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Thermal conductivity of ZrO_2 thin films [1]

Stéphane Orain [a]*, Yves Scudeller [a], Thierry Brousse [b]

[a] *Université de Nantes, ISITEM, Laboratoire de thermocinétique, UMR-CNRS 6607, La Chantrerie, BP 90604, 44306 Nantes cedex 3, France*

[b] *Université de Nantes, Laboratoire de Génie des Matériaux, La Chantrerie, BP 90604, 44306 Nantes cedex 3, France*

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Abstract — The thermal conductivity of thin solid films may be considerably lower than bulk material ones. We have recently developed a new photothermal method which enables the determination of the thermal conductivity of the dielectric films, on various kind of substrates, with an accuracy better than 10%. In this paper, we present the thermal conductivity of two kinds of ZrO_2 thin films (stabilized with Y_2O_3 or not). We observe that a decrease in the dielectric thickness leads to a drastic drop of the thermal conductivity λ_a. The drop in the thermal conductivity has a similar shape for the two ZrO_2 phases. Phonons boundary scattering cannot contribute so significantly to the reduction of λ_a. The most satisfactory explanation is that the thermal conductivity λ_a is affected by an additional thermal resistance R, especially between ZrO_2 and alumina substrate. In the future, we intend to study in more detail the structures of the interfaces. © 2000 Éditions scientifiques et médicales Elsevier SAS

thin film / thermal conductivity / interface / heat transport / ZrO_2 film / thermal resistance

Résumé — **Conductivité thermique des couches minces de ZrO_2.** La conductivité thermique des dépôts d'oxyde de Zircone en couches minces intéresse de nombreux domaines d'application (barrières thermiques des chambres de combustion, piles à combustible...). Nous avons récemment développé une méthode permettant de mesurer la conductivité thermique d'un dépôt submicronique dans la direction normale au substrat sur lequel il est déposé. La méthode est fondée sur l'analyse de l'évolution de la température de surface consécutive à l'absorption d'une impulsion laser. La température est détectée en suivant les variations de la résistance électrique d'un dépôt d'or de 0,2 μm. La précision de la mesure est de l'ordre de 10% pour un dépôt de 1 μm. La conductivité thermique de films de ZrO_2, dont l'épaisseur est comprise entre 50 nm et 1 μm, a été mesurée. Les dépôts ont été réalisés par pulvérisation cathodique. Deux cibles de ZrO_2 ont été utilisées. L'une stabilisée à l'Yttria (15% de Y, 85% de ZrO_2) a permis d'obtenir une cristallisation de forme cubique (taille des cristallites : 20 nm); l'autre, non stabilisée, une cristallisation de forme monoclinique (taille des cristallites : 13 nm). La conductivité thermique de ZrO_2 stabilisée apparaît plus élevée que celle de ZrO_2 non stabilisée en raison de la cristallisation et de la taille des cristallites. Une réduction importante de la conductivité thermique est observée en fonction de l'épaisseur pour les deux types de cristallisation. La conductivité thermique de dépôts de l'ordre micron avoisine celle du matériau massif. Ceci tient à la forte densité des dépôts qui a été confirmée par l'étude structurale et microstructurale (MEB, diffraction rayons X). Cette diminution de conductivité est essentiellement imputable à l'existence d'une résistance thermique d'interface entre le dépôt et le substrat. Nous avons pu la mesurer pour les deux type de cristallisation ($1{,}9\cdot10^{-7}$ $m^2\cdot KW^{-1}$ pour la forme cubique et $2{,}5\cdot10^{-7}$ $m^2\cdot KW^{-1}$ pour la forme monoclinique). © 2000 Éditions scientifiques et médicales Elsevier SAS

couche mince / conductivité thermique / interface / transport de chaleur / film de ZrO_2 / résistance thermique

Nomenclature

$c\rho$	specific heat	$J\cdot m^{-3}\cdot K^{-3}$
e	thickness	m
R	thermal resistance	$m^2\cdot K\cdot W^{-1}$
t	time	s
t_{iso}	time required by the thin film to become an isothermal regime	s
t_l	time during which a thermal gradient is stated in the thin film	s

