



**HAL**  
open science

# Accurate determination of mechanical properties in thin polyimide films with transverse isotropic symmetry using impulsive stimulated thermal scattering

J. Rogers, L. Dhar, K. Nelson

## ► To cite this version:

J. Rogers, L. Dhar, K. Nelson. Accurate determination of mechanical properties in thin polyimide films with transverse isotropic symmetry using impulsive stimulated thermal scattering. *Journal de Physique IV Proceedings*, 1994, 04 (C7), pp.C7-217-C7-224. 10.1051/jp4:1994752 . jpa-00253281

**HAL Id: jpa-00253281**

**<https://hal.science/jpa-00253281v1>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Accurate determination of mechanical properties in thin polyimide films with transverse isotropic symmetry using impulsive stimulated thermal scattering

J.A. Rogers, L. Dhar and K.A. Nelson

*Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, U.S.A.*

**Abstract:** A transient grating method is used to excite and monitor Lamb acoustic waveguide modes in free standing thin polyimide films which are known to have transverse isotropic symmetry. The dispersion of these Lamb modes is used to accurately characterize both the in and out-of-plane elastic moduli in the films. To our knowledge, this is the first example of the noncontact, nondestructive determination of transverse isotropic moduli in a thin film system.

### 1. INTRODUCTION

As a result of the increasingly widespread use of thin films in the microelectronics, optical, biomedical, and aerospace industries, it has become important to clearly understand the chemical, structural, mechanical, and adhesive properties of these materials during and after fabrication. Recently we introduced a method for the real-time, noninvasive characterization of mechanical, thermal and adhesive properties in thin films[1-4]. We believe that this technique can provide information that will aid in the development of a fundamental understanding of these materials which will ultimately allow for optimization of fabrication conditions and for microstructure design choices that will maximize device reliability and performance.

The technique involves a modification of the well developed impulsive stimulated thermal scattering (ISTS) method[5,6]. Briefly, two picosecond excitation laser pulses are crossed spatially and temporally in an absorbing sample. Rapid nonradiative relaxation gives rise to impulsive heating in a grating geometry that images the optical interference pattern. This sudden spatially periodic heating drives thermal and acoustic responses in the material with a well defined wavevector which is a function of the excitation pulse wavelength and intersection angle. The resulting material motions are monitored by resolving the time-dependent diffraction of a quasi-cw probe beam from the material grating with a fast detection and recording apparatus. This arrangement yields real-time data acquisition rates and spatial resolution on the order of 20 microns. The data can be used to determine important information about the mechanical, adhesive, and thermal properties of films, coatings or multi-layer systems. For example, with this technique we have determined the viscoelastic properties in supported and free standing isotropic polyimide films[1-4]. We have also used the data to determine in and out of plane thermal diffusivities[7], and we have demonstrated the ability to locate and map out spatially fine regions of delamination in films bound to substrates[8]. In addition, the data can be used to measure film thicknesses, and to carry out depth profiling in multilayer systems[9].

Our recent work is focussed on quantifying anisotropic mechanical properties in thin films. While an important design parameter, the anisotropic mechanical properties of thin films are not easily

determined. In fact, we are unaware of any other nondestructive noncontact technique which has the ability to accurately determine these properties. While it is clear that anisotropy within the film plane can be characterized through ISTS by orienting the grating wavevector along different directions in the plane, it may not be obvious that in-plane and through-plane properties can also be determined independently. In this report we use ISTS data to quantify both the in and out-of-plane mechanical moduli in six spin cast polyimide film samples which are known to have transverse isotropic symmetry. That is, these films have in-plane properties that are not necessarily the same as out-of-plane properties.

## 2. EXPERIMENTAL

### 2.1. Real-Time ISTS

The ISTS experimental set-up has been described in detail elsewhere[1,3]. The laser pulses used for excitation are derived from the output of a Q-switched, modelocked, and cavity dumped Nd:YAG laser which yields a 1 millijoule 1064 nm pulse of 100 picosecond duration at a repetition rate of up to 1 kHz. The light from this laser is first attenuated and then passed through a lithium triborate (LBO) crystal to yield light at 532 nm. This is then mixed with the remnant 1064 nm radiation in a B-barium borate (BBO) crystal to yield excitation pulses of approximately 20 microjoules at 355 nm. This light was attenuated to yield ~1 microjoule pulses that were used for excitation of the films.

