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Effect of film formation process on residual stress of poly(*p*-phenylene biphenyltetracarboximide) in thin films

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Soluble poly(*p*-phenylene biphenyltetracarboxamine acid) (BPDA-PDA PAA) precursor, which was synthesized from biphenyltetracarboxylic dianhydride and *p*-phenylene diamine in *N*-methyl-2-pyrrolidone (NMP), was spin-cast on silicon substrates, followed by softbake at various conditions over 80–185°C. Softbaked films were converted in nitrogen atmosphere to be the polyimide films of *ca.* 10 μm thickness through various imidizations over 120–400°C. Residual stress, which is generated at the polymer/substrate interface by volume shrinkage, polymer chain ordering, thermal history, and differences between properties of the polymer film and the substrate, was measured *in situ* during softbake and subsequent imidization processes. Polymer films imidized were further characterized in the aspect of polymer chain orientation by prism coupling and X-ray diffraction. Residual stress in the polyimide film was very sensitive to all the film formation process parameters, such as softbake temperature and time, imidization temperature, imidization step, heating rate, and film thickness, but insensitive to the cooling process. Softbaked precursor films revealed 9–42 MPa at room temperature, depending on the softbake temperature and time. That is, residual stress in the precursor film was affected by the amount of residual solvent and by partial imidization possibly occurring during softbake above the onset of imidization temperature, *ca.* 130°C. A lower amount of residual solvent caused higher stress in the precursor film, whereas a higher degree of imidization led to lower stress. Partially imidized precursor films were converted to polyimide films revealing relatively high stresses. After imidization, polyimide films exhibited a wide range of residual stress, 4–43 MPa at room temperature, depending on the histories of softbake and imidization. Relatively high stresses were observed in the polyimide films which were prepared from softbaked films partially imidized and by rapid imidization process with a high heating rate. The residual stress in films is an in-plane characteristic so that it is sensitive to the degree of in-plane chain orientation in addition to the thermal history term. Low stress films exhibited higher degree of in-plane chain orientation. Thus, residual stress in the film would be controlled by the alignment of polyimide chains via the film formation process with varying process parameters. Conclusively, in order to minimize residual stress and to maximize in-plane chain orientation, precursor films should be softbaked for 30 min–2 h below the onset imidization temperature, *ca.* 130°C, and subsequently imidized over the range of 300–400°C for 1–4 h by a two-step or multi-step process with a heating rate of $\leqslant 5.0\,\mathrm{K\,min^{-1}}$, including a step to cover the boiling point, 202°C, of NMP. In addition, the final thickness of the imidized films should be <20 μm. © 1997 Elsevier Science Ltd.

(Keywords: polyimide; poly(amic acid) precursor; imidization)

INTRODUCTION

Aromatic polyimide is known to have excellent thermal stability, high chemical resistance, good mechanical properties, low dielectric constant, and easy processability[1–6]. For these advantageous properties, polyimide is widely used in the fabrication of microelectronic devices as interlayer dielectrics, passivation layers and alpha particle barriers[7,8]. Recently, most high performance microelectronic devices have been composed of multilayer structures in order to condense wiring of metal conductor lines into a compact size, consequently providing electrically high performance, in particular high signal propagation speed[7,8]. In this application, polyimide is commonly interfaced to itself as well as other device components, such as metals, silicons, ceramics, and plastic substrates. Sometimes, high residual stress is generated at the interfaces, causing reliability problems such as curl, bend, displacement, crack, and delamination. Therefore, the stress at all interfaces needs to be as low as possible to avoid the stress associated reliability problems.

In general, residual stress consists of two components, intrinsic stress and thermal stress[9–16]. The intrinsic stress

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results from volume shrinkage due to solvent loss, from molecular structural ordering during formation process, and perhaps from physical properties of the formed film[9–14]. That is, the intrinsic stress arises mainly from constraints on molecular movement by solvent and reaction byproduct loss and by imidization that freezes the polymer chain in a nonequilibrium state, having occurred during film formation[9–14]. A polymer film is commonly fabricated by applying its solution on to a substrate, followed by drying. During drying, the wet polymer film concentrates and its viscosity drastically increases due to solvent evaporation. The wet film starts to solidify when its viscosity reaches a gel point. Below gel point, the molecules in the film are mobile enough to flow and thus residual stress cannot be generated. However, above gel point the film is extremely viscous and its glass transition temperature (T_g) increases. The increase of viscosity and of T_g restrict the molecular motion, leading to a residual stress in the film. The shrinkage due to solvent evaporation takes place in the direction of the film thickness but is constrained in the direction of the film plane, because of the interfacial adhesion between the film and the substrate. Thus, residual stress develops in the film plane interfaced with the substrate.

On the other hand, thermal stress, which is the major contributor to the overall residual stress in polymer films treated at high temperature, in particular above T_g, is a function of the mechanical properties (particularly, Young's modulus E and Poisson's ratio ν), thermal expansion coefficient (TEC), and thermal history of the layers[14–16]. Thus, for interfaced layers, both matching of these properties and lowering heat-treatment temperature are necessary to minimize the thermal stress. In fact, the modulus of metals and inorganic substrates is much higher than that of polymers[17–19]. The Poisson's ratio generally varies in the range of 0.2–0.5, depending on materials such as metals, ceramics, and polymers[18–20]. The TEC of copper, which is commonly used in microelectric devices as a conductor, is 17–20 ppm $^{\circ}C^{-1}$ over 20–500°C, whereas that of ceramic and silocon substrates is 1–6 ppm °C[19]. In contrast to these materials, the TEC of polyimide films (or other polymers) varies from a few ppm $^{\circ}C^{-1}$ to hundreds ppm $^{\circ}C^{-1}$ [17–19].

In general, matching Young's moduli between polymer films and metals or substrates is very difficult because of their large gap, whereas matching their TECs sometimes achievable at limited temperature ranges due to the relatively large TEC window of polymers. The TEC of a polymer film is strongly dependent upon polymer chain rigidity and order as well as chain orientation: That is, the residual stress depends upon polymer rigidity, order and orientation[10,17,18,21–49]. Therefore, the stress at polymer/substrate or polymer/metal interfaces can be minimized by controlling the TEC of the polymer through the modification of polymer backbone and the control of molecular orientation.

The residual stress behaviour of a series of polyimides with various chain rigidities and orders have been previously studied[17,23]: poly(*p*-phenylene pyromellitimide) (PMDA-PDA), poly(*p*-phenylene biphenyltetracaboximide) (BPDA-PDA), poly(*p*-phenylene benzophenonetetracarboximide) (BTDA-PDA), poly(*p*-phenylene 4,4′-oxydiphthalimide (ODPA-PDA), poly(*p*-phenylene 4,4′-hexafluoroisopropylidenediphthalimide) (6F-PDA), poly(4,4′-oxydiphenylene pyromellitimide) (PMDA-ODA), and poly(4,4′-oxydiphenylene benzophenonetetracarboximide) (BTDA-ODA). Rigid polymers such as PMDA-PDA and BPDA-PDA showed relatively low stress, whereas flexible polymers exhibited high stress. Semi-flexible polymers revealed intermediate stress. The stress is dependent primarily on chain rigidity and secondarily on chain order[17].

The residual stress in films varies with film thickness, in addition to chain rigidity and order[10,23,46]. In general, for semi-flexible and flexible polymers the stress increased gradually with increasing film thickness[10,23,46]. For example, PMDA-ODA, which was slowly imidized at 400°C for 1–2 h, exhibited that the residual stress varied with film thickness to 33 MPa from 21 MPa over the thickness range of 1–85 μm. However, rigid polymers, such as PMDA-PDA and BPDA-PDA, exhibited a three-regime behaviour in stress-thickness profile, which is quite different from that of semi-flexible and flexible polymers. The stress varies insensitively in the low thickness region (*regime I*) as well as in the high thickness region (*regime III*) but varies very sensitively in the intermediate thickness region (*regime II*)[23]. For BPDA-PDA films slowly imidized at 400°C for 1–2 h, the stress was *ca.* 6.5 MPa for films of $\leqslant 20\,\mu$m thickness (*regime I*). However, the stress increased steeply with increasing thickness at $>20\,\mu$m (*regime II*) and levelled off at *ca.* 40 MPa at $\geqslant 40\,\mu$m thickness (*regime III*). The thickness dependence in the residual stress has been known to result from the variation of molecular in-plane orientation in the film due to the thickness variation[10,23,46].

