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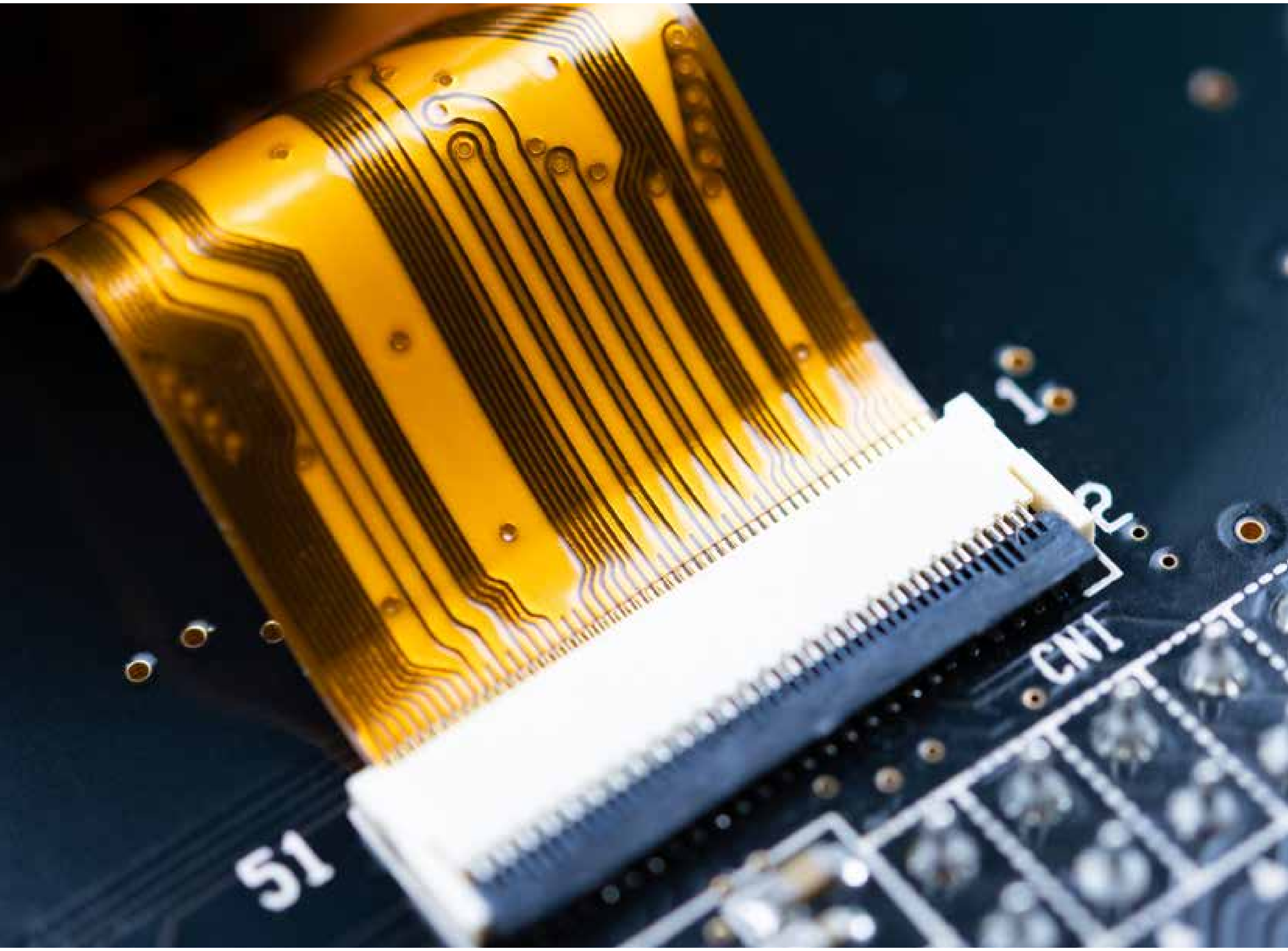
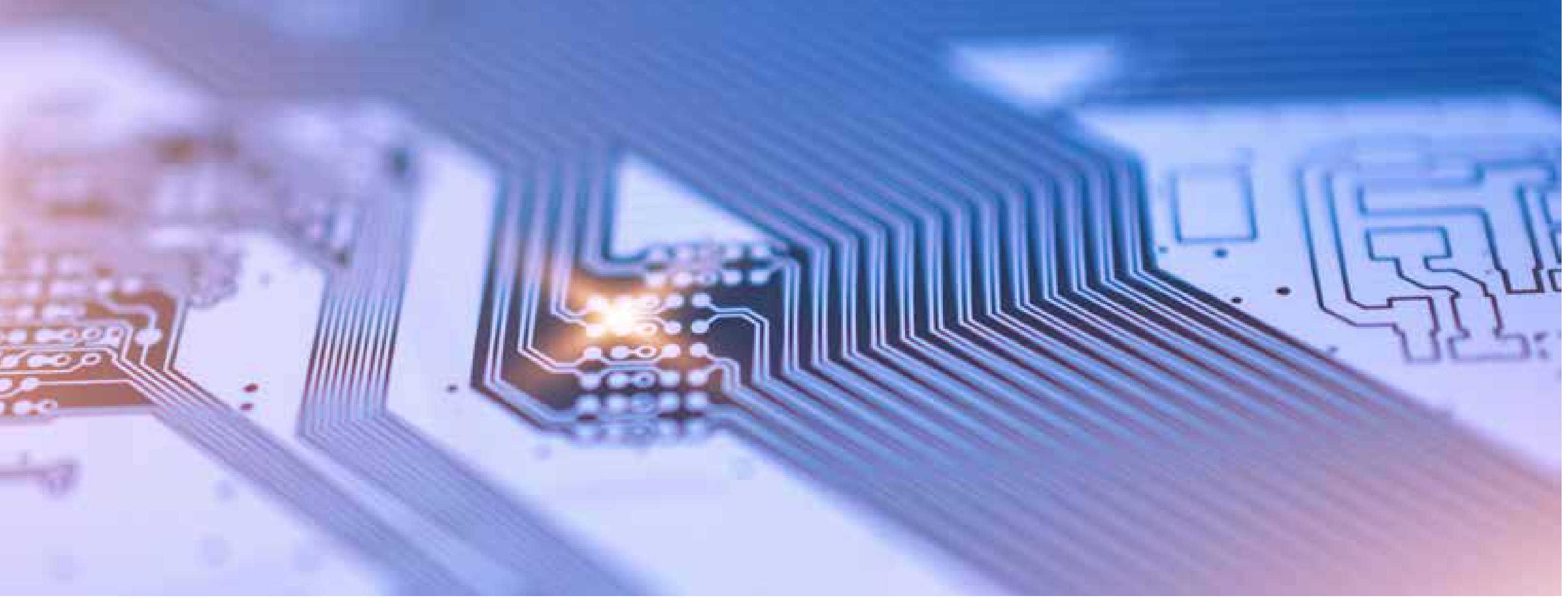


