International Journal of Thermophysics, Vol. 25, No. 1, January 2004 (© 2004)

Measurement of Thermal Conductivity of TiO_2 Thin Films Using 3ω Method

D. J. Kim,[1] D. S. Kim,[1] S. Cho,[1] S. W. Kim,[1,2] S. H. Lee,[3] and J. C. Kim[3]

Received April 29, 2003

TiO_2 film has been used in many industrial components such as laser filters, protection mirrors, chemical sensors, and optical catalysts. Therefore, the thermal properties of TiO_2 thin films are important in, e.g., reducing the thermal conductivity of ceramic coatings in gas turbines and increasing the laser damage threshold of antireflection coatings. The thermal conductivity of four kinds of TiO_2 thin films, prepared by dc magnetron sputtering, was measured using the 3ω method in the temperature range from 80 K to room temperature. The results showed that the thermal conductivity of TiO_2 thin films strongly depends on the thickness and the microstructure of the films. The films with smaller grain size and thinner thickness have smaller thermal conductivities.

KEY WORDS: 3ω method; thermal conductivity; thermal resistance; thin film; TiO_2 film.

1. INTRODUCTION

The determination of the thermal conductivity is of great interest because it contains information about the microstructure of materials, and therefore contributes to an analysis of the performance of various devices, such as thermoelectric power generators and thermoelectric coolers. Optical coatings for high power laser applications [1] are another example where heat transport of a thin film is crucial in the system performance. Data for the thermal conductivity of oxide films often show large variation between different investigations [2–5], and this reveals the difficulty in obtaining

[1] Department of Physics, University of Ulsan, Ulsan 680-749, Korea.
[2] To whom correspondence should be addressed. E-mail: sokkim@ulsan.ac.kr
[3] Division of Physical Metrology, Korea Research Institute of Standards and Science, Taejon 305-600, Korea.

0195-928X/04/0100-0281/0 © 2004 Plenum Publishing Corporation

reliable data for thin films. In the case of thin films or superlattices, the transport properties can be considerably different from equivalent bulk materials and show large scatter depending on sample preparation.

Unfortunately, thermal conductivity measurements are difficult on a two-dimensional structure because problems arise mainly from thermal radiation and heat loss in the temperature measurement. The use of a thin metal strip as both heater and thermometer and an ac current in the 3ω method can overcome these difficulties [6]. Although the 3ω method has originally been developed for the thermal conductivity measurement of isotropic bulk materials exhibiting low thermal conductivity values, this method was successfully applied to thermal conductivity measurement of thin films deposited on high thermal conducting substrates [7].

In this paper, we describe our study of the thermal conductivity of TiO_2 films by the 3ω method and the heat transport behavior of highly disordered TiO_2 thin films. TiO_2 film has been used in many industrial parts such as a laser filter, protection mirror, chemical sensor, and optical catalyst. Therefore, thermal properties of TiO_2 thin films are important in, e.g., reducing the thermal conductivity of ceramic coatings in gas turbines and increasing the laser damage threshold of antireflection coatings.

2. PRINCIPLE OF MEASUREMENT

The sample geometry is shown in Fig. 1. When an ac electric current of angular frequency ω is applied across the heater, it generates Joule heating at 2ω. Two pads are the connections for current leads and voltage leads. A gold strip is used as a heater and thermometer because it is not susceptible to oxidation and has suitable electrical resistivity.

If the amplitude of sinusoidal heating is P, the temperature distribution in the substrate can be calculated as a superposition of temperature modulations by the infinitesimal line heaters. The solution given by Carslow and Jaeger [8] for the temperature modulation by a line heater of infinitesimally narrow width is proportional to $K_0(qr)$, where r is the distance from the heater, $K_0(x)$ is the modified Bessel function of zeroth order, and q is defined as [6]

$$q^2 = \frac{2i\omega C}{\kappa} \tag{1}$$

where C and κ are the heat capacity and thermal conductivity of the sample, respectively. Integrating the solution by varying the position of infinitesimal heaters over the width of the flat heater, the temperature oscillation amplitude T_{ac} at the heater can be obtained in the Fourier k space as

$$T_{ac} = \frac{P}{l\pi\kappa}\int_0^{\infty} \frac{\sin^2(kb)\,dk}{(kb)^2\sqrt{k^2+q^2}} \tag{2}$$

