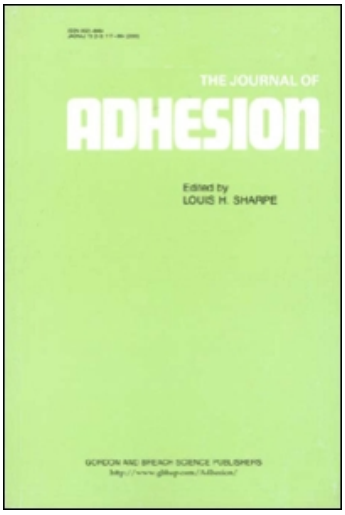

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The Use of Thin Film Thermocouples to Determine the Thermal Conductivity and Young's Modulus of Coatings and Interfaces

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The Use of Thin Film Thermocouples to Determine the Thermal Conductivity and Young's Modulus of Coatings and Interfaces*

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Linear and differential thin film thermocouples, typically 500–1000Å thick, were fabricated on flexible polymer and paper substrates by thermal evaporation. Both types of thermocouples had thermal sensitivities of approximately 4 μV/°C, for temperatures between 20°C and 40°C, on the paper and polymer-coated paper substrates. The transverse thermal conductivity (k_t), *i.e.*, thermal conductivity in the direction perpendicular to the plane of the films, of polyimide (Kapton-H®) films, of a clay-coated paper, and of a polystyrene coating on paper were determined by depositing linear thermocouples on both sides of the films and raising the temperature of one junction and measuring the heat flux and, at equilibrium, the temperature of the other junction. Shear and Young's moduli of the polymer films were estimated from the measured thermal conductivity values, assuming the Debye model of thermal conductivity.

KEY WORDS linear and differential thin film thermocouples; thermal measurements; estimation of Young's and shear modulus of coatings; Debye model of thermal conductivity; polyimide; clay coated paper; polystyrene-polyethylene-paper composite.

INTRODUCTION

The measurement of temperature across an interface and the determination of thermal and mechanical properties of interfacial regions as well as those of different

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thin coatings and films have long been of immense interest. These films and/or substrates of interest may be rigid (metallic, ceramic, *etc.*) or flexible (*e.g.*, polymeric). For example, several processes in xerography and in the melt extrusion of polymers onto substrates require the accurate determination and control of the temperature in an interfacial region or within a thin (10–20 μm) thermoplastic layer.[1–3] Similarly, measurement of the thermal conductivity of semiconductor films[4] and the thermal resistance at interfaces and in thin layers in microelectronic circuits[5] also require the accurate measurement of temperature. Wear of polymeric coatings may be associated with localized heating and better control strategies to reduce/eliminate wear in such polymer coatings can be developed if both the temporal and spatial history of the temperature of the coating is known. Similarly, by determining the thermal conductivity of a coating or of an interfacial region, based on the measurement of the temperature difference and the associated heat flux across the region, it should be possible to estimate the Young's modulus of that region. In many instances, such information can be used to enhance the understanding of particle/surface adhesion characteristics. For example, particle adhesion to a substrate overcoated with a relatively rigid material depends on the Young's modulus of the coating.[6–8]

The thermal and elastic properties of thin coatings, including the Young's modulus, may not be the same as those of bulk materials. In addition to the obvious differences associated with the ratio of surface area to mass, coatings typically contain strains, which can affect their thermal and mechanical properties. Orientation effects may also be present. Finally, the coating methods can result in an alteration of the composition of the coatings. For example, coatings frequently contain significant quantities of residual solvents. Even in the absence of such differences between the properties of coatings and bulk materials, the presence of an interfacial region can alter the physical response of a system. Thus, the presence of an interfacial region can greatly affect the propagation of a thermal wave through the material.

