Spot-Pulse-Heating Method for Measuring Thermal Conductivity and Thermal Diffusivity of Silica Thin Sheets

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The spot-pulse-heating method is based on the relationship between the surface-temperature increase of a sample at the end of each heating interval, the thermal conductivity and the thermal diffusivity of the sample. The relationship is obtained by solving the Fourier's equation. The surface-temperature increase at the end of each heating interval is proportional to the reciprocal of square root of time. The intercept and the slope of this straight line give the values of thermal conductivity and thermal diffusivity.

This method was examined by measuring the thermal conductivity and the thermal diffusivity of fused-SiO₂ and PbO-SiO₂ with about 10 mm thickness at room temperature. The obtained values were in good agreement with ones in literatures.

Next, this method has been successfully applied to fused-SiO₂ with 1 mm to 60 μ m thickness without the influence of substrates. The thermal conductivity and the thermal diffusivity of thin sheets of fused-SiO₂ are independent of the thickness and constant at about $1.05 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and $6.5 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$, respectively.

(Received February 4, 1991)

Keywords: spot-pulse-heating method, thermal conductivity, thermal diffusivity, specific heat, thin silica sheet, thin film

I. Introduction

At present there exists an increasing demand for the thermophysical data of thin films because of the following two reasons. One is the scientific reason that the study on the size effects of heat conduction could yield the informations on the various scattering processes of phonons in materials and their mean-free-path lengths. Another is the industrial reason that the thermal conductivity and the thermal diffusivity of thin films are also of much value in elucidating the heat transfer during film-manufacturing processes, the thermal aging effects in microelectronic circuits and so on.

In spite of the above interests, few studies have been carried out in this field. Some reports describe the development of new methods for measuring the thermal conductivity and the thermal diffusivity of thin plates or films⁽¹⁾⁻⁽⁶⁾ and the size effect of heat conduction⁽⁷⁾.

In these currents we have reported in the previous paper⁽⁸⁾ the spot heating method as a new one for measuring the thermal conductivity and the thermal diffusivity of thin materials. This measurement is based on the following principle: The surface of a sample is continuously heated up by a laser beam with a circular shape and the temperature increase of the surface is measured by means of a thermocouple. The temperature increase is controlled by the thermophysical properties of the sample, such as thermal conductivity and thermal diffusivity. Therefore, these thermophysical data can be obtained by

analyzing the temperature increase on the assumption that the sample is semi-infinite.

The spot heating method can be successfully applied to the fused silica plate of 1 mm in thickness. But the following problems could be caused in applying this method to thinner materials:

(1) The assumption of a sample with semi-infinite length breaks down.

(2) The use of a thermocouple is unsuitable for measuring the surface-temperature increase of a sample because the influence of its heat capacity becomes relatively larger.

In order to avoid the problem (1), the reduction of heat supply to a sample is considered to be effective. The reduction can be attained by supplying a laser beam intermittently in regular pulses by use of an optical chopper. On the other hand, it is considered that the use of thinner thermocouples may successfully solve the problem (2).

On the basis of the above background, in the present work we propose a newly-improved method for measuring the thermal conductivity and the thermal diffusivity of thin films. The method is actually applied to thin silica plates and films which play very important roles in microelectronic devices. Now, this method is called the spot-pulse-heating method because a laser beam is supplied to a sample in regular pulses.

II. Experimental

1. Principle

Heat is periodically supplied over a circle of radius r in the surface of a sample in regular rectangular pulses. For example, a heat input is "on" for time T_1 and "off" for time $T - T_1$, and so on, with period T .

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In this situation the heat input per unit time $q(t)$ may be represented by the function

$$\begin{aligned} q(t) &= 0, & t < 0 \\ q(t) &= Q, & nT < t < nT + T_1, \quad n = 0, 1, 2, \dots \\ q(t) &= 0, & nT + T_1 < t < (n+1)T, \quad n = 0, 1, 2, \dots, \end{aligned} \quad (1)$$

where Q , T and T_1 are constants.

