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Thermal Diffusivity Measurements of Thin Films and Multilayered Composites[1]

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This review discusses the following methods for measuring thermal diffusivity of thin materials: ac calorimetric method, flash method, mirage-effect method, picosecond time-resolved thermoreflectance method, photoacoustic method, etc. The measurements are classified into the following three cases: (a) that yield thermal diffusivity parallel to the surface of a thin material, (b) that yield thermal diffusivity perpendicular to the surface, and (c) that yield thermal diffusivity perpendicular to the surface of a thin material but deposited on a solid substrate. The contribution of inhomogeneity in the spatial distribution of the imparted thermal energy and obscureness at the edge of the restricted region, to which uniform thermal energy is imparted, is considered in each case. The contribution of temporal distortion of the temperature pulse, waves, etc., is considered in each measurement. The proper thickness of samples required for the measurements is discussed. In some of the measurements, the applicable materials are restricted, for instance, thermoreflectance measurements are applicable to metallic samples only.

KEY WORDS: ac calorimetry; composites; flash method; multilayer; photoacoustic method; thermal diffusivity; thin films.

1. INTRODUCTION

Several methods are available to measure the thermal diffusivity of a thin single film. Some of them are applicable to the measurement on a multilayered composite film.

They are classified into the three cases: case A measures the component parallel to the surface of a thin material, case B measures the compo-

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nent perpendicular to the surface, and case C measures the component perpendicular to the surface of a thin material but which is deposited on a solid substrate. In Fig. 1, the components measured in the above cases are illustrated for the composite materials with *n* layers.

Usually in the measurements for thin materials, thermal energy is imparted to an entire or restricted region on the surfaces. The spatial profile of the imparted thermal energy should be considered in the analysis of the data, since the ideal profile is not always available. Generally speaking there are two kinds of typical profiles: one is perfectly flat as shown in Fig. 2a and the other is strictly square as shown in Fig. 2b. However, the spatial profile of the imparted thermal energy in the actual measurements is inevitably more or less deformed as shown in Figs. 3a and b, corresponding to Figs. 2a and b, respectively.

On the other hand, there are three kinds of typical temporal shapes: an instantaneous pulse, a pulse with finite width, and sine waves as shown in Figs. 4a, b, and c, respectively. However, the actual shapes used in the measurements are usually deformed as in Figs. 5a, b, and c, corresponding to Figs. 4a, b, and c, respectively. The deformation in the temporal shapes should be considered carefully in the analysis.

In most of the thin-material measurements, optical excitation is employed for imparting thermal energy, since such a noncontacting method affects minimally the measurements on small samples. When a sample is optically transparent, the mechanism of converting optical energy

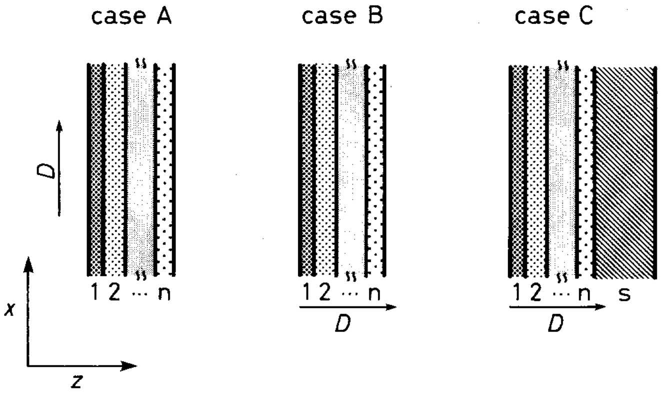

Fig. 1. Observable components of thermal diffusivity, *D*, in *n*-layer materials. If *n* is 1, it tends to a single layer material. Case A is for measuring thermal diffusivity parallel to the surface of a thin material, case B is for the thermal diffusivity perpendicular to the surface, and case C is for the thermal diffusivity perpendicular to the surface of a thin material deposited on a substrate.

