Coating thickness effect on the orientation and thermal expansion coefficient of polyimide films

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From X-ray diffraction experiments, it is observed that on-substrate cured polyimide films are so oriented that the imide chains are preferentially aligned in the plane direction of the films. For films with rigid-rod polyimide, film orientation is especially prominent and decreases significantly as the film thickness increases. The effect of coating thickness on the orientation and ordering of polyimide films is most pronounced in pure pyromellitic dianhydride–*p*-phenylenediamine (PMDA–PDA) films, slightly less in films with 50% pyromellitic dianhydride–4,4'-oxydianiline (PMDA–ODA) and 50% PMDA–PDA, and relatively insignificant in those with 100% PMDA–ODA. According to the C=O and C–N stretching absorption bands from Fourier-transform infra-red–attenuated total reflectance spectroscopic experiments, imide molecules located near the centre of the film exhibit poorer structure ordering than those near the surface. This reveals why the average film orientation decreases and the corresponding thermal expansion coefficient increases with increase of film thickness.

(Keywords: coating thickness; polyimides; orientation; stress; thermal expansion coefficient; X-ray diffraction; Fourier-transform infra-red spectroscopy; attenuated total reflectance)

INTRODUCTION

Recently, polyimides have drawn more and more attention because of their importance in electronic packaging applications[1-4]. Generally speaking, they have relatively high glass transition temperatures, high planarization, high processability, low dielectric constants and low thermal expansion coefficients. All these properties are crucial to device fabrication, performance and/or reliability. However, several problems may arise from the stress in the polyimide film, when it is coated on other materials such as silicon, due to mismatch in thermal expansion coefficients[5-7]. The resulting stress, if too high, may cause serious bending, warpage, delamination, or cracking in a given layered structure or device composed of different materials. To avoid such a high stress, polyimides should be carefully selected so that thermal mismatch can be minimized. Actually, there are numerous polyimides available with wide-ranging thermal expansion coefficients[7,8]. Some of them have thermal expansion coefficients as large as that of copper or aluminium, and some as small as that of silicon or even quartz. Thermal expansion coefficients of various polyimides strongly depend on their molecular structures. Ideally, polyimides can be roughly divided into two classes. Those with semi-flexible chain structures have relatively high thermal expansion coefficients, and those with rigid-rod-like chain structures have relatively low ones.

Polyimides are often used as dielectric layers or protective coatings on some other materials. They are

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insoluble in most common solvents in the imide form. In practice, they are usually applied by casting or spin-coating their soluble precursor, e.g. poly(amic acid) solutions, onto the desired substrate, followed by chemical or thermal curing. Consequently, resulting solid imide films must have been biaxially stretched and exhibit some degrees of in-plane orientation[9-13]. This may have some effect on the film properties, especially thermal expansion coefficient. As recalled, films or fibres with orientation always have lower thermal expansion coefficients and higher tensile moduli in the film plane direction than those without. As clearly shown in other papers[7,14], all the imide films that have been cured 'biaxially fixed' have much lower thermal expansion coefficients than the ones cured freely. This is, of course, due to a difference in the film orientations of the biaxially fixed and free-cured films. The free-cured films do not exhibit orientation, as known[7,14,15]. Therefore, it is thought that thermal expansion coefficients of the on-substrate cured polyimide films must depend on the extents of orientation.

In a preliminary study[16], it is found that, when measuring the stresses as a function of temperature in various polyimide films with different monomeric structures, the slope of the stress–temperature curves increases with increase of coating thickness. As known, the slope is equal to the product of the biaxial modulus of the film studied and the difference between the thermal expansion coefficients of the film and the substrate[17,18]. Therefore, the thicker films, whose slopes are larger, must have higher thermal expansion coefficients if not having higher tensile moduli, and their film orientation must be
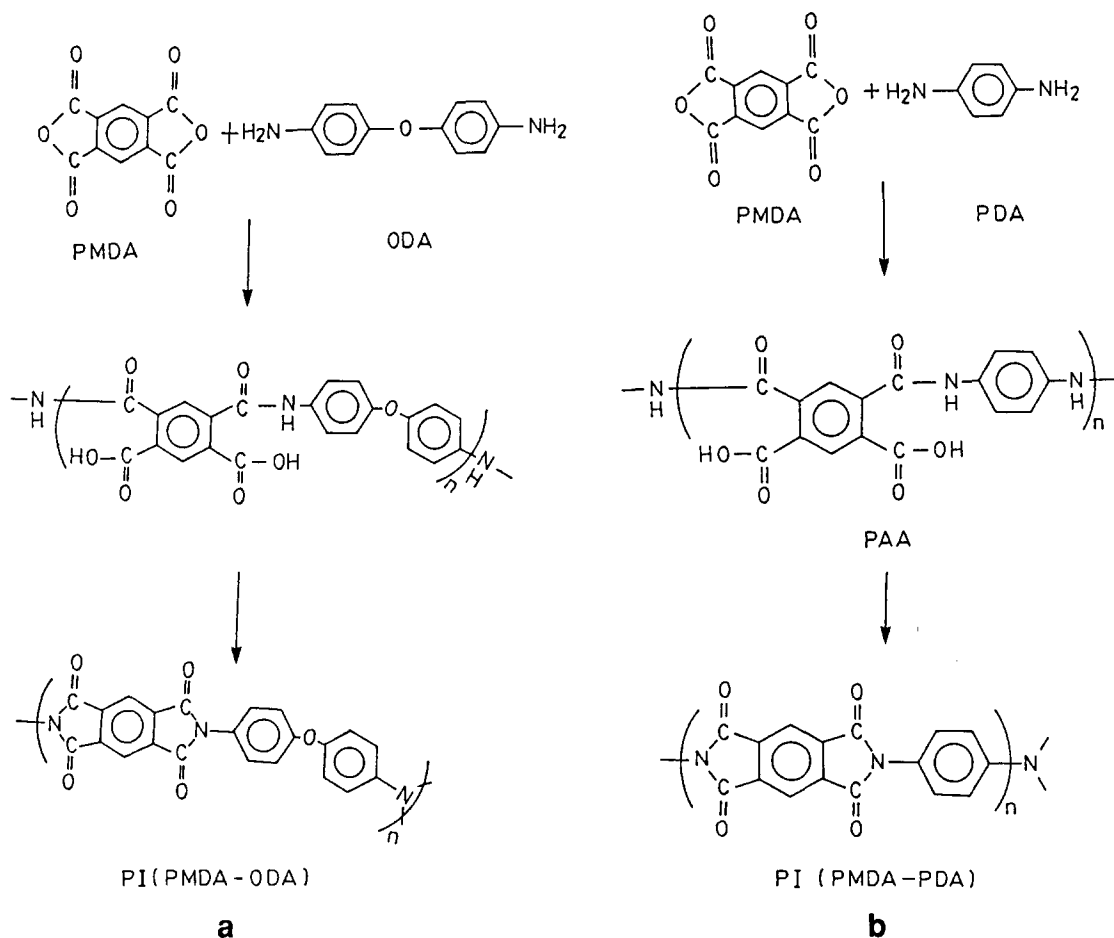
Figure 1 Molecular structures of the resulting poly(amic acids) for preparing aromatic polyimides: (a) PMDA–ODA and (b) PMDA–PDA

