Development of Ultrafast Laser Flash Methods for Measuring Thermophysical Properties of Thin Films and Boundary Thermal Resistances

Tetsuya Baba*, Naoyuki Taketoshi1, and Takashi Yagi2

National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8563, Japan ¹ Standards Planning Office, International Standards Promotion Division, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568, Japan

² Thermophysical Properties Section, Material Metrology Division, National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8563, Japan

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Reliable thermophysical property values of thin films are important to develop advanced industrial technologies such as highly integrated electronic devices, phase-change memories, magneto-optical disks, light-emitting diodes (LEDs), organic light-emitting diodes (OLEDs), semiconductor lasers (LDs), flat-panel displays, and power electronic devices. In order to meet these requirements, the National Metrology Institute of Japan of the National Institute of Advanced Industrial Science and Technology (NMIJ/AIST) has developed ultrafast laser flash methods heated by picosecond pulse or nanosecond pulse with the same geometrical configuration as the laser flash method, which is the standard method to measure the thermal diffusivity of bulk materials. Since these pulsed light heating methods induce one-dimensional heat diffusion across a well-defined length of the specimen thickness, the absolute value of thermal diffusivity across thin films can be measured reliably. Using these ultrafast laser flash methods, the thermal diffusivity of each layer of multilayered thin films and the boundary thermal resistance between the layers can be determined from the observed transient temperature curves based on the response function method. The thermophysical properties of various thin films important for modern industries such as the transparent conductive films used for flat-panel displays, hard coating films, and multilayered films of next-generation phase-change optical disks have been measured by these methods. © 2011 The Japan Society of Applied Physics

1. Introduction

Electrical devices such as central processing units (CPUs), dynamic random access memories (DRAMs), phase-change memories, hard disks, light emitting diode (LEDs), organic LEDs, laser diodes (LDs), flat-panel displays, and power electronics consist of thin films with a thickness of several nanometers to several hundred nanometers. In order to know how heat flows and the distribution of temperature that is induced inside them under operation, the thermophysical properties of thin films and the boundary thermal resistance between thin films are required.^{1–8)}

The thermal properties of such thin films are generally different from those of bulk materials of the same composition. Consequently, it is desirable to measure thin films of the same thickness synthesized under the same deposition conditions by the same deposition method as those of the thin films in devices.^{9,10}

In addition, it is necessary to know the boundary thermal resistances between the layers as well as the thermophysical properties of each layer to understand the internal heat transfer of multilayered films.^{2–6,11,12} However, when multilayered films are measured with conventional measurement methods, it is difficult to separate the contribution of thermal resistance between the layers from the thermal conduction of each layer.

The quantitative measurement of heat transport properties across thin films thinner than 100 nm is not easy because of the fundamental difficulty of temperature detection for layers as thin as 10 nm. It is extremely difficult to measure the temperature difference between both sides of the same thin film, which is much smaller than 1 mK, if steady-state measurements with a similar geometrical configuration to that of the guarded hot plate method used for measuring the heat transport of insulation materials, are applied to measure the thermal conductivity of thin films.

2. Development of Technology for Thermal Diffusivity Measurements

The laser flash method is a well-established and standard method for measuring the thermal diffusivity α of bulk materials such as metals, ceramics, graphite, and semiconductors.^{13–16)} The ultrafast laser flash method is a natural extension of the laser flash method for application to thin films.^{5,8,17–24)} Thermal conductivity λ is calculated by the equation $\lambda = \alpha c \rho$ from specific heat capacity *c* and density ρ after thermal diffusivity α is measured by the ultrafast laser flash method.

2.1 Laser flash method

When thermal diffusivity is measured with the laser flash method, the front face of a planar specimen, kept at constant temperature, is heated uniformly with an impulse of light, as shown in Fig. $1.^{15}$ Heat diffuses one-dimensionally from the heated face to the opposite face, and finally the temperature throughout the specimen becomes uniform. Because the normalized temperature rise at the rear face of the specimen changes proportionally to the thermal diffusivity and inversely proportionally to the square of the specimen's thickness, the thermal diffusivity is calculated from the thickness of the specimen and heat diffusion time.

The following conditions are assumed as ideal:^{13,15)}

- 1) The duration of the laser pulse is negligibly short compared with the heat diffusion time.
- 2) The specimen is adiabatic to the environment.
- 3) The specimen's front face is heated uniformly.
- 4) The temperature change of the specimen's rear face is measured precisely.
- 5) The specimen is dense, uniform, and opaque.
- 6) The change in thermal diffusivity due to the specimen's temperature increase after the pulse heating is negligibly small.

Under the assumptions mentioned above, when the front face of a plate of thermal diffusivity α , specific heat capacity

^{*}E-mail address: t.baba@aist.go.jp



Fig. 1. (Color online) Principle of the laser flash method.



Fig. 2. Normalized temperature rise at the rear face of a specimen after pulsed light heating of the front face of the specimen observed by the laser flash method.

c, density ρ , and thickness *d* is heated impulsively with uniform energy density, the temperature change of the specimen's rear face is expressed by the following equation:^{1,13,17)}

$$T(t) = \Delta T \cdot \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left[-(n\pi)^2 \frac{t}{\tau}\right] \right\}$$
$$= \frac{2}{b\sqrt{\pi t}} \sum_{n=0}^{\infty} \exp\left[-\frac{(2n+1)^2 \tau}{4t}\right],$$
(1)

where $\Delta T = Q/C$, Q is the total energy absorbed by the specimen, C is the heat capacity of the specimen, $b = \sqrt{\lambda c\rho}$ is the thermal effusivity of the specimen, and $\tau = d^2/\alpha$ is the heat diffusion time across the specimen. The graph of eq. (1) is shown in Fig. 2.¹⁷

2.2 Ultrafast laser flash method

The National Metrology Institute of Japan, AIST, has developed the ultrafast laser flash method, 5,7,17-24) which is a natural extension of the laser flash method and the conventional picosecond thermoreflectance method.^{2,24} In the conventional picosecond thermoreflectance method, measurements are made in a front heating/front detection (FF) or rear heating/rear detection (RR) configuration, where the front means the open surface of the thin film synthesized on a substrate and the rear means the boundary between the thin film and substrate as shown in Fig. 3.

In the original configuration of the picosecond thermoreflectance method reported by Paddock and Eesley, an area of the front face of the thin film with a diameter of several tens of micrometers is heated by a picosecond laser beam,



Fig. 3. (Color online) Comparison between rear heating/front detection configuration (ultrafast laser flash method) and front heating/front detection configuration of pulsed light heating thermoreflectance method.

and a probe beam is irradiated to the same position, and the change in the surface temperature is observed.²⁵⁾ In this configuration, thermal diffusivity is calculated from the cooling rate after the picosecond pulse heating, which is dependent on the thermal diffusivity of the thin film. However, it is not easy to make precise and accurate measurements in this configuration since the measured value is sensitively dependent on the absorption coefficients for the laser beams and the conditions of the front face of the thin film.