Assuming the semi-infinite thickness of a sample, Jaeger⁽⁹⁾ and Carslaw and Jaeger⁽¹⁰⁾ solved Fourier's equation under the above conditions and showed the temperature increase $\Delta\theta$ at the center of the heating circle in sample surface at time t as follows:

$$\Delta\theta = (QT_1/\pi r \lambda T) \tau \{ \pi^{-1/2} - \text{ierfc}(1/\tau) \} + v_p. \quad (2)$$

Here λ is the thermal conductivity of sample and τ is the dimensionless number defined as $\tau = 2(\kappa t)^{1/2}/r$, where κ is the thermal diffusivity of the sample. $\text{ierfc}(x)$ is the function defined as $\text{ierfc}(x) = \exp(-x^2)/\pi^{1/2} - x \cdot \text{erfc}(x)$. v_p means the periodic part of the temperature change. The value of v_p at the end of each heating interval for heat supply, i.e., $t = nT + T_1$ is represented by the equation

$$\begin{aligned} v_p &= \pi r^2 \lambda T^{1/2} / QT_1 \kappa^{1/2} \\ &= \{ 2/(\pi a)^{1/2} \} \cdot \{ 1 - \exp(-c^2/4a) \} \\ &\quad + (c/a) \text{erfc}(c/2a^{1/2}) - c \\ &\quad + (2/\pi a) \int_0^\infty [\exp(-a\xi^2) \cdot \{ \exp(-(1-a)\xi^2) \\ &\quad - \exp(-\xi^2) \} \cdot \{ 1 - \cos(c\xi) \} / \xi^2 \{ 1 - \exp(-\xi^2) \}] d\xi \\ &= P \end{aligned} \quad (3)$$

where $a = T_1/T$, $c = r/(\kappa T)^{1/2}$, and ξ is the dimensionless parameter used for solving Fourier's equation.

The values of P as a function of T_1/T are shown in Fig. 1 for various values of c . For $c \geq 1$ they are close to the limiting case of $c \rightarrow \infty$, as pointed out by Jaeger⁽⁹⁾. Thus the suitable choice of the values of r , T and T_1/T can make P constant. In such a case v_p can be represented by the equation

$$v_p = QT_1 \kappa^{1/2} P / \pi r^2 \lambda T^{1/2}. \quad (4)$$

The combination of eqs. (2) and (4) gives $\Delta\theta$ at $t = nT + T_1$.

$$\begin{aligned} \Delta\theta &= (QT_1/\pi r \lambda T) \tau \{ \pi^{-1/2} - \text{ierfc}(1/\tau) \} \\ &\quad + QT_1 \kappa^{1/2} P / \pi r^2 \lambda T^{1/2} \end{aligned} \quad (5)$$

Here for $a = T_1/T = 1$ eq. (5) is reduced to the following simple equation because of $P = 0$ in Fig. 1.

$$\Delta\theta = (Q/\pi r \lambda) \tau \{ \pi^{-1/2} - \text{ierfc}(1/\tau) \} \quad (6)$$

This equation is just for the spot heating method⁽⁸⁾.

Since $\tau \{ \pi^{-1/2} - \text{ierfc}(1/\tau) \}$ in eq. (5) can be approximated to $1 - 0.4358/\tau$ in the error of less than 10% for $\tau \geq 1$ ⁽⁸⁾, eq. (5) can be reduced to the equation

$$\begin{aligned} \Delta\theta &= (QT_1/\pi r \lambda T^{1/2}) \cdot (1/T^{1/2} + \kappa^{1/2} P/r) \\ &\quad - (0.2179 T_1 Q / \pi \lambda \kappa^{1/2} T) \cdot (1/t^{1/2}), \end{aligned} \quad (7)$$

Fig. 1 Relation between P and T_1/T for various values of c . Here P is the calculated values of eq. (3). T_1/T is the ratio of a heating interval to a period and c is the value of $r/(\kappa T)^{1/2}$, where r , κ and T express the radius of the heating circle, thermal diffusivity and a period of heat supply timing, respectively.

