Anisotropic properties of high-temperature polyimide thin films: Dielectric and thermal-expansion behaviors

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Multilayer poly(*p*-phenylene biphenyltetracarboximide) (BPDA-PDA) polyimide films of 172 μm total thickness (11.4 μm per layer) were prepared from the poly(amic acid) precursor solution through repetition of a spin-coat/softbake/cure process. Wide-angle x-ray diffraction results indicate that the polyimide molecules in the multilayer films are highly ordered along the chain axes as well as in the lateral direction and furthermore are highly oriented in the film plane as observed in a single-layer film of 11.4 μm thickness. The multilayer films showed the same dynamic mechanical properties and glass transition behavior ($T_g = 330\,^\circ\mathrm{C}$) as a single-layer film. For the multilayer films both the in-plane dielectric constant (ϵ'_{XY}) and out-of-plane thermal-expansion coefficient (α_Z) were measured using time-domain spectroscopy and conventional thermal mechanical analysis, respectively. The ϵ'_{XY} at room temperature was 3.69 (± 0.08) over a frequency range of 0.35–2.50 THz. A similar ϵ'_{XY} is predicted at frequencies of <0.35 THz. In contrast to the ϵ'_{XY}, a relatively lower out-of-plane dielectric constant (ϵ'_Z) was observed: $\epsilon'_Z = 2.96$–3.03 (± 0.02) at 1 MHz, depending on moisture content in the film. The dielectric loss ϵ''_Z at 1 MHz was 0.011–0.014 (± 0.001), depending on moisture content. The measured α_Z was 74 ppm/°C over the temperature range of 25–150 °C, which was much higher than $\alpha_{XY} = 2.6$–5 ppm/°C. Consequently, large anisotropic ϵ' and α have been observed in the in plane and out of plane of the thermally imidized BPDA-PDA films. The anisotropic ϵ' and α were caused by high in-plane orientation of the polyimide molecules highly ordered along the chain axes in the films.

I. INTRODUCTION

Recently, organic polymer materials have become of interest to the microelectronics industry as insulators in microelectronic devices, owing to their relatively low dielectric constant and easy processability.[1,2] In particular, polyimides, which exhibit high-temperature stability, excellent dielectric properties, excellent mechanical properties, and high chemical resistance, have been widely used as interlevel dielectric layers in the fabrication of semiconductor chips and multichip packaging structures.[1,2] For these applications of a dielectric material, low dielectric constant and low (or zero) interfacial stress are highly desirable for making high-performance devices with excellent reliability. First, the dielectric properties of the material play an important role in the performance of a device since the dielectric constant and dissipation factor influence the signal carrying capacity and propagation speed of the device. A material having a low dielectric constant and a low dissipation factor allows faster signal propagation with less attenuation since the signal propagation speed is inversely proportional to the square root of the dielectric constant of the dielectric material.[1] Second, a dielectric polymer layer in a device is generally interfaced to itself as well as a number of different materials, such as silicon, silicon nitride, silicon oxide, aluminium, copper, chromium, tungsten, ceramic, and so on. At these interfaces, low (or zero) residual stress and high adhesion strength are necessary to avoid reliability problems due to interfacial mechanical failure (displacement, bending, curling, warping, cracking, or delamination), which often occurs because of high stress and weak adhesion. In general, the residual stress at an interface is generated by the mismatch between physical properties of the interfacial layers. The stress is initially generated by the intrinsic stress of the polymer chains constrained through the film formation process (i.e., coating of its solution and drying or curing), and significantly increased by the mismatched thermal-expansion coefficients (TECs) between the layers through thermal cycles. The stress due to the mismatched TECs is further built up by the mismatch between the other physical properties of the layers, such as Young's modulus and Poisson's ratio.

For many microelectronic applications, a representative polyimide is poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA) derived from the condensation polymerization of pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA).[3] This polyimide has been extensively characterized since it was introduced in the early 1960s by Du Pont Chemical Company.[4] This polyimide film is known to have 35 ppm/°C TEC (below 150 °C), about 27 MPa residual stress on silicon wafers, 3.5ϵ' (dielectric constant) at 1 MHz, about 3.0 GPa Young's modulus, and about 100% elongation at break.[5,6] That is, this material has relatively good physical properties for device applications. Another important class of polyimides is poly(*p*-

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phenylene biphenyltetracarboximide) (BPDA-PDA) prepared from the condensation polymerization of biphenylenetetracarboxylic dianhydride (BPDA) and *p*-phenylene diamine (PDA). This polymer film has been reported to have 2–10 ppm/°C TEC (below 150 °C), roughly 7 MPa stress on silicon wafers, 2.9–3.1 ϵ' at 1 MHz, about 10.0 GPa modulus, and about 40% elongation at break.[6,7] Overall, the latter polyimide exhibits superior physical properties to those of the former. For this reason, BPDA-PDA polyimide is currently more attractive for microelectronic applications. In the fabrication of microelectronic devices these polyimdes are usually used as thin films, which are prepared by coating (spin coating, spray coating, or doctor-blade coating) and subsequent drying/curing. For thin polyimide films (usually less than 100 μm), most properties (namely TEC, residual stress, and mechanical properties) have been characterized extensively in the direction of the film plane because of the difficulty of characterizing thin films in the direction of film thickness.[3,6,7] On the other hand, the dielectric properties of thin films have been measured mostly in the direction of the film thickness because of the ease of sample preparation.[3,6]

Because of the lack of experimental measurements, as noted above, we have investigated the out-of-plane TEC and the in-plane dielectric properties of BPDA-PDA polyimide thin films using multilayer films, which were prepared from its poly(amic acid) precursor solution by repeated spin-coat/softbake/cure processes. The TEC and dielectric properties were measured by thermal mechanical analysis and time-domain spectroscopy, respectively. In addition, the out-of-plane dielectric properties and the in-plane dynamic mechanical thermal properties were investigated for single-layer, as well as multilayer, BPDA-PDA films, using a capacitance technique and a dynamic mechanical thermal analyzer. The molecular order and orientation were also investigated with respect to the in plane, as well as the out of plane, of films, by means of wide-angle x-ray diffraction.

