

Processing Effects on Optical Anisotropy in Spin-Coated Polyimide Films

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SYNOPSIS

The effects of spinning speed, substrate material, and thermal treatment on the optical anisotropy of spin-coated polyimide films have been examined using the Metricon 2010 Prism Coupler to measure the birefringence. A decrease in the molecular orientation, as determined by birefringence, with increasing film thickness has been attributed to a stress gradient in the thickness of the film and the presence of air-polymer-substrate interfaces. The extent of the thickness dependence is a function of the polymer chain rigidity associated with the polyimide chemistry. The birefringence of the polymer film is also influenced by the substrate material due to the coefficient of thermal expansion mismatch between the film and the substrate. In addition, as a result of potential interdiffusion of solvent molecules and polymer segments between multiple layers of film, the birefringence in polyimide films obtained from multiple coatings of polyamic acid depends on the thermal treatment between the individual coatings. The birefringence of PMDA/ODA polyimide film derived from polyamic acid solution increases as the imidization temperature is increased to 400°C. For preimidized polyimide, the birefringence initially increases upon solvent removal, but decreases above 200°C, possibly indicating the occurrence of thermal cross-linking. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Thin polyimide films are widely used in microelectronics as passivation layers on top of devices or as dielectric interlayers between two levels of metalization.¹ These films are typically formed by spin-coating and are known to develop an in-plane orientation, resulting in measurable optical anisotropy.²⁻⁵ The in-plane molecular orientation is proposed to be responsible for the variations in the moisture absorption,⁶ electrical,⁷ and thermal-mechanical^{3,8,9} properties that ultimately affect the functionality and the reliability of microelectronic devices. Therefore, the purpose of this study was to gain a better understanding of the relationships between processing variations and the development of molecular orientation in spin-coated polyimide films less than 10 μm .

The processing variations examined in this work include spinning speed, substrate material, and thermal treatment. Greater orientation with increasing spinning speed recently reported³ was investigated further to determine the specific cause for the observed dependency. Considerations are given to variations in the linear velocity, solution concentration, and polymer chemistry. Microelectronic device fabrication utilizes a variety of materials that may affect the orientation of the polymer molecules; however, current literature does not contain information on the substrate effects on the orientation of spin-coated films. The effect of the surface material on the orientation of polyimide films is examined in terms of the coefficient of thermal expansion (CTE) mismatch and the adhesion strength between the polyimide film and the underlying material. Upon thermal treatment, increased molecular ordering in polyimide films is evident from X-ray scattering studies.^{2,10} The prism coupler technique is used here to detect structural changes due to high-temperature treatments for both the polyamic acid-based and the preimidized polyimide films.

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SAMPLE PREPARATION

Four different polyimides are examined in this study, and the structural units that make up each of these polyimides are shown in Figure 1. These polyimides belong to two general types: polyamic acid solution and the preimidized polyimide solution. The polyamic acid solution is derived from the reaction of monomeric dianhydride and diamine in a polar solvent such as *N*-methyl-2-pyrrolidone. The formation of a generic polyamic acid and the subsequent thermal treatment commonly used to yield the resulting polyimide film are illustrated in Figure 2. The polyamic acid solutions studied in this work include DuPont PI2540 and PI2545 (pyromellitic dianhydride [PMDA] with 4,4'-oxydianiline [ODA]); DuPont PI2566 (4,4'-hexafluoroisopropylidene-bis-phthalic anhydride [6FDA] with ODA); and DuPont PI2611 (biphenyldianhydride [BPDA] and *p*-phenylenediamine [PPD]). The preimidized polyimide solution (Olin Ciba-Geigy

[OCG] Probimide 293) is a fully imidized polyimide based on benzophenone-3,3',4,4'-tetracarboxydi-anhydride (BTDA) and trimethyldiamino-phenylindane (DAPI). The DAPI unit promotes the solubility of the resulting polyimide in the solvent, γ -butyrolactone. The solvent is subsequently removed by thermal treatments to yield a solid polyimide film.

The polyimide films are cast by spin-coating the polymer solutions on 2 in.-diameter silicon wafers. An adhesion promoter, DuPont VM-651 based on aminopropyltriethoxysilane in a methanol/deionized water mixture, is used to enhance the adhesion between the polyimide film and the substrate material. The adhesion promoter is first applied to the silicon substrate by static spin-coating, without any thermal treatment, and then the polymer solution is dispensed manually and spin-coated for 30 s.

After spin-coating, thermal imidization is carried out to transform the polyamic acid into polyimide for the DuPont polyamic acid coatings. Typical thermal treatment includes a soft bake for 15 min