Equation (7) means $\Delta\theta$ is linearly proportional to $1/t^{1/2}$. The slope, S , and the intercept for $t \rightarrow \infty$, $\Delta\theta(\infty)$, are represented by the following two equations, respectively.

$$S = -0.2179 T_1 Q / \pi \lambda \kappa^{1/2} T \quad (8)$$

$$\Delta\theta(\infty) = (QT_1/\pi r \lambda T^{1/2}) \cdot (1/T^{1/2} + \kappa^{1/2} P/r). \quad (9)$$

In these equations only λ and κ are unknown. Therefore, λ and κ can be determined by solving these two equations.

In addition, when the density of a sample, ρ , is known, specific heat C_p can be estimated by virtue of the relationship of $C_p = \lambda/(\kappa \cdot \rho)$.

2. Procedure

Figure 2 shows the schematic view of the experimental apparatus of the spot-pulse-heating method. A chromel-alumel thermocouple of 100, 50 or 25 μm in diameter was fixed on the surface of a sample with silver paste. The diameter and thickness of the silver paste were 2 to 3 mm and 100 to 200 μm , respectively. In order to eliminate the reflection of light, the surface of the sample was colored black. The sample surface was heated up by means of a He-Ne or Ar^+ laser with a circular shape. The radius r of the heating circle was 1 mm and the center was adjusted to the location of the thermocouple junction.

When the shutter was opened, the laser beam was supplied to a sample intermittently by means of an optical chopper. The temperature change of the sample surface was measured as the voltage change of the thermocouple by means of a recorder for about 100 s. The

Fig. 2 Schematic diagram of the experimental apparatus for the spot-pulse-heating method.

magnitude of the voltage change was 10 to 40 μV and the ratio of noise to signal voltage was within 1.5%. All measurements were carried out at room temperature.

The laser power Q was changed in the range of 2.5 to 10 mW and measured with a powermeter after each measurement. The values of 1, 2, 3, 4 and 5 Hz were chosen as the frequency f of the chopper. The ratio of a heating interval to a period T_1/T was changed in the range of 0.1 to 0.5. The change of the ratio was attained by varying the ratio of space to mark in the chopper blade.

3. Samples

In order to examine the validity of this method, fused- SiO_2 and 50 mol% PbO-SiO_2 with about 10 mm thickness were employed as samples, because their thermal conductivity and thermal diffusivity were known⁽⁸⁾⁽¹¹⁾⁻⁽¹⁴⁾. PbO-SiO_2 samples were prepared by quenching PbO-SiO_2 melts kept about 1200 K.

Fused- SiO_2 plates of 1000 to 60 μm in thicknesses were employed. The samples of below 200 μm in thickness were obtained by etching fused- SiO_2 of 500 μm in thickness in hydrofluoric acid solution. The thickness of the samples was measured with a micrometer. In this measurement, in order to examine the influence of the substrates, these samples were set on the substrates of silicon or silicone rubber, because the substrates have larger and smaller thermal conductivity than SiO_2 , respectively.

Amorphous SiO_2 films of 0.5 to 4.5 μm in thicknesses were employed as thin films. These thin SiO_2 films were synthesized on the substrates of silicon and/or fused- SiO_2 by means of thermal oxidation of silicon, sputtering, chemical-vapor-deposition (CVD) and spin-on glass (SOG) methods. The thickness of the thin SiO_2 films was determined by the observation with a scanning electron microscope.

III. Results

1. Temperature increase of sample surface

Figure 3 shows the voltage change of a thermocouple in the measurement of fused- SiO_2 with 10 mm thickness. The measurement was carried out under the conditions of $f/\text{Hz}=2$, $T_1/T=0.5$ and $Q/\text{mW}=2.6$. The diameter D of the thermocouple was 100 μm . From this figure, the temperature change is in good agreement with the heat-pulse timing.

Figure 4 shows the relation between the surface-temperature increase $\Delta\theta$ at the end-time t of each heating interval and $t^{-1/2}$, based on Fig. 3. There is a linear relationship between $\Delta\theta$ and $t^{-1/2}$. From the intercept and the slope of this straight line, the thermal conductivity λ and the thermal diffusivity κ of SiO_2 can be obtained through eqs. (8) and (9) as follows:

$$\lambda/W \cdot \text{m}^{-1} \cdot \text{K}^{-1} = 0.95 \quad \text{and} \quad \kappa/\text{m}^2 \cdot \text{s}^{-1} = 7.4 \times 10^{-7}.$$

These values are in good agreement with those measured with the spot heating method⁽⁸⁾.

