Characterization of PMDA-ODA Polyimide Films by External Reflectance Infrared Spectroscopy

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ABSTRACT: Reflectance infrared spectroscopy has been carried out for quantitative structural analysis of polyimide films thinner than 1000 Å. Reflection spectra have been simulated for isotropic polyimide films of specific thickness on a metallic substrate. Structural analysis was based on a number of infrared active vibrations particularly sensitive to changes in chain conformation or packing. The structure of these films was compared with that obtained by annealing experiments on free standing films and crystalline powders. For adsorbed films with thicknesses <150 Å, very low packing order was found. Frequency shifts in films of varying thicknesses were observed to be sensitive to changes in chain conjugation which are dependent on the coplanarity of rings along the backbone. Utilizing vibrations of known transition moment direction allowed one to characterize the degree of segmental orientation relative to the surface normal of variously prepared films. Spectroscopic data also revealed changes in orientation of the rigid planar structures in PMDA-ODA polyimide with respect to the surface normal upon variation of film thickness. The imide ring, preferentially aligned perpendicular to the surface normal in thin films, changes toward an isotropic orientation distribution. The chain orientation reached a constant value of $f = -0.28$. These spectroscopic studies were corroborated by electron diffraction tilting experiments obtained from flat films lifted from their respective gold substrates.

Introduction

Crystallinity and orientation represent important structural parameters in consideration of mechanical, thermal, and electrical properties of polyimide coatings. Coating performance is critical in demanding applications such as interlayer dielectrics in semiconductor integrated circuitry and other packaging applications.[1] Studies were aimed at a better understanding of the solidification process of this polyimide in restricted geometries, such as in very thin coatings, as well as of the interfacial layer between the polyimide and substrate. In these cases, polyimides are confined geometrically so that individual chains are unable to adopt the full range of conformations available in a bulk material. Studies of thin polyimide films are important as both rigid and semiflexible polyimides are known to develop a significant degree of anisotropy when utilized as coatings. The anisotropy of these films in terms of their elasticity coefficients has been previously measured.[2] In addition, the nature of the interfacial layer is important and relevant as bonding of polyimide with substrate may significantly influence the occurrence of the cohesive failure of coatings.

PMDA-ODA is provided by E. I. duPont as a 10-20% solution of polyamic acid precursor in *N*-methyl-2-pyrrolidone (NMP). The in-plane isotropy observed in virtually all polyimide films most probably occurs as a result of film shrinkage under the constraining influence of a substrate. In the absence of a thermal gradient or chemical reaction when spin-cast onto substrates, the orientation process represents a competition between chain relaxation and film shrinkage during solvent loss, resulting in the inability to relieve local stresses and formation of in-plane orientation. Imidization in PMDA-ODA is achieved by heating. Anisotropy is known to be induced during the spin-coating process of the polyamic acid. It is, however, uncertain whether the degree of anisotropy is maintained during curing.

The anisotropic nature of polyimide films has been observed by numerous techniques such as wide-angle X-ray diffraction, birefringence, conoscopy, optical wave guide spectroscopy, dielectric loss measurements, and attenuated-reflectance Fourier transform infrared spectroscopy.[3-8] Quantitative information on the degree of anisotropy and the related microstructures as a function of film thickness for thermally cured polyimide films has yet to be reported. The microstructures and degree of anisotropy in polyimide films can be characterized by orientation of the pyromellitimide groups with respect to the plane of the substrate. This orientation is most conveniently measured by utilizing grazing angle infrared techniques. Vibrational spectroscopy is a localized technique capable of measuring changes in chain conformation and packing, especially when accurate band assignments and polarization characteristics, i.e. transition moments, are defined. PMDA-ODA polyimide band assignments and characterization of transition moment directions have been provided by prior studies.[9,10]