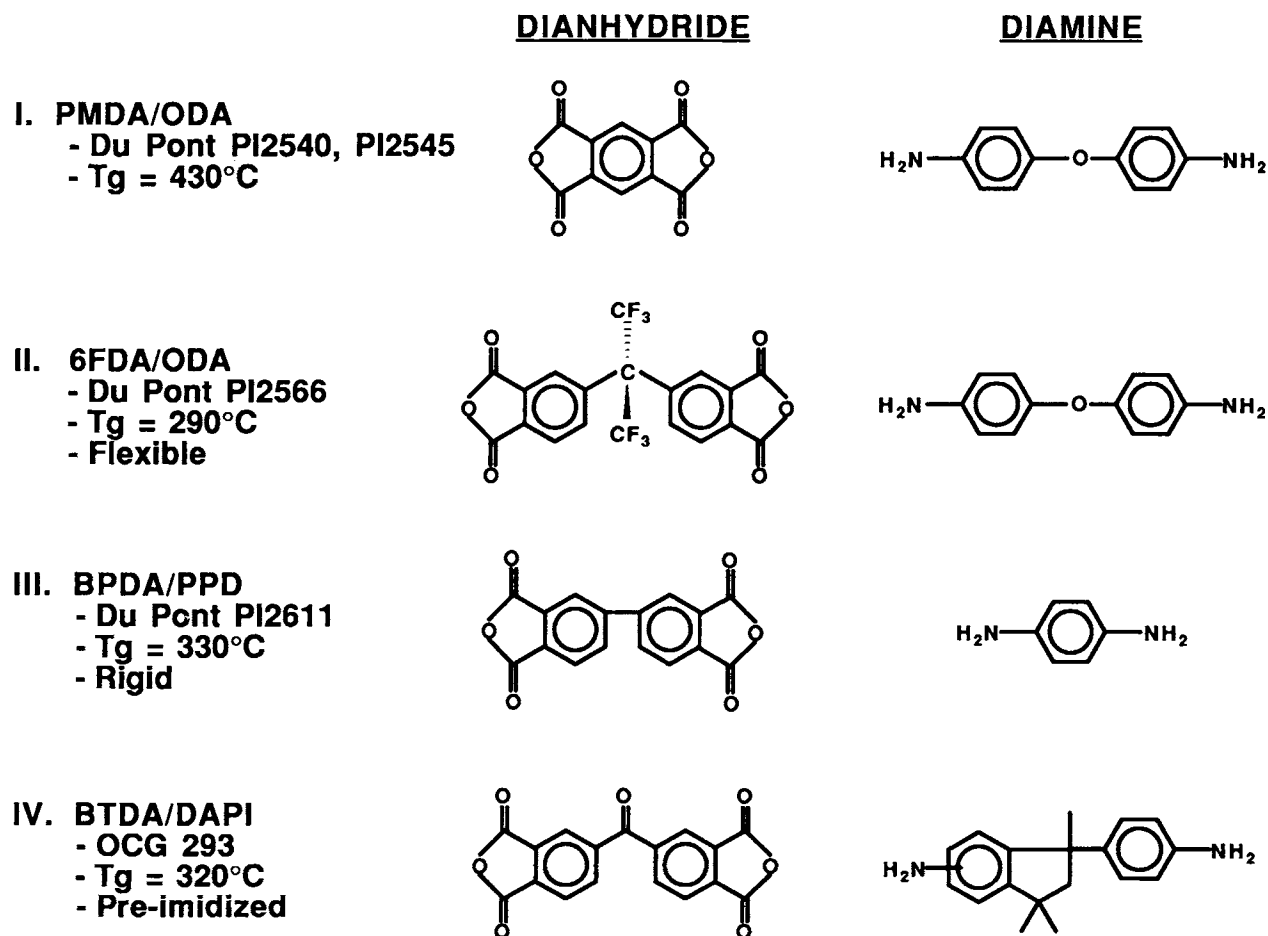


Figure 1 Monomeric units of polyimide chemistries examined.

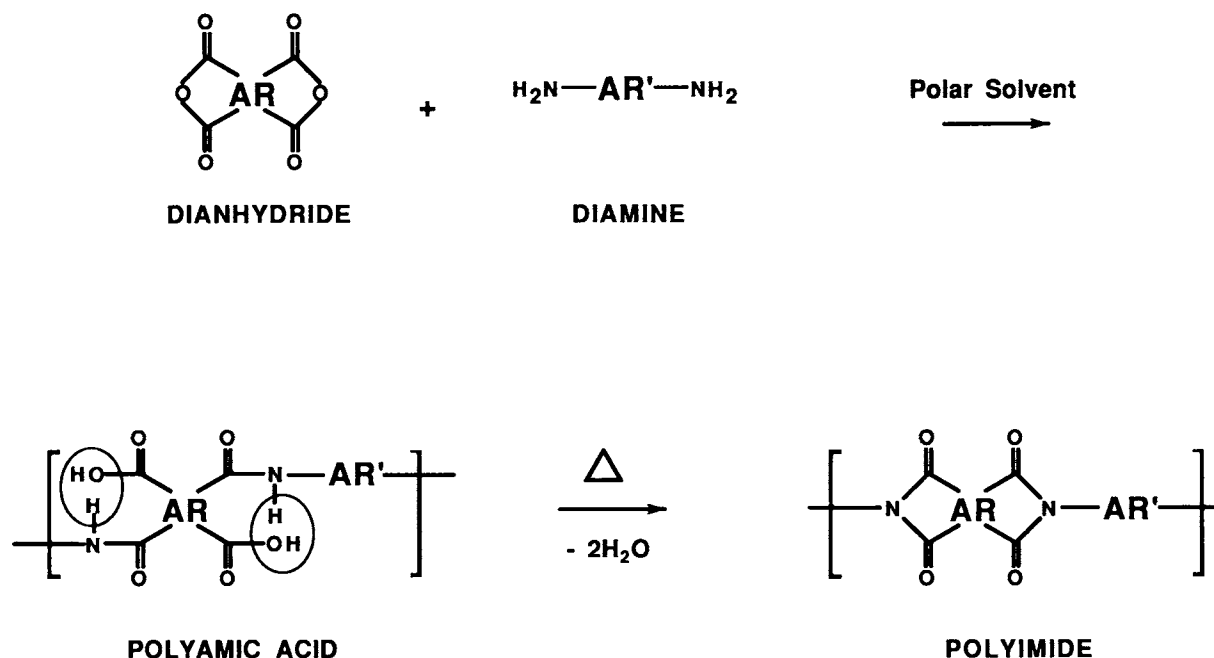


Figure 2 Polyimide formation from thermal imidization of polyamic acid.

at 120°C in air, followed by a hard bake under a flow of nitrogen. The hard-bake schedule consists of ramping the tube furnace temperature at 5°C/min from room temperature to 350°C, holding for 30 min, ramping at 2°C/min to 400°C, and holding for 60 min. For the OCG preimidized polyimide, soft bake is performed at 120°C in air for 15 min, and the hard bake is carried out under nitrogen with heating rate of 2°C/min from room temperature to 150°C, holding for 15 min and continually heating at 2°C/min up to 350°C and holding for another 15 min. The power to the furnace is turned off after the last dwelling, and the samples are removed when the furnace temperature reaches approximately 300°C. Exceptions to the standard sample preparation above are noted where appropriate.

CHARACTERIZATION TECHNIQUE

To preserve the film orientation intrinsically developed through the various processing steps, a nondestructive *in situ* technique to characterize the molecular orientation is desirable. Optical anisotropy, or birefringence, offers a convenient and sensitive method for characterizing the molecular orientation of the spin-coated thin polyimide films.²⁻⁵ The magnitude of the birefringence is dependent on the specific chemical groups and the degree of molecular orientation.¹¹ Therefore, the degree of mo-

lecular orientation for a particular polyimide chemistry may be inferred from the relative magnitude of the birefringence.

Birefringence of polymer films can be determined nondestructively by measuring the retardation of plane-polarized light or by measuring the refractive index of the film in the three dimensions of the Cartesian coordinates. The retardation measurement requires the film sample to be transparent to the light source, which presents difficulty for *in situ* measurement of polyimide films spin-coated on substrates. To circumvent removing the thin film samples from the substrate and possibly altering the inherent molecular orientation, *in situ* measurement of the refractive indices can be obtained by using either the Abbe refractometer or the prism coupler.