The determination of the temperature of such thin polymer films and interfacial regions requires innovative methods. Conventional temperature probes are unsuitable, since they may be large compared to the thin films of interest, and their thermal conductivities and heat capacities can significantly perturb the measurements. Furthermore, their large mass can result in inadequate and slow response times. Non-contact optical methods such as standard pyrometry or calorimetry are not always feasible since they require a direct optical path from the sample film, which may not be possible for opaque coatings, or due to the unique equipment constraints associated with thin film processes.

There has been much experimental and theoretical work aimed at measuring the thermal conductivity of thin films[9,10] deposited on different substrates. Decker *et al.*[11] determined the thermal conductivity of thin films of SiO_2 and Al_2O_3 on sapphire substrates by using a pair of electron beam deposited, 1000Å thick, chromel/alumel thermocouples. While this suggests that similar thin film thermocouples (TFTs) may also be used with flexible thermoplastic films and substrates, the electron beam deposition method may be unsuitable for heat-sensitive polymer substrates. Furthermore, the flexibility of many of the thermoplastic films also demands that the TFTs be sufficiently robust and retain their sensitivity with use.

Recently, Rimai *et al.*[12] demonstrated that copper/constantan and copper/nickel

TFTs and differential thermocouples deposited on several flexible polymer substrates by sequential thermal evaporation were durable and had good temperature sensitivity. They calibrated these thin film devices and the thermal emfs were quite reproducible. These thermocouples are thin enough that heat loss through their leads is negligible. They may also be used in laminated coatings for precise temperature determinations at various depths within the films. This paper describes the use of Cu-Ni linear and differential TFTs to measure the transverse thermal conductivities and the elastic moduli of 0.025 mm thick polyimide (Kapton-H, a registered trademark of DuPont), a 0.1 mm thick clay-coated paper, and a 0.2 mm thick polystyrene-polyethylene-paper composite.

EXPERIMENTAL PROCEDURE

Cu-Ni thin film thermocouples were deposited on 25 μm thick polyimide and 0.1 mm thick clay-coated paper substrates, and on 0.2 mm thick polystyrene-polyethylene-paper composites in a thermal evaporation system consisting of a bell jar type evaporator. The system was pumped by a mechanical and a silicone oil diffusion pump combination, capable of attaining a base pressure of 10^{-6} Torr. Copper (99.9%) and nickel (98%) pellets were evaporated sequentially using tungsten and alumina-coated tungsten boats, respectively. Copper and nickel were used as the thermocouple elements, rather than conventional alloys, to control the composition of the thermocouple junction. Earlier studies[12] have shown that the use of an alloy, such as constantan, resulted in the fractional distillation of one component during deposition and caused variations in the properties of the thermocouple junction. The polymer substrates on which the TFTs were to be deposited were placed on an aluminum support, approximately 11.5 inches (29.2 cm) above the evaporation source. The deposition rates were controlled by varying the voltage across the evaporator boat by means of a voltage transformer. The evaporation was carried out at a base pressure of 3×10^{-6} Torr. Typical deposition rates were 3–7Å/s. The low deposition rates were chosen because scanning electron microscopy showed that the thermocouples deposited under such conditions were in intimate contact with the substrate, yet did not significantly penetrate the polymer coating on the paper support. Metallic masks were used to mask portions of the substrate during the evaporation process. After evaporating the copper, the system was opened, the masks rotated to cover most of the copper film except where the junction was to be located, and the system re-evacuated. Subsequently, the Ni film was deposited.

The copper and nickel films were deposited on glass slides placed inside the deposition chamber, simultaneous with the TFTs. The thickness of the TFTs was determined indirectly by measuring the film thickness on the glass slides using a profilometer (Dektak IIA), thereby avoiding any possible damage to the surface of the thermocouples on the polymer films during the thickness measurements. The leads for the TFTs were fabricated by flattening the tips of copper and nickel wires and contacting the flat ends across the measuring junctions of the TFT. The film and the contacting wires were sandwiched between two glass slides held together mechanically by clips.

