Residual stress behaviour of isomeric PMDA-ODA polyimides

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Poly(3,4′-oxydiphenylene pyromellitimide) (PMDA-3,4′-ODA), an isomer of poly(4,4′-oxydiphenylene pyromellitimide) (PMDA-4,4′-ODA), was synthesized from pyromellitic dianhydride (PMDA) and 3,4′-oxydiphenylene diamine (3,4′-ODA). For these two polyimide isomers and their poly(amic acid) precursors in the condensed state on Si wafers, residual stress behaviour over the range 25–400°C was investigated by the dynamic measurement of wafer bending. During thermal imidization both isomers did not show any difference in stress *versus* temperature behaviour. Once imidized, however, one isomer exhibited a quite different stress behaviour from that of the other during cool-down: the stress of PMDA-3,4′-ODA increased rapidly from zero at 400°C to ≈45 MPa at 40°C, whereas that of PMDA-4,4′-ODA rose gradually from zero to ≈27 MPa. For both cured isomers, stress–temperature profile on heating was the same as that on cooling, with some deviation due to moisture uptake over the temperature range 25–150°C, indicating that their stresses were insensitive to thermal cycling or thermal annealing. From independently measured properties (thermal expansion coefficient, modulus, Poisson's ratio of 0.34) of both polyimides, the thermal stresses were calculated and compared with the measured overall stresses. It is concluded that for both polyimides the overall residual stress results primarily from the thermal stress. In comparison with PMDA-4,4′-ODA, PMDA-3,4′-ODA showed a much higher stress despite its slightly lower thermal expansion coefficient. This leads to the conclusion that the large difference between the stresses of the isomers results from the large difference in their moduli (5.0 GPa for PMDA-3,4′-ODA and 3.0 GPa for PMDA-4,4′-ODA). This behaviour is further supported by the difference in morphological structures of these two isomers as determined by wide-angle X-ray diffraction: PMDA-3,4′-ODA showed a well-developed crystalline structure, whereas the PMDA-4,4′-ODA did not. In addition, the interfacial adhesion between polyimide film and Si wafer primed with A1100 was investigated.

(Keywords: PMDA-ODA; polyimide; residual stress; thermal stress; intrinsic stress; thermal expansion coefficient)

INTRODUCTION

In comparison with inorganic dielectric materials (e.g. borosilicate, lead borosilicates, silicon oxide, and silicon nitride) used in the electronics industry, high-temperature polyimides have several advantageous properties such as a low dielectric constant, low-temperature processability, easier patternability with the aid of a photoresist, high thermal stability, and excellent mechanical properties[1,2]. As a result of these properties, polyimides are widely used in the microelectronics industry as interlayer dielectrics, passivation layers, and alpha-particle barriers. Recently, high-temperature polyimides have been extensively used to fabricate multilayered semiconductor chips and integrated circuits required in making high-performance computers. This special application requires superior properties for a polyimide dielectric, including thermal expansion coefficient (t.e.c.) match, good interfacial adhesion, and low solvent-swelling, besides all the good properties mentioned above.

When the t.e.c.s between layers are not matched in a multilayered structure, residual stress is generated. This residual stress is drastically enhanced by further mismatch of other properties such as Young's modulus, Poisson's ratio, and glass transition temperature. The residual stress of a polymer layer in a multilayered structure is generally dependent upon its processing, loading history, and intrinsic physical properties such as thermal expansion coefficient, Young's modulus, Poisson's ratio, and glass transition or melting temperature. Sometimes the stress causes serious reliability problems such as displacement, cracking and delamination, giving rise to mechanical failures, particularly in a multilayer structure. Mechanical failures can be generally classified into three types[3–5]: loss of dimensional stability (curling, bending, warping, deformation, etc.); cohesive failures (crazing and cracking); and adhesive failures (debonding and delamination). Normally, cracking often occurs when the residual stress in a given layer structure overcomes the strength at break or the bonding strength of the structure material. Furthermore, cracking may also be induced by repeated cyclic loading, inhomogeneous solvent-swelling, thermal and mechanical shock, and defects (microvoids, bubbles and impurities). However, owing to the complex nature of this failure mechanism, residual stress and its role in mechanical failures are not fully understood.

A representative polyimide is poly(4,4′-oxydiphenylene

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pyromellitimide) (PMDA-4,4′-ODA)[1]. This polymer has been widely used since the early 1960s. An isomer of this polyimide was synthesized in the present study: poly(3,4′-oxydiphenylene pyromellitimide) (PMDA-3,4′-ODA). The residual stress behaviours of these two polyimides were investigated over the range of 25–400°C by means of wafer bending measured either by X-ray diffraction or optically with a He–Ne laser. Stresses were dynamically measured during thermal imidization from the precursor polymers and subsequent cooling, as well as upon thermal ageing of the imidized polyimides. The thermal stresses were also calculated from mechanical and thermal properties measured independently, and compared with the measured overall stresses. The stress behaviour was then interpreted in terms of the relationship to morphological structure and physical properties.

EXPERIMENTAL

Materials and sample preparation

Two structural isomers of poly(oxydiphenylene pyromellitimide) (PMDA-ODA) were used in the present study: poly(3,4′-oxydiphenylene pyromellitimide) (PMDA-3,4′-ODA) and poly(4,4′-oxydiphenylene pyromellitimide) (PMDA-4,4′-ODA) (see *Figure 1*). The PMDA-4,4′-ODA poly(amic acid) precursor solution (PI-2540) was obtained from DuPont Chemical Company. This precursor solution was used as received without any further treatment. The PMDA-3,4′-ODA poly(amic acid) precursor solution was synthesized from pyromellitic dianhydride (PMDA) and 3,4′-oxydiphenylene diamine (3,4′-ODA). The two monomers were commercial materials: they were sublimed once through Al_2O_3 to remove coloured contaminants and then a second time to ensure complete dryness. *N*-methylpyrrolidone (NMP) was distilled under argon at reduced pressure from P_2O_5. Polymerizations were conducted in a glove box filled with helium gas, using a predetermined monomer stoichiometry utilizing excess 3,4′-ODA diamine to yield a $\overline{DP}$ of 60. Thus 80.00 mmol of diamine was dissolved in ≈150 ml of dry NMP and then 77.38 mmol of powdered dianhydride was slowly added. The polymerization mixture was stirred for 48 h and stored at 0–5°C in capped Wheaton bottles. The poly(amic acid) precursor solutions were filtered through 1 μm Fluoropore filters before use.