The residual stress is further affected by imidization process parameters, such as heating rate and imidization temperature, in addition to the film thickness[10,46–49]. For semi-flexible PMDA-ODA, the residual stress at room temperature was *ca.* 40 MPa for the film imidized at 230°C for 2 h with a heating rate of 1.0 K min^{-1}, but *ca.* 57 MPa for the film at the same temperature with a heating rate of 10.0 K min^{-1} [47,48]. However, for films rapidly imidized at 350°C, the stress was 34 MPa[49]. These results indicate that the stress is relatively high in rapidly imidized films compared to slowly imidized films, and the high stress in the rapidly imidized films would be reduced by imidization at higher temperature. The stress in PMDA-ODA also depended on imidization temperature[49]. For slowly imidized films, higher imidization temperature gave slightly higher residual stress: 17 MPa for the film imidized at 300°C with a heating rate of 2.0 K min^{-1}, 19 MPa for one imidized at 350°C, 19 MPa for one imidized at 400°C, and 25 MPa for one imidized at 450°C[49]. Similar imidization temperature dependence in the stress was observed for rigid BPDA-PDA[46,49]. The stress was 2 MPa for the films slowly imidized at 300°C or 350°C but 10 MPa for one slowly imidized at 400°C[46,49]. This imidization temperature dependence of the stress is quite different from that observed in rapidly imidized films.

As described above, the residual stress behaviour in polyimides is very complex. That is, the residual stress, which is colligative property, including in-plane TEC and modulus, Poisson's ratio, and thermal history in addition to volume changes due to solvent and by-product loss and shrinkage due to solidification and chain ordering, is a function of chain rigidity, chain order, in-plane orientation, imidization reaction, and film thickness. For this reason, residual stress can be used

as a monitor in order to optimize film formation process including softbake and subsequent imidization process to maximize properties in performance. For BPDA-PDA polyimide, the investigation of its residual stress behaviour has been very limited instead of its practical importance in the microelectronic industry, in comparison to PMDA-ODA. Thus, in the present study, the stress behaviour of BPDA-PDA was investigated in detail in counting effects of film formation process parameters, such as softbake temperature and time, heating rate, imidization step and temperature, and cooling rate. All polyimide films were prepared on silicon substrates from the poly(amic acid) precursor solution in *N*-methyl-2-pyrrolidone (NMP) through a conventional spin-cast/dry/thermal imidization process. Residual stress in films was measured using the wafer bending technique. In addition, the refractive indices in the film plane as well as in the direction of film thickness were determined by prism coupling. The birefringence, which is a measure of molecular orientation, was estimated from the measured refractive indices. Wide-angle X-ray diffraction (WAXD) measurements were also performed for some films.

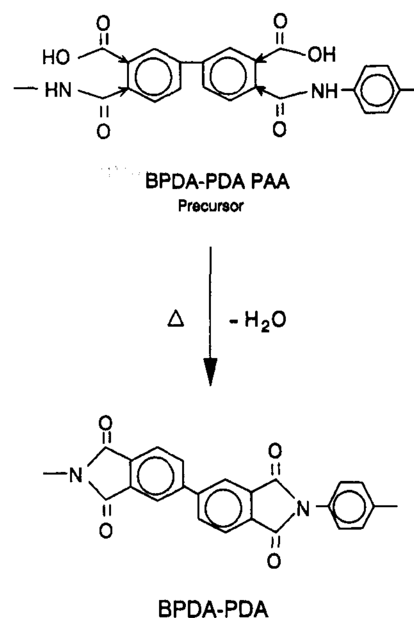


Figure 1 Chemical structures of BPDA-PDA and its poly(amic acid) used in this study

EXPERIMENTAL

Materials and film preparation

Biphenyltetracarboxylic dianhydride (BPDA) and *p*-phenylene diamine (PDA) used in this study were supplied from Chriskev Chemical Company (Leawood, Kansas, USA). The monomers were purified by sublimation under reduced pressure and then used for polymerization. Poly(*p*-phenylene biphenyltetracarboxamic acid) (BPDA-PDA PAA) was prepared in a glove box filled with dry nitrogen gas by slowly adding the sublimed BPDA to the purified PDA in dry *N*-methyl-2-pyrrolidone (NMP). Once the dianhydride addition was completed, the reaction flask was capped tightly and stirring was continued for an additional 2 days to make the polymerization mixture completely homogeneous. The molecular weight of poly(amic acid) precursor was controlled to be *ca.* 40 k $\bar{M}_w$ by stoichiometric imbalance of the monomers using the diamine in small excess. The solid content of precursor solution was 12 wt%. The precursor solution was filtered with silver metal membranes of 1.0 μm pore size, tightly sealed, and stored in a refrigerator before use.

Double side polished Si(1 0 0) wafers with 82.5 mm diameter and *ca.* 380 μm thickness were used as substrates because of their well known physical properties. These wafers were calibrated on a residual stress analyser to determine their initial curvatures before polymer coating. They were precleaned with NMP using a spin-coater, followed by drying on a hotplate of 80°C for a few minutes in ambient air. An adhesion promoter, 0.1 vol% γ-aminopropyltriethoxysilane solution in deionized water, was spin applied on the wafers at 2000 rpm/20 s, followed by drying at 115°C for 5 min in ambient air.

The BPDA-PDA PAA solution was spin coated on the primed Si(1 0 0) wafers and subsequently softbaked at various conditions. Softbaked BPDA-PDA PAA films, as shown in *Figure 1*, were thermally imidized in the hotstage of a stress analyser or a high temperature oven with nitrogen gas flow by various imidization processes over the range of 120–400°C (see *Tables 1–5*). The thickness of all polyimidine films was measured to be *ca.* 10 μm, using a Tencor alpha-stepper.

Residual stress measurements

Curvatures of a silicon wafer with and without a polymer film were measured using a Flexus stress analyser (Model 2-300) or a similar stress analyser made in our laboratory, which was equipped with a He–Ne laser and a hotstage in dry nitrogen gas atmosphere and controlled by a personal computer. Variations in the curvature of the silicon wafer due to the deposited film were measured during softbake and subsequent thermal imidization of the BPDA-PDA PAA precursor. In fact, in the measurement, variations of the angle θ between incident and reflected laser light beams were detected as shown in *Figure 2*. Each measurement for the angle θ requires only 1–5 s, consequently allowing the monitoring of residual stress *in situ* as a function of temperature and time. The distance x between the two beams was 6.0 cm. Therefore, the curvature R of the silicon wafer can be calculated from the angle and the distance $R = x/\theta$. Then, the residual stress (σ_F) of the film was calculated from the radii of the wafer curvatures measured before and after the film deposition using the equation[14,15]

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

Here, the subscripts F and S denote the polymer film and the silicon wafer substrate, respectively. The symbols E, ν, and t are the Young's modulus, Poisson's ratio, and thickness of each layer material, respectively. R_F and R_∞ are the radii of the wafer with and without a polyimide film, respectively. For Si(1 0 0) wafers[50], the biaxial modulus, $E_S/(1-\nu_S)$ is 1.805×10^5 MPa.

For the residual stress composed of intrinsic (σ_i) and thermal (σ_t) stress, the thermal stress component σ_t can be expressed by the equation[9,10,16,18,21]

$$\sigma_t = (\alpha_F - \alpha_S)(T_f - T)\frac{E_F}{(1-\nu_F)} \tag{2}$$

where thermal expansion coefficient α, final imidization temperature T_f ($T_f = T_g$ if glass transition temperature $T_g \leqslant T_f$), and stress measurement temperature T.