Therefore, the procedure in the recently proposed pulsed light heating thermoreflectance method with an FF configuration measurement is to place a metal film as thin as 100 nm on the surface of the specimen²⁶⁾ and calculate the thermal effusivity of the second layer from the time constant of cooling using the heat capacity of the first layer per unit area.²⁷⁾

Figure 3 shows the difference between the geometrical configurations of the ultrafast laser flash method (rear heating/front detection; RF) and the conventional pulsed light heating thermoreflectance method (FF). Thermal diffusivity can be calculated from the heat diffusion time across the thin film and the film thickness with small uncertainty. Although both measurement methods with the two different configurations use almost the same hardware and realize ultrafast temperature measurements by the thermoreflectance method,²⁸⁾ their measurement principles are completely different each other. As shown in Fig. 3, in the ultrafast laser flash method (RF configuration), the thermal diffusivity of the first layer is determined precisely and accurately using the thickness of the first layer. In contrast, in the conventional pulsed light heating thermoreflectance method, the thermal effusivity of the second layer can be determined using the properties of the first layer. Since the temperature response curve of cooling in the FF configuration is also influenced by the factors described in §3, it is not easy to determine the absolute value of the time constant of cooling precisely and accurately.

In contrast, the heat diffusion time is determined from the rising part of the temperature response curve, as shown in Fig. 3, and the thickness of the first layer can be measured precisely and accurately, meaning that the thermal diffusivity of the first layer can be determined reliably with smaller uncertainty by the ultrafast laser flash method. It should be





Fig. 4. Initial setup of the ultrafast laser flash system involving picosecond pulsed laser heating.

pointed out that the ultrafast laser flash method is robust to even moderate amounts of noise and drift of the baseline, with which it is very difficult to derive reliable thermal effusivity values in the FF configuration.

As the critical requirements for measurement, both faces of the specimen must be optically flat and the substrate must be transparent at the wavelength of the heating laser beam in the "RF configuration" and at the wavelength of the laser beam for thermoreflectance measurements in the "RF configuration".

2.2.1 Picosecond light pulse heating

Figure 4 shows the initial setup of the ultrafast laser flash system in which picosecond pulsed lasers were used for pulsed light heating.^{18–24)} The thermal diffusivity of a thin film can be calculated from the thickness of the thin film and the heat diffusion time across the film.

The laser beam emitted from a mode-locked titanium sapphire laser is divided into a transmitted beam and a reflected beam by a quartz plate. About 90% of the beam power is used for pulse heating and the other 10% is used for temperature detection to measure the temperature changes of the thin film surface. An area with a diameter of about 100 μ m on thin film front face is heated by the picosecond laser beam. The temperature detection beam is focused to a spot on the front face of the specimen with a diameter of about 50 μ m, exactly opposite the focus of the heating light.

By adjusting the distance of the path to the specimen after the laser beam is divided, the time difference between the arrival of the heating light and detection light at the specimen surface can be controlled.

The reflected light intensity of the probe beam is in proportion to the change in the temperature of the front face of the specimen, and the change in the reflected light intensity is detected by a photodiode. This detection technique is called the thermoreflectance method.²⁸⁾ The temperature coefficient of reflectivity for a normal metal such as molybdenum is of the order of 10^{-4} to 10^{-5} /K. This configuration is essentially equivalent to the laser flash



Fig. 5. (Color online) Thermoreflectance signals of molybdenum thin films 70, 100, and 200 nm thick observed by ultrafast laser flash method after picosecond pulsed light heating.

method, which is the standard method for measuring the thermal diffusivity of bulk materials.

Since the transient temperature rise of the specimen after picosecond pulsed light heating is smaller than 1° K, the thermoreflectance signal is much smaller than the offset level of the reflected light. Such a small signal can be measured by lock-in detection at the modulation frequency of the heating light by an acoustic optic modulator.^{18,19}

Figure 5 shows thermoreflectance signals of molybdenum thin films of 70, 100, and 200 nm thick observed by the ultrafast laser flash method after picosecond pulsed light heating.¹⁹⁾ The molybdenum thin films were synthesized on a Pyrex glass substrate by magnetron DC sputtering. Since the observed chronological responses of the thermoreflectance signals are similar to those observed by the laser flash method for the bulk specimen, the energy transport of these molybdenum thin films at room temperature can be still expressed by the classical heat diffusion equation.

The thermal diffusivity values for the molybdenum thin films are calculated from the observed curves and the specimen thickness as 3.0×10^{-5} , 3.6×10^{-5} , and $3.0 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ for the 70-, 100-, and 200-nm-thick films, respectively, whereas the thermal diffusivity of bulk molybdenum is $5.4 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$.

2.2.2 Nanosecond light pulse heating

In order to measure thicker films with thicknesses up to several micrometers, nanosecond pulsed lasers were used for pulsed light heating^{5,7,29-31} with the electrical delay method.²¹

Figure 6 shows the initial setup of the nanosecond pulsed light heating measurement system.^{5,29)} The pulse duration of the pump pulse is 2 ns and the pulse interval is $20 \,\mu$ s with intensity modulation of 1 kHz by an acoustic optical modulator. Thin films are deposited on a transparent substrate that is typically a disk of 10 mm diameter or a square of 10 mm side. The specimen is irradiated through the substrate to the rear face of the film by the heating beam, and the reflected light of the probe beam is detected by a photodiode as shown in Fig. 6.

Figure 7 shows the thermoreflectance signal of titanium nitride thin films of 466, 602, and 1206 nm thick observed



Fig. 6. (Color online) Initial setup of the ultrafast laser flash system involving nanosecond pulsed laser heating.



Fig. 7. (Color online) Thermoreflectance signals of TiN thin films 466, 602, and 1206 nm thick observed by ultrafast laser flash method after nanosecond pulsed light heating.

by the nanosecond thermoreflectance method measured with the improved setup.³⁰⁾ Thermal diffusivity values of 2.9×10^{-6} , 2.6×10^{-6} , and $2.6 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ were obtained for the 466-, 602-, and 1206-nm-thick thin films, respectively.

3. Differences between Ultrafast Laser Flash Method and Conventional Laser Flash Method

As explained before, the ultrafast laser flash method is a natural extension of the conventional laser flash method for application to thin films. However, the following important factors must be considered:²³⁾

- 1. Repetitive pulse heating with finite duration.
- 2. Continual heat effusion into the substrate on which the thin film is synthesized.
- 3. Effect of penetration of light into the thin film for pulse heating and temperature detection by thermoreflectance method.



Fig. 8. (Color online) Chronological response observed by repetitive pulse heating with finite duration in RF configuration.

- 4. The Knudsen number of heat carriers (phonons and electrons) might be large.
- 5. The contribution of boundary thermal resistance is large.
- 3.1 Repetitive pulse heating with finite duration and continual heat effusion into the substrate on which the thin film is synthesized

In the conventional laser flash method, each measurement is completed after illuminating a single pulse.^{1,13–17)} On the other hand, in the ultrafast laser flash method, the signal is averaged over the signals of repetitive pulse heating with a finite duration.^{18–22)} Therefore, the shape of the observed signal is dependent on the interval between repetitive pulses as shown in Fig. 8.²³⁾

Since films thinner than $1\,\mu m$ are usually synthesized on substrates, these thin films cannot be adiabatic but heat



Fig. 9. Thin film synthesized on a substrate and heat effusion into the substrate.