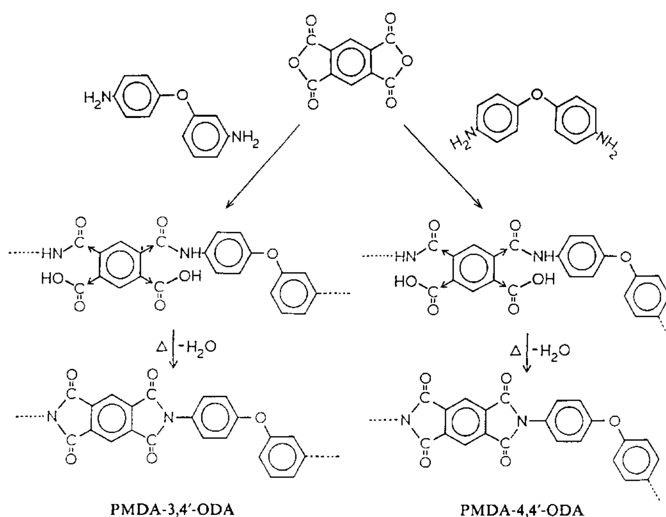

Figure 1 Schematic diagram of the chemical structures of isomeric PMDA-ODA polyimides and their synthesis from pyromellitic dianhydride and oxydiphenylene diamine isomers

All the substrates (silicon wafers and glass slides) were cleaned in a Plasmaline 515 asher of Tegal Corporation (300 W for 5 min and 535 cm^3 min^{-1} oxygen flow rate) before use. For residual stress measurements, double-sided polished silicon wafers (82.5 mm diameter and ≈400 μm thickness) of known curvature were treated with an adhesion promoter (0.1 vol% A1100 (γ-aminopropyltriethoxy silane) solution in 90 vol% ethanol–10 vol% water) at 2000 rev min^{-1} for 20 s, followed by baking at 120°C for 20 min in air. Then a polyimide precursor solution was spin-coated on the primer-coated wafer, soft-baked at 80°C on a hotplate or in a convection oven with nitrogen flow for 1 h, and thermally imidized in a Heraus oven or the hot-stage of a Flexus stress analyser with nitrogen flow by a one-step cure process (400°C/1 h) or a three-step cure process as follows: 150°C/30 min, 230°C/30 min and 400°C/60 min. The heating rate was 2 K min^{-1} in the one-step process, and 2.5 K min^{-1} between steps in the three-step process. The thickness of the thermally imidized polyimide films was ≈12 μm. To study the effect of thermal ageing on the residual stress of the polyimides, some imidized samples were again heated to 400°C by the step cure process and then annealed at 400°C for 10 h. The residual stress was measured again at room temperature.

For dynamic mechanical thermal analysis, stress–strain analysis and thermal expansion measurement, the polyimide film samples were prepared on 82.5 mm silicon wafers or 50 × 75 mm glass slides without using the adhesion primer. The films imidized by the step cure process were diced in strips of 3 and 6 mm width on a dicer with a circular blade before removal from the substrates. Removal consisted of immersion in deionized water for ≈3 h or dilute aqueous hydrofluoric acid for a few minutes. The diced film strips were dried at room temperature for a week before testing.

For peel test samples, A1100 primed wafers were spin-coated twice with the polyimide precursor solutions to yield ≈24 μm final film thickness. The second coating was applied on the first coated layer after it had been partially imidized at 150°C for 30 min following softbake at 80°C. After softbake of the second layer, the wafer was put through the step cure process. In addition, thick films (≈80 μm after cure) were also made for wide-angle X-ray diffraction measurements by doctor-blade coating. For all the film samples, the thickness was measured using a Tencor alpha-stepper.

Residual stress measurement

The radius of curvature of a blank wafer, R_∞, was measured on an automated Lang camera and a Flexus stress analyzer (Model 2-300, Flexus Co.). Once a polymer film was deposited on the wafer, its radius of curvature was measured again in the same way. The change in the wafer curvature before and after polymer film deposition was used to calculate the residual stress in the polymer film. The Lang X-ray camera was employed only for the measurements at room temperature, while the Flexus analyser was used for both room-temperature and high-temperature measurements.

The Lang camera used was a modified Rigaku PMG-A2 horizontal goniometer[6,7]. The detector arm was extended to 30 cm, and a translator stage with a

span of 10 cm was added, together with slits needed to shield the detector from the main beam. The detector was raised or lowered manually to aid in the wafer alignment. A manually driven vertical rotation was also necessary for alignment. The theta drive and translator stepper motors were driven by a microcomputer controller designed and built in-house, itself driven by an IBM Series/1 minicomputer. The Lang camera was mounted on a Rigaku RU300 rotating anode generator with molybdenum target. The source voltage was set to 40 kV while the current was adjusted to provide a peak count intensity of $\approx 10\,000\ s^{-1}$. The source-to-specimen distance was 1 m, of which about 95 cm was taken up by a collimator forming a 15 cm high by 0.5 mm wide beam at the sample. For Si(100) wafers, the detector was fixed at the diffracting position of the Si(220) reflection. Under computer control, the position of the rocking curve maximum was measured at points widely separated on the wafer. For 82.5 mm diameter wafers, the common spacing of these two points, δx, was 6 cm. The angular separation between these maximum positions, $\delta\theta$, was used to calculate the radius of curvature, R:

$$\frac{\delta x}{\delta\theta} = R \tag{1}$$

The Flexus analyser was a He–Ne laser-based optical system equipped with two position-sensitive detectors and a hot stage, controlled by an IBM PC/AT computer[8]. The two laser beams were generated via a beam splitter at the fixed positions with a certain distance, δx. The two laser beams reflected from the wafer were detected by two position-sensitive detectors. Then the angular separation between the two points was measured. The radius of curvature was calculated from equation (1). With this tool, the collecting time for the reflected beams was 5 or 10 s. This allowed dynamic measurement of the change in the radius of wafer curvature during heating and cooling as a function of temperature or time.

The residual stress, σ_F, was calculated from the measured radii of curvature using the following simple equation[9] valid for $t_F \ll t_S$:

$$\sigma_F = \frac{1}{6}\frac{E_S t_S^2}{(1-\nu_S)t_F}\left(\frac{1}{R_F} - \frac{1}{R_\infty}\right) \tag{2}$$

where the subscripts F and S denote the polymer film and the substrate, respectively; E, ν, σ, and t are the Young's modulus, Poisson's ratio, stress, and thickness, respectively; and R_F and R_∞ are the radii of the substrate with and without the polymer film, respectively. For Si(100) wafers[10], $E_S/(1-\nu_S)$ is 1.805×10^5 MPa.

Adhesion to silicon wafers

Four structurally different samples were prepared for peel tests:

1. PMDA-4,4′-ODA(24 μm)//A1100//silicon wafer
2. PMDA-3,4′-ODA(12 μm)/PMDA-4,4′-ODA(12 μm)//A1100//silicon wafer
3. PMDA-3,4′-ODA(24 μm)//A1100//silicon wafer
4. PMDA-4,4′-ODA(12 μm)/PMDA-3,4′-ODA(12 μm)//A1100//silicon wafer

These samples were then diced into strips of 1.6 and 3.2 mm width using a dicer. The peel test was performed on an Instron Tester (Model 1122, Instron Co.) equipped with a 90° peel test fixture and a chart recorder. The cross-head speed was 0.05 to 5 mm min^{-1}.

