Residual Stress Behavior in Spin-cast Films of Soluble Polyimides


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Abstract: Using a bilayer bending technique, intrinsic stress and overall residual stress were measured for three soluble polyimides: poly(2,2'-bis(3-phenyl)hexafluoropropylene diphthallimide), poly(2,2'-bis(4-phenyl)hexafluoropropylene diphthallimide), and poly(4,4'-methylene-3,3'-dimethylidiphenylene benzophenonetetracarboximide). For these polyimides, the intrinsic stress was 29-31 MPa at room temperature at which the films were prepared, indicating that the intrinsic stress is not sensitive to the type of backbone chemistry among these polymers. The measured intrinsic stress is not small enough to be neglected as one usually does. However, the intrinsic stress relaxed out with temperature in the first heating run and its relaxation behavior with temperature was strongly dependent upon the film properties, including mechanical properties, polymer chain stiffness, molecular order, and glass transition temperature. In the subsequent cooling run, the intrinsic stress was never recovered. That is, the intrinsic stress varied irreversibly with temperature. In contrast, once the polymer films were thermally treated, their overall stress was predominated by the thermal stress component which varies reversibly with temperature. In addition, the glass transition temperatures of the polymer films were estimated from the overall stress-temperature profiles and compared with those measured by dynamic mechanical thermal analysis.

Introduction

Aromatic polyimides have found wide application in the microelectronics industry as alpha particle protection, passivation, and intermetallic dielectric layers, owing to their excellent thermal stability, mechanical properties and dielectric properties. Many microelectronic devices, such as VLSI semiconductor chips and advanced multichip modules, are composed of multilayer structures. In multilayered structures, one of the serious concerns related to reliability is the residual stress caused by thermal and loading histories generated through processing and use, since polyimides have different properties (i.e., mechanical properties, thermal expansion coefficient, and phase transition temperature) from the metal conductors and substrates (ceramic, silicon, and plastic) commonly employed. In general, residual stress in a polymer film consists of two major components: One is the so-called thermal stress due to the mismatch of thermal expansion coefficients between film and substrate or metal layer, as well as the thermal history and mechanical properties. The other is the intrinsic stress resulting from volume change due to solvent evaporation and shrinkage, from molecular structural ordering during the film formation process, and perhaps from the physical properties of the formed film. The overall residual stress of a polymer film is usually assumed to be the thermal stress, neglecting the contribution of intrinsic stress. Furthermore, the intrinsic stress in polymer films has got less attention and therefore, is not understood in detail yet.

In the present study we have chosen several soluble preimidized polyimides in order to understand intrinsic stress behavior and its contribution to overall stress: poly(2,2'-bis(3-phenyl)hexafluoropropylene diphthallimide), poly(2,2'-bis(4-phenyl)hexafluoropropylene diphthallimide), and poly(4,4'-methylene-3,3'-dimethylidiphenylene benzophenonetetracarboximide) (Figure 1).

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Residual Stress in PI Films

Figure 1. Chemical structures of preimidized polyimides: 6F-4,4'-6FDA, 6F-3,3'-6FDA, and BTDA-MDA.

These soluble preimidized polymers are good candidate polymer systems for studying the behaviors of stress components, because completely dried films can be made without any solvent complication and imidization which occur in polyimide precursors. For these preimidized polymers, fully dried films were prepared on silicon wafers through room temperature drying under a nitrogen flow and then followed by vacuum drying to avoid the involvement of any thermal history. For these dried polyimide films, intrinsic stress was measured at room temperature using a wafer bending technique, and its variation was monitored in-situ during heating as a function of temperature over the range of 25-400°C. In the subsequent cooling run, overall stress was also measured dynamically as a function of temperature. The thermal stress component was estimated from the measured intrinsic and overall stresses.