II. EXPERIMENT

A. Material and sample preparation

Poly(*p*-phenylene biphenyltetracarboxamic acid) (BPDA-PDA PAA) precursor solution in N-methylpyrrolidone (NMP) (Pyralin PI-2611) was received from Du Pont Chemical Company. The solution was stored in a refrigerator at about 5 °C before use.

Single-side-polished silicon wafers of 127 mm diameter and 0.6 mm thickness were precleaned for 5 min in an oxygen plasma asher (Plasmaline 515, Tegal Corporation) operated at 300 and 535 cm^3/min oxygen flow rate. In the present study, two different types of polyimide film samples were prepared: single-layer and multilayer films. First, single-layer films were prepared for the studies of dynamic dielectric and mechanical properties. Gold or aluminium films were evaporated on some of the precleaned wafers in a metal evaporator operated in vacuum. The BPDA-PDA PAA solution was spin coated at 1700 rpm/30 s on either metallized wafers or precleaned blank wafers and was then softbaked in a convection oven at 80 °C for 30 min. The softbaked precursor films were thermally cured in a Heraeus oven with nitrogen flow (oxygen level of $<$10 ppm) through a step-cure process (i.e., 150 °C/30 min, 230 °C/30 min, 300 °C/30 min, and 400 °C/1 h). Then, after cure, the samples were cooled in the oven with the power off. The thickness of the cured films was about 11.4 μm. Several evaporated metal electrodes of 1.0–5.0 mm diameter were made by the metal evaporation on the top surface of the cured polyimide films on the metallized wafers. These samples were used to measure the out-of-plane dielectric properties, whereas the films prepared on the blank wafers were used to measure the dynamic mechanical and thermal properties. Second, multilayer film samples were prepared on adhesion-primed wafers through repetition of a single-layer film formation process. An adhesion promoter, 0.1 vol % A1100 (γ-aminopropyltriethoxy silane) in deionized (DI) water, was spin applied on the wafers at 2000 rpm/20 s and dried for 10 min in air. The BPDA-PDA PAA solution was applied on the A1100-primed wafers, softbaked at 80 °C for 30 min, and thermally imidized through the step-cure process described above. Then, the cured film samples were treated in the oxygen plasma asher operated at a mild condition (i.e., 150 W and 535 cm^3/min) for 3 min, in order to modify the top surface of the cured film for improving their adhesion to the next film layer. The polyimide precursor solution was again applied on the top of the first polyimide layer with the modified surface, softbaked in the convection oven at 80 °C for 30 min, and followed by the step-cure process. This multilayer film fabrication process was repeated 13 times to make 15-layer films with roughly 170 μm total thickness. Finally, the multilayer films were removed from the wafers by immersion in dilute aqueous hydrofluoric acid for 1–3 days. The removed films were washed several times with DI water and dried in a vacuum oven (about 1 mm Hg) at 50 °C for 1 day. These multilayer films were used for measurements of in-plane dielectric properties and out-of-plane thermal expansion.

B. Dielectric properties

THz time-domain spectroscopy (TDS) was used to measure the in-plane dielectric properties of the BPDA-PDA polyimide films. Although the THz-TDA technique and applications have been previously reported in detail,[8] they will be briefly reviewed here. With this technique two electromagnetic pulse shapes are measured, the input and the propagated pulse, which has changed shape due to its passage through the sample under study. Consequently, via Fourier analyses of the input and propagated pulses, the frequency-dependent absorption and dispersion of the sample can be obtained. The following THz-TDS measurements were performed by measuring subpicosecond, freely propagating THz electromagnetic pulses transmitted through the multilayer film under investigation. These transmitted pulses were then compared to the measured THz pulses with no sample in place. For the actual measurement a free-standing multilayer BPDA-PDA film of