Thermal expansion coefficient

Thermal expansion coefficients were determined using a thermal mechanical analyser (TMA 943, DuPont Instrument Co.) from 80 to 400°C under a nitrogen gas flow. The heating rate was 2 K min^{-1}. Sample strips of 2.0 mm width, $\approx$6.0 mm length (distance between grips), and $\approx$20 μm thickness were used.

Mechanical properties

For the cured polyimide films, the dynamic mechanical properties (storage modulus E', loss modulus E'', and $\tan\delta$) were measured between 25 and 500°C, using a Mark-I tensile-head-based dynamic mechanical thermal analyser of Polymer Laboratories, controlled by a Hewlett-Packard computer. The heating rate was 10 K min^{-1} and the frequency was 10 Hz. These dynamic measurements were carried out in air. The film strips were $\approx$12 μm thick and 6 mm wide. The gauge length was $\approx$15 mm.

The stress–strain curves were also measured using the Instron (Model 1122). Each film strip was mounted on an aluminium foil holder with epoxy glue to simplify mounting in the grips of the tester. For these measurements, the grip gauge length was $\approx$50 mm and the strain rate was 0.2 min^{-1}. The sample strips were $\approx$12 μm thick and 3.2 mm wide.

Wide-angle X-ray diffraction

Diffraction measurements were performed for $\approx$12 μm thick films on a silicon wafer in reflection geometry and for $\approx$80 μm thick films in both reflection and transmission geometry. All measurements were made in a $\theta/2\theta$ mode with a Rigaku horizontal diffractometer in $\approx$20 mmHg vacuum at room temperature. The Cr K_α radiation source was operated at 35 kV and 40 mA. The 2θ scan data were collected at 0.1° step intervals over the range of 2°–80°. The collecting time for the diffracted beam was 35 s per step.

RESULTS AND DISCUSSION

Residual stress behaviour during thermal imidization and cooling

The dynamic stress measurement was performed for both softbaked polyimide precursor films and thermally cured polyimide films over the temperature range 25–400°C. For the polyimide precursor films softbaked at 80°C for 1 h, residual stress changes were measured during thermal imidization and subsequent cooling. During thermal imidization of the softbaked precursor samples, the film thickness changed, owing to the volume reduction associated with solvent evaporation, imidization, and molecular ordering. Thus the film thickness change for the softbaked samples was measured for both cure processes as a function of temperature. For each isomer, the precursor solution was spin-coated on two Si wafers of 82.5 mm diameter and softbaked at 80°C for 1 h. With the aid of a blade and a rule, these two wafers with softbaked films were broken into nine fragments of similar size. The film thickness of these pieces was measured before use. One set of nine pieces was used for the one-step cure and another set of nine pieces was employed for the three-step cure. During imidizing of the nine pieces of precursor films on the Flexus hot stage in nitrogen by the one- or three-step cure process, each

piece was sampled from the hot-stage at various temperatures and quenched to room temperature through contact with a metal plate. The film thickness of the piece sampled at a certain cure temperature was then immediately measured again, using a Tencor alpha stepper. The film thickness variations are plotted in *Figure 2* as a function of temperature. The film thickness change was dependent upon cure process parameters such as heating rate and number of holding steps. With a given cure process, both isomers showed the same behaviour in thickness change. These thickness change profiles with temperature were applied in stress calculations with equation (2) from radii of wafer curvatures measured during imidization. In the calculation of residual stresses for cooling runs from 400°C after imidization, it was assumed that the thickness of the cured film, which was measured at room temperature, was constant over the range 25–400°C. This assumption was also applied for both heating and cooling runs of samples which were thermally imidized in an oven.

Dynamic stress measurements over 25–400°C are shown in *Figures 3–6*. For both isomeric precursor films softbaked at 80°C for 1 h, residual stresses at room temperature were 23–27 MPa. For softbaked precursor films, stresses generally depended upon degree of drying. Residual stresses increased with decreasing solvent content in the precursor films. However, a softbaked (i.e. dried) poly(amic acid) film contains at least ≈30 wt% NMP, owing to complex formation between carboxylic acid groups of precursor molecules and NMP. From this it would be expected that both isomeric precursor films fully dried at 80°C had higher residual stresses than 23–27 MPa.

As shown in *Figure 3*, during thermal imidization at 2 K min^{-1}, the residual stress of PMDA-3,4′-ODA precursor film decreased from ≈23 MPa at room temperature to zero at ≈130°C in spite of continuous NMP evaporation due to heating. This suggests that the softening temperature of the softbaked PMDA-3,4′-ODA precursor film was ≈130°C. Residual stress then reappeared at ≈135°C, rose rapidly with increasing temperature, levelled off at 172°C, and then remained

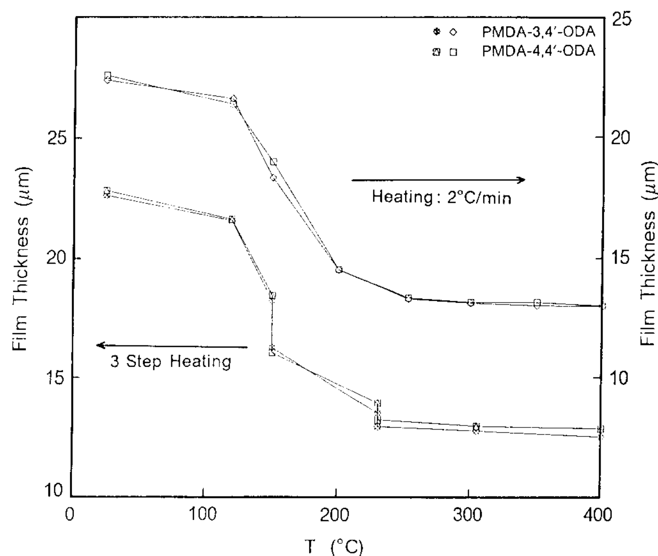

Figure 2 Variation of film thickness with temperature during one-step and three-step thermal curing for polyimide precursor films softbaked at 80°C for 1 h

