Effect of precursor history on residual stress and relaxation behaviour of high temperature polyimides

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Using a wafer bending technique, residual stress and its relaxation were investigated for four different kinds of high temperature polyimides: rodlike PMDA-PDA, semi-rigid BPDA-PDA, semi-flexible PMDA-ODA, and flexible BTDA-ODA. Residual stress was measured *in situ* on silicon wafers during thermal imidization of the polyimide precursors and subsequent cooling of the resulting polyimides as a function of temperature over the range of 25–400°C. The stress of the cured films at room temperature was significantly relaxed by the moisture uptake of the films rather than their creep behaviour. Both residual stress and moisture-induced stress relaxation in the cured polyimide films were strongly dependent upon the molecular nature (that is, molecular chain rigidity, degree of molecular orientation and packing), as well as the precursor origin. In addition, the diffusion coefficients of water in the cured polyimide films were estimated by best-fitting stress relaxation against time profiles.

INTRODUCTION

High temperature polyimides are widely used in the microelectronics industry as interlayer dielectrics, passivation layers and alpha particle barries, owing to excellent properties such as good mechanical properties, high thermal stability, low dielectric constant and high chemical resistance[1]. Recently, most high performance microelectronic devices demand multi-layered structures to be dense and compact[2]. For a multi-layered device there are often reliability problems, such as displacement, cracks, and delamination at interfaces, which are caused by interfacial adhesion and mechanical failures associated with interfacial residual stress due to the mismatch of the physical properties between the layers. Thus, to avoid the reliability problems due to residual stress, zero or low stress is necessary at all the interfaces in multi-layered structures.

There are four different types of aromatic polyimides in terms of molecular chain rigidity: rodlike, semi-rigid, semi-flexible, and flexible. The physical properties of a polyimide, particularly the thermal expansion coefficient (*TEC*), glass transition temperature (T_g) and mechanical properties (Young's modulus and Poisson's ratio), which are critical to the residual stress[3,4], are primarily dependent upon the polymer chain rigidity, which can be expressed by the Kuhn length[5,6]. In the present study, we have chosen fully rodlike poly(*p*-phenylene pyromellitimide) (PMDA-PDA), semi-rigid poly(*p*-

phenylene biphenyltetracarboximide) (BPDA-PDA), semi-flexible poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA), and fully flexible poly(4,4'-oxydiphenylene benzophenonetetracarboximide) (BTDA-ODA) as model polymers which have various molecular chain rigidities, in order to understand residual stress behaviour and its correlation with the nature of the polyimide molecule (see the chemical structures in *Figure 1*). These polyimides are usually prepared through the thermal imidization of
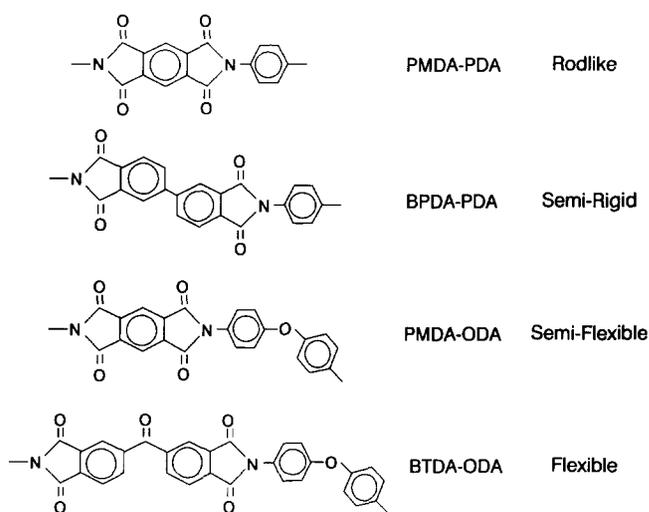
Figure 1 Chemical structures of aromatic polyimides studied in this work

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various types of soluble precursors, such as poly(amic acid), poly(amic dialkyl ester) and photosensitive precursors. As is well known, the imidization kinetic of either a poly(amic dialkyl ester) or a photosensitive polyimide precursor is quite different from that of the conventional poly(amic acid) precursor[7,8]. The different imidization kinetics between precursors of a polyimide may lead to different properties in the resulting polyimide. According to a previous study by Ree et al.[9], the properties (in particular, mechanical properties, residual stress and thermal expansivity) of BPDA-PDA polyimide from its photosensitive precursor were significantly different from those of the corresponding polyimide from the poly(amic acid) precursor. In the present study, the dependency of stress behaviour on the history of precursor origin was extensively investigated for the four different types of polyimides using a wafer bending technique. The stress of the polyimide precursor films was measured *in situ* on a silicon wafer during thermal imidization and subsequent cooling as a function of temperature over the range of 25–400°C. In addition, for the polyimide films cured at 400°C, stress relaxation was monitored in 50% relative humidity (r.h.) at 25°C.