Reproducibility of the thermocouple characteristics and the contacts was verified by measuring the emf across the thermocouples each time at room temperature. Differential thermocouples were formed by depositing two copper films 4 cm apart from each other, followed by the deposition of a nickel film in between the copper films forming two similar Cu-Ni junctions. The junction area was typically about 0.4 cm^2.

The thermocouples were calibrated by immersing the junction in a hot silicone oil (viscosity of 50 centistokes and a flashpoint of 285°C) bath and recording the emf generated between the measuring leads as the bath cooled down. A standard mercury thermometer was used to record the bath temperature and the induced emf was measured using a Keithley 175 autoranging multimeter. All measurements were referenced to the room temperature (20°C).

In this paper, the term transverse thermal conductivity (k_t) denotes the thermal conductivity measured perpendicular to the plane of the film, *i.e.*, when the heat conduction path is determined by the thickness of the film, while the conductivity measured in the plane of the film is denoted as longitudinal thermal conductivity (k_l).

Transverse thermal conductivity was determined by depositing thermocouples on both sides of the polymer film or composite material. A resistive heater consisting of a tungsten wire (25 ohm resistance) wound around an insulating cylindrical core and enclosed in a cylindrical brass casing with a flat base was used as the heating source. The cylindrical portion of the heater was provided with two end leads across which a voltage could be applied to heat it. During the thermal conductivity measurements, one thermocouple junction was heated by placing the flat base of the resistive heater (3.8 cm^2 area) on the junction and allowing it to reach a steady state temperature. The temperature of this heated junction was measured by contacting it with a fine gauge chromel-alumel thermocouple. The thermal response, or the emf output, of both the junctions was recorded. The temperature difference between the junctions was determined from the emf measurements, using the thermocouple calibration curves.

The measurements were repeated with different power inputs, ranging between approximately 0.25 and 0.1 watt, supplied to the resistive heater. The input power was varied so that the measurements could be repeated and averaged to minimize the errors resulting from any possible incomplete energy transfer from the heater to the thermocouple junction. The convective heat losses occurring from the resistive heater's surface to the surrounding air were calculated using the surface area of the heater not in contact with the film and its temperature and using the appropriate heat transfer coefficient.[13] It was estimated that, for the temperature differences involved in this study, approximately 90% of the total heat input to the heater was transferred to the underlying film or substrate. Heat losses due to radiation were negligible for the temperature regimes encountered in this study.

The transverse thermal conductivity, k_t, of the film is related to the thermal power input, Q, the temperature difference, ΔT, the thickness of the film, Y, and the area of the heated region, A, by

$$Q = k_t A \Delta T / Y \tag{1}$$

where A is the area of the film heated by the base of the resistive heater.

Here Q is the energy actually entering into the sample. It can be lower than the energy input into the heater due to convective and radiative heat losses. Such losses, if significant, should manifest themselves in apparent variations of the thermal conductivity with the heater power. As discussed later in this paper, the absence of any such effects beyond the limits of experimental error and the agreement between the presently obtained values of the thermal conductivity of Kapton-H® with previously reported values suggest that any such effects, if present, are small. Similarly, the loss of heat through the thermocouples was estimated to be small.

RESULTS AND DISCUSSION

Calibration

The typical calibration curves for the 1000Å thick linear and differential Cu-Ni thermocouples on the polystyrene-polyethylene-paper composite substrates are shown in Figures 1 & 2, respectively. The sensitivities of the linear and the differential thin film thermocouples, 4.1 ± 0.5 μV/°C, and 2.5 ± 0.1 μV/°C, respectively, as measured by the magnitude of the induced emf at the same junction temperature, is about 20% to 30% that of conventional Cu-Ni wire thermocouples. This may be due to either the thickness of the thermocouples and/or the properties of the junction. Further work is needed to understand this effect more fully. At equal temperature of both junctions, the voltage across the differential thermocouple was zero