Greek symbols

λ	thermal conductivity	$W\cdot m^{-2}\cdot K^{-1}$
λ_a	apparent thermal resistance	$W\cdot m^{-2}\cdot K^{-1}$

1. INTRODUCTION

Thermophysical properties of dielectric thin solid films influence the reliability of various systems in electronics, opto-electronics, photonics or aerospace. Ther-

* Correspondence and reprints.
orain@isitem.univ-nantes.fr

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mal conductivity of such films may be considerably lower than for bulk material. This difference can be assigned to the structural disorder of materials deposited in a thin film, to a large interface thermal resistance or at last, to the limitation of the phonon mean free paths.

We have recently developed a new photothermal method which enables the determination of both the thermal conductivity and the heat capacity of dielectric films on various kinds of substrates. Due to the very short response time of our measuring device, we can investigate the thermal properties of thin layers in the submicron range with a high accuracy.

To clarify the role of these three different phenomena, we have focused our investigations on ZrO_2 thin films of different thickness. Furthermore, two kinds of ZrO_2—stabilized with Y_2O_3 or not—have been studied to investigate the effects of phases and crystallite sizes.

2. EXPERIMENTAL

2.1. Sample film preparation and characterisation

Thin films have been deposited using a RF sputtering technique. Two different batches of films were prepared on polycrystalline Al_2O_3 substrates (corundum).

The first batch was deposited using a pure ZrO_2 target (monoclinic form). The same deposition conditions have been used for all the films (RF power, argon and oxygen flow rates, etc.) except the deposition time which has been varied in order to grow layers of different thickness. According to weight increase, surface profilometry and scanning electron microscope observations, films with thickness ranging from 75 nm to 1 000 nm were grown with this target. X-ray diffraction analyses have shown broad *hkl* reflections of the monoclinic structure of ZrO_2 (Baddeleyite type, JCPDS #37-1484) thus indicating a poorly crystallized layer for every sample (75 nm to 1000 nm). According to the Scherrer formula, the crystallite size never exceeded 13 nm.

For the second batch of films, an yttria stabilized zirconia target (YSZ, 15 at.% of Y, 85 at.% of Zr) was used. The film thickness ranged from 125 nm to 1 000 nm. X-ray diffraction analysis indicated that the deposited material crystallized in the cubic form of ZrO_2 as expected with an YSZ target. The observed *hkl* reflections fitted well with the JCPDS #30-1468 theoretical pattern of yttria stabilized zirconia. However, a small amount of Y_2O_3 (JCPDS #41-1105) has been detected in all the films, thus indicating that an excess of yttrium has been deposited. The energy dispersive X-ray analyses confirmed that the Y/Zr ratio in all the films was close to 20 % instead of 15 % for the target. The films also were poorly crystallized with an average crystallite size of 20 nm, i.e. slightly larger grains than for the monoclinic ZrO_2 layers of the first batch.

2.2. Determination of the thermal conductivity and heat capacity

Details of the measurement photo-thermal technique are described in previous studies [1]. In brief, this photothermal method has been used to measure the thermal conductivity simultaneously with heat capacity. The technique is based on the analysis of transient surface temperature induced by absorption of a short laser pulse. The extremely thin layers have required to set up this new method. A gold layer of 200 nm has been deposited on the dielectric film. Temperature variations are obtained from measurement of the electrical resistivity of the metal. An electrical current is applied through the metal and a differential tension is detected between its two sides. Tension is measured by means of a Wheastone bridge. Before irradiation, the bridge balance eliminates the contribution of the tension corresponding to the initial temperature. Detection is sensitive only to temperature variations. Sensitivity of a few mV/K can be reached. The thermal conductivity is identified simultaneously with heat capacity by fitting theoretical and experimental normalized thermograms over a temporal sequence ranging from about 10^{-7} to 10^{-6} s. Identification is performed by means of a least square technique.

