New Laser-Flash Method for Measuring Thermal Diffusivity of Isotropic and Anisotropic Thin Films

Hiroyuki Shibata*, Hiromichi Ohta** and Yoshio Waseda***

A new laser flash method has been developed for determining thermal diffusivity of thin films in the direction parallel and perpendicular to the sample surface. On the measurement of parallel direction of the sample, a pulsed laser beam which has narrow line-shaped cross section is flashed onto the front surface of a film sample and the temperature response at the back surface at a certain distance away from the line-shaped illuminated area of the laser beam is measured by an InSb infrared rays detector. The thermal diffusivity of the sample can be determined from time required for the temperature to reach the half of the maximum temperature rise finally acquired. On the other hand, the measurement of thermal diffusivity in the direction perpendicular to the sample surface, a pulsed laser beam which has the diameter of about 10 mm is flashed onto the front surface of a film sample and the temperature response at the back surface is measured by an InSb infrared rays detector. For this purpose, an improved temperature response acquisition system is required to cover the very fast sampling speed of 1 μs interval. The measured temperature response is compared with the theoretical solution coupled with measured laser beam intensity as a function of time for estimating the thermal diffusivity of the sample.

The capability of this new method was clearly demonstrated by determining the thermal diffusivities of isotropic ribbon samples for copper(thickness: 18 μm), nickel(thickness: 5 μm) and SUS304 stainless steel(thickness: 50 μm). A new data processing has also been developed for determining thermal diffusivity of anisotropic film samples by considering two-dimensional heat flow. The usefulness of this data processing was demonstrated by measuring thermal diffusivity in the direction parallel to the C-axis of pyrolytic graphite (thickness: 180 μm).

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I. Introduction

The importance of the thermal diffusivity measurements of ribbon samples or thin films less than 100 μm in thickness has recently been recognized, in parallel with the progress in various functional materials such as metallic glasses, superlattice films and highly conductive substrates. There have been several attempts on the thermal diffusivity measurements for thin films. For example, Hatta et al. (1) developed the AC calorimetric method using a thermocouple and Ono et al. (2) proposed the thermographic method by measuring the steady-state temperature distribution of a sample. Several photothermal heating methods were also reported for measuring thermal diffusivity of thin films (3)-(6). However, the full potential of these methods can not be assessed yet.

On the other hand, the laser-flash method, first proposed by Parker et al. (7) has gained a dominant position as one of the powerful tools for measuring thermal diffusivity of various materials (8)-(11). The short measuring time less than a few seconds for obtaining the temperature response in the laser-flash method minimizes the heat leak from a sample, when coupled with the optical temperature detection system such as an infrared rays detector. This is particularly important for the thermal diffusivity measurements of thin films, because the heat leak through a thermocouple frequently produces some difficulties for the measurements in the conventional AC calorimetric method. However, the requirements are not fully given yet for the thermal diffusivity measurements of thin films using the laser-flash method, although the preliminary results are reported by the present authors (12). The main purpose of this paper is to present the fundamentals of a new laser-flash method for determining thermal diffusivity of thin films in the direction parallel and perpendicular to the sample surface, through an attempt of the measurement for isotropic ribbon samples of copper (18 μm), nickel (5 μm) and SUS304 stainless steel (50 μm). In the present study, we will also describe a new data processing for determining thermal diffusivity, of anisotropic film samples by considering two-dimensional heat flow, including the results of pyrolytic graphite (180 μm).

II. Principle of the New Method

1. Thermal diffusivity measurement of thin films in the direction parallel to the sample surface

Figure 1 shows the schematic diagram of the present laser-flash method for the thermal diffusivity measurements of a film sample. A single pulse laser beam is flashed on the surface of a film for measurements of both directions to the sample surface and a laser beam with the diameter of about 10 mm is usually employed.
However, in the case of measurements in the direction parallel to the sample surface, the beam shape is restricted to the line-shaped area on the sample surface perpendicular to the length of a film using a slit system inserted into the beam path (see Fig. 1(a)). This gives us the condition of one-dimensional heat flow in the direction parallel to the length, when the sample is sufficiently thin where the temperature distribution is uniform in the direction of the sample width, but there is no temperature gradient in the direction perpendicular to the sample surface. It is also noteworthy that the short measuring time makes the heat leak from a sample negligibly small. Equations of heat diffusion for this case have been given by the present authors with the preliminary results\(^{12}\). Thus, only the essential points are given below.