effuses into the substrate. Figure 9 shows a schematic of heat effusion from a thin film to a substrate after the surface is heated by a pulsed light.^{17,32)} The temperature at the boundary between the thin film and the substrate after pulsed heating the surface of the thin film is expressed by the following equation based on the response function method and the mirror image method in this front heating/ rear detection (FR) configuration:^{1,5,11,12,17,32}

$$T_{s}(t) = \frac{2}{(b_{f} + b_{s})\sqrt{\pi t}} \sum_{n=0}^{\infty} \gamma^{n} \exp\left[-\frac{(2n+1)^{2}\tau_{f}}{4t}\right]$$
$$= \frac{2b_{f}}{b_{f} + b_{s}} \frac{1}{\sqrt{\pi} \cdot c_{f}\rho_{f}d_{f}} \cdot \sqrt{\frac{\tau_{f}}{t}}$$
$$\times \sum_{n=0}^{\infty} \gamma^{n} \exp\left[-\frac{(2n+1)^{2}\tau_{f}}{4t}\right].$$
(2)

Here, $b_{\rm f}$ is the thermal effusivity of the thin film, $b_{\rm s}$ is the thermal effusivity of the substrate, $\tau_{\rm f} = d_{\rm f}^2/\alpha_{\rm f}$ is the heat diffusion time across the thin film, $d_{\rm f}$ is the thickness of the thin film, $\alpha_{\rm f}$ is the thermal diffusivity of the thin film, $\beta = b_{\rm s}/b_{\rm f}$, and $\gamma = (b_{\rm f} - b_{\rm s})/(b_{\rm f} + b_{\rm s}) = (1 - \beta)/(1 + \beta)$.

This equation corresponds to the temperature response induced by an infinite series of virtual heat sources of the same intensity located periodically and separated by a distance of twice the film thickness as shown in Fig. $10^{.17,32}$. If the temperature response is analyzed from the time of impulse heating, the temperature change follows the first

Fig. 10. (Color online) Mirror images of impulse heating as virtual heat source causing a temperature rise in the film.

term in eq. (2) and is free from the effect of the substrate at the beginning. Later, the contribution of the higher-order terms in eq. (2) is superimposed.

When the pulse interval time is 50 µs in the nanosecond thermoreflectance method, the signal shape for the thin film with a heat diffusion time of 10 ns is similar to that observed upon single-pulse heating if the response of temperature detection is fast enough. However, when the same thin film is heated by repetitive pulses with an interval of 13 ns^{18-21} or 50 ns,³³⁾ the observed signal is distorted from that obtained by heating with a single pulse except for the initial part after each pulse. Thus, it is safe to confine the heat diffusion time of the specimen to considerably shorter than half of the pulse interval for quantitative measurement even in FR or RF configuration heating and reflectivity measurements if a conventional analysis procedure assuming singlepulse heating is applied. In particular, careful and sophisticated analysis is necessary for the determination of thermophysical properties from the cooling rate of the specimen surface in the FF or RR configuration.

After repetitive heating by a pulse train with period τ_p , the temperature response shown in Fig. 8 is expressed by an infinite series as follows:²³⁾

$$T_{\rm rep}(t) = \frac{2}{(b_{\rm f} + b_{\rm s})} \sum_{j=0}^{\infty} \left\{ \frac{1}{\sqrt{\pi(t+j\cdot\tau_{\rm p})}} \cdot \sum_{n=0}^{\infty} \gamma^n \exp\left[-\frac{(2n+1)^2\tau_{\rm f}}{4(t+j\cdot\tau_{\rm p})}\right] \right\}$$

$$= \frac{2b_{\rm f}}{b_{\rm f} + b_{\rm s}} \frac{1}{\sqrt{\pi} \cdot c_{\rm f}\rho_{\rm f}d_{\rm f}} \sum_{j=0}^{\infty} \left\{ \sqrt{\frac{\tau_{\rm f}}{t+j\cdot\tau_{\rm p}}} \cdot \sum_{n=0}^{\infty} \gamma^n \exp\left[-\frac{(2n+1)^2\tau_{\rm f}}{4(t+j\cdot\tau_{\rm p})}\right] \right\}$$
(3)

The first term and higher-order terms can be analyzed separately using the following infinite series involving j.

$$T_{\rm rep}(t) = \frac{2b_{\rm f}}{b_{\rm f} + b_{\rm s}} \frac{1}{\sqrt{\pi} \cdot c_{\rm f}\rho_{\rm f}d_{\rm f}} \cdot \left\{ \sqrt{\frac{\tau_{\rm f}}{t}} \cdot \sum_{n=0}^{\infty} \gamma^n \exp\left[-\frac{(2n+1)^2 \tau_{\rm f}}{4t}\right] + \sum_{j=1}^{\infty} \sqrt{\frac{\tau_{\rm f}}{t+j\cdot\tau_{\rm p}}} \cdot \sum_{n=0}^{\infty} \gamma^n \exp\left[-\frac{(2n+1)^2 \tau_{\rm f}}{4(t+j\cdot\tau_{\rm p})}\right] \right\}$$
(4)

When the heat diffusion time across the thin film, τ_f , is shorter than the period of repetition of the pulsed light heating, the higher terms can be analyzed separately in the infinite series involving *j* and approximated as follows:

$$T_{\rm rep}(t) = \frac{2b_{\rm f}}{b_{\rm f} + b_{\rm s}} \frac{1}{\sqrt{\pi} \cdot c_{\rm f}\rho_{\rm f}d_{\rm f}} \cdot \sqrt{\frac{\tau_{\rm f}}{t}} \cdot \sum_{n=0}^{\infty} \gamma^{n} \exp\left[-\frac{(2n+1)^{2}\tau_{\rm f}}{4t}\right] + \frac{2}{\sqrt{\pi} \cdot c_{\rm f}\rho_{\rm f}d_{\rm f}} \cdot \sum_{j=1}^{l} \exp\left(\frac{t+j\cdot\tau_{\rm p}}{\tau_{\rm s}}\right) \exp\left(\sqrt{\frac{t+j\cdot\tau_{\rm p}}{\tau_{\rm s}}}\right) + \frac{1}{\sqrt{\pi} \cdot b_{\rm s}} \sum_{j=l+1}^{\infty} \frac{1}{\sqrt{t+j\cdot\tau_{\rm p}}}.$$
(5)

$$\frac{2}{\sqrt{\pi} \cdot c_{\rm f} \rho_{\rm f} d_{\rm f}} \cdot \sum_{j=1}^{l} \exp\left(\frac{t+j \cdot \tau_{\rm p}}{\tau_{\rm s}}\right) \operatorname{erfc}\left(\sqrt{\frac{t+j \cdot \tau_{\rm p}}{\tau_{\rm s}}}\right),$$

in eq. (5) corresponds to the temperature response when the heat diffusion time across the thin film, τ_f , is much shorter than the characteristic time of heat effusion from the thin film to the substrate, $\tau_s = (c_f \rho_f d_f / b_s)^2$, where b_s is the thermal effusivity of the substrate and $\operatorname{erfc}(x) = \int_x^\infty \exp(-s^2) ds$ is the complementary error function. This approximation is represented by a model of a thin film synthesized on a substrate of with thermal effusivity b_s where the heat capacity per area of the thin film is $c_f \rho_f d_f$ and the temperature is uniform over the thin film.²⁷⁾