Based on the principle of the critical angle, the Abbe refractometer has been used to obtain structural information for a variety of free-standing polymer films.¹² Utilizing techniques from the field of integrated optics, the prism coupler is a newer technique based on the ability of thin film to act as an optical waveguide.¹³ The prism coupler technique provides an *in situ* and nondestructive means to obtain both the refractive index and the film thickness accurately.¹⁴ The principal component of a commercially available prism coupler (Metricon Model 2010 Prism Coupler) is the optical module shown schematically in Figure 3. The monochromatic He—Ne laser beam enters the high refractive index

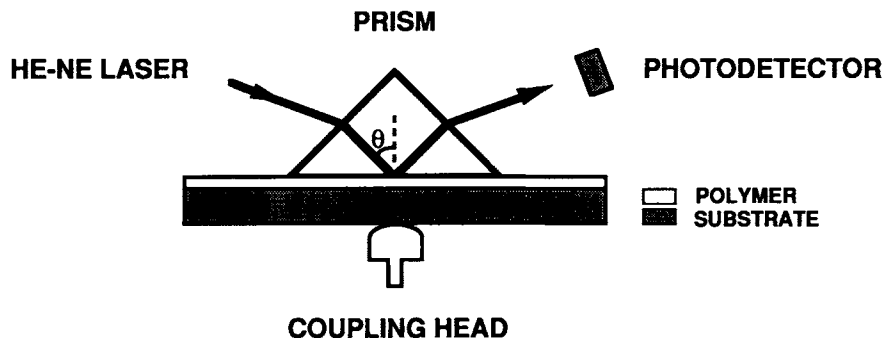


Figure 3 Optical module of the Metricon Prism Coupler.

prism and is reflected onto the photodetector. A pneumatically driven coupling head secures the spin-coated polyimide film sample against the prism that has been designed to leave a small air gap between the film and the prism at the coupling point. At large angles of θ , the laser light is totally internally reflected and the photodetector measures a high intensity. As the angle θ is decreased by moving the rotary table upon which the optical module is fixed, photons are able to tunnel into the film sample at discrete angles, which are referred to as mode or coupling angles. The allowable coupling angles are governed by the thickness of the film and the refractive indices of the prism, the film, and the substrate.¹⁵ When a coupling angle is encountered, the light intensity that reaches the photodetector decreases, and a plot of the intensity vs. the angle θ typically displayed on the computer monitor is shown in Figure 4. With the location of two coupling angles, both the refractive index and the thickness of the film can be calculated if the refractive indices of the prism and the substrate are known.¹⁵ The accuracy of the simultaneous determination of the film refractive index and thickness depends on the precise location of the coupling angles. As film thickness increases, a greater number of coupling angles makes accurate mode location more difficult. For polyimide films, accurate simultaneous refractive index and film thickness data from prism coupler measurements can be expected for films of less than 10 μm . When the film thickness becomes too great for simultaneous refractive index and thickness determination, the Metricon 2010 Prism Coupler may be used for refractive index determination by measuring the critical angle of the film. Distinction of refractive indices in- and through-the-plane of the film is obtained by polarizing the laser source.

In this work, the birefringence is defined as the difference between the refractive index in-the-plane of the film and the refractive index through-the-

plane of the film. The magnitude of the birefringence corresponds to the degree of optical anisotropy, which reflects the molecular orientation. Birefringence measurements, obtained using the Abbe refractometer³ and the prism coupler,^{2,4,5} have been reported for thin polyimide films. As determined in this laboratory, the birefringence values obtained from an Abbe refractometer (with a 589 nm sodium light source) is approximately 0.002 greater than the birefringence value obtained from the Metricon Model 2010 Prism Coupler (with a 633 nm He — Ne laser light source).¹⁶ The discrepancy between the two methods has been attributed to the wavelength difference of the light sources. Unlike the Abbe refractometer, the prism coupler does not require the use of a contact fluid that may affect the polymer film properties and can be hazardous. The prism coupler also has the advantage that it gives both the film thickness and refractive index. Because of the greater convenience and flexibility offered by the

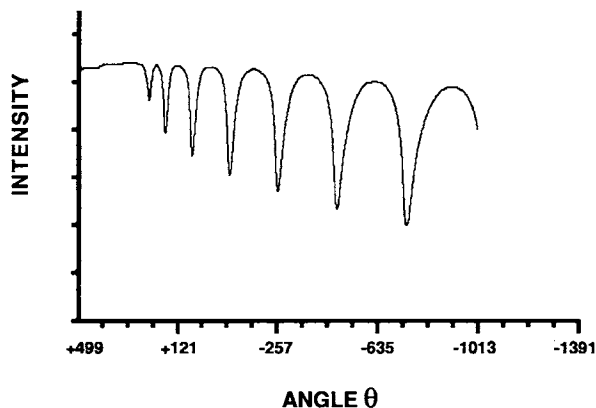


Figure 4 Typical Metricon Prism Coupler plot for PMDA/ODA polyimide film showing locations of mode angles. The numerical θ values on the label represent the internally calibrated rotary table position, not the actual angle in degrees or radians.

prism coupler technique, the molecular orientation of the spin-coated polyimide films is determined in this study using the Metricon Model 2010 Prism Coupler.

RESULTS AND DISCUSSION

The goal of the present work is to gain a better understanding of the development of the in-plane orientation found in spin-coated polyimide thin films. Processing variations in spinning speed, substrate material, and thermal treatments have been employed to investigate the effects on the optical anisotropy of these films. Experimental birefringence data obtained from refractive index measurements using the Metricon 2010 Prism Coupler are presented and discussed.

Spinning Speed

The uniformity of PMDA/ODA film is verified by examining the refractive index and film thickness using the Metricon 2010 Prism Coupler. The average film thickness across the wafer for a film of PI2545 spin-coated at 2500 revolutions per minute (rpm) is $2.24 \mu\text{m}$ with 2% standard deviation after thermal imidization. Optical anisotropy is observed as the in-the-plane refractive index of the film is significantly greater than the through-the-plane refractive index (Fig. 5). Both the in- and through-the-plane

refractive index of the film remain constant with positions across and around the wafer, as the measurements are made by moving the sample radially or rotating it angularly. These observations indicate that the spin-coated polyimide film has an uniform in-plane orientation, in agreement with previous studies.²⁻⁴

In spin-coating, the linear velocity of the rotation increases radially, which translates to increasing shear stress. Therefore, the stress experienced by the molecules across the wafer during the spin-coating process also increases radially. For a 2 in.-diameter silicon wafer spinning at 2500 rpm, the linear velocity increases from 0 mm/s at the center to 6650 mm/s at the edge of the wafer. The invariance of the birefringence with positions on a 2 in. wafer as shown in Figure 5 demonstrates that changes in the linear velocity do not affect the orientation of the spin-coated polyimide film. Examination of PI2540 film on 2, 3, and 4-in.-diameter wafers at 3000 rpm also shows no dependence of birefringence on the linear velocity (Table I). Therefore, the stress imposed on the polyamic molecules by the spin-coating process does not influence the final morphology of the polyimide film.

