Development of certified reference material of thin film for thermal diffusivity

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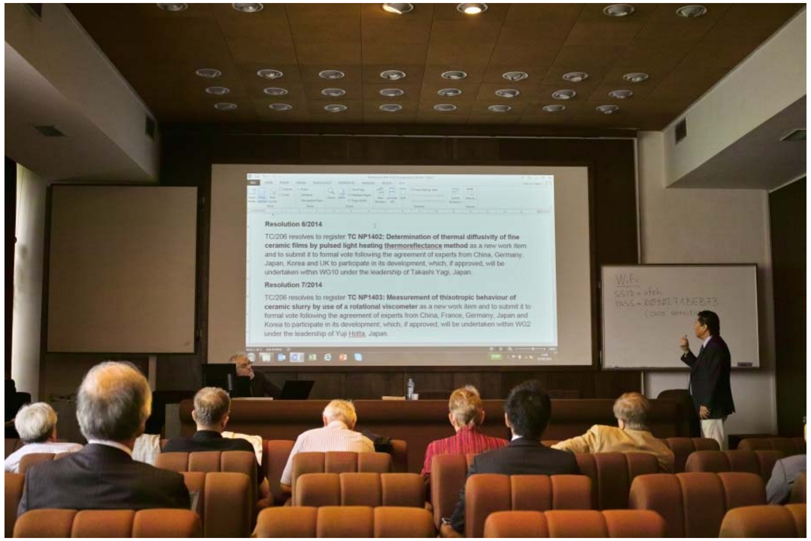
Status of ISO standardization

- ISO/TC206(fine ceramics)

“TCNP1402 - Determination of thermal diffusivity of fine ceramic films by pulsed light heating thermoreflectance method”

- At the last plenary meeting of ISO/TC206, it has bee approved to be treated in WG10(coatings).



TC206 meeting at Praha, Czech, 3, Oct. 2014

Scope of the project

- **Standardization of ISO** for thermal diffusivity of thin films.
- Development of **a reference thin film**.
- Development of **an accurate analysis technique**.

Benefit for instrument users

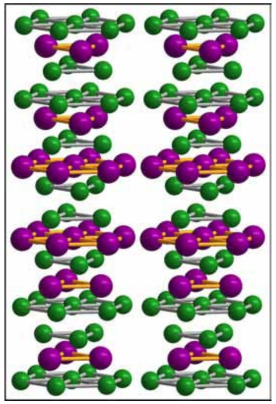
Reliable and quantitative themophysical data

I look forward to new an ongoing collaborations, especially in the area of thermoelectrics and other energy conversion technologies

Thermoelectric element (Dr. Joshua Martin, NIST)

$\boldsymbol{ZT = S^2\sigma T/\kappa} \leftarrow$ Thermal conductivity

- ✓ Electricity from heat
- ✓ Future goal, ZT = 2~4
- ✓ Reliable $\boldsymbol{k}$ data are needed.

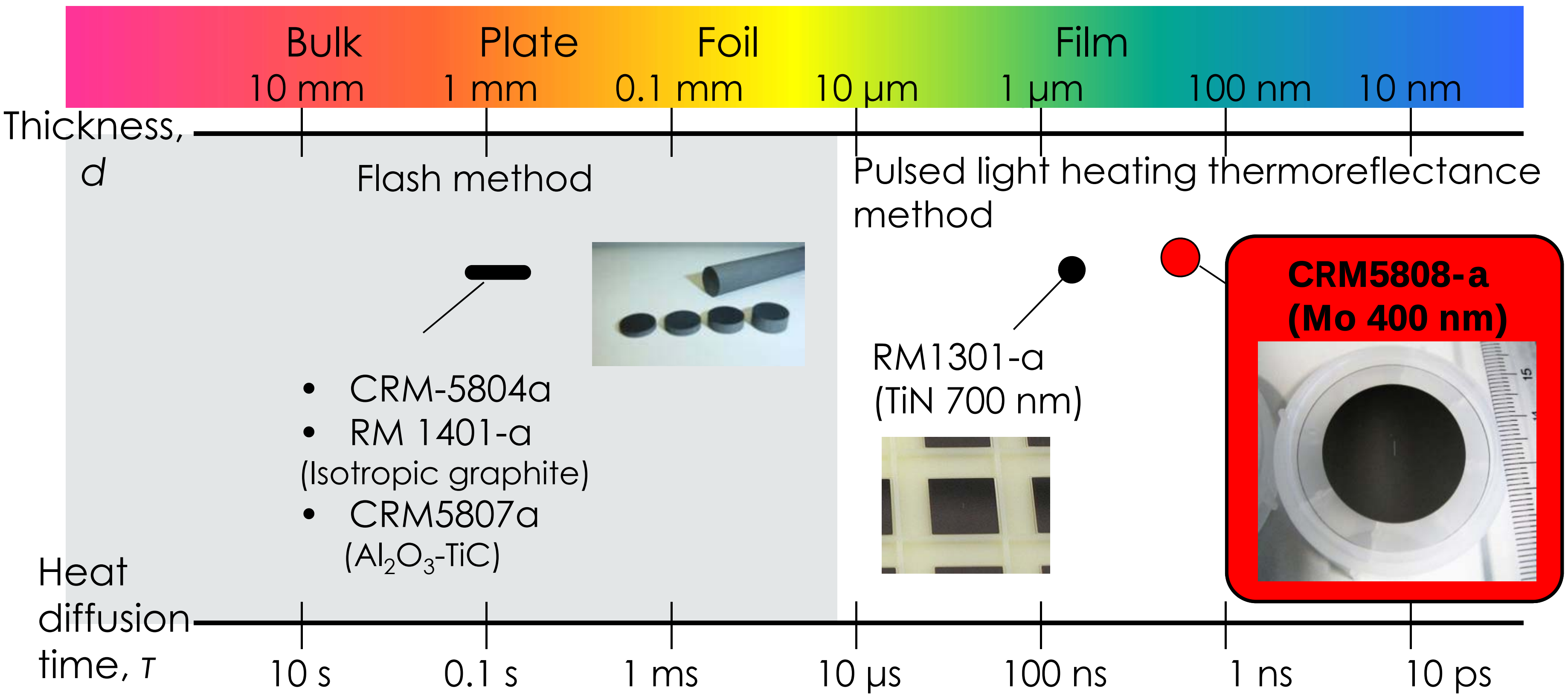


MML, NIST website

"Especially for the case of thin film thermoelectric materials, there are currently no methods to accurately and reproducibly measure the material properties."