The third set of terms,

$$\frac{1}{\sqrt{\pi} \cdot b_{\rm s}} \sum_{j=l+1}^{\infty} \frac{1}{\sqrt{t+j \cdot \tau_{\rm p}}},$$

corresponds to the temperature response of the surface of a semi-infinite uniform material with thermal effusivity b_s after the surface is heated by pulses of energy with unit density per area. The summation of these terms diverges to infinity, as expected for one-dimensional heat effusion over a semi-infinite body upon steady heating. However, the temperature converges to a finite value in real measurements because the substrate is set at a holder with infinitely large heat capacity, which can be approximated as a heat reservoir of constant temperature. This boundary condition can be formulated by replacing the last term in eq. (5) with the following term and setting the initial temperature equal to 0.

$$T_{\text{decline}}(t) = \frac{1}{\sqrt{\pi} \cdot b_{\text{s}}} \cdot \sum_{j=1}^{\infty} \left(\frac{1}{\sqrt{t+j} \cdot \tau_{\text{p}}} - \frac{1}{\sqrt{j} \cdot \tau_{\text{p}}} \right), \quad (6)$$

which is defined in the range $0 \le t \le \tau_p$. Then,

$$T_{\text{decline}}(0) = 0, \ T_{\text{decline}}(\tau_{\text{p}}) = -\frac{1}{\sqrt{\pi} \cdot b_{\text{s}}} \cdot \frac{1}{\sqrt{\tau_{\text{p}}}}.$$

The derivative of eq. (6) is

$$\frac{dT_{\text{decline}}(t)}{dt} = -\frac{1}{2\sqrt{\pi} \cdot b_{\text{s}}} \cdot \sum_{j=1}^{\infty} \frac{1}{(t+j\cdot\tau_{\text{p}})^{3/2}} \\ = \frac{1}{2\sqrt{\pi} \cdot b_{\text{s}}} \cdot \left[\frac{1}{t^{3/2}} - \frac{1}{\tau_{\text{p}}^{3/2}}\zeta\left(\frac{3}{2}, \frac{t}{\tau_{\text{p}}}\right)\right], \quad (7)$$

where

$$\zeta(z,a) = \sum_{n=0}^{\infty} \frac{1}{(a+n)^2}$$

is the Hurwitz zeta function.

Then,

$$T_{\text{decline}}(t) = T_{\text{decline}}(\tau_{\text{p}}) + \int_{\tau_{\text{p}}}^{t} \frac{dT_{\text{decline}}(\delta)}{d\delta} d\delta$$
$$= -\frac{1}{\sqrt{\pi} \cdot b_{\text{s}}} \left\{ \frac{1}{\sqrt{t}} + \frac{1}{2\tau_{\text{p}}^{3/2}} \int_{\tau_{\text{p}}}^{t} \left[\zeta\left(\frac{3}{2}, \frac{\delta}{\tau_{\text{p}}}\right) \right] d\delta \right\}.$$
(8)

If τ_p is much larger than both τ_f and τ_s , and the second set of terms can be approximated by the third set of terms in eq. (5) with l = 0 and j = 1. The observed temperature

response is expressed by replacing the third set of terms with eq. (8):

$$T_{\text{obs}}(t) = \frac{2}{\sqrt{\pi} \cdot (b_{\text{f}} + b_{\text{s}})} \cdot \frac{1}{\sqrt{t}} \cdot \sum_{n=0}^{\infty} \gamma^{n} \exp\left(-\frac{(2n+1)^{2}\tau_{\text{f}}}{4t}\right)$$
$$+ T_{\text{decline}}(t)$$
$$= \frac{2}{\sqrt{\pi} \cdot (b_{\text{f}} + b_{\text{s}})} \cdot \frac{1}{\sqrt{t}} \cdot \sum_{n=0}^{\infty} \gamma^{n} \exp\left(-\frac{(2n+1)^{2}\tau_{\text{f}}}{4t}\right)$$
$$- \frac{1}{\sqrt{\pi} \cdot b_{\text{s}}} \left\{\frac{1}{\sqrt{t}} + \frac{1}{2\tau_{\text{p}}^{3/2}} \int_{\tau_{\text{p}}}^{t} \left[\zeta\left(\frac{3}{2}, \frac{\delta}{\tau_{\text{p}}}\right)\right] d\delta\right\}$$
$$= T_{\text{amp}}\left(\frac{1}{\sqrt{t}} \cdot \sum_{n=0}^{\infty} \gamma^{n} \exp\left[-\frac{(2n+1)^{2}\tau_{\text{f}}}{4t}\right]$$
$$- \frac{1+\beta}{2\beta} \cdot \left\{\frac{1}{\sqrt{t}} + \frac{1}{2\tau_{\text{p}}^{3/2}} \int_{\tau_{\text{p}}}^{t} \left[\zeta\left(\frac{3}{2}, \frac{\delta}{\tau_{\text{p}}}\right)\right] d\delta\right\}\right), (9)$$

where

$$T_{\rm amp} = \frac{2}{\sqrt{\pi} \cdot (b_{\rm f} + b_{\rm s})}.$$

The temperature history curve observed by the ultrafast laser flash method involving picosecond pulsed light heating is fitted by eq. (9) or the general formula derived from eq. (5) over the entire time scale from the impulse pulse heating to that by the next pulse. When the measurements were made by the improved setup of the ultrafast laser flash method,³³⁾ τ_p is fixed to a value such as 50 ns and τ_s is fixed if the substrate is known. *l* is usually 1 or 0, which means that the second term is removed. Then, τ_f , $\gamma = (b_f - b_s)/(b_f + b_s) = (1 - \beta)/(1 + \beta)$ and is determined by fitting with τ_f , then the thermal diffusivity of the thin film is calculated as $\alpha_f = d_f^2/\tau_f$, where d_f is the thickness of the thin film.

If the thermal effusivity of the substrate is unknown, τ_s is determined by fitting, and the thermal effusivity of the substrate is calculated as $b_s = c_f \rho_f d_f / \sqrt{\tau_s}$ if the specific heat capacity c_f , density ρ_f , and thickness d_f of the thin film are known.

Figure 11 shows an example of fitting by eq. (9) for the temperature response curve of a molybdenum thin film of 407 nm of thick synthesized on a fused quartz substrate in the RF configuration observed by the improved picosecond pulse heating system.³³⁾ A picosecond pulse train is generated with a period of 50 ns and the fitting was made over the entire period using eq. (9). The calculated thermal diffusivity of the molybdenum thin film is $3.7 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$.

3.2 Effect of penetration of light into the thin film for pulse heating and temperature detection by thermoreflectance method

When a thin film is illuminated by light for heating and reflectivity measurement from an open face or through a transparent substrate, light penetrates a finite length from the surface, as shown in Fig. 12, in the case of the RF configuration.²³⁾ The thermoreflectance signal after light heating with a single pulse is represented by the dual convolution of an infinite series of Green's function^{1,17,19,23} with heating distribution function for the penetration depth of heating, $\delta_{\rm h}$, and the penetration depth of reflectivity measurement, $\delta_{\rm m}$, by the following equation.



Fig. 11. (Color online) Example of fitting for repetitive pulsed light heating over the repetition period.