less. In order to investigate the structures, especially orientation, of those different films, an X-ray diffractometry method has been applied. Since it is not easy, or almost impossible, to prepare a sample with perfect orientation as a standard, the resulting diffraction patterns have been compared on a relative basis. Also, owing to the 'poorly' focused X-ray beam, each X-ray diffraction pattern only provides average structure information. By using a Fourier-transform infrared–attenuated total reflectance (*FT* i.r.–a.t.r.) method, details about the variation of structure ordering at various positions in the transverse direction of a given thick film have been revealed. Meanwhile, stress–temperature curves of these polyimide films on a silicon substrate have been measured by using a bending-beam apparatus. The stress curves are used to demonstrate the effect of coating thickness on the resulting thermal stresses and thermal expansion coefficients in the polyimide films. In the following section, experimental procedures concerning poly(amic acid) synthesis, imide sample preparations, X-ray diffraction, *FT* i.r.–a.t.r. experiments, and bending-beam stress measurements are described.

EXPERIMENTAL

Materials

The starting materials used in this study are pyromellitic dianhydride (PMDA) and the two diamines, 4,4'-oxydianiline (ODA) and *p*-phenylenediamine

(PDA). The solvent used is *N*-methylpyrrolidone (NMP). These materials were used as received.

Poly(amic acids)

Homopolymers of PMDA–ODA and PMDA–PDA poly(amic acids) were prepared as follows: First, the diamine, ODA or PDA, was dissolved in NMP in a four-necked flask. When the diamine was completely dissolved, dianhydride PMDA of equal molar amount was added gradually[19]. The reaction proceeded for 8 h with stirring. The entire process was done under a nitrogen atmosphere. The molecular structures of the resulting poly(amic acids) are shown in *Figure 1*. The resulting solutions have a solid content of 14 wt%.

Blends of PMDA–ODA with PMDA–PDA were obtained by mixing the resultant poly(amic acids). The mixing was done under nitrogen for 5 min and kept at room temperature overnight. The resulting, mixed solutions were then kept frozen before use.

Imidization

Solid films of the above-mentioned poly(amic acids) were prepared by spin-casting the solutions on glass substrates, followed by prebaking at 80°C for 30 min, curing from 80°C to 350°C in 5 h and heating at 350°C for 30 min. Though polyimide films of PMDA–ODA could be made at a higher ramp rate, those of PMDA–PDA are much less fragile if cured slowly. Therefore, the ramp rate was kept low as described above.

a

b
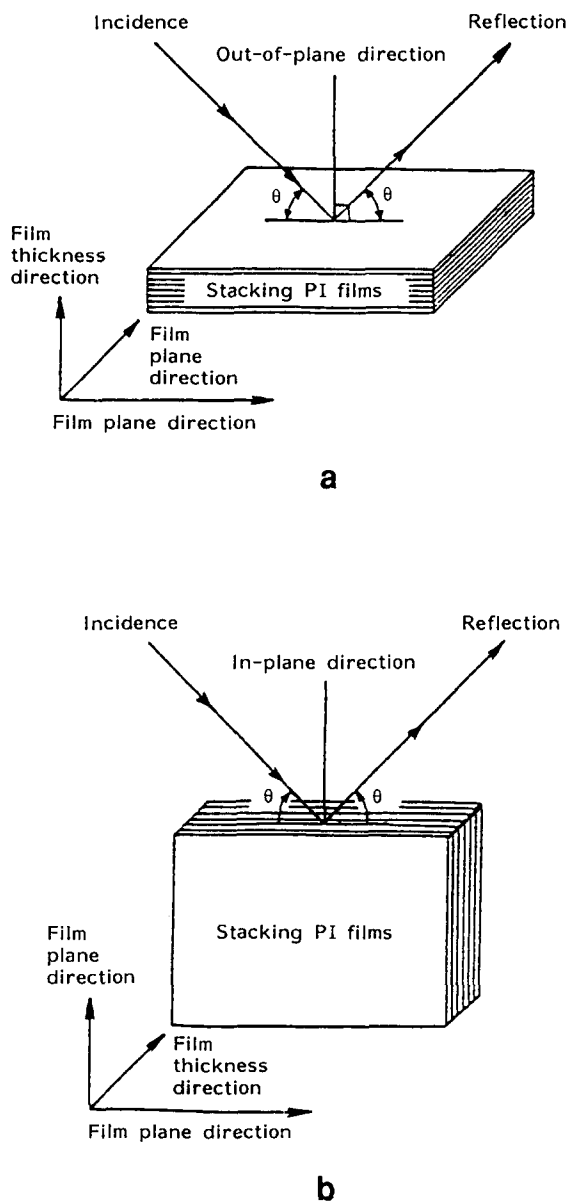
Figure 2 Schematic illustration of the arrangements of X-ray diffraction experiments: (a) the out-of-plane diffraction, in which the sample is so arranged that its film plane is perpendicular to the plane formed by the incident and reflected beams; (b) the in-plane diffraction, in which the film plane is parallel to the plane formed by the incident and reflected beams