Refractive indices and birefringence measurements

For polyimide films, prism-coupling patterns were measured using a Metricon prism coupler (Model 2010) or a similar prism coupler made in our laboratory, which was equipped with a He–Ne laser light source of 632.8 nm wavelength and controlled by a personal computer (see *Figure 3*). Prism-coupling patterns were measured in transverse electric (TE) and transverse magnetic (TM) modes by choosing the appropriate polarization of the incident laser beam as described elsewhere[10,17,22–24,28,30,31,33–38,46,49,51–55]. The refractive index in the film plane, n_{xy} ($= n_{TE}$) was estimated from the prism-coupling pattern measured in the TE mode, whereas the refractive index in the out-of-plane, n_z ($= n_{TM}$) was calculated from the coupling pattern measured in the TM mode. All measurements were performed using a cubic zirconia prism of $n_{TE} = n_{TM} = 2.1677$ at a wavelength of 632.8 nm.

Polyimide films, which were spin-coated and imidized on silicon wafers, exhibited relatively higher refractive index in the film plane than the out-of-plane. In addition, the in-plane refractive index n_{TE} was isotropic within the film plane. Thus, the out-of-plane birefringence (Δ) in films, which is a measure of molecular in-plane orientation, was estimated from the measured refractive indices[17,23].

$$\Delta = n_{xy} - n_z \tag{3}$$

Wide-angle X-ray diffraction measurements

Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature in both reflection and transmission geometries, using a Rigaku horizontal diffractometer (Model D/MAX-200B) with a rotating anode X-ray generator. The CuK_α radiation source was operated at 50 kV and 40 mA. A divergence slit of one-degree was employed together with two receiving slits of 0.15° and 0.3°. All measurements were carried out in $\theta/2\theta$ mode. The 2θ scan data were collected at 0.02° intervals over the range of 3–60° and the scan speed was $0.4°(2\theta)\,\mathrm{min}^{-1}$. The measured WAXD profiles were corrected for background.

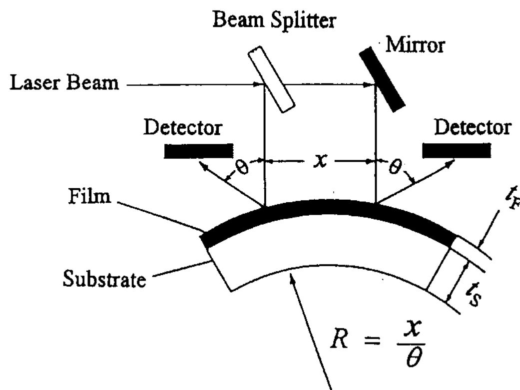


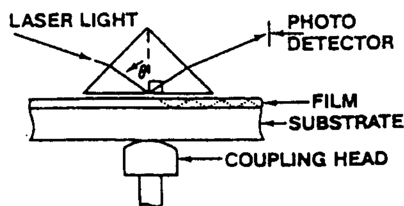
Figure 2 Schematic diagram of residual stress analyzer: R is the curvature of the silicon substrate, t_F is the thickness of the polymer film, and t_S is the thickness of the silicon substrate

RESULTS AND DISCUSSION

BPDA-PDA polyimide in films is well known as an excellent dielectric material with low residual stress and low TEC which are required in the fabrication of microelectronic devices[10,22,24–26,46,49]. However, those film properties are strongly dependent on the film thickness[22,23,56]. According to a previous study[23], a low level of residual stress is achievable for the polyimide films with a thickness of $\leqslant 20\,\mu$m. Furthermore, over this thickness range, the low stress did not vary sensitively with film thickness. For this reason, in the present study all polyimide films were prepared to have a final thickness of *ca.* 10 μm. The residual stress in all films was measured *in situ* during softbake and imidization in specially designed hotstages of residual stress analysers. All stress measurements were conducted in dry nitrogen atmosphere.

Effect of softbake

All precursor films spin-coated on the primed silicon wafers were first softbaked at 80°C for 30 min in atmosphere. The softbaked precursor films exhibited a residual stress of 18–21 MPa at room temperature, depending on the content of residual solvent. Some of the films were further baked over 100–185°C as shown in *Table 1*. During these bakes, variations in the film stress were *in situ* monitored as illustrated in *Figure 4*. *Figure 4a* shows that for a baking run of 100°C, residual stress gradually relaxed with increasing temperature to 9 MPa at 100°C from *ca.* 21 MPa at room temperature and then again increased to 22 MPa during soaking for 2 h at that temperature. In a subsequent cooling run, stress further increased and finally reached 38 MPa at room temperature. Consequently, the stress was increased by further removal of residual solvent from the film through the bake process. Similar stress–temperature profiles were observed for the films baked for 2 h at 120°C and 150°C (see *Figures 4b* and *c*). The film baked at 120°C exhibited 42 MPa at room temperature. This stress level was slightly higher than that of the film baked at 100°C.



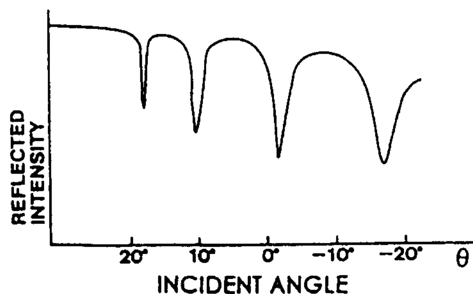


Figure 3 Schematic diagram of prism coupler (left) and typical prism-coupling pattern (right)

However, the film softbaked at 150°C revealed a stress of 30 MPa, which is relatively lower than those of the films baked at 100°C and 120°C. Furthermore, the film baked at 185°C for 2 h showed only 7.5 MPa at room temperature (see *Figure 4d*), which is much lower than those of the films baked over 100–150°C. In comparison, for the baked films, residual stress increased with increasing bake temperature over the range of <150°C, but decreased with increasing bake temperature over ⩾150°C.

In general, residual stress in cast precursor films sensitively depends upon the amount of residual solvent. Higher residual solvent gives lower stress in the film. In fact, softbaking at higher temperature removes more residual solvent from the film, resulting in large shrinkage in the thickness direction of and large increase in the T_g of the film adhered on the substrate which play critical roles to increase residual stress in the resultant film. In addition, higher temperature employed for softbaking produces larger thermal history term ($\Delta T =$

Table 1 Effect of softbake process on residual stress and optical properties in thin films of BPDA-PDA polyimide

Softbake process	Softbaked film[a] Residual stress at 25°C (MPa)	Polyimide film imidized at 400°C/1 h[b] Residual stress at 25°C (MPa)	Optical properties[c] n_{xy}	n_z	Δ
80°C/30 min	18–23	4	1.8549	1.6125	0.2424
80°C/30 min, 100°C/2 h	38	5	–	–	–
80°C/30 min, 120°C/2 h	42	8	–	–	–
80°C/30 min, 150°C/2 h	30	9	–	–	–
80°C/30 min, 185°C/2 h	9	9	–	–	–
80°C/30 min, 185°C/10 min	25	20	–	–	–
80°C/30 min, 185°C/2 min	27	34	–	–	–
115°C/2 min, 185°C/2 min	40	43	1.8247	1.6722	0.1525

[a] The thickness of the softbaked PAA films was 11–22 μm, depending on the softbake conditions
[b] All films were imidized by a step process: 150°C/30 min, 230°C/30 min, 300°C/30 min and 400°C/1 h with a ramping rate of 2.0 K min^{-1}. After imidization, all films were cooled with a rate of 1.0 K min^{-1} to room temperature. The thickness of the imidized films was *ca.* 10 μm
[c] Measured at 632.8 nm (i.e. 474.08 THz)

