Reliable thermophysical property values of thin films are important to develop advanced industrial technologies such as highly-integrated electric devices, optical disks, magneto-optical disks, and thermoelectric devices. In order to meet this requirement, the National Metrology Institute of Japan of the National Institute of Advanced Industrial Science and Technology (NMIJ/AIST) has developed thermoreflectance methods by picosecond pulse heating and nanosecond pulse heating under the same geometrical configuration to the laser flash method which is the standard method to measure thermal diffusivity of bulk materials. These light pulse heating methods observe one-dimensional heat diffusion across well-defined length of the specimen thickness. Thermal diffusivity values across thin films were measured with small uncertainty. Since the geometry is very simple, thermal diffusivity can be determined reliably with uncertainty evaluation based on Guide to the Expression of Uncertainty in Measurement (GUM).

1. INTRODUCTION

According to the ITRS (International Technology Roadmap for Semiconductors) 2006 Update, the pace of change in assembly and packaging has accelerated as packaging is increasingly a limiting factor for both product cost and performance. In order to reflect these rapid changes, “Package Substrate Physical Properties (Table 98) have been updated to incorporate additional parameters for thermal properties that are increasingly critical for higher temperature, smaller form factor packages” in the assembly and packaging part. It is also mentioned that one of the difficult challenges ≥ 32 nm is “Thermal-mechanical-electrical modeling for interconnections and packaging” in the modeling and simulation part and Difficult Challenges (Table 122) have been updated as “Model thermal-mechanical, thermodynamic and electronic properties of low κ, high κ, and conductors for efficient in-chip package layout and power management, and the impact of processing on these properties especially for interfaces and films under 1 micron dimension.” in the modeling and simulation part.

In optical recording storage media, small area is heated by laser beam and it is recorded by changing state (magnetization, crystal phase or an amorphous phase) of the area. Therefore, control of a temperature change in record media by pulse heating becomes key technology.

Thermal properties of such thin films do not agree with those of bulk materials of same name / same composition. Consequently, it is necessary to measure these thin films in situ as the shape of circuit elements or record media, or to measure thin film specimens which are synthesized to the same thickness by the same deposition method as the thin films in the vice [1, 2].

In addition, it is necessary to know a value of a boundary thermal resistance between the layer as well as a thermophysical property of each layer to understand internal heat transfer of multilayered film constituting a semiconductor device or storage media at high integration. However, when multilayered films are measured with conventional measurement methods, it is difficult to separate contribution of thermal resistance between the layers from thermal conduction of each layer.

2. LASER FLASH METHOD

There are varieties of thermal diffusivity measurement methods by combination such as shape and dimension of the specimen, heating position, heating method of the specimen, a temperature measurement position, a temperature measurement method. It is common to measure a thermal diffusivity by the laser flash method for specimens of thickness from several 100μm to several mm of metals, ceramics, semiconductor, and s carbon materials etc. Then, thermal conductivity λ is calculated by equation \( \lambda = \alpha c \rho \) from specific heat capacity c and density \( \rho \) [3-5].
When thermal diffusivity is measured with the laser flash method, front face of a planar specimen kept at constant temperature is pulsewise heated uniformly as shown in figure 1. Heat diffuses one-dimensionally from a heated specimen front face to rear face and temperature of the whole specimen finally becomes uniform. Because speed of a temperature change of specimen rear face is in proportion to a thermal diffusivity and is in inverse proportion to the square of thickness of specimen, a thermal diffusivity is calculated by thickness of specimen and heat diffusion time [3-5].

The following condition is assumed as ideal:
1) Duration of the laser pulse is negligibly short compared with the heat diffusion time.
2) Specimen is adiabatic to the environment.
3) Specimen front face is heated uniformly.
4) Temperature change of specimen rear face is measured precisely.
5) Specimen is dense, uniform, and opaque.
6) Change of thermal diffusivity by temperature rise of specimen after pulse heating is negligibly small.

Under the assumption mentioned above, when front face of a plate of thermal diffusivity \( \alpha \), specific heat capacity \( C \), density \( \rho \), thickness \( d \) is heated pulsewise with uniform energy density, temperature change of the specimen rear face is expressed by the following equation:

\[
T(t) = \Delta T \left[ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-\left(n\pi\frac{1}{\tau}\right)^2 t\right) \right]
\]

where \( \Delta T = Q / C \), \( Q \) is the total energy absorbed by the specimen, \( C \) is the heat capacity of the specimen, \( \tau = d^2 / \alpha \) is the characteristic time of heat diffusion across the specimen. Graph of equation (1) is shown in figure 2.

