Curing Effect on the Relaxation Modulus and Thermal Expansion Coefficient of Rodlike Polyimide Films

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ABSTRACT: For the films of PMDA-PDA (pyromellitic dianhydride–*p*-phenylenediamine) cured on silicon (Si) and gallium arsenide (GaAs) substrates at 400 °C, the corresponding thermal stresses, thermal expansion coefficients, and relaxation moduli increase with the increase of film thickness. The relaxation modulus increases with the increase of observation temperature. This may be attributed to the inherent characteristics of cross-linking and in-plane orientation of the films. With the increase of curing temperature, the variation of thermal stress with respect to temperature lessens and the thermal expansion coefficient decreases. For curing temperature changing from 200 to 250 °C, the decreases in the variation of thermal stress and thermal expansion coefficient and the increase in the relaxation modulus may mainly be attributed to the effect of a further imidization. Above 250 °C, the decreases in the variation of thermal stress, thermal expansion coefficient, and relaxation modulus with respect to curing temperature may presumably be attributed to the conversion of some intermolecular links to imides.

Introduction

Polyimides have been extensively studied for their importance in many applications. Polyimides can be used, for example, in electronics as flexible boards for printed circuit, tape-automated bonding, or solar cell, as an overcoat for α-particle shielding, as dielectric layers for multilayer interconnection, etc. All these applications utilize all or some of the superior characteristics possessed by polyimides, i.e. excellent mechanical strength, high glass transition temperature, high planarization, easy processibility, low dielectric constant, and low thermal expansion coefficient. These properties are indeed crucial to device fabrication, performance, and/or reliability.

Several problems may frequently arise from the stress originated from curing or deposition when a polyimide film is coated on other materials such as silicon, quartz, or glass substrate or deposited by a metal, ceramics, or another polymer thin film. Besides this intrinsic stress, thermal stress may arise when the given multilayer structure is subjected to thermal cycling or temperature variation due to thermal mismatch. These stresses, if too high, may cause serious bending, warpage, delamination, and/or cracking in the structure.[1,2] Minimizing the stresses is the most straightforward and also effective method in avoiding these undesired problems. Thermal stress can be easily minimized by selecting a polyimide or tailoring a polyimide blend or copolymer with a thermal expansion coefficient (TEC) matching that of the substrate material. However, the TEC of a given polyimide film cured on substrate has been found to be strongly dependent on its coating thickness.[3] It may also vary significantly with different curing temperatures. This is since the rigid imide chain is converted from its flexible amic acid counterpart. Obtaining a further understanding, or most ideally a precise quantitative relationship regarding the dependence of the TEC on curing temperature, is therefore necessary.

Furthermore, multilayered structures, such as metal–polyimide–substrate, are often encountered in multichip module packaging.[4-6] Stress will also significantly arise in the metal layer during deposition and/or upon post-annealing. The stress in the metal layer or fine line, especially that being formed after some microlithographic processes, has been realized as a fatal factor to the integrity of metal interconnection.[7-9] The problem would become worse if the stress was higher and the metal line was finer, especially when an electric current was being applied. The stress, however, may be reduced by the usage of a less stiff polyimide layer that exhibits a smaller relaxation modulus.[10,11] Having a thorough understanding regarding the relaxation modulus of a given polyimide film therefore seems useful. Cross-linking, especially for rigid rodlike polyimide films, undoubtedly exist—having been formed through intermolecular links (or called transimides).[12-14] The links that have formed at some lower curing temperatures would break at elevated temperatures since they are thermodynamically unstable. This may greatly affect the mechanical properties, especially relaxation modulus, of the film. Seeing how the relaxation modulus is affected by different curing temperatures would then be very interesting.

A bending beam technique with the usage of two different substrates has been employed for the above purposes. This technique has been previously proven to be an effective method in simultaneously determining the relaxation modulus and TEC of a given polyimide.[3] In the study, only the fully cured films have been investigated. In this study, we have investigated both the effects of curing temperature and coating thickness on the relaxation modulus and TEC of a rodlike polyimide. Procedures concerning sample preparations and bending beam experiments will be described in the following section. A complete review regarding the theory of the bending beam technique has been given in ref 3 and will be omitted here for brevity.

Experimental Section

Materials. The starting materials used here were pyromellitic dianhydride (PMDA) and diamine *p*-phenylenediamine (PDA). The solvent was *N*-methylpyrrolidone (NMP). These materials were used as received. The substrates used were a 3-in. ⟨100⟩ orientation silicon (Si) and a 3-in. ⟨100⟩ orientation gallium arsenide (GaAs) wafers.

Synthesis of Poly(amic acid). The homopolymer of PMDA–PDA polyamic acid was prepared as follows: In a four-neck flask, the diamine, PDA, was dissolved in NMP. Dianhydride PMDA of an equal molar amount was gradually added when the diamine was completely dissolved.[15] The reaction proceeded for 8 h with stirring. The entire process was done in a nitrogen atmosphere. The resulting solutions had a solid content of 14 wt %.

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Imidization. All the samples, before being clamped on the bending beam apparatus for stress measurement, were prepared by spin-casting the resulting poly(amic acid) solutions on the desired substrates and prebaking at 80 °C for 30 min. The resulting samples were then thermally imidized. One batch of the samples was heated up to 400 °C at a ramp rate of 2 °C/min and kept at 400 °C for 30 min. To investigate the effect of curing temperature, another batch of the samples was successively annealed at several different constant temperatures from 200 to 400 °C with a 50-deg increment. The curing time was 20 min for each curing temperature. The samples were cooled to 100 °C each time after curing and before being heated to the next curing temperature. A ramp rate of 1 °C/min was used during heating. The film thickness of each sample was calculated after imidization by measuring its weight, width, and length and by knowing its density. All the prebaking and curing processes were performed in air.