The 355 nm pulses pass through a 50% beam splitter and a cylindrical lens, and are crossed at an angle  $\theta$ . The relative path lengths and mirror positions are adjusted such that the pulses are temporally and spatially coincident at the film surface. Interference between the two excitation pulses gives rise to a grating intensity pattern with a wavevector of magnitude  $q=4\pi\sin(\theta/2)/\lambda_1=2\pi/\Lambda$ , where  $\lambda_1$  is the laser wavelength,  $\theta$  is the crossing angle between the excitation pulses, and  $\Lambda$  is the grating fringe spacing. Absorption of these pulses and subsequent rapid electronic relaxation in the film leads to deposition of heat which is impulsive on the time scale of most mechanical responses at the excitation wavevector. Thermal expansion which follows this heating launches both an acoustic and a thermal response with wavevector  $\pm q$ . The acoustic response consists of counterpropagating waves which give rise to damped oscillatory material motions. The thermal response gives rise to a quasi-steady state material response which persists until thermal diffusion washes out the temperature grating.

These material motions are recorded in real-time by monitoring the time-dependent diffraction of a probe beam that is overlapped with the excitation pulses. The probe pulse is derived from a continuous wave (cw) single-mode Argon ion laser (Lexel 3500) which produces 1 Watt at 514 nm with a flat intensity profile. This output is electro-optically gated (Conoptics 380) to yield a square pulse whose temporal width is adjustable from ~500 ns to many seconds. This probe beam, coupled with a fast amplified photodiode (Antel - 2 GHz bandwidth), and a transient digitizer (Tektronics DSA 602A - 1 GHz bandwidth) effectively provides a 1 GHz bandwidth window through which film oscillatory and relaxational motions can be monitored.

In the set of experiments described here, we collected data at crossing angles which correspond to grating wavelengths  $\Lambda$  of 28.29, 25.30, 23.93, 19.35, 18.21, 16.04, 15.33, 13.75, 12.76, 12.41, 11.04, 10.06, 10.03, 9.05, 8.67, 8.37, 7.49, 7.36, 6.82, 6.67, 6.33, 5.74, 5.67, 5.39, 5.12, 5.11, 4.94, 4.64, 4.56, 4.29, 4.18, and  $3.89 \pm 0.05$  microns. The grating wavelengths were determined with a 3.15 micron unsupported Dupont PI2555 (BTDA/ODA/MPDA) "standard" sample whose acoustic response was calibrated using an optical microscope to measure the wavelength of grating patterns burned into a blank silicon wafer.

### 2.2. Sample Preparation

Six polyimide film-silicon substrate samples were fabricated by spin coating and fully curing Dupont's PI2611 precursor solution (BPDA/PDA) on 10 cm diameter silicon wafers. The thickness of each sample was determined by the spin speed and was measured with a DEKTAK 8000 stylus profilometer after the cure. The samples had thicknesses of 2.40, 2.97, 6.01, 6.95, 7.74, and  $8.50 \pm .05$  microns. After the thicknesses were recorded, each sample was loaded into a teflon jig. Two identical holes in the side of the jig that contacts the silicon side of the sample define the areas to be etched[10]. A 6:1:1 mixture of HF:HNO<sub>3</sub>:CH<sub>3</sub>COOH etchant was poured into the wells formed by the holes in the jig and within 5 minutes the acid mixture removed the silicon in these regions[11]. (It has

been demonstrated that this etch does not alter the intrinsic properties of the polyimide film nor does it change the residual stress[12,13].) After the etch, the samples were rinsed with deionized water and were allowed to dry for 48 hours in a dessicator.

The samples resulting from this procedure consisted of polyimide coated 10 cm silicon wafers with a pair of 2.5 cm holes in each wafer. For each excitation angle, data were collected in two different regions in each of the two areas where the silicon was etched away. We did not observe significant property variation from spot to spot within one etched region or between the two etched regions. We also did not notice any property changes over the six weeks during which experiments were conducted.