A geometrical effect of metal line as a thermal conductor is also neglected in order to get the relation in simpler form. The agreement between calculated and measured T_{ac} shows that this approximation seems to be valid. If the width of the heater is small enough to satisfy the condition $qb \ll 1$, Eq. (2) can be approximated by $-\ln(qb)+\text{const}$. Also, if the heat capacity and thermal conductivity are both real values, q^2 becomes purely imaginary. Then, we can divide T_{ac} into real and imaginary parts to distinguish in-phase and out-of-phase oscillations of temperature as follows:

$$\frac{l\pi\kappa}{P}T_{ac} = -\ln(qb)+\eta = -\frac{1}{2}\ln\left(\frac{2\omega b^2 C}{\kappa}\right)+\eta-\frac{\pi}{4}i \tag{3}$$

where η is a constant.

Finally, thermal quantities can be calculated from $V_{3\omega}$—the measured rms value of 3ω voltages. The $V_{3\omega}$ $(=V'_{3\omega}+iV''_{3\omega})$ is related with the temperature oscillation T_{ac} as

$$\begin{aligned} V_{3\omega} &= \frac{\omega}{2\pi}\int_0^{2\pi/\omega} I(t)\,R(t)\cos(3\omega t)\,dt \\ &= \frac{\omega}{2\pi}\int_0^{2\pi/\omega} 2I_0\cos\omega t\left[R+\frac{dR}{dT}T_{ac}\cos(2\omega t)\right]\cos(3\omega t)\,dt \\ &= \frac{I_0\alpha}{2}T_{ac}, \end{aligned} \tag{4}$$

where α is the temperature coefficient of the resistance R of the heater and I_0 is the rms value of the electric current along the heater generating a power of $P = I_0^2 R$. Equation (3) can be rewritten in terms of $V'_{3\omega}$ as

$$\kappa = -\frac{I_0^3 R\alpha}{4\pi l}\frac{d\ln\omega}{dV'_{3\omega}} \tag{5}$$

We consider now the case when a thin film with a lower thermal conductivity than the substrate is located between the substrate and the strip.

Table I. Description of the Prepared TiO_2 Thin Film Samples

Sample Number	Thickness of Film (nm)	Growth Temperature (°C)
1	150	150
2		30
3	80	150
4		30

The increase of temperature oscillation of the film ΔT_f can be expressed in terms of a thermal conductivity of film κ_f [9]:

$$\Delta T_f = \frac{Pd}{2b\kappa_f} \tag{6}$$

where d is the film thickness.

3. EXPERIMENTS

Four kinds of TiO_2 thin film samples were prepared with two thicknesses of 150 and 80 nm at different substrate temperatures for the thermal conductivity measurements. TiO_2 thin films were prepared by dc magnetron sputtering. During sputtering, the gas pressure of Ar and O_2 mixture was 3.5×10^{-3} torr and the O_2 fraction ($O_2/(O_2+Ar)$) was 4 to 10%. Table I summarizes the prepared samples.

As in Fig. 1, a narrow gold metal strip and the rectangular pads are evaporated onto the sample through a stainless steel mask and the lead lines are electrically connected to the pads. The samples mounted in the sample holder by low temperature epoxy and lead lines are connected to the pads using silver paste. Then, the metal strip is connected to the current and voltage lead lines with a four-probe type coupling. The width of the

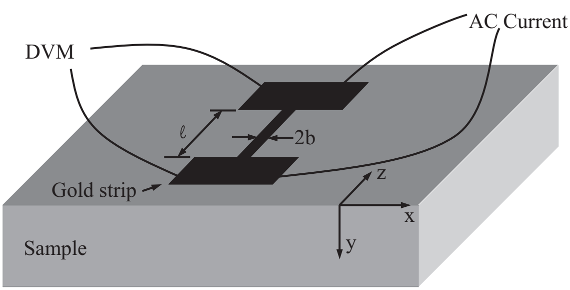


Fig. 1. Shape of a prepared sample.

heater pattern is about 60 μm, and its length is 4 mm. Gold is preferred as a heating element because it is not susceptible to oxidation and has suitable electrical resistivity as a heater and temperature sensor.