The temperature dependence at \( X(X) \) is the distance from the center of the spot of a laser beam as a function of time is given as follows by assuming the length of a sample to be infinite:

\[
\Psi(\alpha t, X) = \frac{1}{\pi} \int_{-\infty}^{\infty} \Psi_0(0, X+2\beta \sqrt{\alpha} t) \exp(-\beta^2) \, d\beta.
\]  

(1)

Here \( \Psi_0(0, X) \) is the initial temperature distribution as given by the following form:

\[
\Psi_0(0, X) = \begin{cases} T_0 & (-l<X<l) \\ 0 & (0 \leq X \leq l \text{ or } l \leq X) \end{cases}
\]  

(2)

\[
T_0 = \frac{Q}{\rho C_p d}
\]  

(3)

where \( T_0 \) is the temperature rise from the ambient temperature, \( \alpha \) is the thermal diffusivity, \( l \) is a half of the laser beam width, \( Q \) is the heat absorbed by a sample from the laser beam per unit area, \( C_p \) is the specific heat, \( \rho \) is the density, and \( d \) is the thickness of the sample.

Note that the present method requires only the relative change (not absolute values) in temperature, proportional to the transient temperature rise. Since the infrared rays detector for obtaining the temperature response of the sample has a certain area (about 3 mm\(^2\) for the InSb crystal case), it is necessary to consider the space distribution of the sensitivity, \( S(X) \), of a detector. Consequently, the signal response \( U(\alpha t, r) \) measured by the detector at the distance of \( r \) is represented by the following equation:

\[
U(\alpha t, r) = \int_{-\infty}^{\infty} \Psi(\alpha t, X) S(X-r) \, dX
\]  

(4)

where \( r \) is the relative distance between the detector and the center of the laser beam. Theoretical signal responses \( U(\alpha t, r) \) are calculated for various values of \( r \) as a function of \( \alpha t \). And next, the values of \( (\alpha t)_{1/2} \) corresponding to one-half of their maximum values, are determined. It may be noted that these values depend on the position of the detector. The values of \( t_{1/2} \), corresponding to the time required for the measured signal response to reach one-half of its maximum value are estimated for various values of \( r \). From the values of \( (\alpha t)_{1/2} \) and the position of the detector, the so-called device constant \( k(r) \) is defined as follows:

\[
\alpha = k(r) / t_{1/2}.
\]  

(5)

Thus, the thermal diffusivity of a film sample in the direction parallel to the sample surface can readily be determined from the position of the detector and the \( t_{1/2} \) value using eq. (5), when the device constant is available with sufficient accuracy.

2. Thermal diffusivity measurement of thin films in the direction perpendicular to the sample surface

The slit system for producing the line-shaped laser beam is not required in the measurement of thermal diffusivity of thin films in the direction perpendicular to the sample surface as shown in Fig. 1(b). The temperature response of the back surface of the area illuminated by a laser beam is governed by the following equation\(^{13,14}\):

\[
\Theta(t) = \int_0^\infty \left\{ 1 + 2 \sum_{n=1}^\infty (-1)^n \exp[-n^2 \pi^2 (t-t')/t_c] f(t') \right\} dt'
\]  

(6)

\[
t_c = d^2 / \alpha
\]  

(7)

where \( f(t) \) is the intensity of a laser beam as a function of time, \( \tau \) is the pulse duration time, \( d \) and \( \alpha \) are the thickness and the thermal diffusivity of a sample, respectively. Figure 2 shows the intensity profile of a ruby laser beam measured as a function of time using the result of a single pulse operated at 6 J as an example. The theoretical temperature responses can easily be calculated for various values of \( t_c \) defined by eq. (7) for \( \alpha \) by integrating from \( t=0 \) to \( t=\tau \). The intensity value of a laser beam shown in Fig. 2 is integrated and the results are given in Fig. 3. The thermal diffusivity of a film sample in the direction perpendicular to the sample surface can be determined by comparing the theoretical temperature response with the measured one where the experimental temperature response is normalized by its maximum value. The following data processing is convenient for this purpose. The hatched area of Fig. 3, \( \Delta S \), surrounded by the theoretical temperature response curve and the integrated beam intensity is provided as a function of \( t_c \), as exemplified by the results of Fig. 4. Therefore, the thermal diffusivity value of a film sample in the direction perpendicular to the sample surface can be estimated...
Fig. 2 The intensity profile of a ruby laser beam as a function of time.