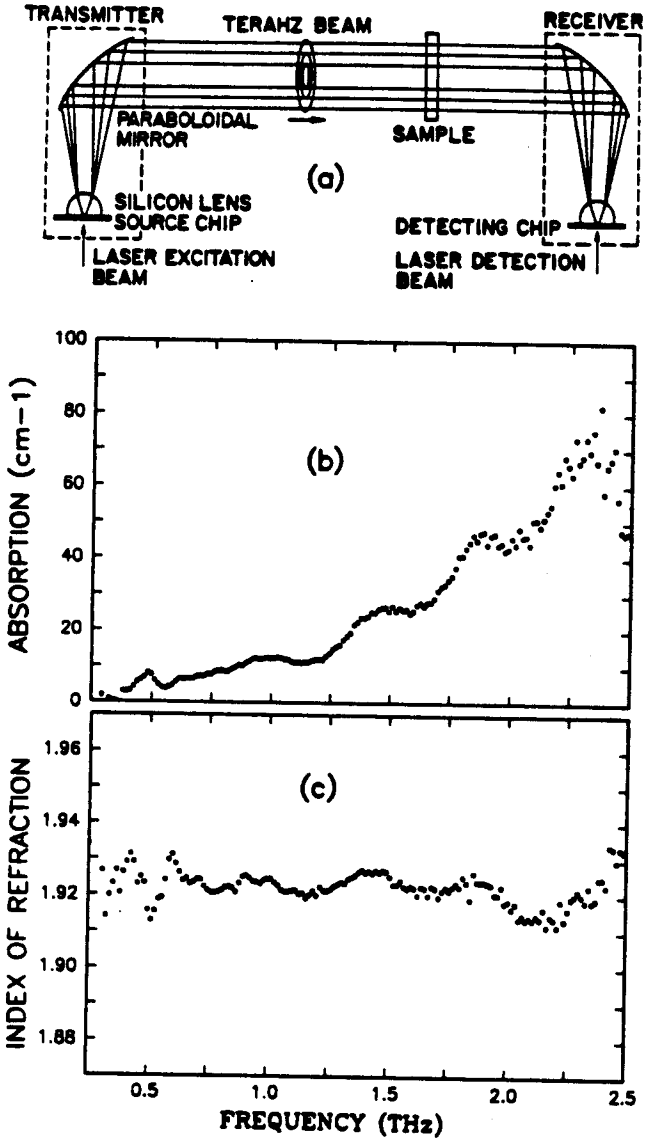

FIG. 1. (a) The optoelectronic THz beam system used for THz-TDS; (b) the measured power absorption (cm^{-1}) of a 15-layer BPDA-PDA film as a function of frequency; (c) the measured index of refraction of a 15-layer BPDA-PDA film as a function of frequency.

dimension 5 cm×5 cm×170 μm was mounted on a sample holder with a 1.5 cm diameter for the transmitted THz beams. This smaller aperture was used to minimize the effect of thickness variations across the film sample. The measurements over the frequency range of 0.35–2.50 THz were performed in a dry nitrogen enclosure.

The setup used to generate and detect the short pulses of THz radiation is depicted in Fig. 1(a) and has been described earlier.[8] Similar transmitting and receiving antennas, consisting of micrometer-sized dipole antennas imbedded in coplanar transmission lines, were optoelectronically driven by 60 fs pulses from a colliding-pulse mode-locked (CPM) dye laser. The generated pulses of THz radiation are collimated by a silicon lens attached to the transmitting chip and directed onto a paraboloidal mirror that recollimates the radiation into a beam directed towards the receiver, where it is focused onto the receiving antenna. The electric field of the focused incoming THz radiation induces a transient bias voltage across the 5 μm gap between the two arms of this receiving antenna, directly connected to a low-noise current amplifier. The amplitude and time dependence of this transient voltage is obtained by measuring the collected charge (average current) versus the time delay between the THz pulses and the CPM laser detection pulses.

The out-of-plane dielectric properties were measured using multifrequency LCR meters (Hewlett-Packard models 4275A and 4192A and a Polymer Laboratories DETA dynamic dielectric analyzer) equipped with hot stages and controlled by IBM PC/AT computers. The dielectric property measurements were performed over the temperature range of 25–200 °C. The frequency range was 100 kHz–4 MHz. Single-layer films of 10–12 μm thickness were used together with gold or aluminium electrodes of 1.0–5.0 mm diameter.

C. Thermal-expansion coefficient

A DuPont Instrument Model 943 thermal mechanical analyzer (TMA) with a compression probe was used in order to measure the out-of-plane thermal-expansion coefficient (*Z*-TEC) of BPDA-PDA polyimide films. The multilayer polyimide films of roughly 170 μm total thickness were cut into specimens of 1×1 mm^2 using a precision polymer film cutter. The specimen was placed on the sample holder equipped with an oven and annealed at 300 °C for 10 min under nitrogen flow and subsequently cooled to 25 °C before measurement. *Z*-TEC (α_Z) measurements of the annealed samples were performed during heating up to 400 °C. The heating rate was 5.0 K/min and the loading was 0.1 g.

D. Dynamic mechanical and thermal properties

The dynamic mechanical properties (storage modulus E' and loss modulus E'') were measured in nitrogen ambient over the temperature range of 25–500 °C, using a tensile-head-equipped dynamic mechanical thermal analyzer (DMTA; Mark-II, Polymer Laboratories) controlled by an IBM PC/AT computer. The heating rate and frequency were 5.0 K/min and 10 Hz, respectively.

E. Wide-angle x-ray diffraction

Wide-angle x-ray diffraction (WAXD) measurements were conducted at room temperature in both reflection and transmission geometries using a Rigaku B/Max horizontal diffractometer with a rotating anode x-ray generator. All measurements were performed in $\theta/2\theta$ mode. The Cu$K\alpha$ radiation source was operated at 40 kV and 40 mA. The 2θ scan data were collected at 0.02° intervals over the range of 3°–60°. The scan speed was 0.4°/min. One half-degree defining slit was used together with two receiving slits of 0.15° and 0.30°. The measured transmission WAXD spectra were corrected for background, whereas the reflection WAXD spectra were not.

