BIPM Workshop
on Challenges in Metrology for Dynamic Measurement

Dynamic measurements of thermophysical properties for material metrology standards

Measurement by impulse heating and analysis by response functions and transfer functions

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BIPM Workshop on Challenges in Metrology for Dynamic Measurement

- Session 1 Dynamic Mechanical Quantities
  Force, Torque, Vibration, etc
- Session 2 Dynamic Fluid and Flowmetry
  Pressure, temperature, and volume of fluid
- Session 3 Thermo Physical Quantities
  Thermal properties, material properties, etc
  Temperature

Dynamic response of sensor, measurement
Frequency response, Step response, Impulse response
Mathematical presentation
Impulse response function
Transfer function
Outline of the presentation

1. Introduction
   • Needs for thermophysical quantities
   • Common interest with dynamic measurement of mechanical quantities, fluid and flowmetry

2. Pulsed light heating methods
   • Laser flash method for thermal diffusivity measurements
   • Ultra fast laser flash method for thin films measurement

3. Analysis by impulse response function and transfer function
   • Analysis of heat diffusion
   • Analysis of finite response time of temperature detection
   • Transfer function and areal heat diffusion time

4. Summary
Needs for thermal metrology 1

• Energy production:
  Electric power generator
  Nuclear power plant
  Natural energy
    Geothermal power generation
    Solar power generation
Needs for thermal metrology 2

• Energy saving:
  Industrial sector
    Production line
    Plants
    Furnaces, kilns, heat treatment
    Steel making, ceramics industry
  Transportation sector
    Automobiles
    Trains, ships, aircrafts
  Commercial and residential sector
    Buildings and houses
Needs for thermal metrology 3

• Electronics:
  Thermal design and management
  PC, server, data center, projector
  Home electric appliance
    LED illumination
    Flat panel display
  Device
    CPU
    Memory and storage
      Phase change memory
      Hard disk (Heat assisted)
      Organic EL
CMC service categories covered by WG9

6. Thermophysical properties

6.1 Thermal transport property
   6.1.1 Thermal conductivity
   6.1.2 Thermal diffusivity

6.2 Caloric property
   6.2.1 Specific heat capacity
   6.2.2 Heat of fusion
   6.2.3 Calorific value

6.3 Radiative property
   6.3.1 Spectral emissivity
   6.3.2 Total emissivity

6.4 Thermo-mechanical property
   6.4.1 Thermal expansion coefficient
Vacuum insulation panel (VIP)

VIP  Urethane form  Glass wool

0.045 W m\(^{-1}\) K\(^{-1}\)
0.024 W m\(^{-1}\) K\(^{-1}\)
0.002 W m\(^{-1}\) K\(^{-1}\)
Measurement of thermal conductivity

Thermal conductivity, $\lambda$, measurement by steady method

Thermal conductivity

$$\lambda = \frac{d \cdot q_0}{T_f - T_r} = \frac{d \cdot q_0}{\Delta T_{fr}}$$
Three pilot studies organized by CCT WG9

CCT-P01 (CCT-S2)
Thermal conductivity of insulating materials

- Temperature range: 0 - 100 °C
- Measurement technique: guarded hot plate method
- Pilot institute: LNE, France

**CCT-S2**

<table>
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<tr>
<th>Information</th>
<th>Description</th>
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<tr>
<td>Metrology area, branch</td>
<td>Thermometry, Thermophysical quantities</td>
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<td>Transfer device(s)</td>
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<td>Comparison type</td>
<td>Supplementary comparison</td>
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<tr>
<td>Consultative Committee Conducted by</td>
<td>CCT (Consultative Committee for Thermometry)</td>
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Ceramics and compound semiconductors

AlN

SiC

Si$_3$N$_4$

GaN
Measurement of thermal conductivity and thermal diffusivity

Thermal conductivity, \( \lambda \), measurement by steady method

\[
\lambda = \frac{d \cdot q_0}{T_f - T_r} = \frac{d \cdot q_0}{\Delta T_{fr}}
\]

Thermal diffusivity, \( \alpha \), measurement by dynamic method

\[
\alpha = \alpha \cdot c \cdot \rho
\]
Laser flash method

Light Pulse heating → One dimensional heat diffusion → Temperature detector → Observation of rear face temperature

Temperature, $T / \Delta T$

Time, $t / \tau_0$

Distance from the surface, $x/d$

Thermal diffusivity, $\kappa = \frac{d^2}{\tau_0} = 0.1388 \frac{d^2}{t_{1/2}}$

Bloch diagram of the laser flash method

Pulse laser

Trigger

Data acquisition

DC amplifier

Radiation thermometer

Specimen

Temperature change at rear face

Controller

Power supply

Heater

Vacuum chamber

Thermocouple
Thermal diffusivity measurement of carbon by the laser flash method
Three pilot studies organized by CCT WG9