Fig. 3 The theoretical temperature response curves at the back surface of a sample for various \( t_C \), and the integrated intensity value of a laser beam.

from the area surrounded by the measured temperature response curve and the integrated beam intensity using the relation of Fig. 4 and eq. (7). It should be kept in mind that a devised data acquisition system is required to cover the very fast sampling speed of 1 \( \mu s \) interval for detecting the temperature response of the back surface of a film sample in the direction perpendicular to the sample surface.

III. Experimental Apparatus

Figure 5 shows the schematic diagram of the apparatus newly constructed for the present purpose of thermal diffusivity measurement of thin films. A concave mirror made of aluminum is used for focusing the infrared rays emitted by the sample on the InSb infrared rays detector. The ruby laser beam (wave length=694 nm) has a diameter of about 10 mm. In the case of measurement for thin films in the direction parallel to the sample surface, the laser beam was restricted to the narrow linear shape area on the specimen perpendicular to the length and parallel to the width of a film by a slit of 2 mm wide inserted into the beam path.

Considering the temperature distribution given by eq. (1), the sample dimension should be regarded to be long enough and the sample width is requested to be shorter than the longitudinal dimension cross section of the laser beam for satisfying one-dimensional heat flow. The size
of ribbon samples tested in this work is 50 mm long and 10 mm wide. They include thin foils of copper (18 μm), nickel (5 μm) and SUS304 stainless steel (50 μm).

The sample holder is required only to set a film sample in the position in the focusing plane of the detector and thus a sample is not affected by any stress and strain throughout the experiment. This is very convenient, especially for a fragile sample. This sample holder was enclosed in a vessel with two windows of CaF<sub>2</sub> and silica glass and evacuated to about 6 Pa if need by a rotary pump. The detector with a concave mirror can be moved along the axis parallel to the film length and its precise location is read by a micrometer. Although the apparatus shown in Fig. 5 was newly constructed for the present study, other experimental details were essentially similar to those employed in our preliminary work on thin foils<sup>12</sup> and not duplicated here. The temperature response signals measured by the remote optical sensing system were stored in a digital transient memory (I·O DATA PIO-9622) of a microcomputer (NEC, PC-9801 RX).

IV. Results and Discussion

1. Examples of thermal diffusivities of isotropic thin films

The feasibility work of the present new method was made using a copper (18 μm in thickness) foil and a nickel (5 μm in thickness) film whose thermal diffusivities are well known<sup>10</sup> for bulk form and their thermal properties are well recognized to be isotropic. As shown in section II, the device constant of \( k(r) \) should be determined with sufficient accuracy. In order to obtain the values of \( k(r) \), the sensitivity of an InSb infrared rays detector as a function of the space distribution was measured by the procedure along the way similar to our previous work on ribbon samples<sup>12</sup> and Fig. 6 shows the results of \( k(r) \) for the apparatus newly constructed. The uncertainties of \( k(r) \) was estimated to be at most 1%.