EXPERIMENTAL

Materials

Poly(*p*-phenylene biphenyltetracarboxamic acid) (BPDA-PDA PAA) (ca. 40 K M_w and 13.5 wt%) and poly(4,4'-oxydiphenylene pyromellitamic acid) (PMDA-ODA PAA) (ca. 35 K M_w and 16.0 wt%) precursor solutions were received from Du Pont Chemical Company. Poly(*p*-phenylene pyromellitamic acid) (PMDA-PDA PAA) (ca. 30 K M_w and 10.0 wt%) and poly(4,4'-oxydiphenylene benzophenonetetracarboxamic acid) (BTDA-ODA PAA) (ca. 40 K M_w and 18.0 wt%) precursor solutions were prepared in *N*-methyl-2-pyrrolidone (NMP) through polymerization from the respective dianhydrides and diamines purified through sublimation. Photosensitive precursor solutions were prepared by attaching photocrosslinkable dimethyl-aminoethyl methacrylate (DMAEM) to the carboxylic acid groups of the poly(amic acid) precursors through acid/amine ionic complex formation as previously described elsewhere[9]: PMDA-PDA/DMAEM, BPDA-PDA/DMAEM and PMDA-ODA/DMAEM. DMAEM of 100 mol% (equivalent to the carboxylic acid groups of a precursor) was added to each precursor solution and mixed at room temperature for 1 day using a roller mixer. Photoneece UR-3840, a photosensitive precursor formulation including a photosensitizer and a photoinitiator, was received from Toray Chemical Company: this was BTDA-ODA PAA precursor functionalized with an aminoalkyl methacrylate by acid/amine salt formation[8]. In addition, two poly(amic dialkyl ester)s were synthesized: poly(4,4'-oxydiphenylene pyromellitamic diethyl ester) (PMDA-ODA ES) precursor was prepared via low temperature solution polycondensation in NMP of diethyl pyromellitate diacyl chloride with 4,4'-oxydiphenylene diamine (ODA) as previously described[10]. Poly(*p*-phenylene *meta*-pyromellitamic diethyl ester) (*m*-PMDA-PDA ES) precursor was synthesized from *meta*-diethyl pyromellitate diacyl chloride with *p*-phenylene diamine (PDA) in the same way as the PMDA-ODA ES was prepared.

Sample preparation and measurement

For all the double-side polished Si(100) wafers of 82.5 mm diameter used in the present study, curvatures were measured before use with the aid of a HeNe laser-beam based stress analyser (Flexus stress analyser: Model 2-300, Flexus Company) equipped with a hot-stage and controlled by an IBM PC/AT computer. The calibrated Si wafers were cleaned for 5 min in an O_2 plasma asher operated at 150 W. Then, an adhesion primer solution, 0.1 v% A1100 (γ-aminopropyltriethoxy silane) solution in 90 v% EtOH/10 v% deionized (DI) water or in DI water, was spin-coated at 2000 rev min⁻¹ for 20 s on the precleaned Si wafers and followed by a bake at 120°C for 20 min in air. All the polyimide precursor solutions were spin-coated on the primer-coated wafers and softbaked at 80°C for 30 min in a convection oven with a nitrogen flow. These softbaked samples were used for dynamic residual stress measurements. Dynamic residual stress measurements were performed in nitrogen ambient during thermal imidization of the softbaked precursor films on Si wafers and subsequent cooling, using the Flexus stress analyser. Here, the imidization was performed by a step-cure 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°C min⁻¹. A rate of 1.0°C min⁻¹ was employed in cooling. The thickness of cured films was ca. 10 μm. The stress relaxation was monitored at 25°C in air ambient with 50% r.h. immediately after the cure. In this measurement, a cured film sample was exposed to the 50% r.h. environment by quickly removing a quartz cover glass from the hotstage and turning off an inlet valve of nitrogen gas (to the hotstage) when the sample temperature reached 25°C in the cooling run. At almost the same time (i.e. within a few seconds), the stress relaxation measurement was started. Here, the measuring time per data point was 5 s.

Residual stress and its relaxation

In stress measurements using a wafer bending technique, the angle (θ) between incident and reflected laser light beams for a wafer is monitored *in situ* as a function of temperature and time. Then, the degree of wafer curvature (that is, radius of wafer curvature: R) is calculated from the angle (θ) and the distance (x) between two light beams: $R = x/\theta$. Residual stress (σ_F), the so-called overall residual stress, is calculated from the radii of wafer curvatures measured before and after the deposition of a polymer film using the following equation[11] valid for $L_F \ll L_S$:

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

Equation (1) can be expressed by the following two terms, thermal stress (σ_t) and intrinsic stress (σ_i)[12,13]:

$$\sigma_F = \sigma_t + \sigma_i \quad (2)$$

where

$$\sigma_t = (\alpha_F - \alpha_S)(T_f - T)\frac{E_F}{(1-\nu_F)} \quad (3)$$

and

$$\sigma_i = \text{intrinsic stress} \quad (4)$$

Here, the subscripts F and S denote polyimide film and Si wafer substrate, respectively. The symbols E, ν, σ, α,

and L are the Young's modulus, Poisson's ratio, stress, thermal expansion coefficient, and thickness of each layer of material. R_F and R_∞ are the radii of a substrate with and without a polyimide film, respectively. T_f and T are the final imidization temperature (or T_g if the glass transition temperature, T_g, is lower than T_f) and the temperature prevailing during the stress measurement, respectively. For Si(100) wafers, $E_S/(1-v_S)$ is 1.805×10^5 MPa (see ref. 14).