Gold was chosen as the substrate because of its limited chemical reactivity with polyamic acid. Extensive studies have been performed on the reflectivity of electromagnetic waves for multilayered systems, including both dielectric and metallic substrates.[11-17] The boundary conditions are such that at grazing angles external reflection infrared spectroscopy of adlayers on metallic substrates measures only the transition moments which have components perpendicular to the substrate surface (p-polarization). Although significant anomalies and spectral distortions exist with utilization of grazing angle infrared spectroscopy,[18,19] application of this technique in studies of polyimides adsorbed onto metals has proven extremely useful.[20,21] Films thicknesses in the range 75-750 Å were examined in this study. Although this technique is applicable for films thicker than 1000 Å, the computational complexity is greatly increased to account for decreases in the mean square electric field intensity as a function of distance from the substrate. The infrared reflectance theory has also recently been modified and applied to optically isotropic and anisotropic monolayers on an

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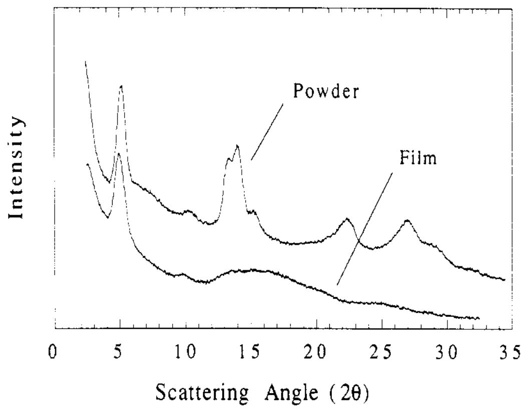

Figure 1. Comparison of the wide-angle X-ray diffraction patterns obtained for PMDA-ODA polyimide samples.

isotropic low-absorbing substrate.[22-25] Utilizing these methods, lateral and axial orientations can be obtained by a quantitative analysis of spectroscopic data. Spectroscopic analysis of PMDA-ODA polyimide films on a metallic substrate is reported in this study. Results on dielectric substrates shall be reported shortly.

Experimental Section

The precursor, polyamic acid, was obtained from duPont and received as 20% of solids by weight in *N*-methyl-2-pyrrolidone (NMP). The solution was diluted with dimethylacetamide (DMAc) to the appropriate concentrations. The solutions were spin-cast onto gold-coated glass slides, obtained from Brysen Optical Corp., at 4000 rpm. The gold layer on these glass slides had an average thickness of ~2000 Å. The samples were then placed on a hot plate for 15 min at 85 °C and cured at 225 °C in nitrogen atmosphere for 1 h. Thickness was determined with a Rudolph Research Ellipsometer AUTOEL-II using the 6328 Å line (0.2 mW) reflected at a 70° angle with respect to the surface normal. A series of nine measurements were performed for gold surfaces with and without the adsorbed polyimide. Film continuity and roughness in the substrate and adsorbed polymer were measured with a Zygo optical phase interference microscope Maxim3D 5800. The average surface roughness was found to be in the range 8-10 Å. 20X, 40X, and 100X Mirau lenses were utilized in these measurements. The smaller magnification lens, 20X, provides a vertical resolution of ~1 Å and a lateral resolution of ~1 μm. If supported on a substrate and with removal of a portion of the film, thickness can also be measured directly by the profilometer.

Electron diffraction studies were performed with a JEOL 100CX TEM. For these experiments, the polyimide films were removed from the gold-coated slides by first shaving the outermost portion of the gold layer partially under water. The films were then picked up with a carbon-coated grid. Samples obtained utilizing this technique were relatively undamaged and unwrinkled. These features are required for acquisition of reliable film-tilting data. Gold still adhered to some sections of the film which facilitated determination of interplanar spacings in the polymer by providing a direct calibration using spacings known for gold.

Infrared spectra were obtained using a Nicolet 60SXB Fourier transform infrared spectrometer equipped with a Specac external reflectance attachment. A total of 1024 scans at a resolution of 2 cm^{-1} were collected. The incident angle of the p-polarized radiation on the sample was maintained at 84° for all measurements. Transmission measurements for the polyimide powder in KBr pellets were obtained in a Bruker 113 FTIR. In this case, 256 scans were signal averaged and the spectral resolution was maintained at 2 cm^{-1}. Highly crystalline polyimide powder samples were created by a one step cure at 200 °C under 200 psi of nitrogen pressure. Details associated with the structure of these powders were previously provided.[26,27] As shown in Figure 1, X-ray diffraction analysis in conjunction with density measurements reveals that this polyimide powder has a much higher degree of crystallinity and larger crystalline domains than thin films. Transmission wide-angle X-ray experiments were performed in vacuum with a Statton camera. Ni-filtered Cu Kα radiation was employed. All film or powder samples were annealed for 1 h at 300 °C.