Experimental

Materials and Sample Preparation. Two fluorinated polyimides, poly(2,2'-bis(3-phenyl)hexafluoropropylene diphthalimide) (6F-3,3'-6FDA) and poly(2,2'-bis(4-phenyl)hexafluoropropylene diphthalimide) (6F-4,4'-6FDA), were supplied as fibers or powders by American Hoechst Chemical Company. These polyimides were dissolved in n-butyl acetate and filtered with 1μm Fluoropore filter membranes. Their concentrations were ca. 10 wt%. Another soluble polyimide, poly(4,4'-methylene-3,3'-dimethylidiphenylene benzophenonetetracarboximide) (BTDA-MDA), was obtained from OCG Chemical Company as a solution with a solid content of 12 wt% in γ-butyrolactone.

Double side polished Si(100) wafers (82.6 mm diameter and ca. 380 μm thickness) were used as substrates for stress measurements. These wafers were cleaned in a Plasmaline asher (Model 515) of Tegal Corporation before use. The curvatures of these wafers were measured using a residual stress analyzer. An adhesion promoter solution, 0.1 vol% A1100 (γ-aminopropyltriethoxysilane) in deionized water, was spin-applied on the calibrated Si wafers at 2000 rpm for 20 sec. Then, the polymer solutions were spin-coated on the primed Si wafers and dried in a convection oven with a nitrogen gas flow at room temperature. The partially dried samples were further dried at room temperature in a vacuum oven with 1×10^−6 torr for 2 weeks. The thicknesses of the films were ca. 12 μm.

Measurements. Residual stress in a polymer thin film is commonly determined by measuring the curvature (deflection) of the bilayer composite structure of the film and a substrate after film deposition. In the case of wafer bending technique using a laser based optical system (Figure 2), the curvature of a wafer substrate is easily measured by determining the variation of angle (θ) between incident beam to and reflected beam from the substrate. The distance (x) between two laser beams is commonly fixed: x = 6.15 cm for a wafer bending apparatus used in the present study. From the angle and the distance, the radius (R) of the wafer curvature is calculated:

\[ R = \frac{x}{\theta} \]  

Figure 2. A schematic diagram of bilayer bending technique using a laser light source.
Therefore, the stress of the film ($\sigma$) in equilibrium with the resultant strain can be calculated from the curvature and mechanical parameters of the substrate using the following simple plate equation:

$$\sigma = \frac{1}{2} \frac{E_L}{2} \frac{t}{(1 - v) R_F} \left( \frac{R_F}{R} \right)$$  \(2\)

Here, the subscripts F and S denote the polymer film and substrate, respectively. The symbols $E$, $v$, and $t$ are the Young’s modulus, Poisson’s ratio, and thickness of each layer of material, respectively. $R_F$ and $R$ are radii of a substrate with and without a polymer film, respectively. For Si(100) wafers, biaxial modulus, $E_S(1 - v_S)$, is $1.805 \times 10^5$ MPa.\(^{14}\)

Eq(2) has been derived under the assumption that stress is isotropic and uniform in the film plane. The application of this equation is limited to bending displacements smaller than the thickness of substrates. In other words, the thickness of a polymer film should be much smaller than that of substrates.

For fully dried polyimide films, residual stress was in-situ measured in nitrogen ambient during thermal heating and subsequent cooling, using a double He-Ne laser beam stress analyzer equipped with a hot-stage and controlled by a personal computer. The collecting time per each data point was only 5 sec, which had allowed in-situ measurements. The baking was conducted for 30 min at a certain temperature in the range of 25-400 °C. Then, the heating and cooling rates used were 2.0 and 1.0 K/min, respectively.

For polyimide films baked at 400 °C for 30 min, dynamic mechanical properties (storage modulus $E'$ and loss modulus $E''$) were measured over 25-500 °C, using a dynamic mechanical thermal analyzer (Polymer Laboratories Model Mark-II) equipped with a tensile head and controlled by a personal computer. The heating rate was 5.0 K/min and the frequency was 10 Hz. The measurements were carried out in nitrogen ambient. The width of film strips was 6.35 mm and the gauge length was 5.0 mm.