CCT-P02 (CCT-S3)
Thermal diffusivity of dense materials

- Temperature range: RT - 1000 °C
- Measurement technique: laser flash method
- Pilot institute: NMIJ, Japan

CCT-S3

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<td>Temperature: 300 K to 1200 K</td>
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<td>Transfer device(s)</td>
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<td>Comments</td>
<td>Measurements using laser flash method for dense materials</td>
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Needs for thermophysical property data by electronics industry

- LSI
- Power device
- Lighting
- Flat panel display

Low K in LSI, AlN and diamond for heat spreader, GaN for LED, ITO and IZO in FPD

Thermophysical property data
- Thermal conductivity
- Thermal diffusivity
- Specific heat capacity

Thermal design and simulation
Recording by phase change in optical recording media

Recording layer (GeSbTe)

0 (Crystal)

Heating beam

1 (Amorphous)

$K_{\text{crystal}}$

$K_{\text{amorphous}}$

$\sim 5\mu m$

$\sim 50 \text{ nm}$
The Structure of Thin Film Stack: HD DVD-ARW Medium

Reliable values are especially needed for ZS, GSTB and boundary resistance between them.

0.6mm thick substrate
405nm

10 – 100 nm each

NA: 0.65

0.6mm thick substrate

ZnS - SiO₂
SiO₂
AlN
ZnS - SiO₂
GeSbTeBi
ZnS - SiO₂
Ag - alloy

(ZS)
(GSTB)
Length and time scale of pulsed light heating methods

Heat diffusion time: \[ \tau = \frac{d^2}{\alpha} \]

Thermal diffusivity

Specimen

Temperature detection

Laser flash method
Bulk materials, 1mm

10ms-10s

Observation of radiation

Nanosecond TR method
Thin films, 1μm

10ns-10μs

Change of reflectivity as a function of surface temperature

Picosecond TR method
Thin films, 30nm

10ps-10ns

\[
R = R_0 + \frac{dR}{dT} \Delta T
\]

\[
\frac{1}{R} \frac{dR}{dT} = 10^{-4} \sim 10^{-5}
\]
Block diagram of measurement system by the picosecond thermoreflectance method

- Ti/sapphire laser
- AOM
- Pump beam
- Specimen generator
- Optical delay line
- Probe beam
- Photo diode
- Lock-in amplifier
- Function generator
Thermal diffusivity of molybdenum thin films measured with the picosecond thermoreflectance method

Synthesized by magnetron DC sputtering
Substrate: Corning 7740 glass

Temperature response curve of Mo thin films

![Graph showing temperature response curves for 70 nm, 100 nm, and 200 nm Mo thin films over time in ps. The x-axis represents time in ps, ranging from 0 to 600, and the y-axis represents thermoreflectance signal in arbitrary units.](image-url)
Thermal diffusivity of molybdenum thin films measured with the picosecond thermoreflectance method

Synthesized by magnetron DC sputtering
Substrate: Corning 7740 glass

<table>
<thead>
<tr>
<th>Nominal thickness (nm)</th>
<th>Measured thickness (nm)</th>
<th>Absorption coefficient ($\times 10^7$ m$^{-1}$)</th>
<th>Thermal diffusivity ($10^{-5}$ m$^2$s$^{-1}$)</th>
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<tr>
<td>70</td>
<td>65.4</td>
<td>5.8</td>
<td>3.0</td>
</tr>
<tr>
<td>100</td>
<td>94.6</td>
<td>5.4</td>
<td>3.6</td>
</tr>
<tr>
<td>200</td>
<td>191.0</td>
<td>5.0</td>
<td>3.0</td>
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<td>Bulk</td>
<td>-</td>
<td>5.5</td>
<td>5.4</td>
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Thermal diffusivity measurements from bulk materials to thin films by pulsed light heating methods

(Thermal diffusivity, $\alpha = 1 \times 10^{-5} \text{ m}^2\text{s}^{-1}$, $\tau = d^2/\alpha$)
Normalized thermoreflectance signal / a.u.