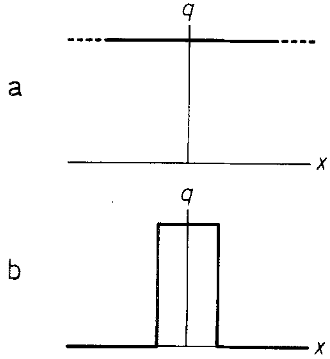

Fig. 2. Ideal spatial profiles of the thermal energy imparted to the surface of a thin material. (a) Uniform thermal-energy distribution over the surface. (b) Thermal energy imparted to a restricted region in the surface.

into thermal energy in the sample should be considered in detail, otherwise the surface of the sample should be treated so as to absorb optical energy at the surface. In addition, the effect of radiation heat transfer in the sample should be taken into account.

To sense the temporal change in temperature, there are both contacting and noncontacting methods. In general, the noncontacting methods

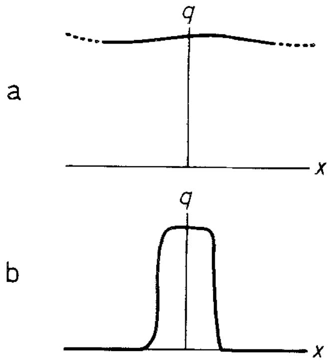

Fig. 3. Practical spatial profiles of the thermal energy on the surface of a thin material. (a) Inhomogeneity appears, in contrast to Fig. 2a. (b) Obscureness takes place at the boundary, in contrast to Fig. 2b.

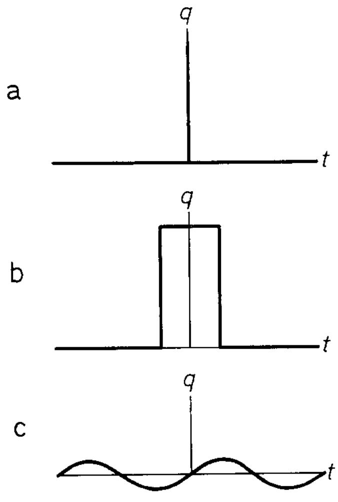

Fig. 4. Ideal temporal shape of the thermal energy: (a) an instantaneous pulse, (b) a pulse with definite width, and (c) sine waves.

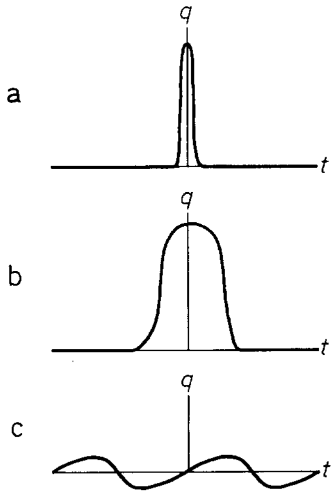

Fig. 5. Practical temporal shape of the thermal energy: (a) a sharp pulse, (b) a broad pulse, and (c) periodically deformed waves, corresponding to Figs. 4a, b, and c, respectively.

have the advantage that they are less likely to disturb the temperature of the thin samples. Furthermore, one should take into account the size of a temperature sensor which holds the key to the spatial resolution of the temperature measurement.

Most of the measurement methods for thin films have been developed quite recently, and in this review they are discussed briefly.

2. METHODS FOR MEASURING THERMAL DIFFUSIVITY OF THIN MATERIALS

2.1. ac Calorimetric Method

In this method [1–3], a part of a thin sample is shadowed by a mask from chopped light irradiation and then periodic thermal energy is imparted to the remaining part of the thin sample. The ac temperature at a position of the sample lying under the mask is detected by a fine thermocouple attached to the sample. To obtain the thermal diffusivity parallel to the plane surface of the thin sample (case A), the ac temperature T is measured as a function of the distance x between the positions of the thermocouple and the edge of the mask. The relation of $|T|$ vs x is given as

$$|T| = (Q/2\omega cd)\exp(-kx) \tag{1}$$

where k is the thermal decay constant, which is defined as $(\omega/2\mathrm{D})^{1/2}$, ω is the angular frequency of the periodic heating, Q is the amplitude of the applied thermal-energy flux per unit area, c is the heat capacity of the sample per unit volume, d is the thickness of the sample, and D is the thermal diffusivity of the sample. Frequently k is called the thermal wave number or $1/k$ is called the thermal diffusion length. From the decay constant given in Eq. (1), one can determine the value of thermal diffusivity.

