# Development of thin film reference material for thermal diffusivity

○Takashi YAGI[1], Naoyuki TAKETOSHI[1], Tetsuya BABA[2]
1. Thermophysical Properties Section, NMIJ, AIST
Tsukuba Central 3, 1-1-1, Umezono, Tsukuba, Ibaraki 305-8563, JAPAN
Corresponding author: Takashi YAGI, E-mail: t-yagi@aist.go.jp
2. Material Properties and Metrological Statistics Division, NMIJ, AIST
Tsukuba Central 3, 1-1-1, Umezono, Tsukuba, Ibaraki 305-8563, JAPAN

There has came into existence some practical instruments to measure the thermophysical properties of thin films, and those instruments have been recognized to be of benefit to R&D in the thin film technology. However, there are no systems to calibrate such instruments by standards that are guaranteed to trace up to national standards or reference materials. Accordingly, NMIJ/AIST has established a high speed laser flash apparatus as a national standard in Japan. The apparatus can measure the thermal diffusivity of thin films normal to the surface with small uncertainty using a thermoreflectance technique. Based on this apparatus, a calibration service of the thermal diffusion time for user's specimen has started at the end of 2007 FY.

We have moved to develop a thin film reference material for thermal diffusivity, since the reference material is more useful to calibrate the practical instrument. The reference material is made of a titanium nitride (TiN) thin film with 700 nm in thickness. The TiN film was deposited on a synthesized silica wafer (76.2 mm in diameter, 0.525 mm in thickness, Shin-Etsu Chemical Co., Ltd.) using a reactive dc magnetron sputtering. The target metal is pure Ti and the sputtering gas is pure $N_2$ gas. The TiN film on the wafer was patterned with each individual chips using a photo-resist and metal-resist coatings by lithography technique. The chip is 10mm x 10 mm, and an etched line of 1 mm x 100 μm is positioned at the center of the film. This etched line is for a surface profiler in order to measure the film thickness. The thermal diffusion time of a typical film is $145.9 \times 10^{-9}$ s, and its expanded uncertainty is 3.6 %. We are planning to establish the thin film reference materials by end of 2008 FY in Japan.

## 1. Introduction

Thermophysical properties for thin films become important in order to manage heat transport in high technology devices. For example, heat management between interconnects and interlayer dielectric materials for a microprocessor will be a critical problem in very near future. In additions, rewritable optical disks, hard disks using heat assisted magnetic recording technology, phase change memories and thermo-electric devices also require reliable thermophysical properties values of the thin film materials for the optimum thermal design. There has came into existence some practical instruments [1-3] and methods [4] to measure the thermophysical properties of thin films, and those instruments have been recognized to be of benefit to R&D in the thin film technology. Accordingly, NMIJ/AIST has established a high speed laser flash apparatus as a national standard in Japan. The apparatus can measure the thermal diffusion time of thin films normal to the surface with small uncertainty using a thermoreflectance technique.

We have moved to develop a thin film reference material for thermal diffusivity. This reference film is of use to guarantee the practical instruments for suppliers, and instrument users also have the benefit with regard to calibration for their own instrument. In this paper, preparation of the reference material and measurement procedure are reported.

## 2. Development of Reference thin film

### 2.1 Standard apparatus for thermal diffusion time

NMIJ/AIST has established a standard apparatus to measure the thermal diffusion time, $\tau_f$ of the reference film. The thermal diffusivity, $\kappa_f$ is represented as follows equation,

$$\kappa_f = \frac{d^2}{\tau_f} \quad (1)$$

where $d$ is a characteristic length, *i.e.* film thickness. Thus, the value of $\kappa_f$ can be derived from the data of $\tau_f$ and $d$. The standard apparatus is shown in Figure 1. Two sub-nanosecond pulsed lasers with wavelength of 1064 nm

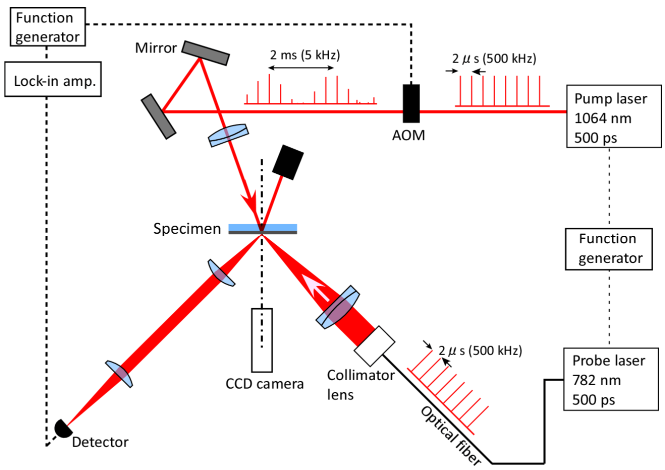


Figure 1 Block diagram of a standard apparatus for the thermal diffusion time measurement.