Thermoreflectance by Pulsed Light Heating

NanoTR/PicoTR

Thermophysical Analysis of Thin Films: Thermal Diffusivity, Thermal Effusivity, Thermal Conductivity and Interfacial Thermal Resistance

Analyzing & Testing



Thermoreflectance

The Laser Flash Method for Thin Films

LASER FLASH METHOD

The Most Established Method for the Determination of the Thermal Diffusivity

In modern industries, knowledge of thermal properties, specifically thermophysical properties, becomes more and more important. They are required, for example, for the development of heat release materials of advanced and miniaturized electronics, thermoelectric materials as sustainable energy, insulating materials for saving energy, TBCs (thermal barrier coatings) for turbine blades, and safety operation of nuclear plants, etc.

Among the thermophysical properties, the thermal conductivity is of paramount importance. The determination of the thermal diffusivity/thermal conductivity can be realized with the established laser flash method (LFA). This method has been known for many years to provide reliable and accurate results. Sample thicknesses typically range from 50 µm to 10 mm.

NETZSCH is a world-wide leading manufacturer of instruments for testing thermophysical properties, specifically laser flash analyzers. These LFA systems are used in the fields of ceramics, metals, polymers, nuclear research, etc.

THERMOREFLECTANCE

The Method for the Determination of the Thermal Diffusivity in the Nanometer Thickess Range

With the significant progress in the design of electronic devices and the associated need for efficient thermal management, accurate thermal diffusivity / thermal conductivity measurements in the nanometer range are crucial more than ever. Materials with such thicknesses are used in phase-change memories (PCM), thermoelectric thin films, light emitting diodes (LED), interlayer dielectrics, and transparent conductive films (FPD), etc.

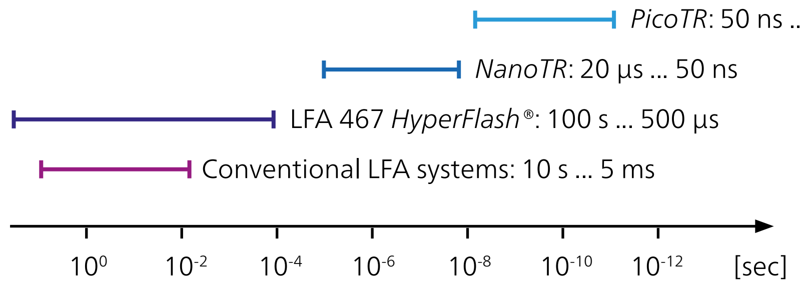
The National Institute of Advanced Industrial Science and Technology (AIST), Japan, already responded to industrial requirements with the development of a "pulsed light heating thermoreflectance method" in the early 90's, which allowed for absolute measurements of the thermal diffusivity of thin films. As an AIST start-up, PicoTherm Corporation was established in 2008 with the launch of a nano-second thermoreflectance apparatus "*NanoTR*" and a picosecond thermoreflectance apparatus "*PicoTR*". These instruments allow for measurements on materials in a thickness range of several 10 µm down into the nanometer range.

In 2020, PicoTherm Corporation joined the NETZSCH Group as a wholly owned subsidiary of NETZSCH Japan, K.K. In combination with our LFA systems, NETZSCH can now offer the solution for thin films in the nanometer range up to bulk materials in the mm range.

Possible Heat Diffusion Times

Heat Diffusion Time $\tau = \frac{d^2}{\alpha}$

where
d = thickness
α = thermal diffusivity



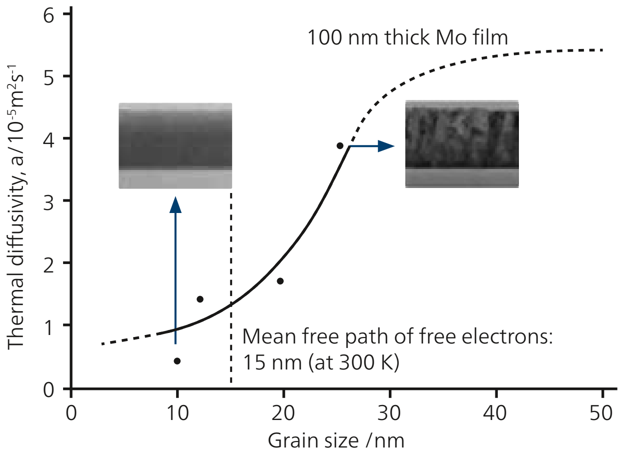
WHY MEASURING THIN FILMS?

Thermophysical Properties of Thin Films are Different from that of Bulk Materials