III. RESULTS AND DISCUSSION

A. In-plane dielectric properties

Time-domain spectroscopic (TDS) measurements were made on a 15-layer BPDA-PDA polyimide film. This multilayer sample was oriented with the plane perpendicular to the beam of THz pulses as indicated in Fig. 1(a), except that the sample was placed at the midpoint between the two mirrors. Consequently, the THz electromagnetic radiation was polarized parallel to the film plane and was thereby sensitive to the in-plane dielectric properties of the film. A 1.5-cm-diam aperture defined the area of the measured film. This aperture was used to limit the thickness variations across the sample. These thickness variations of ±4 μm are the largest source of error in the index of refraction measurements. The thickness nonuniformity resulted from the complicated fabrication procedure for the 15-layer film.

The measured power absorption coefficient in cm^{-1} is presented in Fig. 1(b). Here, the absorption increases monotonically with frequency to relatively high values; although, for electronic applications below 1 THz, the absorption of a thin film would be insignificant. Even though the étalon resonances were numerically removed from the data, there still remains a slight oscillation due to their effect, because of the thickness nonuniformity. The excellent signal-to-noise (S/N) ratio of the measurement indicates the power of the THz-TDS technique.

The index of refraction versus frequency was obtained from the relative phase shifts of the Fourier components of the pulses with and without the sample in place. The measured relative phase shift increases linearly, with a weak oscillation due to the étalon resonances, up to approximately 8.5 rad at 2.5 THz. The resulting index of refraction shown in Fig. 1(c) is remarkably insensitive to frequency. The small observed variations are mainly due to slight changes in the input THz pulses over the time of the measurement. The quoted value of 1.92 is seen to be slightly low and a value of 1.923 would be closer to that determined by the scatter of the data. However, due to the variations in the sample thickness, we assign a conservative error estimate of ±0.02 for the index. Within this relatively large error, the value of 1.92 is appropriate. Here again, the quality of the data is exceptional, illustrating the applicability of THz-TDS to thin-film measurements. Using the Maxwell relationship,[9] the in-plane dielectric constant ϵ'_{XY} was calculated to be 3.69 ± 0.08, the square of the refractive index.

In addition to the in-plane dielectric constant, the out-of-plane dielectric properties were measured by means of dynamic dielectric analysis using multifrequency LCR meters. For a single-layer BPDA-PDA film saturated with roughly 50% RH (relative humidity) in air, the out-of-plane dielectric constant ϵ'_Z was 3.03 ± 0.02 at 1 MHz and dielectric loss was 0.014 ± 0.001. The dielectric properties were again measured at room temperature immediately after drying at 200 °C for 30 min under a nitrogen flow. For the dried film, the dielectric constant ϵ'_Z was 2.96 ± 0.02 and the dielectric loss ϵ''_Z was 0.011 ± 0.001. That is, the dielectric constant and dielectric loss varied slightly with moisture uptake.

From these measurements, a relatively high degree of anisotropy in the dielectric constant was observed in thermally imidized BPDA-PDA polyimide thin film. In the present study, the ϵ'_Z was measured at 100 kHz–1 MHz, whereas the ϵ'_{XY} was measured at 0.35–2.50 THz. Consequently, the frequency dependence of the dielectric constant in the BPDA-PDA polyimide film becomes an important question. For this reason, the ϵ'_{XY} of the multilayer polyimide films has also been investigated in the frequency range of 15–140 GHz by means of coherent microwave transient spectroscopy (COMITS),[10] which is similar to the TDS but is operated with a lower-frequency radiation source. The ϵ'_{XY} was 3.6 ± 0.1 at 15–140 GHz. Recently, Edelstein[11] has studied the in-plane dielectric properties of BPDA-PDA polyimide thin film, using a multifrequency impedence analyzer. He found a value for ϵ'_{XY} at 1 MHz similar to that at 0.35–2.50 THz in the present study. Therefore, it is concluded that the ϵ'_{XY} of the thermally imidized BPDA-PDA polyimide film is relatively frequency independent over the range of 1 MHz–2.50 THz, corresponding to the range of radio to sub-mm microwave frequency. Over the same frequency range, a similar frequency dependence is also expected in the ϵ'_Z of the polyimide films.

However, for the polyimide films a relatively lower dielectric constant is expected at frequencies of >2.5 THz, because of the frequency-dependent polarizability of the polyimide molecules. In general, the greater is the polarizability of molecules, the higher the dielectric constant.[12,13] The overall polarization of a molecule is the sum of electronic, atomic, and orientational polarizations.[12,13] The electronic, atomic, and orientational polarizations occur at the frequencies of visible light to x-ray radiation, of infrared light, and of radio-frequency to microwave radiation, respectively.[12,13] Thus, atomic polarization can not occur at the frequencies of visible light to x-ray radiation, whereas orientational polarization is not allowed at the high frequencies of infrared, visible, and x rays. Therefore, the dielectric constant (or refractive index) of a polymer is in the decreasing order of ϵ' (frequencies of visible to x ray) $<\epsilon'$ (frequencies of infrared) $<\epsilon'$ (frequencies of radio to microwave). Recently, Herminghaus *et al.*[14,15] have studied the dielectric properties of BPDA-PDA polyimide thin films of 0.4–7.8 μm thickness at the frequencies of infrared to visible. They found $\epsilon'_{XY} = 3.43$ ($n_{XY} = 1.852$) and $\epsilon'_Z = 2.60$ ($n_Z = 1.612$) at a wavelength of 632.8 nm and $\epsilon'_{XY} = 3.52$ ($n_{XY} = 1.876$) and $\epsilon'_Z = 2.76$ ($n_Z = 1.660$) at a wavelength of 1064.2 nm. These measured dielectric constants are lower than those at the frequencies of radio to microwave, due to the lack of a contribution from orientational and/or atomic polarizations at those optical frequencies. However, even at the optical frequencies of >10 THz, an anisotropy in the dielectric constant was detected in the BPDA-PDA thin films.

