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DEVELOPMENT OF THERMAL DIFFUSIVITY STANDARD FOR THIN FILMS: REFERENCE THIN FILM AND MEASUREMENT METHOD

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Abstract: The reference thin metal film to calibrate for the thermal diffusivity is being developed in NMIJ. Mo thin film with a nominal thickness of 400 nm is candidate for the reference film. To inspect the fabrication process of the reference material, test films were prepared and estimated in terms of scatter of the physical properties. Thermal diffusivity of those films were measured using the pulsed light heating thermoreflectance apparatus originally developed by NMIJ. The measured thermal diffusivity is 3.46×10^{-5} m^2 s^{-1} and the standard deviation is 0.05×10^{-5} m^2 s^{-1} (1.6%) for 8 films sampled from a total of 75 films. We plan to supply the reference thin films based on above mentioned technology in 2014FY.

Keywords: thermal diffusivity, Mo, reference film

1. INTRODUCTION

Thermophysical property data of thin films is one of the fundamental information for cutting-edge industries; control of heat transport in integrated devices, improvement of thermal barrier properties and heat transfer simulation to test the products under operation. Thermal properties of such thin films often do not agree with those of bulk materials of same name / same composition.

To observe thermal energy transfer within thin films, a measurement technique often requires very fast time resolution such as nano- or pico-seconds time scale, because heat diffusion is very short time phenomenon owing to small dimension of sample. Recently, there are some commercial instruments for measuring the thermal diffusivity /conductivity of thin films. However, there was no system to calibrate or guarantee those instruments by tracing up to national standards or reference materials.

National Metrology Institute of Japan (NMIJ)/AIST is engaged to develop a reference thin film of thermal diffusivity calibrated based on Guide to the Expression of Uncertainty in Measurement (GUM). The reference thin film aims to be utilized for calibration of the commercial instruments and evaluation of analytical procedures. For this purpose, 400 nm-thick Mo films deposited on a high purity and ultra-flat quartz grass substrate were made by means of a large-scale magnetron sputtering apparatus. This paper describes details of the development of the reference thin film and a measurement technique of the thermal diffusivity to calibrate the reference thin films.

2. MEASUREMENT APPARATUS FOR MESURING THERMAL DIFFUSIVITY OF THIN FILMS

For calibrate thermal diffusivity of the reference thin film, a pulsed light heating thermoreflectance apparatus [1-4] was used. A schematic illustration of the apparatus is shown in Fig.1. A rear face of the thin film is heated by pump laser pulses with a wavelength of 1550 nm, duration of 0.5 ps and pulse frequency of 19.9957 MHz. Probe laser pulses, a wavelength of 775 nm, duration of 0.5 ps and pulse frequency of 19.9957 MHz, are focused on the surface of the film opposite to the heated area. The reflected probe pulses are detected by a differential photo detector, and temperature rise of the front surface is observed using thermoreflectance effect[5-7]. This geometry is same as the conventional laser flash method where heat diffusion time, τ_f, *i.e.* the characteristic time that heat diffuses over a thickness of the film is measured. Typical transient temperature curve observed by the apparatus is shown in Fig. 2. Here, pulse heating is applied on the film at t=0. The transient temperature, T is analyzed based on one dimensional heat diffusion model[8] to obtain the value of τ_f.

$$T = \Delta T\alpha d \sum_{n=-\infty}^{\infty} \left\{ \begin{aligned} &\gamma^{|n|} \exp\left(-\frac{(2n-1)^2}{4} \frac{\tau_f}{t} \right) \\ &\times \exp\left(\left(\frac{2n-1}{2} \sqrt{\frac{\tau_f}{t}} + \alpha d \sqrt{\frac{t}{\tau_f}} \right)^2 \right) \\ &\times \operatorname{erfc}\left(\frac{2n-1}{2} \sqrt{\frac{\tau_f}{t}} + \alpha d \sqrt{\frac{t}{\tau_f}} \right) \end{aligned} \right\}, \tag{1}$$

$$\gamma = \frac{b_f - b_s}{b_f + b_s}, \tag{2}$$

where ΔT is maximum temperature rise, α is the absorption coefficient at the wavelength of the pump laser, d is the thickness of the film, b_f and b_s are the heat effusion of the film and substrate, respectively. Then, the thermal diffusivity of the film, k_f is represented as follows equation,

$$\kappa_f = \frac{d^2}{\tau_f}. \tag{3}$$

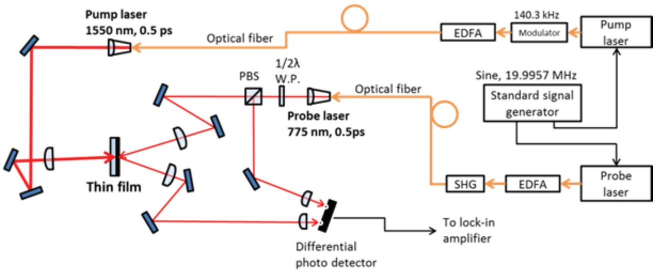


Figure 1 Schematic illustration of the pulsed light heating thermoreflectance for measuring thermal diffusivity of thin metal films.