Thermal diffusivity standard (RM and CRM) distributed by NMIJ

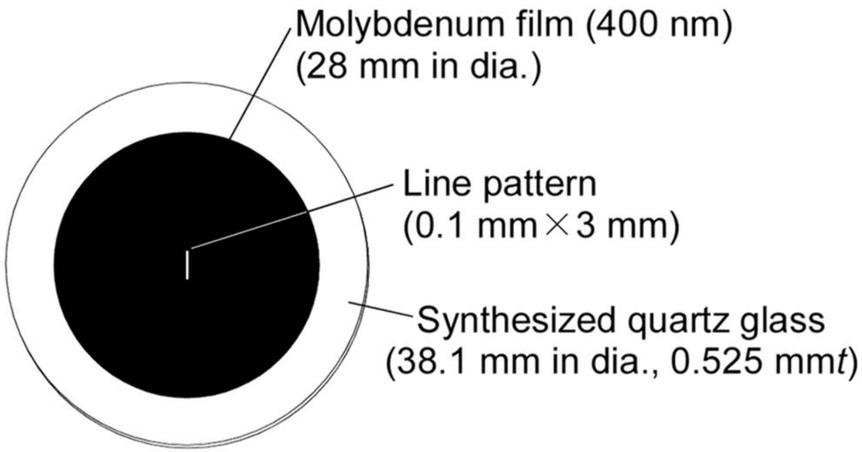
- NMIJ/AIST distributes RMs and CRMs for thermal diffusivity.
- Metal film (Molybdenum, 400 nm) is newly developed.

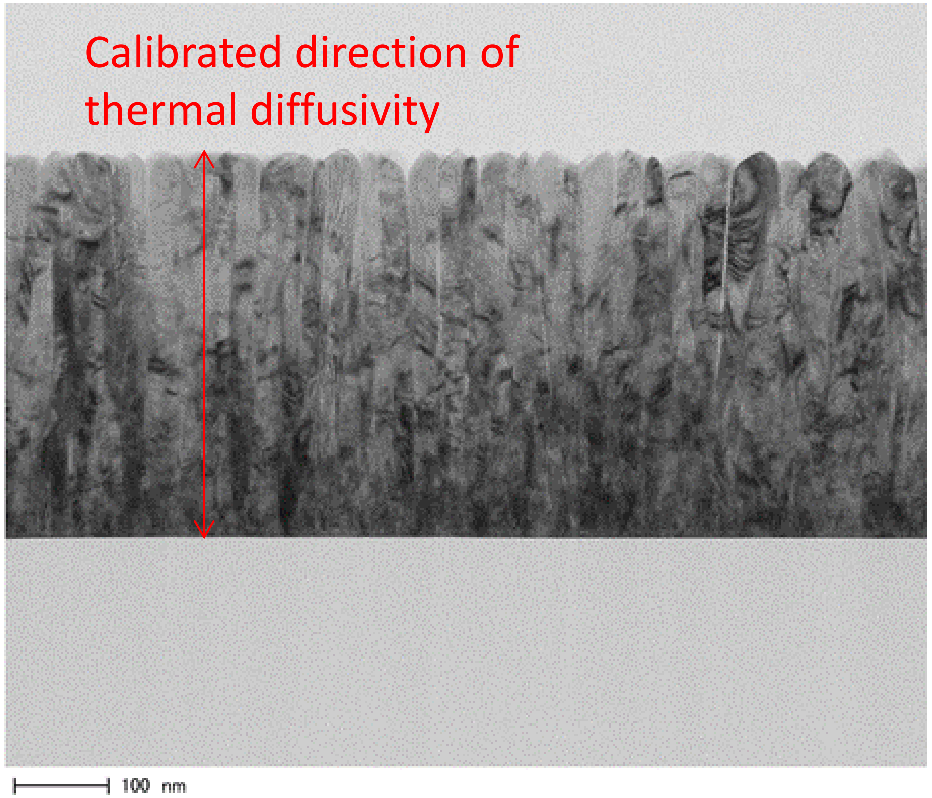


(Thermal diffusivity, $\kappa = 1\times10^{-5}\,\mathrm{m^2 s^{-1}}, \quad \tau = d^2/\kappa$)

CRM 5808-a

- Mo 400 nm (Nominal) was deposited on a quartz glass wafer.
- Thermal diffusivity (normal to plane) has been calibrated.
- 50 films were made and 8 films were sampled for the calibration.

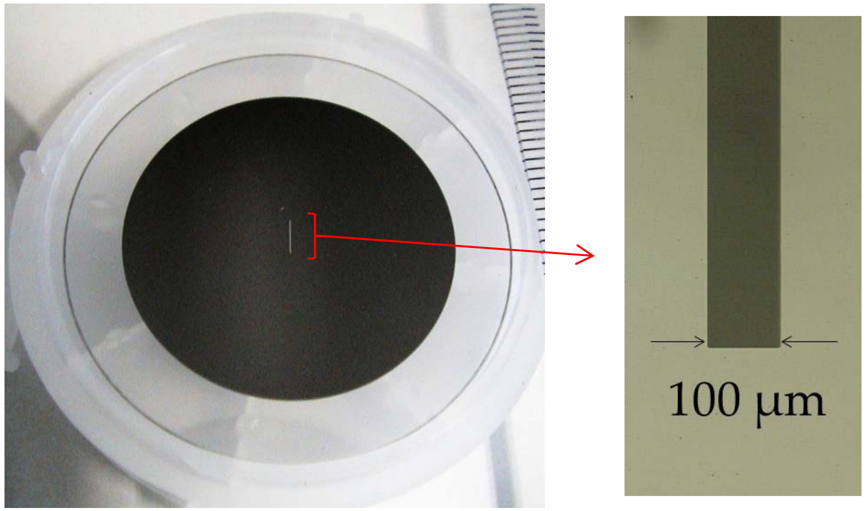




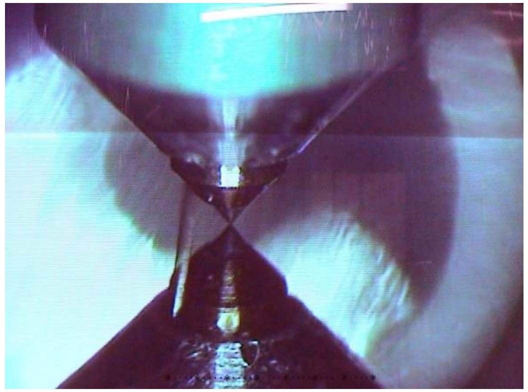
Thickness of the CRM 5808-a

- Thickness is necessary to determine the thermal diffusivity.
- Step of the etched line pattern located at the center of the film was measured using a calibrated stylus profiler.