When 0.1388 times of the characteristic time passed after pulse heating, specimen rear face temperature reaches half of the maximum temperature rise. The characteristic time is determined by fitting theoretical curve to the rear face transient temperature curve, and the thermal diffusivity is calculated. Conventional standard data analysis algorithm is the half time method where the time reaching half of the maximum temperature rise value is determined from measured curve, and calculates thermal diffusivity from the following equation: [3]

\[
\alpha = 0.1388 \frac{d^2}{t_{1/2}}
\]

3. HIGH SPEED LIGHT PULSE HEATING THERMOREFLECTANCE METHODS

3.1 Nanosecond light pulse heating thermoreflectance method

1) Front face heating / front face detection

Picosecond thermoreflectance method was developed to measure thermal diffusivity of subnanometer thick films by Paddock and Eesley [6]. The optical reflection intensity of the temperature detection light is detected by photodiode. Since reflectivity of material surface changes dependent on the surface temperature, the change of specimen front face temperature can be observed by the change of reflected light amplitude. This temperature measurement method with the temperature change of such a reflectivity is called as thermoreflectance method [7]. Thermal diffusivity of submicrometer thick films perpendicular to the surface was calculated from the cooling rate of the surface temperature and the penetration depth of the heating light.
First, NMIJ/AIST developed a system for measuring thermal diffusivity of thin films system under front face heating / front face detection configuration Figure 5 shows the result which observed the change of the front face temperature by the picosecond thermoreflectance method about three kinds of aluminium thin films of different thickness synthesized on a glass substrate [8].

For the specimen of 500 nm thick, the heat has not arrived at the substrate within 120 ps after pulse heating and the front face temperature change represented by red line corresponds to internal heat diffusion of the aluminium thin film.

On the other hand, for the specimen of 100 nm thick, the temperature change speed decreases around 30 ps after pulse heating as show by black line and deviates from the temperature change of the 500 nm thick specimen. Because the thermal diffusivity of glass substrate is much smaller than the thermal diffusivity of aluminium thin film, the heat diffusion to the substrate is suppressed when the heat arrives at the interface between the thin film and the substrate.

As shown by blue line in figure 5, for the specimen of 50 nm thick, the temperature change only for the inside of the thin film cannot be observed because of heat diffusion to the substrate just after pulse heating.

Area of a diameter of several 10 μm on thin film front face is heated by the picosecond laser beam and the same position is irradiated by the probe beam. Then, the history of front face temperature is observed by the conventional thermoreflectance method.

In this method, the thermal diffusivity can be calculated from the cooling rate after pulse heating. However, it is not easy to make quantitative and reproducible measurement because the cooling rate changes sensitively dependent on the condition of thin film front face.

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In this method, the thermal diffusivity can be calculated from the cooling rate after pulse heating. However, it is not easy to make quantitative and reproducible measurement because the cooling rate changes sensitively dependent on the condition of thin film front face.
2) Rear face heating / front face detection

National Metrology Institute of JAPAN, AIST has developed rear face heating / front face detection picosecond light heating thermoreflectance methods which are evolution of the conventional laser flash method and the picosecond thermoreflectance method [9-12]. Figure 7 shows the block diagram of a measurement system. This configuration is essentially equivalent to the laser flash method which is the standard measurement method to measure the thermal diffusivity of bulk materials. The thermal diffusivity of the thin films can be calculated with small uncertainty from the thickness of a thin film and the heat diffusion time across a thin film.

The temperature detection beam is focused to a spot diameter of about 50 μm at the specimen front face just opposite to the heating light focus position. The reflected light intensity of the temperature detection light is in proportion to the change of specimen front face temperature and the change of the reflected light intensity is detected by photodiode. The temperature coefficient of reflectivity for normal metal such as aluminium is small with $10^{-5}/K$ order. Since the transient temperature rise of the specimen front face after picosecond pulse heating is smaller than a few degrees, 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 modulation frequency of heating light by an acoustic optic modulator.