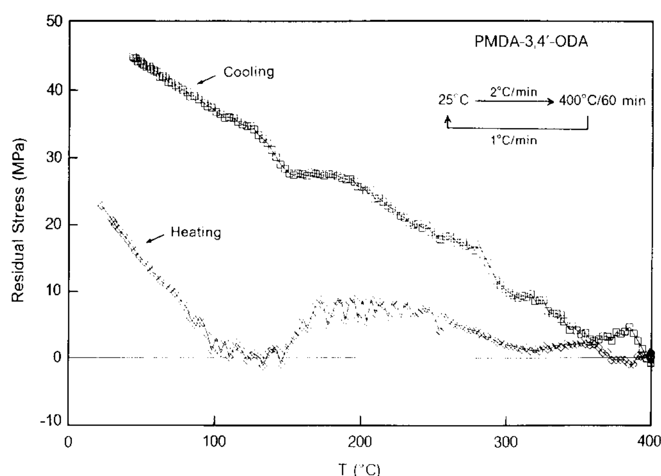

Figure 3 Residual stress variation of PMDA-3,4′-ODA on Si(100) wafer as a function of temperature: 'Heating', during imidization of the softbaked precursor polymer film by one-step cure process; 'Cooling', during cooling of the polyimide film imidized fully by the one-step cure

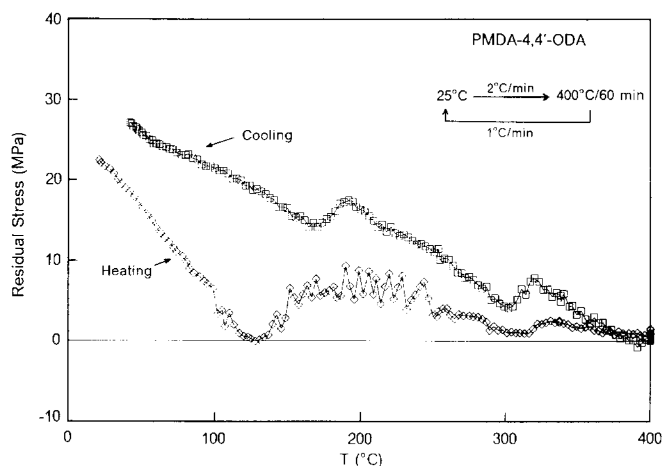

Figure 4 Residual stress variation of PMDA-4,4′-ODA on Si(100) wafer as a function of temperature: 'Heating', 'Cooling', as in *Figure 3*

constant (≈7.3 MPa) up to ≈250°C. In this temperature region, the residual stress was mainly due to the imidization of the poly(amic acid) precursor. The reason is that the physical properties of the imidized PMDA-3,4′-ODA improved significantly when the precursor moleules were imidizing: among the improved properties, both high modulus and high glass transition temperature (T_g) (i.e. high degree of supercooling) in particular contributed significantly to the increase in residual stress. The evaporation of residual NMP solvent may also contribute to the increase in residual stress. Above ≈250°C, the residual stress again decreased gradually with increasing temperature, approaching zero. This decrease of the residual stress above ≈250°C might have been due to low or zero supercooling and low Young's modulus in spite of the relatively high thermal expansion coefficient. During subsequent cooling at 1.0 K min^{-1} after imidization at 400°C for 1 h, the residual stress again built up as the temperature decreased, as shown in *Figure 3*: it increased gradually from zero at 400°C to ≈45 MPa at 40°C.

Similar residual stress behaviour was observed for PMDA-4,4′-ODA isomer during imidization and subsequent cooling (see *Figure 4*). However, upon cooling, its

residual stress rose from zero at 400°C to ≈27 MPa at 40°C. The cooling run showed two maxima at 322–300°C and 191–168°C in the residual stress, as shown in *Figure 4*. The magnitude and location of these maxima were not reproducible. This phenomenon was more significant in PMDA-4,4′-ODA than in PMDA-3,4′-ODA. This behaviour is not yet clearly understood.

The stress variation during three-step cure and subsequent cooling was also monitored for the softbaked polyimide precursor isomer films. The results are shown in *Figures 5* and *6*. The curing steps were reflected in the stress–temperature profile. In *Figure 5*, the residual stress (≈22 MPa at 25°C) of the dried PMDA-3,4′-ODA precursor film decreased with increasing temperature, reaching zero at ≈105°C. The stress reappeared at 150°C and increased with time during isothermal imidization at this first step, reaching ≈14 MPa. The stress decreased slightly with further increasing temperature, but maintained a level of ≈5 MPa owing to the continuation of imidization. At 230°C for 30 min, the stress increased slightly as a result of isothermal imidization but then gradually decreased with increasing temperature, finally reaching zero at 400°C. During subsequent cooling at 1.0 K min^{-1} after the completion of thermal imidization at 400°C for 1 h, the stress of the cured polyimide film gradually increased and finally reached ≈48 MPa at room temperature. This stress behaviour during cooling was very similar to that observed for samples imidized in one step. Similar stress behaviour was observed for PMDA-4,4′-ODA isomer (see *Figure 6*).

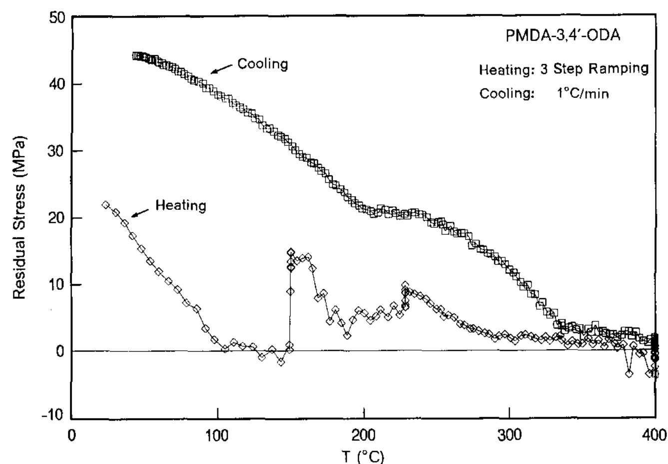

Figure 5 Residual stress variation of PMDA-3,4′-ODA on Si(100) wafer as a function of temperature: 'Heating', during imidization of the softbaked precursor polymer film by three-step cure; 'Cooling', during cooling of the polyimide film imidized fully by the three-step cure

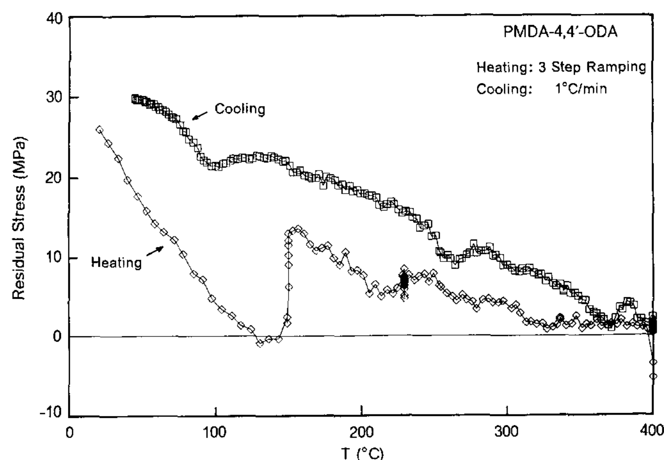

Figure 6 Residual stress variation of PMDA-4,4′-ODA on Si(100) wafer as a function of temperature: 'Heating', 'Cooling', as in *Figure 5*