Results and Discussion

The polyimide films, which were dried at room temperature in a vacuum oven with $1 \times 10^{-5}$ torr for two weeks, were found not to have residual solvent (n-butyl acetate or γ-butyrolactone) by proton nuclear magnetic resonance (1H-NMR) spectroscopy. Here, 1H-NMR spectroscopic measurements were performed after the dried polymers were dissolved in dimethyl-d$_6$ sulfoxide.\(^{15}\)

For the fully dried polyimide films, the intrinsic stress was measured at room temperature to be 31 MPa for 6F-4,4'-6FDA and 6F-3,3'-6FDA and 29 MPa for BTDA-MDA. These results indicate that the intrinsic stress is not sensitive to the type of backbone chemistry among these polyimides.

These intrinsic stresses might arise mainly from constraints on molecular movement during film formation. A polymer film is commonly fabricated by applying the polymer in solution on to a substrate and subsequently drying it. 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 the gel point, the molecules in the film are mobile enough to flow and thus residual stress can not be generated. However, above the gel point the film is extremely viscous and its glass transition temperature ($T_g$) increases. The increases of viscosity and $T_g$ in the film restrict the molecular motion and results in stress. At the same time, the solvent evaporation through the drying process leads the wet film to shrink. The shrinkage takes place in the direction of 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. This stress ($\sigma_0$) generated by the deposition of the polymer film can be expressed by the following equation:\(^{16}\)

$$\sigma_0 = \frac{E_F}{(1 - v_F)} \frac{\phi_0 - \phi}{3(1 - \phi)}$$  \(3\)

where $\phi_0$ is the volume fraction of solvent at which the film solidifies and $\phi$ is the volume fraction of solvent retained in the film.

As is expressed in Eq(3), the stress ($\sigma_0$) is sensitive to the residual solvent in the film. When the polymer film is fully dried at a given temperature, the volume fraction ($\phi$) becomes zero. Then, we
define that the stress \((\sigma_r)\) with \(\phi_r = 0\) is the intrinsic stress of the film:

\[
\sigma_r = \frac{\phi(1 - \nu)}{3(1 - \nu_r)} E_r
\]  

(4)

Here, the intrinsic stress \((\sigma_r)\) is only a function of the biaxial modulus \([E_r/(1 - \nu)]\) and volume fraction \((\phi)\) which are physical characteristics of the polymer film. These parameters are of course a function of temperature, so that the intrinsic stress is also a function of temperature. Using Eq (4), the \(\sigma_r\) in Eq (3) is expressed in terms of the intrinsic stress \((\sigma_r)\):

\[
\sigma = \sigma_r (\phi - \phi_r) \frac{(1 - \nu_r)}{(1 - \nu)}
\]  

(5)

When the polymer film was heated, the measured intrinsic stress was, however, relaxed out with increasing temperature. Figure 3 shows the stress-temperature profile of the 6F-4,4'-6FDA film measured in-situ during heating up to 400 °C and subsequent cooling. In the heating run, the stress decreased to 2.2 MPa at 400 °C from 31 MPa at room temperature. During aging at 400 °C for 30 min, the stress increased slightly from 2.2 to 3.0 MPa. The stress increment due to the aging is only 0.8 MPa. Similar aging behavior was observed at 250 °C: that is, the stress increment is 1.4 MPa. In contrast, this aging effect is more significant at 150 °C: the stress increment is 3.8 MPa. Therefore, the aging effect on the stress of 6F-4,4'-6FDA films is significant at temperatures below 250 °C but becomes very small above 250 °C.

In the subsequent cooling run after heating up to 400 °C, the stress remained at ca. 3 MPa until 300 °C and thereafter started to increase linearly with descending temperature, finally reaching to 50 MPa at room temperature. This result indicates that the residual stress does not build up above 300 °C because of a relatively high chain mobility and, however, generates below 300 °C because of a restricted chain mobility. Thus, from this stress profile the polymer film is expected to have a glass transition at 300 °C. And, this stress profile is quite different from the stress profile monitored in the first heating run. Further, the stress level is always higher than that in the first heating run over 20-280 °C.