An increase in birefringence with increasing spinning speed has been observed for PMDA/ODA films.³ By varying the processing conditions, the underlying cause for greater birefringence with spinning speed is explored here. From the previous discussion of film uniformity, it is unlikely that the

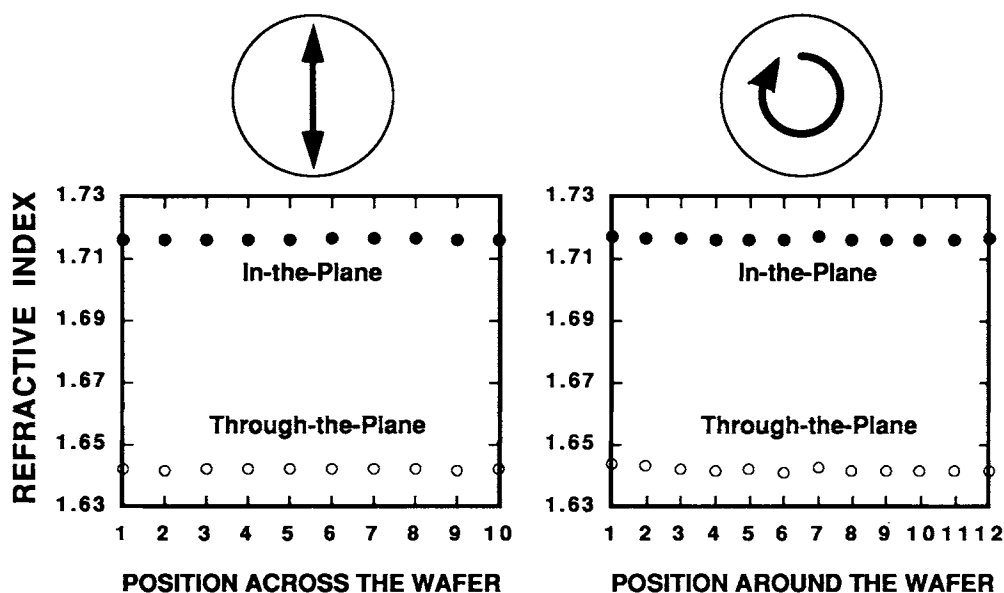


Figure 5 Refractive index variation of PMDA/ODA (DuPont PI2545) polyimide film, indicating in-plane orientation and uniformity of optical anisotropy in the sample.

Table I Effect of Linear Velocity on the Birefringence of PMDA/ODA (DuPont PI2540) Polyimide Film Spin-coated at 3000 rpm on Various Sizes of Substrate

Wafer Diameter (in.)	Linear Velocity Range (mm/s)	Birefringence	Film Thickness (μm)
2	0 to 7.98×10^3	$.0740 \pm .0002$	$4.45 \pm .02$
3	0 to 1.20×10^4	$.0746 \pm .0001$	$4.50 \pm .01$
4	0 to 1.60×10^4	$.0747 \pm .0003$	$4.48 \pm .02$

observed birefringence increase is due to the polymer molecules being oriented by the mechanical stress induced by the spinning. However, the spinning speed directly controls the thickness of the film; as spinning speed is increased, film thickness decreases. Therefore, it is hypothesized that the film thickness is the controlling factor for the observed difference in birefringence. To investigate the effect of film thickness on the birefringence, PI2540 is spin-coated on oxidized silicon wafers at speeds ranging between 2000 and 8000 rpm, which corresponds to a film thickness variation between 6 and 2 μm (Fig. 6). The birefringence and film thickness are both measured by the prism coupler, and the results show a decrease in birefringence as the film thickness increases.

To ascertain whether film thickness is responsible for the observed birefringence increase with increasing spinning speed, dilutions of DuPont PI2540 are used to make polyimide films of similar thickness at different spinning speeds to examine the effect of polyamic acid concentration on the optical anisot-

ropy of spin-coated PMDA/ODA polyimide film. Dilutions of PI2540 are made by adding DuPont T-9039 polyamic acid thinner, composed of 1-methoxy-2-propanol and *N*-methyl-2-pyrrolidone. Three different dilutions of PI2540 with T-9039 by weight are used in this experiment: 3 : 1, 7 : 1, and 1 : 0, which correspond to a range from 10.8 to 14.5 wt % solids in the solution. Independent of the polyamic acid concentration, the birefringence of polyimide films obtained from the three dilutions is simply a function of the film thickness (Fig. 7), which corresponds to the observation by Coburn and Pottinger.¹⁷ Films with similar final thickness made from different dilutions must have varying thicknesses before the thermal treatment, and this is likely to affect the dynamics of solvent evaporation and molecular motion during thermal imidization. In view of the birefringence being independent of the polyamic acid solids content for a given final film thickness, it is hypothesized that the anisotropy variation of polyimide films with thickness is not due to solvent evaporation differences in coatings of different solids content.

The independence of birefringence from both the substrate size (Table I) and the solids content variations (Fig. 7) suggests that the increase in birefringence with increasing spinning speed is due to film thickness variations. There are several possible reasons why the film thickness change may be responsible for the observed orientation variation. Smaller birefringence in thicker films may be due to less complete imidization. Reflectance FTIR is used to detect *in situ* any variations in the extent of imidization for the films. The imide peak near 1370 cm^{-1} normalized to an aromatic peak at 1500

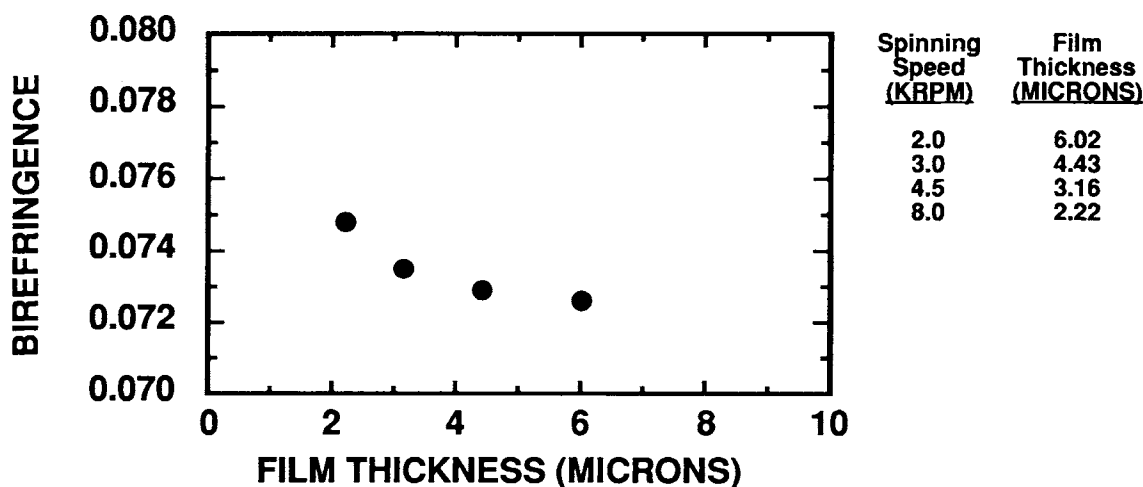


Figure 6 Effect of film thickness on the birefringence of PMDA/ODA polyimide film.