The measurement circuit is shown in Fig. 2. Since the ω component of the ac voltage at the heater causes a spurious signal at the lock-in amplifier, a Wheatstone bridge is used. R_1 and R_2 are fixed resistances, and R_v and R_s are the rheostat resistance and resistance of the gold pattern, respectively. Since R_2 and R_v are a few tens of kΩ and R_1 and R_s are a few tens of Ω, most of the current flows through R_1 and R_s. In the experimental apparatus of Fig. 2, to balance the bridge circuit, we adjusted the value of R_v to suppress the signal of ω and then to separate only the 3ω component of the voltage signal. In order to prevent rapid temperature variation and to maintain a thermally stable state, the sample is put into the capsule whose temperature is controlled by the temperature controller LakeShore 330 over the temperature range from liquid nitrogen to room temperature. Using an EG&G 5302 lock-in amplifier, the amplitude and phase of 3ω signal voltage were measured through the third harmonic mixer in the lock-in amplifier. All the apparatus were controlled by GPIB card and LabView control program.

4. RESULTS AND DISCUSSION

In this experiment, it is necessary to know the variation of the resistance of a strip for measurement of the exact thermal conductivity as a

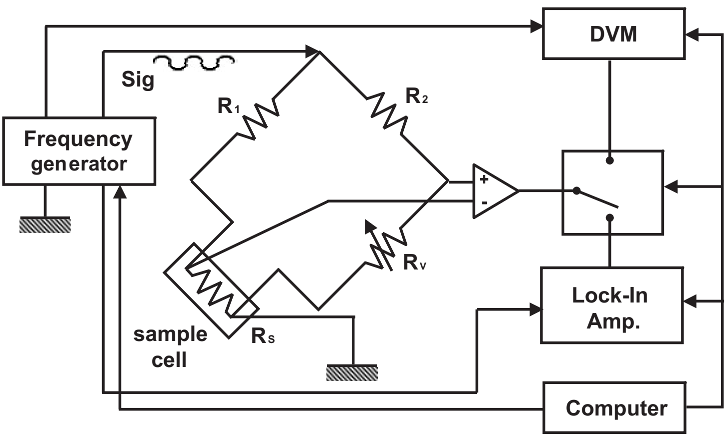


Fig. 2. Schematic of the apparatus for 3ω thermal conductivity measurements.

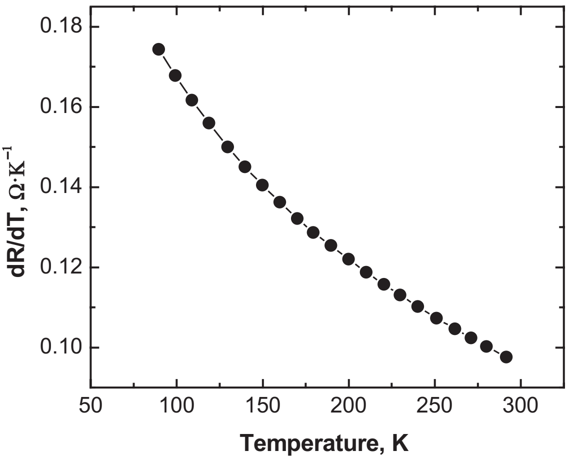


Fig. 3. Measured variation of dR/dT as a function of temperature.

function of temperature. Figure 3 shows the measured $\frac{dR}{dT}$ of a strip as a function of temperature. During the deposition of the gold strip, the TCR, defined as $\frac{1}{R}\frac{dR}{dT}$, and the resistance could be changed for many other reasons such as an impurity; therefore, it has to be checked accurately.

