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Thermal conductivities of thin, sputtered optical films

C. H. Henager, Jr. and W. T. Pawlewicz

The normal component of thin-film thermal conductivity has been measured for the first time, to the best of our knowledge, for several advanced sputtered optical materials. Included are data for single layers of boron nitride, silicon aluminum nitride, silicon aluminum oxynitride, silicon carbide, and for dielectricenhanced metal reflectors of the form $Al(SiO_2/Si_3N_4)^n$ and $Al(Al_2O_3/AlN)^n$. Sputtered films of more conventional materials such as SiO_2 , Al_2O_3 , Ta_2O_5 , Ti, and Si have also been measured. The data show that thin-film thermal conductivities are typically 10 to 100 times lower than conductivities for the same materials in bulk form. Structural disorder in the amorphous or fine-grained films appears to account for most of the conductivity difference. Conclusive evidence for a film-substrate interface contribution is presented.

Key words: Thermal conductivity, sputtered optical films, thermal comparator, dielectric-enhanced metal reflectors, structural disorder, film-substrate interface.

Introduction

A wide variety of dielectric and metal films is currently being examined for advanced optical elements in which high power densities are encountered. Both high and low refractive-index materials are necessary for building multilayered dielectric stacks, and all the materials are required to be thermally and environmentally stable. Oxides and nitrides have the necessary optical properties, are easily deposited as high-quality films, and are stable. High thermal conductivities are also required, since the ability of an optical element to dissipate heat is often a limiting factor in optical designs. Uncertainties in optical film thermal conductivities can impose limitations on design accuracy.¹ This is especially true since it is now accepted that thin dielectric films have thermal conductivities that are much lower than comparable bulk materials. This means that indiscriminate use of bulk conductivity data in optical element design and damage calculations is highly inaccurate.

A variety of measurement techniques has been utilized to make thin-film thermal conductivity mea-

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surements: thermal comparators,^{2–4} specialized film geometries (including measurements on freestanding films),^{5–8} laser calorimetry,^{9,10} and flash radiometry.¹¹ The use of specialized film geometries^{7,12-14} offers the greatest potential to achieve an understanding of thin-film thermal and electronic processes, but these methods are impractical for optical film development research. The thermal comparator technique allows standard film-substrate geometries to be used in a nondestructive manner and is rapid and easy to use. This technique was developed to measure thermal conductivities of bulk specimens² but has been adopted for thin film use.^{3,4} Briefly, a heated probe is brought into contact with the film-substrate system mounted on a heat sink. A temperature difference develops between the probe tip and a probe reference heat reservoir. The difference is proportional to the conductivity of the film-substrate system: small for poor conductors and large for good conductors.

All the above techniques have consistently indicated that thin-film thermal conductivities, when measured parallel to the film growth direction, are much smaller than bulk values. Boiko *et al.*⁵ and Nath and Chopra⁶ measured in-plane thermal conductivities of deposited metal films and found good agreement with bulk values for films thicker than ~5000 Å. This immediately suggests that there is a large thermal resistance at the film–substrate interface. However, Decker *et al.*⁸ observed low thermal conductivity of freestanding SiO₂ films when measured parallel to the film growth direction, suggesting

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that structural disorder also plays a major role in determining thin-film conductivities.

The majority of other studies have examined oxide films such as SiO₂ and Al₂O₂. Lambropoulos *et al.*³ also measured fluoride films. Ristau and Ebert⁹ measured electron-beam deposited films of Al₂O₃, TiO₂, HfO₂, Ta₂O₅, and SiO₂ on fused-silica substrates and found that only Al₂O₃ had a value close to the bulk. The other films had from one to several orders of magnitude lower thermal conductivities than bulk values. Lambropoulos *et al.* observed large differences between thin films and bulk materials such as TiO₂, Al₂O₃, and MgF₂. Ogden *et al.*⁴ observed that thick (as thick as 85-µm) films of anodized aluminum coatings, nominally Al₂O₃, had average thermal conductivities of 0.73 W/(mK) compared with 30 W/(mK) for bulk, polycrystalline Al₂O₃.

The silica glass system has been studied extensively by these thin-film techniques; measured thin-film thermal conductivities are found to be from a factor of 2 to an order of magnitude smaller than bulk conductivities. Decker et al.⁸ measured SiO₂ films between 0.5 and 1 μ m thick and found values an order of magnitude lower than in bulk SiO₂, 0.17-0.28 W/(mK) compared with 1.4 W/(mK) for bulk fused silica.¹⁵ Ristau and Ebert⁹ measured thin-film values of 0.1 W/(mK) for 1- μ m-thick SiO₂ films. Lambropoulos et al.³ reported values of 0.45-0.61 W/(mK) for electron-beam evaporated SiO₂ and 0.41-1.05 W/(mK) for ion-beam-sputtered SiO₂. Swartz and Pohl⁷ observed thin-film conductivities approximately a factor of 2 smaller than bulk SiO_2 . The work of Swartz and Pohl⁷ suggests that the filmsubstrate interface or near-interface region contributes to phonon scattering that is sufficient to account for these differences. This additional scattering is proposed to come from local structural disorder.