Method for Interpreting Film Anisotropy

The use of vibrational spectroscopy as an analytical tool to measure anisotropy is based on the measurement and analysis of relative band intensity and width. To derive structural information from reflection infrared experiments, care must be exercised in analysis to separate structural features from optical anomalies. This section provides analytical expressions from which reflected spectra can be computed for planar electromagnetic waves incident on optically anisotropic and absorbing thin films adsorbed on a metallic isotropic substrate. Several variations have been presented in the literature.[11-14] Because of the metallic substrate, only the p-polarized waves are present in the adsorbed film. A quantitative analysis is sought for the absorption coefficient and transition moment direction of vibrational modes relative to the surface normal. With determination of the absorption coefficient and transition moment direction, structural information in terms of changing chain conformation and orientation may be derived.

The anisotropy of the polyimide film can be obtained by comparing the reflected spectrum to that obtained for an isotropic sample of the same thickness. Equation 1 relates

$$\theta = \cos^{-1}\left(\frac{R_{\mathrm{obs}}}{3A_{\mathrm{calc}}}\right)^{1/2} \tag{1}$$

the observed band intensity in the reflected spectrum to the expected value.[28] Here, θ is the angle that a particular transition moment makes relative to the surface normal (z axis), R_{obs} is the experimentally obtained absorbance from reflection experiment, and A_{calc} is the calculated absorbance for a film of the same film thickness. A direct analysis utilizing relative band intensity cannot be meaningful, as reflected data are distorted due to dispersion effects. Transmission data from an isotropic polyimide sample were utilized to compute the frequency dispersion of the real part of the complex refractive index. The optical coefficients are necessary for generation of *isotropic* spectra of different film thicknesses. Molecular orientation in coatings can then be computed by comparison of peak absorbances of the experimental and calculated spectra of the same thickness. The intensity of a given mode is related to the transition moment by

$$I \propto \left|\frac{\partial\mu}{\partial q}E\right|^2 \tag{2}$$

where E is the electric field vector, μ is the dipole moment, and q is the normal coordinate direction. If z is to be the direction parallel to the surface normal, the transition moment for a thin film geometry where only the parallel component of the electric field is a significant contributor to the intensity is dependent on θ at the surface by

$$\cos^2\theta \propto \left|\frac{\partial\mu}{\partial q}z\right|^2 \tag{3}$$

As mentioned earlier, many variations for derivation of Fresnel's law for complex refractive indices exist. It is not the intent of this section to derive another variation but rather to show how the present analysis is applied in determining the absorption coefficient and transition moment direction of various vibrations for molecules at

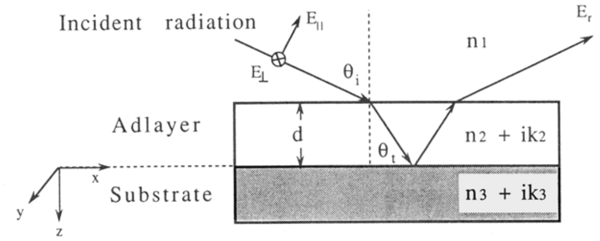

Figure 2. Coordinate frame used to define the interaction of radiation with adsorbed polyimide film on a metallic substrate.