Heat diffusion time across the film $\tau = \frac{d^2}{\alpha}$ Thickness, Thermal diffusivity



Etched line pattern (100 um x 3 mm)

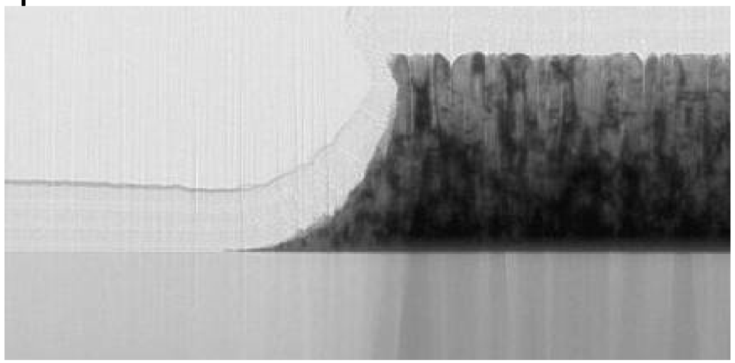


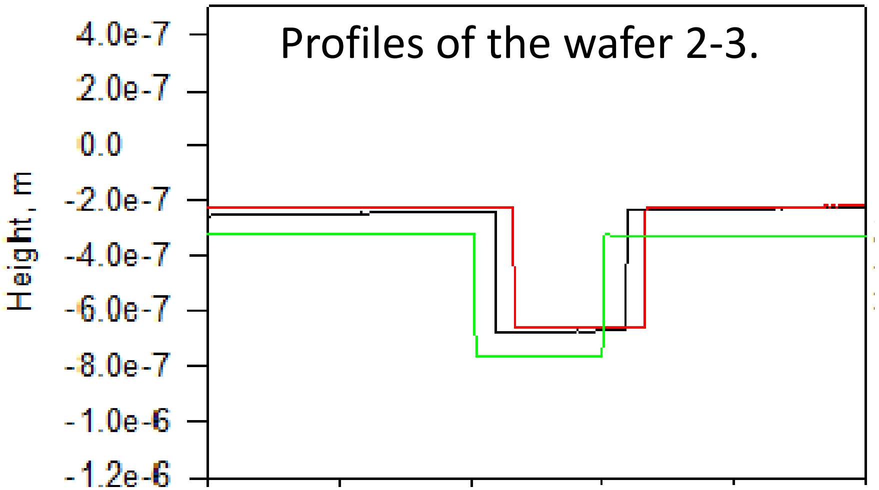
- ✓ Nanostep 2, Taylor-Hobson
- ✓ 2 um stylus
- ✓ UKAS standard(0.41 um) was used for calibration.

Thickness of the CRM 5808-a

- The average thickness and standard deviation of the sampled 8 films were 421.3 nm and 0.53 nm.

Cross-sectional TEM at the etched pattern of the film.



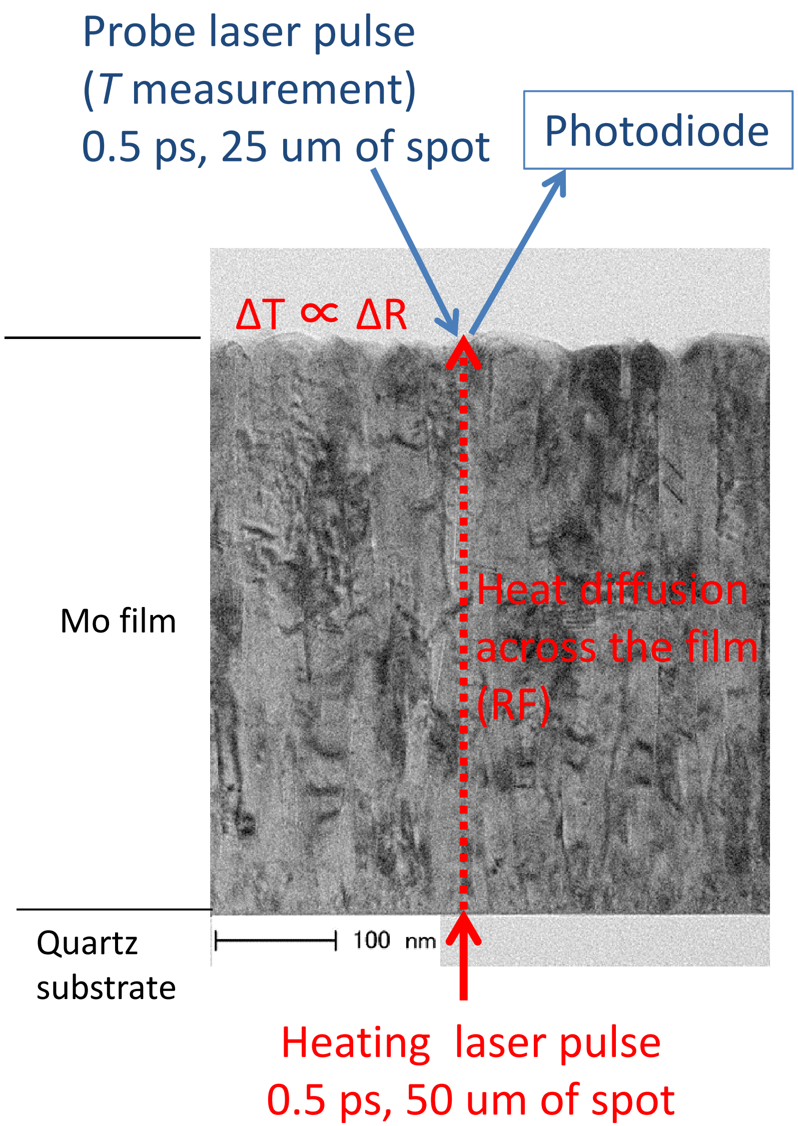


Profiles of the wafer 2-3.