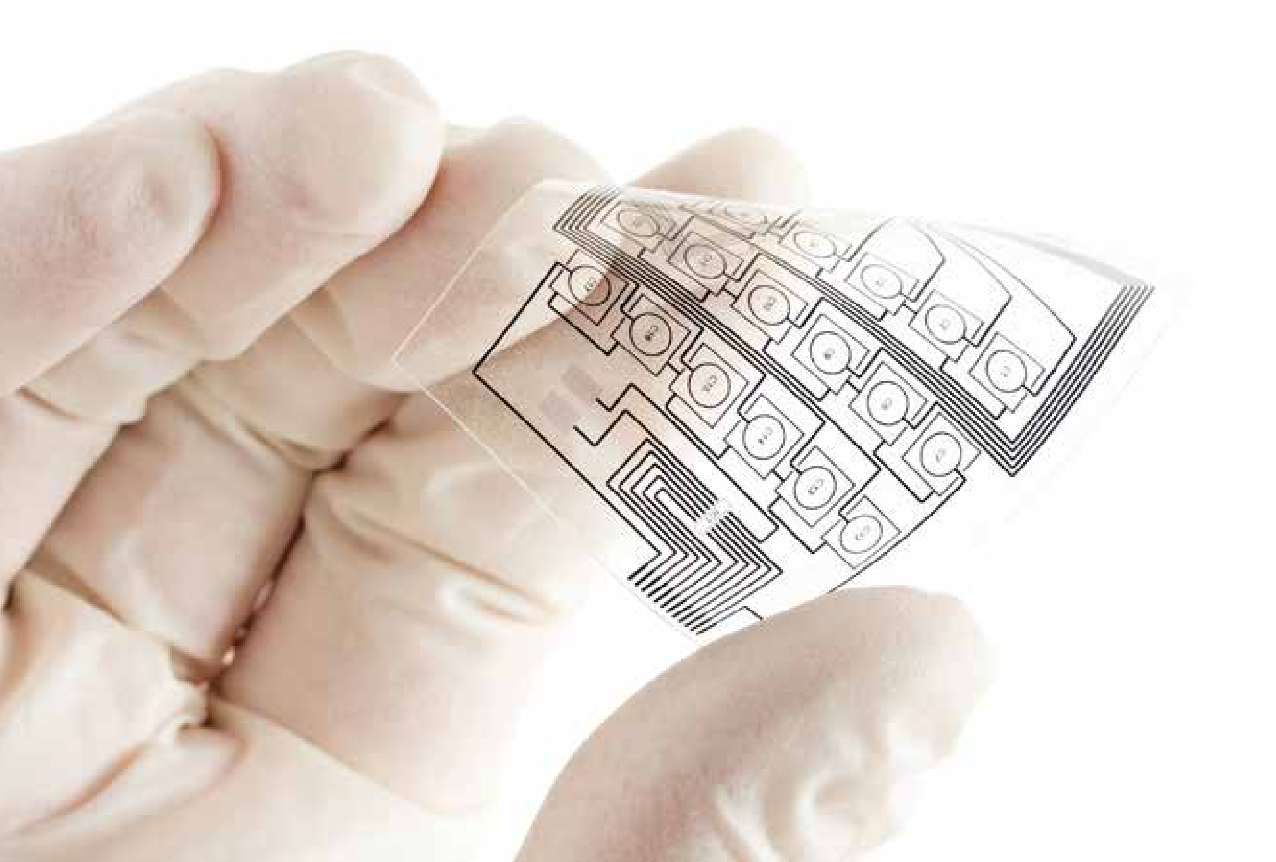
The thicknesses of nanometer-thin films are often less than the typical grain size. Consequently, their thermophysical properties differ significantly from the bulk material.

The plot below indicates the dependency of thermal diffusivity on the grain size. At decreasing grain size (film thickness), the thermal diffusivity values decrease, especially close to the mean free path of electrons (~1.5×10^{-5} m²/s at 15 nm). The thermal diffusivity of bulk material is ~5.4×10^{-5} m²/s and therefore three to four times higher.

For this reason, it is essential to determine the thermal diffusivity of thin films as well.



Thermal diffusivity of a molybdenum (Mo) thin film compared to bulk material; Japanese Journal of Applied Physics 48 (2009) O5ECO1; Furnished by AIST



Thermoreflectance Measures the Change in Reflected Light Due to a Change in Temperature

The thermoreflectance technique makes use of the material's temperature-dependent reflectivity. By measuring the reflected energy of a constant laser probe, the surface temperature fluctuations can be accurately monitored. Thermoreflectance usually performs much faster than the conventional radiation-sensing IR detector.

$$\Delta T = \left[\frac{1}{R}\frac{\partial R}{\partial T}\right]^{-1} \frac{\Delta R}{R}$$

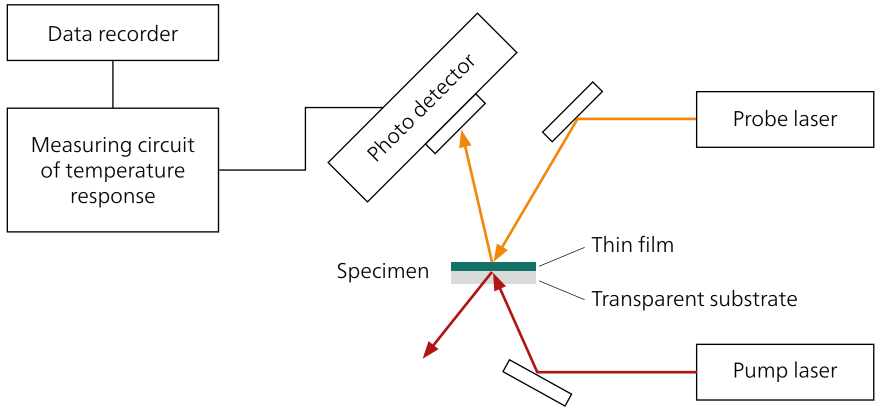
where

ΔT = change in temperature
R = reflectivity
ΔR = change in reflectivity

Application Range

- Thermoelectric materials, solar cells, fuel cells, OLEDs
- Semiconductor memory, storage, metals, FeRAM, MRAM, PRAM, LSI, power devices, phase changes and magnetic recording films, diffusion barrier films
- LED, ceramic composites, electronics, resins for insulation films, transparent conductive films for FPD, interlayer dielectrics, gate insulators

WHAT IS THERMOREFLECTANCE?



Measurement Principle

The front surface of a thin film on a transparent substrate is heated by a pulsed laser source for heating (pump laser). At the same time, the front or rear surface of the thin film is irradiated by a laser source for temperature monitoring (probe laser).

Combined with the photo detector, the reflectivity can be evaluated as a function of time, and the curve of the temperature rise can be obtained. By fitting the mathematical model to the history curve of the temperature, the thermal diffusivity can be determined.