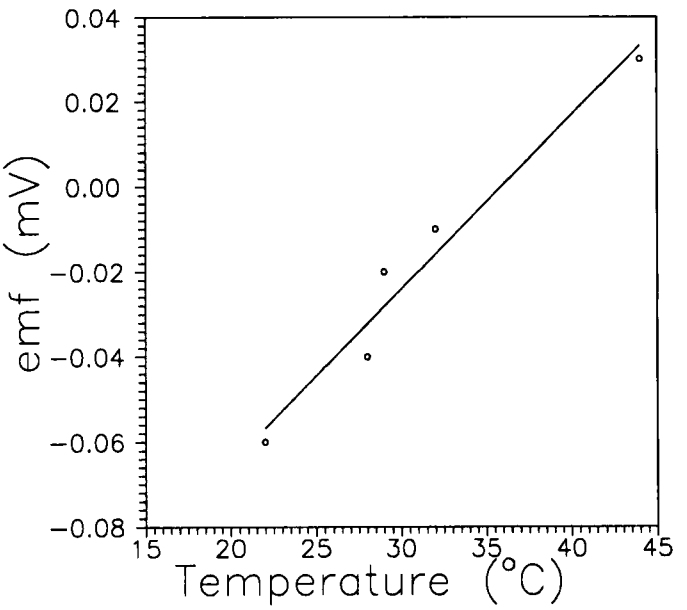

FIGURE 1 The calibration curve of a 1000Å thick Cu-Ni thermocouple on the polystyrene-polyethylene-paper composite. The observed linear response ranges between 20% and 30% of that of bulk thermocouples. The slope of the straight line is 4.1 ± 0.5 μV/°C.

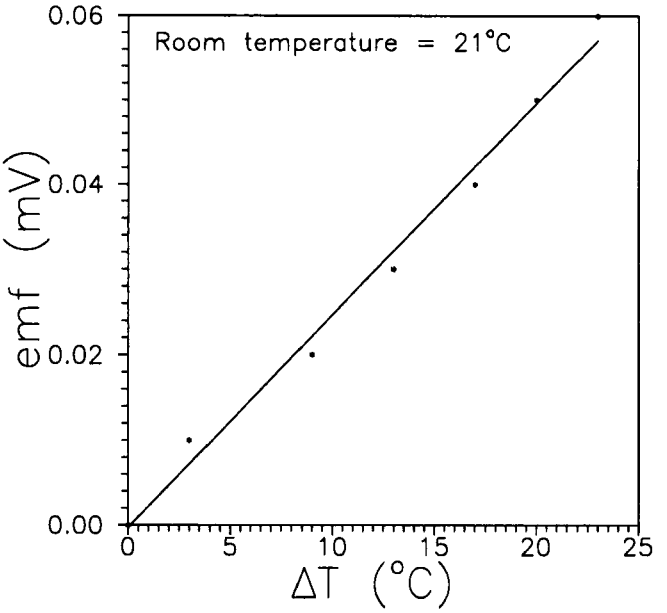

FIGURE 2 The calibration curve of a differential thermocouple on the polystyrene-polyethylene-paper composite. The slope of the straight line is 2.5 ± 0.1 μV/°C.

suggesting that the variations between junctions prepared under similar conditions are minimal. The linear response of both types of thermocouples was sufficiently large and stable so as to permit their use as precise temperature measuring devices. The Cu-Ni thermocouples deposited on the Kapton-H® films and the clay-coated paper were also calibrated. Their response was linear and their sensitivities were 11 ± 0.2 μV/°C and 3 ± 0.04 μV/°C, respectively. All the thermocouple sensitivities and the corresponding deviations reported in this paper were determined using standard linear regression analysis. The relatively low sensitivity of the thermocouple on the paper is probably due to the highly inhomogeneous surface of the paper. These substrates were chosen to be sufficiently thick so as to have bulk rather than surface properties dominate the thermal conductivity. Therefore, it is unlikely that the sample thickness can account for these variations. The reasons for the differences in sensitivities are not presently fully understood. However, it appears that, as long as the thermocouples are calibrated, they can be used as precise temperature measuring devices.