### 2.3. Qualitative Description of Data Features

Typical data collected from the PI2611 free standing film samples are shown in figure 1. The upper frame illustrates acoustic wave propagation which is typically damped out due to viscous losses in the film after several hundred nanoseconds. The decay illustrated in the lower frame of figure 1 is due to thermal diffusion in and out of the plane of the film which washes out the material diffraction efficiency on microsecond time scales. In this paper we focus on the acoustic waveguide velocities which are determined by the excitation angle and a fourier transform analysis of data like that shown in the upper frame of figure 1.

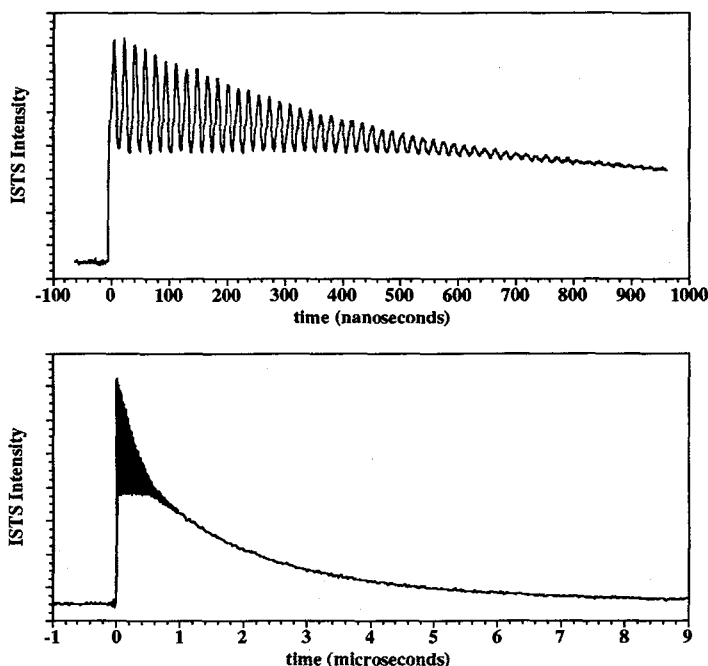


Figure 1: ISTS data from an unsupported 2.40 micron film of BPDA/PDA polyimide. This data are the result of 50 averages and required a few seconds to obtain. The upper frame shows the acoustic response which damps away on nanosecond time scales. As shown in the lower frame, thermal diffusion washes out the material grating on longer time scales.

## 3. THEORY

### 3.1. General Considerations

The theory of ISTS excitation and probing of acoustic disturbances in isotropic thin films systems has been given previously[1-4]. Briefly, for the entire range of acoustic wavelengths excited in these experiments, the acoustic wavelength is comparable to or larger than the sample thickness. For this reason, there are strong waveguide effects in all of the samples. This means that in general there are

many modes, known as Lamb modes, that can propagate. The number, velocity and spatial character of these modes scales with the product of the acoustic wavevector and the film thickness. The lowest four modes that propagate in a typical unsupported polyimide film at a wavevector times thickness value of 2.5 are illustrated in figure 2.

