Impact of molecular orientation on thermal conduction in spin-coated polyimide films

K. Kurabayashi and K. E. Goodson
Department of Mechanical Engineering, Stanford University, Stanford, California 94305-3030

(Received 4 February 1999; accepted for publication 6 May 1999)

Polymer films are serving as passive regions in fast logic circuits and as active regions in organic optoelectronic devices, such as light-emitting diodes. Recent data illustrated the strong anisotropy in the thermal conductivity of polyimide films of thickness near 1 μm, with the in-plane value larger by a factor of approximately six. This manuscript extends previous theoretical work on heat conduction in stretched bulk polymers to model the conductivity anisotropy in spin-coated polymer films. Predictions are based on the standard deviation of the angle of molecular orientation with respect to the film in-plane direction, which can be investigated using birefringence data, and the expected conductivity anisotropy in a material with perfectly aligned chains. The modeling and previous data indicate that the anisotropy factor could increase to a value larger than 10 for polyimide films much thinner than 1 μm. © 1999 American Institute of Physics.

I. INTRODUCTION

Polymer films are promising as inter-level dielectric regions for metallization in fast integrated circuits and as active layers for optoelectronic devices.1–3 The precise simulation of these circuits and devices demands an in-depth knowledge of the properties of the polymer films. The thermal conductivities of these polymer films govern the temperature fields in device and interconnect structures, which govern failure rates due to thermomechanical debonding and diffusion processes such as electromigration. Polymer film properties are sensitive to their molecular structure and can differ strongly from those of bulk materials. The partial orientation of molecular chains during the film spin-coating process can cause the thermal conductivity to be strongly anisotropic. This anisotropy has been reported for a variety of material properties, including the index of refraction,4,5 the dielectric constant,6 the Young’s modulus,7,8 and the coefficient of thermal expansion.9,10 Kurabayashi et al.11 reported measurements of both the lateral and vertical thermal conductivities of spin-coated polyimide films of thickness between 0.5 and 2.5 μm. Their data showed that the thermal conductivity anisotropy factor lies between approximately four and six and favors lateral conduction. Because measurements on thinner films may prove difficult, it will be important to understand the manner in which further orientation of molecules in such films might augment the anisotropy. However, no effort had been made to model the impact of molecular orientation on the thermal conductivity anisotropy of spin-coated polymer films.

Previous studies12,13 showed that uniaxially stretched polymers exhibit anisotropic properties similar to those in spin-coated polymer films. The stretching causes the molecular chains to be oriented along the draw direction. The molecules are connected by covalent bonds along the chain while they are weakly coupled with neighboring molecules, primarily through van der Waals interaction. Hence, the molecular chain linkage is direction dependent and causes the orientation of the chains to be responsible for the material anisotropy. While atomic vibrational energy conducts effectively along the chains due to the strong covalent bonding of atoms, the weak van der Waals coupling of atoms in neighboring chains results in relatively poor thermal conduction perpendicular to the chain orientation.14 Henning12 showed mathematically that the physical properties parallel and perpendicular to the stretching direction of uniaxially oriented bulk polymers can be related to those of perfectly aligned polymer chains. The calculation considers the statistical distribution of the chain orientation with respect to the stretching direction. This theoretical approach can also be used to calculate the thermal conductivity anisotropy of spin-coated polymer films as a function of molecular orientation. However, the physical meaning of the thermal conductivities along and perpendicular to the perfectly aligned chains is not clear. Furthermore, the influence of the film thickness on molecular orientation is not known.

The present work predicts the impact of molecular orientation on the thermal conductivity anisotropy of fully amorphous spin-coated polymer films. The calculations assume a Gaussian distribution for the angles of polymer chains with respect to the film in-plane direction. The qualitative level of orientation in the film is therefore quantified using a single parameter, the standard deviation angle in the Gaussian distribution function. This manuscript discusses a procedure for determining the average molecular orientation of spin-coated polymer films using birefringence data. The theory of Henning12 has been adapted to calculate the lateral and vertical thermal conductivities of spin-coated films from assumed intrinsic thermal conductivities along and perpendicular to perfectly aligned polymer molecules. For fully amorphous polymers, these intrinsic thermal conductivities can be understood as those that would be measured in an
idealized material with perfectly oriented molecules.

II. THEORY

Figure 1 summarizes the modeling approach used in this manuscript, which calculates the anisotropy using: (1) the degree of polymer chain alignment along the film plane and (2) the expected conductivity anisotropy in a material with identical stoichiometry and molecular weight, which has perfectly oriented chains.

