Thermal diffusion in thin plates and coatings: influence of thickness and substrate material

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Abstract: The dependence of thermal diffusivity/conductivity on thickness for a variety of coatings and free-standing thin metallic plates was measured using a traveling photothermal technique. The selected materials have large differences in terms of their thermal conductivity. Measurements were carried out on coatings prepared on substrates with two widely different values for thermal conductivity to bring out the influence of substrate thermal conductivity on the thermal diffusivity/conductivity of the coating. Thermal diffusivity/conductivity increases exponentially with coating thickness with the value saturating at a definite thickness. The variation follows an empirical relation, which can predict thermal diffusivity of a coating at any thickness in the low thickness regime. In the region where thermal diffusivity increases exponentially with thickness, thermal diffusivity of the coating is lower when the substrate is a better thermal conductor, implying that thermal waves diffuse into substrate causing an overall reduction in thermal diffusivity. However, beyond the saturation thickness the thermal diffusivity is independent of substrate material. Thermal conductivity of coatings as well as thin metallic plates follows analogous variations with thickness and substrate material. The results will help in providing a better theoretical description of heat transport in low dimensional structures.

Key words: Thermal conductivity, thin plates, coatings, photothermal technique

1. Introduction

In all applications involving heat transport through material media, the most important parameter of interest is thermal conductivity. The methods employed to measure thermal conductivity in different types of materials and media, as well as its values, are extensively documented in the literature [1–3]. Theoretical techniques to evaluate thermal conductivity of solid media with variations in sizes, shapes, and dimensions were developed during the first half of the 20th century [4]. The most popular techniques to measure thermal conductivity involve setting up a steady temperature difference between two points in the medium and measuring the corresponding temperatures at these points. Since the energy transported through the medium is measured, this technique is susceptible to errors due to radiative heat losses from the sample. This issue becomes even more serious when one tries to measure thermal conductivity of thin plates, coatings, or films as the surface area of the sample becomes very large compared to its thickness or volume.

One solution to the above problem is to measure thermal diffusivity, rather than thermal conductivity, for such samples. Since thermal diffusivity is a measure of the rate at which thermal energy is transported through a medium, it is independent of heat losses from the sample. Once the thermal diffusivity α is obtained,

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thermal conductivity λ can be evaluated from the well-known relation

$$\lambda = \alpha \rho C_p, \tag{1}$$

where ρ and C_p are the mass density and specific heat capacity of the material respectively. Again, a number of techniques have been developed to measure the thermal diffusivity of bulk samples [5,6]. Of late photothermal techniques employing the photoacoustic [7,8], photothermal deflection [9,10], or photopyroelectric [11,12] effects have become very popular for the measurement of the thermal diffusivity of bulk samples. However, these techniques are limited to bulk samples with minimum thickness of about 1 mm or so.

With advancements in semiconductor device fabrication and use of oxide layers and thermal barrier coatings in many devices, it has become necessary to measure thermal diffusivity or conductivity of thin layers and coatings. Now the question is whether the thermal conductivity/ diffusivity of such thin layer coatings and plates, with thickness in the micrometer or even nanometer ranges, is different from the corresponding values for bulk samples with thickness in the millimeter range or higher. We try to provide an answer to this question with the results presented in this paper.

There have been several attempts in the past to measure thermal diffusivity of thin coatings, plates, and films. One of the early attempts in this direction was by Hatta et al. [13], who measured thermal diffusivity of thin films by an *ac* calorimetric method. Measurements were reported in thin films of nickel, silicon, stainless steel, and aluminum with thickness in the range 50 to 300 μm. However, the dependence of film thickness on thermal diffusivity was not reported in that work. Later, by measuring the phase lag of a thermal wave propagating along a free-standing diamond sheet, Kosky [14] reported its thermal diffusivity. Necessary theory of the technique was developed by this author, which was extended later to other materials and films by other researchers [15–17]. The latter authors used an optical beam deflection technique or pyroelectric detection to monitor traveling thermal waves for these measurements. Among these authors, Bhusari et al. [15] reported an exponential dependence for thermal conductivity on thickness for Al films, while Chattopadhyay et al. [16] reported similar dependence for aluminum films and a-SiC_xN_y films. Philip et al. [17] have reported exponential variation for thermal diffusivity with thickness for paint coatings in the low thickness regime (<0.2 mm).