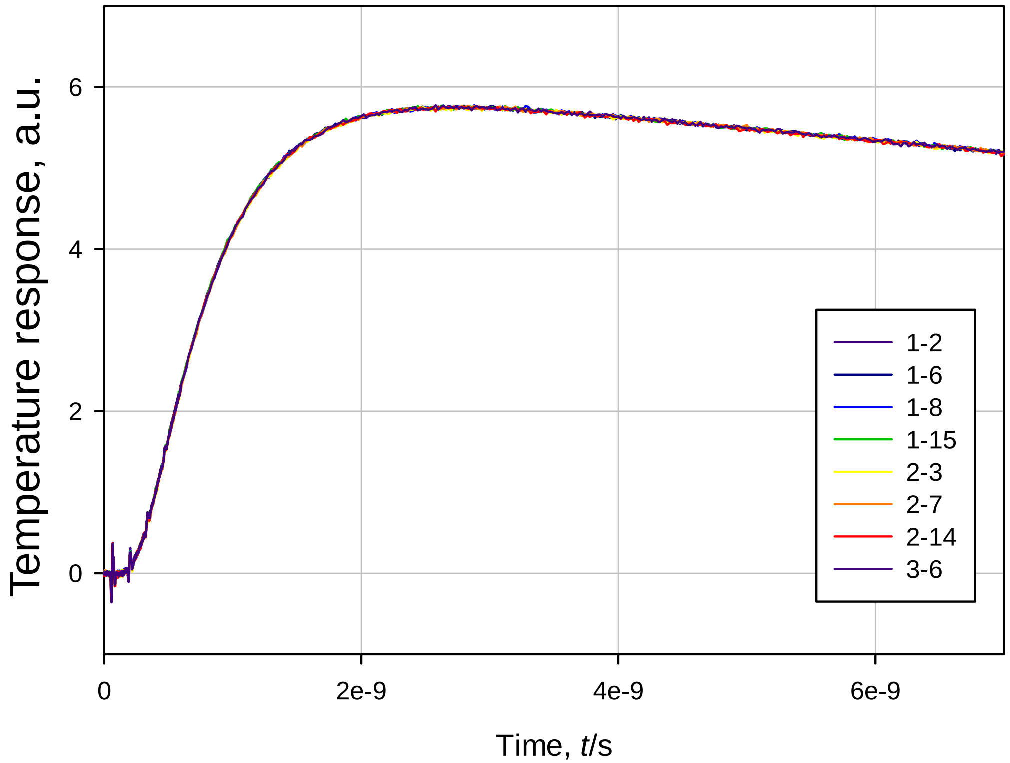
Measurement result for sampled 8 wafers.

Wafer No.	*d* (nm)
1-2	420.5
1-6	420.6
1-8	421.5
1-15	421.4
2-3	421.5
2-7	421.0
2-14	421.5
3-6	422.1
Average	421.3
Std	0.53

Heat diffusion across the film
(Pulsed light heating thermoreflectance)

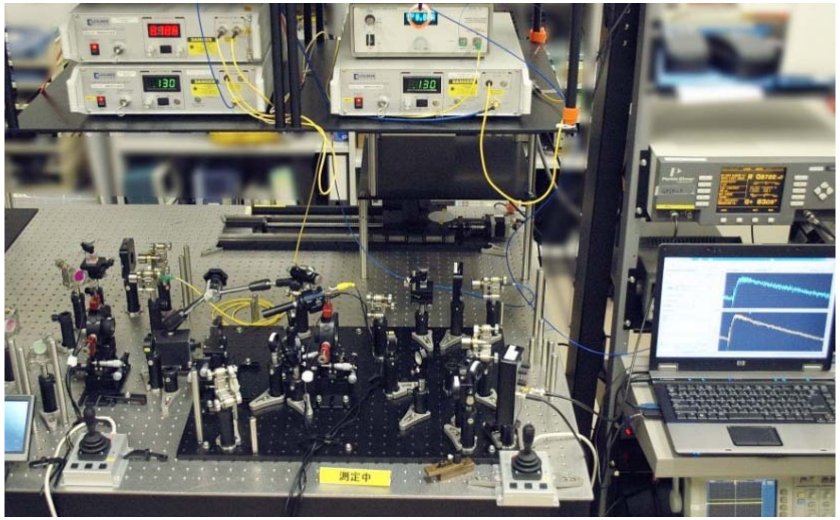


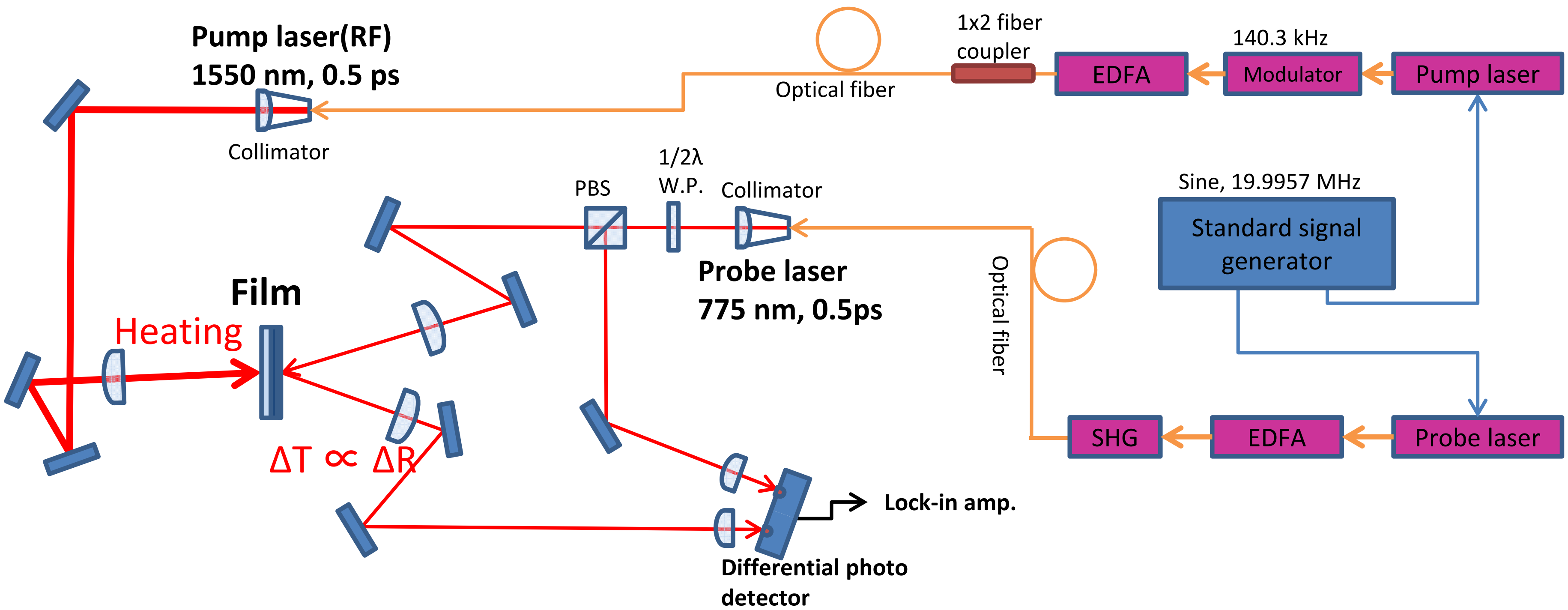
Transient temperature response at the film surface after the pulse heating for the sampled 8 films.