Delay time / ns

Mo 140 nm

SiO$_2$ thickness

- 0.5 nm
- 1.0 nm
- 3.0 nm

Mo 70 nm
Definition of areal heat diffusion time

Areal heat diffusion time

\[ A = \int_0^\infty \left[ 1 - \frac{T_r(t)}{T_{\text{max}}} \right] dt \]

\[ = \lim_{\xi \to 0} \int_0^\infty \exp(-\xi t) \left[ 1 - \frac{T_r(t)}{T_{\text{max}}} \right] dt \]

\[ = \lim_{\xi \to 0} \left[ \frac{1}{\xi} - \frac{T_r(\xi)}{T_{\text{max}}} \right] \]

\[ = \lim_{\xi \to 0} \left[ \frac{1}{\xi} - \frac{\tilde{R}_{rf}(\xi)}{T_{\text{max}}} \right] \]

Transfer function

Normalized temperature rise

Laplace transformation

\[ \tilde{f}(\xi) = \int_0^\infty \exp(-\xi t)f(t)dt \]
Temperature history curves of 3 layer specimens with different thickness of nonmetal thin film

\[ \text{Normalized temperature rise} \]

\[ A_1 \]

\[ \text{Time} \]

\[ A_2 \]

\[ \text{Time} \]
適電気導体（インターレイヤ）の厚さと遅延時間の関係を示すグラフです。 graft トレータ レクフレクタンスを示すグラフです。
Experimental value

Calculated value
$k_{\text{SiO}_2} = 8.8 \times 10^{-7}$ m$^2$/s, $R_{\text{SiO}_2/\text{Mo}} = 2 \times 10^{-9}$ m$^2$K/W

Calculated value 2
$k_{\text{SiO}_2} = 5.9 \times 10^{-7}$ m$^2$/s, $R = 0$
Thin films and boundary thermal resistances measured by this study

- Metals: Al, Mo, W, Pt, etc.
- Oxides: SiO$_2$, Al$_2$O$_3$, In$_2$O$_3$, ZnO, etc.
- Nitrides: TiN, AlN, etc.
- Compounds composed of 3 elements: Mg(OH)$_2$, GeSbTe, etc
- Compounds composed of 4 elements: AgInSbTe, etc
- Boundary thermal resistance between metal layer and nonmetal layer: Mo/SiO$_2$, Mo/Al$_2$O$_3$, Mo/In$_2$O$_3$, etc.
Major factors contributing uncertainty of dynamic thermophysical quantity measurement

- Heating function
  - Impulse, step, sinusoidal, etc.
  - Intensity variation in time domain
- Geometry
  - Heat conduction equation
  - Shape and dimensions of the specimen
  - Heating method and position
  - Temperature detection method and position
- Response of temperature detection
  - Nonlinearity
  - Response time
- Impulse response function

Finite duration of heating

Finite response

Detector response

$t_{qcg}$
time

$t_{qcg}$
time
Block diagram of dynamic thermophysical quantity measurement

- Heating
- Heat diffusion
- Response of detector

\[
\tilde{q}(\xi) \rightarrow \tilde{R}(\xi) \rightarrow \tilde{T}(\xi) \rightarrow \tilde{D}(\xi) \rightarrow \tilde{\theta}(\xi)
\]

\[
\tilde{\theta}(\xi) = \tilde{D}(\xi) \cdot \tilde{R}(\xi) \cdot \tilde{q}(\xi)
\]

\[
\tilde{R}(\xi) = \frac{\tilde{\theta}(\xi)}{\tilde{D}(\xi) \cdot \tilde{q}(\xi)}
\]
Infrared radiation thermometer for laser flash thermal diffusivity measurements
Frequency response of the infrared radiation thermometer

Frequency, Hz

Amplitude

Phase shift, degree

Phase shift, degree
Frequency response of the infrared radiation thermometer

\[ F_D(\omega) = \tilde{D}(i\omega) = \frac{\omega_n^2}{(i\omega)^2 + 2\eta(i\omega)\omega_n + \omega_n^2} = \frac{\omega_n^2}{\omega_n^2 - \omega^2 + 2i \cdot \eta \cdot \omega \cdot \omega_n} \]

\[ = \frac{\omega_n^2 \cdot (\omega_n^2 - \omega^2)}{(\omega_n^2 - \omega^2)^2 + 4(\eta \cdot \omega \cdot \omega_n)^2} - i \cdot \frac{2\eta \cdot \omega \cdot \omega_n^3}{(\omega_n^2 - \omega^2)^2 + 4(\eta \cdot \omega \cdot \omega_n)^2} \]

\[ |F_D(\omega)| = \frac{\omega_n^2}{\sqrt{(\omega_n^2 - \omega^2)^2 + 4(\eta \cdot \omega \cdot \omega_n)^2}} \]

\[ \omega_n = 54.6 \text{ kHz} \]
\[ \eta = 0.135 \]
Transfer function of detector

\[ \tilde{D}(\xi) = \frac{\omega_n^2}{\xi^2 + 2\eta\xi\omega_n + \omega_n^2} \]