Thermoreflectance Methods

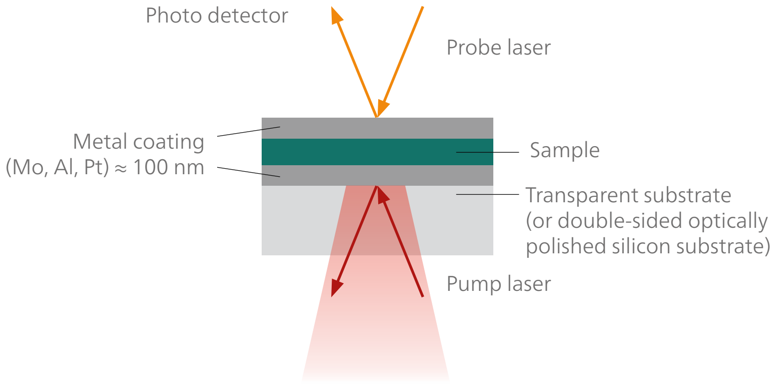
TIME DOMAIN THERMOREFLECTANCE – REAR HEATING/FRONT DETECTION (RF)

Determination of Thermal Diffusivity and Interfacial Thermal Resistance

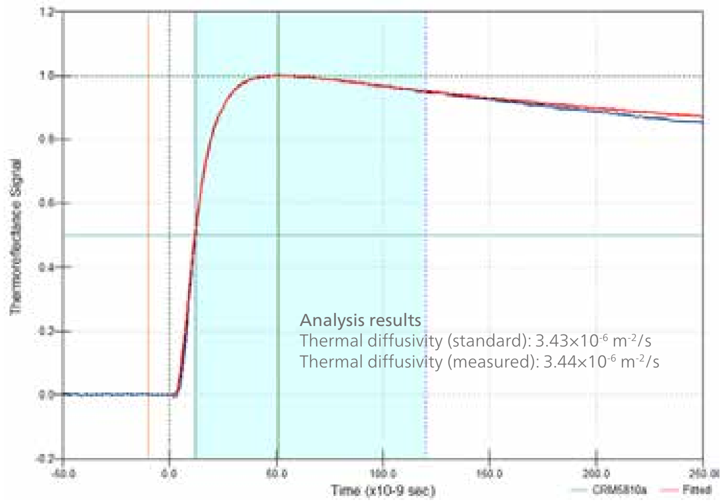
The fact that the thermophysical properties of thin layers and films differ considerably from those of the corresponding bulk material requires a technique which overcomes the limitations of the classical laser flash method (LFA). This so-called ultrafast laser flash technique is also known as rear heating/front detection (RF) mode.

The measurement setup is similar to the conventional LFA: detector and laser are on opposite sides of the sample which is located on a transparent substrate. The measured thermal diffusivity is the component through the thickness perpendicular to the sample's surface. The pump laser irradiates the sample's rear side (upper picture).

As the sample heats up, its surface thermoreflectance varies. The thermal diffusivity is calculated from the temperature rise (lower plot). Here, the thermal diffusivity of a titanium nitride (TiN) thin film was determined to 3.44×10^{-6} m²/s.



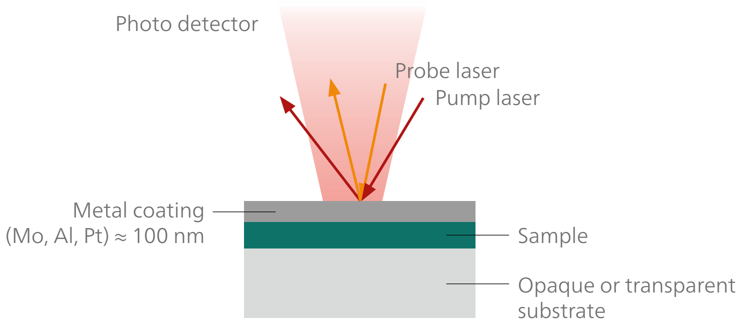
RF configuration specifically for transparent substances



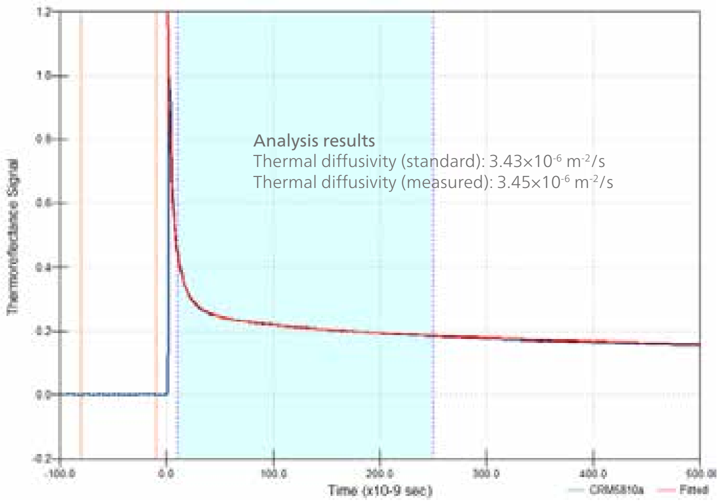
Temperature history curve by RF mode
Measurement with a certified reference material for thermal diffusivity (NMIJ CRM 5810-a: titanium nitride thin film 543.8 nm on quartz glass)

TIME DOMAIN THERMOREFLECTANCE – FRONT HEATING/FRONT DETECTION (FF)

Determination of Thermal Effusivity and Interfacial Thermal Resistance



FF configuration specifically for opaque substrates



Temperature history curve by FF mode
Measurement with a certified reference material for thermal diffusivity (NMIJ CRM 5810-a: titanium nitride thin film 543.8 nm on quartz glass)

In addition to the RF mode, measurements can also be made in a front heating/front detection (FF) configuration. The term "front" refers to the outermost surface of the thin film deposited on a substrate, while "rear" refers to the boundary between the thin film and the substrate.

In the FF mode setup (upper picture), the detector and laser are on the same side of the sample. An area of the front face of the thin film with a diameter of several tens of micrometers is heated by a pump laser, and a probe laser points at the same position. The change for the surface temperature is observed.

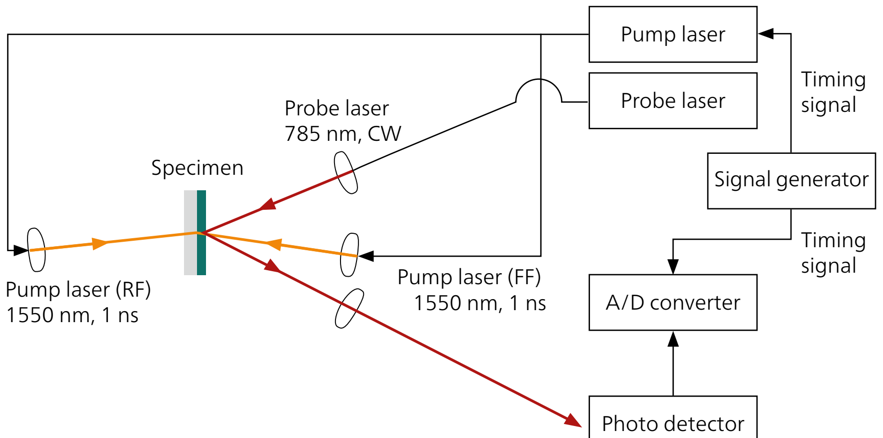
This method can be applied to thin layers on non-transparent substrates for which the RF technique is not suitable.