Fig. 12. (Color online) Penetration of illuminated light for pulse heating and reflectance detection.

$$T_{obs}(t) = \frac{1}{2b_{\rm f}\sqrt{\pi t}} \int_0^\infty \int_0^\infty D(x_{\rm m}) \\ \times \sum_{n=0}^\infty \left(\begin{array}{c} \gamma^n \left(\exp\left\{ -\frac{\left[(2n+1)d - x_{\rm m} - \chi_{\rm h}\right]^2}{4\alpha_{\rm f}t} \right\} + \exp\left\{ -\frac{\left[(2n+1)d + x_{\rm m} - \chi_{\rm h}\right]^2}{4\alpha_{\rm f}t} \right\} \right) \\ + \gamma^{n+1} \left(\exp\left\{ -\frac{\left[(2n+1)d - x_{\rm m} + \chi_{\rm h}\right]^2}{4\alpha_{\rm f}t} \right\} + \exp\left\{ -\frac{\left[(2n+1)d + x_{\rm m} + \chi_{\rm h}\right]^2}{4\alpha_{\rm f}t} \right\} \right) \right) Q(\chi_{\rm h}) d\chi_{\rm h} dx_{\rm m}, \quad (10)$$

where

$$D(x_{\rm m}) = \frac{1}{\delta_{\rm m}} \exp\left(-\frac{x_{\rm m}}{\delta_{\rm m}}\right)$$
 and $Q(x_{\rm h}) = \frac{1}{\delta_{\rm h}} \exp\left(-\frac{\chi_{\rm h}}{\delta_{\rm h}}\right)$

This equation can be solved analytically as the following equation. The derivation is described in the Appendix.

$$T_{\text{obs}}(t) = \frac{2}{\sqrt{\pi}c_{\text{f}}\rho_{\text{f}}} \cdot \frac{1}{\delta_{\text{h}}^{2} - \delta_{\text{m}}^{2}} \cdot \begin{pmatrix} \delta_{\text{h}} \exp\left(\frac{\alpha_{\text{f}}t}{\delta_{\text{h}}^{2}}\right) \cdot \sum_{n=0}^{\infty} \begin{cases} \exp\left(-\frac{D_{n}}{\delta_{\text{h}}}\right) \cdot \left[\gamma^{n} \operatorname{erfc}\left(\frac{-D_{n}}{2\sqrt{\alpha_{\text{f}}t}} + \frac{\sqrt{\alpha_{\text{f}}t}}{\delta_{\text{h}}}\right)\right] \\ + \exp\left(\frac{D_{n}}{\delta_{\text{h}}}\right) \cdot \left[\gamma^{n+1} \operatorname{erfc}\left(\frac{D_{n}}{2\sqrt{\alpha_{\text{f}}t}} + \frac{\sqrt{\alpha_{\text{f}}t}}{\delta_{\text{h}}}\right)\right] \\ - \delta_{\text{m}} \exp\left(\frac{\alpha_{\text{f}}t}{\delta_{\text{m}}^{2}}\right) \cdot \sum_{n=0}^{\infty} \begin{cases} \exp\left(-\frac{D_{n}}{\delta_{\text{m}}}\right) \cdot \left[\gamma^{n} \operatorname{erfc}\left(\frac{-D_{n}}{2\sqrt{\alpha_{\text{f}}t}} + \frac{\sqrt{\alpha_{\text{f}}t}}{\delta_{\text{m}}}\right)\right] \\ + \exp\left(\frac{D_{n}}{\delta_{\text{m}}}\right) \cdot \left[\gamma^{n+1} \operatorname{erfc}\left(\frac{D_{n}}{2\sqrt{\alpha_{\text{f}}t}} + \frac{\sqrt{\alpha_{\text{f}}t}}{\delta_{\text{m}}}\right)\right] \end{cases} \end{cases} \right).$$
(11)

Here, $D_n = (2n + 1)d$.

This equation is symmetric for the penetration of heating and the penetration of temperature detection and converges to eq. (2) when the penetration lengths of both heating and temperature detection are negligibly small. If the effect of the penetration of heating is only considered and the penetration of temperature detection is neglected, this equation is the same as eq. (7) of ref. 19 after the correction of the factor $2/\sqrt{\pi}$ assigned to the different definition of the complementary error function.

3.3 Contribution of boundary thermal resistance

The boundary thermal resistance across dense solid materials is considerably smaller than $10^{-7} \text{ W}^{-1} \text{ m}^2 \text{ K}$ if two layers bond at the atomic scale without a gap.^{11,34-37)} The boundary thermal resistance of $10^{-9} \text{ W}^{-1} \text{ m}^2 \text{ K}$ corresponds to the resistance of a 100-nm-thick metal thin film with a thermal conductivity of $100 \text{ Wm}^{-1} \text{ K}^{-1}$ and that of a 5-nm-thick

oxide thin film with a thermal conductivity of $5 \text{ Wm}^{-1} \text{ K}^{-1}$. Therefore, it is necessary to consider the boundary thermal resistance in the analysis of heat transfer across multilayered thin films even though these boundary thermal resistances are too small to be detected at the macroscopic scale.

If thermal conductivities and thermal boundary resistances can be determined by steady-state measurements across multilayered thin films, the analysis is very simple, and the thermal resistance is expressed as the sum of the resistance of all layers and all boundary thermal resistances analogous to the serial connection of resistances in an electric circuit. However, since it is very difficult to measure transport properties across thin films by steady-state measurements, as mentioned in the last paragraph of the introduction, transient measurement methods such as the ultrafast laser flash method are suitable for measuring boundary thermal resistance.





Fig. 13. (Color online) Temperature response curves of three-layered thin films of molybdenum/indium tin oxide (ITO)/molybdenum deposited on fused quartz substrate observed by the ultrafast laser flash method involving picosecond pulse heating.

Therefore, the systematic analysis of heat transfer across thin film layers and the boundary between thin films is of primary importance in order to derive the thermal diffusivity and thermal conductivity of each layer and the boundary thermal resistance separately from transient measurements. A systematic analysis with a detailed mathematical derivation of one-dimensional heat diffusion considering boundary thermal resistance is described in ref. 17.

Figure 13 shows examples of temperature response curves of three-layered thin films of molybdenum/indium tin oxide (ITO)/molybdenum deposited on a fused quartz substrate measured with the ultrafast laser flash method involving picosecond pulse heating.³⁴⁾ Three specimens with ITO layer thicknesses of 27, 46, and 62 nm were prepared and the thickness of the molybdenum layers on both sides was kept constant at 70 nm. The areal heat diffusion time was defined as the area surrounded by the vertical line during impulse heating, the horizontal line representing the normalized maximum temperature, and each temperature history curve as shown in Fig. 13. The dependence of the areal heat diffusion time on the thickness of the ITO layer can be fitted to an analytical equation derived from the response function method as shown in Fig. 14.¹⁷⁾ The thermal diffusivity of the ITO layer is determined as $1.2 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ and the boundary thermal resistance between the ITO layer and the molybdenum layer is determined as $5 \times 10^{-9} \,\mathrm{Km^2 W^{-1}}$ by this series of measurements and analysis.

3.4 Knudsen number of heat carriers (phonons and electrons)

In the gas phase, heat is carried by gas molecules and the mean free path of molecules can increase to a macroscopic scale under low pressure. Heat is mainly carried by phonons in electrically insulating solids and by electrons in pure metals. Although the mean free path of these carriers increases to a macroscopic scale at lower temperatures, the mean free path is considerably smaller than 100 nm above room temperature. This is why we observe that heat transfer is diffusive and the Fourier law of heat diffusion is valid.



Fig. 14. Dependence of the areal heat diffusion time on the thickness of the ITO layer fitted to analytical equation.



Fig. 15. (Color online) The Knudsen number is defined as the mean free path of carriers divided by the thickness of the film.