\( \omega_n = 54.6 \text{ kHz} \)
\( \eta = 0.135 \)

\[ \bar{D} = \int_0^\infty D(t) \, dt = \lim_{\xi \to 0} \int_0^\infty \exp(-\xi t) D(t) \, dt = \lim_{\xi \to 0} \tilde{D}(\xi) = 1 \]

\[ t_{\text{Deg}} = \frac{\int_0^\infty t \cdot D(t) \, dt}{\bar{D}} = \lim_{\xi \to 0} \int_0^\infty \exp(-\xi t) \cdot t \cdot D(t) \, dt = \lim_{\xi \to 0} \left[ -\frac{d\tilde{D}(\xi)}{d\xi} \right] \]

\[ = \lim_{\xi \to 0} \left[ -\frac{d}{d\xi} \left( \frac{\omega_n^2}{\xi^2 + 2\eta\xi\omega_n + \omega_n^2} \right) \right] = \lim_{\xi \to 0} \left[ \frac{\omega_n^2 \cdot (2\xi + 2\eta\omega_n)}{(\xi^2 + 2\eta\xi\omega_n + \omega_n^2)^2} \right] \]

\[ = \frac{2\eta}{\omega_n} = \frac{2 \times 0.135}{5.46 \times 10^4 \text{ Hz}} = 4.9 \times 10^{-6} \text{ s} \]
Analysis of observed areal heat diffusion time

\[ A_\theta = \int_0^\infty \left[ 1 - \theta(t)/\theta_{\text{max}} \right] dt = \lim_{\xi \to 0} \int_0^\infty \exp(-\xi t) \left[ 1 - \theta(t)/\theta_{\text{max}} \right] dt \]

\[ = \lim_{\xi \to 0} \left[ \frac{1}{\xi} - \frac{\widetilde{\theta}(\xi)/\theta_{\text{max}}}{\theta_{\text{max}}} \right] = \lim_{\xi \to 0} \left[ \frac{1}{\xi} - \frac{\widetilde{D}(\xi) \cdot \widetilde{R}_{rf}(\xi) \cdot \widetilde{q}_f(\xi)}{\widetilde{D} \cdot R_{rf_{\text{max}}} \cdot \bar{q}} \right] \]

\[ = \lim_{\xi \to 0} \left[ \frac{1}{\xi} - \frac{(1 - \xi \cdot t_{Dcg}) \cdot \widetilde{D} \cdot \widetilde{R}_{rf}(\xi) \cdot (1 - \xi \cdot t_{qcg}) \cdot \bar{q}}{\widetilde{D} \cdot R_{rf_{\text{max}}} \cdot \bar{q}} \right] \]

\[ = \lim_{\xi \to 0} \left[ \frac{1}{\xi} - \frac{\widetilde{R}_{rf}(\xi)}{R_{rf_{\text{max}}}} \right] + t_{Dcg} + t_{qcg} = A_T + t_{Dcg} + t_{qcg} \]

\[ A_T = A_\theta - t_{Dcg} - t_{qcg} \]
Correction of observed areal heat diffusion time for finite duration of the heating function and finite response of temperature detector

**Ideal signal**

\[ A = A_\theta - t_{qcg} - t_{Dcg} \]

**Observed signal**

\[ A_\theta = A + t_{qcg} + t_{Dcg} \]

- **Impulse heating**
- **Infinitely fast response**
- **Finite duration of heating**
- **Finite response**
Uncertainty evaluation for pulsed light heating methods

1. Heat diffusion time: $\tau_0$  
   - Evaluated by transfer function and areal heat diffusion time
   - Heating
   - Heat conduction equation
     - Shape and dimensions of the specimen
     - Boundary conditions
     - Heating method and position
     - Temperature detection method and position
   - Temperature detection
     - Nonlinearity
     - Response time

2. Thickness of the specimen: $d$

3. Steady temperature of the specimen: $T$

Thermal diffusivity at $T$

$$\alpha = \frac{d^2}{\tau_0}$$
Summary

• Light pulse heating methods have been developed to measure thermal diffusivity from bulk materials thicker than 1 mm to films thinner than 100 nm.

• One dimensional heat diffusion can be analyzed by the response function method and the areal heat diffusion time method.

• Uncertainty of finite heating distribution, evaluation of heat diffusion in material and finite response of detector can be universally analyzed by transfer functions and areal heat diffusion time.