2.3. Experimental details

The experimental setup (*figure 1*) is composed of a laser YAG : Nd, the sample integrated in the Wheastone bridge, an acquisition and data processing system. The laser (wavelength 1.06 μm) supplies high energy pulses (0–4 J) of about 20 ns. Laser spot has a diameter of 10 mm. A He–Ne laser aligns the target with the incident beam. The sample is held on a microstage $xyz\theta$.

The sample (*figure 2*) is composed of a ZrO_2 layer sputtered on a bulk substrate. A gold sensor is deposited on the sample and is connected with two copper blocks by means of a connecting paste. The gold film of about 100 nm is supplied by a current of 50 mA. The sensor shape is achieved by means of a deposition mask which

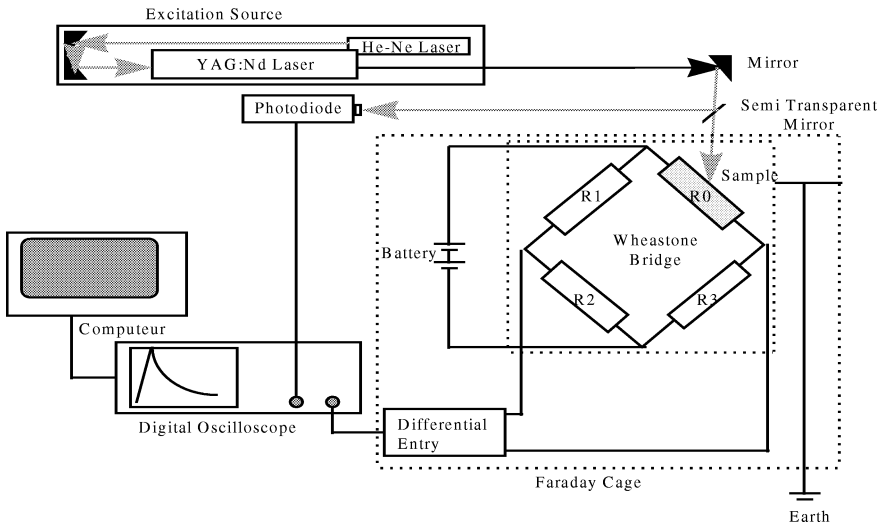

Figure 1. Experimental arrangement.

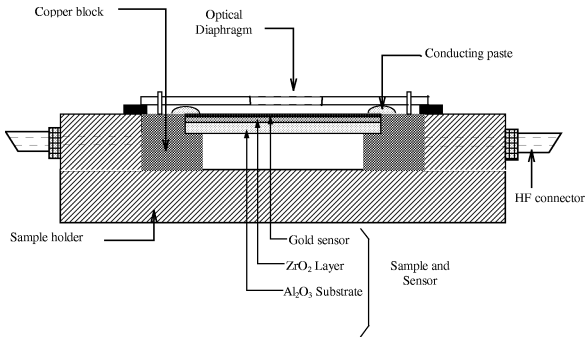

Figure 2. Test sample and its holder.

has a role of an optical diaphragm during laser shots. The sample and its Wheastone bridge are enclosed in a Faraday cage to reduce electromagnetic perturbations. The digital oscilloscope operates with a sampling frequency of 100 MHz and has an analog bandwidth of 100 MHz. Data are processed on a computer.

2.4. Sensitivity of the method

Our preliminary studies have demonstrated that it was possible to measure the thermal conductivity of SiO_2 and ZrO_2 thin films deposited on alumina substrates. Thermal conductivity and specific heat of ZrO_2 thin films were found very close to those of bulk material. On the other hand, the thermal conductivity of submicron layers

TABLE I
Effect of thickness on thermal conductivity and on specific heat for ZrO_2 thin film.

Thickness (nm)	230	920	Bulk material
λ ($W{\cdot}m^{-1}{\cdot}K^{-1}$)	0.6	1.3	1.5–2.5
$c\rho$ ($J{\cdot}m^{-3}{\cdot}K^{-3}$)	$2{\cdot}10^6$	$2.8{\cdot}10^6$	$2.4{\cdot}10^6$–$3{\cdot}10^6$

was strongly reduced, whereas the specific heat remained unchanged (*table I*).