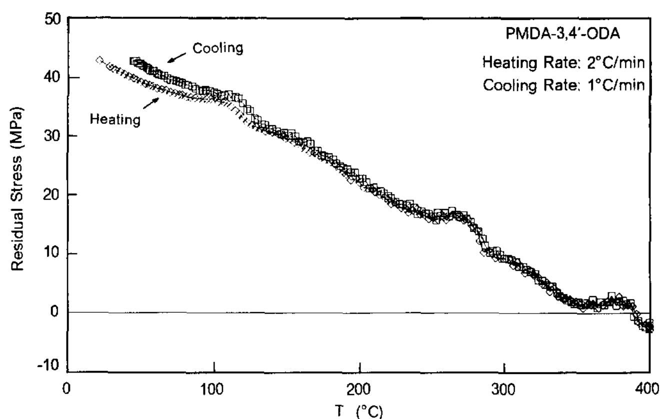

Figure 7 Residual stress *versus* temperature for the imidized PMDA-3,4′-ODA on Si(100) wafer during a thermal cycle (25–400°C)

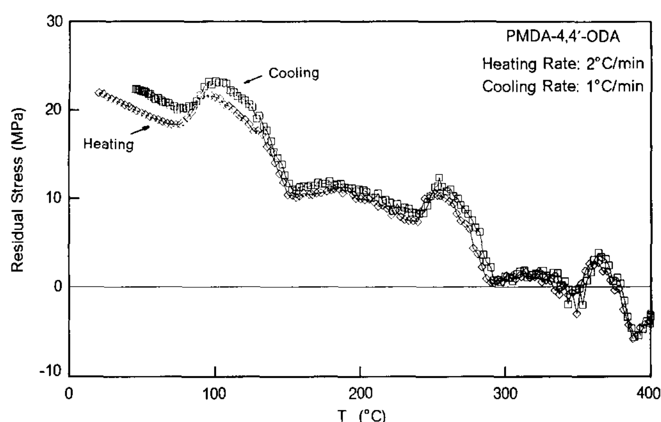

Figure 8 Residual stress *versus* temperature for the imidized PMDA-4,4′-ODA on Si(100) wafer during a thermal cycle (25–400°C)

Effects of thermal cycling and annealing on residual stress

The residual stress of the polyimide films thermally imidized may be sensitive to thermal cycling or annealing. For this reason, stresses were measured for both polyimides through a thermal cycle over 25–400°C, in which the heating and cooling rates were 2.0 and 1.0 K min^{-1}, respectively, and the soaking time at 400°C was 30 min. The results are shown in *Figures 7* and *8*. The stress behaviour as a function of temperature for both heating and cooling was identical except in the 25–150°C region. The difference in this region might have been due to moisture-induced stress relaxation. In fact, the imidized samples were exposed to atmosphere in the laboratory for 1 day before the thermal cycle run. Of course, stress relaxation may also have been a result of creep of the polyimide. However, the latter contribution to stress reduction is expected to be very small, owing to the high T_g of completely imidized samples[11].

In addition, the effect of thermal ageing on the stresses was studied. The polyimide samples were thermally aged at 400°C for 10 h in nitrogen. For these aged samples,

stress was measured again at room temperature, using the Lang X-ray camera. After annealing, the stress increased slightly, from 26.0 to 29.8 MPa for PMDA-4,4'-ODA, and from 48.5 to 53.0 MPa for PMDA-3,4'-ODA.

Adhesion of polyimides to Si wafer

In general, good interfacial adhesion between polymer film and substrate is essential in measuring residual stress of a polymer film with the aid of the bilayer technique. For this reason, peel tests were performed at room temperature, using an Instron tester equipped with an L-type sample holder for 90° peeling. The results are shown in *Table 1*. For both isomer films, adhesion to Si wafers primed with A1100 was excellent; the peel strength was 126.0–157.4 g mm^{-1} for PMDA-3,4'-ODA and 75.6–105.8 g mm^{-1} for the other isomer, depending upon peeling rate. As shown in *Table 1*, the peel strength increased with increasing peel rate.

It is well known that peel strength is also dependent upon the mechanical properties of a peeling layer[12]. Thus, in order to average out the variations due to the differences between the mechanical properties of the two isomer films, the film of some samples was composed of two polyimide layers, one of one isomer and the other of the other isomer, each 12 μm thick. For the single-layer film structure, the peel strength was 138.6–157.4 g mm^{-1} for PMDA-3,4'-ODA and 75.6–100.8 g mm^{-1} for PMDA-4,4'-ODA. On the other hand, for the double-layer structure, the peel strength was 126.0–143.0 g mm^{-1} for PMDA-3,4'-ODA and 93.2–105.8 g mm^{-1} for PMDA-4,4'-ODA. Overall, PMDA-3,4'-ODA isomer exhibited higher peel strength than did PMDA-4,4'-ODA.

Structure and properties

As discussed above, PMDA-3,4'-ODA polyimide exhibits a much higher residual stress than does the corresponding polyimide derived from the 4,4'-ODA isomer, despite their identical elemental composition. This large difference in the residual stresses may be due to the differences in their physical properties (i.e. thermal expansion coefficient, Young's modulus, etc.) and morphological structures (i.e. molecular chain orientation and molecular packing). For this reason, it was imperative to characterize these two materials with respect to wide-angle X-ray diffraction patterns, thermal expansion coefficients, mechanical stress–strain behaviour, and dynamic mechanical thermal properties.

For both isomeric polyimide films of ≈80 μm thickness, diffraction patterns were measured in both reflection and transmission geometry (see *Figures 9* and *10*). The patterns indicate that PMDA-3,4'-ODA polyimide exhibits a well-developed crystalline structure, whereas PMDA-4,4'-ODA does not. The morphological structure has been well characterized for PMDA-4,4'-ODA by Takahashi *et al.*[13] and for PMDA-3,4'-ODA by Ree *et al.*[14]. According to these studies, PMDA-3,4'-ODA polyimide molecules in the solid state are in the frozen smectic-E liquid-crystalline state, whereas the PMDA-4,4'-ODA molecules are in the frozen smectic-A state. Thus PMDA-3,4'-ODA polyimide exhibits a highly ordered molecular orientation and lateral packing based on an orthorhombic crystal unit cell with its fully extended pseudo-rodlike *trans* conformation chains. On the other hand, PMDA-4,4'-ODA shows only a molecular orientation along the chain axis, without any good lateral packing. The diffraction measurement in reflection geometry was extended to the thin films of ≈12 μm on wafers previously employed for the stress measurements. The results are shown in *Figures 11* and *12*. In *Figure 11* for PMDA-3,4'-ODA, three major strong peaks at