In order to treat the thermal system as a one-dimensional system, the thickness of the sample should satisfy the following condition:

$$kd \leqq 0.1, \tag{2}$$

that is, the thickness d should be smaller than 10% of the thermal diffusion length $1/k$. Then, the maximum thickness at 1 Hz is 2 mm for a diamond type IIa crystal, 0.6 mm for copper, 0.2 mm for a sapphire crystal, 0.05 mm for glass, 0.02 mm for polystyrene, etc. From the above consideration, one can perform the measurement on almost any kind of thin material. In addition, the size of the thermocouple for the ac temperature measurement should be smaller than the thermal diffusion length. It is worthwhile to point out that the addenda used for the attachment of the thermocouple do not affect the determination of the thermal diffusivity [2]. From this viewpoint, this method has the advantage that the measurement is not influenced by contacting a temperature sensor.

In this measurement, the ac temperature is observed using a lock-in amplifier with which, notwithstanding the periodic deformation in the shape such as given in Fig. 5c, only the fundamental sine-wave component is detected. Therefore, the deformation of waves does not affect the measurement at all.

The contributions of the inhomogeneity of the spatial distribution of the imparted thermal energy and of the obscureness of the imparted thermal energy at the edge of the mask should be considered. The profile of the imparted thermal energy should be flat over a wider region compared to the distance x required for the measurement. The obscureness which is shown partly in Fig. 3b does not affect the measurement, if the mask is moved beyond the distance corresponding to the obscrured region.

This method can also be applied to a multilayer material as far as the following condition is satisfied:

$$k_i d_i < 1 \tag{3}$$

where k_i means k of the ith layer and d_i is the thickness of the ith layer. Under the condition of Eq. (3), we can obtain the thermal diffusivity of such a composite material (case A). The overall thermal diffusivity is given as

$$D = \sum c_i D_i d_i \Big/ \sum c_i d_i \tag{4}$$

where c_i and D_i are c and D for the ith layer, respectively.

In the case where a sample is not optically opaque, the surface of the sample should be coated so as to absorb the optical energy at the surface. The measurement in the coated sample corresponds to that in a bilayer material, in which the thermal diffusivity is given by Eq. (4) with $i = 1$ and 2.

The measurement of thermal diffusivity perpendicular to the surface of a thin material (case B) has been achieved in principle. But delicate care should be paid for carrying out the measurement at present.

2.2. Flash Method

This is one of the most well-known methods in the thermal diffusivity measurement of plate-like samples [4]; thus, it is not necessary to discuss here in detail. In this method, thermal energy is imparted instantaneously to the front surface of the plate-like sample by a light pulse, and the temperature of the rear surface is measured (case B). By analyzing the temperature vs time function the thermal diffusivity can be evaluated according to the following relation.