Since most poly(amic acids) would almost fully imidize at temperatures higher than 300°C, and varying degrees of imidization have an effect on chain ordering[20], curing to 350°C seems adequate.

X-ray specimen preparation

For X-ray specimen preparation, the resultant imide films were removed from the glass substrates after immersing in water for 2–3 days. The film thicknesses of the resulting polyimide ranged from 5 to 40 μm. In a previous X-ray experiment, it is found that these polyimide films must be thicker than 200 μm for the X-rays not to penetrate through the films. In order for quantitative comparison, relatively thick samples are therefore required. This was done by stacking many pieces, such as 50 or so, of the films together. By so doing, one has the other advantage that structure information not only in the out-of-plane (film thickness) direction

but also in the in-plane (film plane) direction can be obtained.

X-ray experiment

X-ray experiments were done using a Rigaku Wide-Angle X-Ray Diffractometer with nickel-filtered copper $K_{\alpha 1}$ radiation. Its power setting was at 40 kV and 20 mA. The line-focus slot has dimensions of 8 mm × 0.04 mm. The arrangements of the X-ray diffraction experiments are illustrated schematically in *Figure 2*. For the in-plane diffraction, the sample is so arranged that its film plane is parallel to the plane formed by the incident and reflected beams. For the out-of-plane diffraction, the film plane is perpendicular to the plane formed by the incident and reflected beams. Here, the in-plane direction means the film plane direction, and the out-of-plane direction means the film thickness or transverse direction. Since the length of the monomeric repeat units of either one of the two studied polyimides is much larger than the spacing between any two neighbouring imide chains, which are usually around 0.4 to 0.5 nm, one expects to see a characteristic peak corresponding to 'intramolecular' ordering of the former at a small angle, and one corresponding to 'intermolecular' ordering of the latter at a large angle, if these polymers are more or less crystalline. One important point should be kept in mind. If a given film is isotropic or has no orientation, its in-plane and out-of-plane diffraction patterns will be the same. Conversely, differences existing between the in-plane and out-of-plane patterns will indicate structure anisotropy or orientation. If polymeric chains of the studied film are preferentially aligned in the plane direction, the intensity of the peak that corresponds to intramolecular ordering should be somewhat higher in the in-plane pattern than in the out-of-plane pattern. Likewise, the intensity of the peak that corresponds to intermolecular ordering should be somewhat lower in the in-plane pattern than in the out-of-plane pattern.

### F.T.*i.r.–a.t.r.* specimen preparation

Poly(amic acid) was spread on a glass substrate and then cured on a hotplate. The curing process is the same as mentioned above. The resultant polyimide film is 50 μm thick. After its structure ordering at the film surface has been measured, the film is then abraded by a fine emery paper so that the inner structure ordering can also be determined. Before each measurement, the specimen was dried at 120°C overnight in a vacuum chamber.

F.T.*i.r.–a.t.r.* experiments

*FT*i.r.–a.t.r. experiments were done by using a Bomem DA 3002 Spectrometer with a KRS-5 crystal under vacuum conditions. The spectra were obtained after 200 scans with an incident angle of 60°. The penetration depth of the i.r. beam in the film is 0.25–0.50 μm. Spectra with wavenumber ranging from 550 to 2000 cm^{-1} were recorded. To determine the structures at several different depths of a given film, the film surface was mechanically abraded successively after each measurement. The abrasion direction was from the surface near the air toward the centre of the film.