This reduction of the thermal conductivity has been experimentally observed on various sputtered solid thin films such as oxides (TiO_2, HfO_2, Al_2O_3, etc.), fluorides (AlF_3, HfF_4, YF_3, etc.) and on others like ZnS [2]. But, in most cases only few thicknesses have been investigated except for silicon oxide, which has been particularly studied [3, 4, 8]. So, in order to investigate the influence of the thickness on the thermal conductivity, we have deposited a large number of ZrO_2 thin films ranging from about 50 nm to 1 μm.

Thermal conductivity measurement requires a temperature gradient inside the material. The major difficulty of the photothermal method is to generate a significant thermal gradient and then to detect accurately fast transient temperature response. *Figure 3* shows temporal variations of temperature measured for three ZrO_2 thicknesses (125 nm, 375 nm and 1 μm) with the same substrate and sensor. The aspect of thermograms are typical: it corresponds to the cooling of the sample by heat diffusion through dielectric and substrate. The strong differences

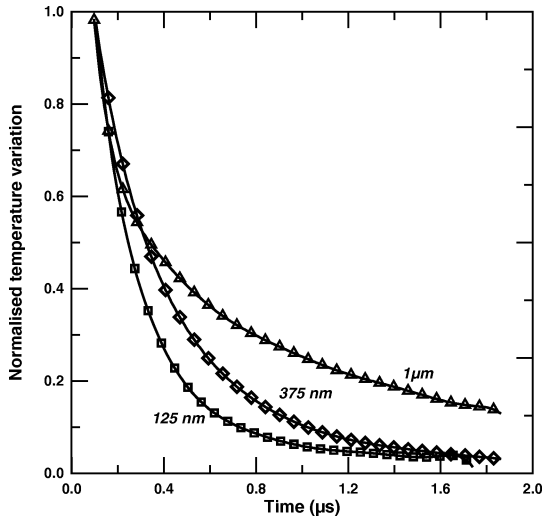

Figure 3. Temperature drops for three different ZrO_2 thicknesses (125 nm, 375 nm, 1 µm).

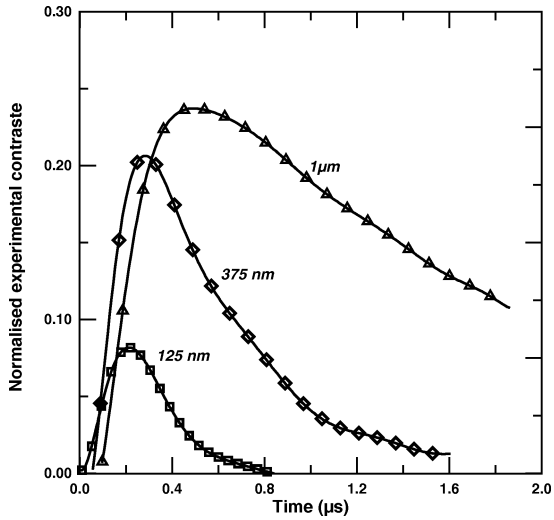

Figure 4. Experimental thermal contrast for three different ZrO_2 thicknesses (125 nm, 375 nm, 1 µm).

between each cooling down are only due to the state of dielectric layer. Temperature variations are normalized by their values at time $t = 100$ ns.

Before $t = 300$ ns, temperature responses are similar, because the ZrO_2 layer is as a semiinfinite body. Time lag t_{iso}, required by ZrO_2 films to become an isothermal regime, increases with thickness. t_{iso} is ranging from 1 to 2 microseconds.

Figure 4 shows three "experimental" thermal contrasts. Here, we define the contrast as the difference between temperature rise with and without ZrO_2 thin film. On one hand, it reveals the time lag t_1 during which a thermal gradient is stated in ZrO_2 layer. t_1 is about 200 ns for 125 nm of ZrO_2 and raised up to more than 2 µs for 1 µm. On the other hand, the contrast highlights the effects of ZrO_2 on temperature response. The maximum of contrast increases and drifts in time with ZrO_2 thickness. It follows that a high contrast induces an accurate measurement of the thermal conductivity. The contrast is significant even for a thin film thicker than 50 nm; it corresponds to 5 K increase for 100 nm.