Experimental Procedures

Thermal Comparator Technique

A thermal comparator was built and used to obtain thermal conductivities by using an approximate analytical expression for the thermal resistance of the comparator-film-substrate system (see Appendix A). The comparator consists of an oxygen-free high conductivity (OFHC) copper probe with a fine tip $(r_p \sim 0.2)$ mm) machined on the end, a large OFHC copper plate heat sink (15-cm diameter \times 2.5 cm thick), and a Plexiglas enclosure (Fig. 1). The probe was mounted on a stem attached to an x-y-z manipulator, which allows accurate positioning of the probe tip on the specimen. A Constantan wire was placed down the stem through a hole drilled in the probe and makes a soldered copper-Constantan (type T) thermocouple junction at the probe tip. Small weights were placed on the probe assembly to give a total probe mass of ~ 200 g. A reference thermocouple was placed in the probe body and a thermocouple was placed in the copper heat sink. The probe was heated to 85°C by using a small heater wrapped around the probe body and the temperature was controlled to $\pm 0.5^{\circ}C$ by using a standard three-mode controller for operating a 200-W power supply. The specimens were placed on the copper heat sink held at ambient temperature. The Plexigas enclosure shelters the comparator from laboratory air currents. An HP-85 computer with an HP data-acquisition box was used to acquire the comparator data, which consists of the probe reference temperature, the temperature difference between the probe tip and probe body (reservoir) at contact, and the heat sink temperature. An operational amplifier with a gain of 10^4 was used to amplify the probe tip-probe body temperature difference signal, which typically ranged from 4 to 30 μ V (using



Fig. 1. Photograph of the thermal conductivity apparatus.

 $45.7\ \mu V/K$ for copper–Constant n type T thermocouple).

As a check of the comparator, we measured several bulk standards to demonstrate the square root dependence of the change in temperature between the probe tip and reservoir as a function of thermal conductivity observed by Powell² (Fig. 2). Figure 2 illustrates how the comparator can be used as a calibration curve to determine the thermal conductivity of an unknown bulk material in a comparative manner. The line on the plot is a fitted line to the data (passing also through the origin) and illustrates the approximate nature of the comparator data when bulk materials are measured. Note the discrepancy between the measured value for SiO₂ and the square root fitted line suggesting that large uncertainties would be encountered when a comparator technique is used over such a large range of thermal conductivities.

Use of the comparator with thin-film specimens required the development of an experimental technique and analysis method distinct from that used to measure bulk conductivities. Measurements of coated substrates indicated a large reduction in thermal conductivity from the uncoated substrates, which for the experiments reported here was polished singlecrystal silicon. This reduction in conductivity was used to extract that portion of the thermal resistance that was due to the coating (film) but can only be used to give the effective conductivity of the film plus film-substrate interface system (see Appendix A). The analysis method requires that films of several different thicknesses be deposited and measured to determine the film thermal conductivity.

A probe temperature of 85°C and a heat sink temperature of 22°C (ambient) were chosen to give a large temperature difference signal without heating the heat sink. Typically, the heat sink temperature would rise ~ 1°C during a several-hour data-acquisition session. The probe mass of 200 g was chosen by trial and error to give a reproducible probe tipspecimen contact. As with other thermal comparators, when the probe tip makes contact with the specimen, a temperature difference is established between the probe tip and the probe body (reservoir)



Fig. 2. Probe tip/probe body voltage difference as a function of $\sqrt{k_{\rm th}}$ for various bulk standards.

as heat flows from the probe into the specimen. For this thermal comparator, a steady-state temperature difference was established within 2 s after contact. The computer data-acquisition system was programmed to discard temperature data acquired before this steady-state temperature was reached. Average temperature differences were computed by using probe reference temperatures acquired several seconds before and after probe tip contact was made. Contact was made for 5 s, with the first 2 s of data discarded as discussed above. Typically seven to ten contacts were made for a given film thickness to obtain a single data point. Since the probe tip-film contact resistance was of concern during this measurement, a high thermal conductivity grease was applied to the probe tip to ensure uniform contact between the probe tip and specimen. All seven to ten contacts for a given data point were made at the same location by using the same thermal grease spot. New grease was applied to the probe tip after the measurement was shifted to a new location or new specimen.

Sputtered Optical Films

A wide variety of films (Table 1) was deposited on (111) single-crystal, highly polished (5-Å rms) Si substrates (3.8-cm diameter \times 0.64 cm thick), a standard substrate used in optical film research. When possible, several film thicknesses were chosen to give a range that spans the thickness of interest. For example, typical single-layer dielectric film thicknesses for optical applications range from 0.5 to $2 \mu m$, while multilayered stacks range from 1 to 5 μ m. The silicon aluminum nitride (Si:Al:N) and silicon aluminum oxynitride (Si:Al:O:N) films ranged from 10 to 60 µm in thickness. A limited amount of data was obtained from films of only a single thickness by using a bare Si substrate as a zero thickness film. Films were sputtered by using a variety of techniques, which included rf diode reactive sputtering from 15-cm targets and both large chamber (2-m substrates) and small chamber (35-cm substrates) magnetron sputtering.^{16,17} No evaporated films were measured.