A. Molecular chain orientation distribution

Figure 2 provides approximate schematics of the molecular structure of spin-coated polymer films, which have molecular chains oriented partially along the in-plane direction. Each chain consists of a large number of linked molecular segments. These segments are usually defined in terms of monomer units, and their size and geometrical dimensions are determined by the molecular mass and the chemical structure of the monomer molecule. The orientation of a given segment can be defined by the polar $\theta$ and azimuthal $\phi$ angles of the segment with respect to the fixed global axes (the $x_1, x_2, x_3$ coordinates) as shown in Fig. 3, where $x_1$ and $x_2$ describe directional components in the film plane and $x_3$ describes the out-of-plane direction. The $x_1', x_2'$, and $x_3'$ coordinates are orthogonal Cartesian coordinates taken such that the $x_3'$ axis is parallel to the principal axis of the segment. For the present work, the molecular orientation refers to the local angle of the molecular chain with respect to the statistically averaged value of $\theta$ for all chains. The key to determining the degree of molecular orientation is the distribution function of the segmental orientations with respect to the reference axis. The distribution function $\rho_{\alpha}(\theta, \phi)$ of the $x_3'$ axis direction is assumed to be given as the product of separate functions for $\theta$ and $\phi$

$$\rho_{\alpha}(\theta, \phi) = P(\theta)Q(\phi).$$  

(1)

Sakamoto et al.\textsuperscript{15} experimentally studied the distribution of the polymer chain orientation using polarized infrared absorption spectroscopy. Their analysis assumes a Gaussian distribution for the variable $\theta$, which in the present notation yields

$$P(\theta) = \exp\left[-\frac{(\theta - \pi/2)^2}{2\sigma^2}\right].$$  

(2)

The standard deviation $\sigma$ defines the degree of the polymer chain alignment with respect to the film in-plane direction, which is defined by $\theta = \pi/2$. The standard deviation $\sigma$ quantifies the extent of deviation of the chain segments from the direction along the film plane. Poon et al.\textsuperscript{16} examined x-ray diffraction patterns for fully amorphous spin-coated polymer films and found no preferred chain orientations in the film plane. Based on their experimental observation, the current model assumes that $Q(\phi)$ is invariant with $\phi$. Therefore,

$$\rho_{\alpha}(\theta, \phi) = \rho_0 \exp\left[-\frac{(\theta - \pi/2)^2}{2\sigma^2}\right].$$  

(3)

where $\rho_0$ is constant. The probability of finding the segment within $\theta - \theta + d\theta$ and $\phi - \phi + d\phi$ in the $x_1$, $x_2$, and $x_3$ coordinates is $\rho_{\alpha}(\theta, \phi)\sin\theta d\theta d\phi$. The spatial average of a physical quantity over the aggregate of the chain segments, $\langle X \rangle$, can therefore be calculated using

$$\langle X \rangle = \int \int X(\theta, \phi)\rho_{\alpha}(\theta, \phi)\sin\theta d\theta d\phi.$$

(4)

In using Eq. (4) to calculate the thermal conductivity, we are simply performing a weighted average of the intrinsic in-plane and out-of-plane conductivity values for the perfectly

---

FIG. 1. Elements of the modeling process for the anisotropic thermal conductivity of spin-coated polymer films.

FIG. 2. Schematic of the partially oriented molecular structure of spin-coated polymer films. Each molecular strand consists of a large number of segments, called monomers.
oriented material, where the weighting factor is governed by the assumed distribution of molecular orientation in the film. While this approach is attractive for its simplicity, it is highly approximate. For example, Eq. (4) neglects the impact of the chain misalignment on the coupling of thermal energy across neighboring chains.

B. Model for partially oriented polymers

Henning\textsuperscript{12} developed a model for the properties of single-phase polymers oriented with respect to a reference direction. The properties of these polymers can be represented by a tensor of second order \( a \), which is described in terms of a transformation

\[
a_i = (a_2 - a_1)\langle \cos^2 \varphi \rangle + a_1,
\]

\[
a_\perp = \frac{1}{2} [(a_2 + a_1) - (a_2 - a_1)\langle \cos^2 \varphi \rangle],
\]