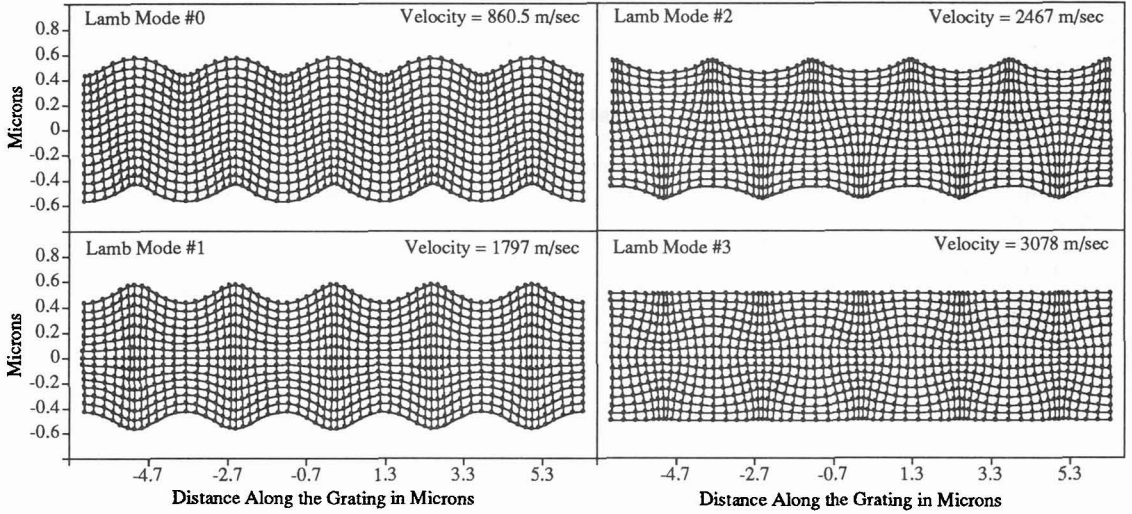


Figure 2: Grid distortion diagrams of the four lowest Lamb acoustic modes at wavevector\*thickness = 2.5.

The important feature for our present purposes is that although these modes all propagate along the surface of the film, the motion associated with each involves shear and longitudinal strains both in and out of the plane of the film. To make this clear, we show in figure 3 a diagram of the lowest order Lamb mode in the large wavevector time thickness limit. The inset illustrates the dramatic in and out-of-plane shear and longitudinal motions that are associated with this mode. Although the diagrams illustrated in figures 2-3 were generated assuming the film to be isotropic, it is clear from the spatial character of each that if the in and out-of-plane moduli of the film are different, then this anisotropy should induce changes in the phase velocities and therefore in experimentally observed frequencies.

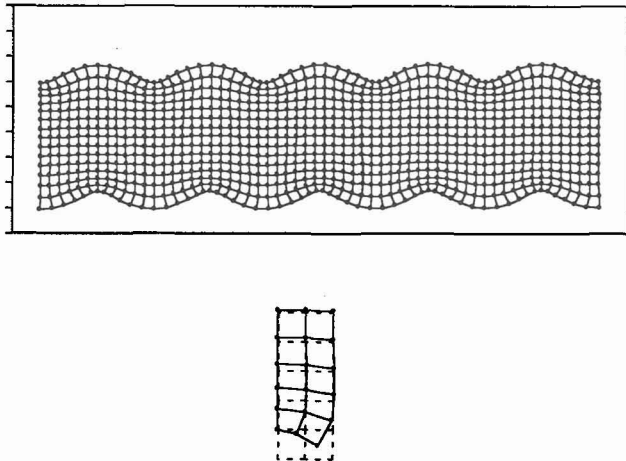


Figure 3: Grid distortion diagram of the lowest order Lamb waveguide mode in the large wavevector times thickness limit. As highlighted with the inset, this mode involves shear and longitudinal motion both in and out of the plane of the film.

### 3.2. Waveguide Propagation in Transverse Isotropic Media

As mentioned at the outset, PI2611 is known to have transverse isotropic symmetry. This symmetry arises due to a preferential ordering of the polymer chains in the plane of the film. The existence of such ordering is common in spin cast polyimide films, and is inferred from significant differences between in and out-of-plane indices of refraction[14,15], large differences between the in and out-of-plane thermal expansion coefficients[16], anisotropy in fluid transport properties[17,18], and, most directly, from x-ray diffraction measurements[19-22]. Although anisotropy of the mechanical moduli has not been measured in thin polyimide films, it has been suggested that in light of the anisotropy seen in other material parameters, the in and out-of-plane moduli should be different. In particular, one would expect that in-plane ordering of the polymer chains would give rise to in-plane moduli which are larger than the out-of-plane moduli simply because there is more covalent (stronger) bonding in the plane than out of the plane of the film.