The precision of the thermal conductivity measurement mainly depends on the knowledge of thickness and thermal properties introduced in the identification algorithm. There are three main parameters: the gold and ZrO_2 thickness, the effusivity of the substrate. The determination of different thickness has been performed by quartz balance, ellipsometer and profilometer. Conductivity and specific heat of the alumina substrate have been measured respectively by hot plat guarded method and differential scanning calorimeter. The thermal conductivity has been identified by fitting theoretical and experimental normalized temperature. The fitted value has been obtained considering the measurement of gold and ZrO_2 thickness as well as the alumina effusivity. In each *figure 5*, the experimental curve of 110 nm ZrO_2 thin film is plotted in empty squares, temperatures calculated with different parameter values are plotted in dotted line and the fitted curve is plotted in bold line. On these figures, the gold layer is 142 nm thick, and the effusivity of the alumina substrate is taken as 9 700 $J{\cdot}m^{-2}{\cdot}K^{-1}{\cdot}s^{-0.5}$ in accordance with measurements.

Figure 5a shows the good fit achieved with a thermal conductivity of 0.15 $W{\cdot}m^{-1}{\cdot}K^{-1}$. Different curves generated with lower or higher thermal conductivity have been plotted to highlight the sensivity of the method. On *figure 5b*, while keeping the ZrO_2 thickness parameter and the effusivity of the substrate constant in our model, we can highlight the role of the gold layer thickness. Thus, we can see that a small error in the gold thickness induces a difference in the cooling down and so, in the thermal conductivity estimated. On *figure 5c*, the same effect is observed when the ZrO_2 thickness is changed (gold thickness and effusivity of the substrate are constant). On the other hand, *figure 5d* shows that the effusivity has a small effect on the cooling down (gold and ZrO_2 thickness are constant). Clearly, a precise knowledge of gold and ZrO_2 thickness is required. The model is in very good agreement with experiments. Considering the sensivity of the method and experimental errors, we estimate that the incertitude of thermal conductivity measurements is less than 15 %.