Pulsed light heating thermoreflecatance

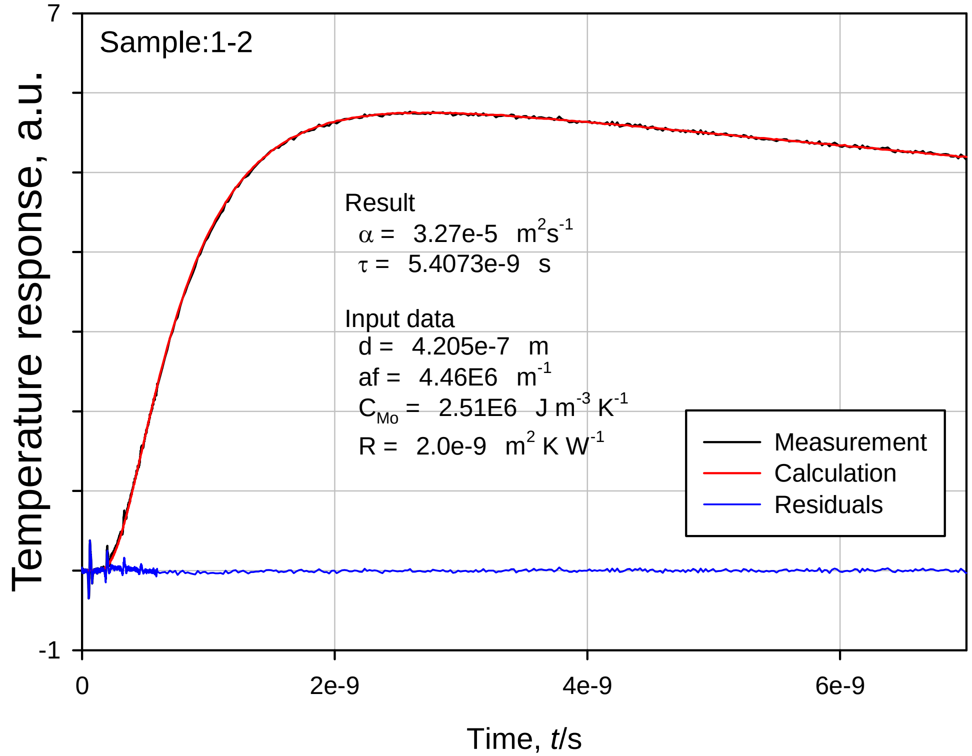
- Measurement of **heat diffusion time across the film**.
- Two mode-locked Er-doped fiber lasers (0.5 ps) were used for heating and temperature change measurement.
- 1 ps of delay time control with maximum 50 ns of length.
- Available thickness: 100 nm to 1000 nm (metal film)

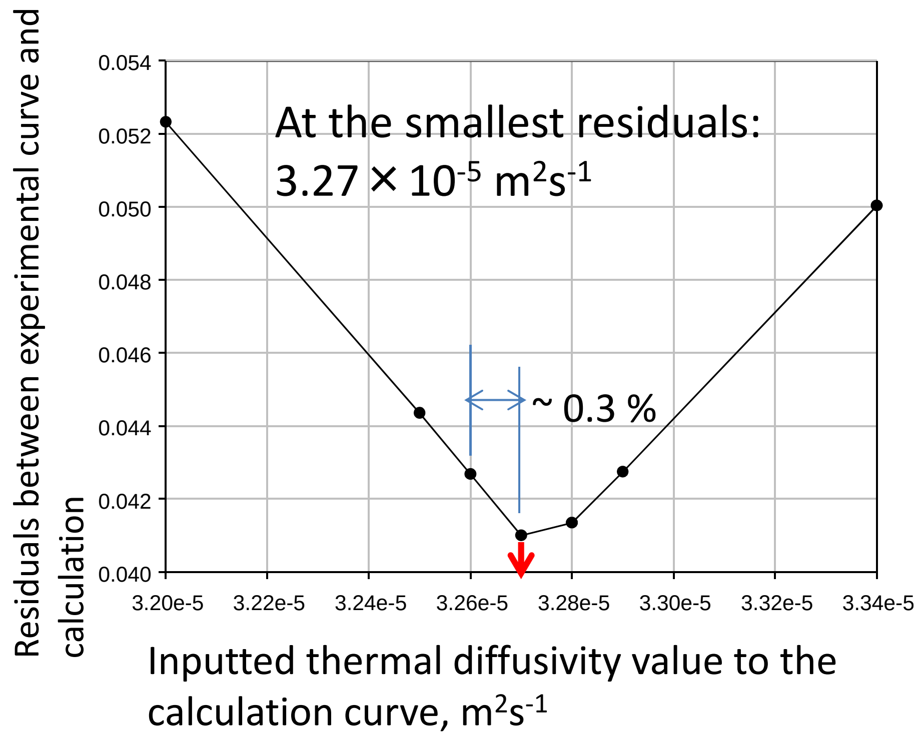




Sensitivity of analysis

- Difference of 0.3% of thermal diffusivity can be detected.





Error budget for CRM5808-a

Material:	Molybdenum
Average thickness:	421 nm
Thermal diffusivity:	3.28×10^{-5} m2s^{-1}
Expanded Uncertainty (*k*=2):	6.2 %

For example, NMJ Laser flash method (bulk materials) : 3.1 % (*k*=2)

Factor	Value		Sensitivity		Uncertainty, m^2s^{-1}	Relative uncertainty
Analysis, u_{calc}	1.0×10^{-7}	m^2s^{-1}	$1/\sqrt{3}$		0.0058×10^{-5}	0.18 %
Thermophysical values used for analysis, u_v	3.0×10^{-7}	m^2s^{-1}	$1/2\sqrt{3}$		0.0087×10^{-5}	0.26 %
Time, u_0	2.0×10^{-12}	s	76376.26	$m^2\,s^{-2}$	0.015×10^{-5}	0.47 %
Thickness, u_d	6.3×10^{-9}	m	155.5291	$m\,s^{-1}$	0.098×10^{-5}	3.00 %
Reproducibility of measurement, u_r	1.0×10^{-7}	m^2s^{-1}	1		0.010×10^{-5}	0.32 %
Inhomogeneity, σ_B	1.8×10^{-7}	m^2s^{-1}	1		0.018×10^{-5}	0.53 %
Combined uncertainty (*k* = 1)					**0.10×10^{-5}**	**3.1 %**
Expanded uncertainty(*k* = 2)					**0.20×10^{-5}**	**6.2 %**

We will distribute the CRM5808 as soon as possible.

We aim to add the CRM to the ongoing ISO, e.g. informative annex.

Summary

- We developed the measurement technique for thermal diffusivity of thin films and the CRM. Those results will be involved in the ongoing ISO proposal.