Method of Analysis of Thin-Film Data and Principal Measurement Uncertainties

An analysis of the series of thermal resistances involved in the comparator measurement is shown in Appendix A and an approximate expression for the film thermal conductivity is obtained as [see also Eq. (A18) in Appendix A]

$$K_3 = k_{\rm th}{}^f = \frac{4K_1 r_1}{mA_3}, \qquad (0)$$

where $k_{\text{th}}{}^{f}$ is the film thermal conductivity (including the film–substrate interface), K_1 is the thermal conductivity of the probe body and is equal to that of OFHC copper, 401 W/(mK), r_1 is the probe tip radius and is set equal to $r_p{}^{\text{eff}}$, m is the slope of a fitted line for the temperature ratio [Eq. (A14) in Appendix A] as a

Fable 1.	Summar	of Thin-Film Thermal Conductivity Measurements
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		Thermal Conductivity (W/mK)			
Material	Film Structure	PNL ^a Data Thin Film	Other Data Thin Film	Bulk Conductivity	Ratio
Ti	(001) Texture 200-Å grains	1.6–2.0		21.9	11:14
Si	(111) Texture 300-Å grains	1.0		148	148
SiO_2 (Ref. 16)	Glassy	0.12	0.1 (Ref. 10) 0.17–0.28 (Ref. 8) 0.41–1.05 (Ref. 3)	1.3	11
Al_2O_3 (Ref. 16)	Glassy	0.12	0.25 (Ref. 8) 0.72 (Ref. 3) 0.73 (Ref. 4)	28	233
Ta_2O_5 (Ref. 16)	Glassy	0.12			
BN (Ref. 16)	Glassy	0.32		62 (a axis) 1.5–2.9	194 4.7:9.1
Si_3N_4 (Ref. 16)	Glassy	0.15		10	67
SiC (Ref. 16)	Glassy	0.12		25	208
$Si_{0.7}Al_{0.3}N$ (Ref. 20)	(111) Texture microcrystalline	0.82			
$Si_{0.6}Al_{0.4}N$ (Ref. 20)	(111) Texture microcrystalline	0.88			
$Si_{0.6}Al_{0.4}NO (Ref. 20)$ N:O = 2:1	(111 Texture) microcrystalline	0.83			
$Si_{0.6}Al_{0.4}NO (Ref. 20)$ N:O = 1:2	(111) Texture microcrystalline	0.62			
$Al(SiO_2/Si_3N_4)^n$ (Ref. 16)	Glassy	0.25			
$Al(Al_2O_3/AlN)^n$ (Ref. 16)	Glassy	0.32			

^aPacific Northwest Laboratory.

function of film thickness, and A_3 is the probe tipspecimen contact area, πr_p^{eff2} . Making these substitutions then gives

$$k_{\rm th}^{f}\left(\frac{\rm W}{\rm mK}\right) = \frac{1.604 \times 10^{3} \left(\frac{\rm W}{\rm mK}\right)}{\pi r_{p}^{\rm eff}({\rm m}) m \,(\mu {\rm m}^{-1}) 10^{6}}\,, \qquad (2)$$

where r_p^{eff} is 1.5×10^{-4} m as determined from micrographs of probe tip contact imprint areas from actual measurement spots by using thermal grease (Fig. 3) and *m* is determined by using a least-squares fitted line to the temperature ratio versus film thickness data. In Figure 3, the imprint area is not circular and r_p^{eff} was calculated by using the actual imprint area measured from the micrograph. Thus, r_p^{eff} is smaller than the actual probe tip radius and may vary from imprint to imprint. The temperature ratio is given by $(T_p - T_b)/(T_p - T_t)$, where T_p is the probe reference temperature, T_b is the heat sink temperature, and T_t is the probe tip temperature after the steady-state contact temperature is established.

The temperatures are measured and controlled to $\pm 0.5^{\circ}$ C, which implies an uncertainty of $\pm 1\%$ for T_p and T_i and $\pm 2.5\%$ for T_b . Further, because of the 1°C temperature drift in T_b , the uncertainty in T_b is actually $\pm 5\%$. Treating the propagation of these uncertainties in the normal manner gives an estimated uncertainty in the temperature ratio of $\pm 8\%$.