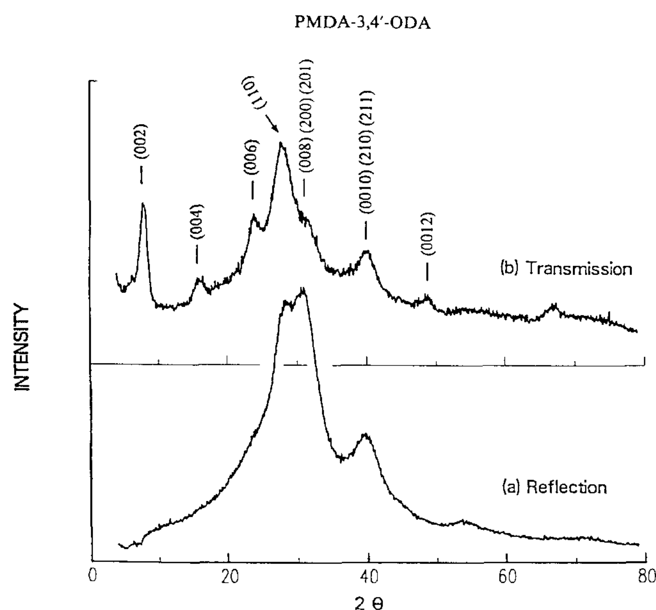

Figure 9 Wide-angle X-ray diffraction patterns of PMDA-3,4'-ODA polyimide in (a) reflection and (b) transmission. Peak indices are from Ref. 13. Film thickness ≈80 μm

Table 1 Adhesion of structural isomeric PMDA-ODA polyimides to silicon wafers as a function of peeling rate

	Peel strength (g mm^{-1})						
	Peeling rate (mm min^{-1})						
Wafer[a]	5.0	2.0	1.0	0.5	0.2	0.1	0.05
34'ODA-1	157.4	153.1	149.6	147.4	143.3	141.7	138.6
34'ODA-2	143.0	139.8	136.7	133.5	130.4	127.9	126.0
44'ODA-1	100.8	98.9	96.7	94.5	92.9	89.8	75.6
44'ODA-2	105.8	103.3	100.8	98.9	97.6	95.7	93.2

[a]Film layer structure on wafer:

34'ODA-1: PMDA-3,4'-ODA(24 μm)//A1100//silicon wafer (SW)
34'ODA-2: PMDA-4,4'-ODA(12 μm)/PMDA-3,4'-ODA(12 μm)//A1100//SW
44'ODA-1: PMDA-4,4'-ODA(24 μm)//A1100//SW
44'ODA-2: PMDA-3,4'-ODA(12 μm)/PMDA-4,4'-ODA(12 μm)//A1100//SW

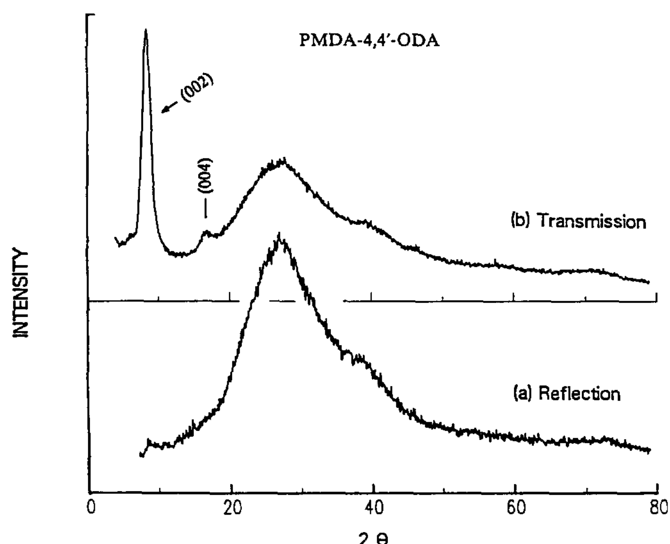

Figure 10 Wide-angle X-ray diffraction patterns of PMDA-4,4'-ODA polyimide in (a) reflection and (b) transmission. Film thickness ≈80 μm

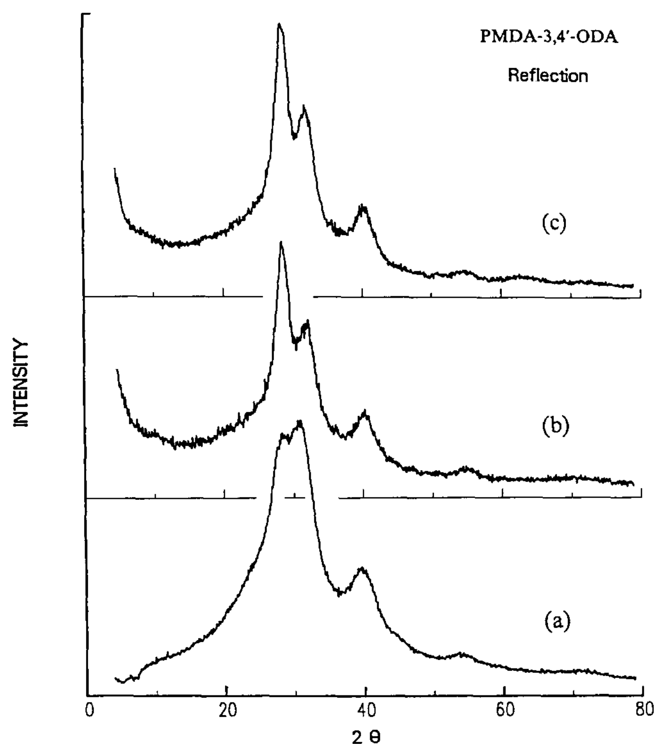

Figure 11 Wide-angle X-ray diffraction patterns of PMDA-3,4'-ODA in reflection: (a) ≈80 μm thick film, free-standing, cured at 400°C for 1 h; (b) ≈12 μm thick film on Si wafer, cured at 400°C for 1 h; (c) ≈12 μm thick film on Si wafer, annealed at 400°C for 10 h

25°–45° (2θ) appear to depend upon both film thickness and annealing at 400°C. In *Figure 11*, the three reflection peaks of (b) for the wafer-supported thin film are much stronger in intensity and much sharper in shape than those of (a). Of those peaks, the (110) peak of (b) is significantly enhanced in both intensity and shape in comparison with that of (a). These enhancements were further refined slightly by annealing at 400°C (see *Figure 11(c)*). These results indicate that the degree of molecular packing order is higher in thin films than in thick films and is further increased by annealing. In contrast to PMDA-3,4'-ODA, the reflection diffraction pattern of PMDA-4,4'-ODA was relatively insensitive to both film thickness and annealing. As shown in *Figure 12*, the diffraction patterns are dominated by the broad amorphous halo peak regardless of film thickness and annealing, indicative of inherently poor molecular packing in PMDA-4,4'-ODA polyimide.