In the second heating run to 400 °C, the stress followed reversibly the same stress profile which was measured in the first cooling run. Furthermore, the stress profile in the second cooling run was exactly same with that in the first cooling run. Similar stress behaviors were previously reported for other polyimide films prepared from thermal imidization of their precursor polymers.

These stress results inform us indirectly that the residual stress generated by the first thermal heating and subsequent cooling is different from the intrinsic stress developed in the film by its forming process at room temperature. Here, there arises a question: that is, how much intrinsic stress component is involved into the overall residual stress term which is known to consist of intrinsic and thermal stress components. However, the intrinsic stress in the film prepared at room temperature was relaxed out almost completely above ca. 300 °C (Figure 3). In the subsequent cooling, thermal stress component was always involved in the polymer film. Thus, the intrinsic stress could not be recovered after the heating treatment: that is, the intrinsic stress may follow an irreversible process with temperature. In contrast, for the film treated thermally the linear variation of stress with temperature suggests that the overall residual stress in the film is predominated by the thermal stress component which is gener-

![Figure 3. Stress versus temperature behavior of the 6F-4,4'-6FDA film dried at room temperature measured on a Si(100) wafer during heating up to 400 °C and subsequent cooling: \(\sigma_r\) overall stress; \(\sigma_i\) intrinsic stress, The heating and cooling rates were 2.0 and 1.0 K/min, respectively.](image-url)
ated by the heat-treatment. Further, the measured stress behaviors suggest that the thermal stress component in the polymer film varies reversibly with temperature in the heating and subsequent cooling process. Here, the thermal stress ($\sigma_t$) is generally known to result from the mismatched thermal expansion coefficients (TECs) of the film and substrate, as well as the mechanical properties and thermal history of the film as is indicated in the following equation:\[\text{(6)}\]

$$\sigma_t = (\alpha_f - \alpha_s)(T_f - T)(E_f/(1 - v_f))$$

with TECs ($\alpha_f$ and $\alpha_s$), final heat-treat temperature ($T_f$), stress measurement temperature ($T$), modulus ($E_f$) and Poisson’s ratio ($v_f$).

The in-situ measurement of residual stress was extended to 6F-3,3’-6FDA and BTDA-MDA films. Representative results are shown in Figures 4 and 5. For 6F-3,3’-6FDA, the stress level is comparable to that of the 6F-4,4’-6FDA. However, its variation with temperature in the first heating run is different from that of the 6F-4,4’-6FDA films. As shown in Figure 4, on heating the intrinsic stress rapidly relaxed out with increasing temperature and then leveled off at 1.5 MPa above 150°C. For cooling, the overall residual stress started to increase from 230°C, due to the contribution of thermal stress generated in the supercooled state below $T_g$ and finally reached 45 MPa at room temperature. Similar stress-temperature behaviors were observed for BTDA-MDA films. In the heating run, the stress of 29 MPa decreased to ca. 4 MPa at 400°C (Figure 5). On cooling after the bake, overall stress increased continuously with temperature and reached 56 MPa at room temperature.

As described above, all the three polyimides exhibited almost the same intrinsic stress (29-31 MPa) at the drying temperature, regardless of the different chemical backbone. This indicates that the mechanical properties (particularly Young’s modulus and Poisson’s ratio) of those polyimides are nearly the same. On heating, the intrinsic stress relaxed out with temperature. The stress relaxation was strongly dependent on $T_g$, that is, polymer chain flexibility. The $T_g$ of the 6F-3,3’-6FDA is relatively low so that its stress relaxation is faster than that of the other polyimides. The stress-temperature profiles indicate that $T_g$ is in the increasing order 6F-3,3’-6FDA < 6F-4,4’-6FDA < BTDA-MDA.