In Fig. 4, the experimental values are obtained from the silicon substrate coated with the TiO_2 layer and the expected values are calculated from the assumption that only the substrate contributes to the oscillation

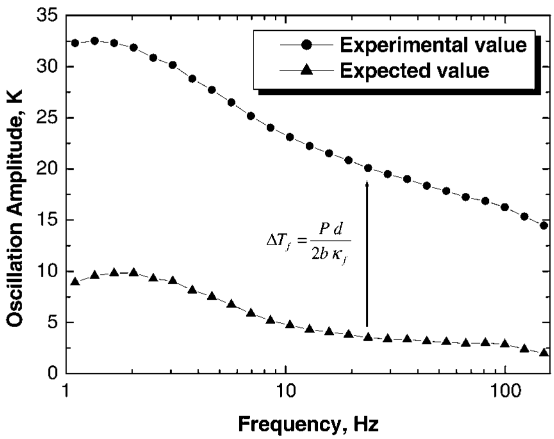
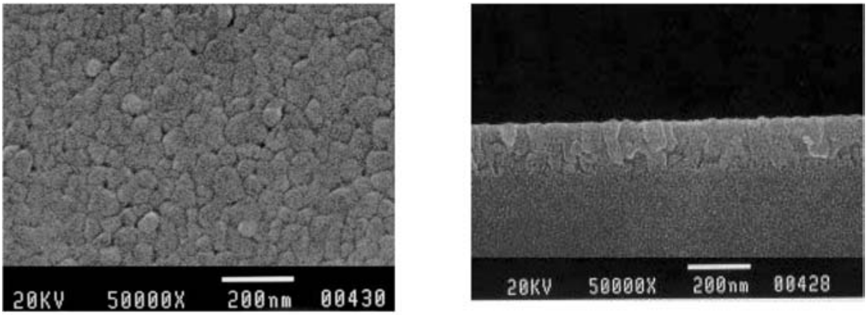


Fig. 4. Variation of oscillation amplitude with frequency.



(a) (b)

Fig. 5. Microphotograph of (a) surface and (b) side of TiO_2 thin film sputtered on Si with 150 nm thickness.

amplitude in Eq. (3). Assuming the TiO_2 layer acts as a thermal resistance, the through-plane thermal conductivity of the film can be calculated using Eq. (6).

Figure 5 shows SEM microphotographs of sputtered TiO_2 thin film sample 1. The thickness of the film was about 150 nm, and the average grain size was about 50 nm. The grain size of sample 2 (for which we did not obtain a clear image) has a smaller value than that of sample 1 because of a lower growth temperature. We observed significant changes in the average grain size because of the temperature of the substrate.

Figure 6 shows the measured thermal conductivity of TiO_2 films with several other literature data [10] and a reference value of bulk TiO_2 [11]. As the temperature increases, the thermal conductivities of samples 1 to 4 increase and reach a maximum at about 250 K and then begin to decrease, showing a different trend compared to literature values that increase gradually. This is assumed to be caused by the fact that the grain size of our samples changes while the film thickness changes as shown qualitatively in Fig. 5, and it needs additional quantitative investigation and analysis. All of the measured values are in the range from 1 to 10 $W \cdot m^{-1} \cdot K^{-1}$ which agrees with the literature values.

From the result, we can see that films grown at lower temperature have lower thermal conductivities and this may be due to the increased phonon scattering with smaller grain size. Therefore, the thermal conductivity of TiO_2 films strongly depends on the growth temperature and begins to approach the thermal conductivity of bulk TiO_2 ceramics when $T \approx 350$ K. The results of Lee and Cahill [10] show that the thermal conductivity of sputtered films depends on the deposition temperature and approaches the thermal conductivity of bulk ceramics when $T_s \cong 400$ K.

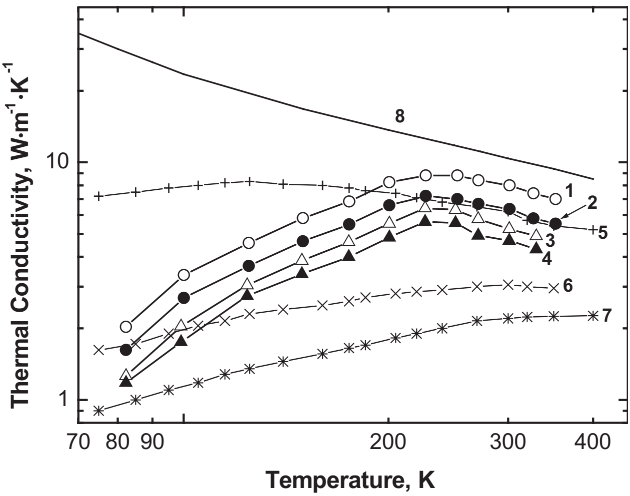


Fig. 6. Measured thermal conductivities of TiO_2 thin film samples compared with several other literature data and a reference value of bulk TiO_2. 1 to 4: our samples 1 to 4, respectively; 5: film deposited at 400°C [10]; 6: film deposited at 250°C [10]; 7: amorphous sample [10]; 8: recommended values for TiO_2 single crystals [11].

