APPLICATION NOTE

Thin Film – *NanoTR*

Thermal Diffusivity Measurements on PEDOT: PSS Thin Film by Means of *NanoTR*

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Introduction

The Japanese National Institute of Advanced Industrial Science and Technology (AIST) has developed a measurement technique called "pulsed light heating thermoreflectance method", which is a faster version of the laser flash method, and has thus succeeded in measuring the thermophysical properties of thin films ahead of other companies in the world.

The pulsed light heating thermoreflectance method, one of the Time Domain Thermoreflectance (TDTR) methods, is a technique in which a thin film formed on a substrate is instantaneously heated by irradiating it with a picosecond or nanosecond pulsed laser, and the high-speed temperature change due to thermal diffusion after heating is measured by the reflected intensity change of laser light for temperature measurement.

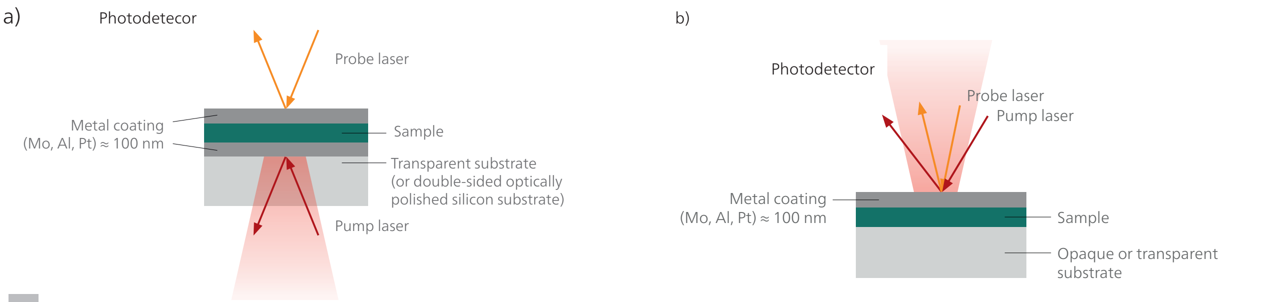
Rear Heating/Front Heating Versus Front Heating/Front Detection

There are two types of this method: An arrangement in which the sample is heated from the transparent substrate side (in the case of infrared light, Si is also a transparent substrate) and the temperature rise of the sample surface is measured (Rear heating / Front detection (RF) mode, fig 1b), and an arrangement in which the sample surface is heated and the temperature rise of the same location on the sample surface is measured (Front heating / Front detection (FF) mode, fig. 1a).

In principle, the RF mode is identical to the laser flash method, which is the standard thermal diffusivity measurement method for bulk materials, and features excellent quantitative reliability. Contrary to the RF mode, the FF mode can measure thin films on opaque substrates and is important as a practical measurement technique.

Since the discovery of conductive polymers (doped polyacetylene) by the Nobel prize winners H. Shirakawa, A. J. Heeger and A.G. MacDiarmid [1], they have been extensively developed and used in various products such as antistatic films, solid electrolytic capacitors and organic EL*. More recently, the focus has been more on the development of organic transistors and organic thermoelectronic materials, and it is expected that poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) will turn out to be a promising material for this application.

The efficiency of thermoelectric materials is represented by the dimensionless figure of merit, *ZT*. The dimensionless figure of merit, *ZT,* is expressed by $ZT=S^2T/(\rho\cdot\kappa)$, where S(V/K) is the Seebeck coefficient, ρ(Ω·m) is the electrical resistivity, κ(W/(m·K)) is the thermal conductivity, and T(K) is the absolute temperature.



1 a) RF mode and b) FF mode

*Organic EL: organic electroluminescent

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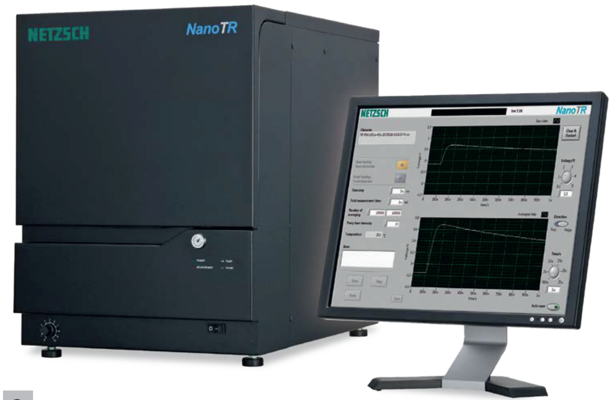


2 *NanoTR*

In this example, the thermal diffusivity of a PEDOT: PSS thin film (70 nm) was measured by means of *NanoTR* figure 2). The sample was formed on a quartz glass substrate of 0.5 mm by spin coating, and sandwiched between Al layers.

Analysis

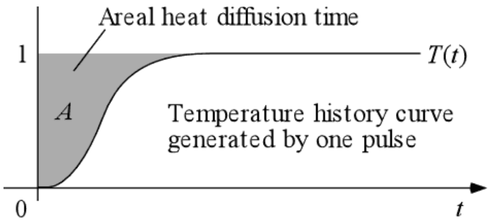
Temperature history curves are fit with the following equation for front surface temperature response to rear surface heating [2] to obtain heat diffusion time τ_f.

$$T(t) = \frac{a}{\sqrt{t}} \sum_{n=0}^{\infty} \gamma^n \exp\left(-\frac{(2n+1)^2}{4t} \tau_f \right) \qquad (1)$$

$$\tau_f = \frac{d^2}{k_f} \qquad (2)$$

Here a is the amplitude, and γ is the intensity of a virtual heat source. Because the vertical axis of the temperature history curve is relative, α is an arbitrary parameter that is determined by curve fitting.