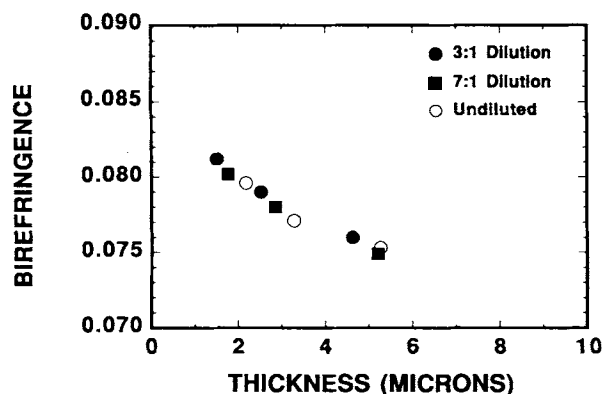


Figure 7 Effect of polyamic acid solids content on the thickness dependence of birefringence for PMDA/ODA polyimide film.

cm^{-1} is used to compare the extent of imidization.¹⁸ As shown in Table II (for imidization temperature of 350 and 400°C), the peak height ratio increases with film thickness, indicating a greater extent of imidization in thicker films. It has been observed that the optical anisotropy of PMDA/ODA polyimide increases with thermal imidization.²³ If the extent of imidization should influence the optical anisotropy, thicker films are expected to have greater birefringence; however, the birefringence of PMDA/ODA polyimide films decreases with increasing film thickness. Therefore, the dependence of birefringence on film thickness must be dominated by factors other than variations in the extent of imidization.

Under the same thermal treatment, thicker films are likely to retain molecular motion for a longer period of time for the solvent to diffuse out of the film.¹⁹ Prolonged plasticization by the solvent would increase the segmental mobility of the polymer chains for molecular relaxation and allow thicker films to attain a more random structure with less birefringence. However, the result in Figure 7 shows that variations in the solvent evaporation for films derived from different polyamic acid concentrations do not explain the dependence of birefringence on film thickness. As the thickness dependence of birefringence cannot be fully explained by differences in either the extent of imidization or variations in solvent evaporation, the most probable explanation is a skin effect due to a stress gradient in the thickness of the film and the presence of air-polymer-substrate interfaces.

For a film under tension, such as the polyimide film on a silicon wafer that has a lower coefficient of thermal expansion (CTE) than the polymer, the biaxial shrinkage of the film is limited by the sub-

strate shrinkage. As a result of the CTE mismatch, the molecules at the polymer-substrate interface are expected to be under the greatest stress. Additionally, the presence of a substrate disrupts any random orientation of the molecules in the bulk of the film; therefore, the molecular orientation should be greatest at the polymer-substrate interface. In support of a stress gradient and the presence of a substrate causing orientation variation in the thickness of the film, the existence of a very thin polyimide layer of higher anisotropy at the substrate-polymer interface has been reported.²⁰ The spatial discontinuity at the polymer-air interface can also introduce structural inhomogeneity. In fact, a more perfect ordering at the polymer-air interface has been recently observed by grazing incidence X-ray scattering.²¹ The prism coupler measures an average refractive index for the entire film assuming insignificant index variation; therefore, it cannot distinguish between surface and bulk index differences. If the ordered skin layer observed by Russell et al.²¹ is assumed to have greater birefringence, the decrease in birefringence with increasing film thickness may be explained as a result of a decreasing contribution of the skin layers with film thickness.

Although a dependency of birefringence on film thickness exists for PMDA/ODA polyimide film, this effect is not universal for all polyimides. For example, the birefringence for stiff polyimide films is reportedly independent of film thickness.²⁰ In an attempt to understand the effect of chemical structure on the film thickness dependency of birefringence, polyimides of different chemistries are examined. A number of polyamic chemistries have been developed to reduce moisture absorption or film stress in the polyimide film by incorporating fluorinated molecules (6FDA/ODA) or increasing chain rigidity (BPDA/PPD), respectively (Fig. 1). By considering the length of the polymer segment needed to describe the polymer chain as a freely jointed coil,⁵ PI2566, composed of 6FDA/ODA, has

Table II Effect of Final Bake Temperature on the Extent of Imidization Based on the Peak Height Ratio of the 1370 cm^{-1} Imide Absorption and the 1500 cm^{-1} Aromatic Absorption

Film Thickness (μm)	Schedule 1 (400°C)	Schedule 2 (350°C)
2.3	0.59	0.58
3.3	0.74	0.87
4.4	1.34	0.94
6.4	1.28	0.98

a relatively flexible structure, whereas PI2611, based on BPDA/PPD, is much more rigid. Birefringence-thickness data for these two polyimide chemistries with significant different chain rigidity are compared in Figure 8, where it is seen that 6FDA/ODA films have much less optical anisotropy than that of the BPDA/PPD films. Two possible explanations for the observed difference in the magnitude of birefringence between 6FDA/ODA and BPDA/PPD are the backbone rigidity and the glass transition temperature of the polymers. Backbone rigidity enhances the ordering along the substrate and thus increases the polarizability of the molecules, giving rise to greater birefringence. The glass transition temperature (290°C for 6FDA/ODA and 330°C for BPDA/PPD) affects the ability of the molecules to relax to a more isotropic state.

Besides its contribution to the magnitude of the birefringence, polyimide chemistry also affects the thickness dependence of the birefringence. As shown in Figure 8, the birefringence of BPDA/PPD films ranging from 1.0 to 6.5 μm is independent of the film thickness, in accord with results reported by Herminghaus et al.²⁰ Composed of the same diamine portion in the backbone, films of PMDA/ODA and 6FDA/ODA both show decreasing birefringence with increasing film thickness (Figs. 6 and 8). As the rigidity of the polyimide backbone affects the magnitude of the birefringence, the backbone rigidity also influences the effect of the skin layers on the thickness dependence of the birefringence. The substrate-polymer and polymer-air interfaces force molecular alignment along the interfaces, resulting in a greater influence of the backbone structure on the orientation in the skin layers than in the bulk material. Therefore, the relative contribution of the

skin layers to the overall birefringence is more pronounced in the less rigid systems (PMDA/ODA and 6FDA/ODA) than in the more rigid system (BPDA/PPD).

Assuming a finite skin-layer thickness for a particular polyimide chemistry, the effect of the skin layer on the film birefringence is expected to decrease with film thickness as the orientation of the bulk material dominates the overall birefringence. Although film thicknesses greater than 6 μm have not been extensively characterized in this laboratory, the birefringence of PMDA/ODA is becoming independent of film thickness at the critical film thickness of approximately 4 μm . A distinct critical film thickness is not yet evident for 6FDA/ODA polyimide film below 6 μm , as shown in Figure 8.

Although the thickness dependence of orientation is independent of solids content for the three PMDA/ODA solutions diluted in-house as shown in Figure 7, a significant birefringence variation is observed for two commercial dilutions of PMDA/ODA (Fig. 9). PI2540 (14.5 wt % solids) yields films with greater orientation than that of the PI2545 (13.5 wt % solids). Earlier studies on the optical anisotropy for solvent-cast polystyrene films have shown that as the molecular weight of the polymer solution increases the birefringence of the resulting film also increases.¹⁵ Polyamic acids are typically formed by adding solid dianhydride in diamine solution, and the molecular weight of the polyamic acid is extremely sensitive to the reaction conditions: both the amount and the order of monomer addition.²² Therefore, the optical anisotropy difference for polyimides processed from PI2540 and PI2545 may be due to variations in the molecular weight of the two polyamic acid solutions.