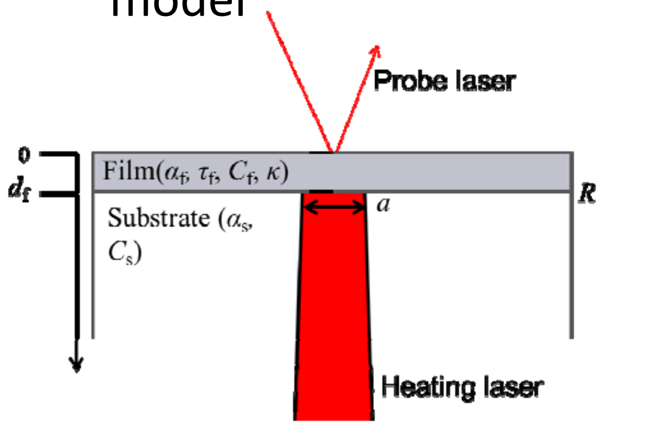
- The above results can be utilized for the scope of the MML, NIST, especially thermoelectric materials.

Analysis technique

Experimental data includes following effects,

- temperature response of pulse heating,
- Conversion from *T* to TR signal,
- Lock-in detection (= Fourier transform) for photo diode signal.

1. Heat conduction model → 2. Conversion → Reproducing measurement data

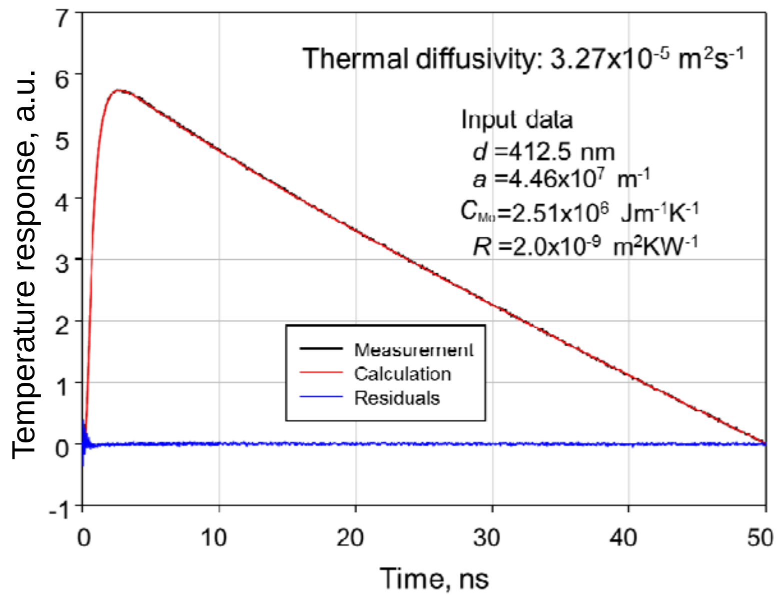


- ✓ Thermophysical properties of film, substrate and interface.
- ✓ Apparatus constants (pulse width, spot diameters, etc.)

2. Conversion

- ✓ TR signal
- ✓ Lock-in detection

Reproducing measurement data



*Front heating data is also available based on the analysis manner.

Thermoreflectance
-for temperature change probe-

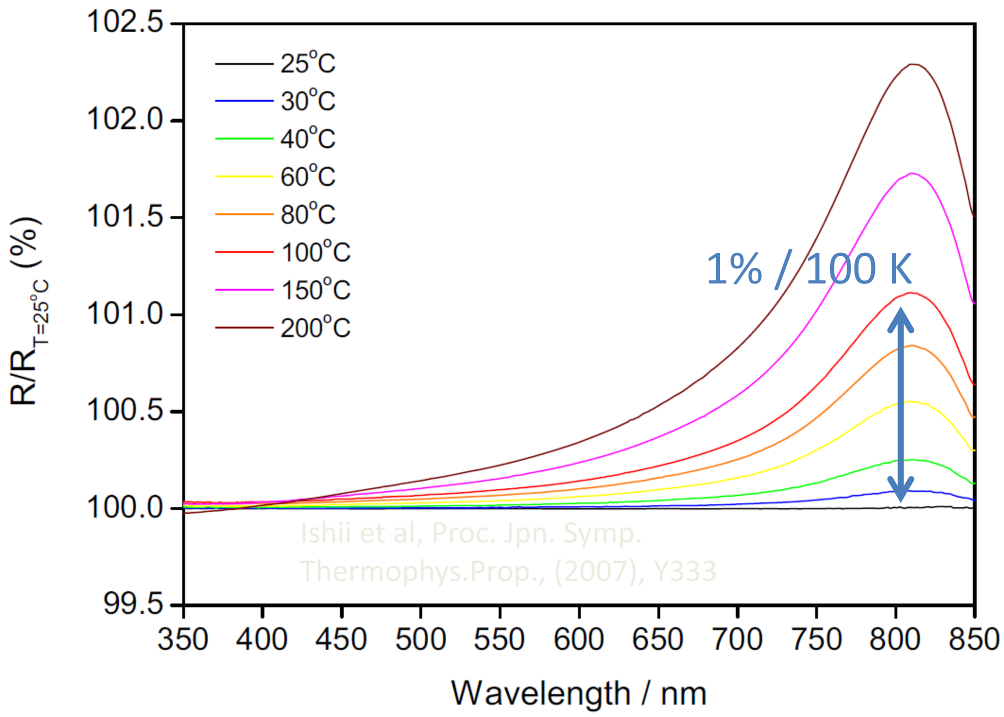
- Reflectivity change can be useful probe to detect a temperature change of materials.
- If we use a pulsed laser beam as a probe, nano- ~ pico-second time resolution can be achieved.