Uncertainties in the slope m are a ratio of the temperature ratio and the film thickness. Film thicknesses are measured to $\pm 10\%$ accuracy by using optical techniques. Therefore, uncertainties in mare $\pm 18\%$. K_1 , the thermal conductivity of the OFHC copper, was not measured, and an estimated uncertainty of $\pm 5\%$ is assigned to K_1 . The largest experimental uncertainties are the determination of r_p^{eff} and the assumption that it remains relatively constant from specimen to specimen. Underlying this are the assumptions, discussed in Appendix A, that lateral heat flow in the films can be neglected and that the actual probe tip-specimen contact area can be used for $r_p^{\text{eff.}}$ Obviously, the former assumption is best for low conductivity films. The uncertainty in r_p^{eff} is estimated to be ±50%. Measured thermal conductivities, therefore, are estimated to be uncertain by $\pm 73\%$. Statistical tests suggest that there is also a measure-

Statistical tests suggest that there is also a measurement uncertainty related to lack of repeatability in probe tip placement from data set to data set for the same specimens, although not within a given data set. Typical standard deviations from the mean for a given data set (repeated contacts on the same thermal grease spot) are less than 5% and often less than 2%, which is excellent reproducibility. However, statistical t tests occasionally indicate that separate data sets do not satisfy the hypothesis that (1) a given data set belongs to the parent population (using a one-sample, two-tailed t test at the 95% confidence level as shown



Fig. 3. Micrographs of (a) comparator probe tip, (b) probe tip imprint in thermal grease.

in Fig. 4) or (2) two data sets belong to the same population (using an unpaired, two-tailed t test at the 95% confidence level as shown in Fig. 5). These statistical t tests suggest a systematic error in the measurement technique, most likely the probe tip contacting the specimen at a slight angle or with a different part of the probe tip than in the other data set. Still, it is concluded that the thermal comparator technique developed here provides data of useful accuracy where none existed previously, although the measurement uncertainties may be more than the $\pm 73\%$ estimated uncertainty.

Results and Discussion

Measured thin-film thermal conductivities are shown (Table 1, Fig. 6) for a wide variety of dielectric and metal films and for two multilayered stacks. For many of the materials, to the best of our knowledge,



Fig. 4. Comparison of the mean and standard deviations of four data sets taken from the same specimen, sputtered Si on Si, showing a low probability of set four belonging to the entire population. these are the first measurements ever reported. The sputtered Ti and Si films were studied for calibration purposes and to explore differences between a metal film (electron-dominated heat conduction) and a dielectric (phonon-dominated heat conduction). Ti was chosen because it is a poor thermal conductor for a metal and because reasonable signal levels (temperature differences) could be expected for Ti films in the micrometer thickness range.

First examination of Table 1 reveals a large discrepancy between measured thin-film thermal conductivities and handbook bulk values. This comparison is, of course, not meaningful without an appreciation of the structural differences between the films and the bulk materials in the handbooks. Thin dielectric films are typically amorphous (glassy) or microcrystalline, resulting in reduced thermal conductivity be-



Fig. 5. Mean and standard deviations of two separate data sets for each of three specimens (three thicknesses) of sputtered Si_3N_4 on Si showing lack of correlation for the two sets taken on the thickest specimen, specimen 3. Other data sets are well correlated.



Fig. 6. Measured thin-film thermal conductivities of various sputtered optical films and multilayered stacks.

cause of increased phonon scattering from lattice imperfections.

However, a more complete explanation is needed since the structure of sputtered SiO_2 is not appreciably different from that of bulk glasses and yet the measured thermal conductivity of SiO_2 films is an order of magnitude lower than handbook bulk values. In particular, the interface between the film and the substrate must be considered as a barrier to phonon transport (barrier to heat transfer).⁷ Studies of these interfaces, in which the films nucleate and grow from the vapor, support this idea since structural disorder, in the form of lattice strain and growth defects, tends to be concentrated there.^{7,12,13,18,19}

Therefore, the two leading mechanisms for the reduced thermal conductivities of sputtered thin films are (1) structural disorder within the film and (2) a barrier to heat transfer at the film-substrate interface. As is discussed below, it is difficult at the present time to distinguish between these mechanisms, both of which play important roles. The barrier that is postulated to exist at the film-substrate interface may actually be local structural disorder at the film-substrate near-interface region and may extend only a few angstroms within the film.^{7,12,13} The thermal comparator technique and analysis used in this research gives a measure of the thermal response of the film-substrate system as a whole and cannot separate distinct components. However, comparison of thin-film thermal conductivities of both phonondominated and electron-dominated thermal conductors does indicate that, although the film-substrate interface is a common denominator for all the films tested, it appears to be more significant for dielectric films in which the heat conduction is phonon dominated.

