 3 (circles). (b) For sample 2, denoted (circles) as a reference, for sample 4 (squares), and for sample 5 (triangles).

The experimental results are plotted in Fig. 4. As may be seen, the behavior of apparent thermal diffusivity is similar to that shown in Fig. 2, that is, the results are well expressed by Eq. (2). It can clearly be seen in Fig. 4 that apparent thermal diffusivity saturates at high frequencies. We estimated the true thermal diffusivity for each sample from the saturated value. The results are summarized in Table II. The thermal diffusivity of diamond/Si composite films decreases as the methane concentration in chemical vapor deposition decreases. As indicated in Table II, thermal diffusivity was determined within an accuracy of ± 1 %. However, it should be noted that the moving region of the mask was limited to the region as discussed in Ref. 3. For the accurate determination of the thermal diffusivity

Table II. Thermal Diffusivity of Diamond/Si Composite Film for Samples 1, 2, 3, 4, and 5

Sample	Thermal diffusivity ($cm^2 \cdot s^{-1}$)
1	1.488 ± 0.005
2	1.122 ± 0.003
3	0.926 ± 0.008
4	0.826 ± 0.003
5	0.738 ± 0.002

of the film samples, thickness of the sample plays an important role, i.e., the accuracy depends on the uniformity of the sample thickness.

An analysis concerning the thermal diffusivity of each layer of a bilayer composite will be presented in paper II, the next paper in this issue.

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