There have been many other reports on the thermal diffusivity of thin films and coatings. Zhang and Grigoropoulos [18] measured the thermal diffusivity of free-standing silicon nitride thin films and reported that the thermal diffusivity of a film of thickness 0.6 μm is about 35% lower than that of a film of the same material of thickness 1.4 μm. Lee and Cahill [19] measured the thermal conductivity of dielectric films of SiO_2 and SiN_x with thickness in the range 20–300 nm following the 3ω method. They found a decrease in thermal conductivity with decreasing film thickness and interpreted the results in terms of interface thermal resistance. Yamane et al. [20] measured the thermal diffusivities of metallic thin films using an *ac* calorimetric method and found that thermal diffusivity decreases as the thickness of the films decreases. This decrease is interpreted as due to decrease in crystallite size.

The thermal conductivities or diffusivities of dielectric thin films coatings [21], CVD diamond films [22], and nanocrystalline diamond films [23] have been reported by different authors, all of them reporting significantly reduced thermal conductivity/diffusivity for films compared to respective bulk materials.

Even though the above experiments and respective results on selected materials have given some insight into the mechanisms responsible for the decrease in thermal conductivity/ diffusivity with reduction in film thickness, results on a wider spectrum of samples with wide difference in thermal conductivity are necessary to

obtain a clearer picture of the mechanism involved. Analysis of the available results shows that the thickness dependence of thermal diffusivity/conductivity does depend on the magnitude of thermal conductivity of the material in the bulk form. The influence of substrate, if any, on the thermal diffusivity of films is another aspect that has not been considered by earlier authors.

In this paper we report the results obtained on the thickness dependence of thermal diffusivity and conductivity for a variety of coatings, films, or thin plates of materials with a wide range of thermal conductivities from as low as 1.14 W/m-K (solid polyvinyl alcohol) to as high as 401 W/m-K (copper).

A traveling photothermal technique, described earlier [17], was employed to measure thermal diffusivities of thin coatings, films, or plates with thickness in the micrometer to millimeter regime. Our results show that the thickness dependence of thermal diffusivity of thin material coatings, plates, or films can be described by a general expression irrespective of the thermal conductivity of the material in the bulk form. The influence of thermal conductivity of the substrate material on thermal diffusivity of the coatings was also investigated and reported in this work.

2. Experimental methods

2.1. Sample preparation

Thin coatings, films, or plates of a variety of materials with widely different thermal conductivities were the subject of the present investigations. Specifically the following samples were prepared for the present studies:

1. Black enamel paint coatings on glass and copper substrates.

2. Aluminum paint coatings on glass and copper substrates.

3. Polyvinyl alcohol (PVA) coatings on glass and copper substrates.

4. Metallic copper coatings on ebonite substrate.

5. Free-standing thin copper plates.

6. Free-standing thin aluminum plates.

7. Soda lime glass plate.

All the samples were prepared with great care to ensure that the thickness of the coatings or plates was uniform throughout. Samples 1, 2, and 3 were prepared by hand coating and samples 4, 5, and 6 by removing materials by etching out from thick enough starting materials.

2.2. Thermal diffusivity measurement

The thermal diffusivities of the coatings or plates were measured employing a traveling thermal wave technique described elsewhere [15,17]. The method involved measurement of the phase lag undergone by a thermal wave while propagating over a finite distance through the coating. In the present experiment we used laser-based photothermal excitation to generate thermal waves in the film and a pyroelectric detector to detect them after traveling over a defined distance [17]. The phase difference of the pyroelectric output signal was continuously measured as a function of the separation between the points of excitation and detection. The technique was tested with known samples (of fixed thickness) before carrying out the present measurement. It was shown that the technique provided accuracy better than 5% in thermal diffusivity for a coating.

For the thermal diffusivity and conductivity plots shown in Figures 1 and 2 for metallic copper and aluminum, the values for plate thicknesses 0.01 mm and 0.02 mm were obtained from corresponding metallic films coated on an insulating substrate like ebonite. Other values in these figures were obtained with free-standing thin plates. Measurements were also carried out on a soda lime glass plate (slide) for comparison. The excitation region was darkened with India ink to enhance optical absorption for the generation of thermal waves in the glass plate. Measurement of the variation of thermal diffusivity with thickness was not done for the glass plate.
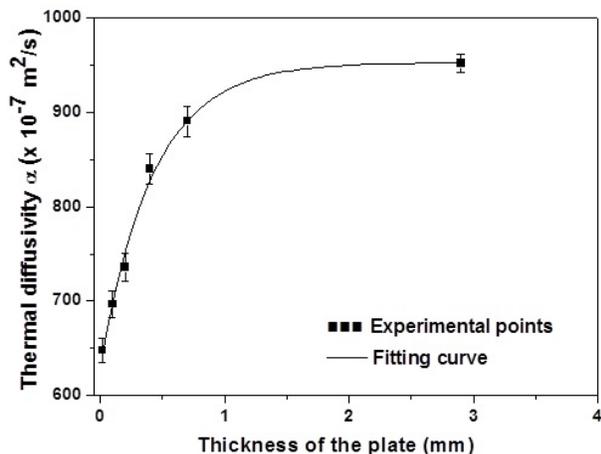