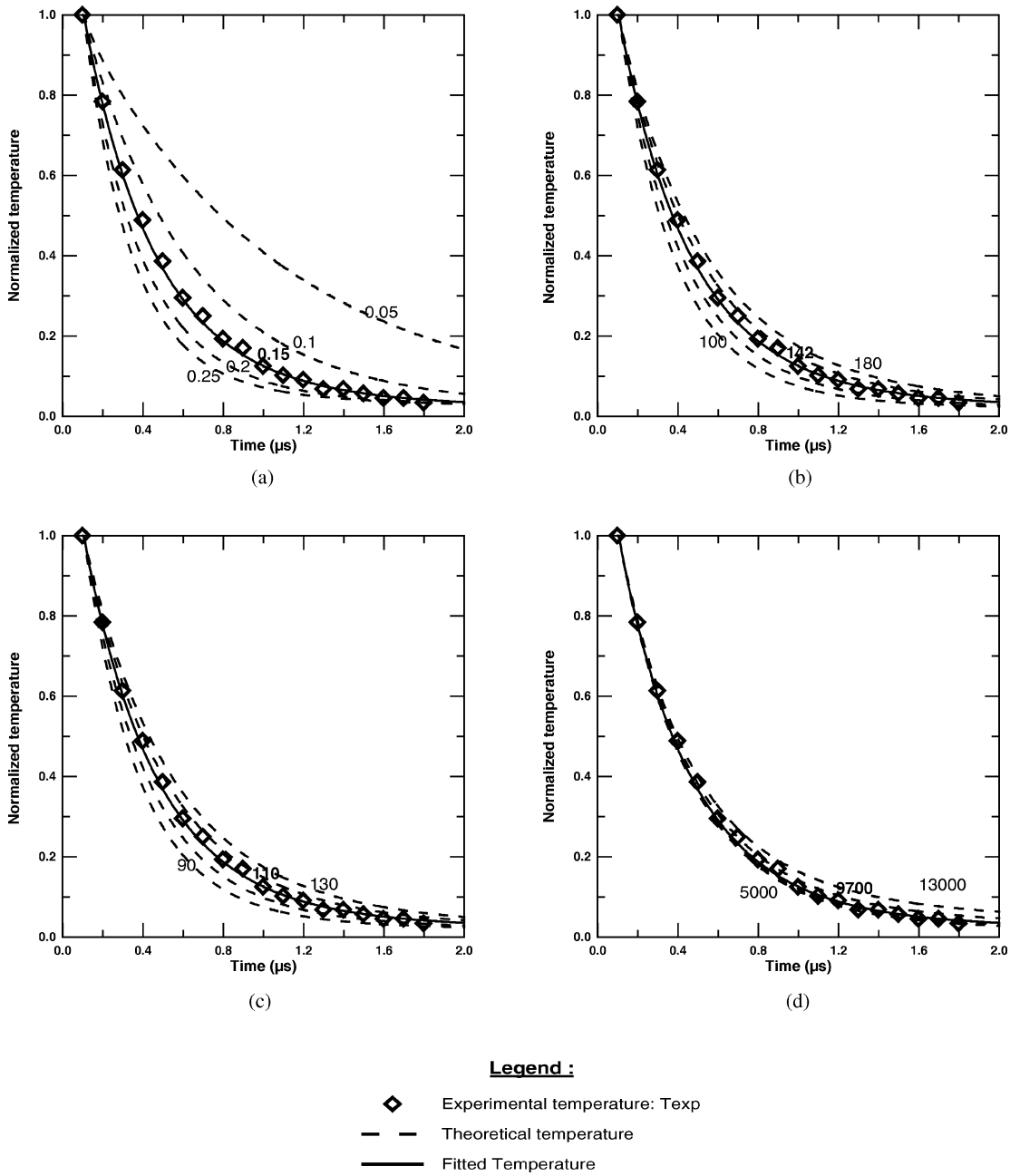

Figure 5. Influence of the main parameters on cooling down for a 110 nm ZrO_2 thin film. (a) ZrO_2 thermal conductivity (0.05, 0.1, **0.15**, 0.2, 0.25 $W{\cdot}m^{-1}{\cdot}K^{-1}$). (b) Gold thickness (100, 120, **1420**, 160 and 180 nm). (c) ZrO_2 thickness (90, 100, **110**, 120,130 nm). (d) Substrate effusivity (5000, 8000, **9700**, 11000, 13000 $J{\cdot}m^{-2}{\cdot}K^{-1}{\cdot}s^{-0.5}$).

3. RESULTS AND DISCUSSION

We have measured separately the thermal resistance between the gold sensor and the ZrO_2 by the technique described in [5]. It has been estimated to be $1.7{\cdot}10^{-7}$ $m^2{\cdot}K{\cdot}W^{-1}$ and taken into account to identify the thermal conductivity λ_a of ZrO_2. On *figure 6*, we have plotted λ_a versus the thickness e of the layer for

two kinds of ZrO_2 phases. *Figure 6* denotes a strong decrease of λ_a with e. For example, the thermal conductivity of nonstabilized ZrO_2 is divided by 8 between 1 μm to 100 nm. The drop in the thermal conductivity has a similar shape for the two ZrO_2 phases. Phonons boundary scattering cannot explain this decrease because the phonon mean free paths of ZrO_2, of the order of 0.5 nm, are much smaller than our thinnest film (73.5 nm) and so could not contribute so significantly to the reduction of λ_a. This argument is in good accordance with measurements performed on SiO_2 [6, 7]. The most satisfactory explanation is that the thermal conductivity λ_a is affected by an additional thermal resistance R. In fact, the thermal resistance of the ZrO_2 layer can be viewed as the contribution of two thermal resistances [8]:

$$\frac{e}{\lambda_a} = \frac{e}{\lambda_i} + R \qquad (1)$$

- e/λ_i is the intrinsic thermal conductivity of the ZrO_2 layer in absence of defect, λ_i being only determined by ZrO_2 phases, crystallite size and grain boundary density.
- R is due to a volume distribution of defects inside the layer, particularly near the transition region, as well as a boundary resistance located at ZrO_2/substrate interface.