Bending-beam specimen preparation

The substrates used for stress measurement are silicon strips with 7.5 cm length, 0.8 cm width and 390 μm
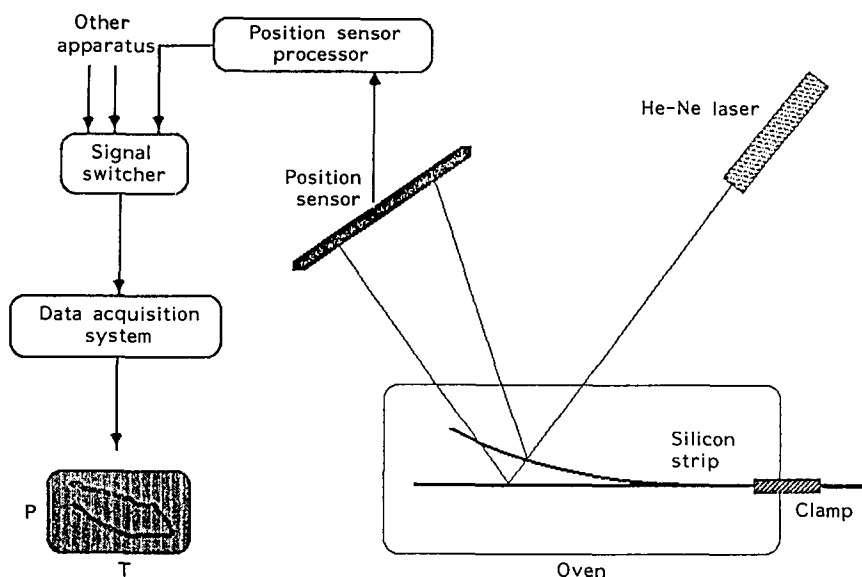
Figure 3 Schematic diagram of the experimental set-up of a bending beam apparatus used for stress measurement

thickness. These silicon strips were prepared by slicing (1 0 0) silicon wafers along the (1 0 0) crystal plane. Polyimide films were prepared by spin-casting their poly(amic acid) solutions on the substrates, followed by prebaking at 80°C for 30 min. During the prebake, part of the solvent is removed in order to solidify the film. Since one end of the substrate must be mounted on a clamp and the other end must reflect the laser beam to a sensor, the two ends of the solid film were separated by 1 cm.

Bending-beam experiment

After the prebake of the polymer film, the sample is mounted on a clamp with a thermocouple tip placed near the middle of the Si wafer, and then enclosed in a thermocontrolled oven with an optical window to admit laser light. A nitrogen purge is used during the cycle to prevent moisture uptake of the film at low temperature. The temperature is ramped upwards at a rate of 1°C min^{-1}. The zero-stress position is determined by measuring the position of the He–Ne laser beam reflected from the silicon substrate after removing the polyimide film. To remove the film, a condensed acid solution was added to the substrate so that the polyimide film could be easily stripped from the silicon substrate.

The film thickness is determined by measuring the weight density and dimensions of the film after the cure. This technique gives us the average thickness of the film, accurate to 0.5 μm.

Figure 3 shows a schematic diagram of the experimental set-up for *in situ* bending-beam experiments. The specimen was mounted on a clamp. The deflection of the end of a specimen was measured continuously by a computer-controlled system during thermal cycling. The change in the deflection was detected by a position-sensitive detector. The measured analogue signals were amplified and transformed to digital signals by a signal processor. The processed signals were then transferred via a multi-operation signal switch to a data acquisition system. The data acquisition system consisted of a PC/AT and a 14 bits A/D + D/A + DIO control card. After calculation, the obtained position data were

converted to bending curvature, $1/R$, according to the geometry of the set-up.

Stress in the polyimide film can be readily calculated from the bending curvature, $1/R$, according to the following equation[17]:

$$\sigma_{2,r} = \frac{1}{6R} \frac{E_1}{(1 - v_1)} \frac{d_1^3}{d_2(d_1 + d_2)} \qquad (1)$$

where $\sigma_{2,r}$ is the average stress in the polymer film, R is the radius of curvature of the specimen, E_1, v_1 and d_1 are Young's modulus, Poisson's ratio and thickness of the substrate, respectively, and d_2 is the thickness of the polymer film.

In the above equation, it has been assumed that the tensile modulus of the polyimide film is much smaller than the Young's modulus of the silicon substrate. A more simplified formula can be reached if the thickness of the polyimide film is comparatively small[21]. However, in this stress experiment, the film thickness ranges from 4 to 33 μm and the thickness of the silicon substrate is 390 μm. The calculated stresses will be overestimated by 1.0 to 7.8% if the oversimplified formula is applied. In order to investigate the effect of coating thickness on the resulting stress more precisely, the oversimplified formula is avoided. Instead, equation (1) is used for stress calculation.

Upon thermal cycling, the difference in the film stress at any two given temperatures can be attributed to the mismatch in the thermal expansion coefficients of the polyimide film and the silicon. It can be expressed as:

$$\Delta\sigma_{2,r} = \frac{E_2}{(1 - v_2)} \int_{T_i}^{T_j} \Delta\alpha \, dT \qquad (2)$$

where $\Delta\sigma_{2,r}$ is the residual stress change in the polymer film, E_2 and v_2 are the relaxation modulus and Poisson's ratio of the polymer film, respectively, $\Delta\alpha = \alpha_2 - \alpha_1$, α_2 is the thermal expansion coefficient of the polymer film, and α_1 is the thermal expansion coefficient of the substrate.