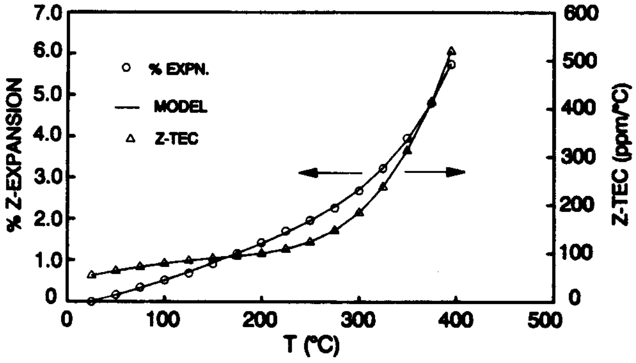

FIG. 2. Thermal expansion in the out of plane of a 15-layer BPDA-PDA polyimide film of 172 μm total thickness measured by a common thermal mechanical analysis as a function of temperature. The heating rate was 5.0 K/min.

B. Out-of-plane thermal expansion

Thermal mechanical analysis (TMA) is commonly used to measure the thermal-expansion behavior of a polymer film. However, in the case of thin polymer films this technique is usually limited to measuring the in-plane thermal-expansion coefficients α_{XY} rather than the out-of-plane α_Z coefficients, since its sensitivity is not enough to monitor small variations in the thickness of thin polymer films. For this reason, the 15-layer BPDA-PDA polyimide films, which were used in the in-plane dielectric properties measurements, was used for measurements of the out-of-plane TEC. Using small pieces (1×1 mm^2) of the multilayer films, the dimension change in the direction of film thickness was measured using TMA. The thermal expansion ($\Delta l/l_0$ in percentage) was calculated with the initial film thickness at 25 °C. The α_Z (*Z*-TEC) was obtained as the first derivative of the thermal expansion with respect to temperature. The thermal expansion ($\Delta l/l_0$ in percentage), as well as the out-of-plane TEC (α_Z in %/°C), was fitted by an interactive program of least-squares polynomial function of temperature (T in °C). The results were best fitted by the following polynomial functions:

$$\begin{aligned}\frac{\Delta l(T)}{l_0}\,100 = {} & -0.113\,45+4.4680\times 10^{-3}T\\ & +1.7000\times 10^{-5}T^2+5.5000\times 10^{-8}T^3\\ & -5.3000\times 10^{-10}T^4+1.1000\times 10^{-12}T^5, \quad (1)\end{aligned}$$

$$\begin{aligned}\alpha_Z(T) = {} & d\left(\frac{\Delta l(T)}{l_0}\,100\right)(dT)^{-1}\\ = {} & 4.4680\times 10^{-3}+3.4000\times 10^{-5}T\\ & +1.6500\times 10^{-7}T^2-2.1200\times 10^{-9}T^3\\ & +5.5000\times 10^{-12}T^4. \quad (2)\end{aligned}$$

As shown in Fig. 2, the *Z*-TEC (α_Z) increased almost linearly with temperature up to about 250 °C and thereafter increased rapidly with increasing temperature due to the softening of the polyimide film. The α_Z varied from 54 ppm/°C at 25 °C to 520 ppm/°C at 395 °C (see Table I and Fig. 2). The α_Z averaged over the range of 25–150 °C was 74 ppm/°C.

TABLE I. Out-of-plane TECs of a 15-layer film of thermally cured BPDA-PDA polyimide at various temperatures. *Z*-TEC data were obtained from Fig. 2.

T (°C)	*Z*-TEC (ppm/°C)
25	54
50	63
75	72
100	79
125	85
150	90
175	94
200	100
225	109
250	124
275	148
300	185
325	238
350	313
375	415
395	520

The α_{XY}, compared to the α_Z for the BPDA-PDA film, is relatively small. Over the range of 25–150 °C, the averaged α_{XY} is 2.6–5.0 ppm/°C for the polyimide films of 5–20 μm thickness thermally imidized on substrates.[16,17] In the comparison, the α_Z (74 ppm/°C) is at least 15 times higher than the α_{XY} (2.6–5.0 ppm/°C), indicative of very large anisotropy in the TECs in the directions parallel and vertical to the film plane.

Recently, several techniques have been developed to measure the α_Z of polymer thin films: the capacitance change technique,[18] Fabry–Perot laser interferometry,[18] and Fizeau laser interferometry.[19,20] Tong and coworkers[18] have measured the α_Z of Upilex-S films (Trademark of Ube Chemical Company; chemically imidized BPDA-PDA polyimide films which were mechanically drawn under heat treatment) of 51 or 127 μm thickness over the range of 50–160 °C, using both the capacitance change technique and the Fabry–Perot laser interferometric technique. They found that α_Z was 51 ppm/°C for the 51-μm-thick film and 58 ppm/°C for the 127-μm-thick film. The α_{XY} of Upilex-S film was known to be 8 ppm/°C for a 25-μm-thick film over the range of 20–100 °C. Based on these available data, the α_Z of the Upilex-S films is approximately 7 times higher than the α_{XY}. Using the Fizeau laser interferometry, Chen and Wagner[21] have investigated the out-of-plane thermal-expansion behavior of BPDA-PDA polyimide films thermally imidized on substrates: roughly 2-μm-thick single-layer film and roughly 23-μm-thick multilayer film (total of 8 layers). They found that for both single-layer and multilayer films, the average α_Z was 113 ppm/°C over the range of 25–150 °C.