Figure 1. Variation in thermal diffusivity of thin free-standing copper plates with thickness, and the corresponding fitting curve. The two lowest thickness readings (0.02 mm and 0.1 mm) are for copper films coated on an insulating substrate (ebonite).
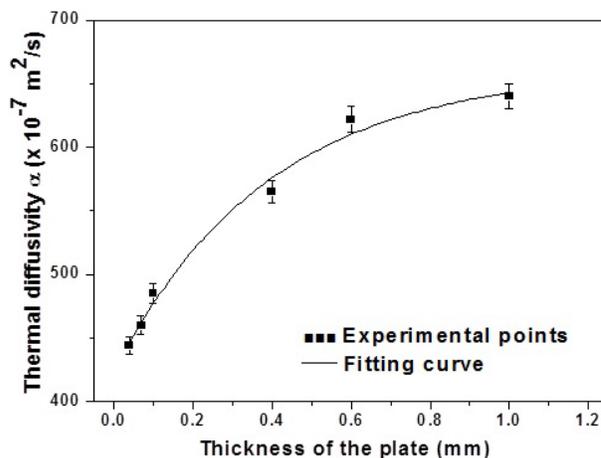
Figure 2. Variation in thermal diffusivity of free-standing aluminum plates with thickness, and the corresponding fitting curve.

3. Results and discussion

The variations in thermal diffusivity with coating or plate thickness for different samples are shown in Figures 1 to 5. Figures 1 and 2 are for two free-standing plates (copper and aluminum), while Figures 3 to 5 are for three coatings indicated in the respective figures. The variations for coatings on glass as well as copper substrate are shown in the respective figures. The corresponding values of thermal conductivity, obtained using Eq. (1), were calculated from the measured values of thermal diffusivity and plotted against the coating or plate thickness. Since the variations in thermal conductivity for all samples are similar to the corresponding variations in thermal diffusivity, thermal conductivity curves are not reproduced here. While plotting the thermal conductivity variations, values of heat capacity and density taken from the literature were used. From these two sets of figures it is clear that in the low thickness regime all the coatings and plates investigated have exponential thickness dependence for thermal diffusivity as well as conductivity. It is obvious from the figures that thermal diffusivity vanishes as the coating thickness becomes negligibly small. At a high enough thickness value, which strongly depends on the thermal conductivity of the respective material in its bulk form, thermal diffusivity (as well as thermal conductivity) assumes constant steady values. Between zero thickness and the above high enough thickness value, say Ts, thermal diffusivity increases exponentially with thickness.

The exponential increase in thermal diffusivity between zero thickness and Ts follows an equation of the form
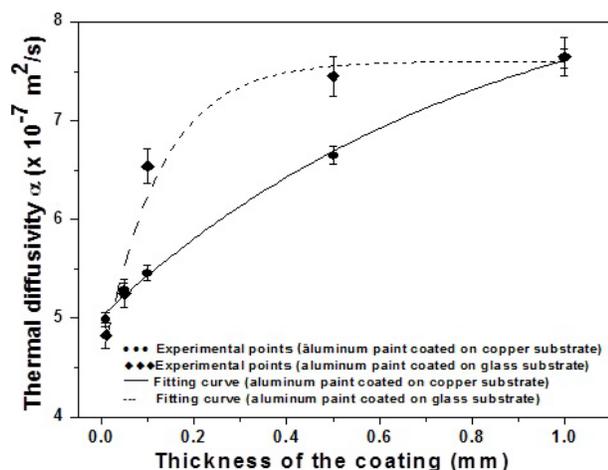
Figure 3. Variation in thermal diffusivity of dry aluminum paint coatings with thickness, coated on glass and copper substrates, and the corresponding fitting curves.
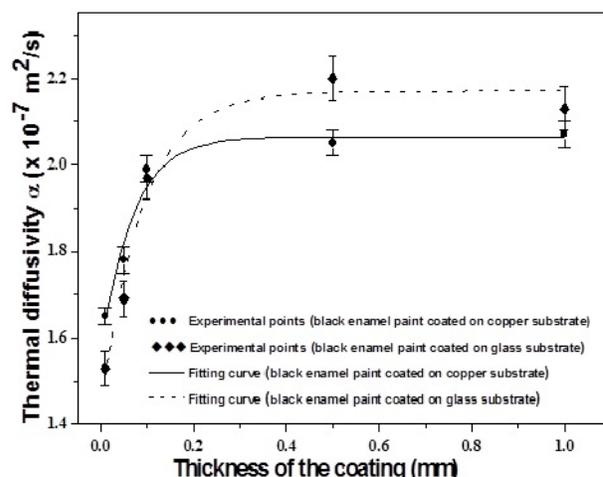