The work of Lambropoulos *et al.*³ shows that for some films there is a thickness effect on the thermal conductivity. The analysis presented here assumes that there is no thickness effect and, in fact, requires films of different thicknesses to determine $k_{\rm th}$ ^f. Thus, any thickness effect would be averaged out. The question is would a 100-µm-thick sputtered film have the same thermal conductivity as a 1-µm-thick sputtered film deposited under identical conditions? That question is not answered here. It is well known that the film microstructure is a function of film thickness¹⁸ and that the number of scattering centers per unit volume in a thick film would be reduced compared with a thin film because of the reduced importance of the film-substrate interface volume in the thick film. Research on thicker, sputtered films²⁰ has shown that the microstructure gradually evolves from fine columnar growth near the interface to much coarser columnar growth farther out. However, similar interface barriers would exist in either film. Another possibility is that there is a contribution to phonon scattering by the free surface of the films that is more dominant for thin films than for thick ones. It is suggested that thicker films will have higher thermal conductivities than thin films, but no quantitative information can be determined from this work.

The analysis presented in Appendix A is similar to a more rigorous analysis developed by Lambropoulos et al.³ which is not available before the completion of this work. Our analysis is more simplified and rests on a number of assumptions (discussed in Appendix A) that, while they appear reasonable, have not been rigorously verified. Future comparator measurements would be improved by using the analysis of Lambropoulos et al., but our current data cannot, unfortunately, be reevaluated by using their analysis because of the differences in our experimental procedures. It is especially useful to be able to separate the film conductivity from the interface resistance as shown in their work and to be able to determine differences in conductivities of films of varying thickness. However, our reported results for SiO_2 are in reasonable agreement with the measurements of Decker et al.⁸ and Akhtar et al.¹⁰ Also, it is worth noting that our values in Table 1 are thermal conductivities of the film-substrate assembly and may not be so easily compared with the data of Lambropoulos et al. for this reason.

Sputtered Ti and Si Films

Thin sputtered films of Ti (Ti 1: 1.7, 4.2, and 8.5 µm thick; and Ti 2: 1.2, 2.9, and 5.7 µm thick), and Si $(2.2, 4.9, and 9.9 \ \mu m \text{ thick})$ were sputtered onto Si substrates in a quadrant arrangement such that one Si substrate contained three quadrants of sputtered film, one of each of the above thicknesses, and one bare quadrant. Sputtering was performed by using small (5-cm) magnetron sources operating at 420-Vdc and 2 A at a pressure of 2.2-mTorr Ar. Sputtering rates were 570 Å/min for Ti 1, 380Å/min for Ti 2, and 667 Å/min for Si by using sputtering times of 30, 75, and 150 min for each quadrant, respectively. We used a Sloan M-200 Angstrometer with Na vapor illumination to measure the film thickness of the thinnest quadrant and to obtain the other quadrant thicknesses by assuming similar sputtering rates. X-ray diffraction indicated that the Ti films were (001) oriented with a 200- \pm 20-Å grain size and the Si films were (111) oriented with a 300- \pm 30-Å grain size.

Each quadrant was measured by using the thermal comparator technique, and the thin-film thermal conductivities were determined (Fig. 7). The value of $k_{\rm th}^{f}$ for sputtered Ti (2.0 W/mK) is 11 times smaller than that for bulk Ti (21.9 W/mK), while that for sputtered Si (0.97 W/mK) is 150 times smaller than bulk polycrystalline Si (148 W/mK). Additionally, four-point-probe in-plane electrical conductivity measurements of sputtered Ti gave an average value of $\sigma_{\rm Tf}^{f} = 1.6 \times 10^{4} ~(\Omega ~{\rm cm})^{-1}$, which is 68% of the measured bulk value of $\sigma_{\rm Ti} = 2.34 \times 10^{4} ~(\Omega ~{\rm cm})^{-1}$. No electrical measurements were made for the Si films.

The measured reduction in electrical conductivity is consistent with the observed fine-grain-sized Ti structure, with a grain size of 200 ± 20 Å calculated from x-ray diffraction peak broadening. Additional grain boundary scattering and the structural disorder associated with the columnar structure observed in sputtered metal films could easily account for this reduction. Grain boundaries and disorder would also be expected to reduce the measured thermal conductivity by this same factor in compliance with the Wiedemann–Franz law, which states that $\kappa/(\sigma T)$, the Lorenz number, is approximately constant for metallic materials. For bulk Ti at 273 K the Lorenz number is $3.43 \times 10^{-8} \text{ W} \Omega/\text{K}^2$. Sputtered Ti films should have a thermal conductivity approximately 0.68 times lower than the bulk or ~15 W/(mK). whereas the measured value of 2 W/(mK) is 7.5 times smaller. Clearly, additional factors are acting to reduce the film thermal conductivity. Since the electrical conductivity was measured in plane and the thermal conductivity was measured through the thickness and includes the film-substrate interface, it can be inferred that additional scattering centers are present at this interface that do not influence inplane measurements.