It is straightforward to determine the Lamb acoustic waveguide dispersion in a transverse isotropic plate. Briefly, the acoustic field equations which govern motion in the film are given by[23],

$$\rho \frac{\partial^2 u_i}{\partial t^2} - c_{ijkl} \frac{\partial^2 u_k}{\partial x_i \partial x_j} = 0 \quad (1)$$

where  $\rho$  is the density,  $u$  is the displacement, and  $c$  is the stiffness tensor. If we define our coordinate system such that the grating wavevector points in the  $z$  direction (direction index 3) and is assumed to extend infinitely in the  $x$  and  $y$  directions (directions 1 and 2 respectively), then derivatives along  $x$  can be ignored. Using this fact, the equations in (1) reduce to

$$\rho \frac{\partial^2 u_y}{\partial t^2} - c_{11} \frac{\partial^2 u_z}{\partial y^2} - c_{44} \frac{\partial^2 u_z}{\partial z^2} - (c_{23} + c_{44}) \frac{\partial^2 u_z}{\partial y \partial z} = 0 \quad (2)$$

$$\rho \frac{\partial^2 u_z}{\partial t^2} - c_{44} \frac{\partial^2 u_z}{\partial y^2} - c_{11} \frac{\partial^2 u_z}{\partial z^2} - (c_{23} + c_{44}) \frac{\partial^2 u_z}{\partial y \partial z} = 0 \quad (3)$$

where the  $c$ 's are components of the transverse isotropic stiffness tensor written in matrix form[24,25],

$$c_{ij} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{22} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{22} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(c_{11} - c_{22}) \end{bmatrix} \quad (4)$$

If we perform a Laplace transform along  $t$ , a Fourier transform along  $z$ , and postulate solutions to  $u_y$  and  $u_z$  of the form  $\sim \exp(iky)$ , where  $b$  is unknown, the dispersion of the Lamb modes can be found by imposing the appropriate boundary conditions at the two film-air interfaces. Operationally, calculation of the Lamb mode frequencies reduces to finding the position of zeroes in a  $6 \times 6$  determinant which is a function only of the wavevector-thickness product and the in and out-of-plane shear and longitudinal sound speeds in the film. (We note that the density and longitudinal sound speed in the surrounding air are also needed. However, the dispersion of the Lamb modes which involve significant motion in the film are highly insensitive to the properties of the air.) It is straightforward to incorporate a function which locates the zeroes of this determinant into a non-linear least squares fitting algorithm for data analysis and property determination.

4. DATA ANALYSIS

4.1. Results

Although there is sufficient data for moduli determination in each of the six polyimide film samples individually, we found that there is negligible property variation from sample to sample. For this reason, we make use of the fact that the waveguide velocities scale with the product of the wavevector and the film thickness to fit data from all six samples simultaneously. Figure 4 shows the measured (symbols) and calculated (lines) Lamb mode phase velocities. It is clear that the transverse isotropic model can very accurately describe the measured waveguide dispersion. The fit determines the in and out of plane shear and longitudinal acoustic speeds. The values of these parameters are given in table 1 and are consistent with the belief that there is in-plane ordering of the polymer chains in this material. (Note the presence of a non-dispersive slow mode in figure 4. This mode can only be accounted for by properly including the air that surrounds the film. This mode is localized at the interface of the film and the air, and disappears when the air is removed[26].)

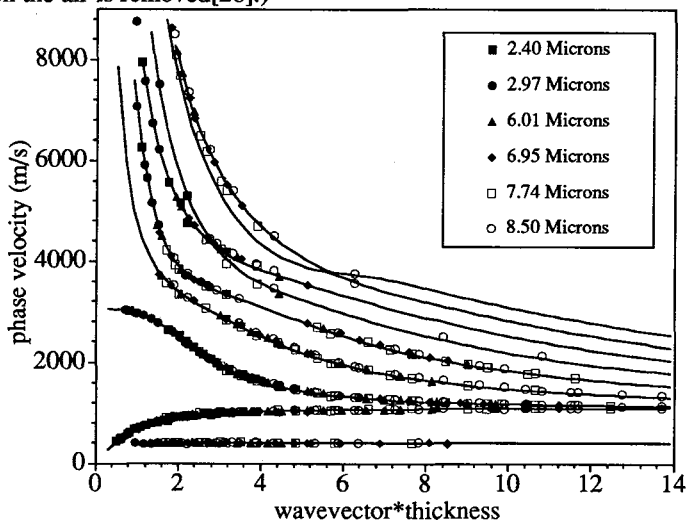


Figure 4: Measured (symbols) and calculated (lines) Lamb waveguide dispersion. The transverse isotropic model for the film accurately describes the observed response. Film thicknesses are given in the legend.