$$D = 0.139 d^2 / t_{1/2} \tag{5}$$

where d is the sample thickness and $t_{1/2}$ is the time corresponding to a rise in the temperature to one-half of its maximum value. In the ideal case, the imparted thermal-energy pulse should be as shown in Fig. 4b, and spatially it should spread uniformly as shown in Fig. 2a. However, in the actual case, the shape is deformed as shown in Fig. 5b and the spatial distribution of the imparted thermal energy is not perfectly uniform as shown in Fig. 3a. Owing to the former fact, the minimum thickness of the sample is limited in such a way that the duration of the heating pulse is shorter than the time interval required for the propagation of the temperature pulse across the sample [4]. For a heating pulse 1 ms in duration, the thickness [according to Eq. (5)] of the sample should be significantly greater than 840 μm for aluminum ($D = 0.972\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$), 78 μm for fused quartz ($D = 0.00844\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$), 26 μm for polystyrene ($D = 0.00095\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$), etc. Not only the finite width of the heating pulse but also the deformation of the pulse shape requires a correction to Eq. (5) [5]. It has been pointed out that one of the largest errors is due to the inhomogeneity of the spatial distribution of the imparted thermal energy on the sample surface [4], however, this point has not been thoroughly discussed.

The flash method is also extended to the measurement of the thermal diffusivity parallel to the surface of a thin sample (case A). In this case, radial heat flow is measured and is called the radial flash method [6, 7]. In this type of measurement an error results from the sharpness at the edge of heating region, in addition to the errors appearing in the usual method. A method in which the imparted thermal energy is converged into an annular-shaped heating region has been studied [8].

2.3. Mirage-Effect Method

A mirage-effect thermal-wave method has been first applied to the thermal diffusivity measurements of a bulk material [9, 10]. The working principle is similar to that in the ac calorimetric method [10] or to that in the photoacoustic method [9]. For the ac temperature detection, the deflection of a probe optical beam is used. The method related to the photoacoustic method has been extended to the measurement in a thin material deposited on a substrate (case C). In comparison to the photoacoustic method this method has the advantage that the measurement can be performed over a wide frequency range, and the detection of the periodic deflection due to the temperature oscillation is rather easy since the dample cell is not necessarily closed as is in the case of the photoacoustic method.

In this method the ac thermal energy is imparted uniformly over the surface of an opaque sample and the probe beam passes close to the surface in a parallel direction to it. When one measures the thermal diffusivity of a thin material deposited on a substrate, a high-frequency measurement is required. In this measurement, the size of the probe beam affects the spatial resolution of the ac temperature detection. To avoid this problem a method using two phase measurements has been developed [11]. The measurement of the periodic deflection has been done, for instance, in a $CuInSe_2$ film of 3.5 μm thick evaporated on a glass at frequencies up to a few kilohertz [11].

2.4. Picosecond Time-Resolved Thermoreflectance Method

Using the criteria that reflectance of metals changes linearly with temperature, one can detect the temperature change on the surface of metals. When an instantaneous thermal energy, as indicated in Fig. 4a, is imparted to the surface of a bulk material, the temperature change with time t at the surface is given by [12]

$$T = Q/2\sqrt{\pi Dt} \tag{6}$$

where the quantity of heat liberated in this experiment is given by Qc per unit area (c: heat capacity per unit volume). The characteristic length associated with the thermal diffusion is of the order of $(Dt)^{1/2}$. For a typical metal ($D = 0.15\ \mathrm{cm^2 \cdot s^{-1}}$), the heat imparted to the surface diffuses a distance of 55 nm after 200 ps. Thus, the measurement of the surface temperature within the above time interval yields the thermal diffusivity in the above distance. Therefore, this method can be used for measurements in a single-layer material on a substrate (case C), for instance, a 30-nm nickel film deposited over a 300-nm-thick copper underlayer and in a multilayer film (case B), for instance, a –Ni–Cu–Ni–Cu– multilayer with a composition modulation wavelength of 8 nm [13]. The results give rise to an understanding of electron scattering and transport across a metallic boundary.

As discussed in the subsection on the flash method, the shape of a heating pulse affects considerably the shape of the response. Since the full width at half-maximum (FWHM) of the pulse is about 4 ps [14], the problem related to its actual shape is more serious than that in the flash method. Therefore, one cannot introduce a shift only with a small correction. In this case the raw data have been used to solve directly the one-dimensional heat conduction equation, assuming a Gaussian-shaped heating pulse (Fig. 5a), for instance, with the FWHM of 4 ps. An analysis has been performed using the data taken beyond a time delay of approximately five pulse widths (about 20 ps) after the arrival of the heating pulse [14]. From such a procedure, one obtains the thermal diffusivity, although a lot of ambiguous points still remain in this analyses.