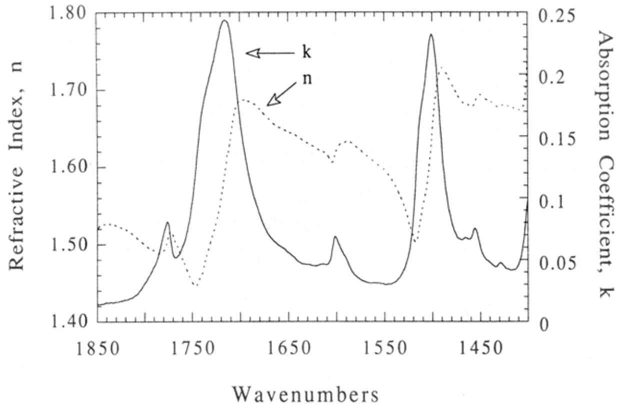

Figure 3. Refractive index, $n(\nu)$ and $k(\nu)$, calculated for PMDA–ODA polyimide.

the interface. Transmission data at normal incidence from the material in isotropic form are necessary as an initial estimate in calculation of the optical constants n and k. This can be expressed by

$$\frac{I}{I_0} = \exp(-4\pi\nu k d) \tag{4}$$

where I_0 is the incident intensity, I is the transmitted intensity with the absorbing material present, ν is the wavenumber, d is the linear optical path through the pellet, and k is the absorption coefficient when the sample concentration in the pellet is considered. The complex refractive index of the jth layer of an absorbing material is defined as

$$\hat{n}_j(\nu) = n_j(\nu) + ik_j(\nu) \tag{5}$$

The fundamental relationship between n and k is given by the Kramers–Kronig relationship

$$n(\nu_j) = n_\infty + \frac{2}{\pi}\int_0^\infty \frac{k(\nu)\nu}{\nu^2 - \nu_j^{\,2}}\,\mathrm{d}\nu \tag{6}$$

where $n(\nu)$ and $k(\nu)$ are the frequency dependent real and imaginary components of the complex refractive index, respectively. These optical coefficients are then utilized to simulate reflection data for the geometry used in the experiment. The value of n_∞, i.e. the index of refraction at an extremely high frequency as compared to that with infrared radiation, is estimated to be 1.65.[5,29] In this study, eq 6 can only be approximated due to the finite frequency range of measurement. The transmission data of an isotropic sample serve as the initial *estimate* to compute the refraction index. A new spectrum is then calculated and compared with the experiment. This process is reiterated until a match is obtained for the calculation and experiment. Upon refinement of the refraction index, both real and imaginary, an isotropic spectrum at any angle of incidence can be calculated. The coordinate frame used for this calculation is shown in Figure 2. The optical coefficients obtained as a function of frequency for the in-plane region are shown in Figure 3.

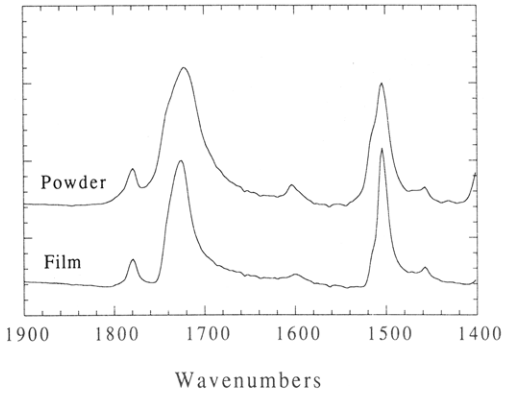

Figure 4. Comparison of the infrared spectra obtained for PMDA–ODA polyimide powder and film. The samples were mixed with KBr and then studied in the pellet form.

Computation of dispersion in the optical coefficients for the metallic substrate has been performed using the Drude model, as described earlier.[30] The complex refractive index in the metal is given by

$$\hat{n}_3 = n_3 + ik_3 \tag{7}$$

Here, the real component of the complex refractive index and the absorption coefficient are given as

$$n_3 = \left[\frac{1}{2}(\epsilon'^2 + \epsilon''^2)^{1/2} + \epsilon'\right]^{1/2} \tag{8}$$

$$k_3 \left[\frac{1}{2}(\epsilon'^2 + \epsilon''^2)^{1/2} - \epsilon'\right]^{1/2} \tag{9}$$

where prime and double prime denote the real and imaginary parts of the dielectric constant, respectively. Frequency dependencies are shown in eqs 10 and 11,

$$\epsilon' = \epsilon_\infty - \frac{\omega_p^{\,2}}{\omega^2 + \omega_\tau^{\,2}} \tag{10}$$

$$\epsilon'' = \frac{\omega_p^{\,2}\omega_\tau}{\omega^3 + \omega_\tau^{\,2}\omega} \tag{11}$$

where ω_τ is the damping frequency, ω_p is the plasma frequency of the substrate, and ϵ_∞ is the dielectric constant at infinite frequency. For gold, these constants are ω_τ = 216 cm^{-1}, ω_p = 72 500 cm^{-1}, and ϵ_∞ = 1.0.