γ is determined by the thermal effusivity between the thin film and the substrate, and ranges between -1 and 1. When the thermal effusivity of the substrate is extremely small and the thin film can be viewed as thermally insulated, γ=1. When the thermal effusivity of the film and substrate are equal (including when the film and substrate are equal and semi-infinite), γ = 0. When the thermal effusivity of the substrate is extremely large and the interface between the film and the substrate is isothermal, γ=-1.



3 Areal diffusion time

For multilayer films, the analysis of thermal diffusivity is based upon temperature history curves using areal heat diffusion times* figure 3 [3].

According to areal heat diffusion time analysis and including interfacial thermal resistance between layers, for a three-layer film, the areal heat diffusion time A is given by equation (3).

$$A = \frac{\left(C_Z d_Z + \frac{4}{3} C_M d_M \right) \frac{d_M^2}{k_M} + \left(\frac{C_M^2 d_M^2}{C_Z d_Z} + \frac{1}{6} C_Z d_Z + C_M d_M \right) \frac{d_Z^2}{k_Z}}{C_Z d_Z + 2 C_M d_M} \qquad (3)$$

$$A = \frac{\tau_f}{6} \qquad (4)$$

C: volumetric heat capacity (product of specific heat capacity and density)
d: film thickness, *k*: thermal diffusivity, *R*: interfacial thermal resistance,
subscripts Z and M refer to subject layer and Mo layer on both sides

When a subject layer Z is sandwiched between Mo layers in a three-layer film and measured using the RF mode, the thermal diffusivity k_Z of layer Z and the interfacial thermal resistance $R_{Z\text{-}M}$ between layer Z and the Mo layers are both unknown values.

These values are determined by measuring heat diffusion times τ_f (areal heat diffusion times being determined from these values) for multiple films for which the subject films are qualitatively the same but have differing thicknesses. Areal heat diffusion times are then determined as a function of thickness by fitting the equation.

The thermal conductivity λ of the subject thin film is determined using the equation below.

$$\lambda = k_Z C_Z \qquad (5)$$

*Areal heat diffusion time: Referencing the maximum value of the temperature history curve, the areal heat diffusion time is defined as the area A between this maximum value and the measured temperature history curve.

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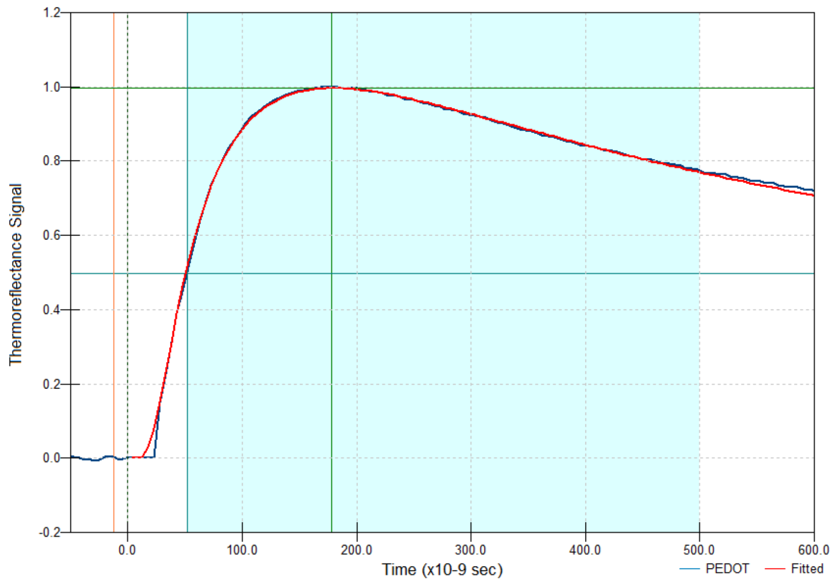

4 Temperature history curve of PEDOT:PSS (measured by means of *NanoTR*, RF mode)

Table 1 Analysis Results

Sample name	**Al/PEDOT/Al** Heat diffusion time τ_f s	**Al/PEDOT/Al** Areal heat diffusion time *A* s	**PEDOT** Thermal diffusivity κ_z m^2/s	**PEDOT** Thermal Conductivity λ W/(m x K)
PEDOT:PSS	3.8×10^{-7}	6.3×10^{-8}	6.9×10^{-8}	0.21

Test Results

The temperature history curve is shown in figure 4. As shown in table 1, by applying three-layer analysis, the thermal diffusivity of the PEDOT layer was calculated as 6.9×10^{-8} m^2/s (0.21 W/mxK) using the multi-layered analysis described before.

Conclusion

The thermal conductivity of PEDOT: PSS thin film was measured by *NanoTR* in RF mode.

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In the case of *NanoTR*, the temperature history curve is obtained as the summation of each result (typically 10,000 times in a minute) for the periodic pulsed light heating. The actual pulse energy is only several nJ and causes no thermal damage to the sample.

For thin film measurement by *NanoTR,* periodic pulsed light heating has a great advantage over other commercially available TDTR systems, which is based on single pulse heating with high pulse energy.

References

[1] Synthesis of electrically conducting organic polymers: halogen derivates of polyacetylene, (CX)x
Hideki Shirakawa, Edwin J. Louis, Alan G. MacDiarmid, Chwan K. Chiang and Alan J. Heeger; J. Chem. Soc., Chem. Commun., 1977, 578-580

[2] Analytical equations for rear heating/front detection using pulse thermoreflectance
Progress in Heat Transfer, New Series, Vol. 3 (The Japan Society of Mechanical Engineers), pp. 187-188 (in Japanese)

[3] Areal heat diffusion times by response function, Tetsuya Baba, JJAP 48 (2009), pp. 05EB04-1~9

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