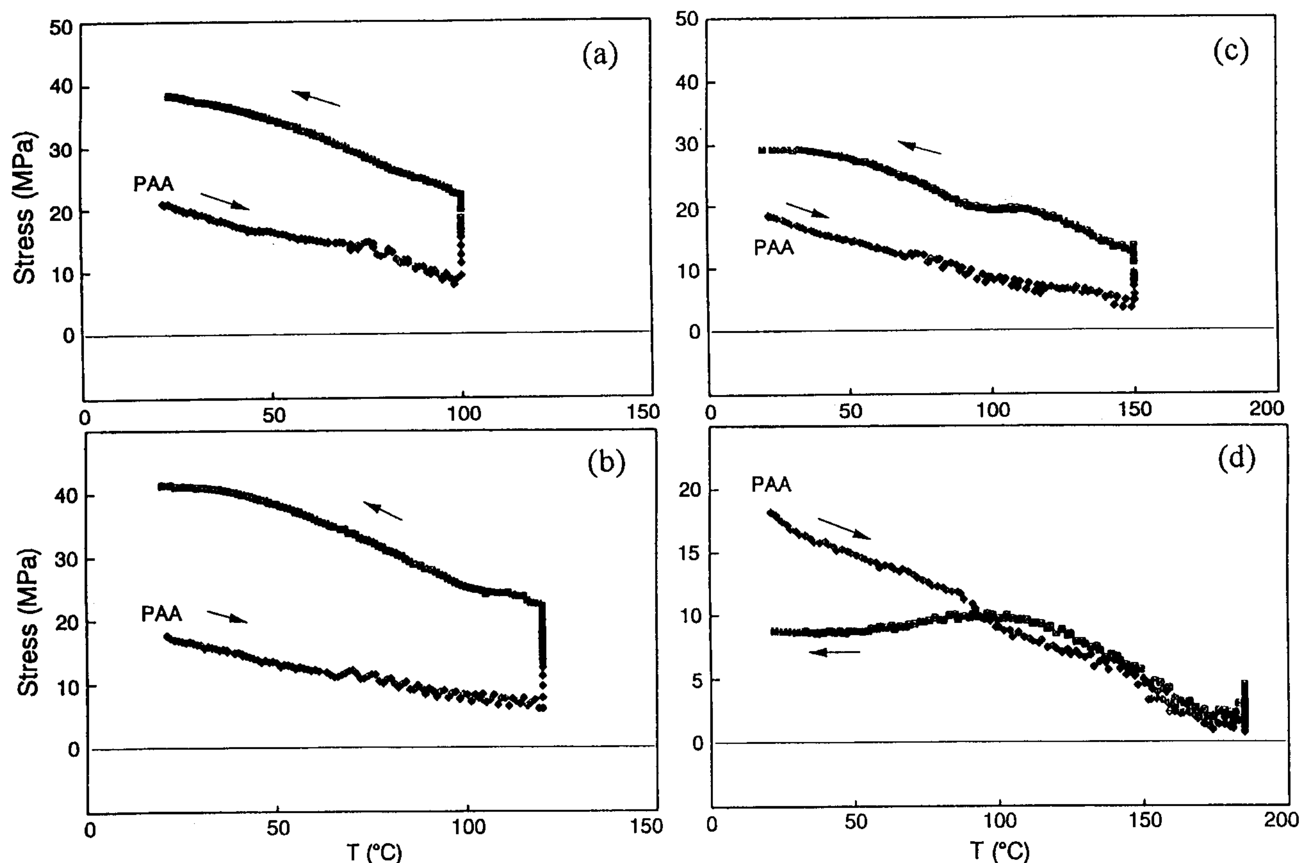


Figure 4 Residual stress variations with temperature in BPDA-PDA poly(amic acid) films measured *in situ* during softbake at various conditions after primarily softbaked at 80°C for 30 min: (a) 100°C for 2 h; (b) 120°C for 2 h; (c) 150°C for 2 h; (d) 185°C for 2 h. The heating and cooling rates were 2.0 K min^{-1} and 1.0 K min^{-1}, respectively

$T_f - T$) to the thermal stress component as illustrated in equation (2), consequently increasing the residual stress. Therefore, for films softbaked at higher temperature, higher stress might result from these contributions.

However, for films baked at ≥150°C, higher temperature softbaking produced relatively lower stress in the film. This might result from partial imidization occurring during softbaking. According to imidization studies of BPDA-PDA PAA precursor by dynamic i.r. spectroscopy and WAXD in the literature[57,58], the imidization started at *ca.* 130°C, and its conversion increased by elevating temperature and by increasing soaking time at a chosen temperature. In a heating run with a rate of 5.0 K min^{-1}, the degree of imidization was *ca.* 30% at 150°C, *ca.* 67% at 185°C, and finally reached 100% at ≥300°C[57]. From this result, the degree of imidization would be estimated to be >30% for the film baked at 150°C/2 h and >67% for the film baked at 185°C/2 h. The imidizations contributed to lower residual stress in the films.

The residual stress of softbaked films also depended upon the soaking time, in addition to the softbake temperature, because both amount of residual solvent and degree of imidization are a function of soaking time. For example, precursor films, which were first softbaked at 80°C for 30 min or 115°C for 2 min, were further baked at 185°C for various times. For these films, the stresses measured at room temperature are summarized in *Table 1.* The stress varied sensitively with soaking time: 9 MPa for the 2 h baked film, 25 MPa for the 10 min baked film, and 27 MPa for the 2 min baked film. These indicate that shorter baking time at 185°C gave higher residual stress in films. In fact, during the baking, both imidization and evaporation of residual solvent occur simultaneously. These contradict each other in contribution to the stress. That is, the imidization lowers stress, whereas the removal of residual solvent enhances stress. Therefore, these two factors contribute competitively to the residual stress.

Softbaked precursor films, which were prepared in various conditions as described above, were thermally converted in dry nitrogen atmosphere to the polyimide films through a four-step imidization process: 150°C/30 min, 230°C/30 min, 300°C/30 min, and 400°C/1 h with a ramping rate of 2.0 K min^{-1}. After the imidization, polyimide films were cooled to room temperature with a rate of 1.0 K min^{-1}. Stress measurements were performed *in situ* during the imidization and subsequent cooling process. Some of the stress–temperature profiles measured are shown in *Figures 5a–c.* The final stresses measured at room temperature are compared in *Table 1.* Despite all the polyimide films prepared by the same imidization condition, their stresses depended significantly on the softbake history.

For polyimide films prepared from the precursor films softbaked at various temperatures over 80–185°C, the residual stress at room temperature varied in the range of 4–43 MPa, depending on the softbake temperature and time. Softbakes below the onset temperature (*ca.* 130°C) of imidization led relatively low stress in the resultant polyimide film. Overall, higher softbake temperature caused relatively higher residual stress in the polyimide