for a pump beam and 782 nm for a probe beam are used. The pulse width of both lasers is 500 ps. The pump laser pulse is irradiated at a rear surface of the film through the substrate, which induces heat flux inside the film. This thermal diffusion is one-dimensional normal to the film surface, since the spot diameter of the pump laser is 300 μm, which is much larger than the typical film thickness such as 1 μm. In order to measure the thermal diffusion time of the film thickness, the transient temperature change at the bare surface is measured using a thermoreflectance technique as follows. The probe beam is focused on the bare surface opposite to the heated area with a spot diameter of 100 μm. The power of the probe beam is 0.2 mW. Intensity change of the probe beam is detected by a Si photo detector. The pulse repetition frequencies of the both lasers are locked by signals with 500 kHz from a function generator. Then, the phase of the signal for pump beam to that for probe beam is controlled to record a temperature history curve.

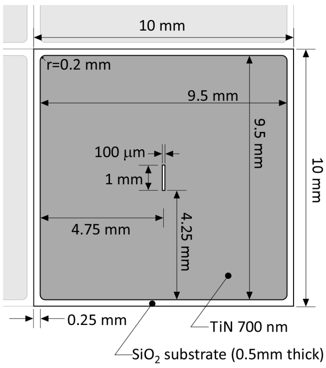


Figure 2 Illustration of thin film reference material for thermal diffusivity.

## 2.2 Fabrication of Reference material

The reference thin film made of TiN was prepared using a dc reactive magnetron sputtering. Ohtsuka et al[5] has reported that the thermal diffusivity of TiN films changes from 0.2 to 1.4 × $10^{-5}$ $m^2/s$ according to the nitrogen concentrations. The films of under- or over-stoichiometric composition show smaller thermal diffusivity than that of stoichiometric composition. Consequently, we chose the over-stoichiometric composition, since a small thermal diffusivity is suitable for reducing the film thickness. A synthesized silica wafer (76.2 mm in diameter, 0.525 mm in thickness, Shin-Etsu Chemical Co., Ltd.) is used for the substrate. The surface roughness of the wafer is smaller than 0.2 nm. The target metal is pure Ti and the sputtering gas is pure $N_2$ gas. The nominal thickness of the film was 700 nm.

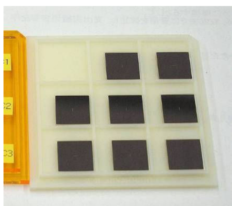

Figure 3 Appearance of the reference thin films made of TiN.

The synthesized TiN film on the wafer was patterned with individual chips using a photo-resist and metal-resist coatings by a lithography technique as shown in Figure 2. The chip size is 10 mm x 10 mm, and 32 pieces of chip was made from a wafer. There is an etched line of 1 mm x 100 μm positioned at the center of the chip. This etched line is for a surface profiler in order to measure the film thickness. The detail of the patterning procedure is as follows; a Cr/Au layer was deposited over the TiN film. Then a photo-resist was coated over the Cr/Au layer. The chip pattern as shown in Figure 2 was copied on the photo-resist. The photo-resist was developed and the Cr/Au layer was etched as the pattern. Subsequently, the exposed part of TiN layer was etched. Finally, the Cr/Au layer was perfectly removed. After patterning, the wafer was cut into each chip.

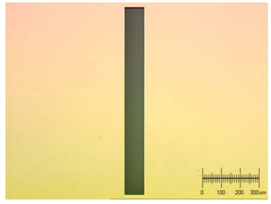

Figure 4 Etched line positioned at the center of the reference film.

# 3. Results and Discussion

## 3.1 Physical properties of reference material

Figure 3 is appearance of the reference thin films. Figure 4 shows a microscope photograph of the typical etched line positioned at the center of the film. Users can use this etched line for a film thickness measurement by a surface profiler. Figure 5 is a cross sectional photograph for the film by a transmitted electron microscope (TEM). Columnar structure is clearly seen in the photograph. The microscopic surface roughness originates in these columns. However, this roughness is relatively smaller than the uncertainty of the surface profiler (several percent).