2. Results of thermal conductivity and thermal diffusivity for thick silica and lead silicate glasses

Figures 5 and 6 show the thermal conductivities and the thermal diffusivities of fused- SiO_2 and PbO-SiO_2

Fig. 3 Electromotive force change of thermocouple set on fused- SiO_2 sample.

Fig. 4 Relation between the surface temperature increase, $\Delta\theta$, and the reciprocal of the square root of time at the end of each heating interval, $t^{-1/2}$.

Fig. 5 Dependence of thermal conductivities, λ , on the frequency of heat input, f . Different marks of the plots mean different runs.

Fig. 6 Dependence of thermal diffusivities, κ , on the frequency of heat input, f .

with 10 mm thickness each as a function of the chopper frequency f . The other parameters were $T_1/T=0.5$, $Q/\text{mW}=2.7$ and $D/\mu\text{m}=100$. The different marks of plots mean the different runs and show the magnitude of the reproducibility. The measurements at $f/\text{Hz}=0$ correspond to those with the spot heating method.

The thermal conductivities and the thermal diffusivities are constant within scattering errors and

independent of chopper frequency. Table 1 shows the comparison of thermal conductivities of fused-SiO₂ and PbO-SiO₂ measured at room temperature with various methods. The thermal conductivities of fused-SiO₂ measured with the spot-pulse-heating method are in agreement with those measured with the spot heating method by Susa *et al.*⁽⁸⁾, with the hot strip method by Li *et al.*⁽¹¹⁾ and with the steady-state method by Wray and Connolly⁽¹²⁾, but are about 1.2 times smaller than those by the other investigators^{(13-a)-(13-b),(14)}. This difference results might be caused from fused-SiO₂ in non-equilibrium state.

On the other hand, the thermal conductivities of PbO-SiO₂ in the present study are in good agreement with those measured with the spot heating method⁽⁸⁾, with the hot wire and the hot strip methods⁽¹¹⁾, with the absolute method of electrically heated disc^(13-b) and with the steady-state method⁽¹³⁻ⁱ⁾.

Table 2 shows the comparison of thermal diffusivities of fused-SiO₂ and PbO-SiO₂ measured at room temperature with various methods. The thermal diffusivities of fused-SiO₂ measured with the spot-pulse-heating method have scattering error of $\pm 30\%$ in magnitude but their average is in agreement with those measured with the other methods^{(8)(11)(13-c)(13-f)(13-j)(14)}.

On the other hand, the thermal diffusivities of PbO-SiO₂ in the present study are in good agreement with those measured with the spot heating method⁽⁸⁾ but about 2 times larger than those with the hot strip method⁽¹¹⁾.

From the above results, it has been concluded that the spot-pulse-heating method is reliable for measuring thermal conductivity and thermal diffusivity of thick materials. Furthermore, it has been experimentally demonstrated that these thermal properties by the present method are independent not only of the chopper frequency but also of the other parameters such as T_1/T and Q .

3. Dependence of the linearity of $\Delta\theta$ against $t^{-1/2}$ on parameter T_1/T

Figure 7 shows the relation between $\Delta\theta$ and $t^{-1/2}$ for fused-SiO₂ with 500 μm thickness under the different values of the parameter T_1/T . The other parameters were fixed as $f/\text{Hz}=2$, $Q/\text{mW}=2.6$ and $D/\mu\text{m}=50$. In each measurement $\Delta\theta$ has a linear relationship with $t^{-1/2}$ in shorter time range than deviation time, t_d , but positively deviates from the straight line in the long time range. This deviation is due to the breakdown of the assumption of a semi-infinite medium because of the influence of silicone rubber substrate with smaller thermal conductivity than SiO₂.