Results

The transmission infrared spectra obtained for two different polyimides shown in Figure 4 exhibit significant differences in band frequency, width, and relative intensity. Particular attention has been given to previously assigned localized vibrations associated with symmetric and C=O asymmetric stretching vibrations or skeletal bending (tangential stretching) such as the band near 1500 cm^{-1}. This tangential stretching vibration is designated as mode 19a using Wilson's classification.[31] These spectroscopic features can be attributed to different structures or orientations. Curing history which provides for a longer solvent residence time will produce samples of higher degrees of crystallinity as well as to reduce in-plane orientation for PMDA–ODA polyimides. Spectroscopic and wide-angle X-ray diffraction studies of PMDA–ODA

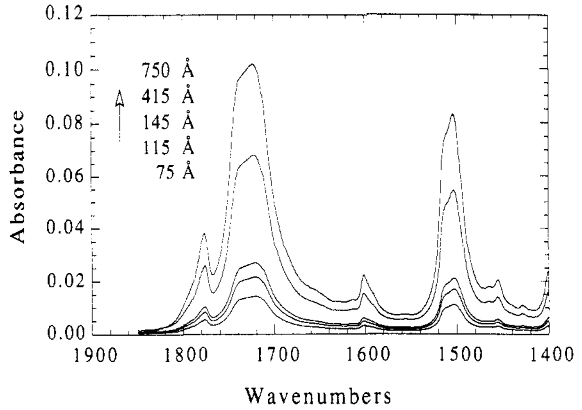

Figure 5. Calculated reflection spectra for polyimide films of various thicknesses.

polyimide produced with rapid curing exhibit spectroscopic features similar to those shown above.[32,33]

Due to the extreme difficulty in obtaining thin isotropic polyimide films, the transmission spectrum obtained for the polyimide powder mixed with KBr was chosen to simulate the reflection spectrum for specific thicknesses on gold. It is emphasized that the simulated reflection spectrum used for comparison, i.e. that based on polyimide powder, represents a sample of a higher degree of crystallinity than expected for a thin film. Thin films possess noncrystalline domains as high as 85%. These regions are not designated as amorphous, as a "smectic-like" liquid crystalline order is present due to the rigid nature of these chains.[34] Thermal annealing is known to remove conformational defects while increasing the degree of crystallinity and crystallite size. The obvious differences observed for the simulated and experimental spectra can then be used for analysis of the degree of order in thin polyimide films prepared on a gold substrate.

To provide greater accuracy in calculation of the orientation angle from these spectra, it is important to utilize the noncrystalline or higher frequency component of the asymmetric C═O stretching vibration. Correction of peak intensities is necessary to account for population differences arising from changes in crystalline content between powder and film samples. Utilizing X-ray diffraction methods, a 65% crystalline content was computed for the powder and 10% was assumed for the films.

Orientation Analysis. The symmetric and asymmetric stretching and out-of-plane bending vibrations of the C═O's are those most convenient for use in characterizing of segmental orientational distribution. Deviations from an idealized planar zigzag conformation will occur due to flexibility of the ether linkage. M_1 and M_2 represent transition moments associated with the symmetric and asymmetric stretching vibrations, respectively. M_1 has been determined to be mainly along the chain axis, and M_2, to be in the plane of the imide ring.[9] Chain orientation with respect to the substrate's surface normal can be computed using the polarization measured for M_1. Similarly, the PMDA ring tilt can be obtained by analyzing the average direction of M_2 in the film. The transition dipole moment designated as M_3 is the C—N—C out-of-plane bending which appears at ~725 cm^{-1}. The other mode which can be analyzed is the para-substituted phenyl ring CH out-of-plane vibration at 825 cm^{-1}.