The residual stress of a polymer film on a substrate generally relaxes due to creep phenomenon as well as moisture (or any other solvent) swelling of the film[9]: the so-called 'creep induced stress relaxation' ($\sigma_C(t)$) and 'moisture induced stress relaxation' ($\sigma_W(t)$). The overall stress relaxation ($\sigma_F(t)$) in a humid environment can be described as:

$$\sigma_F(t) = \sigma_C(t) + \sigma_W(t) \tag{5}$$

Here,

$$\sigma_C(t) = \sigma_0 - \Delta\sigma f(T_g) \tag{6}$$

and

$$\sigma_W(t) = \sigma_0 - \Delta\sigma\left[1 - \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n-1)^2}\exp\left\{-\left[\frac{\pi(2n-1)}{2L_F}\right]^2 Dt\right\}\right] \tag{7}$$

where σ_0 is the initial stress at time $t=0$, and $\Delta\sigma$ is the difference between the stresses at $t=0$ and $t=\infty$. $f(T_g)$ is a function of T_g of the film, D is the diffusion coefficient of water and L_F is the film thickness. Equation (7) is valid under several assumptions: (i) surface concentration is constant; (ii) concentration gradient is zero at the interface; and (iii) initially, there is no water present[15,16].

RESULTS AND DISCUSSION

PMDA-PDA: fully rodlike polyimide

For the precursor films softbaked at 80°C for 30 min, stress at room temperature was 15.5 MPa for the PMDA-PDA PAA, 11.2 MPa for the PMDA-PDA/DMAEM and 26.8 MPa for the *m*-PMDA-PDA ES. If a polymer film was completely dried, its stress would solely depend on the nature of the polymer molecule, that is, its structure and properties. The drying time of 30 min at 80°C is not enough to remove NMP solvent completely from the precursor films. In the case of poly(amic acid), it is well known that the precursor forms a complex with NMP through acid/amine interaction so that the precursor film cannot be dried completely. Furthermore, the PMDA-PDA/DMAEM photosensitive precursor is the PMDA-PDA PAA complexed with DMAEM. The complexed DMAEM groups plasticize the polyimide precursors in a dried state and consequently lower the stress level. Overall, the stress level of the softbaked precursor films on silicon wafers is primarily dependent upon the degree of drying (that is, amount of residual NMP solvent).

These precursor films were imidized through a step cure process: 150°C/30 min, 230°C/30 min, 300°C/30 min and 400°C/1 h. During the step curing and subsequent cooling, residual stress was dynamically measured as a function of temperature. First, during the thermal

imidization, the stresses of the softbaked precursor films initially decreased with increasing temperature until starting imidization and then varied with further elevating temperature, reflecting both evaporation of the residual solvent and imidization (see *Figure 2*). In the curing run, the contribution of thermal stress is negligible, particularly above 80°C, the temperature at which the precursor films have been softbaked. Therefore, the stress–temperature profile monitored in the curing presents the variation of the intrinsic stress of the softbaked precursor film as a function of temperature. After the cure, the intrinsic stress of the resulting PMDA-PDA polyimide at 400°C was dependent upon the precursor origin. For example, intrinsic stress at 400°C was 13.5 MPa for the PMDA-PDA PAA, 9.9 MPa for the PMDA-PDA/DMAEM and 3.6 MPa for the *m*-PMDA-PDA ES.

In cooling from 400°C, residual stress decreased with decreasing temperature in the resulting polyimide films from both PMDA-PDA PAA and PMDA-PDA/DMAEM but increased in the polyimide film from the *m*-PMDA-PDA ES (see *Figure 2*). After cooling, stress at room temperature was -7.1 MPa for the PMDA-PDA PAA precursor origin, -1.3 MPa for the PMDA-PDA/DMAEM and 17.7 MPa for the *m*-PMDA-PDA ES: here, the negative sign indicates the stress in compression mode and the positive sign the stress in tension mode. The temperature for the inversion of
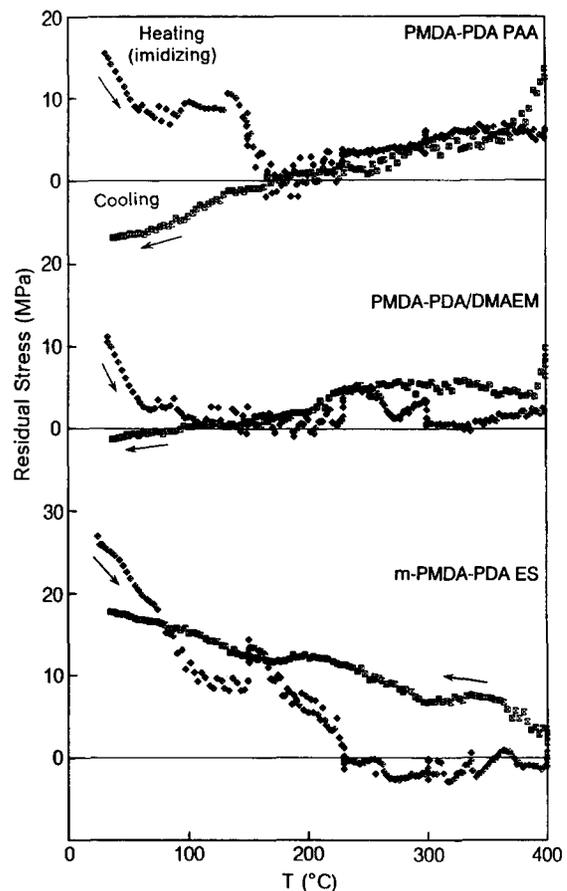
Figure 2 Residual stress *versus* temperature profiles of various PMDA-PDA precursors on Si(100) wafers measured during thermal curing through a step cure process (150°C/30 min, 230°C/30 min, 300°C/30 min and 400°C/1 h: 2.0°C min⁻¹ ramping rate for each step) and subsequent cooling at 1.0°C min⁻¹. All the precursor films were softbaked at 80°C for 30 min. The thickness of the cured films was 10 μm