By knowing the thermal expansion coefficient (or tensile modulus and Poisson's ratio) of the film, its biaxial
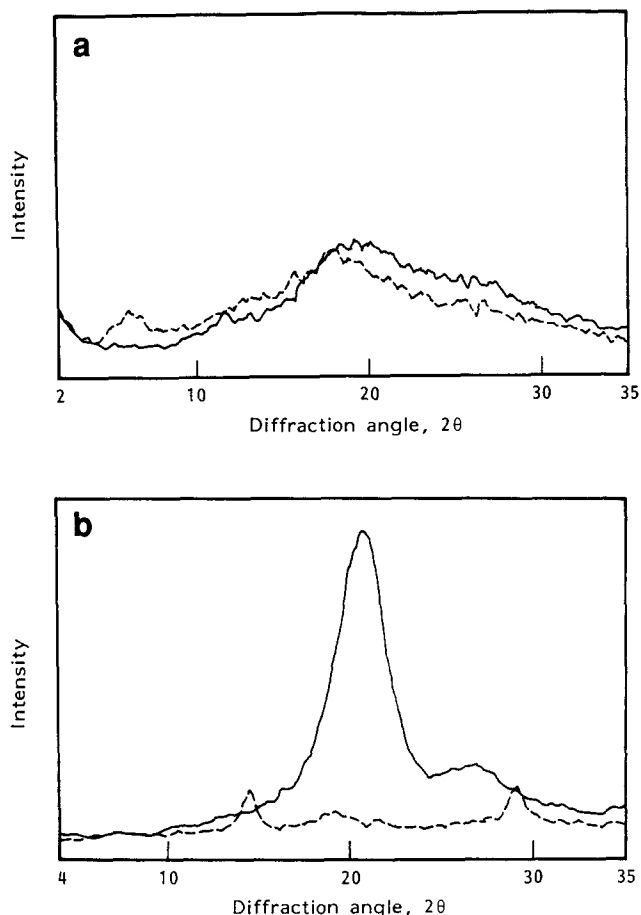
Figure 4 X-ray diffraction patterns of (a) PMDA–ODA and (b) PMDA–PDA polyimide films: (———) in-plane diffraction pattern; (————) out-of-plane diffraction pattern

modulus (or thermal expansion coefficient) can be obtained according to the slope of the resulting curve of stress *versus* temperature. This relationship can be written as:

$$\frac{d\sigma_{2,r}}{dT} = \frac{E_2}{(1 - v_2)} \Delta\alpha \qquad (3)$$

RESULTS AND DISCUSSION

Figure 4 shows the X-ray diffraction patterns of PMDA–ODA and PMDA–PDA polyimide films. For PMDA–ODA, the in-plane and out-of-plane diffraction patterns are not very different to each other over the entire range of diffraction angles, except at small angle. At small angle, there is a peak in the in-plane diffraction pattern. This peak is characteristic of the intramolecular ordering of the monomeric repeat units[13]. This result means that polymeric chains of this polyimide are more or less preferably aligned in the plane direction of the films. In other words, the PMDA–ODA film exhibits some degree of orientation.

For PMDA–PDA, the in-plane and out-of-plane diffraction patterns are very different. The characteristic peak, corresponding to the intermolecular spacing[13], in the out-of-plane diffraction pattern is very prominent, while it can be barely seen in the in-plane diffraction pattern. This result indicates not only that these polymeric chains are predominantly aligned in the plane direction of the film, but also that PMDA–PDA has

formed a much higher ordering structure when comparing with PMDA–ODA.

From the results shown above, it can be seen that degrees of orientation of the PMDA–ODA and PMDA–PDA films are apparently different. As is well understood, with the same extent of stretching or drawing, the resulting orientation in an amorphous polymer will be much less than that in a crystalline polymer. PMDA–ODA is a semi-rigid polymer and has relatively low structure symmetry. Its characteristic diffraction peaks, as shown, are relatively broad and weak, which indicates that the molecular structure of the PMDA–ODA film is nearly amorphous. Therefore, its film orientation is relatively low. In contrast to PMDA–ODA, PMDA–PDA is a rigid polymer and has relatively high structure symmetry. Its characteristic diffraction peaks are relatively sharp, as seen. The molecular structure of the PMDA–PDA film is highly crystalline. Therefore, its film orientation is comparatively high.

Figure 5 shows the effect of film thickness on the in-plane diffraction patterns of two different specimens, both with 80% PMDA–ODA and 20% PMDA–PDA. At small angle, the diffraction intensity of the specimen stacked with many layers of 36.2 μm thick films is much lower than that of 5.4 μm; while at higher angle, the intensities of the two specimens are comparable. Apparently the thicker film has a poorer orientation.
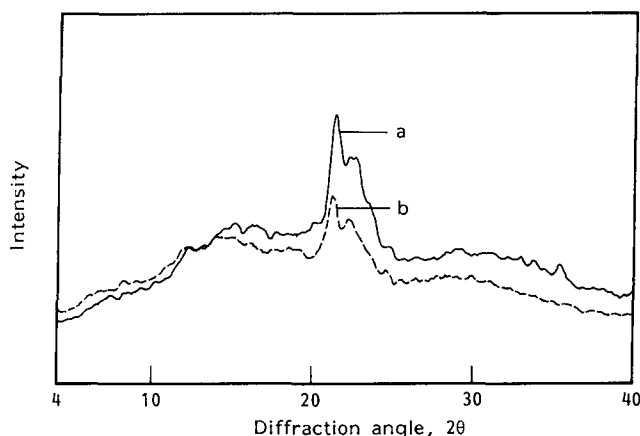
The effect of film thickness on the resulting film orientation increases as the composition of PMDA–PDA increases. This trend can be clearly observed in the in-plane diffraction patterns of the samples with 60% PMDA–ODA and 40% PMDA–PDA and with 50% PMDA–ODA and 50% PMDA–PDA as demonstrated in *Figures 6* and *7*, respectively. For the samples composed of thicker films, the diffraction intensities corresponding to the intramolecular ordering are relatively low, while those corresponding to the intermolecular ordering are significantly higher. Here, it becomes more obvious that thicker films exhibit a lower degree of film orientation, and the converse is also true. Indeed, this can be attributed to the increase of the content of PMDA–PDA, which can form a much better crystalline structure. These results again imply that thicker coating thickness results in films with poorer orientation.
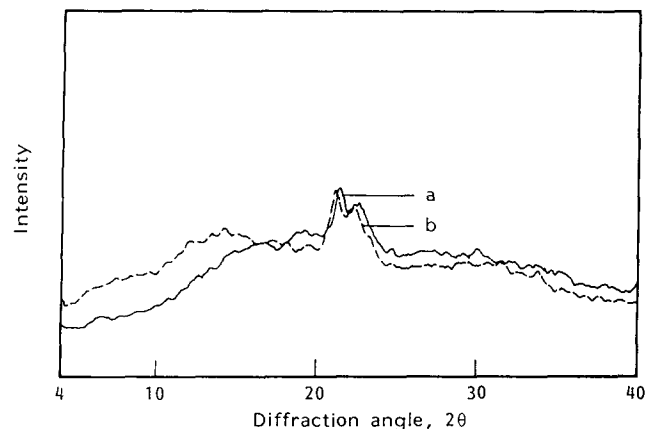
Figure 5 The effect of film thickness on the in-plane diffraction patterns of two different specimens, both with 80% PMDA–ODA and 20% PMDA–PDA: (a) 36.2 μm and (b) 5.4 μm
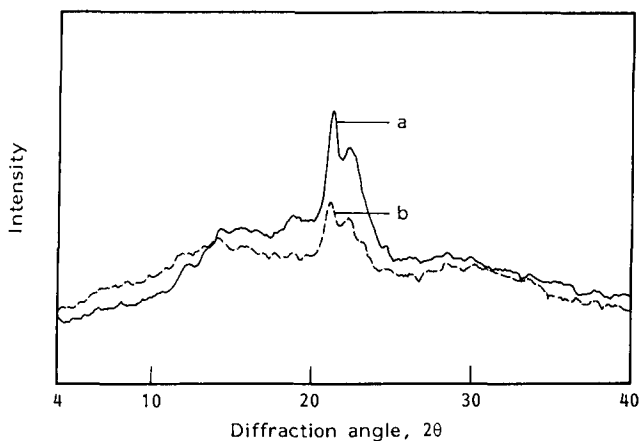
Figure 6 The effect of film thickness on the in-plane diffraction patterns of two different specimens, both with 60% PMDA–ODA and 40% PMDA–PDA: (a) 13.9 μm and (b) 6.1 μm