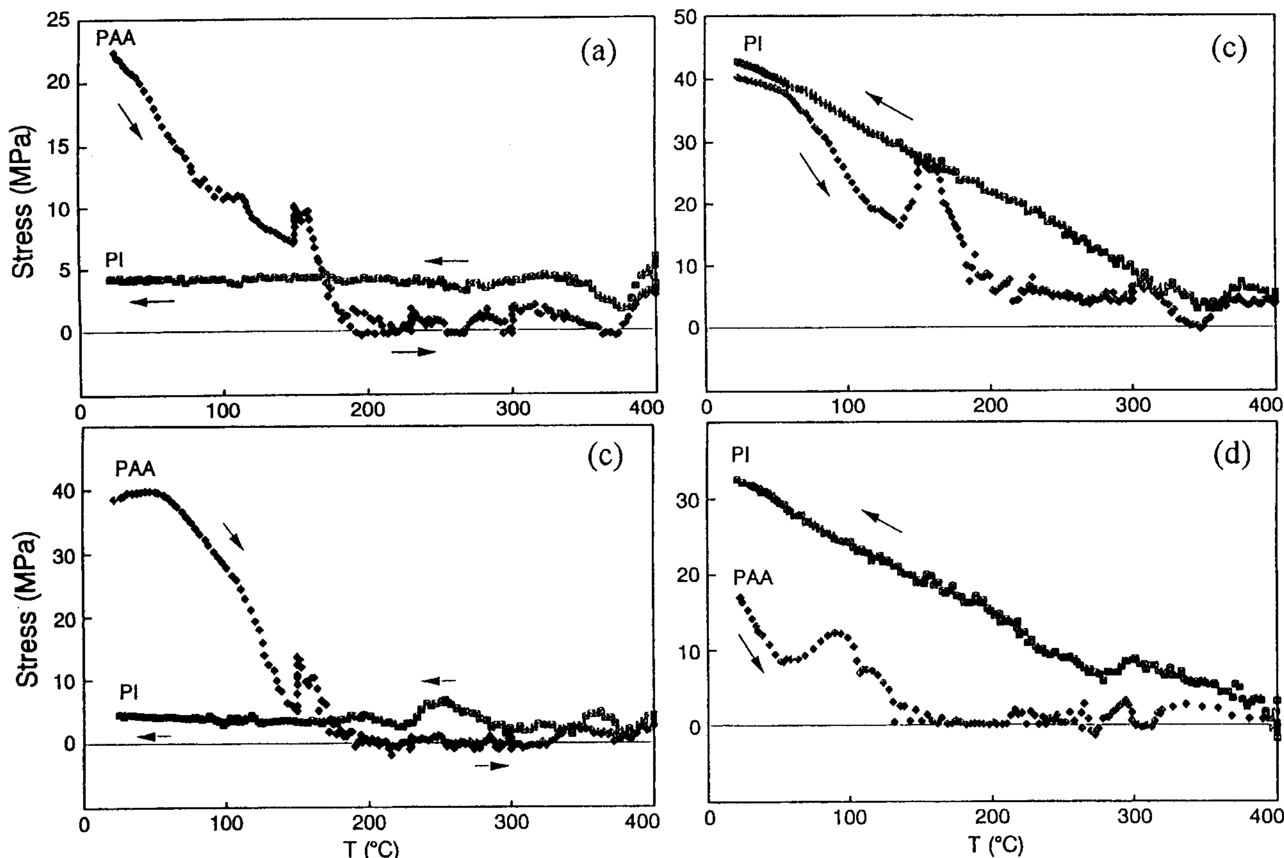


Figure 5 Residual stress variations with temperature in BPDA-PDA poly(amic acid) films measured *in situ* during imidization at 400°C after softbakes at various conditions: (a) 100°C for 2 h; (b) 120°C for 2 h; (c) 150°C for 2 h; (d) 185°C for 2 h. Here, all the precursor films were primarily softbaked at 80°C for 30 min. All the imidizations were conducted by a four-step process (i.e. 150°C 30 min, 230°C/30 min, 300°C/30 min and 400°C/1 h. The heating and cooling rates were 2.0 K min^{-1} and 1.0 K min^{-1}, respectively

film. However, softbakes above the onset temperature (*ca.* 130°C) of imidization led to relatively high stress. Overall, higher softbake temperature caused relatively higher residual stress in the polyimide film.

In particular, for films imidized from the precursor films softbaked at 185°C, residual stress widely varied over the range of 9–40 MPa, depending on the softbake time (see *Table 1*). Shorter softbake time caused higher stress in the resultant polyimide film. These stress results may relate to the degree of in-plane orientation of polymer chains partially imidized during softbake and its memory effect through the subsequent imidization process. Shorter softbake time may allow only lower conversion of imidization and lower removal of residual solvent in the cast precursor film. These circumstances would lead the partially imidized polymer chains to orient randomly rather than in the film plane, resulting in higher stress in the cast film. The randomly oriented polymer chains are then frozen by a subsequent cooling process after the softbake. The partially imidized chains with the random orientation may have a tendency to keep their random orientation during further imidization process. This tendency in the chain orientation plays as an obstacle in which polymer chains being imidized are oriented in the film plane under the unidirectional shrinkage in the direction of film thickness due to removal of residual solvent and of water byproduct during imidization, consequently leading to relatively low degree of in-plane chain orientation in the film. The low in-plane chain orientation causes high stress in the resultant film.

In contrast, a longer softbake time at 185°C causes relatively high conversion of imidization to allow the formation of a more rigid imide chain, in comparison to the full precursor chain, as well as large removal of residual solvent from the cast film to lead to high shrinkage in the out-of-plane. The high volume shrinkage in the out-of-plane leads the rigid polyimide chains or chain segments partially imidized to orient favourably in the film plane, consequently producing low stress in the baked film. The high in-plane orientation is further enhanced through the subsequent imidization, finally giving relatively low stress in the polyimide film.

In order to get information on polymer chain orientation, some of the fully imidized films were further characterized by prism coupling. Results are illustrated in *Table 1*. A polyimide film exhibited a low stress of 4 MPa, which was prepared by softbaking at 80°C/30 min and subsequent imidization at 400°C, revealed an in-plane refractive index (n_{xy}) of 1.8549 and an out-of-plane refractive index (n_z) of 1.6125, giving a relatively high out-of-plane birefringence (Δ) of 0.2424. On the other hand, a high stress film with 40 MPa, which was prepared by softbaking at 115°C/2 min and at 185°C/2 min and subsequent imidization at 400°C, 1.8247n_{xy} and 1.6722n_z, resulting in 0.1525Δ. In comparison, the high stress film showed relatively lower Δ than that of the low stress film. For positively birefringent BPDA-PDA polyimide in which the polarization is higher along the chain axis than in the direction normal to the chain axis, a high out-of-plane birefringence qualitatively means that the polymer chains are highly oriented in the film plane. Therefore, it is concluded that in the film, higher in-plane orientation of polyimide chains causes lower residual stress.

Molecular in-plane orientations in the films were further detected on WAXD patterns. The diffraction peaks in *Figure 6* were indexed in accordance to previous X-ray diffraction studies[32,59] which reported the orthorhombic crystal formation of BPDA-PDA with its highly extended chain conformation. For the low stress film, the transmission pattern, in which the diffraction vector is in the film plane, revealed multiple (0 0 *l*) peaks and other (*h k l*) peaks such as (1 1 0), (2 0 0) and (2 1 0) reflections, whereas the reflection pattern, in which the diffraction vector is in the out-of-plane, showed only (*h k l*) peaks without (0 0 *l*) peaks. The results indicate that the rigid BPDA-PDA polyimide chains were preferentially oriented in the film plane rather than randomly. In contrast, the high stress film exhibited a similar transmission pattern was observed for the low stress film. In the transmission pattern, the (0 0 *l*) peaks were relatively weakened in intensity, whereas the other (*h k l*) peaks were strengthened, in comparison to those of the low stress film. However, the reflection pattern was quite different from that of the low stress film. That is, the (0 0 4) peak appeared with a weak intensity and the (2 0 0) peak almost diminished in intensity. These results indicate that for the high stress film, the polyimide chains are oriented not only in the film plane but also in the out-of-plane. However, the population of polyimide chains oriented in the film plane is still higher than that of those oriented randomly or in the out-of-plane. Therefore, it is concluded that the molecular in-plane

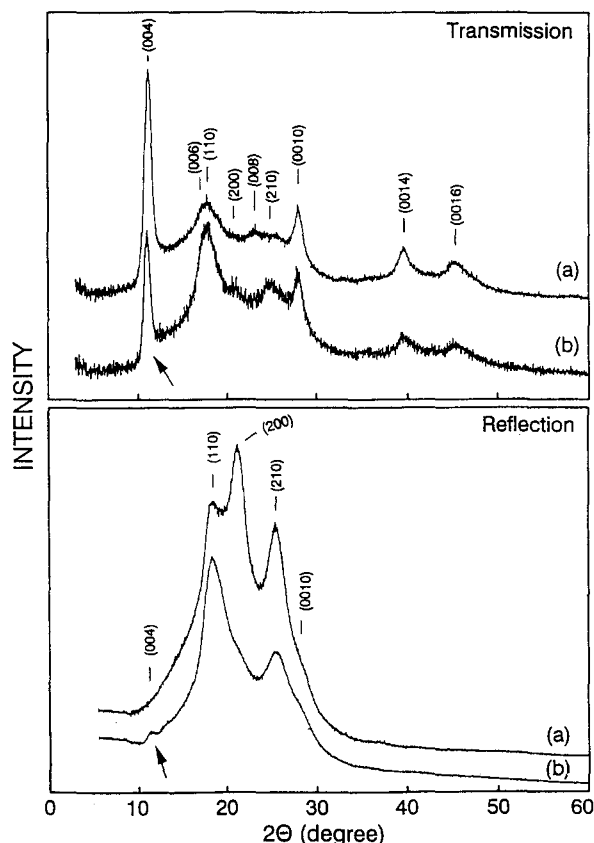


Figure 6 Transmission and reflection X-ray diffraction patterns of BPDA-PDA polyimide films imidized slowly by a four-step protocol (i.e. 150°C/30 min, 230°C/30 min, 300°C/30 min, and 400°C/1 h with a rate of 2.0 K min^{-1}) from precursor films softbaked at two different conditions: (a) precursor film softbaked at 80°C for 30 min; (b) precursor film softbaked at 115°C/2 min and 185°C/2 min. The CuK_α radiation source was used

orientation in the high stress film is relatively lower than in the low stress film.