tension to compression in stress was 166°C for the PMDA-PDA PAA precursor and 94°C for the PMDA-PDA/DMAEM. If the stress–temperature profiles of the cure films are predominated by their thermal stresses, it is presumed that at those inversion temperatures, their thermal expansion coefficients (TECs) are matched with that (3 ppm/°C) of Si(100)[12]. Furthermore, below the inversion temperatures their TECs are smaller than 3 ppm/°C. However, for the resulting polyimide from the *m*-PMDA-PDA ES, stress is in tension mode over the range of 25–400°C, indicating that its TEC is always greater than 3 ppm/°C. This stress–temperature behaviour is quite different from that of the polyimide films from both PMDA-PDA PAA and PMDA-PDA/DMAEM.

For the cured polyimide films, stress relaxation behaviour was also investigated in the present study. Stress relaxation is generally due to creep phenomenon, as well as moisture (or solvent) swelling in a polyimide film: creep induced stress relaxation and moisture induced stress relaxation. However, for high temperature polyimides having high glass transition temperature (T_g), creep induced stress relaxation is relatively slow at room temperature because of the relatively high degree of supercooling and consequently, its contribution to the overall stress relaxation is small[9]. For example, the creep induced stress relaxation in BPDA-PDA polyimide film is slow and the degree of relaxation is ca. 1 MPa or less[9]. Thus, for the PMDA-PDA polyimide films which do not exhibit any T_g over the range of 25–400°C, regardless of the precursor origin[10], the stress relaxation measured in 50% r.h. at room temperature results mainly from moisture uptake. The results are shown in *Figure 3*. The stress relaxed with time in the resulting polyimide films from both PMDA-PDA PAA and *m*-PMDA-PDA ES, but surprisingly built up further in the film from the PMDA-PDA/DMAEM. The stress behaviour in the
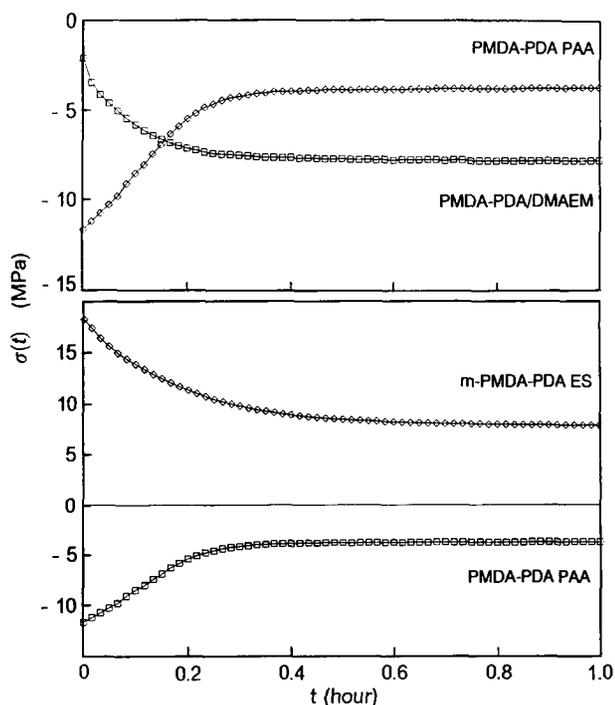
Figure 3 Residual stress relaxation of the PMDA-PDA polyimide films on Si(100) wafers from various PMDA-PDA precursors measured at 25°C in 50% r.h. as a function of time. The thickness of the polyimide films was 10 μm

Table 1 Diffusion coefficients for water sorption in thermally imidized poyimide films[a]

| | D^b (cm^2 s^{-1}) (× 10^{-10}) | | |
| | Polyimide precursor origin | | |
Polyimide film	PAA	ES	PSPI
PMDA-PDA	9.23	8.1	–
BPDA-PDA	1.4	–	6.8
PMDA-ODA	16.8	37.8	42.1
BTDA-ODA	7.1	–	34.2

[a] All the polyimide films were cured at 400°C for 1 h
[b] Diffusion coefficient for water sorption at 25°C and in 50% r.h.

polyimide film from the PMDA-PDA/DMAEM is abnormal and not fully understood at this moment. For the polyimide films from both PMDA-PDA PAA and *m*-PMDA-PDA ES precursor, the diffusion coefficient (D) for water sorption was estimated by the best-fit of the measured stress–time profiles with equation (7), under the assumption that the stress relaxation results from moisture uptake. D was 9.2×10^{-10} cm^2 s^{-1} for the PMDA-PDA PAA and 8.2×10^{-10} cm^2 s^{-1} for the *m*-PMDA-PDA ES (see *Table 1*). That is, they did not show any significant difference in the diffusion coefficient of water sorption.