Reflectivity of metals

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

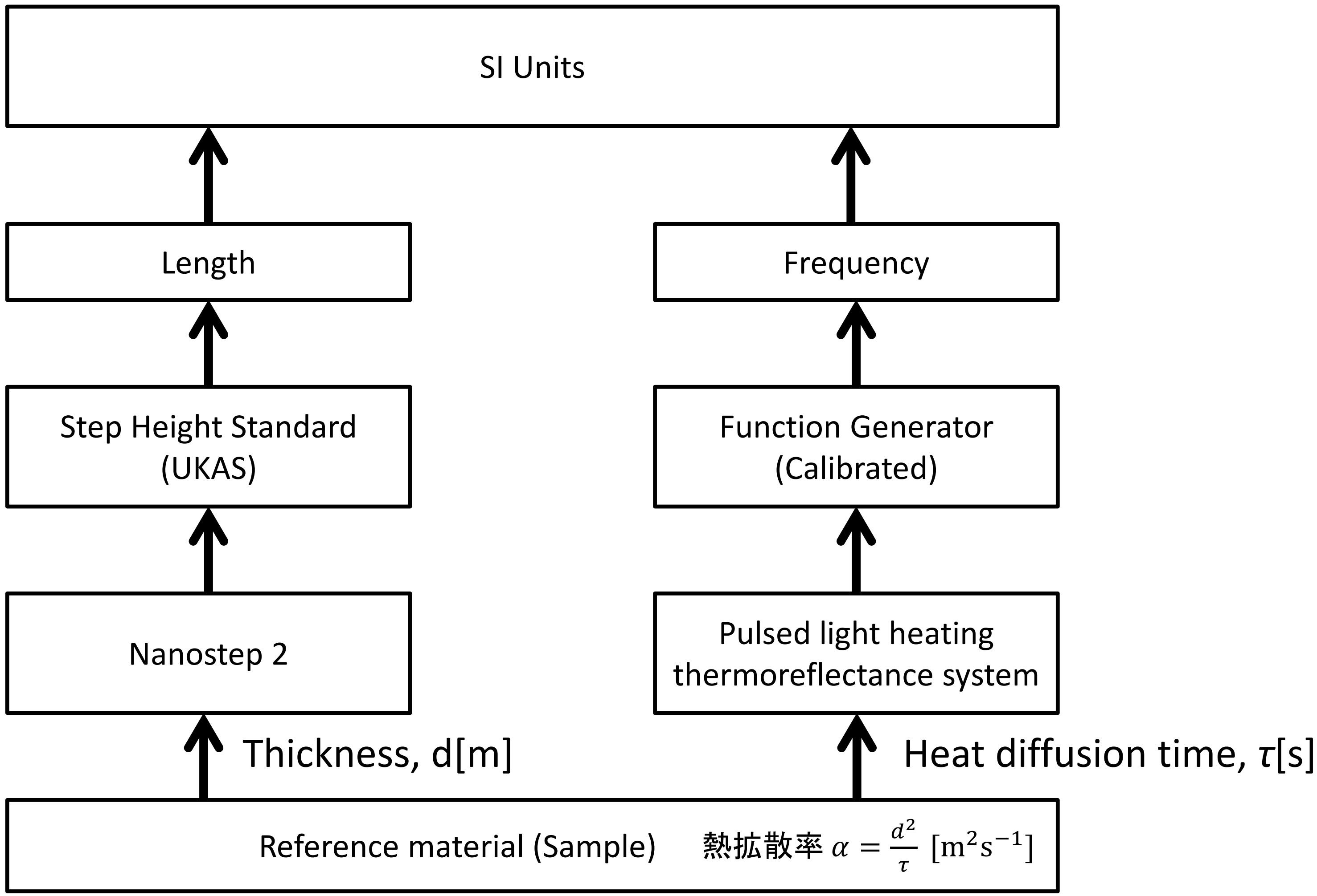
$$\frac{1}{R}\frac{dR}{dT} = 10^{-4} \sim 10^{-5}\ K^{-1}$$