In the example on the left, the thermal diffusivity of a titanium nitride (TiN) thin film was determined to 3.45×10^{-6} m²/s by applying the FF mode. The results prove the high agreement between RF and FF modes (deviation < 1%).

NanoTR

Principle of *NanoTR*

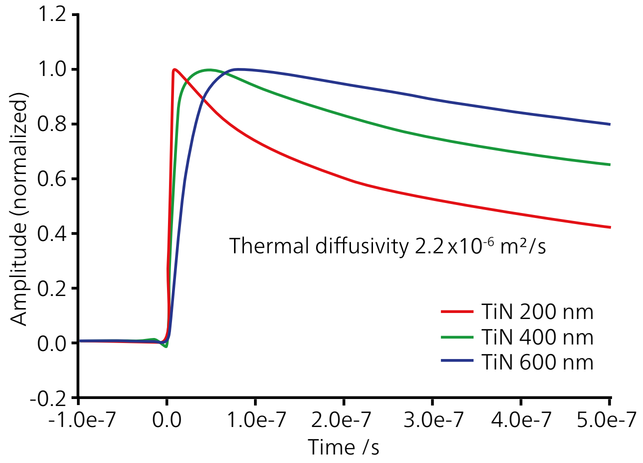
NanoTR's state-of-the-art signal processing technology allows high speed measurements. With this thermoreflectance apparatus, a laser pulse of 1-ns pulse width is periodically (20 µs) irradiated to the sample. The resulting temperature response is applied to a CW laser (probe laser). Excellent s/n ratio can be attained by high speed integration of repetitive signals. It can be easily switched between the RF and FF configurations though the software for a wide variety of samples.



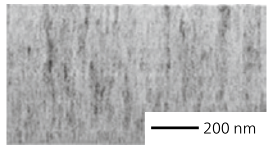
Instrument setup of the *NanoTR* apparatus

NanoTR is in accordance with JIS R 1689, JIS R 1690, and SI traceable by the thin film standard of thermal diffusivity (CRM5810-a), supplied from AIST.

Temperature History Curve of TiN Thin Films Consisting of Different Thicknesses

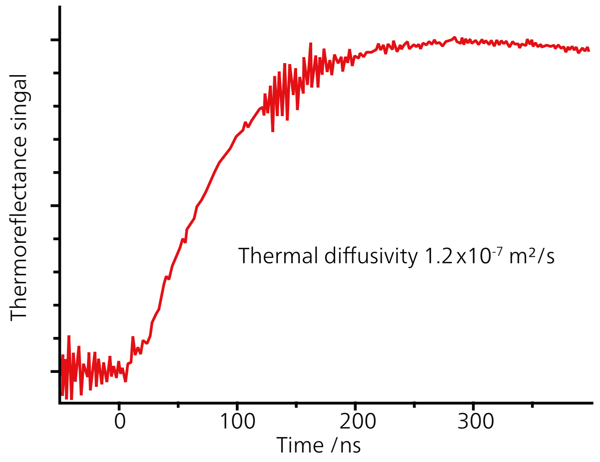


Thermoreflectance signals of TiN films obtained by RF mode

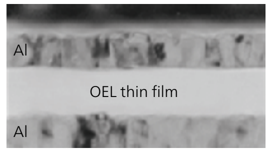


This plot shows temperature excursions of TiN thin films, 200-, 400- and 600-nm thick, measured in the RF configuration. The front surface of the thin films was heated by laser pulses, and the resultant temperature rise of the back surface was monitored.

Temperature History Curve of an OEL Thin Film Between Two Metal Layers



Thermoreflectance signals of an OEL thin film obtained by RF mode



This plot shows the temperature history curve of an OEL thin film, measured in RF configuration. Since the OEL thin film is transparent to the wave length range of the pump and probe laser, Al thin layers were deposited on both sides of the OEL. A threelayer analysis was applied to the temperature curve, resulting in a calculated thermal diffusivity value of the OEL layer of 1.2×10^{-7} m²/s.

Applications

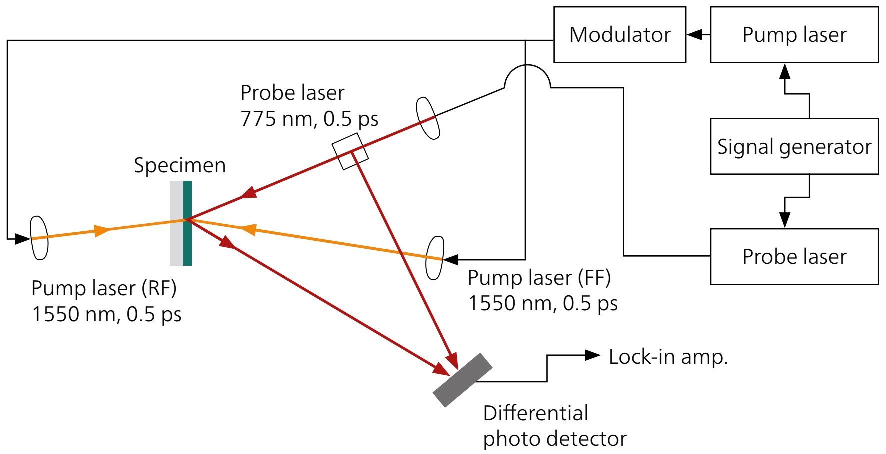
PicoTR

Principle of *PicoTR*

With picosecond thermoreflectance analyzer *PicoTR*, laser pulses (pump laser) of 0.5-ps pulse width are applied to the sample with the time period of 50 ns. The temperature response is detected with the probe laser.

PicoTR allows for easy switching between RF and FF modes by the user.