Thermal expansion coefficients as a function of temperature are shown in *Figure 13*. The t.e.c. of PMDA-3,4'-ODA isomer was slightly lower than that of PMDA-4,4'-ODA, in spite of its higher residual stress. This result suggests that PMDA-3,4'-ODA polyimide chains are generally more extended in the solid state, particularly in the film plane, than are PMDA-4,4'-ODA chains. The reason is that the t.e.c. of a polymer primarily depends upon the polymer chain linearity[15]. As shown in *Figure 13*, the t.e.c.s of both isomers gradually increased with increasing temperature, indicating that their t.e.c.s with temperature are not linear even in the frozen state below T_g.

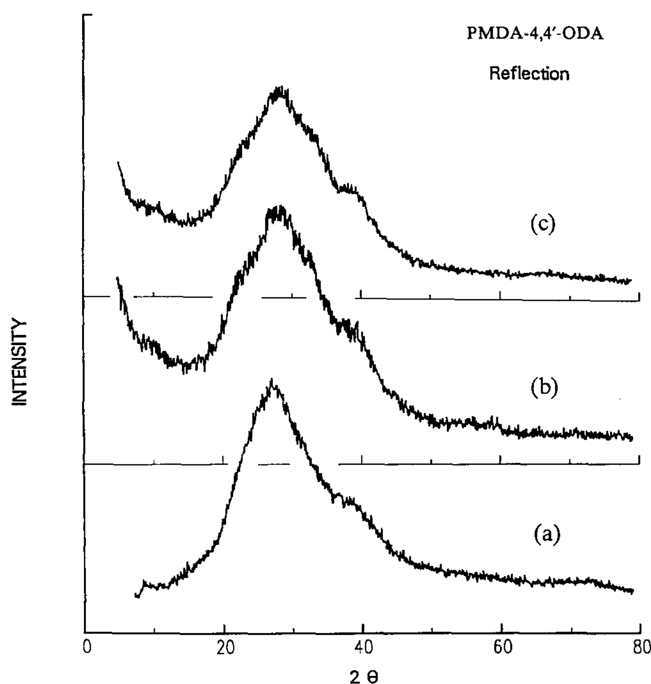

Figure 12 Wide angle X-ray diffraction patterns of PMDA-4,4'-ODA in reflection: (a), (b), (c), as in *Figure 11*

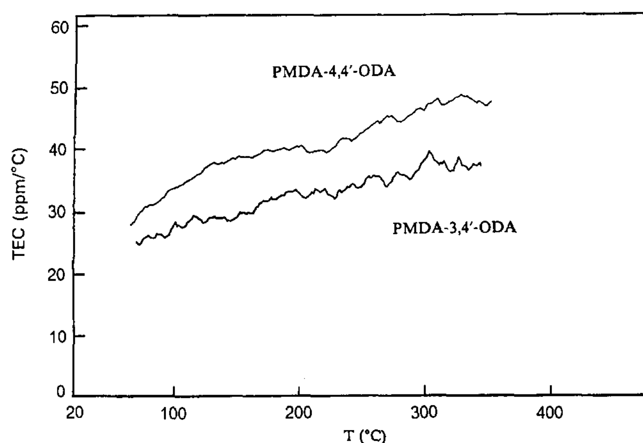

Figure 13 Thermal expansion coefficient (t.e.c.) variations of the isomeric PMDA-ODA polyimides over the temperature range 80–350°C. Heating rate 2.0°C min^{-1}

The mechanical properties, which were obtained by stress–strain measurements at room temperature, are summarized in *Table 2*. The Young's modulus was 3.0 GPa for PMDA-4,4′-ODA and 5.0 GPa for PMDA-3,4′-ODA. The latter isomer exhibited a typical yield behaviour (10% strain and 129.0 MPa stress at the yield point), whereas the former showed none. The tensile strength and elongation at break were 281.0 MPa and 83% for the former, and 235.6 MPa and 130% for the latter isomer. From the comparison of mechanical properties, one can expect that PMDA-3,4′-ODA has better drawability than PMDA-4,4′-ODA. Overall, the mechanical properties of PMDA-3,4′-ODA were superior to those of PMDA-4,4′-ODA. In addition, dynamic mechanical and thermal properties were measured at 10 Hz frequency and 10 K min^{-1} heating rate over the range 25–500°C. The results are shown in *Figure 14*. The storage modulus E' of PMDA-3,4′-ODA was always higher than that of PMDA-4,4′-ODA over the range 25–480°C. The glass transition temperature was ≈400°C for PMDA-4,4′-ODA and ≈475°C for PMDA-3,4′-ODA. PMDA-4,4′-ODA showed a relatively weak, broad glass transition, whereas PMDA-3,4′-ODA exhibited a much sharper phase transition. This indicates that below T_g the degree of molecular order is higher in PMDA-3,4′-ODA than in PMDA-4,4′-ODA. This is consistent with the results of the diffraction study.

Overall stress versus *thermal stress*

The overall stress measured in the present study consists of two major components: *thermal stress* and *intrinsic stress*[16]. In general the thermal stress of a polymer film on a substrate results from the different thermal expansion coefficients of the polymer film and the substrate, combined with Young's modulus and Poisson's ratio of polymer film and the difference (ΔT) between the final heat-treatment temperature (T_f) and the temperature prevailing during the measurement (T). On the other hand, the intrinsic stress arises generally from process-related factors such as film contamination and defects, thickness or volume reduction due to removing solvent, and incomplete structural ordering processes. In fact it is more difficult to understand the overall stress of a polymer system in which mass change and chemical reaction are involved during stress measurement. A good example is the imidization runs of the precursor films as shown in *Figures 3–6*. In this case, the stress measured during imidization results from mass (or volume) reduction by removing residual NMP and water (i.e. the by-product of the imidization reaction) and from the chemical structural change in addition to the film properties. The thermal stress σ_t was calculated only for both thermally cured isomeric polyimide films, using the following equation[16,17]:

$$\sigma_t = (\alpha_F - \alpha_S)E_F(T_f - T)/(1 - \nu_F) \qquad (3)$$

where T_f and T are the final temperature of film heat-treatment (or glass transition temperature of the polymer film if the final temperature is higher than the glass transition temperature) and the temperature of the curvature radius measurement, respectively; $\Delta T = T_f - T$.