Figure 8 shows the temperature history curves of an aluminium single-layered thin film of 100 nm thick and a molybdenum single-layered thin film of 100 nm measured by the picosecond light pulse heating thermoreflectance method [9]. Both films were synthesized on a Pyrex glass substrate by magnetron DC sputtering method. Here, film thicknesses are nominal values.
Since thermoreflectance signals are similar to those observed by the laser flash method for bulk specimen suggest, the heat energy transport of these metallic thin films of about 100 nm thick at room temperature in time scale of several 100 ps can be expressed by the classic thermal diffusion equation.

3.2. Nanosecond light pulse heating thermoreflectance method

Initially, the electrical delay method was developed to expand the observation time of the picosecond light pulse heating thermoreflectance method longer for measurements of thicker films [12]. Since the pulse duration can be longer than picosecond and the repetition period of pulses is flexible, nanosecond pulse laser can be used for light pulse heating thermoreflectance method [2, 11]. For the pump pulse, pulse duration is 2 ns and pulse interval is 20 μs with intensity modulation of 1 kHz by an acoustic optical modulator. Typical size and shape of the specimen are a disk of 10 mm in diameter or a square of 10 mm on each side. The specimen is irradiated from bottom to the rear face of the specimen by the heating beam and the reflected light of the probe beam is detected by a photodiode. The thermoreflectance signals are detected using a lock-in amplifier. In this system it is possible to measure the thermal diffusivity of thin films with thickness up to several micrometers.

After the laser flash method and high speed light pulse heating thermoreflectance methods (the picosecond thermoreflectance method and the nanosecond thermoreflectance method) have been established, thermal diffusivity of materials ranging from thin films of several 10 nm thick to bulk specimens of several mm thick can be measured the light pulse heating methods under the same geometrical configuration of one dimensional heat diffusion after impulse heating as shown in figure 9.

4. ANALYSIS OF MULTILAYERED FILM AND BOUNDARY THERMAL RESISTANCE

Thin films constituting light heating phase change storage media, transparent conductive films, and interlayer dielectric of semiconductor device are semitransparent to visible light, near infrared light whereas metallic thin films are nontransparent to these lights. Consequently both faces of the film are coated with metal thin film for surface heating by heating laser beam and surface temperature detection by probe laser pulse based on the thermoreflectance method. Therefore, analysis of heat diffusion across three layer thin films on substrate must be considered in order to calculate thermal diffusivity of the thin film sandwiched by metal thin films.

It is necessary to know boundary thermal resistance between the layers as well as thermophysical property of each layer of multilayered film to understand internal heat transfer of multilayered films constituting a semiconductor device or storage. However, when multilayered films are measured with conventional measurement methods, it is difficult to measure thermal conductivity of each layer and thermal resistance between the layers separately.

In this section, the response function method that is general technique to analyze heat diffusion of such a
multilayer films is described [13 - 15].

Following symbols are used in this section:
- $t$: time, $\xi$: Laplace parameter, $d$: thickness,
- $\alpha$: thermal diffusivity, $b$: thermal effusivity,
- $T(t)$: temperature,
- $\tilde{T}(\xi)$: Laplace transform of temperature,
- $q(t)$: heat flux density,
- $\tilde{q}(\xi)$: Laplace transform of heat flux density,
- $\tau = d^2/\alpha$: heat diffusion time across film or layer.

4.1 Areal heat diffusion time

The areal heat diffusion time is defined as the area surrounded by the horizontal line at the height of the maximum temperature rise and the transient temperature response curve at the rear face after pulse heating as shown in Figure 10 [2, 16 - 18]. Based on the response function method, the areal heat diffusion time is calculated by the following equation (3) when the temperature is normalized by the maximum temperature rise $T_{\text{max}} = 1/(b\sqrt{\pi})$:

$$A = \int_0^\infty [1 - b\sqrt{\pi} \cdot \tilde{T}(\xi)] d\xi = \lim_{\xi \to 0} \left[ 1 - b\sqrt{\pi} \cdot \tilde{T}_\alpha(\xi) \right]$$  (3)

where $\xi$ is a Laplace parameter and $\tilde{T}_\alpha(\xi)$ is Laplace transform of $T(t)$ defined by

$$\tilde{T}_\alpha(\xi) = \int_0^\infty T(t) \exp(-\xi t) dt.$$  

Figure 10 Area surrounded by the maximum temperature rise line and the temperature response at the specimen rear face after the pulse heating

4.2 Single layer thin film

The transient temperature response at rear face of an adiabatic mono-layer thin film is identical to equation (1) which is the theoretical solution for the laser flash thermal diffusivity measurement under the ideal condition given by Parker et al. Thus, the areal heat diffusion time is expressed by the following equation:

$$A = \int_0^\infty \left[ 1 - \left( 1 + 2\sum_{n=1}^\infty (-1)^n \exp\left(-\frac{n^2\pi^2 t^2}{d^2}\right) \right) \right] dt$$

Thus, the heat diffusion time $\tau$ is calculated from the areal heat diffusion time $A$ and the thermal diffusivity is calculated as $\alpha = d^2/\tau$, where $d$ is the thickness of the thin film.