Figure 7 The effect of film thickness on the in-plane diffraction patterns of two different specimens, both with 50% PMDA–ODA and 50% PMDA–PDA: (a) 19.1 μm and (b) 6.6 μm
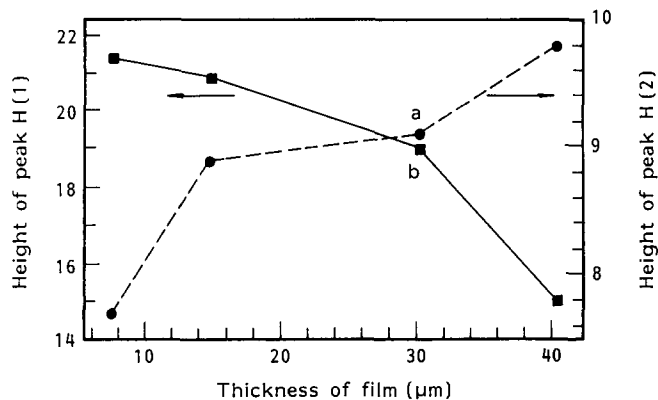
Figure 8 shows the relationship between the height of the characteristic peak at 20.96°, which corresponds to the intermolecular ordering, and that at 6.42°, which corresponds to the intramolecular ordering, and film thickness. The films in these samples are composed of 50% PMDA–ODA and 50% PMDA–PDA. As seen in *Figure 8a*, when the film becomes thicker, a lesser amount of the polyimide chains aligns in the plane direction, according to the intramolecular diffraction intensities. In *Figure 8b*, similarly, when the film becomes thicker, more of the polyimide chains align in the direction perpendicular to the plane, according to the intermolecular diffraction intensities. By dividing the heights as shown in (a) by those in (b), relative orientations of the various films with respect to thickness can be obtained. As shown in *Figure 9*, the relative film orientation decreases with increase of film thickness.

In the in-plane diffraction experiments, the reflected intensities give only average structure information. This is because the width of the line-focus slot for the X-rays is much larger than the thickness of every single piece of the films studied, and the 'poorly' focused X-ray beam could then be used to provide an overall picture of any given 'thin' film. If there exists any orientation variation in the transverse direction of a given film, this X-ray diffraction method is no longer valid.
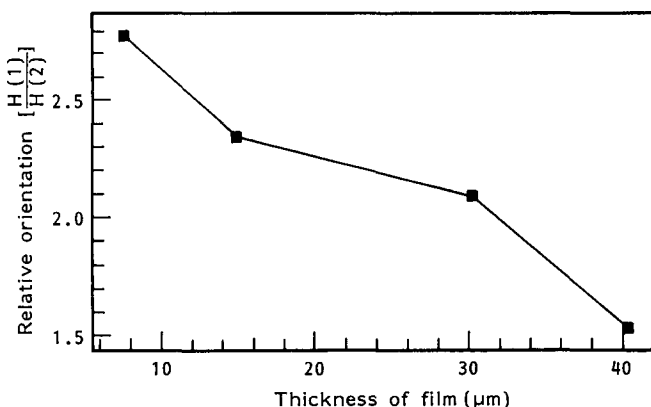
Figure 10a shows the peak wavenumber of the absorption band of the C=O stretch of a 50 μm thick polyimide film with 50% PMDA–ODA and 50% PMDA–PDA from *FT*i.r.–a.t.r. experiments. As shown, the peak wavenumber changes from 1714.7 to 1717.6 cm^{-1} when measuring from the film surface towards the centre of the film. As mentioned elsewhere[22], when changing from crystalline to amorphous, the peak will shift from a low to a high wavenumber. It is therefore indicated that this thick film is more crystalline at the surface and less so in the centre. The peak wavenumber of a 12 μm thick film is also given in the plot. It seems that the structures at both surfaces of the thinner film are slightly more ordered than those of the thicker film.