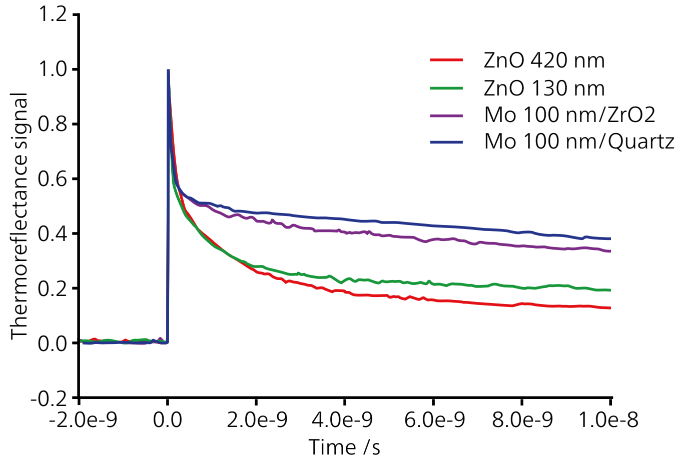
PicoTR is in accordance with JIS R 1689, JIS R 1690.



Instrument setup of the *PicoTR* apparatus

Applications

Temperature History Curve of a ZnO Thin Film on a Transparent Substrate

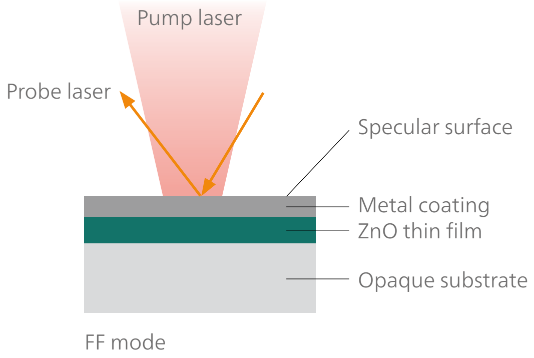


PicoTR measurements on ZnO samples in FF configuration (see picture below): 100 nm Mo on ZnO 420 nm (red); 100 nm Mo on ZnO 130 nm (light green); 100 nm Mo on ZrO$_2$ (purple); 100 nm Mo on quartz (blue)

Due to its wide band gap and large exciton-binding energy, ZnO has been attractive for applications in optoelectronic devices, ultra-violet emitters, sensors, etc.

The plot shows the temperature history curves of translucent ZnO thin films coated by deposited Mo layers on their surface. Sharp peaks are observed immediately after irradiation of the pump laser beam. With increasing time, the decrease in surface temperature can be monitored due to the heat diffusion into the Mo layer. After approximately 1 ns, the heat wave reaches the boundary and starts diffusing into the ZnO layer. The thermal effusivity* (also known as the heat penetration coefficient) is determined to 8570 $J/(m^2 \cdot s^{0.5} K)$.

As expected, this example demonstrates that the cooling rate of the surface temperature is influenced by the thermal effusivity of the second layer.



We kindly thank the National Institute for Material Science (NIMS) for the measurements.

* The thermal effusivity of a material is the square root of the product of the thermal conductivity, density and heat capacity. It is a measure of the material's ability to exchange thermal energy with its surroundings.

Temperature History Curve of SiO_2 Thin Films

The upper plot shows the temperature history curves of SiO_2 thin films with different thicknesses, measured with the *PicoTR* in the RF configuration.

Mo thin layers were deposited on both sides of the SiO_2 thin films, and triple layer analysis was applied.

For each of the curves obtained with the different layers of SiO_2, the areal heat diffusion time* was calculated and plotted as α function of thickness.

Based on these results, the thermal resistance of the SiO_2/Mo interface and the thermal diffusivity (α) of the SiO_2 layer can be calculated to 8.8×10^{-7} m²/s using the formula:

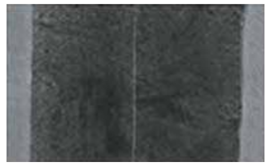
$$\alpha = \frac{d^2}{6 \cdot A}$$

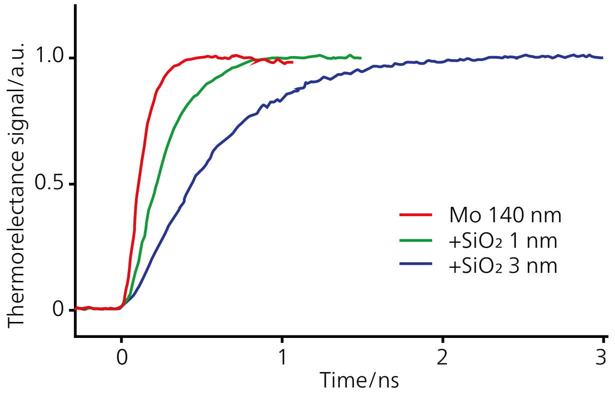
where:

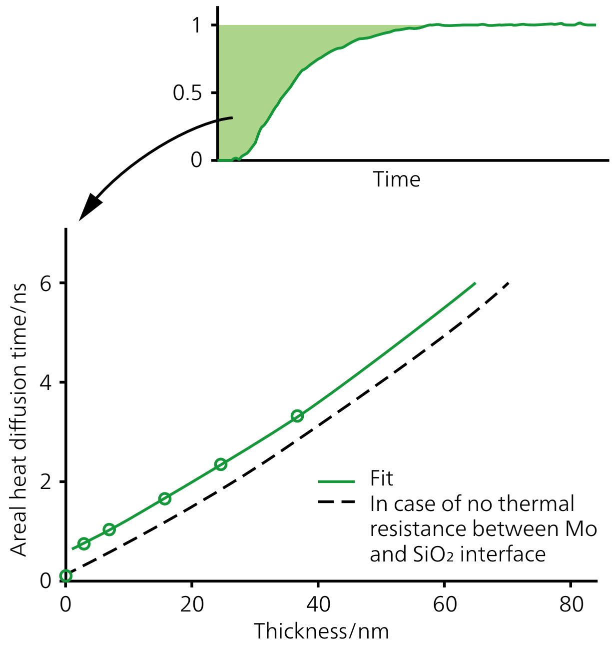
α = thermal diffusivity
d = thickness
A = areal heat diffusion time

The interfacial thermal resistance can be determined to 2.0×10^{-9} m²·K/W.

The principle of the three-layer analysis can be seen in Jpn.Appl. Phys. 50(2011) 11RA01.