Figure 4. Variation in thermal diffusivity of dry black enamel paint coatings with thickness, coated on glass and copper substrates, and the corresponding fitting curves.
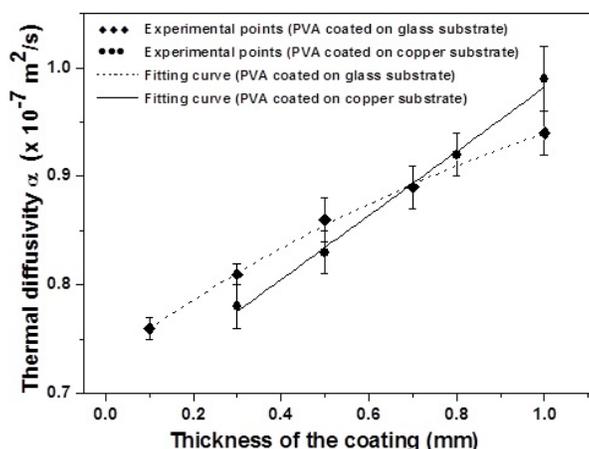

Figure 5. Variation in thermal diffusivity of PVA coatings with thickness, coated on glass and copper substrates, and the corresponding fitting curves.

$$\alpha\left(t\right)=\alpha\left(b\right)-\left[\alpha\left(b\right)-\alpha\left(0\right)\right]\exp\left(-t/\gamma\right), \tag{2}$$

where $\alpha(b)$ is the thermal diffusivity of a very thick coating of the material, which is close to that of the bulk material, and γ is a fitting parameter, which corresponds to the thickness at which $\alpha(t) \rightarrow \alpha(b)$. Here $\alpha(b)$ can be expected to be smaller than the bulk thermal diffusivity for the material of the coating. The exponential decrease in thermal diffusivity with decrease in sample thickness, following the above equation, is the combined effects of reflection, scattering, and diffusion of thermal waves at the boundaries.

The measured thermal properties of the materials involved in the experiments discussed in this work are tabulated in the Table. The bulk thermal diffusivity, conductivity, and specific heat capacity values quoted in the Table are all taken from standard tables from the literature. Citations to such data are given below the Table for reference. All measured values of thermal diffusivity for coatings, with thickness more than Ts, are

260

Table. Thermal properties of materials reported in this work. Measured values of surface thermal diffusivity and conductivity are given in the last two columns.

Material	Bulk thermal diffusivity ($\times 10^{-7}$ m^2/s)	Bulk thermal conductivity W/m-K	Specific heat capacity J/kg-K	Measured surface thermal diffusivity (for coating thickness more than Ts) ($\times 10^{-7}$ m^2/s)	Surface thermal conductivity W/m-K
Free-standing copper plate	1110.00 [24]	401.00 [25]	385.00 [26]	952.00 ± 15.00	328.00 ± 8.00
Free-standing aluminum plate	841.00 [27]	204 [28]	902.00 [26]	640.00 ± 10.00	157.00 ± 4.00
Dry aluminum paint	9.53 ± 0.12*	3.05 ± 0.44*	2640.00 ±50.00	7.65 ± 0.12	2.44 ± 0.12
Dry black enamel paint	3.69 ± 0.20*	2.02 ± 0.05*	4569.00 ± 9.00*	2.13 ± 0.05	1.18 ± 0.04
Glass plate (soda lime glass)	3.76+	0.80 [29]	840.00 [26]	2.27 ± 0.20	0.51 ± 0.04
PVA (polyvinyl alcohol) coating	1.18 ± 0.20*	1.14 ± 0.20*	9104.00 ± 170.00*	0.91 ± 0.02	0.91 ± 0.02
Atmospheric air (for comparison)	190.00 [30]	0.024 [25]	1005.00 [26]	--	--

*Values measured following photopyroelectric technique [12]; + Value calculated from thermal conductivity data

less than the corresponding bulk values quoted in the Table. This is due to the fact that what we measure in our experiments is the thermal diffusivity along the surface of the sample, or surface thermal diffusivity, rather than bulk thermal diffusivity. The thermal properties of air and glass are also quoted in the Table for comparison. The values of surface thermal diffusivity and conductivity quoted in the last two columns are from measurements following the present technique.