The thermal diffusivity measurements in the direction parallel to the sample surface were carried out using copper foil and nickel film. The back surface of the sample was coated by spraying with a carbon powder to increase the signal to the noise ratio in the measurements of the temperature response. The profile of the temperature response was found to be unchanged by this carbon coating from a comparison with the measurements for the sample without carbon coating. The heat flow reaches the back surface in the time less than 2 μs for these samples. The heat diffusion in the direction perpendicular to the sample surface is very short compared with the time for which the heat flow reaches the measured point. The beam profile of a ruby laser is known to be somewhat inhomogeneous. However the distance, \(|r| < 4.0 \text{ mm}\), between the center of the laser beam and the measured point is shorter than the laser beam width. Therefore, the one-dimensional heat flow in the direction parallel to the sample surface could be well accepted. The temperature response curve is shown in Fig. 7 using the nickel film of 5 μm at the distance of \( r = 3.0 \text{ mm} \) as an example. Measured thermal diffusivities in vacuum of 6 Pa at room temperature are summarized in Fig. 8 as a function of the position of a detector for copper foil and nickel film together with the literature values cited in the compilation of Ref. (15) for the bulk form. It is clearly found that the present results of ribbon samples are in good agreement with the literature values, as long as the appropriate distance \(|r| = 2.5 \sim 4.0 \text{ mm} \) in the present case is selected. The average values obtained in this range of \( r \) are 1.17 cm<sup>2</sup>/s for a copper foil and 0.196 cm<sup>2</sup>/s for a nickel film. When the location of the detector, \(|r|\), is less than 2.5 mm, the scatter in the results is detected in both cases. This is probably attributed to the fact that the heat diffusion in the pulse duration time is not negligible. The measurements were also made without a vacuum chamber at room temperature in order to investigate the heat leak from the sample to the air. It is well recognized from the measurements in the air that no significant difference from the results of Fig. 8 in vacuum is detected. This implies that the heat leak to the air by convection is negligibly small in the present ex-
Experimental condition. This is also supported by the following reason. The maximum temperature rise of the sample is about 10 K in the present case. The radiative heat loss $Q$, emitted from the sample of the temperature of $T_n$, can be given by the following Stefan-Boltzmann formula.

$$Q = e\sigma(T_n^4 - T_s^4)$$  \hspace{1cm} (8)

where, $e$ is the emissivity of the sample, $\sigma$ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8}$ Wm$^{-2}$K$^{-4}$), $T_n$ is the ambient temperature. $T_s$ and $T_c$ are 300 K and the order of 310 K respectively in the present experimental condition. On the other hand, the emissivity of the bare surface of copper foil is about 0.02 and that of the carbon coated surface is about 0.8. Thus, the decrease in the sample temperature arising from the radiative heat leak is less than 0.05 K in the range of 100 ms. Therefore, the errors of the heat leak by radiation are considered insignificant. The absolute value for the experimental uncertainty in this method is difficult to estimate. However the following points are suggested.

1. The device constant $k(r)$ includes errors less than 1%.
2. The errors in the determination of $t_{1/2}$ is order of 3% errors.
3. The measurement of the detector position includes errors less than 5%.

Thus, the total experimental uncertainty is estimated to be 9% for the thermal diffusivity measurements in the direction parallel to the sample surface.

The time delay of the order of 20 $\mu$s for obtaining the signal response is suggested in the apparatus constructed in this work. This is due to the inherent limitation of an InSb crystal and the relevant electric circuit, although a data acquisition system is improved to cover the fast sampling speed of 1 $\mu$s interval. For this reason, the present facility is subjected to restriction for samples of $t_c = d^2/\alpha > 4 \times 10^{-4}$ s in the thermal diffusivity measurements of thin films in the direction perpendicular to the sample surface. Thin foil of copper (18 $\mu$m) and thin film of nickel (5 $\mu$m) exceed this restriction. Thus, the thermal diffusivity measurements in the direction perpendicular to the sample surface by the method proposed in this work was made using a thin foil of SUS304 stainless steel (50 $\mu$m). It is worth mentioning that thermal propagation in the direction parallel to the sample surface is almost insignificant because the time required for the preset measurement is very short less than 0.5 ms. Figure 9 shows the signal response of a SUS304 stainless steel foil at the back surface. The intensity of a laser beam was also measured using a PIN photo diode. The area of $\Delta S$ as shown in Fig. 3 was calculated to be $1.02 \times 10^{-4}$ and the value of $t_c$ defined by eq. (7) is estimated to be $6.58 \times 10^{-4}$ s by using the results of Fig. 4. Then, the thermal diffusivity of a SUS304 stainless steel foil in the direction perpendicular to the sample surface was determined to be 0.0380 cm$^2$/s which agrees with the literature value (0.0356 cm$^2$/s±5%) for the bulk form(9). This is also supported by reproducing the experimental results as shown in Fig. 9 where the dashed-dotted line corresponds to the theoretical temperature response calculated from the value of 0.0380 cm$^2$/s.