In regards to film preparation, our multilayer BPDA-PDA film samples are comparable with the film samples of Chen and Wagner, rather than the Upilex-S films. However, the α_Z of our film samples is relatively lower than that of their film samples. This may result from the differences in the thicknesses and thermal histories between the films as well as in the instrumental resolutions. Among these suspected factors, first, the molecular in-plane orientation in BPDA-PDA polyimide films is known to be dependent upon the film thickness.[22] The molecular in-plane orientation is increased as the film thickness decreases. A relatively higher α_Z is expected for a film with a higher molecular in-plane orientation, since the vertical thermal expansion in the highly in-plane-oriented film is mainly caused by the lateral expansion of the molecules. Second, the morphological structure and properties of a polymer are generally dependent upon its thermal history. Thus, the difference in the thermal histories of the polyimide films may lead to a difference in the α_Z. Finally, the TMA has relatively less resolution than the other techniques. Among the techniques mentioned earlier, the Fizeau laser interferometer has the highest resolution, about 10 Å in thickness change, whereas the Fabry–Perot laser interferometer has a resolution of about 0.3 μm.[18–20] The capacitance technique is relatively more sensitive than the Fabry–Perot laser technique.[18] The resolution of the TMA is roughly 0.5 μm,[23] and requires a thicker film to obtain an accurate α_Z value. In addition to these concerns, a uniform film thickness and platness through a specimen are necessary to minimize errors in the α_Z measured by these techniques. In our study, the multilayer polyimide films of 172 μm total thickness were prepared through repeating a spin-coat/softbake/cure film formation process 15 times in order to overcome the resolution limit of the TMA. The small film specimens (1×1 mm^2) were used to avoid errors due to thickness and platness nonuniformity of the large film specimens. Consequently, we have successfully demonstrated in this study that through the multilayer approach of making thick films composed of thin single layers, the use of the conventional TMA technique can be extended to measure the out-of-plane thermal expansion of single polymer films of <25 μm thickness.

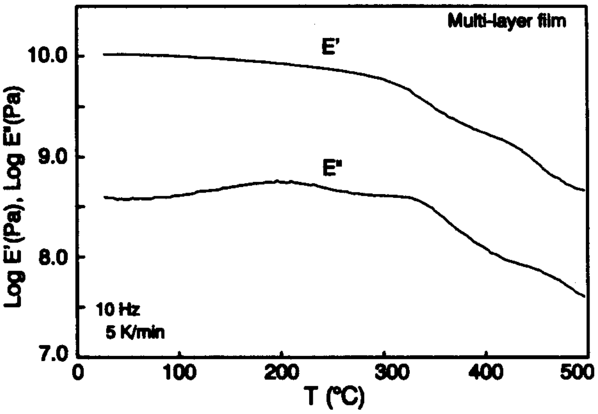

FIG. 3. Dynamic mechanical properties (storage modulus E' and loss modulus E'') of a 15-layer BPDA-PDA polyimide film of 172 μm total thickness as a function of temperature.

C. Dynamic mechanical properties and morphological structure

The dynamic mechanical properties and phase transition behavior of both single-layer and multilayer BPDA-PDA polyimide films were measured in a tensile mode with 5.0 K/min heating rate and 10 Hz frequency by means of DMTA. The results are presented in Figs. 3 and 4. The DMTA spectra (E' and E'' with temperature) of the multilayer film are virtually indentical with those of the single-layer film, regardless of their different thermal histories. This indicates that both dynamic storage E' and loss E'' moduli of each film layer in the multilayer film have not been changed significantly by the multiple thermal cycles over the range of 25–400 °C because of the repeated film forming process. In heating runs, the storage modulus E' decreased slowly with temperature until about 280 °C and then started to drop rapidly with temperature through phase transitions. The polyimide films showed two transitions above 280 °C. One occurred at 280–390 °C and the other at 390–500 °C. The latter was very weak in the single-layer film but slightly pronounced in the multilayer film (see Figs. 3 and 4). A similar enhancement in the latter peak was previously observed in a thick single-layer BPDA-PDA film.[6] On the other hand, three broad peaks were observed in the loss modulus E'' versus temperature plot. The very broad peak below 280 °C, which is assigned by β relaxation, is due to the localized motion of aromatic moieties on the polymer backbone, as typically observed in various aromatic polyimides.[24,25] This β relaxation peak sometimes overlaps with the β' relaxation due to water, if the film absorbs moisture. The contribution of the β' peak may make the β relaxation peak appear broader. Above 280 °C, two relaxation peaks are due to the two different phase transitions, as observed in the storage modulus variation with temperature. Again, the latter peak did not appear clearly in the single-layer film. For these relaxation peaks the phase transition temperatures are 330 and 450 °C, respectively, if the peak maximum temperature is chosen as the phase transition temperature. The morphological structure of BPDA-PDA polyimide films has been extensively studied by Ree *et al.*[6,22] They found that the BPDA-PDA polyimide molecules in thermally imidized

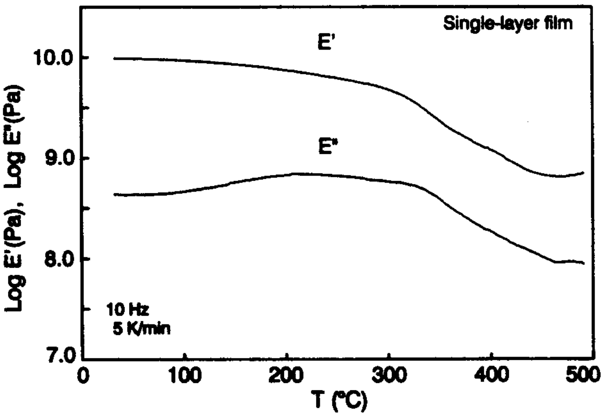

FIG. 4. Dynamic mechanical properties (storage modulus E' and loss modulus E'') of a single-layer BPDA-PDA polyimide film of 11.4 μm thickness as a function of temperature.