Phonon heat conduction, as occurs in Si, is ex-



Fig. 7. Measured temperature ratio as a function of film thickness for sputtered Ti and Si films in quadrant geometry. The slope of the fitted lines shown are proportional to the film thermal conductivity [Eq. (1) and Appendix A]. Thermal conductivities are in units of W/(mK).

pected to be more sensitive to scattering centers present at the film-substrate interface, perhaps because of a local increase in umklapp processes. This hypothesis is supported by the much greater decrease in thermal conductivity observed for the sputtered Si compared with the sputtered Ti (150 times smaller for phonon heat conduction compared with 7.5 times smaller for electronic heat conduction) for similar fine grain size and, presumably, similar microstructure. It is concluded, therefore, that for dielectric films, in which heat conduction is phonon dominated, large heat transfer barriers will exist due to the presence of the film-substrate interface and that these barriers will dominate the measured thin-film thermal conductivities. However, structural disorder in the film will also affect thermal conductivities.

Dielectric Films (Single Layer and Multilayered)

Measured thermal conductivities of dielectric films (Table 1, Fig. 6) show a narrow range of values $(0.12-0.88 \,\mathrm{W/mK})$ consistent with either an interfacedominated heat transfer barrier or structural disorder. The relative constancy of these values is perhaps more fundamentally important than any relationship between thin-film values and bulk values (Fig. 8). As shown in Fig. 8, the films are best distinguished by both their bulk and film structural characteristics. Comparisons between bulk and film conductivities are meaningless unless structural effects are taken into account. One cannot compare data for materials that are polycrystalline in bulk form but glassy as thin films with others that are both bulk glasses and thin-film glasses. The different symbols in Fig. 8 are meant to aid in sorting out this variable and allow valid comparisons to be made. In general, dielectric materials that are crystalline in bulk form but are glassy in thin-film form have thin-film conductivities that are in a narrow range from 0.12 to 0.32 W/(mK) even though their bulk conductivities range from ~ 2 to 62 W/(mK). Not surprisingly, these materials also have the highest bulk/film conductivity ratios since both structural disorder and film-substrate interface effects are present in the thin films but not present in the bulk materials.7,12,13,18,19



Fig. 8. Comparison of handbook bulk thermal conductivities with measured thin-film conductivities. The data are grouped according to bulk and film structure, polycrystalline or glassy.

Structural effects can cause large differences in observed thin-film conductivities, as can be seen by considering the data for SiO_2 (Refs. 3 and 7-9) and the Si:Al:O:N materials.²⁰ SiO₂ is the sole example here of a bulk glass material also having glassy thin films. Structural differences are minimized between bulk and film structures so that the decreased thinfilm conductivity is consistent with interface losses.⁷ From the SiO_2 and the Ti data it can be inferred that the film-substrate interface accounts for approximately a 10-20-fold decrease in thermal conductivity from bulk materials. Therefore, additional reductions in thin-film conductivities compared with bulk conductivities are most likely associated with structural differences in the body of the film, particularly for those materials that are bulk polycrystals but are glassy thin films. These bulk-film microstructural effects must contribute an additional order of magnitude decrease in measured conductivities (Table 1, Fig. 6) to account for the BN, Si_3N_4 , Al_2O_3 , and SiC data. Structural effects are also apparent when the Si:Al:O:N data is examined since these films were microcrystalline on the Si substrates and not glassy. The structural differences between the Si:Al:O;N films and the other dielectric films are due to good lattice matching between the Si:Al:O:N materials and the Si substrate and the fact that these depositions were performed at $\sim 250^{\circ}C.^{20}$ Increased structural ordering probably accounts for the observed differences between the Si:Al:O:N films and the glassy dielectrics.

Compositional effects can also be observed in the data. Addition of AlN to Si_3N_4 to form a Si:Al:N material does increase thermal conductivity slightly, and addition of oxygen to Si:Al:N to form Si:Al:O:N materials does decrease thermal conductivity (Table 1, Fig. 6). Both of these changes are consistent with simple rule of mixture calculations. For example, by using bulk conductivity values for Si_3N_4 (10 W/mK) and AlN (140-200 W/mK) a mixture of 60% Si_3N_4 and 40% AlN (corresponding to $\rm Si_{0.6}Al_{0.4}N)$ should have a conductivity of 62–86 W/(mK), or approximately six to nine times that of pure Si₃N₄. This is in good agreement with the measured ratio (1.5/8.8 = 5.9) for the thin films of Si₃N₄ and Si_{0.6}Al_{0.4}N. Addition of AlN to the multilayered stack coating system increases the thermal conductivity slightly, again consistent with rule of mixture arguments. However, these compositional effects are small relative to the roles played by structural disorder in the film and at the film-substrate interface.

The measured thermal conductivities of the two multilayered dielectric stacks, $Al(SiO_2/Si_3N_4)^n$ (0.25 W/mK) and $Al(Al_2O_3/AlN)^n$ (0.32 W/mK), are more difficult to rationalize from the above arguments because these conductivities are larger than those measured for individual films of SiO₂, Si₃N₄, and Al_2O_3 . The absence of detailed microstructural and interfacial structural data prevents a complete understanding. Perhaps the presence of the Al underlayer

reduces the film–substrate interface effects. However, an obvious question is: Why are there are not additional internal losses that are due to the series of film–film interfaces in these multilayered stacks? One can only speculate that, since these individual layers are glassy in these multilayered stacks (as observed in limited transmission electron microscopy examinations,¹⁹ interface losses at amorphous interfaces are small compared with observed film–substrate losses. It is interesting to note that the dielectric stack containing AIN, Al(Al₂O₃/AlN)ⁿ, possesses a higher thermal conductivity than the Al(SiO₂/Si₃N₄)ⁿ stack, which is consistent with the higher conductivity of AlN compared with Si₃N₄.