4.3 Two-layer thin film

Heat diffusion across a multi-layer thin film is systematically analyzed by the response function method [2, 13-18]. Figure 11 shows a cascade connection of quadra-pole matrices to represent heat diffusion across a two-layer thin film. In Laplace transformed space, the heat flux flowing into the layer 1 from outside is expressed as $\tilde{q}_1(\xi)$, the temperature of the open face of the layer 1 is expressed as $\tilde{T}_1(\xi)$, the heat flux penetrating through the boundary from the layer 1 to the layer 2 is expressed as $\tilde{q}_2(\xi)$, the temperature at the boundary between the layer 1 and 2 is expressed as $\tilde{T}_2(\xi)$, and the quadra-pole matrix of the layer 1 is expressed as $\tilde{S}_1(\xi)$. They are related by the following equation if the boundary thermal resistance is negligibly small [13, 15]:

$$\begin{bmatrix} \tilde{q}_2(\xi) \\ \tilde{T}_2(\xi) \end{bmatrix} = \begin{bmatrix} \tilde{S}_1(\xi) \\ \tilde{T}_1(\xi) \end{bmatrix} \begin{bmatrix} \tilde{q}_1(\xi) \\ \tilde{T}_1(\xi) \end{bmatrix}$$  (5)

Each component of this equation is expressed as follows:

$$\tilde{q}_2(\xi) = \cosh(\sqrt{\xi} t_1) \tilde{q}_1(\xi) - b_1 \sqrt{\xi} \cdot \sinh(\sqrt{\xi} t_1) \tilde{T}_1(\xi)$$  (6)

$$\tilde{T}_2(\xi) = -\frac{1}{b_1 \sqrt{\xi}} \cdot \sinh(\sqrt{\xi} t_1) \tilde{q}_1(\xi) + \cosh(\sqrt{\xi} t_1) \tilde{T}_1(\xi)$$  (7)

Similarly, the heat flux flowing from the layer 2 to outside is expressed as $\tilde{q}_1(\xi)$ and the temperature of the open face of the layer 2 is expressed as $\tilde{T}_1(\xi)$ in Laplace transformed space. Then, the pair of $\tilde{q}_2(\xi)$ and $\tilde{T}_2(\xi)$ are related to the pair of $\tilde{q}_1(\xi)$ and $\tilde{T}_1(\xi)$ by inverse of the quadra-pole matrix of layer 2 $\tilde{S}_1(\xi)$:

$$\begin{bmatrix} \tilde{q}_1(\xi) \\ \tilde{T}_1(\xi) \end{bmatrix} = \begin{bmatrix} \tilde{S}_1(\xi)^{-1} \\ \tilde{T}_1(\xi)^{-1} \end{bmatrix} \begin{bmatrix} \tilde{q}_2(\xi) \\ \tilde{T}_2(\xi) \end{bmatrix}$$  (8)

$$\tilde{q}_1(\xi) = \cosh(\sqrt{\xi} t_2) \tilde{q}_2(\xi) + b_2 \sqrt{\xi} \cdot \sinh(\sqrt{\xi} t_2) \tilde{T}_2(\xi)$$  (9)

$$\tilde{T}_1(\xi) = \frac{1}{b_2 \sqrt{\xi}} \cdot \sinh(\sqrt{\xi} t_2) \tilde{q}_2(\xi) + \cosh(\sqrt{\xi} t_2) \tilde{T}_2(\xi)$$  (10)
When \( b_1 \to 0 \) and \( \tau_2 \to 0 \), equation (13) converges to
\[
\bar{T}_{3b}(\xi) = \frac{1}{\sqrt{\xi}} \left[ b_1 b_3 R_2 \sqrt{\xi} \sinh(\sqrt{\xi} \tau_1) \sinh(\sqrt{\xi} \tau_2) \right. \\
+ b_1 \sinh(\sqrt{\xi} \tau_1) \cosh(\sqrt{\xi} \tau_2) \\
+ b_1 \cosh(\sqrt{\xi} \tau_1) \sinh(\sqrt{\xi} \tau_2) \\
\left. + b_1 \cosh(\sqrt{\xi} \tau_1) \cosh(\sqrt{\xi} \tau_2) \sinh(\sqrt{\xi} \tau_1) \right]
\] (15)