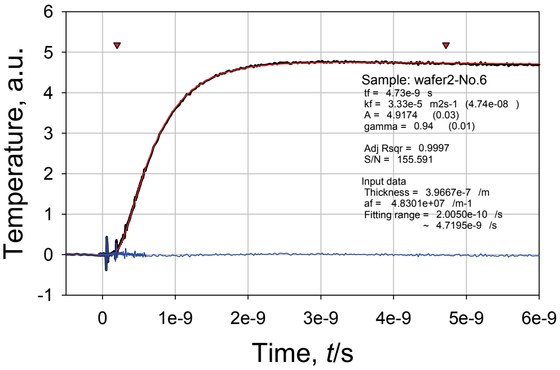


Figure 2 Typical transient temperature curve obtained by the pulsed light heating thermoreflectance method.

3. FABRICATION PROCEDURE OF REFERENCE THN FILMS

The candidate of the reference film is Mo film with a nominal thickness of 400 nm deposited on a high purity quartz glass substrate. Here, we describe a feasibility study on fabrication procedure of the reference films.

The Mo film deposition was carried out using dc magnetron sputtering apparatus, which equips a Mo target (8 inch in diameter) and 4 substrate holders (396 mm in diameter) with rotary and revolutionary motion. High purity and low roughness (Ra<0.3 nm) quartz glass wafers with a diameter of 1.5 inch were used for the substrate. 75 wafers were set on the substrate holders. The dimension of wafers and substrate holder is shown in Fig. 3. Here, the samples are labelled as X-Y, where X and Y represent the substrate holder (from 1 to 4) and position of the wafer in the each substrate holder (from 1 to 26). A sputtering chamber was evacuated by 8×10^{-4} Pa, and the substrate was heated at 473 K. Then, a pure Ar gas with 0.3 Pa was introduced into the chamber. The sputtering dc power was 2000 W.

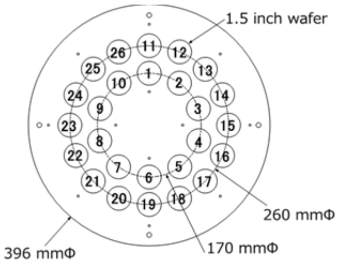
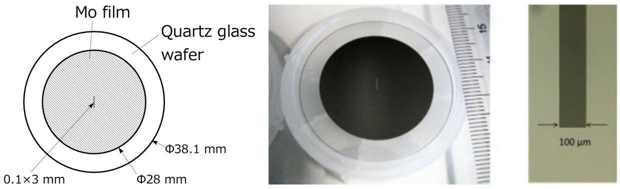


Figure 3: Dimension of the substrate holder and assignment of the wafer's position for the Mo deposition. There are 4 holders set in the sputtering chamber. The samples were labeled as X-Y, which represents X: substrate holder (1 to 4) and Y: wafer position (1 to 26) at the holder.

In order to inspect uniformity of the films, we sampled 8 wafers from total 75 wafers (2 wafers from each substrate holder) for physical properties measurements such as thermal diffusivity, thickness, absorption coefficient at the wavelength of the pump laser, electrical resistivity, X-ray diffraction (XRD), and transmittance electron microscope (TEM).

The deposited films were etched as shown in Figure 4(a) and (b). The outer of the film was removed by the etching process, because the film thickness was ununiform around the outer position. At the center of the film, there is a rectangle pattern with dimension of 0.1×3 mm (Fig.3(c)), which is utilized for a thickness measurement by a surface profiler. Figure 5 shows a typical XRD pattern of the deposited film. The film shows a polycrystalline structure and a preferred orientation of (110) plane. A halo pattern seen around $2\theta = 20°$ was attributed to the quartz glass substrate. Figure 6 shows a cross-sectional TEM image at the edge of the etched part of the film. Aspect ratio of the etching profile was about 1:1, which is enough sharp for the surface profile measurement.



(a) (b) (c)

Figure 4: (a) illustration of the sample after etching process, (b) photograph of the sample, (c) optical microscope image for part of the rectangle etched pattern.

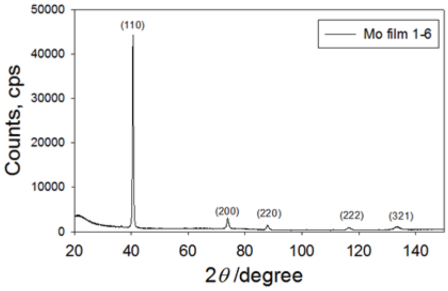


Figure 5: XRD pattern of the Mo film.