However, since the thicknesses of thin films and the mean free path of heat carriers can be of the same order, it is primarily important to consider the possibility that the diffusive response no longer occurs. As shown in Fig. 15, the index for this effect is represented by the Knudsen number N defined as follows.

$$N = \frac{\Lambda}{d},\tag{12}$$

where *d* is the thickness of the thin film and Λ is the mean free path of the carriers. If *N* is sufficiently large, it is expected that the observed signal with deviate from that expected by the diffusion equation.

As shown in Fig. 5, the measurement results for molybdenum thin films of thickness 70 nm and above at room temperature demonstrate that the temperature response of the front face after impulse heating of the rear face follows the curves given by the classical heat diffusion equation. The obtained thermal diffusivity values were close to each other, and there was no systematic dependence of thermophysical properties on the film thickness.

As shown in Fig. 13 and Fig. 14, the measurement results for ITO thin films of thickness 27 nm and above, on both sides of which molybdenum thin films of 70 nm thickness were synthesized, were also explained by the same thermal diffusivity for a set of ITO thin films and the same boundary thermal resistance between the ITO thin film and molybdenum thin film obtained from the response function method and the areal heat diffusion time method.

This experimental approach has been applied to a variety of nonmetal thin films including those of silicon dioxide (silica) and aluminum oxide (alumina).^{35,37)} Our results demonstrate

that both the thermal diffusivity and boundary thermal resistance between a measured nonmetal thin film and a coated metal film are independent of the thickness of the measured thin film. Therefore, the inherent values of thermal diffusivity and boundary thermal resistance can be measured and defined independent of the film thickness when the films are synthesized stationarily over the deposition apparatus.³⁸

According to these experimental results and analyses, the following have been deduced.

- Heat transfer is expressed by the diffusion equation for metal thin films such as those of molybdenum with thickness greater than 100 nm and oxide thin films such as those of ITO, silica and alumina with thickness greater than 10 nm at room temperature.
- 2) Thus, thermal diffusivity can be defined for such thin films independently of the film thickness.
- 3) The boundary thermal resistance between a metal thin film and an oxide thin film can be measured and a boundary having the same thermal resistance can be reproduced by a well-controlled synthesis process.
- Thin films of the same quality having the same thermal diffusivity can be synthesized by a well-controlled synthesis process.
- 5) Therefore, the Knudsen numbers N are small enough in these thin film specimens for the diffusion equation to still be valid.
- 6) The reliability of thermal diffusivity measurements can be confirmed if consistent values of thermal diffusivity can be observed by a series of measurements for a set of thin film specimens of the same quality but different thickness.

4. Metrological Standard and Traceability for Measurements of Thin Film Thermophysical Properties

In order to establish traceable measurements for thermophysical properties of thin films, the following have been performed investigated systematically as shown in Fig. 16.^{24,38)}

- Metrological standards for thin film thermophysical properties
- Reference materials for thin film thermophysical properties
- Documented standards for measurements of thin film thermophysical properties
- Database for thin film thermophysical properties

The National Metrology Institute of Japan has established heat diffusion time standards for thin films after systematic and comprehensive investigation of the factors that might induce bias and error in thermophysical property measurements. All measuring instruments, including their the time scale and the electrical sensitivity of the transient memory, are calibrated with traceability to the national standards, and the measured results are critically evaluated in accordance with a guide for the expression of uncertainty in measurement.³⁹⁾ Thus, heat diffusion time standards have been supplied by NMIJ with an expanded relative uncertainty of 8% for picosecond pulse heating and 5% for nanosecond pulse heating with the coverage factor k = 2 under the quality management system in accordance with ISO 17025 operated by NMIJ.³⁹⁾

Based on these metrological standards, NMIJ is ready to supply reference materials to calibrate heat diffusion time



Fig. 16. (Color online) Metrological standards, reference materials, and standardization of measurement methods in order to establish traceability system for supply of reliable thermophysical property data for thin films.

that will meet the requirement of the quality management systems for certified reference materials.⁴⁰

5. Applications of the Measurements: From Industrial Applications to Basic Physics

The ultrafast laser flash method can measure a wide variety of thin films. If the optical property of the thin film does not satisfy the requirement of the method, coating with a metal thin film such as molybdenum is one of the solutions.^{12,17)} Thus, thin films of semiconductors, carbon materials, oxides,^{34,35,37,41-43)} nitrides,^{44,45)} carbides, and polymers⁴⁶⁾ can be measured as well as metal thin films.^{35,36)}

Examples of measured materials are transparent conductive films for flat-panel displays,^{34,41-43)} phase-change materials for optical media, PRAM^{4,6,47-51)} polymer thin films for organic electroluminescence,⁴⁶⁾ and hard coating films.⁴⁴⁾ Thin films developed for thermoelectric applications⁵²⁾ have also been measured.

The ultrafast laser flash method was successfully applied to thermal diffusivity measurements under high pressures in a diamond anvil $cell^{31}$ and was also applied to thin films synthesized on a silicon substrate.⁵³⁾

Moreover, heat transfer across metal thin films as thin as 100 nm was observed down to the liquid helium temperature for the first time in order to investigate the limit of applicability of the diffusion equation at a large Knudsen number.⁵⁴⁾

6. Summary

Ultrafast laser flash methods involving picosecond pulsed light heating and nanosecond pulsed light heating have been developed with the same configuration as the laser flash method, which is the standard method to measure the thermal diffusivity of bulk materials. Since these extended laser flash methods can be used to observe one-dimensional heat diffusion across a film, thermal diffusivity values across thin films can be calculated reliably from the heat diffusion time and specimen thickness with small uncertainty.

Using the ultrafast laser flash methods, the thermal diffusivity of each layer of multilayered thin films and the boundary thermal resistance between the layers can be determined from the observed transient temperature curves based on the response function method.

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Reliable thermal design can be realized by heat conduction simulation using these reliable thermal diffusivity values of thin films and boundary thermal resistance values between thin films measured with the ultrafast laser flash methods.

A detailed mathematical derivation of the analytical expression for one-dimensional heat diffusion is described in previous reports.^{17,55,56}

The thermophysical property data of thin films measured by NMIJ, Aoyama Gakuin University, and collaborating groups mentioned in this paper are going to be stored in the thermophysical properties database developed by NMIJ⁵⁷⁾ and accessible via the internet.⁵⁸⁾

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Appendix

Calculation of Effect of Penetration of Light into the Thin Film for Pulse Heating and Temperature Detection by Thermoreflectance Method.