Effect of imidization temperature

As mentioned in the previous section, softbaking at 80°C does not cause any partial imidization in the precursor film. Thus, all the cast precursor films were softbaked at 80°C for 30 min in order to avoid their partial imidization during the softbake. Subsequently, softbaked precursor films were thermally imidized through various imidization protocols as illustrated in *Table 2*. In imidizations, all precursor films were slowly heated with a rate of 2.0 K min^{-1} to a chosen temperature of imidization. Residual stress in films was measured *in situ* during the imidizations, as shown in *Figures 4b–d* and *Figure 7*. Residual stresses measured at room temperature, after the imidizations, are compared in *Table 2* as a function of final imidization temperature.

Table 2 Effect of final imidization temperature on residual stress and optical properties in thin films of BPDA-PDA polyimide[a]

Softbake	Final imidization temperature	Residual stress at 25°C (MPa)	Optical properties[b]		
			n_{xy}	n_z	Δ
80°C/30 min	120°C[c]	42	–	–	–
80°C/30 min	150°C[d]	30	–	–	–
80°C/30 min	185°C[e]	9	–	–	–
80°C/30 min	230°C[f]	6.5	1.8234	1.6211	0.2023
80°C/30 min	300°C[g]	3.5	1.8339	1.6204	0.2135
80°C/30 min	350°C[h]	3	1.8461	1.6187	0.2274
80°C/30 min	400°C[i]	4	1.8549	1.6125	0.2424

[a] The thickness of films imidized over 120–185°C was 11.5–15.5 μm; the thickness of films was imidized over 230–400°C was *ca.* 10 μm. After imidization, all films were cooled with a rate of 1.0 K min^{-1} to room temperature
[b] Measured at 632.8 mm (i.e. 474.08 THz)
[c] Imidized at 120°C/2 h with a heating rate of 2.0 K min^{-1}
[d] Imidized at 150°C/2 h with a heating rate of 2.0 K min^{-1}
[e] Imidized at 185°C/2 h with a heating rate of 2.0 K min^{-1}
[f] Imidized by a 2-step process: 150°C/30 min and 230°C/2 h with a heating rate of 2.0 K min^{-1}
[g] Imidized by a 3-step process: 150°C/30 min, 230°C/30 min and 300°C/1 h with a heating rate of 2.0 K min^{-1}
[h] Imidized by a 4-step process: 150°C/30 min, 230°C/30 min, 300°C/30 min and 350°C/1 h with a heating rate of 2.0 K min^{-1}
[i] Imidized by a 4-step process: 150°C/30 min, 230°C/30 min, 300°C/30 min and 400°C/1 h with a heating rate of 2.0 K min^{-1}

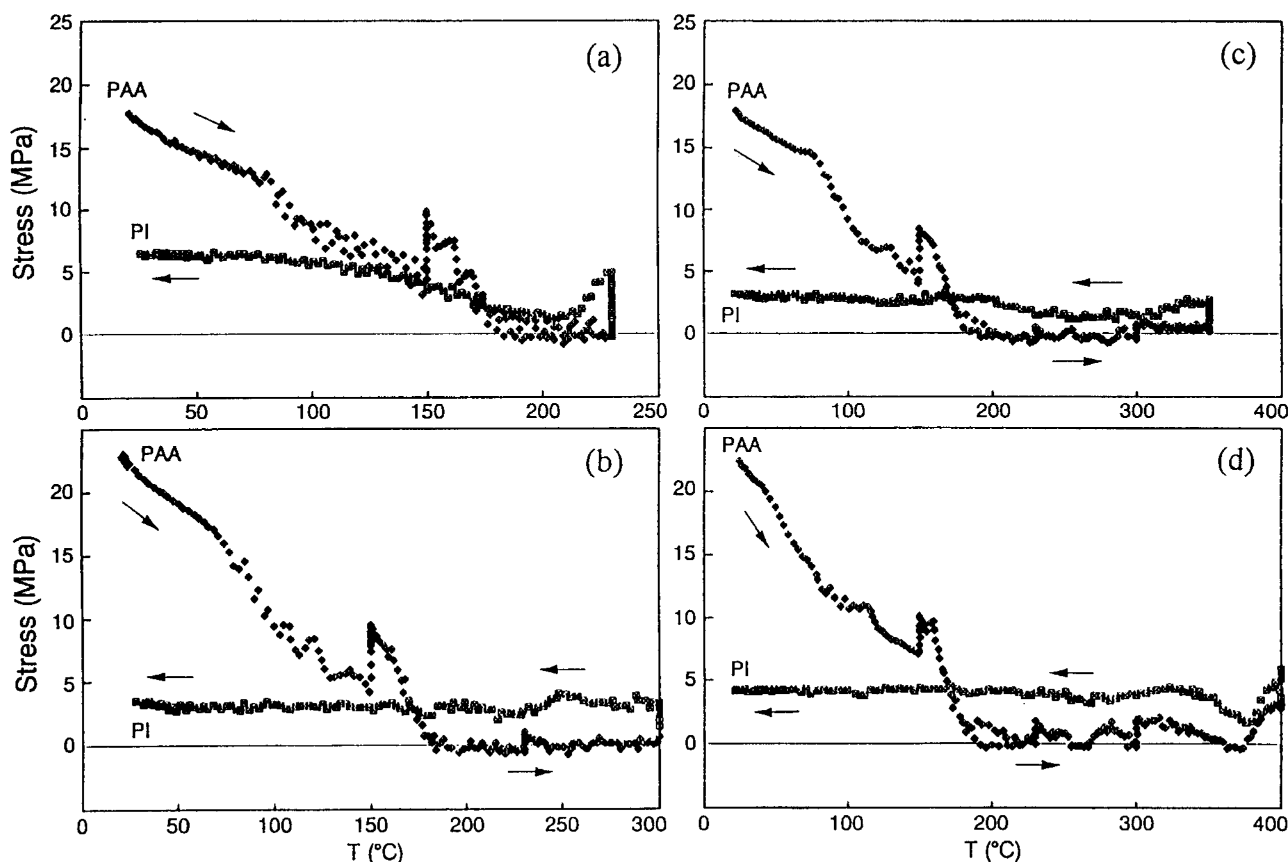


Figure 7 Residual stress variations with temperature in BPDA-PDA poly(amic acid) films measured *in situ* during imidization through various protocols after softbake at 80°C for 30 min: (a), 150°C/30 min and 230°C/2 h; (b), 150°C/30 min, 230°C/30 min and 300°C/1 h; (c), 150°C/30 min, 230°C/30 min, 300°C/30 min and 350°C/1 h; (d), 150°C/30 min, 230°C/30 min, 300°C/30 min and 400°C/1 h. The heating and cooling rates were 2.0 K min^{-1} and 1.0 K min^{-1}, respectively