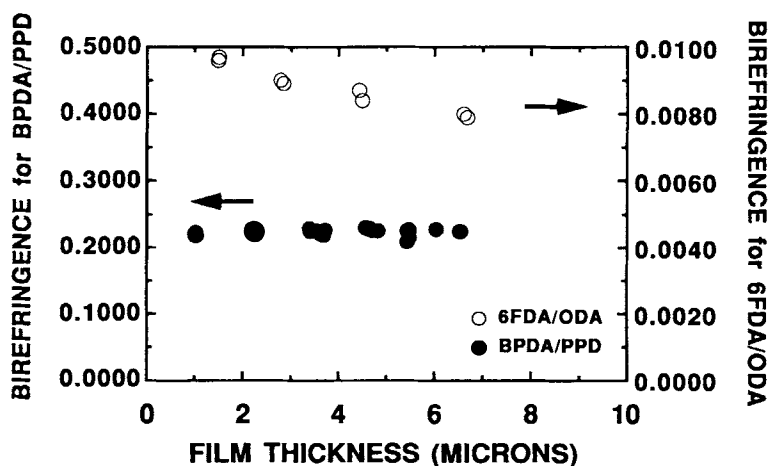


Figure 8 Effect of chemical structure on the thickness dependence of birefringence.

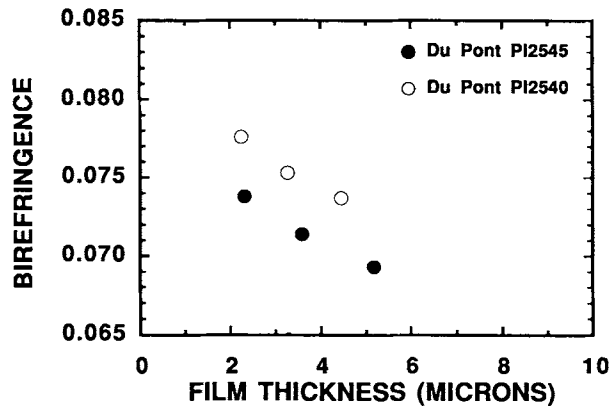


Figure 9 Effect of solids content in commercially available PMDA/ODA polyamic acid solutions on the thickness dependence of birefringence: (●) 13.5% solids; (○) 14.5% solids.

Substrate Effect

In microelectronic fabrication, polyimide thin films are spin-coated on a variety of materials. The effect of substrate surface on the anisotropy is investigated by examining the birefringence of PMDA/ODA polyimide on materials commonly used in microelectronic processing. Literature coefficient of thermal expansion (CTE) values for PMDA/ODA polyimide²³ range from 22 to 35 $\times 10^{-6}/^{\circ}\text{C}$. As shown in Table III, aluminum and silicon dioxide have different CTEs,²⁴ but similar adhesion properties;²⁵ gold and nickel have different adhesion properties,²⁶ but similar CTEs.²⁷ Therefore, examining the birefringence of polyimide on aluminum vs. polyimide on silicon dioxide gives the effect of a CTE mismatch. The effect of adhesion between the polyimide and the substrate materials can be observed by measuring the birefringence of polyimide on gold vs. polyimide on nickel. Cleaned silicon wafers are modified selectively with 0.5 μm of the aluminum, silicon dioxide, gold, or nickel. Aluminum and gold are deposited by DC sputtering, nickel by

filament evaporation, and silicon dioxide by dry thermal oxidation. PI2540 is spin-coated on the surface-modified silicon wafers and thermally imidized using the standard schedule with the soft bake at 135 $^{\circ}\text{C}$ for 15 min but without the 30 min temperature hold at 350 $^{\circ}\text{C}$. As shown in Table III, neither the CTE mismatch nor the adhesion property difference between the polyimide and the surface-modified substrate significantly affects the birefringence.

The effect of metal layer thickness is studied by varying the thickness of aluminum evaporated on the silicon wafer. For films spin-coated on aluminum layers between 0.5 to 2.5 μm , the birefringence remains unaffected. However, the 2 in.-diameter silicon wafers used in this work are between 250 and 280 μm in thickness, and the CTE of a silicon wafer sputtered with a few microns of another material is dominated by the CTE of the silicon. Therefore, polyimide films are spin-coated on bulk aluminum disks to examine the effect of CTE.

Aluminum disks are cut from 650 μm -thick extruded aluminum sheets (2024T3) with a CTE of $23.2 \times 10^{-6}/^{\circ}\text{C}$, compared with the CTE of silicon, which is $3 \times 10^{-6}/^{\circ}\text{C}$. The surface of the aluminum disks is treated with 2 μm of sputtered aluminum. The resulting birefringence for 2.38 μm PMDA/ODA films on the aluminum disks is approximately 0.0024 lower than that for 2.54 μm films spin-coated on silicon wafers. From the thickness dependency of PMDA/ODA observed in Figure 6, a 2.38 μm film should have a greater birefringence than that of a 2.54 μm film. Therefore, the birefringence difference on aluminum and silicon cannot be a result of thickness variation. As the CTE of PMDA/ODA polyimide film matches more closely to the CTE of aluminum than to the CTE of silicon, lower birefringence for polyimide films on aluminum than on silicon substrate may be attributed to a smaller CTE mismatch.

Although a thin layer of modifying material does not affect the birefringence of polyimide films, as

Table III Effect of Substrate Material on the Birefringence of PMDA/ODA (DuPont PI2540) Polyimide Film

Metal on Wafer	Al ^a	SiO ₂ ^a	Au ^b	Ni ^b
CTE ($\times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$)	25.0	0.40	14.2	13.0
Adhesion ($\times 10^5 \text{ dyn/cm}$)	3.89	3.94	3.04	8.43
Birefringence	0.0757	0.0755	0.0752	0.0752
Polyimide thickness (microns)	2.10	2.21	2.15	2.08

^a CTE data from Ref. 24 and adhesion data from Ref. 25.

^b CTE data from Ref. 27 and adhesion data from Ref. 26.

seen in Table III, the effect of the underlying substrate surface is evident in multiple coatings of polyamic acid and should not be neglected. As described in the sample preparation section, thermal treatment of polyimide film from polyamic acid involves two distinct steps: a soft bake and a hard bake. To make multiple coatings of polyamic acid, the first layer of coating may be either processed using the standard schedule (Method A) or simply soft-baked (Method B), as depicted in Figure 10. Then, a second layer is spin-coated, and the standard imidization schedule is carried out for the multilayer structure. The effective difference between Methods A and B is whether the hard bake is performed before spin-coating the second layer of film on the first layer.

A difference in birefringence is observed between PMDA/ODA polyimide films processed by Methods A and B. For two-layer structures of approximately 4 μm produced by Method A, the birefringence is approximately 0.0018 higher than that for the 4 μm two-layer structures fabricated by Method B. Also, the birefringence of two-layer structures made by Method A is essentially the same as for a single-layer film with the same thickness as the top layer.