where \( a_i \) and \( a_\perp \) are the observed macroscopic properties parallel and perpendicular to the orientation direction, respectively, \( a_1 \) and \( a_2 \) are the microscopic properties of the perfectly oriented material perpendicular and parallel to its molecular chains, respectively, \( \varphi \) is the angle between the principal axis \( x_3^i \) of a statistical segment and the orientation direction, and \( \langle \rangle \) denotes a statistical mean value over the ensemble of the segments. The property can be the dielectric constant \( \varepsilon \), the linear compressibility \( \gamma \), the thermal expansion coefficient \( \alpha_T \), or the thermal resistivity \( k^{-1} \), where \( k \) is thermal conductivity. The model assumes that the tensor components of the macroscopic material parameters can be calculated using a normalized sum of the tensor components of the microscopic parameters, which are translated into the fixed global coordinates. For the purpose of modeling heat conduction, this assumes that all of the chains within a local volume element contribute independently to heat flow. This is a rather large approximation, since the coupling between neighboring molecules, which is described using one of the microscopic thermal conductivity tensor components, will depend in part on the degree of orientation of the molecules. However, the assumption of independent molecular contributions allows the relatively simple form of Eq. (5) and (6) and is presented here as a first approximation.

The meaning of \textit{perfectly aligned} polymer chains needs to be clarified for polymers having fully amorphous structure. Amorphous polymers have, by definition, local fluctuations of the molecular orientation which prevent perfect crystalline bonding. Therefore, the perfectly oriented structure of amorphous polymers is a hypothetical condition which assumes that the alignment could be achieved together with a weak van der Waals force coupling neighboring molecules. However, amorphous materials subjected to sufficient uniaxial stress will exhibit properties approaching the anisotropic thermal conductivities of such a hypothetical sample, for which data are available.

Since \( \varphi \) is defined in terms of the angle from the in-plane direction for the case of spin-coated polymer films, \( \varphi = \pi / 2 - \theta \). Accordingly, Eq. (4) can be employed to calculate \( \langle \cos^2 \varphi \rangle = \langle \sin^2 \theta \rangle \) using the orientation distribution function represented by Eq. (3)

\[
\langle \cos^2 \varphi \rangle = \int_0^\pi \int_0^{2\pi} \rho_\varphi(\theta, \varphi) \sin^3 \theta \, d\theta \, d\varphi
\]

\[
\int_0^\pi \int_0^{2\pi} \rho_\varphi(\theta, \varphi) \sin \theta \, d\theta \, d\varphi.
\]

It should be noted that \( \langle \cos^2 \varphi \rangle \) is a function of the standard deviation of chain orientation \( \sigma \) in Eq. (3). For the isotropic state where all the polymer chains are randomly oriented, \( \rho_\varphi(\theta, \varphi) \) is constant and \( \langle \cos^2 \varphi \rangle = 1/3 \), yielding

\[
a_1 + 2a_\perp = 3a_0,
\]

\[
a_1 + 2a_\perp = 3a_0.
\]

where \( a_0 \) is the macroscopic property of the isotropic state where all the polymer chains are randomly oriented.

The goal of this work is to predict the impact of the polymer chain orientation distribution on the macroscopic thermal conductivity anisotropy of polymer films. To apply the approach of Henning\textsuperscript{12} for calculating the thermal conductivity anisotropy, an approximate description of heat conduction by a single molecule needs to be developed. This work assumes that the heat flow parallel and perpendicular to the polymer chain is proportional only to the component of the temperature gradient in the respective direction. This yields the thermal conductivity tensor of the chain segment with respect to the local coordinate system \( x_3^i \)

\[
k^c = \begin{pmatrix} k_1^c & 0 & 0 \\ 0 & k_1^c & 0 \\ 0 & 0 & k_2^c \end{pmatrix},
\]

where \( k_1^c \) and \( k_2^c \) are the \textit{intrinsic} thermal conductivity elements governed by the van der Waals interaction of atoms perpendicular to \textit{perfectly aligned} polymer chains and by the covalent bonding of atoms along these chains, respectively. Because the thermal energy more efficiently propagates along the chain, \( k_1^c < k_2^c \). The use of the values of the intrinsic thermal conductivities for the thermal conductivity tensor components in Eq. (10) assumes (a) that the coupling between neighboring chain molecules do not depend on their orientations and (b) that these molecules contribute independently to the heat flow. Another important limitation of this model is that heat transport locally is assumed to be governed only by local chain orientation in the film, without any dependence on the nature or extent of crosslinking. While crosslinking is absent in many organic layers, its presence may strongly improve conduction between chain segments separated by tens of nanometers within a given film and render the present localized approach inappropriate. The lateral, vertical, and bulk thermal conductivities of the polymer films, \( k_{pl}, k_{pn}, \) and \( k_{bulk} \), respectively, can be calculated in terms of \( k_1^c, k_2^c, \) and \( \sigma \) substituting \( a_1 = k_1^{-1}, \ a_\perp = k_2^{-1}, \ a_1 = k_1^c, \ a_\perp = k_2^c, \ a_0 = k_{bulk} \), and Eq. (7) into Eqs. (5), (6), and (9). The anisotropy factor \( A \) is given by
In this case, which is also valid for uniaxially stretched bulk polymers. In this case, \( k_{\|} \) and \( k_{\perp} \) correspond to the thermal conductivities parallel and perpendicular to the draw direction, respectively.