Equation (10) can be analytically solved by coordinate conversion and using the Jacobian determinant as expressed by the following equations.

$$x_{\rm m} + \chi_{\rm h} = \eta$$
$$x_{\rm m} - \chi_{\rm h} = \mu$$

Then,

$$dx_{\rm m} d\chi_{\rm h} = \left(\frac{dx_{\rm m}}{d\eta} \frac{d\chi_{\rm h}}{d\mu} - \frac{dx_{\rm m}}{d\mu} \frac{d\chi_{\rm h}}{d\eta}\right) d\eta \, d\zeta = \frac{1}{2} \, d\eta \, d\mu$$

Equation (10) is transformed to

$$\begin{split} T_{\text{obs}}(t) &= \frac{1}{2b_{\text{f}}\sqrt{\pi t}} \int_{0}^{\infty} \int_{-\eta}^{\eta} \frac{1}{\delta_{\text{m}}} \exp\left(-\frac{\eta+\mu}{2\delta_{\text{m}}}\right) \\ &\times \sum_{n=0}^{\infty} \left[\begin{array}{c} \gamma^{n} \left(\exp\left\{-\frac{\left[(2n+1)d-\eta\right]^{2}}{4\alpha_{f}t}\right\} + \exp\left\{-\frac{\left[(2n+1)d+\mu\right]^{2}}{4\alpha_{f}t}\right\}\right) \\ &+ \gamma^{n+1} \left(\exp\left\{-\frac{\left[(2n+1)d-\mu\right]^{2}}{4\alpha_{f}t}\right\} + \exp\left\{-\frac{\left[(2n+1)d+\eta\right]^{2}}{4\alpha_{f}t}\right\}\right) \end{array} \right] \frac{1}{\delta_{\text{h}}} \exp\left(-\frac{\eta-\mu}{2\delta_{\text{h}}}\right) \cdot \frac{1}{2} \, d\mu \, d\eta \\ &= \frac{1}{4\delta_{\text{m}}\delta_{\text{h}}b_{\text{f}}\sqrt{\pi t}} \int_{0}^{\infty} \int_{-\eta}^{\eta} \exp\left[-\frac{1}{2}\left(\frac{1}{\delta_{\text{m}}} + \frac{1}{\delta_{\text{h}}}\right) \cdot \eta\right] \cdot \exp\left[-\frac{1}{2}\left(\frac{1}{\delta_{\text{m}}} - \frac{1}{\delta_{\text{h}}}\right) \cdot \mu\right] \\ &\times \sum_{n=0}^{\infty} \left[\begin{array}{c} \gamma^{n} \left(\exp\left\{-\frac{\left[(2n+1)d-\eta\right]^{2}}{4\alpha_{f}t}\right\} + \exp\left\{-\frac{\left[(2n+1)d+\mu\right]^{2}}{4\alpha_{f}t}\right\}\right) \right] d\mu \, d\eta \\ &+ \gamma^{n+1} \left(\exp\left\{-\frac{\left[(2n+1)d-\mu\right]^{2}}{4\alpha_{f}t}\right\} + \exp\left\{-\frac{\left[(2n+1)d+\eta\right]^{2}}{4\alpha_{f}t}\right\}\right) \right] d\mu \, d\eta \\ &= \frac{1}{4\delta_{\text{m}}\delta_{\text{h}}b_{\text{f}}\sqrt{\pi t}} \left[\begin{array}{c} \int_{0}^{\infty} \exp\left[-\frac{1}{2}\left(\frac{1}{\delta_{\text{m}}} + \frac{1}{\delta_{\text{h}}}\right) \cdot \eta\right] \cdot \int_{-\eta}^{\eta} \exp\left[-\frac{1}{2}\left(\frac{1}{\delta_{\text{m}}} - \frac{1}{\delta_{\text{h}}}\right) \cdot \mu\right] \\ &\times \sum_{n=0}^{\infty} \left(\gamma^{n} \exp\left\{-\frac{\left[(2n+1)d+\mu\right]^{2}}{4\alpha_{f}t}\right\} + \gamma^{n+1} \exp\left\{-\frac{\left[(2n+1)d-\mu\right]^{2}}{4\alpha_{f}t}\right\}\right) d\mu \, d\eta \\ &+ \int_{0}^{\infty} \exp\left\{-\frac{1}{2}\left(\frac{1}{\delta_{\text{m}}} + \frac{1}{\delta_{\text{h}}}\right) \cdot \eta\right] \cdot \sum_{n=0}^{\infty} \left(\gamma^{n} \exp\left\{-\frac{\left[(2n+1)d-\mu\right]^{2}}{4\alpha_{f}t}\right\}\right) d\mu \, d\eta \\ &+ \gamma^{n+1} \exp\left\{-\frac{\left[(2n+1)d+\mu\right]^{2}}{4\alpha_{f}t}\right\}\right) \int_{-\eta}^{\eta} \exp\left\{-\frac{\left[(2n+1)d-\eta\right]^{2}}{4\alpha_{f}t}\right\} d\mu \, d\eta \\ &+ \gamma^{n+1} \exp\left\{-\frac{\left[(2n+1)d+\eta\right]^{2}}{4\alpha_{f}t}\right\}\right) \int_{-\eta}^{\eta} \exp\left\{-\frac{\left[(2n+1)d-\eta\right]^{2}}{4\alpha_{f}t}\right\} d\mu \, d\eta \\ &+ \gamma^{n+1} \exp\left\{-\frac{\left[(2n+1)d+\eta\right]^{2}}{4\alpha_{f}t}\right\}\right) \int_{-\eta}^{\eta} \exp\left\{-\frac{\left[(2n+1)d-\eta\right]^{2}}{4\alpha_{f}t}\right\} d\mu \, d\eta \\ &+ \gamma^{n+1} \exp\left\{-\frac{\left[(2n+1)d+\eta\right]^{2}}{4\alpha_{f}t}\right\}\right) \int_{-\eta}^{\eta} \exp\left\{-\frac{\left[(2n+1)d-\eta\right]^{2}}{4\alpha_{f}}\right\} d\mu \, d\eta \\ &+ \gamma^{n+1} \exp\left\{-\frac{\left[(2n+1)d+\eta\right]^{2}}{4\alpha_{f}t}\right\}\right\} \int_{-\eta}^{\eta} \exp\left\{-\frac{\left[(2n+1)d-\eta\right]^{2}}{4\alpha_{f}t}\right\} d\mu \, d\eta \\ &+ \gamma^{n+1} \exp\left\{-\frac{\left[(2n+1)d+\eta\right]^{2}}{4\alpha_{f}t}\right\}\right\} \int_{-\eta}^{\eta} \exp\left\{-\frac{\left[(2n+1)d-\eta\right]^{2}}{4\alpha_{f}t}\right\} d\mu \, d\eta \\ &+ \gamma^{n+1} \exp\left\{-\frac{\left[(2n+1)d+\eta\right]^{2}}{4\alpha_{f}t}\right\}\right\} \int_{-\eta}^{\eta} \exp\left\{-\frac{\left[(2n+1)d-\eta\right]^{2}}{4\alpha_{f}t}\right\} d\mu \, d\eta \\ &+ \gamma^{n+1} \exp\left\{-\frac{\left[(2n+1)d+\eta\right]^{2}}{4\alpha_{f}t}\right\}\right\} \int_{-\eta}^{\eta} \exp\left\{-\frac{\left[(2n+1)d-\eta\right]^{2}}{4\alpha_{f}t}\right\} d\mu \, d\eta \\$$

To simplify the equation, the following parameters are defined:

$$\kappa_{+} = \frac{1}{2} \left(\frac{1}{\delta_{\mathrm{m}}} + \frac{1}{\delta_{\mathrm{h}}} \right)$$
$$\kappa_{-} = \frac{1}{2} \left(\frac{1}{\delta_{\mathrm{m}}} - \frac{1}{\delta_{\mathrm{h}}} \right)$$