Figure 10b shows the peak wavenumber of the absorption band of the C–N stretch of the same sample. As shown, the peak changes from 1362.4 to 1356.7 cm^{-1} when measuring from the film surface towards the centre of the film. As also mentioned elsewhere[22], when changing from crystalline to amorphous, the peak will shift from high to low wavenumber. This again proves that this thick film is more crystalline at the surface and less so in the middle. Furthermore, the structures at both surfaces of the thinner film are also slightly more ordered than that of the thicker film.

From the above results, one can see that, when the coating thickness of the studied film is increased, more and more less ordered structure will result in the centre within the film. This may be attributed to the fact that

Figure 8 The relationship between the heights of the characteristic peak (a) at 20.96° and (b) at 6.42° and film thickness of the X-ray diffraction patterns of the 50% PMDA–ODA and 50% PMDA–PDA films

Figure 9 The relationship between the relative film orientation and film thickness of the 50% PMDA–ODA and 50% PMDA–PDA films
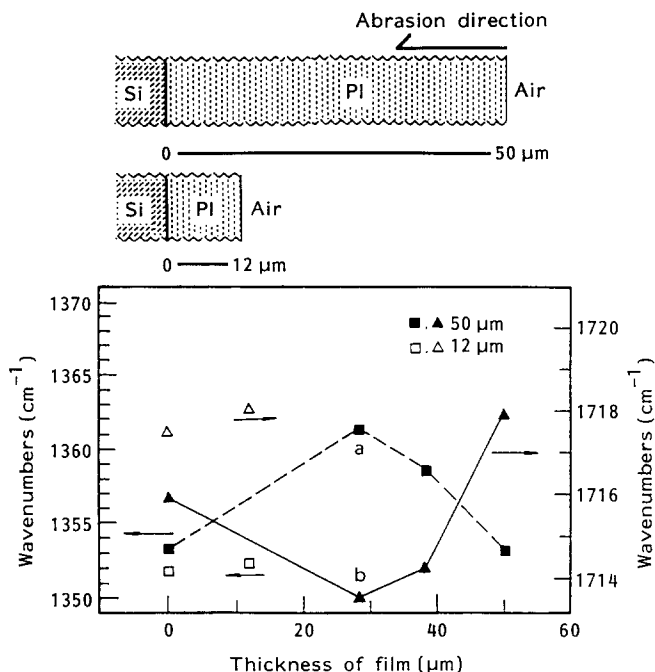
Figure 10 Peak wavenumber of the absorption band of a 50 µm thick polyimide film with 50% PMDA–ODA and 50% PMDA–PDA from *FT*i.r.-a.t.r. experiments: (a) C=O stretch and (b) C–N stretch

the precursor polymer chains in the centre have least restraints since they are, relatively speaking, far away from the substrate surface to which the film is adhered. They are also a distance away from the air. Upon solidifying, they can shrink more freely than those near the substrate and air. Those near the air will, of course, solidify first. When solidifying, they will be immediately restrained by the substrate, provided the edges of the film are solidified. The solidified film edges, which are adhered to the substrate, can transfer the restraint from the substrate to the solidified chains in the surface near the air. If the edges are still liquid-like when the surface near the air has solidified, the chains will shrink freely. Those near the substrate will be, of course, restrained by the substrate directly. In other words, those chains in the centre are more likely to be cured at least partly freely due to less restraint. Since their precursor poly(amic acids) are random coil-like and isotropically distributed in the solution state after prebaking and curing, a less crystalline structure should result. Likewise, a poorer oriented film would occur. In thicker films, these phenomena should be enhanced. These can, supposedly, be used to reveal why the average film orientation decreases with increase of film thickness and why the thicker film exhibits less structure ordering in the centre.

Figure 11 shows the effect of coating thickness on the stress–temperature behaviours of three different imide films with different compositions. As demonstrated in *Figure 11a*, the slopes of the stress curves of pure PMDA–ODA do not vary much with thickness. This result indicates that little structure or orientation difference can be observed among the different PMDA–ODA films with various thicknesses. This phenomenon matches what is observed from the X-ray diffraction results.

For the films with 50% PMDA–ODA and 50% PMDA–PDA, as shown in *Figure 11b*, the stress curve becomes steeper as film thickness increases. In other words, the absolute magnitudes of the slopes of the curves