From Fig. 7, the deviation time, t_d , shifts to longer time with decreasing the value of T_1/T . Concludingly, smaller values of T_1/T is suitable to use for thin films.

4. Thermal properties of thin silica plates and films

Figure 8 shows the relation between $\Delta\theta$ and $t^{-1/2}$ for fused-SiO₂ with 100 μm thickness set on silicon or silicone rubber substrates under the conditions of

Table 1 A comparison of thermal conductivity of fused-SiO₂ and PbO-SiO₂ at room temperature.

Sample	Author	$\lambda/W \cdot m^{-1} \cdot K^{-1}$	Method	Ref.
Fused-SiO ₂	Present Study	0.920 ~ 1.17	Spot-Pulse-Heating Method	—
	Susa <i>et al.</i>	0.911 ~ 1.09	Spot Heating Method	8
	Li <i>et al.</i>	1.16 ~ 1.29	Hot Strip Method	11
	Wray and Connolly	1.09 ~ 1.38	Steady-State Method	12
	Devyatkova <i>et al.</i>	1.38	Steady-State-Plate Method	13-a
	Ratcliffe	1.32 ~ 1.40 (273 K) (323 K)	Absolute Method of Electrically Heated Disc	13-b
	Vasiliev	1.40	Quasi Steady-State Method	13-c
		1.35 ~ 1.37	Modified Method for Small Values of Furie Criterion	
	Sugawara	1.35 ~ 1.44 (273 K) (323 K)	Dual Combined Method	13-d, e
	Corning	1.38	?	13-f
	Sergeev and Chadovich	1.36	?	13-g
	Muratov and Chernyshov	1.33	Quasi Steady-State Method	13-h
Gustafsson <i>et al.</i>	1.42	Hot Strip Method	14	
PbO-SiO ₂ (50-50 mol%)	Present Study	0.522 ~ 0.676	Spot-Pulse-Heating Method	—
	Susa <i>et al.</i>	0.588 ~ 0.621	Spot Heating Method	8
	Li <i>et al.</i>	0.6	Hot Wire Method	11
		0.45 ~ 0.52	Hot Strip Method	
	(51.9-48.1 mol%)	Ratcliffe	0.515 ~ 0.561 (273 K) (323 K)	Absolute Method of Electrically Heated Disc
(49.3-50.7 mol%) (66.2-33.8 mol%)	Van Velden	0.5447(313 K)	Steady-State Method	13-i
		0.469 (313 K)		

Table 2 A comparison of thermal diffusivity of fused-SiO₂ and PbO-SiO₂ at room temperature.

Sample	Author	$\kappa/m^2 \cdot s^{-1}$	Method	Ref.
Fused-SiO ₂	Present Study	$5.02 \sim 9.21 \times 10^{-7}$	Spot-Pulse-Heating Method	—
	Susa <i>et al.</i>	$7.33 \sim 9.03 \times 10^{-7}$	Spot Heating Method	8
	Li <i>et al.</i>	$8.40 \sim 9.68 \times 10^{-7}$	Hot Strip Method	11
	Vasiliev	8.23×10^{-7}	Quasi Steady-State Method	13-c
	Corning	8.4×10^{-7}	?	13-f
	Hattori and Fukumoto	8.9×10^{-7}	Ångström's Method	13-j
	Gustafsson <i>et al.</i>	8.63×10^{-7}	Hot Strip Method	14
PbO-SiO ₂ (50–50 mol%)	Present Study	$2.54 \sim 3.90 \times 10^{-7}$	Spot-Pulse-Heating Method	—
	Susa <i>et al.</i>	$3.38 \sim 3.83 \times 10^{-7}$	Spot Heating Method	8
	Li <i>et al.</i>	$1.75 \sim 1.95 \times 10^{-7}$	Hot Strip Method	11

$f/Hz=2$, $T_1/T=0.1$ and $Q/mW=5$. The diameter of a thermocouple was 25 μm .