Table 1: Mechanical properties of polyimide films (BPDA/PDA)

MECHANICAL PROPERTY	BEST FIT VALUE
In-Plane Longitudinal Acoustic Speed	3500 ± 200 m/s
In-Plane Shear Acoustic Speed	2000 ± 150 m/s
Out-of-Plane Longitudinal Acoustic Speed	2330 ± 150 m/s
Out-of-Plane Shear Acoustic Speed	1090 ± 75 m/s

4.2. Sensitivity Analysis

We can estimate uncertainties in the fitted parameters by varying the best fit value of each by some fixed amount followed by re-fitting the data allowing the other parameters to float. As an example we show in figure 5 data and "best fit" calculations arrived at by fixing the out-of-plane transverse velocity at a value ten percent higher than the best fit value followed by re-fitting the data allowing the other three fitting parameters to float. The fact that there are significant deviations of the calculated from the measured dispersion in this case leads us to the conclusion that the out-of-plane transverse velocity is

determined to better than ten percent of its actual value. From similar sensitivity tests for the other three fitting parameters, we conclude that the uncertainties for each of the four fitted parameters are less than ten percent.

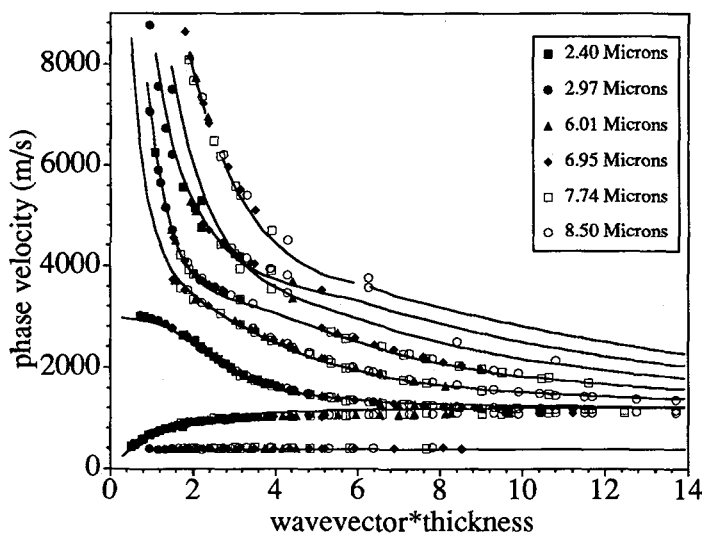


Figure 5: Results of a sensitivity test for the out-of-plane shear speed. The out-of-plane shear speed was fixed at a value ten percent higher than its best fit value. The data were then re-fit, allowing the other three parameters to float. The resulting "best fit" is shown with solid lines in this figure. It is clear that the calculated curves show systematic deviations from the measured dispersion and inadequately fit the data.

## 5. CONCLUSIONS

We have shown that ISTS can accurately determine the in and out-of-plane mechanical properties in thin films. Detailed sensitivity analyses indicate that the in and out-of-plane acoustic velocities are determined to better than ten percent of their values. To our knowledge, this study represents the first time that a single nondestructive, noncontact technique has been used to accurately determine the transverse isotropic properties of a thin film.

## 6. ACKNOWLEDGEMENTS

We wish to thank D. Volfson and F. Trusell for assistance with sample preparation. This work was supported by NSF Grant No. DMR-9002279, by the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Electronics Packaging Program at M.I.T. J.A.R. acknowledges the support of a NSF doctoral fellowship, and L.D. acknowledges receipt of a GRPW grant from AT&T Bell Laboratories and a DoD fellowship.