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* Thickness dependence of the areal heat diffusion time of SiO_2: The areal heat diffusion time is defined as the integral of the rising segment of the normalized temperature response curve over the thermoreflectance axis. It is a measure of the material's ability to exchange thermal energy with its surroundings.

Technical Specifications

	NanoTR	*PicoTR*
Pump laser	Pulse width: 1 ns Wave length: 1550 nm Beam diameter: 100 µm	Pulse width: 0.5 ps Wave length: 1550 nm Beam diameter: 45 µm
Probe laser	CW laser Wave length: 785 nm Beam diameter: 50 µm	Pulse width: 0.5 ps Wave length: 775 nm Beam diameter: 25 µm
Physical properties/ quantities	Thermal diffusivity and effusivity, interfacial resistance	Thermal diffusivity and effusivity, interfacial resistance
Measureument time	Less than 30 seconds	Less than 5 minutes
Sample film thickness (RF mode)	Resins: 30 nm ... 2 µm Ceramics: 300 nm ... 5 µm Metals: 1 µm ... 20 µm	Resins: 10 nm ... 100 nm Ceramics: 10 nm ... 300 nm Metals: 100 nm ... 900 nm
Sample film thickness (FF mode)	Thicker than 1 µm	Thicker than 100 nm
Substrate	Optical properties: opaque/transparent Size: 10 ... 20 mm square Thickness: 1 mm or less	Optical properties: opaque/transparent Size: 10 ... 20 mm square Thickness: 1 mm or less
Thermal diffusivity	Range: 0.01 ... 1000 mm²/s Accuracy: ±7.9% (for CRM 5810-a in RF mode, 543.8-nm thickness TiN) Repeatability: ±5%	Range: 0.01 ... 1000 mm²/s Accuracy: ±6.2% (for CRM 5808-a in RF mode, 421-nm thickness Mo) Repeatability: ±5%
Software	Calculation of thermal properties, multi-layer analysis, database	Calculation of thermal properties, multi-layer analysis, database
Power supply	AC100 V ~240 V (±10%); 50/60 Hz, 0.5 kVA	AC100 V ~240 V (±10%); 50/60 Hz, 1.5 kVA
Weight	40 kg	90 kg
Temperature range (selectable)	RT / RT ... 500°C	RT / RT ... 500°C / -100 ... 500°C
X-Y scanning in FF mode (optional)	10 x 10 mm area, 1µm resolution	8 x 14 mm area, 2 µm resolution

TRACEABILITY TO NATIONAL STANDARD

NanoTR and *PicoTR* allow for absolute measurement of the thermal diffusivity in the case of an opaque sample and a transparent substrate. For all other cases such as opaque substrates and transparent thin films, reference materials are available made of molybdenum (CRM 5808-a, for *PicoTR*) and TiN (CRM 5810-a, for *NanoTR*). It is supplied by AIST, the Japanese National Institute of Advanced Industrial Science and Technology. This guarantees traceability to national standard.

NanoTR and *PicoTR* are calibrated to ensure traceability to Japanese standards. The instruments are in accordance with the Japanese Industrial Standards (JIS):

- JIS R 1689 "Determination of thermal diffusivity of fine ceramic films by pulsed light heating thermoreflectance method"
- JIS R 1690 "Determination of interfacial thermal resistance between fine ceramic films and metal films"

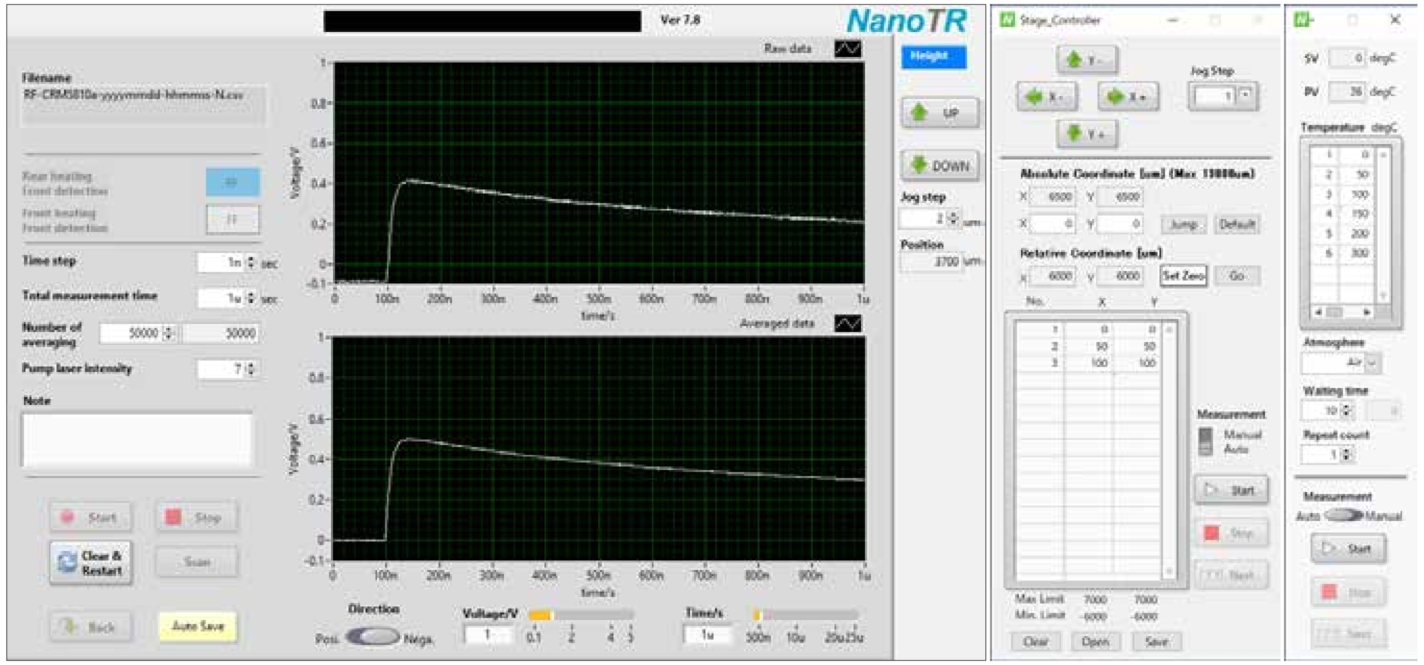
Software

IN-SITU DISPLAY AND ANALYZING

100.000 Shots

The state-of-the-art measurement/analysis software of *NanoTR/PicoTR* has an easy-to-handle user interface which allows for precise determination of the thermal properties of thin films. Focusing of the laser beam can be adjusted by the software and a CCD picture can be obtained.