Spectral reflectivity change of Aluminum



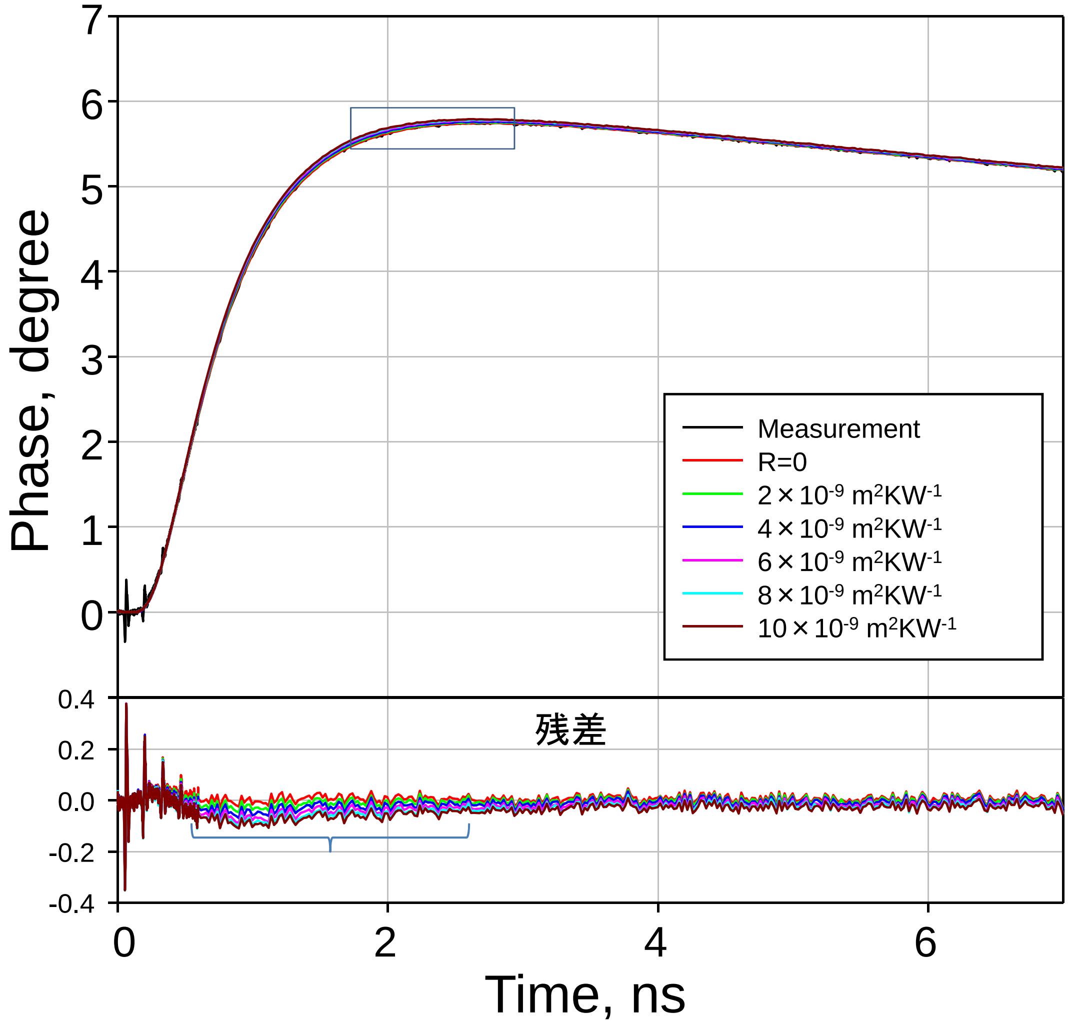
Traceability for thermal diffusivity

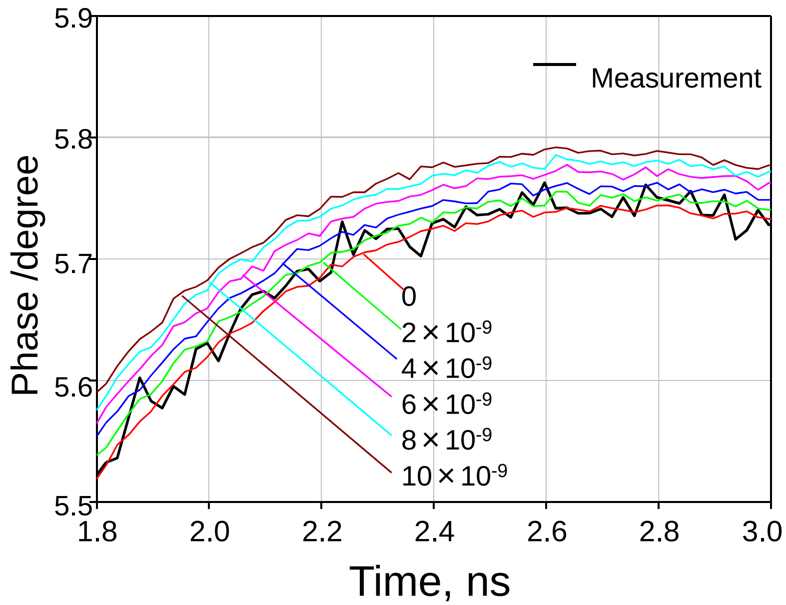
- Thermal diffusivity value is traceable to Length and Frequency.



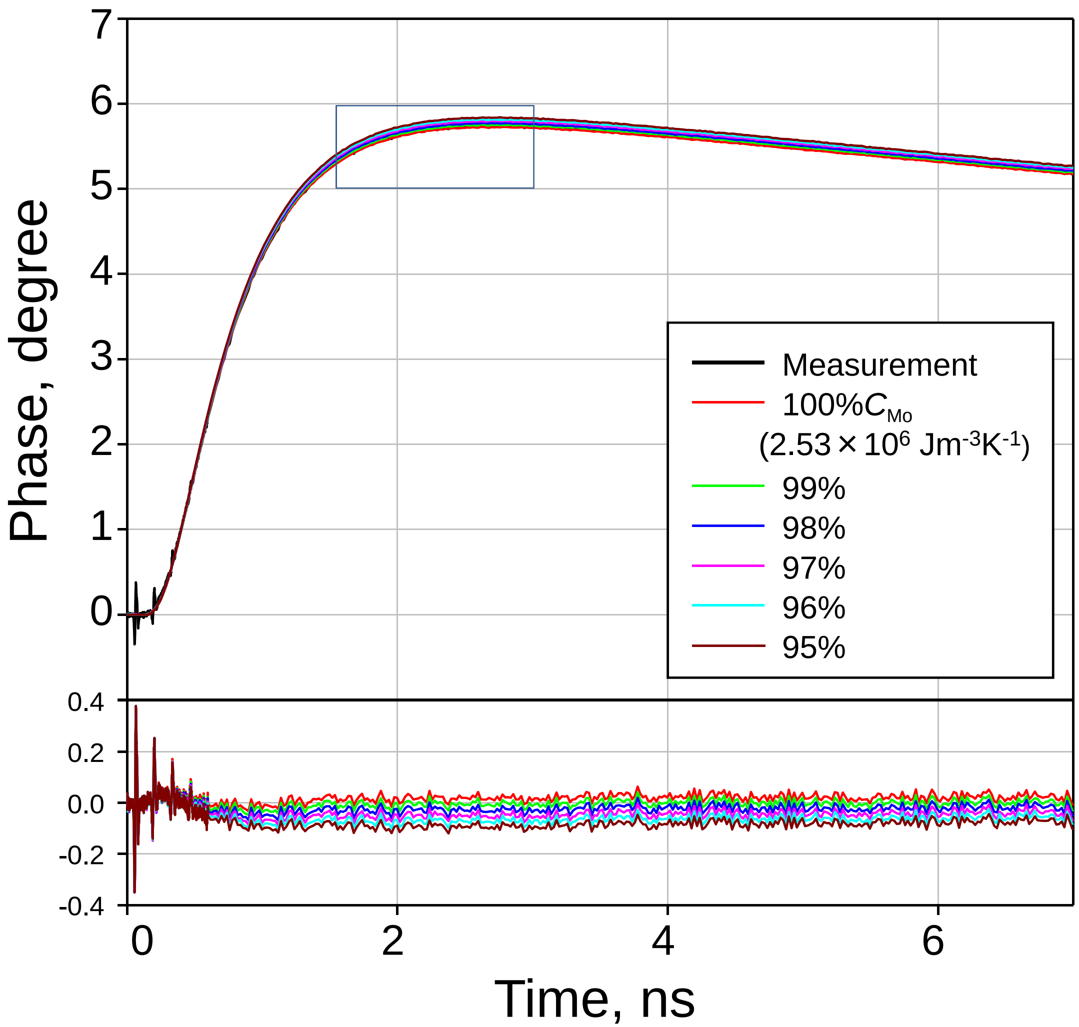
Effect of interfacial thermal resistance between film and substrate

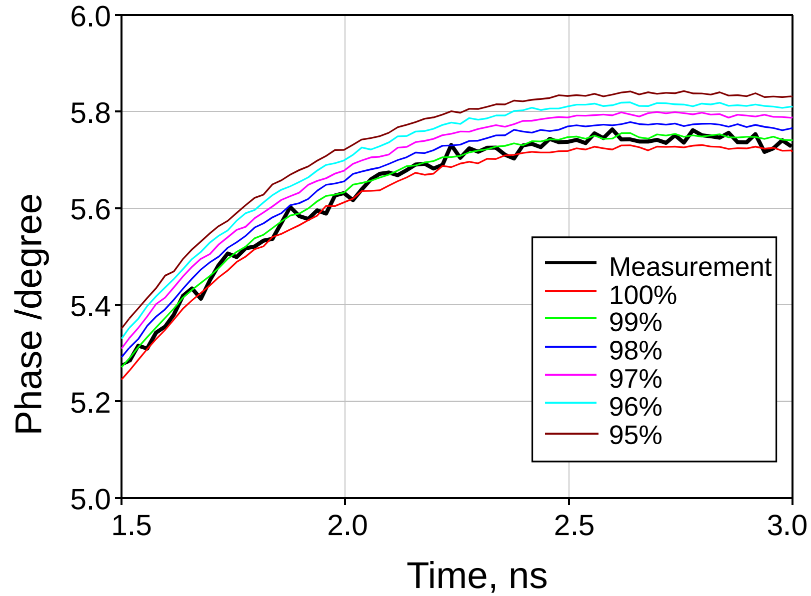
R : 0～10 × 10^{-9} m^2K/W





Example of analysis: effect of heat capacity of the film





Moの熱容量の減少は位相値の増加にはたらく。

Rと効果は似ているが、より長時間まで影響は続く。