### III. EXPERIMENTAL EVALUATION OF THE CHARACTERISTIC PARAMETERS

The previous section models the thermal conductivity anisotropy using the intrinsic chain conductivities and the standard deviation of the molecular segment orientation. This section discusses the ways in which these parameters can be experimentally determined.

#### A. Intrinsic thermal conductivity measurement

The intrinsic thermal conductivities, \( k_{\|} \) and \( k_{\perp} \), can be experimentally investigated using thermal conductivity anisotropy data for stretched bulk polymers, measured using one of several techniques.\(^{17-19}\) The stretching causes the polymer chains to be aligned along the draw direction. The molecular orientation distribution of the stretched polymer as a function of draw ratio \( \lambda = L/L_0 \) is given by\(^ {20}\)

\[
dn/n = \left[ \frac{1}{2} + \frac{1}{4n_\nu} \left( 3 \cos^2 \varphi - 1 \right) \right] d(\cos \varphi), \tag{12}
\]

where \( dn/n \) is the relative number of the statistical segments for which \( \cos \varphi \) lies between \( \cos \varphi \) and \( \cos \varphi + d(\cos \varphi) \), and \( n_\nu \) is the number of segments per polymer chain. Using Eq. (12), the statistical average of the molecular orientation is

\[
\langle \cos^2 \varphi \rangle = \int \cos^2 \varphi \frac{dn}{n} = \frac{1}{3} + \frac{2}{15n_\nu} \left( \lambda^2 - \frac{1}{\lambda} \right). \tag{13}
\]

Inserting Eq. (13) into Eq. (11) yields the thermal conductivity anisotropy factor \( A \) with respect to the draw direction as a function of \( \lambda \). This means that the intrinsic thermal conductivity ratio \( k_{\|}/k_{\perp} \) can be extracted by measuring \( A \) at a given value of \( \lambda \) for the stretched polymer. However, one should be cautious while using this approach. The derivation of Eq. (12) assumes a molecular orientation change associated with the perfectly elastic deformation of polymers. The alignment can be substantially different for the case of viscoelastic deformation, whose importance increases with draw ratio and temperature.

In addition to the ratio \( k_{\|}/k_{\perp} \), it is also possible to obtain the absolute values of \( k_{\perp} \) from thermal conductivity measurement performed on a stretched polymer which exhibits rubber elastic properties, i.e., a polymer which can be stretched to several times its original length without breaking and which, on release of the stress, immediately returns to its original length. This is called a stress-thermal conductivity measurement. The molecular chains of the rubber elastic polymers are crosslinked with one another. For the case of a rubbery crosslinked polymer subjected to a constant uniaxial stress, the following stress-strain expression can be derived\(^ {21,22}\)

\[
\frac{\sigma_s}{M_c} = \frac{\rho RT}{\lambda^2 - \frac{1}{\lambda}}, \tag{14}
\]

where \( \sigma_s \) is the stress applied to the stretched polymer, \( M_c \) is the number average molecular mass of the chains between the crosslinks, \( \rho \) is the density of the polymer, \( R = 8.314 \text{ J K}^{-1} \text{mol}^{-1} \) is the gas constant, and \( T \) is the temperature. Using Eq. (14) and the molecular orientation distribution given by Eq. (12), Henning\(^ {12}\) derived the following stress-thermal conductivity relationship for the earlier polymer

\[
\frac{1/k_{\perp} - 1/k_0}{1/k_{\|} - 1/k_0} = \frac{2}{5} \frac{M_c \sigma_s}{n_\nu \rho RT}, \tag{15}
\]

where \( k_{\perp} \) is the thermal conductivity of the polymer measured perpendicular to the draw direction, \( k_0 \) is the thermal conductivity of the polymer at the unstrained state. Using Eq. (15), \( k_{\|} \) can be extracted measuring \( k_{\perp} \) for a given \( \sigma_s \). Following this approach, Henning\(^ {12}\) estimated the value of \( k_{\|} \) for fully amorphous polymers to be nearly 0.15 W m\(^{-1}\) K\(^{-1}\).