Before about 3.5 s there is a linear relationship between $\Delta\theta$ and $t^{-1/2}$ in each measurement. The slopes of

the straight lines are in good agreement with that obtained in the measurement of thick fused-SiO₂. After about 3.5 s the temperature increase deviates from the straight lines. The direction of deviation depends on ther-

Fig. 7 Variation of the surface-temperature increases, $\Delta\theta$, with the change of the ratio of a heating interval to a period T_1/T for thin fused-SiO₂ plates with 500 μm thickness set on silicone rubber substrate.

Fig. 8 Surface temperature increase, $\Delta\theta$, against $t^{-1/2}$ for thin fused-SiO₂ plates with 100 μm thickness formed on silicon or silicone rubber substrate.

mal conductivity of the substrate. From these results, the temperature increase within about 3.5 s for the thinner fused-SiO₂ are not affected by the substrates. Thus, in the present study, the data in this time range were employed.

Figure 9 shows the thermal conductivity and the thermal diffusivity of fused-SiO₂ as a function of the thickness, d , of sample. The different marks of the plots mean the different substrates. The thermal conductivity and the thermal diffusivity have scattered around 1.05 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and $6.5 \times 10^{-7} \text{ m}^2\cdot\text{s}^{-1}$, respectively, and been independent of the substrates. It has been shown that the thermal conductivity and the thermal diffusivity of fused-SiO₂ are independent of the sample thickness and constant within the scattering errors.

Then the spot-pulse-heating method can be applied to the fused-SiO₂ with more than 60 μm thickness.

Sequently, this method was employed for the SiO₂ film of 3 μm in thickness. The film was manufactured on

Fig. 9 Thermal conductivity and thermal diffusivity of fused-SiO₂ set on silicon or silicone rubber substrate as a function of the SiO₂ thickness, d .

the substrates of silicon and fused-SiO₂ with a sputtering method. The thermal conductivity and the thermal diffusivity of the thin SiO₂ film could not be determined, because the temperature increases were affected by the substrates from the beginning of measurement. The same results were obtained for the SiO₂ films manufactured with thermal oxidation of silicon, CVD and SOG methods.

It has been clarified that the spot-pulse-heating method in the present stage cannot be applied to thin SiO₂ films in magnitude of several micrometers in thickness.

IV. Discussion

1. Errors for thermal conductivity and thermal diffusivity

From eqs. (8) and (9), the following equations for λ and κ can be obtained.

$$\lambda = QT_1 / 2\pi r (\Delta\theta(\infty)) T + \{ (QT_1 / 2\pi r (\Delta\theta(\infty)) T)^2 - 0.2179 Q^2 P T_1^2 / \pi^2 r^2 S (\Delta\theta(\infty)) f^{1/2} T^2 \}^{1/2}. \quad (10)$$

$$\kappa = (0.2179 QT_1 / \pi \lambda S T)^2. \quad (11)$$

By applying the law of error propagation to eqs. (10) and (11), the relative errors for thermal conductivity and thermal diffusivity can be obtained, as follows.

$$(\Delta\lambda)^2 = (\partial\lambda/\partial Q)^2 (\Delta Q)^2 + (\partial\lambda/\partial(T_1/T))^2 \{\Delta(T_1/T)\}^2 + (\partial\lambda/\partial P)^2 (\Delta P)^2 + (\partial\lambda/\partial f)^2 (\Delta f)^2 + (\partial\lambda/\partial(\Delta\theta(\infty)))^2 \{\Delta(\Delta\theta(\infty))\}^2 + (\partial\lambda/\partial S)^2 (\Delta S)^2 + (\partial\lambda/\partial r)^2 (\Delta r)^2. \quad (12)$$

$$(\Delta\kappa)^2 = (\partial\kappa/\partial Q)^2 (\Delta Q)^2 + (\partial\kappa/\partial(T_1/T))^2 \{\Delta(T_1/T)\}^2 + (\partial\kappa/\partial\lambda)^2 (\Delta\lambda)^2 + (\partial\kappa/\partial S)^2 (\Delta S)^2. \quad (13)$$

Substituting eq. (11) into eq. (13), eq. (13) can be simplified as follows:

$$|\Delta\kappa/\kappa| = 2\{(\Delta Q/Q)^2 + (\Delta(T_1/T)/(T_1/T))^2 + (\Delta\lambda/\lambda)^2 + (\Delta S/S)^2\}^{1/2}. \quad (14)$$