BPDA-PDA: semi-rigid polyimide

After the softbake, residual stress at room temperature was 20.9 MPa for the BPDA-PDA PAA and 17.3 MPa for the BPDA-PDA/DMAEM. After curing at 400°C through the step cure process, the intrinsic stress at that temperature was 2.7 MPa for the BPDA-PDA PAA and 3.1 MPa for the BPDA-PDA/DMAEM. That is, the intrinsic stress at 400°C was not sensitive to the precursor origin. This result might correlate with the glass transition. BPDA-PDA polyimide films cured at 400°C exhibit a very broad glass transition over the range of 320–460°C, regardless of the precursor origin[17]. The BPDA-PDA polyimide molecules at the glass transition are relatively mobile and respond easily to the residual stress generated at the interface between the film and silicon wafer to result in a relatively low stress level. This mobility of the molecules might minimize the difference between intrinsic stresses of the films from the two different precursors. This kind of molecular mobility is very much restricted in the PMDA-PDA polyimide, which does not exhibit any glass transition over the considered temperature range, so that the difference in the intrinsic stress due to the different precursor origin cannot be minimized easily.

In cooling after the cure, the BPDA-PDA polyimide showed a stress–temperature profile very sensitive to the history of precursor origin. In the case of the BPDA-PDA PAA precursor, the stress of the resulting polyimide increased very slowly with decreasing temperature and finally reached 6.7 MPa at room temperature. However, for the BPDA-PDA/DMAEM photosensitive precursor, the stress of the resulting polyimide built up rapidly with decreasing temperature and reached 28 MPa at room temperature. These results indicate that the overall stress behaviour in the BPDA-PDA polyimide is very sensitive to the history of precursor origin. As shown in *Figure 4*, the photosensitive bulky DMAEM groups attached on the BPDA-PDA PAA precursor severely affect the stress
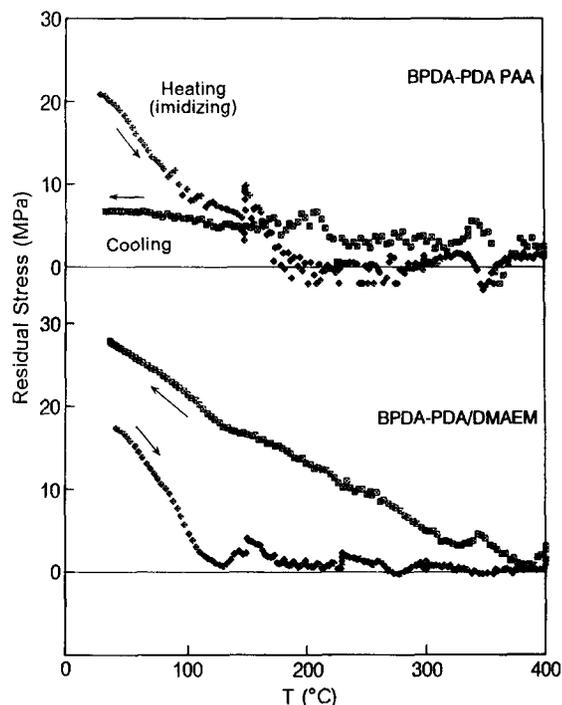
Figure 4 Residual stress *versus* temperature profiles of various BPDA-PDA precursors on Si(100) wafers measured during thermal curing through a step cure process (150°C/30 min, 230°C/30 min, 300°C/30 min and 400°C/1 h: 2.0°C min⁻¹ ramping rate for each step) and subsequent cooling at 1.0°C min⁻¹. All the precursor films were softbaked at 80°C for 30 min. The thickness of the cured films was 10 μm

diffusion coefficient of water as illustrated in *Table 1*: 1.4×10^{-10} cm² s⁻¹ for the BPDA-PDA PAA and 6.8×10^{-10} cm² s⁻¹ for the BPDA-PDA/DMAEM. That is, the diffusion of water is almost five times faster in the polyimide film from the BPDA-PDA/DMAEM than in the corresponding polyimide from the BPDA-PDA PAA. The stress difference before and after relaxation represents the amount of absorbed water in the film. After 4 h, this stress difference was 2.9 MPa for the BPDA-PDA PAA and 10.0 MPa for the BPDA-PDA/DMAEM, indicating a relatively higher water uptake in the latter polyimide film.