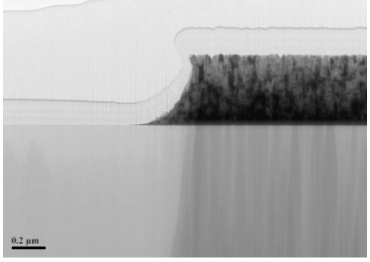


Figure 6: Cross-sectional TEM image of the Mo film. The observed position is the edge of the etching pattern.

4. SCATTER OF THERMAL DIFFUSIVITY AND OTHER PROPETIES

The thermal diffusivity (at 300 K ± 1 K), thickness, electrical resistivity and absorption coefficient at 1550 nm (pump laser's wavelength) of the 8 sampled films are shown in Fig.7. At the present time, uncertainty estimation of thermal diffusivity based on GUM has not been finished yet. Thus, the values in Fig.7 do not include the uncertainty. The error bars for other properties are also not uncertainties but standard deviations. The average of the thermal diffusivity for 8 films is 3.46×10^{-5} m^2 s^{-1} and its standard deviation is 0.05×10^{-5} m^2 s^{-1} (1.6%). This value is comparable with that for the certified reference material of bulk thermal diffusivity, NMIJ CRM 5804a [9], which is designed for flash apparatuses. The relative uncertainty caused by inhomogeneity of NMIJ CRM 5804a is 1.9% [10] with coverage factor k =1. Accordingly, inhomogeneity of our thin films can be permissible level for practical use. On the other hand, the thermal diffusivity values seem to have correlation with other properties. For example, the thermal diffusivity is plotted against electrical conductivity (inverse of resistivity) as shown in Fig.8. There is a weak linear relation between those values. In addition, the white and black points represent those of samples putted on outer and inner circles of the substrate holders during the film deposition (see Fig. 3). It can be clearly seen that the group of the inner circle (black points) has higher thermal diffusivity and electrical conductivity in comparison with that of the outer circle (white points). During the Mo film deposition, the substrate holders rotated and revolved in order to reduce fluctuation of the film thickness and physical properties. As seen in Fig. 8, inhomogeneity of the physical properties, however, still remains toward the radial direction of the holder. For fabrication of the CRM, we plan to use only the outer positions of the substrate holders to reduce scatter of the physical properties.

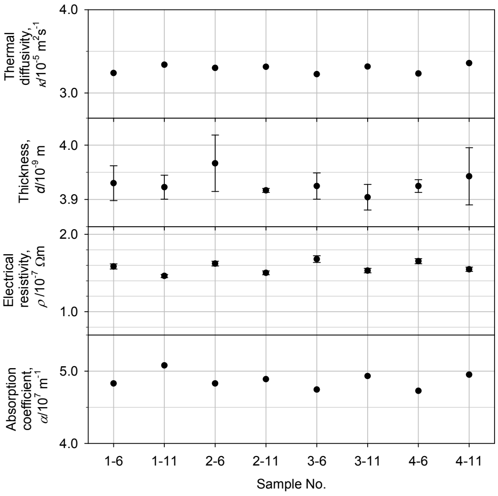


Figure 7 Thermal diffusivity, thickness, electrical resistivity and absorption coefficient at 1550 nm for 8 sampled Mo films. See Fig. 3 for Sample No.

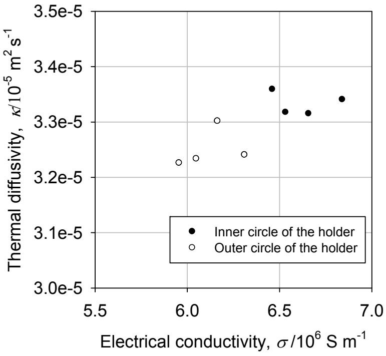


Figure 8 Thermal diffusivity of the Mo films as a function of the electrical conductivity. Black and white circles represent those of samples putted on outer and inner circles of the substrate holders during the deposition process, respectively (see Fig. 3).

5. SUMMARY

The reference thin metal film calibrated for the thermal diffusivity is being developed in NMIJ. Mo thin film with a nominal thickness of 400 nm is candidate for the reference film. Test films to inspect the fabrication process of the reference material were prepared and estimated in terms of scatter of the physical properties. Thermal diffusivity of those films were measured using the pulsed light heating thermoreflectance apparatus originally developed by NMIJ. The measured thermal diffusivity is 3.46×10^{-5} m^2 s^{-1} and the standard deviation is 0.05×10^{-5} m^2 s^{-1} (1.6%) for 8 films sampled from a total of 75 films. We plan to supply the reference thin films based on above mentioned technology in 2014FY.

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