In order to check this assumption, we have plotted in *figure 7* the apparent thermal resistance e/λ_a versus the ZrO_2 thickness e. For the two kinds of ZrO_2 phase, it presents a straight line for thickness larger than 100 nm. Thus, in accordance with equation (1), λ_i and R can be extracted respectively from the slope and the intercept of the straight line with the ordinate.

The intrinsic thermal conductivity is very close to that of bulk material (*table II*). The difference is probably due to the presence of grain boundary. In addition, we note that the λ_i of the stabilized phase is approximately 30 % larger than for the nonstabilized phase one. This result can be explained by the difference of phase and crystallite size. R, of about $2{\cdot}10^{-7}$ $m^2{\cdot}K{\cdot}W^{-1}$, is comparable with those found by other authors [4, 9].

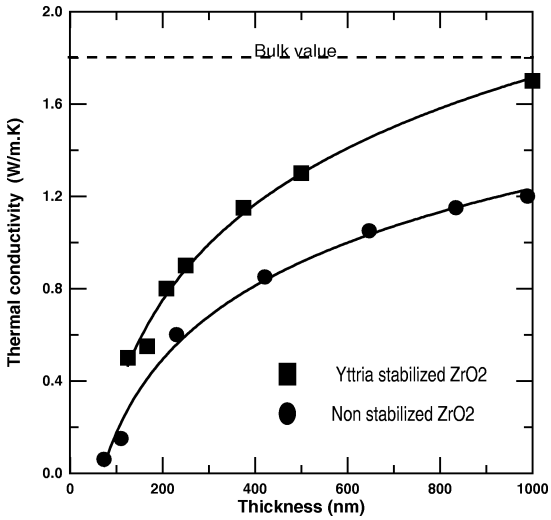

Figure 6. Evolution of thermal conductivity λ_a with thickness.

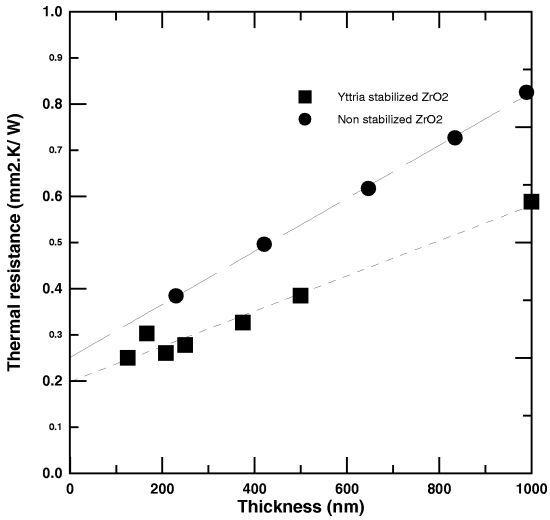

Figure 7. Evolution of thermal contact resistance.

TABLE II
λ_i and R values for the two ZrO_2 phases.

	Crystallization	Crystallite size (nm)	λ_i bulk value ($W{\cdot}m^{-2}{\cdot}K^{-1}$)	λ_i ($W{\cdot}m^{-2}{\cdot}K^{-1}$)	R ($m^2{\cdot}K{\cdot}W^{-1}$)
Stabilized ZrO_2	cubic form	20	2.3	2.5	$1.9{\cdot}10^{-7}$
Nonstabilized ZrO_2	monoclinic	13	1.9	1.7	$2.5{\cdot}10^{-7}$

4. CONCLUSION

The thermal conductivity of ZrO_2 thin films ranging from 50 nm to 1 μm has been measured by using an original photothermal technique. The precision of measurements is better than 15 %.

It was found that the thermal conductivity of ZrO_2 is as much as one order of magnitude lower than the thermal conductivity of the bulk materials. The thermal conductivity is affected by an additional thermal resistance, strongly dependent on the interface structure.

We are intending to lead more investigations on the effects of type of phase, crystallite sizes and interface structure.

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