PMDA-ODA: semi-flexible polyimide

Figure 6 shows the stress–temperature profiles of the resulting PMDA-ODA polyimide films from the three different types of precursors. After the softbake, stress at room temperature was 18.9 MPa for the PMDA-ODA PAA, 19.3 MPa for the PMDA-ODA/DMAEM and 4.6 MPa for the PMDA-ODA ES. The softbaked PMDA-ODA ES film exhibited an unexpectedly low stress level of 4.6 MPa. This might result from a relatively high amount of NMP in the precursor film due to its improper softbake. Otherwise, for this precursor film one would expect a stress level similar to those of the other precursor films. After the cure, the intrinsic stress in the resulting polyimide films was relatively small, ≤0.6 MPa, at 400°C, regardless of the precursor origin. This means that at that temperature, the degree of the molecular

Figure 5 Residual stress relaxation of the BPDA-PDA polyimide films on Si(100) wafers from various BPDA-PDA precursors measured at 25°C in 50% r.h. as a function of time. The thickness of the polyimide films was 10 μm

of the resulting BPDA-PDA polyimide. According to a previous study by Ree *et al.*[9], the DMAEM functional groups significantly increase the *TEC* and residual stress and decrease the Young's modulus, in addition to disturbing the molecular chain order in the resulting polyimide film.

Figure 5 shows the stress relaxation behaviours of the resulting polyimide films in 50% r.h. at room temperature. The stress relaxed very slowly in the polyimide from the BPDA-PDA PAA but relaxed very rapidly in the film from the BPDA-PDA/DMAEM. The difference in the stress relaxation is reflected in the

Figure 6 Residual stress *versus* temperature profiles of various PMDA-ODA precursors on Si(100) wafers measured during thermal curing through a step cure process (150°C/30 min, 230°C/30 min, 300°C/30 min and 400°C/1 h: 2.0°C min⁻¹ ramping rate for each step) and subsequent cooling at 1.0°C min⁻¹. All the precursor films were softbaked at 80°C for 30 min. The thickness of the cured films was 10 μm

mobility in the polyimide films is relatively higher than that in the BPDA-PDA polyimide or the PMDA-PDA polyimide: the glass transition of the PMDA-ODA polyimide appears in the range of 384–465°C (see ref. 3).

In cooling after the cure, stress increased with decreasing temperature in all the polyimide films, as shown in *Figure 6*. At room temperature, stress was 29.3 MPa for the PMDA-ODA PAA, 26.2 MPa for the PMDA-ODA/DMAEM and 28.3 MPa for the PMDA-ODA ES. In contrast to both rodlike PMDA-PDA and semi-rigid BPDA-PDA polyimide, the PMDA-ODA polyimide did not show any strong dependency of the precursor origin on its stress behaviour. This might result from the poor molecular lateral packing order with its Kuhn length of 60–70 Å, which is relatively shorter than that (ca. 120 Å) of the BPDA-PDA polyimide in the *smectic-E* crystalline state or that of the PMDA-PDA polyimide in a poor lateral packing ordered state (that is, *smectic-A*)[6].

However, the effect of precursor origin appeared in the stress relaxation behaviour due to moisture uptake (see *Figure 7*). Stress relaxation was relatively slow in the polyimide from the PMDA-ODA PAA, intermediate in the film from the PMDA-ODA ES and fast in the film from the PMDA-ODA/DMAEM. The diffusion coefficient of water was 16.8×10^{-10} cm^2 s^{-1} for the PMDA-PDA PAA, 37.8×10^{-10} cm^2 s^{-1} for the PMDA-ODA ES and 42.1×10^{-10} cm^2 s^{-1} for the PMDA-ODA/DMAEM. After 30 min, the degree of stress relaxation was 3.6 MPa for the PMDA-ODA PAA, 4.0 MPa for the PMDA-ODA ES and 6.7 MPa for the PMDA-ODA/DMAEM. These results indicate that the degree of water sorption is much higher in the
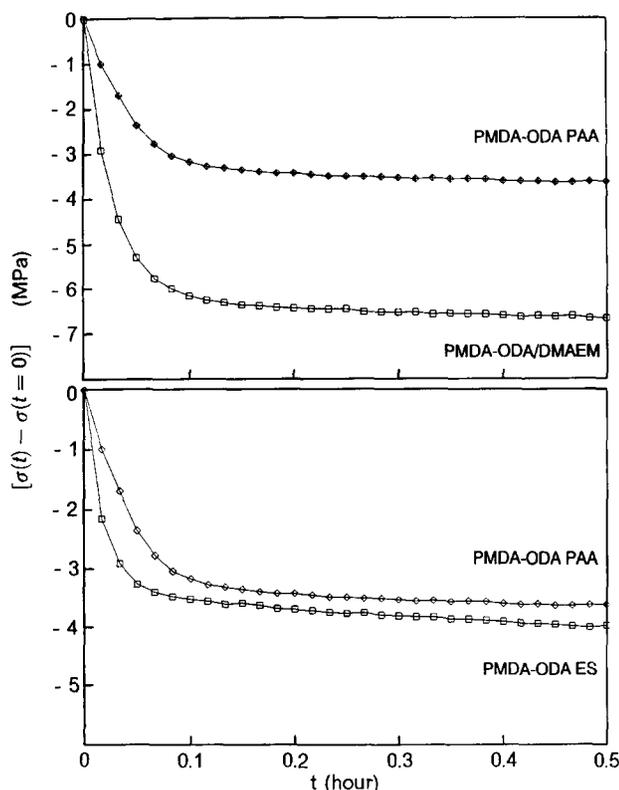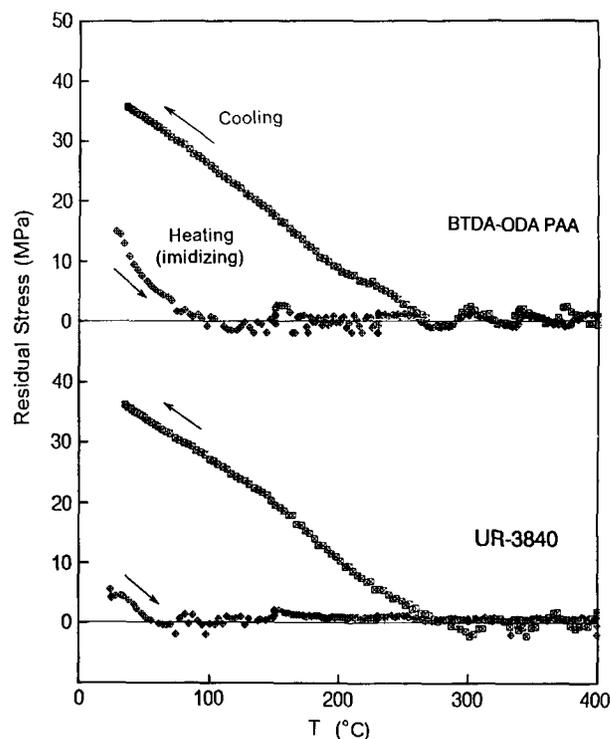
Figure 8 Residual stress *versus* temperature profiles of various BTDA-ODA precursors on Si(100) wafers measured during thermal curing through a step cure process (150°C/30 min, 230°C/30 min, 300°C/30 min and 400°C/1 h: 2.0°C min^{-1} ramping rate for each step) and subsequent cooling at 1.0°C min^{-1}. All the precursor films were softbaked at 80°C for 30 min. The thickness of the cured films was 10 μm