Replacing a pair of \( b_3 \) and \( \tau_3 \) with a pair of \( b_2 \) and \( \tau_2 \), substituting \( \bar{T}_{3b}(\xi) \) to \( \bar{T}(\xi) \) in equation (3), and normalizing by the maximum temperature rise, the areal heat diffusion time is expressed by the following equation:
\[
A_{2b} = \lim_{\xi \to 0} \left[ \frac{1}{\sqrt{\xi}} - \left( b_1 \sqrt{\xi} \tau_1 + b_2 \sqrt{\xi} \tau_2 \right) \right] \bar{T}_{3b}(\xi)
\] (16)
where \( A_2 \) is the areal heat diffusion time of a two-layer thin film without boundary thermal resistance as shown in figure 10 [2, 16]. From equation (16), the boundary thermal resistance is expressed as follows:
\[
R_{1b} = \frac{b_1 \sqrt{\xi} \tau_1 + b_2 \sqrt{\xi} \tau_2}{b_1 \sqrt{\xi} \tau_1 + b_2 \sqrt{\xi} \tau_2} (A_{2b} - A_2)
\] (17)
where \( A_2 \) and \( A_{2b} \) are explained in figure 10.

5. THIN FILM THERMO PHYSICAL PROPERTY
REFERENCE MATERIAL AND TRACEABILITY
The high-speed laser flash method in extended definition mentioned above can be generally used and popular after commercial instruments are available and traceability to the national standard and/or the international standard is established.

The national standard of the laser flash method was established in 2002 by NMIJ/AIST. Uncertainty of thermal diffusivity standard by the laser flash method was evaluated based on “Guide to the Expression of Uncertainty in Measurement, GUM” [19] and a quality system corresponding to ISO 17025 was constructed [5]. Now, evaluation of homogeneity and stability of high density isotropy graphite is under progress. The standard value of thermal diffusivity of the graphite is to be determined with uncertainty evaluation based on GUM and will be supplied as a reference material in 2005.

NMIJ/AIST is also developing the standard of thin film thermophysical property by the high-speed laser flash method under the same scheme as shown in Table 1. It is planned to establish the national standard in 2005 for picosecond thermoreflectance method. The national standard and thin film reference material are developed and to be supplied in 2008 for nanosecond thermoreflectance method.
Table 1 Program to develop thermal diffusivity standards by light pulse heating methods planned by NMIJ/AIST

<table>
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<tr>
<th>Light pulse heating methods</th>
<th>Observable Heat diffusion Time</th>
<th>Planned year to start service</th>
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<td>Laser flash method</td>
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<tr>
<td>Conventional</td>
<td>1ns~10s</td>
<td>FY2002</td>
<td>FY2005</td>
<td></td>
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<tr>
<td>Application to thin plates and coatings</td>
<td>1μs~10μs</td>
<td>under consideration</td>
<td>under consideration</td>
<td></td>
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<tr>
<td>Nanosecond thermoreflectance method</td>
<td>10μs~100μs</td>
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<td>Picosecond thermoreflectance method</td>
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<td>Electrical delay</td>
<td>100ps~10ns</td>
<td>FY2005</td>
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<tr>
<td>Optical delay</td>
<td>10ps~1ns</td>
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6. SUMMARY
Thermoreflectance methods by picosecond pulse heating and by nanosecond pulse heating have been developed under the same geometrical configuration as the laser flash method which is the standard method to measure thermal diffusivity of bulk materials. Thermal diffusivity values across thin films were measured with small uncertainty. These high speed light pulse heating thermoreflectance methods observe heat diffusion time across well-defined length of the specimen thickness under one-dimensional heat flow. Since the geometry is very simple, thermal diffusivity can be determined reliably with uncertainty evaluation based on GUM [16]. NMIJ/AIST is engaged in research for establishment of national standard, international standard for thermal diffusivity measurements of thin films.

REFERENCES