Transverse Thermal Conductivity

Kapton-H® was chosen as one of the substrates, because it is sufficiently thick and homogeneous so as to permit comparison between the presently-obtained experimental results and literature values of the corresponding bulk properties. The average thermal conductivity of the six samples examined was found to be 0.13 ± 0.02 W m^{-1} K^{-1}, which is in good agreement with the value of 0.12 W m^{-1} K^{-1}, reported

TABLE I
Typical measured transverse thermal conductivities for different polymer materials

Polymer film	k_t (W m^{-1} K^{-1})
Kapton-H® (0.025 mm)	0.13 ± 0.02
Polystyrene-polyethylene-paper composite (0.2 mm)	0.036 ± 0.006
Clay-coated paper (0.1 mm)	0.018 ± 0.004

by DuPont. The measured thermal conductivities of Kapton-H®, the polystyrene-polyethylene-paper composite, and the clay-coated paper substrates are shown in Table I. In these calculations, eq. (1), it is assumed that the entire heat supplied to the film propagates in the transverse direction only, without accounting for the flow of heat in other directions, *i.e.*, to regions outside the area covered by the heater. Hence, the reported values should be regarded as the upper limits for the transverse thermal conductivity values.

The transverse thermal conductivity of a clay-coated paper composite, averaged over five samples (Table I), was found to be approximately 0.018 ± 0.004 W m^{-1} K^{-1} which is 15% of that of Kapton-H® films. The clay coating, being an insulator, does not readily conduct heat, in the transverse direction, from the heated junction to the cold junction. Hence, the top surface of the clay-coated paper, in contact with the resistive heater, becomes quite hot while the bottom surface remains relatively cold, causing the measured temperature difference (Δ T) between these surfaces to be rather high, compared with that for other materials under similar conditions. Hence, the reported thermal conductivity for the clay-coated paper should be regarded as the lower limit value. The thermal conductivity of air is approximately 0.02–0.03 W m^{-1} K^{-1}, which is comparable with or slightly greater than, the measured thermal conductivity of the clay-coated paper. This suggests that the thermal conductivity of the paper may be dominated by that of the air in the fibrous paper and/or that the interfacial resistance between the coating and the paper is high. Moreover, the dominant effect of the clay may be to impede the flow of the air. The transverse thermal conductivity of the polystyrene-polyethylene-paper composite, averaged over six samples, shown in Table II, was found to be

TABLE II
Transverse thermal conductivity values for six different samples of 0.2 mm thick polystyrene-polyethylene-paper composites

Sample	Power (Watts)	ΔT (°C)	k_t (W m^{-1} K^{-1})
TC1A	0.7	10.1	0.029
TC2A	1.3	17.0	0.042
TC1B	0.7	10.5	0.034
TC2B	0.4	7.1	0.029
TC3	0.5	8.9	0.037
TC4	0.8	8.7	0.043

Average $k_t = 0.036$ W m^{-1} K^{-1}.

approximately 0.036 ± 0.006 W m^{-1} K^{-1}, which is about one-fourth that of Kapton-H® or polystyrene[14] (0.14 W m^{-1} K^{-1}). Again, it is assumed that all the heat supplied to the film propagates in the transverse direction, *i.e.*, along the thickness, through the different layers of the composite material. However, this assumption is not strictly valid for a composite material consisting of paper coated with consecutive polymer films of high thermal conductivities since, for such materials, a considerable portion of the heat supplied might travel along the length of the film, *i.e.*, to portions of the sample not covered by the heater base, and heat the film surface.

The polystyrene-polyethylene-paper composite used in this study had an intermediate coating of polyethylene (30 μm) between the polystyrene coating (10 μm) and the paper. Since the thermal conductivity of polyethylene[14] is approximately three to four times that of polystyrene, this intermediate layer could conduct a significant portion of the heat in the longitudinal direction, and diminish the actual amount of heat conducted in the transverse direction, across the polyethylene-paper interface. The actual contribution of the interfacial region to the measured thermal conductivity needs to be investigated further.