polyimide film from the PMDA-ODA/DMAEM than in the films from both PMDA-ODA PAA and PMDA-ODA ES. Similar behaviour was observed in the BPDA-PDA polyimide from the BPDA-PDA/DMAEM. This relatively high moisture uptake might be due to several morphological factors related to the complexed DMAEM groups: (i) structural changes; (ii) microvoids formed by the outgassing of bulky DMAEM groups during curing, and (iii) residues related to DMAEM. In particular, microvoids in the polyimide films might contribute significantly to the high moisture uptake.

BTDA-ODA: flexible polyimide

For both PMDA-ODA PAA and UR-3840 photosensitive precursor formulation, stress–temperature profiles are shown in *Figure 8*. After the softbake, stress was 14.8 MPa for the BTDA-ODA PAA and 5.5 MPa for the UR-3840. After the cure, intrinsic stress at 400°C was ≤1.5 MPa for the polyimide films from both precursors. On cooling from 400°C, the stress in the polyimide films from both precursors remained at almost zero until 275°C, and thereafter increased rapidly, indicating that the T_g of the resulting BTDA-ODA polyimide films was ca. 275°C. Finally, at room temperature, stress was 35.6 MPa for the BTDA-ODA PAA and 36.0 MPa for the UR-3840. As observed on the semi-flexible PMDA-ODA polyimide, the BTDA-ODA polyimide did not show any dependency of the precursor origin on its stress–temperature profile once it imidized.

However, the stress relaxation due to moisture uptake is still faster in the polyimide film from the UR-3840 than in the film from the BTDA-ODA PAA, despite their relatively low T_g (ca. 275°C) (see *Figure 9*). The diffusion coefficient of water sorption (34.2×10^{-10} cm^2 s^{-1}) in the

Figure 7 Residual stress relaxation of the PMDA-ODA polyimide films on Si(100) wafers from various PMDA-ODA precursors measured at 25°C in 50% r.h. as a function of time. The thickness of the polyimide films was 10 μm
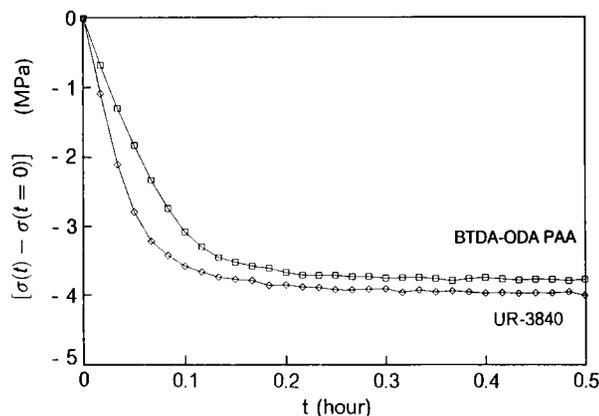
Figure 9 Residual stress relaxation of the BTDA-ODA polyimide films on Si(100) wafers from various BTDA-ODA precursors measured at 25°C in 50% r.h. as a function of time. The thickness of the polyimide films was 10 μm