The calculated and experimental infrared spectra of PMDA-ODA polyimide films of various thicknesses are shown in Figures 5 and 6. Differences observed in the two sets of spectra result from the effects of orientation and crystallinity. The lower frequency component of the C═O stretching vibration has considerable intensity in the simulated spectra. In contrast, the higher frequency component at 1738 cm^{-1} is more prominent in the measured spectra. The C═O stretching vibrations in the polyimide consistently exhibit multiple components which are less obvious in the adsorbed film but quite clear in the highly crystalline samples. The high-frequency component is assigned to the disordered phase.[33,35] Changes in chain conformation affect chain conjugation and thus the intensity and frequency of various observed vibrations. For example, when crystallization occurs, the C═O stretching mode decreases by as much as 8 cm^{-1} from 1725 to 1717 cm^{-1}. This frequency change is assigned to the increase in chain conjugation in ordered state. Polyimide chains exist in a planar form in the highly ordered state.[27,28,36]

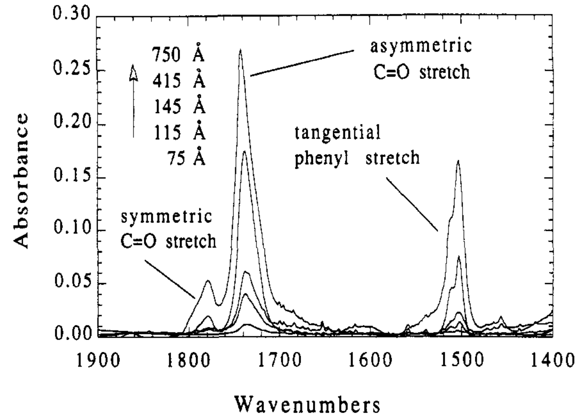

Figure 6. Experimentally observed reflection spectra of PMDA-ODA polyimide films of various thicknesses.

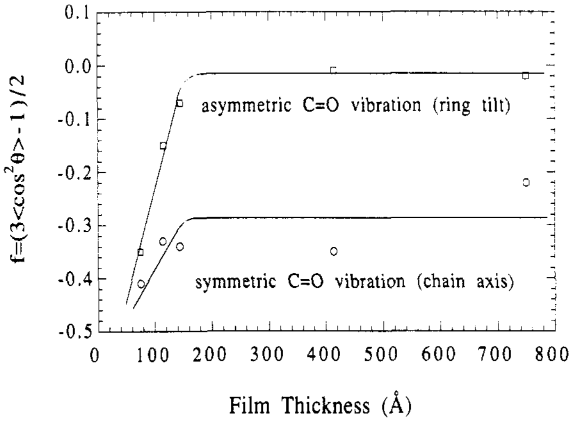

Figure 7. Orientational distribution function calculated for the imide ring and the chain.

In reflection spectra obtained for an adlayer on metal, the components of vibrations aligned parallel to the substrate surface have an intensity lower than those perpendicular to the substrate. As stated previously, the boundary conditions are such that for this system only those vibrations having a component parallel to the plane normal will be observed. Due to the high in-plane orientation of the polyimide chains, bands such as the tangential phenyl stretching at 1505 cm^{-1} possess a much lower intensity than that of the asymmetric carbonyl stretch.

The second moments of the orientation distribution function of the chain and imide rings are plotted in Figure 7. Data in this figure suggest that imide rings orient preferentially flat on the substrate. The average angle measured for the transition moment, M_2, is approximately 76° (measured relative to the surface normal) for extremely thin films. It is clear that these rings disorient as a function

Figure 8. Electron diffraction pattern obtained for the 115 Å thick PMDA–ODA film. This pattern was obtained by tilting the film 30° from normal with respect to the incident beam.