Summary and Conclusions

Measurement of the normal component of the thermal conductivity for an assembly of advanced and conventional single-layer and multilayered sputtered optical materials shows that thin-film thermal conductivities are usually 10–100 times lower than conductivities for the same materials in bulk form. In agreement with earlier measurements by other techniques for evaporated optical films, these data clearly demonstrate the importance of using measured thinfilm conductivity values for optical system design calculations and performance estimates. The measured data also allow selection of the best materials for applications requiring high thermal conductivity and are expected to be of great utility to optical film designers, fabricators, and performance testers. Structural disorder in the amorphous or fine-grained films appears to account for most of the conductivity difference. Structural disorder, for example, explains most of the orders of magnitude reduction in conductivity between amorphous Al_2O_3 and bulk crystalline sapphire, between Si and Ti films with 200–300-Å grain size and their single-crystalline counterparts, and between carbide and nitride films and bulk ceramic materials.

A film-substrate interfacial impedance is also apparent in the data and must be accounted for in future thin-film design and analysis. The interface barrier explains, for example, the difference in thermal conductivity for glassy SiO₂ films compared with bulk SiO₂ glass and eliminates the apparent Wiedemann– Franz law violation for the in-plane electrical conductivity and the normal-component thermal conductivity in Ti films. The interface barrier appears to be much larger for dielectric phonon-transport materials than for metallic electron-transport materials. Such a barrier may consist of a region near the film-substrate interface of a high degree of disorder extending only a few phonon wavelengths into the film. This observation suggests that dielectricenhanced metal reflectors are better choices than all-dielectric reflector designs for heat dissipation or cooling.

The first measured values of thermal conductivity are reported for single layers of advanced materials

such as BN, Si:Al:N, Si:Al:O:N, SiC, and for dielectricenhanced metal reflectors of the form $Al(Al_2O_3/AlN)^n$ and $Al(SiO_2/Si_3N_4)^n$. The nitrides are seen to be better thermal conductors than the oxides in thinfilm form, just as they are in bulk form. These data will aid in development of high-thermal-conductivity materials and multilayer structures. The single carbide examined (SiC) was found to be surprisingly low in thermal conductivity.

Rule of mixture calculations are found to be predictive of thermal conductivity for more advanced and complex ternary nitride and oxynitride compositions and for multilayer optical stacks. By replacing Si_3N_4 with $Si_{0.6}Al_{0.4}N$, for example, we increased measured conductivities by the amount expected from the rule of mixtures. These findings suggest use of rule of mixture calculations as a new thermal design tool for future film development.

The thermal comparator technique has been shown to be a simple, inexpensive, rapid, and nondestructive technique for measuring the thermal performance of thin films in single or multilayer form.

Appendix A

The following analysis was developed to extract thinfilm thermal conductivities from a thermal comparator apparatus. This analysis is similar to the analysis of Lambropoulos *et al.*,³ which was published after the completion of this work, but it is simplified compared with their analysis and rests on a number of assumptions that have not been rigorously verified. In particular, their analysis allows one to extract the film thermal conductivity and the thermal resistance of the film–substrate interface whereas the analysis presented here cannot separate the two.

Figure 9 identifies the various components that constitute the thin-film thermal conductivity measurement technique. At each interface, heat flow is assumed to be proportional to the temperature difference and inversely proportional to the thermal resistance as defined by

$$T_i - T_j = \Delta T_{ij} = R_i Q, \tag{A1}$$

where ΔT_{ij} is the temperature difference between adjacent regions (numbered 1–5 in Fig. 9), R_i is the thermal resistance of the *i*th interface, and Q is the steady-state heat flow across the interfaces. Conservation of energy requires that Q have the same value



Fig. 9. Schematic of the probe tip-film-substrate-heat sink region of the thermal conductivity apparatus.

at each interface at steady state. As an example,

$$T_1 - T_2 = \Delta T_{12} = R_1 Q, \tag{A2}$$

and R_1 is the thermal resistance to heat flow from the reservoir into the probe. The thermal resistance terms are conventionally written as a product of the thermal conductivity and geometrical factors as follows:

Probe Resistance (Region 1)

1

$$1/R_1 = 4K_1r_1, (A3)$$

where K_1 is the probe thermal conductivity and r_1 is the probe tip radius. Here it is assumed that the heat flux through the probe tip does not vary with the radial coordinate, r (see Fig. 9). This assumption is aided by the use of thermal grease to improve the thermal contact of the probe tip with the film surface. This solution is for heat flow from a circular region into a semi-infinite cylinder and is from Ref. 21.