 $D_n = (2n+1)d$

Then, the double integral in the second to last line of eq. $(A \cdot 1)$ becomes

$$\int_{0}^{\infty} \exp(-\kappa_{+} \cdot \eta) \cdot \int_{-\eta}^{\eta} \exp(-\kappa_{-} \cdot \mu) \cdot \sum_{n=0}^{\infty} \left\{ \gamma^{n} \exp\left[-\frac{(D_{n}+\mu)^{2}}{4\alpha_{f}t}\right] + \gamma^{n+1} \exp\left[-\frac{(D_{n}-\mu)^{2}}{4\alpha_{f}t}\right] \right\} d\mu d\eta$$

$$= \int_{0}^{\infty} \exp(-\kappa_{+} \cdot \eta) \cdot \int_{0}^{\eta} \left(\exp(-\kappa_{-} \cdot \mu) \cdot \sum_{n=0}^{\infty} \left\{ \gamma^{n} \exp\left[-\frac{(D_{n}+\mu)^{2}}{4\alpha_{f}t}\right] + \gamma^{n+1} \exp\left[-\frac{(D_{n}-\mu)^{2}}{4\alpha_{f}t}\right] \right\} \right) d\mu d\eta. \quad (A\cdot2)$$

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 $\neg \infty$

This equation can be integrated by parts as follows:

$$\left[\frac{\exp(-\kappa_{+}\cdot\eta)}{-\kappa_{+}}\cdot\int_{0}^{\eta}\left(\exp(-\kappa_{-}\cdot\mu)\cdot\sum_{n=0}^{\infty}\left\{\gamma^{n}\exp\left[-\frac{(D_{n}+\mu)^{2}}{4\alpha_{f}t}\right]+\gamma^{n+1}\exp\left[-\frac{(D_{n}-\mu)^{2}}{4\alpha_{f}t}\right]\right\}\right)d\mu\right]_{0}^{\infty}\right] \\
-\int_{0}^{\infty}\frac{\exp(-\kappa_{+}\cdot\eta)}{-\kappa_{+}}\cdot\left(\exp(-\kappa_{-}\cdot\eta)\cdot\sum_{n=0}^{\infty}\left\{\gamma^{n}\exp\left[-\frac{(D_{n}+\eta)^{2}}{4\alpha_{f}t}\right]+\gamma^{n+1}\exp\left[-\frac{(D_{n}-\eta)^{2}}{4\alpha_{f}t}\right]\right\}\right)d\eta \\
=\frac{1}{\kappa_{+}}\cdot\int_{0}^{\infty}\left(\exp[-(\kappa_{+}+\kappa_{-})\cdot\eta]\cdot\sum_{n=0}^{\infty}\left\{\gamma^{n}\exp\left[-\frac{(D_{n}+\eta)^{2}}{4\alpha_{f}t}\right]+\gamma^{n+1}\exp\left[-\frac{(D_{n}+\eta)^{2}}{4\alpha_{f}t}\right]\right\}\right)d\eta. \quad (A\cdot3)$$

The double integral in the last line of eq. (A·1) becomes

$$\int_{0}^{\infty} \exp(-\kappa_{+} \cdot \eta) \cdot \sum_{n=0}^{\infty} \left\{ \gamma^{n} \exp\left[-\frac{(D_{n}-\eta)^{2}}{4\alpha_{f}t}\right] + \gamma^{n+1} \exp\left[-\frac{(D_{n}+\eta)^{2}}{4\alpha_{f}t}\right] \right\} \left[\int_{-\eta}^{\eta} \exp(-\kappa_{-} \cdot \mu) d\mu \right] d\eta$$

$$= \int_{0}^{\infty} \exp(-\kappa_{+} \cdot \eta) \cdot \sum_{n=0}^{\infty} \left\{ \gamma^{n} \exp\left[-\frac{(D_{n}-\eta)^{2}}{4\alpha_{f}t}\right] + \gamma^{n+1} \exp\left[-\frac{(D_{n}+\eta)^{2}}{4\alpha_{f}t}\right] \right\} \frac{\exp(-\kappa_{-} \cdot \eta) - \exp(\kappa_{-} \cdot \eta)}{-\kappa_{-}} d\eta$$

$$= \int_{0}^{\infty} \frac{-\exp[-(\kappa_{+}+\kappa_{-}) \cdot \eta] + \exp[-(\kappa_{+}-\kappa_{-}) \cdot \eta]}{\kappa_{-}} \cdot \sum_{n=0}^{\infty} \left\{ \gamma^{n} \exp\left[-\frac{(D_{n}-\eta)^{2}}{4\alpha_{f}t}\right] + \gamma^{n+1} \exp\left[-\frac{(D_{n}+\eta)^{2}}{4\alpha_{f}t}\right] \right\} d\eta. \quad (A.4)$$

Here,

$$\int_{0}^{\infty} \left\{ \exp\left[-\frac{(D_{n}-\eta)^{2}}{4\alpha_{f}t}\right] \exp(-k\eta) \right\} d\eta$$

$$= \int_{0}^{\infty} \exp\left(-\frac{D_{n}^{2}-2D_{n}\eta+\eta^{2}+4\alpha_{f}kt\eta}{4\alpha_{f}t}\right) d\eta$$

$$= \exp(-kD_{n}) \exp(\alpha_{f}k^{2}t)$$

$$\times \int_{0}^{\infty} \exp\left[-\frac{(\eta-D_{n}+2\alpha_{f}kt)^{2}}{4\alpha_{f}t}\right] d\eta$$

$$= 2\sqrt{\alpha_{f}t} \cdot \exp(-kD_{n}) \exp(\alpha_{f}k^{2}t) \cdot \operatorname{erfc}\left(\frac{-D_{n}+2\alpha_{f}kt}{2\sqrt{\alpha_{f}t}}\right)$$

$$= 2\sqrt{\alpha_{f}t} \cdot \exp(-kD_{n}) \exp(\alpha_{f}k^{2}t) \cdot \operatorname{erfc}\left(\frac{-D_{n}}{2\sqrt{\alpha_{f}t}} + k\sqrt{\alpha_{f}t}\right)$$
(A·5)

Similarly,

$$\begin{split} &\int_{0}^{\infty} \left\{ \exp\left[-\frac{(D_{n}+\eta)^{2}}{4\alpha_{f}t}\right] \exp(-k\eta) \right\} d\eta \\ &= \int_{0}^{\infty} \exp\left(-\frac{D_{n}^{2}+2D_{n}\eta+\eta^{2}+4\alpha_{f}kt\eta}{4\alpha_{f}t}\right) d\eta \\ &= \exp(kD_{n}) \exp(\alpha_{f}k^{2}t) \\ &\times \int_{0}^{\infty} \exp\left[-\frac{(\eta+D_{n}+2\alpha_{f}kt)^{2}}{4\alpha_{f}t}\right] d\eta \\ &= 2\sqrt{\alpha_{f}t} \cdot \exp(kD_{n}) \exp(\alpha_{f}k^{2}t) \cdot \operatorname{erfc}\left(\frac{D_{n}+2\alpha_{f}kt}{2\sqrt{\alpha_{f}t}}\right) \\ &= 2\sqrt{\alpha_{f}t} \cdot \exp(kD_{n}) \exp(\alpha_{f}k^{2}t) \cdot \operatorname{erfc}\left(\frac{D_{n}}{2\sqrt{\alpha_{f}t}} + k\sqrt{\alpha_{f}t}\right) \end{split}$$

$$(A.6)$$

By substituting these results into eq. (A·3), the final equation is obtained, which is eq. (11) in the main text.

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