increase with increase of film thickness. Apparently, the film structure varies systematically with thickness. This can be attributed to the variation in the film orientations as observed in the X-ray experiments. As demonstrated in equation (3), the slopes of the stress–temperature curves are a function of the tensile moduli of the films and the thermal mismatches between the films and the silicon substrate. Hence, the increase in the slope with
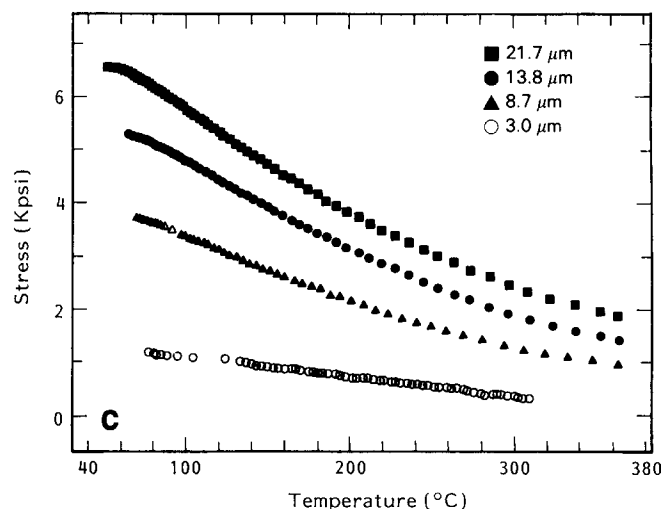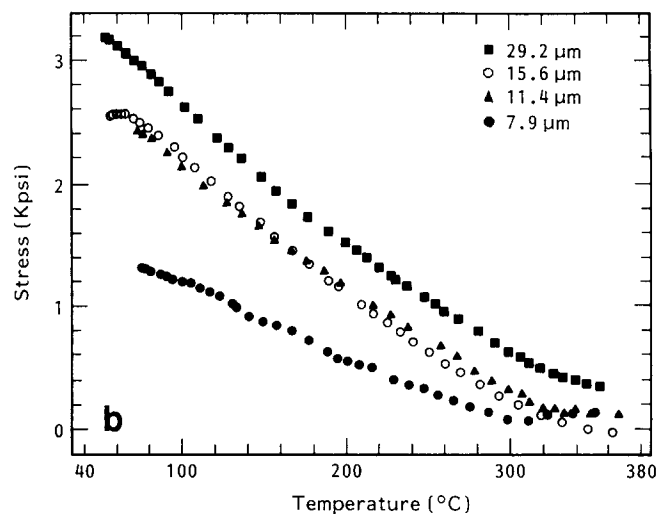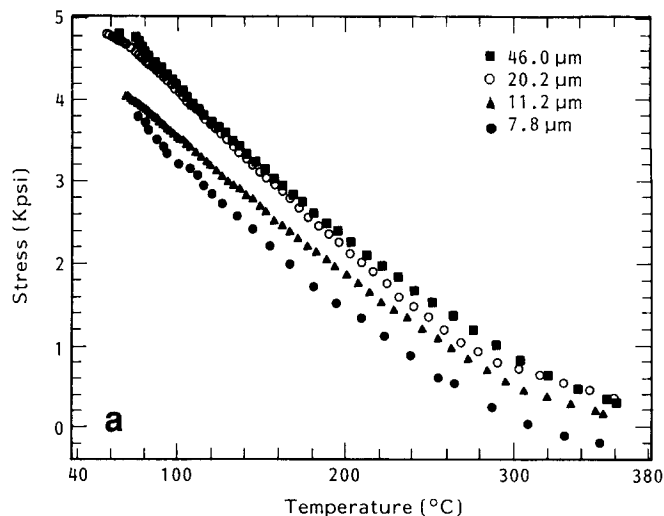
Figure 11 The effect of coating thickness on the stress–temperature behaviours of three different imide films with different compositions: (a) PMDA–ODA; (b) 50% PMDA–ODA with 50% PMDA–PDA; (c) PMDA–PDA

respect to thickness may be attributed to the increase of either the film modulus or thermal mismatch. As demonstrated in the above studies, thicker films have lower degrees of film orientation. If the thicker films studied here have lower degrees of film orientation, they should, presumably, have smaller moduli and higher thermal expansion coefficients. A smaller film modulus would result in a smaller magnitude of the slope. The increase in the slope with respect to thickness should therefore be attributed to the increase in the thermal expansion coefficient. These stress–temperature results imply that the thickest film has the highest thermal expansion coefficient and conversely.

Similar to the blend of 50% PMDA–ODA and 50% PMDA–PDA, the stress–temperature behaviours in the films of 100% PMDA–PDA vary significantly with thickness, as demonstrated in *Figure 11c*. The stress curve becomes steeper as the film thickness increases. Since the film of PMDA–PDA is quite fragile, the films could not be made too thick. However, based on the same thickness range, variation in the slopes of the stress–temperature curves is most pronounced in the films with 100% PMDA–PDA in comparison with those with less or no content of PMDA–PDA.

CONCLUSIONS

From this study, several points can be drawn. First, the on-substrate cured imide molecules are, more or less, preferentially aligned in the plane direction of the films and show some degrees of orientation, which increase with increase of the content of the rigid polyimide, PMDA–PDA.

Secondly, the film orientation decreases with increase of coating thickness. The effect of the coating thickness on the orientation and ordering of the polyimide films can be seen most prominently in the pure PMDA–PDA films, slightly less in the films with 50% PMDA–ODA and 50% PMDA–PDA, and relatively insignificantly in those with 100% PMDA–ODA. This can be attributed to the on-substrate cured PMDA–PDA film being highly crystalline and PMDA–ODA film being highly amorphous. Therefore, higher degrees of orientation are obtained in the highly crystalline PMDA–PDA and its mixture. For the amorphous-like polymer, PMDA–ODA, the resulting orientation is not very marked.

Thirdly, in a studied thick film, relatively speaking, the imide molecules located at positions near the centre of the film exhibit less structure ordering than those near the film surface. Furthermore, the structure ordering at both surfaces of a studied thin film is slightly higher than that of the thick film.

These phenomena reveal why the average film orientations in all the studied polyimide films decrease with increase of film thickness. These also reveal why the thermal expansion coefficients of the polyimide films increase with increase of film thickness.

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