Some further improvements such as the reduction in time delay for obtaining the signal response due to the electric circuit is, of course, required in order to exclude the present restriction for samples of $t_c > 4 \times 10^{-4}$ s. Nevertheless, the present authors maintain the view that the capability of the new laser-flash method is well recognized by the results of SUS304 stainless steel foil for determining thermal diffusivity of thin films in the direction perpendicular to the sample surface. The following points are suggested with respect to the experimental uncertainty in this method.

1. The measurements of $f(t)$ include the uncertainty of 1% at most.
2. The errors in the measurements of the temperature response is the order of 4%.
3. The temperature decrease by the radiative heat loss is estimated by the same procedure as the case of the direction parallel to the sample surface. It is found that the errors of the radiative heat loss are insignificant in the
present experimental condition. Then, the total experimental uncertainty of 5%, is suggested for the thermal diffusivity measurements in the direction perpendicular to the sample surface.

It can also be added that the thermal diffusivity of this SUS304 stainless steel foil in the direction parallel to the sample surface was determined to be 0.0390 cm²/s.

2. Extension of the present method to thermal diffusivity measurement of anisotropic thin films

Various substances such as pyrolytic graphite and lithium fluoride single crystal are known to show the anisotropic properties. For this reason, an attempt has also been made in order to extend the present method to the thermal diffusivity measurement of anisotropic thin films by considering two-dimensional heat flow. The usefulness of a new data processing has been examined by determining the thermal diffusivities of pyrolytic graphite, in the direction parallel and perpendicular to the sample surface.

The data processing using eqs. (6) and (7) described in section II can be applied without any additional requirement in the measurement of the thermal diffusivity of an anisotropic film in the direction perpendicular to the sample surface. On the other hand, the following new data processing has been developed for determining the thermal diffusivity of an anisotropic film in the direction parallel to the sample surface, although the temperature response itself is measured by the same method with isotropic film samples described in section II. It is noticed that thick samples, of course, requires such two-dimensional heat flow.

The coordinate system shown in Fig. 10 employed in this work for considering two-dimensional heat flow. Since the homogeneous intensity profile of a laser beam is quite feasible in the z axis, the heat flow along the z axis can be excluded. Therefore, the heat diffusion equation is given as follows:

\[
\frac{\partial T}{\partial t} = \alpha_x \frac{\partial^2 T}{\partial x^2} + \alpha_y \frac{\partial^2 T}{\partial y^2}
\]

where \( T \) is the absolute temperature at time \( t \) and, \( \alpha_x \) and \( \alpha_y \) denote thermal diffusivities along x axis and y axis, respectively. When the quantities of \( y, X, Y, \Theta \) are defined as eq. (10), eq. (9) can readily be converted to the normalized form of eq. (11).

\[
y = \alpha_x t / l^2, \quad X = x / l, \quad Y = y / l, \quad \Theta = (T - T_o) / (T_{max} - T_o)
\]

\[
\frac{\partial \Theta}{\partial t} = \frac{\partial^2 \Theta}{\partial X^2} + \frac{\alpha_x}{\alpha_y} \frac{\partial^2 \Theta}{\partial Y^2}
\]

Here \( l \) is a half of the laser beam width, \( T_o \) is ambient temperature and \( T_{max} \) is the maximum temperature. Equation (10) was solved by the finite element method (FEM) of numerical calculation under the adiabatic boundary condition at the sample surface. Since the sample was considered to be symmetrical for Y axis, the calculation was carried out with respect to only the hatched area shown in Fig. 10 using triangle elements. Here, we used, in practice, the number of FEM elements of about 300, the number of points of about 200. In order to confirm the validity of the present FEM calculation, the theoretical temperature response curve was estimated as a function of the normalized time, \( \gamma \), for the case of \( d=180 \mu m, x=2.5 \) mm and \( \alpha_x / \alpha_y = 1.0 \) where only one-dimensional heat flow along the sample surface is well recognized. Figure 11 shows a comparison of the FEM result with that calculated using the analytical solution of eq. (1). The two results agree well with each other and this prompts us to further analysis for determining thermal diffusivity of anisotropic thin films coupled with the FEM calculation.