#### B. Molecular orientation measurement

The molecular orientation of polymers can be studied using wide-angle x-ray diffraction,\(^ {23}\) small-angle x-ray diffraction,\(^ {24}\) polarized infrared absorption spectroscopy,\(^ {15}\) and birefringence measurements.\(^ {4}\) The x-ray diffraction methods are most effective if the polymer samples possess crystalline regions that yield distinct diffraction peaks in the detected signals. However, many of the spin-coated polymer films used as inter-level dielectric (ILD) layers have fully amorphous structures. Birefringence measurements are more robust for studying these spin-coated polymer films because they can determine molecular orientation for both amorphous and crystalline materials. The angle between the polymer chains and the film in-plane direction governs the anisotropy. The birefringence measurement can provide the statistical distribution of the angle for oriented polymers.\(^ {25}\) The birefringence \( \Delta n \) of spin-coated films can be related\(^ {23}\) to their molecular orientation \( \langle \cos^2 \varphi \rangle \) using

\[
\Delta n = n_\parallel - n_\perp = \Delta n_{\max} \left( \frac{3(\cos^2 \varphi) - 1}{2} \right), \tag{16}
\]

where \( n_\parallel \) is the index of refraction lateral to the film, \( n_\perp \) is the index of refraction vertical to the film, and \( \Delta n_{\max} \) is the maximum birefringence at perfect molecular alignment when \( \langle \cos^2 \varphi \rangle = 1 \).

The conventional apparatus of the birefringence technique can measure only in-plane optical anisotropy of transparent films. However, as indicated by Eq. (16), the optical anisotropy of spin-coated polymer films needs to be measured within their cross section. Furthermore, these films are normally deposited on opaque silicon substrates. These conditions require a special experimental setup as shown in Fig. 4, which was originally developed by Tien, Ulrich, and...
Martin. The approach of Tien, Ulrich, and Martin is to measure the indices of refraction of the film by determining the allowed optical modes in the film medium. A prism with a large index of refraction is placed in close proximity to the sample surface. Monochromatic incident radiation is completely reflected at the prism-air interface in a normal condition. However, the radiation propagates into the film sample at discrete angles of incidence, a phenomenon that is based on the evanescent electromagnetic field within the gap. The light propagating into the film sample serves as an optical probe. The thickness of the film and the indices of refraction of the prism, the film, and the substrate govern the allowable coupling angles. With the location of two coupling angles, both the index of refraction and the thickness of the film can be calculated if the refractive indices of the prism and the substrate are known. For polarized incident light, the measurement yields different indices of refraction for the transverse component of the electric field and the transverse component of the magnetic field. The indices of refraction measured for the components are therefore the in-plane and the out-of-plane indices of the film. Therefore, the birefringence of the film is

$$\Delta n = n_{TE} - n_{TM},$$

where $n_{TE}$ and $n_{TM}$ are the refractive indices measured for the TE and the TM modes, respectively. A previous study measured the birefringence of spin-coated polymer films using this approach and studied their molecular orientation.

IV. Predictions and Discussion

This section predicts the impact of both the molecular orientation and the film thickness on the thermal conductivity anisotropy of polymer films.

A. Impact of molecular orientations

Figure 5 plots the lateral and the vertical thermal conductivities normalized by the bulk, isotropic thermal conductivity value as functions of $\sigma$. The intrinsic thermal conductivity ratio, $k_2/k_1$, varies between 5 and 15. The modeling shows that for $\sigma<1^\circ$, both of these conductivities are nearly constant and reach their respective maximum and minimum values. The maximum anisotropy ratio, which is given by the maximum value of $k_{pl}$ divided by the minimum value of $k_{pn}$, is nearly identical to $k_2/k_1$. While the lateral thermal conductivity is influenced by both $\sigma$ and $k_2/k_1$, and significantly differs from the bulk value, the minimum vertical thermal conductivity differs from the bulk isotropic value by less than 30%. This indicates that the out-of-plane thermal conductivity of the polymer film can be roughly estimated by the thermal conductivity measured in bulk, unoriented samples. For the application of polymer films in multilevel interconnection, the out-of-plane thermal conductivity has a dominant influence on the maximum temperature rise. Figure 5 indicates that a random molecular structure could help with conduction cooling by increasing the out-of-plane conductivity. However, the maximum increase of the vertical thermal conductivity would be limited to approximately 40%.