polyimide from the UR-3840 was approximately five times higher than that $(7.1 \times 10^{-10} \, \text{cm}^2 \, \text{s}^{-1})$ in the film from the BTDA-ODA PAA. However, in the polyimide film from the UR-3840, the stress difference $(\Delta\sigma = \sigma_F(0) - \sigma_F(30 \, \text{min}))$ was 4.0 MPa, which was very close to that (3.8 MPa) of the corresponding polyimide from the BTDA-ODA PAA. This means that the degree of water uptake in the polyimide from the UR-3840 is only slightly higher than that in the corresponding polyimides from the BTDA-ODA PAA despite its five times higher diffusion coefficient of water. The T_g of BTDA-ODA polyimide is ca. 275°C, which is much lower than 400°C, the final cure temperature. Thus, microvoids in the resulting polyimide film from the UR-3840, which were possibly generated by outgassing of bulky photoactive groups and photopackages (that is, photo-initiator and photosensitizer) during curing, might be healed to a certain degree by the high polyimide chain mobility above T_g and consequently, the effect of the photosensitive precursor and its photopackage was minimized.

CONCLUSIONS

In situ stress measurements have been performed on silicon wafers for four different types of polyimides from their various precursors during thermal imidization and subsequent cooling over the range of 25–400°C using a wafer bending technique: fully rodlike PMDA-PDA, semi-rigid BPDA-PDA, semi-flexible PMDA-ODA and flexible BTDA-ODA polyimides. After 400°C cure from the poly(amic acid) (PAA) precursors, stress at room temperature was −7.1 MPa (in compression) for the PMDA-PDA polyimide, 6.7 MPa (in tension) for the BPDA-PDA, 29.3 MPa for the PMDA-ODA and 35.6 MPa for the BTDA-ODA. These results indicate that the residual stress of a polyimide film is primarily dependent upon the polymer chain rigidity: the order of increasing polymer chain rigidity is PMDA-PDA > BPDA-PDA > PMDA-ODA > BTDA-ODA. The higher polymer chain rigidity gives either the lower residual stress in tension or the higher stress in compression on Si wafer substrates. Among the polyimides studied here, the BTDA-ODA polyimide exhibits the highest overall stress (35.6 MPa) in spite of its relatively low T_g (ca. 275°C) and modulus (3.0 GPa). Therefore, it is evident that the overall residual

stress of a polyimide film on a silicon wafer is generated primarily by mismatch of the TECs between the polymer film and the silicon substrate and further accelerated by thermal history and mismatch in the other physical properties (that is, Young's modulus and Poisson's ratio). Therefore, TEC increases in the order BTDA-ODA > - PMDA-ODA > BPDA-PDA > PMDA-PDA.

We have found that the stress of a polyimide is dependent upon the origin of the precursor — poly(amic acid) (PAA), poly(amic dialkyl ester) (ES) and photosensitive precursor (that is, PAA/DMAEM in this study). At room temperature, the stress of PMDA-PDA polyimide film was −7.1 MPa for the PMDA-PDA PAA precursor, −1.3 MPa for the PMDA-PDA/DMAEM and 17.7 MPa for the m-PMDA-PDA ES. The stress of BPDA-PDA polyimide was 6.7 MPa for the BPDA-PDA PAA and 28.0 MPa for the BPDA-PDA/DMAEM. That is, the stress of both fully rodlike PMDA-PDA and semi-rigid PMDA-PDA polyimides is strongly dependent upon the history of their precursor origin. However, this precursor effect was not observed as readily on the stresses of both semi-flexible PMDA-ODA and flexible BTDA-ODA polyimide. These results suggest that the TEC of both PMDA-PDA and BPDA-PDA polyimides, which have a relatively long Kuhn length of > 120 Å, is significantly influenced by the history of their precursor origin, whereas that of both PMDA-ODA and BTDA-ODA polyimides with a relatively short Kuhn length of < 70 Å is little varied with the history of the precursor type. Furthermore, it is also suggested that in both rodlike PMDA-PDA and semi-rigid BPDA-PDA polyimides morphological structure (molecular in-plane orientation, molecular chain order and lateral packing order) and properties (Young's modulus and Poisson's ratio) are sensitive to the precursor origin, whereas in both PMDA-ODA and BTDA-ODA they are not sensitive.

For the polyimide films, stress relaxation due to moisture uptake was dynamically monitored in 50% r.h. at room temperature as a function of time. The diffusion coefficients of water sorption in the polyimide films were estimated from the stress relaxation profiles with time. In the polyimides from the poly(amic acid)s, the diffusion coefficient of water decreases in the order BPDA-PDA < BTDA-ODA < PMDA-PDA < PMDA-ODA. Their moisture-induced stress relaxation behaviour was dependent strongly upon the history of the precursor origin: the stress relaxation was in the decreasing order PAA < ES < DMAEM (photosensitive). Both the diffusion coefficient of water and the degree of water uptake were relatively low in the polyimides from the PAA precursors, intermediate in the film from the ES precursors and high in the films from the photosensitive precursors. These behaviours might result from morphological changes and microvoids generated by outgassing photosensitive groups or ethyl groups during thermal curing. In the case of photosensitive precursors, residues due to the photosensitive groups and photopackages, which may affect the moisture uptakability, are additionally expected in the resulting polyimides films.

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