of film thickness. This angle decreases to a value of 56° for thicker films. Values of $f = 1.0$ and $f = -0.5$ correspond to perfect parallel and perpendicular alignment with the surface normal. A value of $f = 0$ is indicative of random orientation of the transition moment direction with respect to the surface normal. For thin films, orientation of chain segments is very high with a value near −0.45. The degree of segmental orientation also decreases as a function of film thickness. A constant value of $f = -0.28$ was obtained for the chain axis direction for film thicknesses greater than 150 Å. For these films, imide rings no longer maintain any orientation. These observations agree well with values derived from out of plane bending vibrations (M_3). A value of $f = -0.24$ was calculated with wide-angle X-ray diffraction for thermally cured spin-coated PMDA–ODA films.[3] Studies on films with thicknesses >25 μm suggest that structural anisotropy is present even at values which approach bulk. Optical anisotropy has been shown to be nearly independent of film thickness for PMDA–ODA films in the range 0.5–4 μm.[6] Importantly, our measurements are averaged values for each film. Features observed for thick films contain features observed for thin films.

Electron diffraction patterns of polimide films at different tilt angles were obtained to confirm the anisotropy observed using vibrational spectroscopy. At normal incidence, the diffracted intensity is a ring. As the film is tilted with respect to the incident radiation propagation direction, a pattern (Figure 8) characteristic of molecular anisotropy emerges. The intensities of interplanar spacing ($d = 4.3$ Å) are concentrated along the equator as shown in Figure 8.[37] In addition to the anisotropic features observed, diffraction patterns of the film also indicate a lower dimensional order when compared to that found in the powder samples.

It has previously been suggested that for polyamic acid on unreactive metals, such as gold, titanium, and aluminum, the aryl ether rings are oriented nearly parallel to the metal surface with interconnecting amic acid or ester rings perpendicular to the surface.[38] In the vicinity of the substrate, this arrangement does not change with thermal imidization. Our results are consistent with the suggestion that an interfacial region with a thickness of 150 Å exists between the bulk polyimide and an weakly interacting substrate. This disordered interphase can be considerably thicker if strong chemical interaction occurs between coating and substrate. This has been observed for polyimides on reactive substrates such as copper where its precipitates diffuse as far as 500 Å into the PMDA–ODA coating.[39]

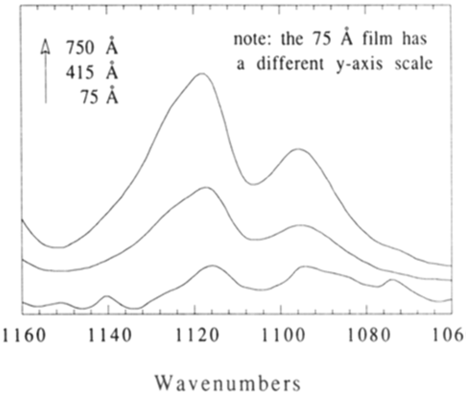

Figure 9. Reflection infrared spectra in the 1060–1160 cm^{-1} region obtained for films of various thicknesses on gold.

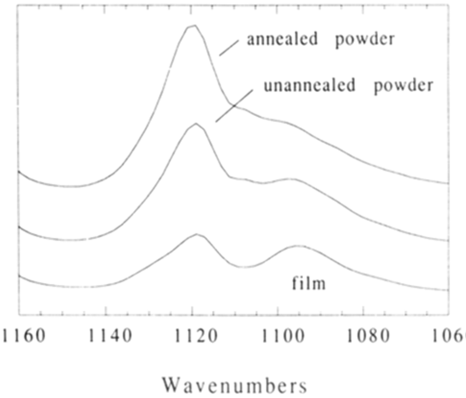

Figure 10. Transmission infrared spectra in the 1000–1200 cm^{-1} region obtained for highly crystalline powders (KBr pellet) and a free standing film of 3000 Å in thickness.

Packing Order in Thin Polyimide Films. As mentioned above, in the observed spectra the lower frequency out-of-phase component (1717 cm^{-1}) assignable to ordered regions is seen only as a shoulder of the higher frequency band. It is to be noted that for the transmission and therefore the simulated spectrum, the lower frequency band has a higher intensity than the component located at 1737 cm^{-1}. The relatively strong intensity of this disorder band observed for thin films suggests perturbative effects of the substrate on packing efficiency. There is little question that structures of low order exist for thin films. Evidence of a decrease in order can also be found in the 1200–1000 cm^{-1} region (Figures 9 and 10). The intensity of the 1117 cm^{-1} vibration decreases with a decrease in film thickness. The intensity of this band increases for samples of increasing order. With the combination of infrared and X-ray diffraction analysis, one can conclude that the intensity of this vibration is extremely sensitive to the degree of order in polyimides. The mode observed at 1117 cm^{-1} involves imide ring distortion and deformation of the carbon–nitrogen bond.[10] For annealed samples with little structural disorder, the 1117 cm^{-1} band is very intense.