Figure 6 plots thermal conductivity anisotropy of spin-coated Du Pont PI 2556 (benzophenone tetracarboxylic dia-
hydride 4, 4-oxydianiline m-phenylene diamine, BTDA–ODA) polymer films as a function of film thickness based on data obtained by Kurabayashi et al.11 The data indicate that the anisotropy factor \( k_{pl}/k_{pn} \) lies between 4 and 8 for the polymer films of thickness between 0.5 and 2.5 \( \mu \text{m} \). A direct comparison of the data shown in Fig. 6 with the theoretical calculations in Fig. 5 requires knowledge of the intrinsic thermal conductivities, \( k_1^s \) and \( k_2^s \), and the standard deviation of the molecular orientation, \( \sigma \), for the polymer films. Since these data are not available here, this work calculates possible sets of the intrinsic thermal conductivity ratio, \( k_{pl}^s/k_{pn}^c \), and \( \sigma \) which yield the thermal conductivity anisotropy shown in Fig. 6. Figure 7 shows values of the standard deviation \( \sigma \) that are consistent with the model and the thermal conductivity data has been calculated for 5 \( k_{pl}^s/k_{pn}^c \) and \( k_{pl}^s/k_{pn}^c = 8 \), respectively.

B. Impact of film thickness

Lin and Bidstrup4 studied the molecular orientation of spin-coated pyromellitic dianhydrideoxydianiline (PMDA–ODA) films of thickness varying between 1.5 and 6 \( \mu \text{m} \) using birefringence. Their results show that the degree of the molecular chain alignment of spin-coated polymer films increases with decreasing thickness. Sakamoto et al.15 derived a formula for calculating the dielectric constants of the completely oriented PMDA–ODA film. Using their formulation, it is found that \( \varepsilon_1 = 2.57 \) and \( \varepsilon_2 = 3.01 \) for the light wavelength used in the birefringence measurements \( \lambda_1 = 633 \text{ nm} \), where 1 and 2 denote the directions perpendicular and parallel to the molecular orientation, respectively. By definition, the index of refraction \( n_{1(2)} \) and the extinction coefficient \( K_{1(2)} \) of the completely oriented film are given by

\[
\sqrt{\varepsilon_{1(2)}} = n_{1(2)} + iK_{1(2)}. \tag{18}
\]

Using Eq. (17) and the earlier values of \( \varepsilon_1 \) and \( \varepsilon_2 \)

\[
\Delta n_{max} = n_2 - n_1 = \sqrt{\varepsilon_2} - \sqrt{\varepsilon_1} = 0.13. \tag{19}
\]

The molecular orientation \( \langle \cos^2 \varphi \rangle \) of PMDA–ODA films can be estimated using the measured birefringence data and Eqs. (16) and (19) for different film thickness as shown in Fig. 8. Figure 8 compares the birefringence and the calculated molecular orientation \( \langle \cos^2 \varphi \rangle \) for film thicknesses between 1.5 and 6 \( \mu \text{m} \). This calculation indicates that the value of \( \sigma \) lies approximately between 20° and 30° for these films. The relatively small degree of molecular alignment of the films may result from the zigzag shape of the PMDA–ODA molecular chain. This chain shape makes it harder to form a high degree of molecular alignment compared to other polymers.

Employing these values of \( \langle \cos^2 \varphi \rangle \) in the formulation described in Sec. II, the lateral and vertical thermal conductivities of PMDA–ODA films can be predicted as functions of film thickness. Figure 9 shows the predictions for the thermal conductivity anisotropy of the PMDA–ODA films for \( k_{pl}^s/k_{pn}^c \) varying between 5 and 25. The calculations predict...
that the anisotropy decreases with the increasing film thickness. The variation of the thermal conductivity with the film thickness for a given value of $k_\parallel/k_\perp$ is approximately 15% for the lateral direction and is negligible for the vertical direction. The predicted anisotropy factor for the PMDA–ODA films is between 2 and 3. A more accurate study on PMDA–ODA films will require both birefringence and thermal conductivity measurements on the same samples.

**ACKNOWLEDGMENTS**

This work was supported by the Semiconductor Research Corporation under Contracts Nos. 98-PJ-357 and 98-SJ-461. K. E. G. appreciates the support of the Office of Naval Research through the Young Investigator Program and the National Science Foundation through a CAREER Award. The authors thank Dr. S. Uma for her helpful comments.

---