For films imidized at ⩽230°C, residual stress varied in the range of 6.5–42 MPa, depending on the imidization temperature: 42 MPa for the film imidized at 120°C, 30 MPa for the film imidized at 150°C, 9 MPa for the film imidized at 185°C, and 6.5 MPa for the film imidized at 230°C. In fact, the high stress value in the film imidized at 120°C is a residual stress in the dried precursor film because its imidization is negligible at that temperature which is lower than the onset temperature of imidization. Furthermore, it might still contain *ca.* 20–30 wt% residual solvent by a strong interaction between the carboxylic acid group of the precursor and the tertiary amino group of NMP with a high boiling point of 202°C. Therefore, in this film, the residual stress is very sensitive to the amount of residual solvent which can lower T_g of the film and enhance precursor chain mobility in the film: lower amount of residual solvent gives higher residual stress in the film. However, when the softbaked films were heat-treated above the onset imidization temperature (*ca.* 130°C), imidization of the precursor chains occurs. During the imidization, precursor molecules are converted to partially or fully imidized rigid chains, whereas residual solvent molecules are detached from the precursor chains and evaporated out from the film. At the same time water, which is the imidization byproduct, is evaporated out. Furthermore, the fully or partially imidized polymer molecules are involved in chain ordering. Consequently, all these cause a volume shrinkage in the direction of film thickness. This unidirectional shrinkage leads the orientation of polymer chains in the film plane. The conversion of imidization increases with increasing temperature, leading to higher molecular in-plane orientation. Therefore, lower stress in the film which was imidized at higher temperature results from higher in-plane chain orientation generated by higher imidization conversion accompanied with larger volume shrinkage. In particular, the film imidized at 230°C exhibited a relatively low stress of 6.5 MPa. However, this stress level is still higher than that of films imidized at >230°C. This might result from incomplete imidization and removal of residual solvent at 230°C.

In contrast, for films imidized at ⩾300°C, residual stress varied very little with the imidization temperature, as compared in *Table 2* and *Figure 7*: that is, all the films exhibited a low stress of 3–4 MPa. According to Pryde's *FT*i.r. spectroscopic study[57], BPDA-PDA PAA precursor completely imidized above *ca.* 290°C when the precursor film was thermally heated to 400°C with a rate 5.0 K min^{-1}. Therefore, the low film stresses measured might result from high in-plane orientations of fully imidized polymer chains and complete removal of residual solvent and reaction byproduct achieved during the imidizations.

In addition, measurements of refractive indices and birefringence were performed for low stress films. Results are compared in *Table 2.* Birefringence varied in the range 0.2023–0.2420, depending upon the imidization temperature. The film imidized at 230°C revealed a slightly low birefringence of 0.2023. Even for films imidized over the range 300–400°C, which showed almost the same level of stress, 3–4 MPa, the birefringence was gradually increased to 0.2420 from 0.2135 by elevating imidization temperature. This indicates that the in-plane orientation of polyimide chains is more favourable in the film imidized at higher temperature. The high in-plane chain orientation might lead to lower in-plane TEC which is a critical parameter to the thermal stress component. However, the high in-plane chain orientation increases Young's modulus, which is another parameter to the thermal stress. In addition, the higher temperature imidization should result in a high value in the thermal history term, $\Delta T [= (T_f - T)]$ [see equation (2)]. These three parameters contribute competitively to the thermal stress: that is, low TEC decreases the thermal stress, whereas both high modulus and thermal history term increase it. Therefore, the apparent independence of imidization temperature in the stresses of the films, which were imidized over 300–400°C, would result from the mixed roles of these three parameters which are correlated to the in-plane chain orientation and the imidization temperature.

Effect of heating rate

Precursor films, which were softbaked at 80°C for 30 min, were thermally imidized with various heating rates. With a one-step imidization process, precursor films were directly heated to 400°C with various ramping rates and soaked for 4 h at that temperature. After imidization, polyimide films were cooled down to room temperature with a rate of 1.0 K min^{-1}. Residual stresses measured at room temperature are summarized in *Table 3.* The residual stress in polyimide films depended sensitively upon the heating rate: 33 MPa for the film imidized with a rate of 30 K min^{-1}, 25 MPa for one imidized with 26 K min^{-1}, 17 MPa for one imidized with 12.5 K min^{-1}, 9 MPa for one imidized with 10.0 K min^{-1}, and 8 MPa for one imidized with 2.0 K min^{-1}.

Table 3 Effect of heating rate on residual stress and optical properties in thin films of BPDA-PDA polyimide prepared by single step imidization process[a]

1-Step imidiziation processes with various heating rates	Residual stress at 25°C (MPa)	Optical properties[b]		
		n_{xy}	n_z	Δ
25°C $\xrightarrow{30\ \mathrm{K\,min^{-1}}}$ 400°/4 h	33	1.8415	1.6419	0.1996
25°C $\xrightarrow{26\ \mathrm{K\,min^{-1}}}$ 400°/4 h	25	1.8384	1.6370	0.2014
25°C $\xrightarrow{12.5\ \mathrm{K\,min^{-1}}}$ 400°/4 h	17	1.8416	1.6310	0.2106
25°C $\xrightarrow{10.0\ \mathrm{K\,min^{-1}}}$ 400°/4 h	9	1.8418	1.6219	0.2199
25°C $\xrightarrow{2.0\ \mathrm{K\,min^{-1}}}$ 400°/4 h	8	1.8536	1.6137	0.2215

[a] All precursor films were softbaked at 80°C/30 min. After imidization, all films were cooled with a rate of 1.0 K min^{-1} to room temperature. The thickness of the imidized films was *ca.* 10 μm

[b] Measured at 632.8 nm (i.e. 474.08 THz)

the film plane. The orientation of chains or segments imidized is possibly fixed in the film because the film would be frozen by elevating its T_g due to the imidization. This chain orientation, which is far from the in-plane orientation, would not be healed completely by subsequent imidization at higher temperature, that is, 400°C, so that fully imidized chains are poorly oriented in the film plane. The low in-plane orientation causes high residual stress in the film.

In contrast, when a precursor film was slowly heated to 230°C and followed by soaking at that temperature, precursor molecules slowly imidize above 130°C, the onset imidization temperature, and at the same time, water byproduct and residual solvent detached from the precursors being imidized and evaporated out. These evaporations lead volume shrinkage in the direction of film thickness, causing the polymer chain imidized or being imidized to be oriented in the film plane. The tendency of the in-plane chain orientation is further enhanced by subsequent imidization at higher temperature, 400°C, with a slow heating rate. Consequently, a high in-plane chain orientation is produced in the film, resulting in low residual stress.

Effect of the imidization step

Precursor films, which were prepared by softbaking at 80°C for 30 min, were imidized at 400°C by various step imidization protocols (see *Table 5*). The first group of precursor films were directly heated up to 400°C with a rate of 2.0 K min^{-1} and imidized for 2 h at that temperature: that is, they were imidized by a single-step process. The second group of precursor films were imidized by a two-step process: 230°C/30 min and 400°C/2 h with a ramping rate of 2.0 K min^{-1}. The final group of films were imidized by a four-step process: 150°C/30 min, 230°C/30 min, 300°C/30 min, and 400°C/2 h with a ramping rate of 2.0 K min^{-1}. After cooling with a rate of 1.0 K min^{-1}, stresses measured at room temperature are compared in *Table 5*.

The films imidized by the single-step process exhibited a stress of 8 MPa and a birefringence of 0.2215, whereas the films imidized by both the two-step and the four-step processes revealed stresses of 4 MPa and birefringences of 0.2424–0.2426. Conclusively, multi-step processes, including an imidization step of 230°C, provide lower residual stress and higher in-plane chain orientation in the polyimide film than single-step process, even though the same heating rate is used. However, for films prepared by multi-step processes with a chosen heating rate, including an imidization step of 230°C, film properties are insensitive to the number of steps used in the imidization.

Effect of cooling rate

Precursor films softbaked at 80°C were imidized at 400°C by the four-step process as illustrated in *Table 6*. After imidization, some of the polyimide films were slowly cooled with a rate of 1.0 K min^{-1} to room temperature. The other polyimide films were quenched to room temperature. Residual stresses and birefringences of the polyimide films were measured at room temperature. All the polyimide films revealed the same stress level, 4 MPa. In addition, their birefringences were almost the same, 0.2424–0.2422. From these results, it is concluded that film properties, such as residual stress and birefringence are not affected by variations in the subsequent cooling process, once precursor films are imidized by a chosen imidization process.