The relative errors are estimated from the following data:

$$\Delta\theta(\infty)/K = 0.2275, \quad S/K \cdot s^{1/2} = -0.02152, \\ \lambda/W \cdot m^{-1} \cdot K^{-1} = 1.01 \quad \text{and} \quad \kappa/m^2 \cdot s^{-1} = 7.18 \times 10^{-7}.$$

The data were obtained under the conditions of $Q/mW = 2.7$, $T_1/T = 0.1$, $f/Hz = 2$, $r/mm = 1$ and $P = 2.79$. The error of each factor is

$$\Delta Q/mW = \pm 0.1, \quad \Delta(T_1/T) \sim 0, \quad \Delta f/Hz = \pm 0.1, \\ \Delta r/mm = \pm 0.05, \quad \Delta P = \pm 0.01, \\ \Delta(\Delta\theta(\infty))/K = \pm 1.95 \times 10^{-3} \quad \text{and} \\ \Delta S/K \cdot s^{1/2} = \pm 3.88 \times 10^{-3}.$$

The errors of $\Delta(\Delta\theta(\infty))$ and ΔS are the respective standard deviations by the method of least squares.

Substituting the above values to eqs. (12) and (14), the relative errors are estimated to be

$$|\Delta\lambda/\lambda| = 0.095 \quad \text{and} \quad |\Delta\kappa/\kappa| = 0.41.$$

Then, relative errors for thermal conductivity and thermal diffusivity are about 10% and 40%, respectively.

In the present study, ΔS is the biggest error and controls the net relative error. Therefore, the accurate measurement of temperature increase is most important for improving the spot-pulse-heating method.

On the other hand, the present method has eight error factors: (1) the deviation of the timing of heat input from regular rectangular pulses, (2) the influence of a thermocouple, (3) the reflection and the permeation of a laser beam, (4) the heat transfer by radiation, (5) the heat transfer to air by convection and conduction, (6) the influence of silver paste, (7) the heat resistance at sample surface and (8) the influence of the power profile of a laser beam.

In the previous paper on the spot heating method⁽⁸⁾, the factors of (3) to (8) were discussed in detail and the errors by the factors of (4) to (8) were below 1% or negligible. The previous discussion is consistent in the spot-pulse-heating method because of the similarity of the principles in both methods.

The error of factor (1) is caused from the characteristic of the spot-pulse-heating method and that of factor (2) is more important with decreasing the thickness of a sample. The factor (3) is again discussed, because the laser power used in the present method is higher than that in the spot heating method. The following discussions are on the factors of (1) to (3).

(1) Deviation of the timing for heat input from regular rectangular pulses

The solution of the Fourier's equation, that is the eq. (2), assumes that heat is supplied on the sample surface in regular rectangular pulses. This assumption holds true for an ideal point heat-source. But the timing for heat input actually deviates from regular rectangular pulses

because the laser beam has the finite radius of 1 mm.

The heat input Q could be overestimated due to this deviation. The error can be geometrically evaluated from the diameter of the heating circle, an arc length of the space in the chopper blade, the chopper frequency f and the ratio of a heating interval to a period T_1/T .

The error is estimated to be about 2.6% for $f/Hz = 2$ and $T_1/T = 0.5$, while about 13% for $f/Hz = 2$ and $T_1/T = 0.1$. The latter value can not be negligible.

In this paper, however, the data of thermal conductivity and thermal diffusivity were not corrected by use of the above error. In order to reduce the magnitude of the error, longer arc length of the space in the chopper blade is preferable for use.

(2) Influence of a thermocouple

Figure 10 shows the dependence of the thermal conductivity and the thermal diffusivity of fused-SiO₂ with 10 mm thickness on the diameter of thermocouples. The thermal conductivity and the thermal diffusivity are constant within scattering errors and independent of the diameter of thermocouples.

As shown in Fig. 9, the thermal conductivity and the thermal diffusivity are also independent of the thickness of the samples in the range of 60 μm to 10 mm.