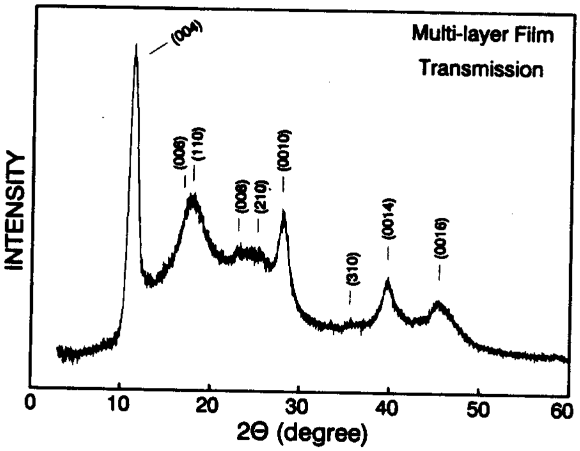

FIG. 5. Wide-angle x-ray-diffraction pattern of a 15-layer BPDA-PDA polyimide film of 172 μm total thickness as a function of 2θ (degree): transmission pattern. The Cu*Kα* radiation source was used.

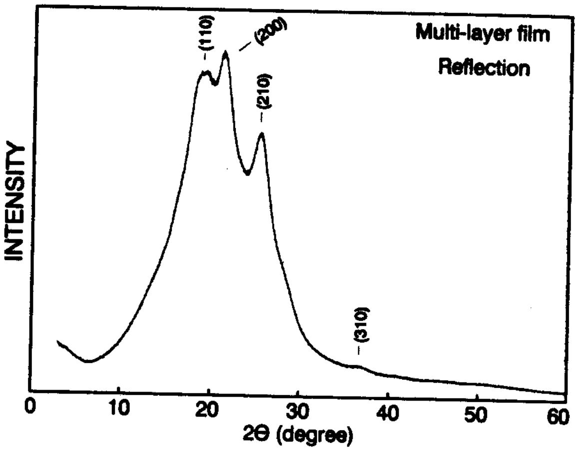

FIG. 6. Wide-angle x-ray-diffraction pattern of a 15-layer BPDA-PDA polyimide film of 172 μm total thickness as a function of 2θ (degree): reflection pattern. The Cu*Kα* radiation source was used.

films are in the frozen smectic-*E* crystalline state, based on orthorhombic unit crystal packing with the extended chains. With this structural information, the relaxation peak at 330 °C may be assigned to the α transition due to the glass transition and the peak at 450 °C to the order-disorder transition due to the phase transition of the smectic-*E* ordered state to a less ordered state. However, at this time a detailed analysis is needed for a better understanding of the latter transition. The glass transition ($T_g = 330\,^{\circ}\mathrm{C}$) measured by DMTA is consistent with that observed in the *Z*-TEC (or % *Z* expansion) variation with temperature (see Fig. 2).

The morphological structure of the multilayer films was characterized by means of wide-angle x-ray diffraction (WAXD) and compared with that of the single-layer film. In this study, WAXD patterns were measured in both transmission and reflection geometries. The diffraction vector in a transmission run with a $\theta/2\theta$ mode is in the film plane and, therefore, the transmission run can give structural information (polymer chain orientation and packing order) in the plane. A reflection run with the diffraction vector normal to the film plane can provide structural information in the out of plane. The WAXD results are shown in Figs. 5 and 6. In this study, the measured diffraction peaks were assigned in accordance with the structural analysis result of Ree *et al.*[6,26] The multilayer film exhibited clearly the multiple (00*l*) peaks in the transmission pattern: (004), (008), (0010), (0014), and (0016). From these diffraction peaks, we conclude that the BPDA-PDA polymer chains are highly ordered along the chain axes in the multilayered film. Besides these (00*l*) peaks, several (*hk*0) diffraction peaks appeared: (110), (210), and (310). These (*hk*0) peaks indicate that the BPDA-PDA polymer chains are relatively well packed. That is, a relatively high degree of lateral packing order was developed in the multilayer BPDA-PDA film. In contrast to the transmission pattern, only the reflection pattern shows a (200) peak, in addition to the (*hk*0) peaks which were observed in the transmission pattern. These diffraction patterns are almost identical with those of the single-layer film (see Fig. 7), indicating that the molecular order and orientation in the single-layer film were undisturbed in the multilayer film prepared through the repeated film formation processes.