## 7. REFERENCES

- [1] Duggal A.R., Rogers J.A. and Nelson K.A., *J. Appl. Phys.* **72** (1992) 2823-2839; Rogers J.A., S.M. Thesis, Massachusetts Institute of Technology, (1992).
- [2] Duggal A.R., Rogers J.A., Nelson K.A. and Rothschild M., *Appl. Phys. Lett.* **60** (1992) 692-694.
- [3] Rogers J.A. and Nelson K.A., *J. Appl. Phys.* **75** (1994) 1534-1556.
- [4] Rogers J.A., Yang Y. and Nelson K.A., *Appl. Phys. A*, in press.
- [5] Eichler H.J., Gunter P. and Pohl D.W., *Laser-Induced Dynamics Gratings* (Springer, 1986)
- [6] Nelson K.A. and Fayer M.D., *J. Chem. Phys.* **72** (1980) 5202-5218; Nelson K.A., Lutz D.R., Fayer M.D. and Madison L., *Phys. Rev. B* **24** (1981) 3261-3275.



- [7] Rogers J.A., Mindas C., Yang Y. and Nelson K.A., "Non-invasive Real-Time Evaluation of the Anisotropic Thermal Diffusivity in Thin Polymer Films for Electronics Packaging", to appear in MRS Symposium J Proceedings (1993).
- [8] Rogers J.A. and Nelson K.A. *J. of Adhes.*, in press.
- [9] Rogers J.A. and Nelson K.A. unpublished.
- [10] Pan J.Y., Ph.D. Thesis, Massachusetts Institute of Technology, (1991).
- [11] Robbins H. and Schwartz B., *J. of the Electrochemical Soc.*, **107** (1960) 108-111.
- [12] Maseeh F., Schmidt M.A., Allen M.G. and Senturia S.D., "Calibrated Measurements of Elastic Limit, Modulus and the Residual Stress of Thin Films Using Micromachined Suspended Structures", IEEE Solid-State Sensor and Actuator Workshop 1988.
- [13] Maseeh F. and Senturia S.D., *Polyimides: Materials, Chemistry, and Characterization* (Elsevier Science Publishers B. V., Amsterdam, 1989) 575-586.
- [14] Noe S.C., Pan J.Y. and Senturia S.D., "Optical Waveguiding as a Method for Characterizing the Effect of Extended Cure and Moisture on Polyimide Films", Annual Meeting of the Society of Plastics Engineers, 1991 (ANTEC 37, 1991) pp. 1598-1601.
- [15] Noe S.C., Ph.D. Thesis, Massachusetts Institute of Technology, (1992).
- [16] Elsner G., Kempf J., Bartha J.W. and Wagner H.H., *Thin Solid Films* **185** (1990) 189-197.
- [17] Denton D.D., Ph.D. Thesis, Massachusetts Institute of Technology, (1987).
- [18] Shih D-Y., Cataldo J., Galligan E., Graham R., McGouey R., Nunes S., Paraszczak J., Serino R., *J. of Vac. Sci. and Tech.: A* **8** (1990) 1521-1528.
- [19] Takahashi N., Yoon D.Y., Parrish W., *Macromolecules* **17** (1984) 2583-2588.
- [20] Russell T.P., Gugger H., Swalen J.D., *J. of Polym. Sci.: Polym. Phys. Ed.* **21** (1983) 1745-1756.
- [21] Nakagawa K., *J. of Appl. Polym. Sci.* **41** (1990) 2049-2058.
- [22] Russell T.P., *J. of Polym. Sci.: Polym. Phys. Ed.* **22** (1984) 1105-1117.
- [23] Farnell G.W. and Adler E.L., Elastic Wave Propagation in Thin Layers, in *Physical Acoustic Principles and Methods* **9** (1972) 35-127.
- [24] Nye J.F., *Physical Properties of Crystals*, (Oxford University Press, London, 1957).
- [25] Smirnova V.E. and Bessonov M.I., *Polyimides: Materials, Chemistry and Characterization* (Elsevier Science Publishers B. V., Amsterdam, 1989) 563-574.
- [26] Rogers J.A. and Nelson K.A., unpublished.