The determination of the longitudinal thermal conductivities (k_l) of these films and coatings needs a radically different experimental set-up and approach requiring the use of differential thermocouples. In addition, a precise estimate of the heat flux along the film surface is required. The required experiments and calculations are in progress and the results will be reported in due course.

Shear Modulus and Young's Modulus

Thermal conductivities have been related to parameters such as phonon velocities and phonon scattering lengths in several models. Following common procedure, we have chosen to analyze the present results according to the Debye model. According to the Debye model, the thermal conductivity k ($k = k_t = k_l$) of a homogeneous and isotropic material is related to the phonon velocity, v, the phonon mean free path, l, and the specific heat of the material, C_p, by the equation

$$k = 1/3 C_p v l \tag{2}$$

If the thermal wave is propagated primarily by the transverse phonons, then the shear modulus, G, is related to the phonon velocity, v, and the material density, ρ, by the equation

$$G = \rho v^2 \tag{3}$$

It is recognized that both transverse and longitudinal phonons contribute to the thermal conductivity. Moreover, the phonon mean free path depends on parameters such as frequency and can be difficult to predict. Therefore, associating the shear modulus with the phonon velocity calculated from eq. (2) is not strictly valid. However, because the Debye model is only an approximate representation of the thermal conductivity, the phonon mean free path can be used as an adjustable parameter when relating the measured thermal conductivity to the phonon velocity.[15] The approach pursued here is to use literature values of typical phonon mean free paths

in polymer films, to determine the phonon velocity from eq. (2) and to assume that these velocities are directly related to the shear modulus. The appropriate modulus of the film/coating can then be estimated. While this method may not allow for accurate determinations of the shear and Young's moduli, it can be used to determine if the coating moduli differ from those of the bulk.

Finally, for an isotropic solid, Young's modulus, E, is determined once the shear modulus, G, and Poisson ratio, γ, are known because

$$G = E/[2(1+\gamma)]. \tag{4}$$

The specific heat and density of Kapton-H® ($C_p = 1.1$ J g^{-1} K^{-1}, $\rho = 1.42$ g cm^{-3}) were obtained from the existing literature values.[16] The shear and Young's moduli for Kapton-H®, calculated assuming a phonon mean free path[14,17] of approximately 4 Å, and a Poisson ratio of 1/3, are approximately 1.35 GPa and 3.62 GPa, respectively. These are typical values for such polymers,[17] and the latter is in reasonable agreement with the tensile modulus (2.5 GPa) published by DuPont, particularly since the tensile modulus is typically lower than the compressive modulus for most polymers. However, even though the thermal conductivity values reported here agree with those of DuPont, the discrepancy in the values of the tensile modulus (3.62 GPa *vs.* 2.5 GPa of DuPont) suggests that the assumed value for the mean free path is suspect. Thus, it would be preferable to determine the mean free path from an independent measurement of sound velocity in Kapton-H®. However, that is beyond the scope of this paper. While the approach taken in this manuscript is clearly not rigorous, due to the uncertain mean free path values, it can yield useful estimates of elastic moduli which can be difficult to obtain otherwise. Similar calculations cannot be readily made for the composite films since eqs. (2)–(4) need modification.

CONCLUSIONS

Thin film thermocouples are very useful in determining the thermal conductivity of thin, flexible materials. Due to their intimate contact with the substrate and negligible heat losses, they are useful devices for measuring the thermal conductivity of films, coatings and interfacial regions. Transverse thermal conductivities of Kapton-H® films, a clay-coated paper, and a polystyrene-polyethylene-paper composite have been determined using linear thin film thermocouples. Finally, the elastic moduli of homogeneous films and coatings can be estimated from the thermal conductivity of these films, provided an accurate value for the phonon mean free path is available.

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