From these results, the influence of thermocouples can be negligible for the sample with above 60 μm in thickness when the thermocouple of 25 μm in diameter is used.

But for thinner samples than 60 μm in thickness the heat capacity of thermocouples would affect thermal conductivity and thermal diffusivity. In such a case, an optical thermometer would be available because it is not in contact with sample and temperature can be measured in good response with the chopper frequency.

Fig. 10 Influence of the diameter, D , of the chromel-alumel thermocouples on the thermal conductivity, λ , and thermal diffusivity, κ , of fused-SiO₂.

(3) Reflection and permeation of laser beam

In order to estimate these errors, the following experiment was carried out. A glass plate with 200 μm thickness was coated with silver paste and colored black. The Ar^+ laser beam with the power of 10 mW was irradiated to the glass plate. The powers of reflection and permeation light were measured by a powermeter.

The power of the reflection light was below 0.1 mW. The value is within the driftage of the powermeter. Therefore, the error by the reflection of light can be considered to be below 1% for thermal conductivity.

On the other hand, the power of the permeation light was also below 0.1 mW. The error by the permeation of light can be also below 1%.

2. Experimental limit for the spot-pulse-heating method

Figure 11 shows the relation between the deviation time t_d and the thickness of fused- SiO_2 d under the conditions of $f/\text{Hz}=2$, $T_1/T=0.1$ and $Q/\text{mW}=5\sim 7$. In this figure, t_s is the time when $\Delta\theta$ begins to fall on a straight line and 0.55 s. Here t_s was estimated from the equation, $1=2(\kappa t_s)^{1/2}/r^{(8)}$.

t_d is linearly proportional to d according to the following equation:

$$t_d = 0.04d. \quad (15)$$

A linear relationship between $\Delta\theta$ and $t^{-1/2}$ is required to obtain λ and κ . Furthermore, at least three data on $\Delta\theta$ are necessary for drawing a straight line in the figure of $\Delta\theta$ vs. $t^{-1/2}$. The datum on $\Delta\theta$ in the first cycle should be negligible because of the condition of $\tau \geq 1$, so three data can be obtained by the fourth cycle. Since the time at the end of a heating interval in the fourth cycle is 1.55 s for $f/\text{Hz}=2$ and $T_1/T=0.1$, the deviation time, t_d , should be more than 1.55 s. Therefore, the limit for the

Fig. 11 Relation between the deviation time, t_d , and the thickness of fused- SiO_2 , d .

sample thickness can be estimated to be about 40 μm through Fig. 11.

However, if the values of T_1/T and Q are decreased to shift t_d to longer time and f is increased to shorten thermal penetration thickness, $(4\kappa t)^{1/2}$, the spot-pulse-heating method could be applied to thinner samples. But in such a case temperature change considerably decreases.

Therefore, the improvement of the temperature measurement system is the most important for applying the spot-pulse-heating method to thin films.

V. Summary

The spot-pulse-heating method has been studied as a new method for measuring thermal conductivity and thermal diffusivity of thin films.

This method has been examined by measuring the thermal conductivity and the thermal diffusivity of fused- SiO_2 and PbO-SiO_2 with about 10 mm thickness at room temperature. The obtained values have been in good agreement with those in literatures.

Secondly, this method has been successfully applied to fused- SiO_2 with 1 mm to 60 μm thicknesses without the influence of substrates but not to thin SiO_2 films with below 4.5 μm thickness. The thermal conductivity and the thermal diffusivity of fused- SiO_2 are independent of the sample thickness, about $1.05 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and $6.5 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$, respectively.

Finally, errors and the experimental limit to the sample thickness have been discussed. The spot-pulse-heating method may be considered to be of great promise for the measurements of thermal conductivity and thermal diffusivity of thin films by increasing the accuracy of temperature measurement.

Acknowledgments

The authors would like to express their sincere thanks to Professor Emeritus J. F. Elliott of Massachusetts Institute of Technology and Associate Professor T. Maruyama of Tokyo Institute of Technology for valuable discussion, comments and encouragement.

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