Grazing angle X-ray scattering of PMDA–ODA polyimide reveals that the degree of crystalline order is higher within 70 Å from the air/polymer interface.[40,41] For a 400 Å film, this crystalline-like layer was present at the free surface of the film but undetected near the polymer/substrate interface. The development of a crystalline-like structure is sensitive to curing conditions. In this study, more densely packed or more ordered packing can also be revealed by frequency shifts observed in the reflection spectra for the 1117, 1240, 1374, 1735, and 1775 cm^{-1} vibrations. These changes are summarized in Figure

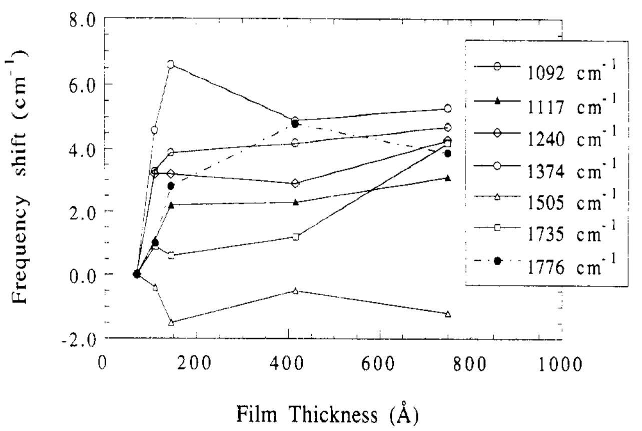

Figure 11. Frequency shift observed for various vibrations found for polyimide films as a function of thickness.

11. As mentioned earlier, a number of spectroscopic studies suggest that vibrational frequency is sensitive to changes in chain conformation. Frequency shifts in PMDA-ODA polyimides have been discussed previously.[34] The frequency shifts can be as large as 13 cm^{-1} between the CN modes of crystalline and noncrystalline samples. Similarly, the asymmetric COC stretching showed increases of 5 cm^{-1}. Frequency shifts usually accompany crystallization or changes in chain conjugation. Data suggest that increases in chain conjugation occur in thicker films. Chain packing order can be concluded to be lower in thinner films. This effect should not be confused with frequency shifts due to optical effects which may arise in going from transmission to reflection modes. In any event, abrupt transitions from an interface layer to the bulk may lead to increases in the likelihood of cohesive failure. As shown here, films thicker than 150 Å exhibit more efficient average packing but random imide ring plane orientation. In our particular case, an adhesive weakness may arise not only from less efficient packing and different ring unit tilt but also from weaker chemical interaction with the substrate.

Conclusions

Calculations based on the intensity of simulated and experimental asymmetric and symmetric C=O stretching have provided results describing the orientation of the imide ring plane with respect to the surface normal. These results show that the tilt of PMDA ring units and the chain axis exhibit preferential orientation for films thinner than 150 Å. This structural anisotropy decreases rapidly as a function of increasing film thickness. On the other hand, the chain axis direction maintains a constant value of $f = -0.28$, even for thick films, indicating that a good degree of anisotropy exists at all times. Electron diffraction film tilting experiments have confirmed the molecular orientation observed by spectroscopy.

Films thinner than 150 Å were found to exhibit lower packing efficiency, evidenced by the decrease in the transverse CNC stretch (1117 cm^{-1}) for thinner films. Better packing would induce a higher degree of ring coplanarity, which, in turn, would increase conjugation. Frequency shifts would then be observed as a function of coating thickness for differing packing efficiencies. Indeed, frequency shifts were observed below 150 Å but constant frequency values were attained for thicker films. The work described here presents the possibility that different chain conformations and/or various degrees of packing exist near the polymer/hard wall interface for PMDA-ODA polyimides.

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