The temperature response of the back surface of a film sample is known to strongly depend on the values of \( \alpha_x / \alpha_y \) and the sample thickness. Therefore, the normalized time of \( \gamma_{1/2} \), corresponding to the theoretical temperature response to reach one-half of its maximum temperature rise, were calculated as a function of \( \alpha_x / \alpha_y \) for various distances. The results are exemplified in Fig. 12 using the cases of \( x=2.5, 3.0 \) and 3.5 mm. The sample

![Fig. 10 The coordinate system employed in this work for considering two-dimensional heat flow. The hatched area is calculated by the finite element method.](image)

![Fig. 11 Comparison of the FEM calculation with that of the analytical solution given for the case of \( d=180 \mu m, x=2.5 \) mm and \( \alpha_x / \alpha_y = 1.0 \).](image)
thickness $d=180 \mu m$ was fixed in these FEM calculations. The measured signal is convoluted the space distribution of the sensitivity of the infrared ray detector and the temperature distribution, so that the present calculations involve such factors. The following points could be deduced from the results of Fig. 12. Decreasing the value of $\alpha_x/\alpha_x$ corresponding to the highly oriented film, $\gamma_{1/2}$ varies abruptly so that the two-dimensional heat flow should be considered even in the case of $d=180 \mu m$. Increasing the value of $\alpha_x/\alpha_x$, the value of $\gamma_{1/2}$ becomes constant which is close to the value of isotropic thin films expressed by eq. (1) and then the effect of two-dimensional heat flow appear to be insignificant.

With these results in mind, the measured temperature response has been analyzed for determining the thermal diffusivities ($\alpha_x$) of a pyrolytic graphite foil (10 × 40 mm, 180 μm in thickness) in the direction parallel to the sample surface using the value of 0.0134 cm$^2$/s for the thermal diffusivity ($\alpha_x$) in the direction perpendicular to the sample surface. This $\alpha_x$ value was determined by the same method for isotropic thin films.

The temperature response curves of a pyrolytic graphite foil in the direction parallel to the sample surface were measured at the distances of $x=2.5$, 3.0 and 3.5 mm. The solid dots in Fig. 13 denote the values estimated along the way described in section II using eq. (4) and eq. (5). However, it is clearly found that these $\alpha_x$ values increase and depend on the distance $x$ due to the two-dimensional heat flow. Then, $\alpha_x$ was calculated by considering the two-dimensional heat flow as follows. At first, the value of $\alpha(0)$ is set for the first iteration using the $\alpha_x$ value estimated with the condition of no two-dimensional heat flow, and then $\gamma_{1/2}$ corresponding to $\alpha_x/\alpha(0)$ is calculated from the results of Fig. 12. Next, $\alpha(2)$ for the second iteration is estimated from the results measured $l_{1/2}$ and $\gamma_{1/2}(l)$. Then, the calculation is iterated until $|\alpha(n) - \alpha(n-1)| < 10^{-4}$. When the convergence is recognized, we may obtain a true value of $\alpha(0)$. Such convergent values of $\alpha_x$ are shown in Fig. 13 by open circles, and they appear to be almost independent of the distance x. Thus, the thermal diffusivity, $\alpha_x$, of a pyrolytic graphite foil in the direction parallel to the sample surface is estimated to be 4.4 cm$^2$/s by averaging the values obtained at different distances. The experimental uncertainty in this case is considered to be 9% similar to the measurement in the direction parallel to the sample surface.

V. Concluding Remark

A new laser-flash method has been proposed for measuring thermal diffusivity of thin films in the direction parallel and perpendicular to the sample surface. The validity and usefulness of this new method including a new apparatus with a very fast data acquisition system was demonstrated by successfully measuring thermal diffusivity of the thin foil of copper (18 μm), the thin film of nickel (5 μm) and SUS304 stainless steel (50 μm).

We have also carried out the extension of this new method to the thermal diffusivity measurement of highly oriented thin films. It is found from the measurements of pyrolytic graphite foil (180 μm) that the method proposed in this study works well when coupled with a new data processing considering two-dimensional heat flow.

The method for measuring thermal diffusivity of thin films has not yet been completed, although it would be interesting to extend the present method to systematically determine the thermal diffusivities of various thin films in a variety of states, so that its usefulness may be tested in a rather wider base. Nevertheless, the laser-flash method itself is known as an easy way to prepare samples. Only a simple and quick operation is required and then the results can be obtained within a few seconds. Thus, the present laser-flash method might become one of the powerful techniques for determining thermal diffusivity of thin films.

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