The three polyimides baked at 400°C exhibited ca. 3.0 GPa Young’s modulus at room temperature, regardless of the polymer backbone. An equivalent Poisson’s ratio is expected for these
polyimides: it would be ca. 0.35. Therefore, the difference in the overall stresses of the polyimides may result from the differences in the $T_s$'s as well as in the TECs. Considering polymer chain flexibility and $T_s$, TEC may be relatively high in the 6F-3,3'-6FDA, intermediate in the 6F-4,4'-6FDA, and low in the BTDA-MDA. However, the thermal stress was in the decreasing order BTDA-MDA > 6F-4,4'-6FDA > 6F-3,3'-6FDA. Consequently, the difference in the overall stresses of these polyimides was predominantly driven by the difference in $\Delta T$'s due to different $T_s$'s.

In addition, the $T_s$ of the films may be estimated from the stress-temperature profile as mentioned qualitatively above. In general, stress is not built up above $T_s$ because of high polymer chain mobility. However, the chain mobility is restricted in the glassy state below $T_s$, allowing the generation of stress. In the overall stress-temperature profile measured on cooling, the temperature at which the stress started to increase was chosen as $T_s$. $T_s$ was estimated to be 235°C for the 6F-3,3'-6FDA, 300°C for the 6F-4,4'-6FDA, and > 400°C for the BTDA-MDA.

For the same samples, DMTA measurements were performed to verify their $T_s$. The DMTA spectra measured are shown in Figure 6-8. In the DMTA, the temperature at which the storage modulus ($E'$) started to decrease significantly in the region of glass transition was selected as $T_s$. The $T_s$ was 253°C for the 6F-3,3'-6FDA, 327°C for the 6F-4,4'-6FDA, and 405°C for the BTDA-MDA.

**Figure 6.** Dynamic storage modulus ($E'$) and loss modulus ($E''$) of the 6F-4,4'-6FDA film treated at 400°C as a function of temperature. The heating rate and frequency were 5.0 K/min and 10 Hz, respectively.

**Figure 7.** Dynamic storage modulus ($E'$) and loss modulus ($E''$) of the 6F-3,3'-6FDA treated at 400°C as a function of temperature. The heating rate and frequency were 5.0 K/min and 10 Hz, respectively.

**Figure 8.** Dynamic storage modulus ($E'$) and loss modulus ($E''$) of the BTDA-MDA film treated at 400°C as a function of temperature. The heating rate and frequency were 5.0 K/min and 10 Hz, respectively.
to the region of high temperature as the frequency employed increases. Second, in determining $T_{s}$, the measurement of stress by wafer bending technique may be less sensitive than the measurement of modulus (or displacement) by DMTA, since the generation of thermal stress requires that molecular mobility be limited otherwise it relaxes out quickly. Thus, thermal stress cannot be built up easily at a low degree of supercooling, that is, near or slightly below $T_{s}$, where polymer molecules are still relatively mobile. This may lead one to underestimate $T_{s}$ in the stress-temperature analysis.

**Conclusions**

For the films of three different polyimides which were prepared at room temperature, their intrinsic stresses were successfully measured to be 29-31 MPa, depending on the chemical backbone structures. These intrinsic stresses, which had been generated mainly by the solidification of spin-cast polyimide solution through solvent evaporation, are apparently not sensitive to the backbone chemistry. The intrinsic stress is not small enough to be neglected. However, in the heating run the intrinsic stress was relaxed out above $T_{s}$ and seemed to be never recovered in the subsequent cooling. That is, the intrinsic stress seems to undergo an irreversible process with temperature. In other word, the intrinsic stress is valid only at a temperature where the film is formed.

In contrast, the thermal stress was built up in the heat-treated film and seemed to play a key role to the overall residual stress. That is, the overall residual stress in the thermally treated film seems to be predominated by the thermal stress component rather than the intrinsic stress component. And, the thermal stress appears to follow a reversible process with varying temperature.

In addition, the $T_{s}$'s of the polyimides were estimated from the overall stress-temperature profiles and compared with those measured by DMTA.

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