An explanation for this phenomenon is that the hard bake performed on the first layer drives the imidization to completion, resulting in a film that is insoluble to the second coat of polyamic acid. Solvent molecules and polymer segments cannot penetrate the hard-baked polyimide surface; therefore, the orientation of the second layer develops as if it were on an impenetrable surface. Conversely, a soft-baked film is only partially imidized so that interdiffusion of solvent molecules and polymer segments can take place at the polyimide-polyamic acid interface. For two-layer polyimide structures in which the first layer has been thermally treated at 80°C for 30 min and 150°C for 60 min, significant interdiffusion between the two layers has been observed using forward recoil spectroscopy upon thermal treatment of the entire structure.²⁸ Therefore, Method B may allow interdiffusion of solvent molecules to plasticize the entire thickness of the two-layer structure and give the polymer segments greater mobility to become less oriented. For two-layer structures made by Method B, the effective coating thickness for structural development may approach the sum of the two coatings, resulting in an orientation similar to that of a single coating of the entire thickness.

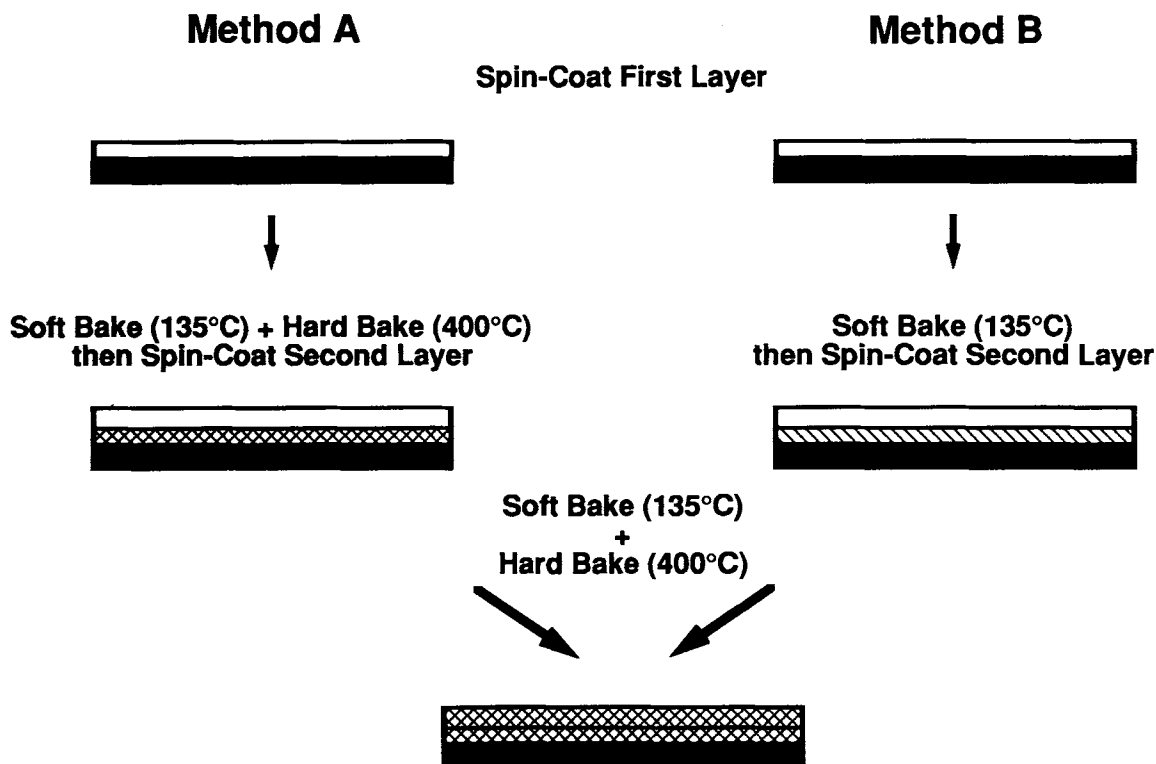


Figure 10 Processing variations for multilayer polyimide film structures: (■) silicon; (□) polyamic acid coating; (▨) soft-baked polymer; (▩) imidized polymer.

Thermal Treatment

Molecular orientation of polyimide thin films is known to be sensitive to the heat treatment.¹⁰ The effect of the hard-bake temperature on the dependence of molecular orientation on film thickness is presented for PI2540 using two hard-bake schedules. The first schedule (Schedule 1) involves ramping at 5°C/min from room temperature to 350°C, then ramping at 2°C/min to 400°C and holding for 60 min. The second schedule (Schedule 2) follows ramping at 2°C/min from room temperature to 200°C and holding for 30 min, then ramping at 2°C/min to 350°C and holding for another 30 min. Schedule 1 takes 3 h to complete, whereas schedule 2 takes 3.5 h. The effect of final bake temperature on the orientation for different thicknesses of PMDA/ODA films is shown in Figure 11, where films made according to Schedule 1 have greater birefringence than that of films made using Schedule 2 for thicknesses greater than 3 μm. A fast heating rate, achieved by inserting soft-baked films in a preheated oven at 350°C, has been shown to result in less oriented films.^{3,29} If the heating rate variation in Schedules 1 and 2 were to influence the orientation, films made by Schedule 1 should have lower birefringence since Schedule 1 has a faster heating rate. However, just the opposite effect is observed in Figure 11. Therefore, the variation in the optical anisotropy of films processed by Schedules 1 and 2 must be dominated by factors other than the heating rate difference.

In Figure 11, the birefringence difference between the films treated using Schedules 1 and 2 increases with film thickness. For the thinner films, the thermal schedule used does not affect the birefringence significantly. However, for films greater than 3 μm,

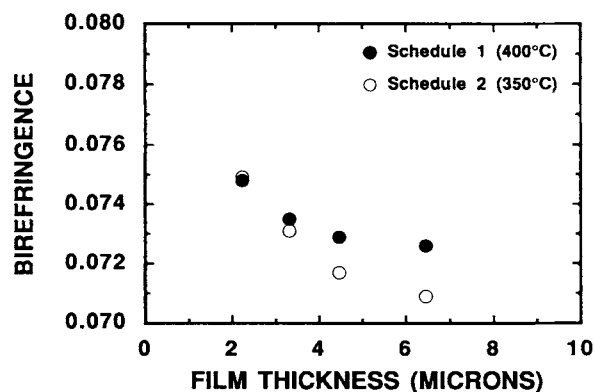


Figure 11 Effect of final bake temperature on the birefringence of PMDA/ODA (DuPont PI2540) polyimide film.