The (*hk*0) reflections indicating the molecular lateral packing order were observed in both reflection and transmission patterns. This is evidence that the BPDA-PDA polyimide chains are regularly packed in both in-plane and out-of-plane directions. The (200) peak observed only in reflection indicates that one (namely, the *a* axis in the orthorhombic crystal packing) of the molecular lateral packing directions is in the out of plane of the film. The overall crystallinity of the multilayer film was estimated to be 20%–23% by the diffraction peaks deconvolution and integration based on Gaussian functions fitting.[22]

In addition to this packing order, both polyimide chain order and orientation in the films are important to the understanding of the anisotropic dielectric constant and

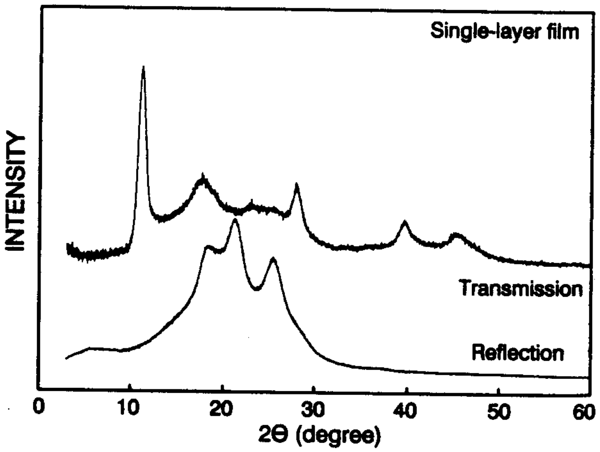

FIG. 7. Wide-angle x-ray-diffraction patterns of a single-layer BPDA-PDA polyimide film of 11.4 μm thickness as a function of 2θ (degree). The Cu*Kα* radiation source was used.

thermal-expansion behavior. In contrast to the ($hk0$) reflections, the multiple ($00l$) peaks were observed only in the transmission. This indicates that the polyimide chains are preferentially aligned in the film plane. The coherence length for the (004) peak was estimated by the Scherrer relationship[27] with an instrument broadening of 0.15° (2θ). The estimated coherence length was 90 Å, corresponding to five or six chemical repeat units. Consequently, the BPDA-PDA polyimide molecules are highly ordered along the chain axes and their chain axes are highly oriented in the plane of the single-layer film, as well as in the serially processed multilayer film.

The preferential in-plane orientation of the highly ordered BPDA-PDA polyimide molecules is correlated with the high anisotropic dielectric constant and thermal expansion of the multilayer film. First, the dielectric constant of a polymer material is dependent upon the overall polarizability (electronic, atomic, and orientation polarizability) of the polymer chains under an applied electric field.[12,13] The overall polarization (in particular, atomic and orientation polarizations) is sensitive to the degree of orientation of the polymer chains in the films. In highly ordered polyimide molecules, the overall polarization is relatively higher along the chain axes than in the lateral direction. Consequently, for the BPDA-PDA polyimide films, composed of molecules highly oriented in the film plane, the dielectric constant is higher in the plane than out of the plane. Second, the thermal expansion of a polymer film is also sensitive to the molecular chain order and orientation. In a polymer, atoms are covalently bonded in the polymer chain but the polymer chains are packed by the interaction of van der Waals force, electron donor to acceptor, ion to ion, or hydrogen bonding. In general, the covalent bond energy is much higher than the others. For this reason, in a polymer film with a high molecular in-plane orientation thermal expansion occurs more favorably in the lateral (out of plane) direction than along the polymer chain axis (in plane). Furthermore, the thermal expansion of a polymer chain along the chain axis is dependent upon the chain rigidity or linearity.[16] BPDA-PDA polyimide exhibits a relatively high rigidity or linearity with roughly 100 Å Kuhn segment length.[28] Therefore, due to the nature of in-plane orientation of the highly rigid BPDA-PDA polyimide chains in thin films, thermal expansion is much higher out of the plane than in the film plane, although the polyimide molecules are intermolecularly well packed.

IV. CONCLUSIONS

The 15-layer BPDA-PDA polyimide films with 11.4-μm-thick layers were prepared from the poly(amic acid) precursor through repeating of a spin-coat/softbake/cure process. It has been verified by WAXD analysis that the molecular order and chain orientation in the 15-layer BPDA-PDA polyimide films are nearly identical with those of a 11.4 μm single layer in spite of their different thermal histories. The polyimide molecules are highly ordered along the chain axes as well as in the lateral direction and furthermore are highly oriented in the film plane. The multilayer films showed the same dynamic mechanical properties and glass transition behavior as the single-layer films. Through the multilayer film approach, adequate measurements of the ϵ'_{XY} and α_Z of the BPDA-PDA thin films with 11.4 μm thickness have been demonstrated using the newly developed THz time-domain spectroscopy and a thermal mechanical analysis. The measured ϵ'_{XY} was 3.69 (± 0.08) over the frequency range of 0.35–2.50 THz. Because of the small frequency dependence, the same ϵ'_{XY} is predicted at the low frequencies of <0.35 THz. The ϵ'_Z and ϵ''_Z measured by capacitance technique were 2.96–3.03 (± 0.02) and 0.011–0.014 (± 0.001) at 1 MHz, depending upon the moisture content in the films. The measured α_Z was 74 ppm/°C over the temperature range of 25–150 °C, which was much higher than $\alpha_{XY} = 2.6$–5 ppm/°C. Consequently, large anisotropic ϵ' and α have been observed in the in plane and out of plane of the thermally imidized BPDA-PDA thin films. These anisotropic ϵ' and α originate from the anisotropic polarization and thermal expansion which, in turn, are mainly due to the high in-plane orientation of the polyimide molecules and the high chain order along the chain axes.

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