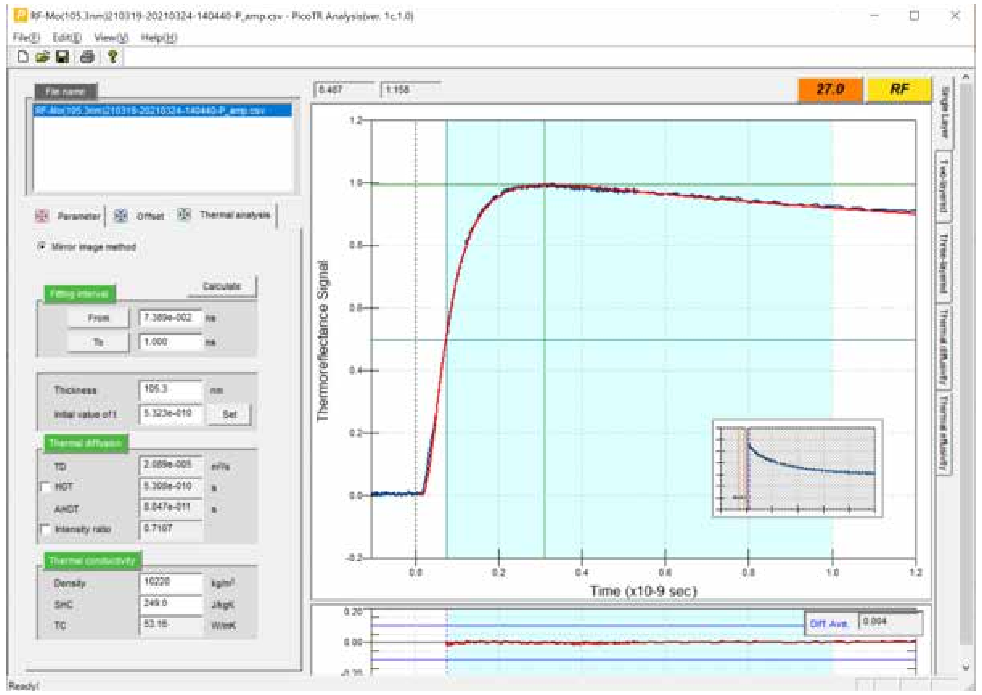
NanoTR/PicoTR software runs under Microsoft Windows.



Measurement

- Choose point distance: 1 ns **NanoTR*
- Measurement time (duration): 1 - 20 µs (for one measurement curve) **NanoTR*
- Averaged: Temperature rise on the base of 100,000 single measurements

OBTAINING RESULTS IN SECONDS

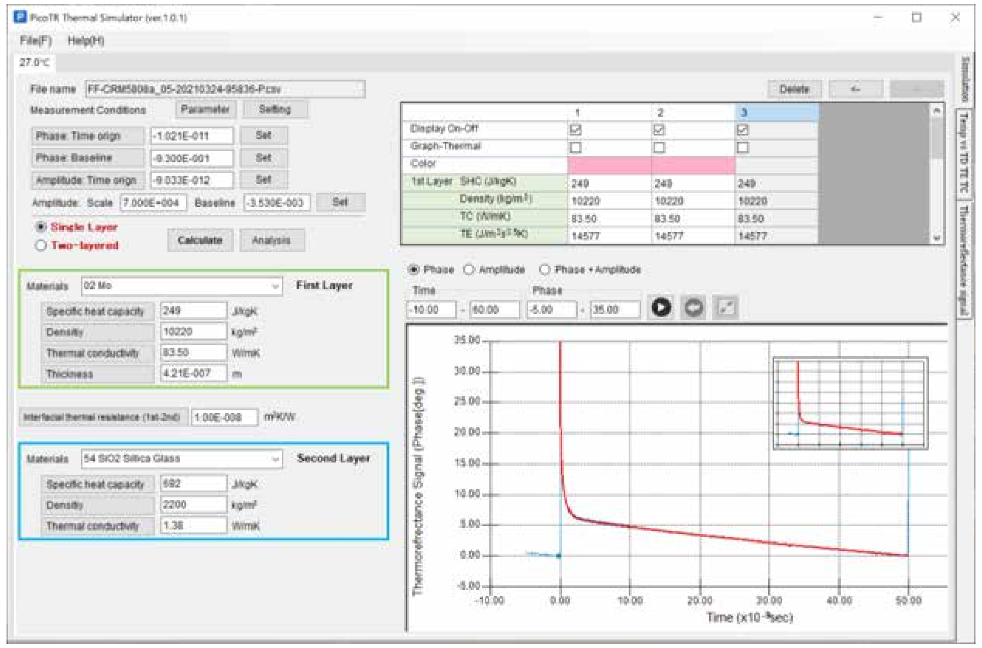


Rear heating/front detection (RF mode)

The thermal diffusivity is measured cross sectionally using RF configuration. The obtained temperature rise curves fit with the theoretical equation to determine heat diffusion times (Mirror image method).

Front heating/front detection (FF mode)

The thermal effusivity is measured cross sectionally using FF configuration. The obtained temperature rise curves of the lock-in phase signals fit with the simulated thermoreflectance signals that are calculated based on the desired estimated values for the thermal effectivity and interfacial thermal resistance (*NanoTR/PicoTR* Thermal Simulator).



Analysis

- Model fit
- Temperature rise
- Calculated thermal diffusivity; results obtained within a few seconds based on several single measurements

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Our performance standards are high. We promise our customers Proven Excellence – exceptional performance in everything we do, proven time and again since 1873.

When it comes to Thermal Analysis, Calorimetry (adiabatic & reaction), the determination of Thermophysical Properties, Rheology and Fire Testing, NETZSCH has it covered. Our 60 years of applications experience, broad state-of-the-art product line and comprehensive service offerings ensure that our solutions will not only meet your every requirement but also exceed your every expectation.

Proven Excellence.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42
95100 Selb, Germany
Tel.: +49 9287 881-0
Fax: +49 9287 881-505
at@netzsch.com
www.analyzing-testing.netzsch.com

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