CONCLUSIONS

Residual stress–temperature profiles of BPDA-PDA PAA precursor and its polyimide in thin films were measured *in situ* during softbake and subsequent imidization in various conditions. Polymer films imidized were characterized by prism coupling and X-ray diffraction.

For precursor films softbaked over 80–185°C, residual stress varied in the range 9–42 MPa at room temperature, depending on the amount of solvent remaining and the degree of imidization occurring in the film. A low level of residual solvent in the film causes a high stress in the film, because removal of solvent from the film constrains the mobility of polymer chains and increases

Table 5 Effect of imidization step on residual stress and optical properties in thin films of BPDA-PDA polyimide[a]

Imidization processes	Imidization steps	Residual stress at 25°C (MPa)	Optical properties[b]		
			n_{xy}	n_z	Δ
400°C/2 h	1	8	1.8536	1.6137	0.2215
230°C/30 min, 400°C/2 h	2	4	1.8556	1.6130	0.2426
150°C/30 min, 230°C/30 min, 300°C/30 min, 400°C/2 h	4	4	1.8549	1.6125	0.2424

[a] All precursor films were softbaked at 80°C/30 min. During imidization, a rate of heating between steps was 2.0 K min^{-1}. After imidization, all films were cooled with a rate of 1.0 K min^{-1} to room temperature. The thickness of the imidized films was *ca.* 10 μm

[b] Measured at 632.8 nm (i.e. 474.08 THz)

Table 6 Effect of cooling rate on residual stress and optical properties in thin films of BPDA-PDA polyimide[a]

Imidization processes	Cooling rate	Residual stress at 25°C (MPa)	Optical properties[b]		
			n_{xy}	n_z	Δ
150°C/30 min, 230°C/30 min, 300°C/30 min, 400°C/2 h	1.0 K min^{-1}	4	1.8549	1.6125	0.2424
150°C/30 min, 230°C/30 min, 300°C/30 min, 400°C/2 h	Quenched	4	1.8552	1.61390	0.2422

[a] All precursor films were softbaked at 80°C/30 min. During imidization, a rate of heating between steps was 2.0 K min^{-1}. The thickness of the imidized thickness of the imidized films was *ca.* 10 μm

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In contrast, when a precursor film was slowly heated to 230°C and followed by soaking at that temperature, precursor molecules slowly imidize above 130°C, the onset imidization temperature, and at the same time, water byproduct and residual solvent detached from the precursors being imidized and evaporated out. These evaporations lead volume shrinkage in the direction of film thickness, causing the polymer chain imidized or being imidized to be oriented in the film plane. The tendency of the in-plane chain orientation is further enhanced by subsequent imidization at higher temperature, 400°C, with a slow heating rate. Consequently, a high in-plane chain orientation is produced in the film, resulting in low residual stress.

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Precursor films, which were prepared by softbaking at 80°C for 30 min, were imidized at 400°C by various step imidization protocols (see *Table 5*). The first group of precursor films were directly heated up to 400°C with a rate of 2.0 K min^{-1} and imidized for 2 h at that temperature: that is, they were imidized by a single-step process. The second group of precursor films were imidized by a two-step process: 230°C/30 min and 400°C/2 h with a ramping rate of 2.0 K min^{-1}. The final group of films were imidized by a four-step process: 150°C/30 min, 230°C/30 min, 300°C/30 min, and 400°C/2 h with a ramping rate of 2.0 K min^{-1}. After cooling with a rate of 1.0 K min^{-1}, stresses measured at room temperature are compared in *Table 5*.

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Effect of cooling rate

Precursor films softbaked at 80°C were imidized at 400°C by the four-step process as illustrated in *Table 6*. After imidization, some of the polyimide films were slowly cooled with a rate of 1.0 K min^{-1} to room temperature. The other polyimide films were quenched to room temperature. Residual stresses and birefringences of the polyimide films were measured at room temperature. All the polyimide films revealed the same stress level, 4 MPa. In addition, their birefringences were almost the same, 0.2424–0.2422. From these results, it is concluded that film properties, such as residual stress and birefringence are not affected by variations in the subsequent cooling process, once precursor films are imidized by a chosen imidization process.

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[a] All precursor films were softbaked at 80°C/30 min. During imidization, a rate of heating between steps was 2.0 K min^{-1}. After imidization, all films were cooled with a rate of 1.0 K min^{-1} to room temperature. The thickness of the imidized films was *ca.* 10 μm
[b] Measured at 632.8 nm (i.e. 474.08 THz)

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[a] All precursor films were softbaked at 80°C/30 min. During imidization, a rate of heating between steps was 2.0 K min^{-1}. The thickness of the imidized films was *ca.* 10 μm
[b] Measured at 632.8 nm (i.e. 474.08 THz)

the T_g of the film. When precursor films are softbaked above *ca.* 130°C, the onset imidization temperature, imidization partially occurs, depending on the softbake temperature and time. Higher softbake temperature and longer softbake time result in higher degree of imidization, causing lower residual stress in the film. The lower stress in the film might be due to the favourable amount of in-plane orientation of the imidized polymer chains or chain segments made under relatively higher volume shrinkage in the direction of film thickness.

Residual stress in polyimide films was very sensitive to all parameters of softbake and imidization processes. When a cast precursor film was dried at a temperature in which imidization was not involved, the residual stress in the final polyimide films was insensitive to the softbake history. Otherwise, the residual stress in the polyimide film varies sensitively with the parameters of the softbake process, namely, softbake temperature and time. That is, the orientation of the polymer chains or chain segments, which are imidized during softbaking, would not be completely healed by subsequent imidization and consequently affect the final chain orientation in the polyimide film, reflecting into the residual stress. Therefore, cast precursor films should be softbaked below the onset temperature of imidization, *ca.* 130°C for a proper time (for example, 2 h or less, depending on temperature). Imidization temperature also influences the residual stress of polyimide film. Residual stress varied sensitively with the imidization temperature for films imidized over the range of <300°C. However, for films imidized over 300–400°C, residual stress varied little with the imidization temperature. The residual stress of polyimide films was influenced significantly by the heating rate employed in the imidization process. Higher heating rate caused higher residual stress. The residual stress was further affected by the imidization steps. Multi-step imidizations, including a step to cover the b.p. of the used solvent, provided lower stress in the film than the single-step imidization process. Including a step to the b.p. (202°C) of the used NMP solvent, only two steps in the imidization process are good enough to provide a low level of residual stress. One example of two-step processes consists of 230°C/30 min and 400°C/2 h with a ramping rate of $<5.0\,\mathrm{K\,min^{-1}}$. In this case, a slow heating rate for the first step, 230°C, is critical in order to lower the level of residual stress in the film.

However, once a precursor film was imidized, the residual stress in the resultant polyimide film was not influenced by the cooling process. That is, both slow cooling and quenching processes gave the same level of stresses in the films.

Residual stress in films, which is an in-plane characteristic is sensitive to the degree of in-plane chain orientation, in addition to the thermal history. Low stress films exhibited higher degree of in-plane chain orientation. Thus, controlling the residual stress in the film is consequently the subject of how the polyimide chains are preferentially aligned in the film plane through all process conditions including coating, softbaking and imidization.

Therefore, in order to minimize film stress, BPDA-PDA PAA precursor should be softbaked below the onset imidization temperature, *ca.* 130°C for <2 h, depending on the softbake temperature, and subsequently imidized over the range of 300–400°C for 1–4 h by a two-step or multi-step process with a heating rate of $<5.0\,\mathrm{K\,min^{-1}}$, including a step to cover the b.p. of the used solvent. After imidization, films would be cooled as convenient. The final thickness of the imidized films should be $<20\,\mu\mathrm{m}$[22]. In particular, the imidization has to be conducted under oxygen free condition in order to avoid oxidation of the polymer at high temperature. Otherwise, BPDA-PDA polyimide films are no longer low stress dielectric materials.

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