Typical physical properties of the reference film are given in Table 1. The resistivity data shows that the film is a good electrical conductor. Thus, the film exhibits a metal like reflectivity. At the measurement of thermal diffusion time, $\tau_f$ for the film, almost optical energy of the pump laser pulse is absorbed within the skin depth and converted to heat. The values of the skin depth are 21 nm at 1065.3 nm, and the effect of this penetration on the thermal diffusion is considered when the temperature history curve of the film is analyzed.

Table 1 Physical properties of the reference film (TiN).

| Thickness $d$/nm | Resistivity, $\rho/\Omega$m | Refractive index, $n$ | Extinction coefficient, $k$ | Reflectivity, $R$ | Skin depth, $l$/nm |
|---|---|---|---|---|---|
| 640 | 1.4×$10^{-6}$ | 1.530* | 2.584* | 0.53* | 24* |
| | | 1.800** | 3.952** | 0.69** | 21** |

*Values at 781.9 nm in wavelength
**Values at 1065.3 nm in wavelength

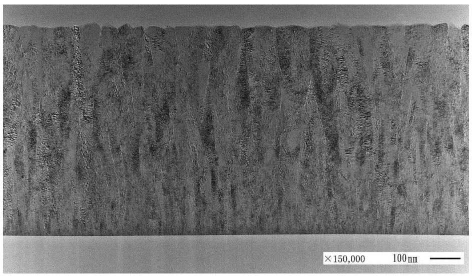


Figure 5 Cross sectional TEM image of the reference film.

### 3.2 Calibration result

Figure 5 shows the typical temperature history curve of the reference film obtained by the standard apparatus for thermal diffusion time measurement. The shape of the curve is very similar to that obtained by the conventional laser flash method, because the configuration of the apparatus is also same as that of the laser flash. Thus, from this temperature history curve, the thermal diffusion time can be determined reliably with uncertainty evaluation based on Guide to the Expression of Uncertainty in Measurement (GUM).

The uncertainty evaluation was carried out with respect to the time scale, the origin of the pulse heating for the apparatus, analysis of the value of $\tau_f$ based on the analytical solution[6] and the effect of steady temperature rise of the film due to the laser heating. The result of the calibration is given in Table 2 along with the expanded uncertainty. The calibrated value of $\tau_f$ is $145.9\times10^{-9}$ s with the expanded uncertainty of 3.6 %. The value of the thermal diffusivity for the film calculated from the value of $\tau_f$ and the film thickness $d$ using eq. (1) is $2.8\times10^{-6}$ $m^2/s$, which coincides with the value of that for over-stoichiometric TiN film[5] reported by Ohtsuka *et al.*

Table 2 Calibration results of the reference thin film.

| Thermal diffusion time, $\tau_f$ for the reference film (TiN 640 nm) | Expanded uncertainty, $U(k=2)$ |
|---|---|
| $145.9\times10^{-9}$ s | $5.2\times10^{-9}$ s (3.6 %) |

## 4. Conclusions

The development of the reference thin film for thermal diffusivity is under way. This reference thin film is expected to be of use to guarantee and calibrate the practical instruments widely. We are planning to establish the reference material by end of 2008FY.

## 5. Acknowledgement

This work was supported by the Nanotechnology Material Metrology Project of the New Energy and Industrial Technology Development Organization (NEDO).

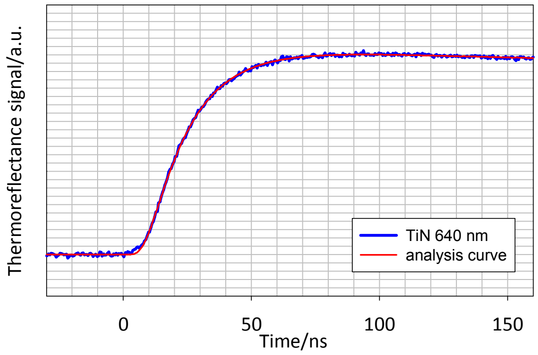


Figure 5 Temperature history curve for the reference thin film. Thickness of the film is 640 nm.

## NOMENCLATURE

| | |
|---|---|
| $\kappa_f$ | :thermal diffusivity, $m^2/s$ |
| $\tau_f$ | :thermal diffusion time, s |
| $d$ | :thickness, m |
| $\rho_f$ | :resistivity, Ωm |
| $n$ | :refractive index |
| $k$ | :extinction coefficient |
| $R$ | :reflectivity |
| $l$ | :skin depth, m |

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