In this method, the heating pulse and the probe laser pulse are used, and therefore, the measurement is carried out in a noncontacting way. Since the energy supplied by the heating pulse is absorbed in a volume roughly 20 μm in diameter and 15 nm in depth, the rather large aspect ratio of the heated volume permits a one-dimensional treatment of the heat flow [13, 14].

2.5. Photoacoustic Method

Using this method, various measurements have been tried for obtaining the thermal diffusivity of a thin material. This is quite similar to one of the mirage-effect methods except for using sound signal in the detection of the ac temperature. Periodically modulated uniform thermal energy is imparted to the surface of a thin material deposited on a substrate, which is called a backing material. In our consideration, we deal only with an optically opaque thin material for simplicity. The sample is placed inside a closed cell containing a gas, such as air, and a sensitive microphone. When the surface of the thin material is heated with chopped light, in the photoacoustic cell an acoustic signal is generated due to the periodic heat flow from the surface to the surrounding gas. The phase and the amplitude of the photoacoustic signal are measured as a function of the chopping frequency for the thin material deposited on the substrate.

This method was applied to the measurement of the thermal diffusivity of polymer films having thicknesses of the order of a few thermal diffusion lengths (several 10 μm) at chopping frequencies up to 400 Hz [16]. Since the films were transparent to visible light, the front surface was coated with a bismuth layer of approximately 80 nm in thickness [16]. The method was also applied to the measurement of the thermal diffusivity of an As_2Se_3 layer in 2-μm thickness deposited on a KCl substrate, at chopping frequencies from 5 Hz to 5 kHz [17]. For a single thin polymer film of 18 μm in thickness, another method was developed in which the film was floated on water, ethanol, etc., as the backing material [17, 18].

The photoacoustic method is also applicable to multilayer materials [19]. However, further investigations are necessary before the establishment of the method.

2.6. The Other Methods

There are some other methods more or less related to the methods discussed above. In the pulse method described in Section 2.4, temperature detection can be performed using a pyroelectric detector attached to a thin material instead of thermoreflectance detection [20]. The pulse method can also be used for the measurement of thermal diffusivity parallel to the surface of a thin material [21].

To characterize the thermophysical properties of thin films, not only thermal diffusivity but also thermal conductivity offers useful information. There is a method which makes use of radiation heat transfer in thin films [22]. The method has been applied to the measurement of thermal conductivity in a diamond film. For a polymer sheet, the differential scanning calorimeter is used [23], in which the film is placed between a reference material, such as indium, and the top of the calorimeter. When the heating rate is kept constant, the reference material undergoes a melting transition with a steep slope; and on the other hand, if there is a film with a low thermal conductivity, the slope becomes less steep. From both results, one can obtain a crude value for the thermal conductivity of the sheet.

3. CONCLUSIONS

There are a large number of methods for measuring the thermal diffusivity of thin materials. Some of the methods are applied to the measurement of thermal diffusivity parallel to the surface of thin materials (case A) and the other to that perpendicular to the surface of thin materials (case B and C).

Generally, a method having a variety of applicabilities is good, that is, the measurement method is superior when it can be performed for a wide variety of thin materials, which have thicknesses less than 100 μm, are not only opaque but also transparent, have low as well as high thermal diffusivities, lie in a wide temperature range, etc. On the other hand, there may be a method for a specific purpose. If it definitely provides a good understanding of the thermophysical properties of a particular thin or multilayer film, it is worthwhile to establish the method.

Although the author did not discuss the accuracy of thermal diffusivity determinations in detail for each method, it should be understood that this is one of the important facts. It is also needless to say that attention should be paid to satisfy the adiabatic condition during the measurements. When one is interested in determining the detail temperature dependence of thermophysical properties, the temperature rise caused by imparting thermal energy should be kept small.

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