In the thermal stress calculation the independently measured thermal expansion coefficients α and Young's moduli E were used. An α_S of 3×10^{-6} K^{-1} was employed for Si wafer substrate[18] and a Poisson's ratio

Table 2 Mechanical properties of structural isomeric PMDA-ODA polyimides[a]

	PMDA-4,4′-ODA	PMDA-3,4′-ODA
Modulus (GPa)	3.0	5.0
Tensile strength at break (MPa)	281.0	235.6
Elongation at break (%)	83	130
Tensile strength at yield (MPa)	–	129.0
Elongation at yield (%)	–	10

[a]Strain rate 0.2 min^{-1}

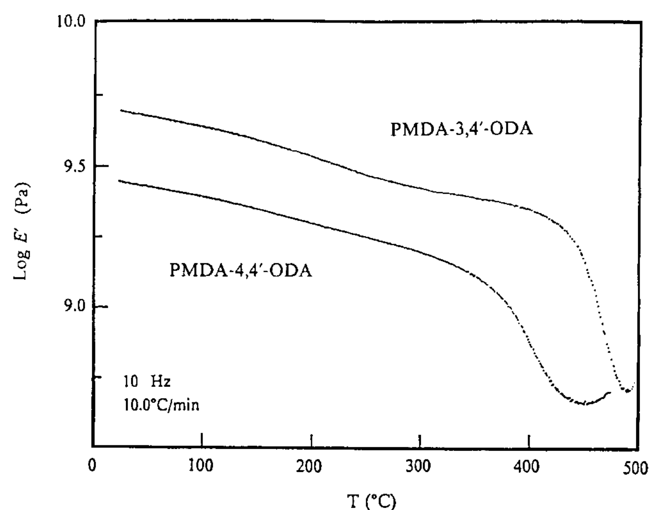

Figure 14 Variation in the dynamic storage modulus E' measured for isomeric PMDA-ODA polyimides as a function of temperature

Table 3 Comparison of calculated thermal stress with measured overall stress as a function of temperature

		PMDA-4,4′-ODA				PMDA-3,4′-ODA			
T (°C)	ΔT	α (10^{-6} K^{-1})	E (GPa)	σ_t (MPa)	σ_F (MPa)	α (10^{-6} K^{-1})	E (GPa)	σ_t (MPa)	σ_F (MPa)
70	330	29.50	2.79	37.0	27.4	25.11	4.66	51.5	41.1
100	300	33.94	2.65	37.3	25.6	28.33	4.39	50.5	36.9
150	250	38.89	2.39	32.5	21.9	29.44	3.95	39.6	30.9
200	200	40.72	2.13	24.4	18.1	32.78	3.45	31.1	25.6
250	150	43.22	1.92	17.6	14.1	35.00	2.99	21.8	18.9
300	100	47.22	1.70	11.4	8.8	38.89	2.70	14.7	10.3
340	60	47.89	1.46	6.0	5.8	37.67	2.53	8.0	5.4

of 0.34 was chosen for both isomers[19]. The results are listed in *Table 3* and compared with the measured overall stresses σ_F over the temperature range 70–340°C. For PMDA-4,4′-ODA, thermal stress σ_t varied from 37.0 MPa at 70°C to 6.0 MPa at 340°C, while its overall stress σ_F changed from 27.4 MPa at 70°C to 5.8 MPa at 340°C. For PMDA-3,4′-ODA, thermal stress varied from 51.5 MPa at 70°C to 8.0 MPa at 340°C, whereas the overall stress decreased from 41.1 MPa at 70°C to 5.4 MPa at 340°C. For both isomeric polyimides, the calculated thermal stresses varied with temperature in the same direction as did the overall stresses. The calculated thermal stresses were always higher than the overall stresses over the temperature range considered. The apparent overestimation of the thermal stresses might be caused both by uncertainties in the independent measurements of the physical parameters (α, E, and σ_F) and by the assumption of constant Poisson's ratios (ν_F and ν_S) independent of temperature. However, although the magnitudes of the calculated thermal stresses are unrealistically high, it is felt that any errors in their estimation are small. Thus, in comparison with the overall stress, it is clear that the thermal stress is the major component.

From the above examination, it is concluded that the measured overall residual stress for the two isomers is primarily due to the thermal stress. Here, the thermal stress is a function of t.e.c., ΔT, modulus E, and Poisson's ratio. PMDA-3,4′-ODA showed a slightly lower t.e.c., while PMDA-4,4′-ODA exhibited a significantly lower modulus. In the comparison with PMDA-4,4′-ODA, PMDA-3,4′-ODA exhibited a much higher stress despite its slightly lower t.e.c. Therefore it is obvious that the high stress in PMDA-3,4′-ODA isomer has been a result of the high modulus. In other words, the difference between the residual stresses of the isomeric polyimide films was mainly due to the difference between their Young's moduli.

CONCLUSIONS

The residual stresses of both PMDA-ODA precursor isomer films softbaked at 80°C for 1 h were 23–27 MPa at room temperature. The minor differences were caused by different degrees of drying. The residual stresses of these softbaked precursor films on Si wafers, profiled as a function of temperature during thermal imidization by a one-step or a three-step cure process from 25 to 400°C, reflected the type of cure process, and both isomers showed the same stress profile. However, the two isomeric films exhibited quite different stress behaviour during cooling from 400°C to room temperature after the imidization: the stress for PMDA-3,4′-ODA isomer increased rapidly, whereas that for PMDA-4,4′-ODA isomer rose gradually. During the additional thermal cycle over 25–400°C, each polyimide isomer showed the same stress–temperature profile in both heating and cooling between 150°C and 400°C. The deviation between the heating and cooling stress profiles of each isomer between 25°C and 150°C is attributed to moisture uptake in that temperature range. For both isomers annealed at 400°C for 10 h, the increase in the stresses was only 9.3–14.6% at room temperature. The results lead to the conclusion that the stresses of both isomeric polyimides are insensitive to the thermal cycle or thermal annealing.

The thermal stress calculated for both isomeric polyimides on the basis of the thermal expansion coefficient and Young's modulus showed the same trend *versus* temperature as observed for the measured overall stress *versus* temperature. However, for both polyimides the calculated thermal stress was slightly higher than the overall stress. From this comparison, it can be concluded that for both polyimides the overall residual stress results primarily from the thermal stress.

PMDA-3,4′-ODA isomer exhibited a slightly lower t.e.c. and a much higher Young's modulus than did PMDA-4,4′-ODA. Despite this slightly lower t.e.c., PMDA-3,4′-ODA showed a much higher stress than did PMDA-4,4′-ODA. Therefore the large difference between the stresses of the isomers was due to the large difference in their moduli. These properties of the isomeric polyimides correlate quite well with their morphological structure. In X-ray diffraction patterns in both reflection and transmission, PMDA-3,4′-ODA showed a well-developed crystalline structure, whereas PMDA-4,4′-ODA did not. The interfacial adhesion between polyimide film and primed Si wafer, as assessed by peel strength, was higher for PMDA-3,4′-ODA than for PMDA-4,4′-ODA. Overall, both isomers exhibited an excellent adhesion to the primed Si wafer.

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