Probe Tip/Film Resistance (Contact Resistance) (Region 2)

$$1/R_2 = K_2 A_2 / t_2, \tag{A4}$$

where K_2 is the contact conductivity, A_2 is the contact area, and t_2 is the contact layer thickness.

Film Resistance (Region 3)

$$1/R_3 = K_3 A_3 / t_3, \tag{A5}$$

where K_3 is the film conductivity, A_3 is the contact area, and t_3 is the film thickness. Here we assume that there is no lateral heat flow in the film, which is a valid assumption if the film thermal conductivity is low and the film thickness is small compared to the probe tip radius, i.e., $t_3 \ll r_1$. Typical ratios of t_3/r_1 are 0.03.

Substrate Resistance (Region 4)

$$1/R_4 = 4K_4r_1,$$
 (A6)

where K_4 is the substrate conductivity and r_1 is the probe tip radius. Here we assume that heat flow from film into the substrate also obeys the semiinfinite solution discussed above. As discussed in Ref. 3, it is also required that $K_3 \ll K_4$ if one is to sum Eqs. (A5) and (A6) to calculate $R_3 + R_4$. Typical ratios of K_3/K_4 are 1×10^{-3} .

Heat Sink Resistance (Region 5)

 $R_5 \approx 0$ since $T_4 \approx T_5$. Assume that $R_5 \ll R_1, R_2, R_3$, R_4 . This assumes that there is little barrier to heat flow from the substrate material into the heat sink. Calculation of Q and K_3

The resistances are considered to be in series such that

$$(T_1 - T_5) = \sum_{i}^{1-5} R_i Q = Q \sum_{i}^{1-5} R_i,$$
 (A7)

which can be solved for Q to give

$$Q = \frac{(T_1 - T_5)}{\sum_{i=5}^{1-5} R_i}$$
 (A8)

Thus, we can write

$$T_1 - T_2 = R_1 Q = R_1 \frac{(T_1 - T_5)}{\sum_{i=5}^{1-5} R_i}$$
, (A9)

which can be used to give

$$\frac{(T_1 - T_5)}{(T_1 - T_2)} = \frac{1}{R_1} \sum_{i}^{1-5} R_i = 1 + \frac{R_2}{R_1} + \frac{R_3}{R_1} + \frac{R_4}{R_1} + \frac{R_5}{R_1} \cdot$$
(A10)

Using the definitions for the R_i and neglecting R_5 gives

$$\frac{(T_1 - T_5)}{(T_1 - T_2)} = 1 + 4K_1r_1\left(\frac{t_2}{K_2A_2}\right) + 4K_1r_1\left(\frac{t_3}{K_3A_3}\right) + \frac{K_1r_1}{K_4r_1} \cdot$$
(A11)

Therefore this gives

$$\frac{(T_1 - T_5)}{(T_1 - T_2)} = \left(\frac{4K_1r_1}{K_3A_3}\right)t_3 + \left[1 + \left(\frac{4K_1r_1}{K_2A_2}\right)t_2 + \frac{K_1r_1}{K_4r_1}\right],$$
(A12)

which is of the form for a line

$$y = mx + b, \tag{A13}$$

where

$$y = \frac{(T_1 - T_5)}{(T_1 - T_2)} = \text{temperature ratio}, \quad (A14)$$

$$x = t_3 =$$
film thickness, (A15)

$$m = \frac{4K_1r_1}{K_3A_3} = \text{slope},\tag{A16}$$

$$b = \left[1 + \left(\frac{4K_1r_1}{K_2A_2}\right)t_2 + \frac{K_1r_1}{K_4r_1}\right] = \text{intercept.} \quad (A17)$$

A plot of the temperature ratio as a function of film thickness is fit with a line by using a least-squares procedure. The resulting slope is used to solve for the film thermal conductivity, K_3 , as

$$K_3 = k_{\rm th}{}^f = \frac{4K_1r_1}{mA_3}, \qquad (A18)$$

where A_3 is the contact area between the probe tip and the film, r_1 is the probe tip contact radius, and K_1 is the thermal conductivity of the probe material.

100 APPLIED OPTICS / Vol. 32, No. 1 / 1 January 1993

We determined the contact area by measuring the impression of the probe left on the film surface. The probe tip contact radius and the probe thermal conductivity are known and thus the film conductivity can be calculated. Note that the probe contact resistance appears only in the intercept term and does not affect the measured value of the film thermal conductivity.

The simplifying assumptions made here have not been rigorously verified. The radial temperature distribution at the probe tip-film interface is not known, nor is it known if there is appreciable lateral heat flow in the films. It is argued that these are reasonable assumptions based on our knowledge of the comparator and the poor thermal conductivity of the films. However, the uncertainty in the measurements is likely to be greater than the $\pm 73\%$ calculated in this work. Future comparator measurements will benefit from the more rigorous analysis given in Ref. 3.

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