The thickness-dependent thermal conductivity of samples may be due to the effect of the thermal resistance of the interface between the dielectric layer and Si substrate and between the strip and dielectric layer. Because of phonon boundary scattering at the interface between the film and substrate, the thermal resistance for the case of films of smaller thickness increases at the interface between the film and substrate. This effect produces a smaller thermal conductivity. The theoretical explanation has been examined by Swartz and Pohl [12]. The thermal resistance R_i at the interface was expressed as $\kappa_a = \frac{\kappa_i}{1+R_i\kappa_i/d}$ by Lee and Cahill [13] and Yamane [14], where k_i is the intrinsic thermal conductivity assumed to be constant and independent of thickness and k_a is the measured, thickness-dependent thermal conductivity found from Eq. (6). The thermal resistance for the interface of the TiO_2 film at 250 K was calculated using the estimated value of 12 $W \cdot m^{-1} \cdot K^{-1}$ as k_i for several curve fits with this equation. We found that the thermal resistances of the samples were in the range of 10^{-9} to 10^{-8} $K \cdot m^2 \cdot W^{-1}$ at 200 K. The thermal resistances at other temperatures can be found in the same way.

5. CONCLUSIONS

We have prepared TiO_2 thin films on Si using dc magnetron sputtering and measured the thermal conductivity using the 3ω method in the temperature range from 80 K to room temperature. We have observed that the thermal conductivity of TiO_2 thin films deposited at higher growth temperatures has a large thermal conductivity. Thus, we suppose that the temperature of the substrate may affect the thermal conductivity of the thin film. We have also observed that the thermal conductivity of TiO_2 thin films depends on the thickness of the film and the microstructure of the films. The samples with smaller grain size and thinner thickness have smaller thermal conductivities.

ACKNOWLEDGMENT

This work was supported by the Korea Science and Engineering Foundation under Grant No. 2000-1-11400-002-3.

REFERENCES

1. A. H. Guenther and J. K. Mclver, *Thin Solid Films* **163**:203 (1988).
2. D. Ristau and J. Ebert, *Appl. Opt.* **25**:4571 (1986).
3. J. C. Lambropoulos, M. R. Jolly, C. A. Amsden, S. E. Gilman, M. J. Sinicropi, D. Diakomihalis, and S. D. Jacobs, *J. Appl. Phys.* **66**:4230 (1989).
4. C. H. Henager, Jr. and W. T. Pawlewicz, *Appl. Opt.* **32**:91 (1993).
5. M. Okuda and S. Ohkubo, *Thin Solid Films* **213**:176 (1992).
6. D. G. Cahill, *Rev. Sci. Instrum.* **61**:802 (1990).
7. D. G. Cahill, H. E. Fischer, T. Klitsner, E. T. Swartz, and R. O. Pohl, *J. Vac. Sci. Technol. A* **7**:1259 (1989).
8. H. S. Carslow and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford University Press, Oxford, 1959), p. 193.
9. S. M. Lee and D. G. Cahill, *J. Appl. Phys.* **81**:2590 (1997).
10. S. M. Lee and D. G. Cahill, *Phys. Rev. B* **52**:253 (1995).
11. Y. S. Touloukian, R. W. Powell, C. Y. Ho, and M. C. Nicolaou, *Thermophysical Properties of Matter*, Vol. 2 (Plenum, New York, 1973), p. 203.
12. E. T. Swartz and R. O. Pohl, *Appl. Phys. Lett.* **51**:2200 (1987).
13. S. M. Lee and D. G. Cahill, *J. Appl. Phys.* **81**:2590 (1997).
14. T. Yamane, N. Nagai, S. Katayama, and M. Todoki, *J. Appl. Phys.* **91**:9772 (2002).