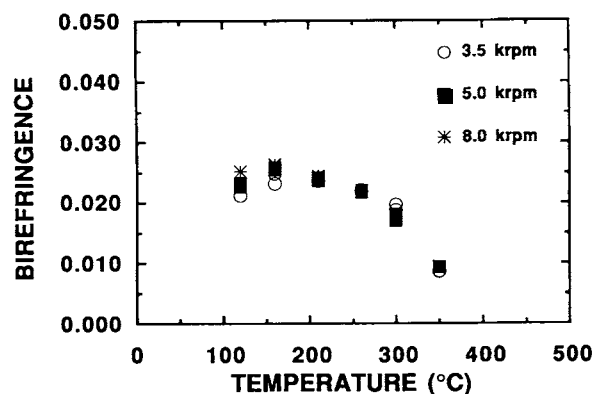


Figure 12 Effect of the final bake temperature on the birefringence of OCG 293 preimidized polyimide film.

the birefringence is greater for films treated up to 400°C than to 350°C. As given in Table II, the peak height ratio of the imide absorption near 1370 cm^{-1} and the aromatic absorption at 1500 cm^{-1} is used to compare the extent of imidization¹⁸ for the two thermal schedules used. For films less than 4 μm, the ratios are not readily distinguishable for the two thermal schedules. However, for the thicker films, the ratios are significantly lower for films treated to 350°C than to 400°C, indicating less imidization attained at 350°C than at 400°C. This illustrates that the final bake temperature is critical to the chemical and structural development of films greater than 4 μm.

As evident in Figure 11, the optical anisotropy of PMDA/ODA polyimide films spin-coated from polyamic acid solution increases with increasing final bake temperature of the thermal treatment. In fact, the birefringence of a 2.25 μm PMDA/ODA film after the soft bake is approximately 0.03, compared with a birefringence of greater than 0.07 after the hard bake. The increase in the birefringence upon thermal imidization may be attributed to film densification due to both solvent evaporation and imidization upon thermal treatment. Thermal formation of solid polyimide films from preimidized polymer solution involves solvent evaporation without imidization. The influence of thermal treatment on the anisotropy of polyimide film spin-coated from preimidized OCG Probimide 293 is presented in Figure 12. The birefringence is measured after each of the following thermal treatment steps: 15 min at 120°C in air, 25 min at 160°C in nitrogen, 15 min at 210°C in nitrogen, 15 min at 260°C in nitrogen, 15 min at 300°C in nitrogen, and 15 min at 350°C in nitrogen. A slight increase in the birefringence is evident between the soft bake at 120°C and the hard

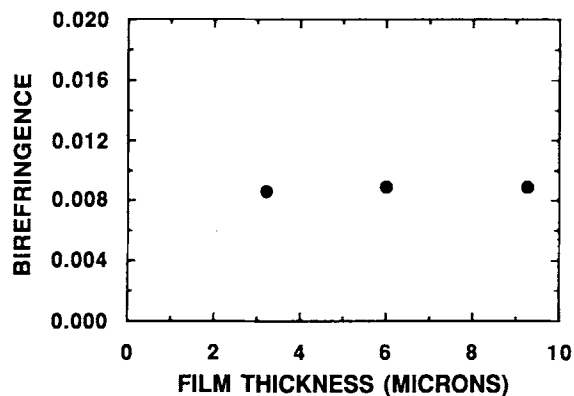


Figure 13 Effect of film thickness on the birefringence of OCG 293 preimidized polyimide film.

bake at 160°C. However, the birefringence begins to decrease after exposure to higher temperatures.

Probimide 293 reportedly undergoes thermal cross-linking at 300–320°C.^{24,30} The exact mechanism for the cross-linking reaction is still unclear, although an increase in the chemical resistance of the film occurs upon high-temperature treatments. Development of a three-dimensional network is associated with any cross-linking reaction, which should result in less optical anisotropy. Thus, the decrease in birefringence with increasing temperature of thermal treatment is a probable indication of thermal cross-linking. For Probimide 293 films that have undergone the standard thermal treatment for preimidized polyimide (described in the sample preparation section), the birefringence is not dependent on film thickness (Fig. 13). This may be due to the rigid and nonplanar configuration of the DAPI component that consists of two amino groups held out of plane of one another (Fig. 1).

CONCLUSIONS

The effects of processing variations on the molecular orientation of some commercially available polyimide thin films have been characterized *in situ* by measuring the birefringence of the films. As determined using a Metricon Model 2010 Prism Coupler, spin-coated polyimide films have a uniform in-plane orientation in both the radial and the angular directions. Therefore, the measured thickness dependence of birefringence is not due to the stress from the spin-coating mechanism, but, rather, from the resulting film thickness. Since the polyamic acid concentration does not influence the thickness dependence of birefringence, the dynamics of solvent

evaporation and thermal imidization are not the controlling factors in the observed thickness dependence. In light of the reported ordered layer at the polymer–air interface and the greater anisotropy at the polymer–substrate interface, lower birefringence with film thickness may be a consequence of skin-layer formation due to a stress gradient and the presence of the interfaces. Both the magnitude and the thickness dependence of birefringence in spin-coated polyimide films processed from polyamic acid solution are affected by the rigidity of the polyimide segments. For a rigid polyimide like BPDA/PPD, the birefringence is relatively high and independent of the film thickness. For polyimides that are less rigid, including PMDA/ODA and 6FDA/ODA, the birefringence is lower and decreases with increasing film thickness.

The substrate upon which polyimide is spin-coated can affect the molecular orientation of the film. As seen in the invariance of birefringence for polyimide films of approximately 2 μm , spin-coated on aluminum, silicon dioxide, gold, and nickel surfaces, the optical anisotropy is independent of the substrate surface modification by thin film addition. Also, the adhesion between the polyimide film and the substrate does not affect the orientation of the film. However, the birefringence of the polyimide film is influenced by the coefficient of thermal expansion (CTE) of the bulk substrate; less CTE mismatch results in a less oriented film. In addition, the molecular orientation is influenced by the solubility of the substrate material by the polyamic acid coating.

The birefringence determination using the prism coupler technique is sensitive to structural development at high temperatures. Greater optical anisotropy is observed for PMDA/ODA films processed at 400°C than at 350°C, due to greater extent of imidization. For preimidized OCG 293 polyimide in which no imidization reaction occurs during thermal treatment, the prism coupler measurements indicate a reduction in the optical anisotropy, which may be attributed to the reported thermal cross-linking reaction. Also, the birefringence of OCG 293 polyimide films is independent of the film thickness.

The development of molecular orientation for several commercially available polyimide films has been characterized using the Metricon Model 2010 Prism Coupler. From the studies of processing variations on the birefringence of spin-coated polyimide films, the optical anisotropy in thin polyimide films is influenced by the film thickness, the polyimide chemistry, the substrate material, and the final bake temperature. The birefringence, which varies from

0.01 to 0.20 for different polyimide chemistries, is likely to produce anisotropic material performance properties in the spin-coated films. Since both in- and through-the-plane properties are important for advanced multilayer microelectronic devices, understanding the origin of the molecular orientation is crucial for using polyimide films in microelectronic applications.

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