For all samples for which data are available it can be noted that surface thermal diffusivity is only 55% to 85% of the corresponding bulk value for the material of the coating or plate. This observation has correspondence with velocity of acoustic waves in solid media, where it is known that surface acoustic wave velocity is less by 10% to 40% of the corresponding bulk velocity.

It follows from Eq. (2) that the value of γ for which $\alpha(t) \to \alpha(b)$ strongly depends on the thermal conductivity of the material. The higher the value of thermal conductivity is, the smaller the value of γ is. This means that for a coating or a plate with high thermal conductivity, $\alpha(t)$ rises from 0 to $\alpha(b)$ very fast and vice versa. As is evident from Figures 1 to 5, although the value of $\alpha(b)$ is nearly independent of the thermal conductivity of the substrate material, the rate at which thermal diffusivity increases with thickness depends on the substrate thermal diffusivity or rather the thermal diffusivity contrast between the coating and substrate. We can see that the higher this contrast is, the higher the rate of increase in thermal diffusivity with coating thickness is. These discussions apply to thin metallic free-standing plates as well, with air acting as the substrate material.

One can note a few interesting aspects related to the influence of thermal diffusivity of substrate on the thermal diffusivity of the coating:

(i) For coating thickness more than Ts, the thermal diffusivity of the coating is more or less independent of the thermal diffusivity of the substrate. If there is a difference at all, it is well within experimental uncertainties.

(ii) In the region where thermal diffusivity increases exponentially with thickness, thermal diffusivity of the coating is lower when the substrate is a good thermal conductor. It seems thermal waves tend to diffuse into the substrate, causing an overall reduction in thermal diffusivity in this regime.

(iii) The increase in thermal diffusivity with thickness is smaller in the exponential region when the thermal diffusivity of the substrate is very high compared to that of the coating. This is in tune with the observation cited as (ii) above.

(iv) As is evident from Figure 5, thermal diffusivity of PVA coating at low values of coating thickness (less than ≈ 0.7 mm) on glass substrate is larger than that on copper substrate, while thermal diffusivity of the same coating at high values (more than ≈ 0.7 mm) of thickness is larger on copper substrate. This shows the influence of thermal diffusion in coatings on the relative thermal diffusivities of the coating and substrate. When substrate has very high thermal diffusivity compared to coating, there is high thermal diffusion into the substrate, which slows down thermal diffusion along a thin coating. However, as the coating thickness increases thermal waves get confined more to the coating and only a small amount of heat diffuses into the substrate, irrespective of the thermal diffusivity of the substrate. Correspondingly we measure the actual thermal diffusivity of the coating, which is higher than for a thin coating. For a substrate like glass with a lower thermal diffusivity, thermal diffusion from coating to substrate is low. What we measure then is more the thermal diffusivity of the coating itself, influenced less by the substrate. As the coating thickness increases, thermal diffusivity increases following Eq. (2). It may also be noted that the changes in values of thermal diffusivity due to effects outlined above are not far from the uncertainty limits of the respective experimental values.

Analysis of the results presented in this work points to the requirement for deriving Eq. (2) for the thermal diffusivity of a coating on a substrate, starting from the basic Fourier diffusion equation for thermal energy. Such a theoretical approach will throw more light on the mechanisms involved in heat transport through two-dimensional structures like films and coatings. A theoretical treatment of the problem is also required to understand the diffusion of thermal energy into the substrate and the influence of substrate thermal conductivity on the thermal conductivity of the film, particularly when the film thickness is smaller than Ts.

4. Conclusions

The thickness dependence of thermal diffusivity and conductivity for thin coatings or plates, with wide variations in their bulk thermal conductivity, was measured following a traveling thermal wave technique and the results analyzed. Work was reported on materials coated on copper and glass substrates to bring to light the influence of substrate thermal conductivity on the thickness dependence of thermal diffusivity/conductivity of coatings. It was found that irrespective of the thermal conductivity of the coating material or substrate the thermal diffusivity as well as conductivity of the coating or plate increases exponentially with thickness following a single relation, the rate of increase being determined by the thermal conductivity and related properties of the material of the coating. The results throw light on the possible mechanisms responsible for the reduction in thermal diffusivity/conductivity for material structures with reduced dimensionality such as two-dimensional ones like thin coatings and plates. The results will have implications on heat transport though low dimensional structures such as coatings in miniature devices and microstructures. They also call for a more detailed theoretical description of the observed effects, starting from the basic heat diffusion equation.

Acknowledgments

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