Bending Beam Experiment. A schematic illustration of the setup of a bending beam apparatus used for the film stress measurements can be referred to in ref 14. A thermocontrolled oven with an optical window to admit laser light was enclosed after the sample was mounted on a clamp. The deflection positions of the reflected laser beam from the silicon strip were recorded while cooling down after curing. Bending curvature variation of the specimen at various temperatures could be calculated from the change in the deflection position. This was calculated according to the geometry of the experimental setup. Variation in the thermal stress in the film could likewise be readily calculated from the obtained bending curvature change according to eq 1. This was deduced from a stress analysis model for multilayer structures presented in the paper.[16]

$$\sigma_{t,i} = \frac{1}{6}\frac{E_i}{1-\nu_i}\frac{d_i^3}{(d_i+d_f)}\left(\frac{1}{R}-\frac{1}{R_0}\right) \quad (1)$$

where R and R_0 are the respective bending curvature radii at any given observation temperature and at any chosen reference temperature. $E_i/(1-\nu_i)$ is the biaxial modulus of the ith substrate, and d_i and d_f are the respective thicknesses of the ith substrate and the film.

Results and Discussion

Effect of Thickness on Thermal Stress. The thermal stress, σ_t, exhibited in a given film varies with the different substrates used due to the difference in thermal mismatch. The thermal stress variations in the films of PMDA–PDA on Si during cooling from a curing temperature of 400 °C are shown in Figure 1a. The stresses were presented on a relative basis. These films apparently have a thermal expansion coefficient (TEC) higher than that of Si. This is since they became more tensile when being cooled to a lower observation temperature. A similar behavior has been observed for the films cured on GaAs, as shown in Figure 1b. The stress variations for the films on Si were more marked than those on GaAs since the TEC of Si is smaller than that of GaAs. The stress variation with respect to temperature, $d\sigma_t/dT$, varied systematically with the variation of thickness as observed.

Parts a–c of Figure 2 show the dependencies of $d\sigma_t/dT$ on coating thickness for the films of PMDA–PDA on Si and GaAs at three respectively different observation temperatures, 150, 200, and 250 °C. No reliable results could be obtained at temperatures below 150 °C since the experiments were performed in an open system and the films would absorb moisture. The absolute magnitude of the $d\sigma_t/dT$ data, however, increases with the increase of thickness. This indicates that either TEC or the relaxation modulus of the film increases with the increase of thickness.

Effect of Thickness on TEC. A thickness-dependent TEC can be calculated for these imide films according to eqs 1 and 2 in ref 3. The obtained TECs of the films for PMDA–PDA with different thicknesses at the three

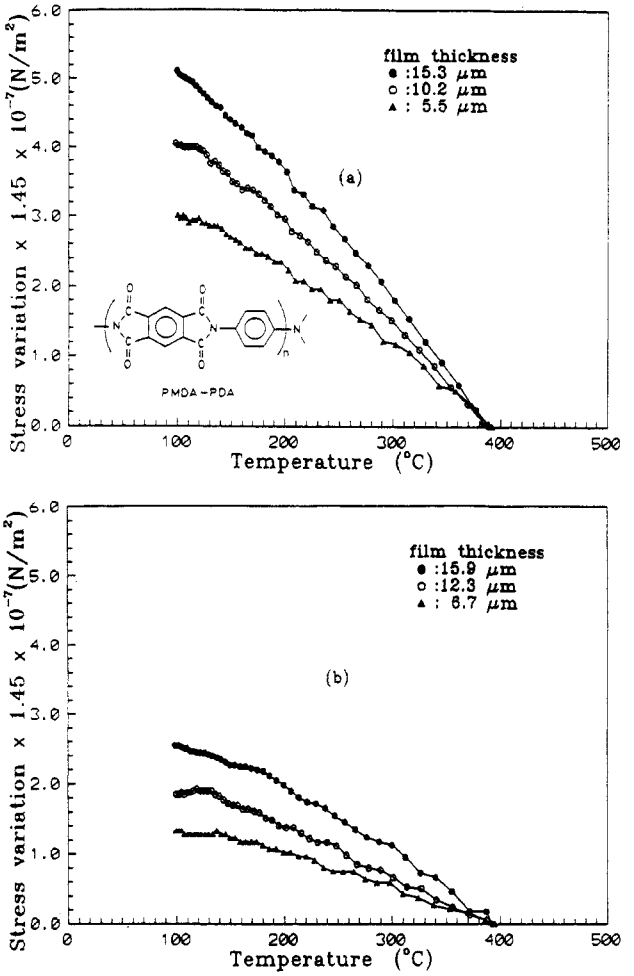

Figure 1. Stress variations with respect to observation temperature for PMDA–PDA films with different thicknesses coated on (a) Si and (b) GaAs substrates.

different observation temperatures are shown in Figure 3. They are seen to increase with the increases of thickness and observation temperature. These phenomena are in accordance with those being observed for the films of PMDA–B.[3] The increase in TEC with respect to thickness can be attributed to the decrease in film orientation.[17] The thickness range studied for PMDA–PDA was much more narrow than that for PMDA–B. This was due to the film of PMDA–PDA being relatively fragile and breaking into pieces if too thick. The film of PMDA–PDA, however, has exhibited a somewhat smaller TEC dependence on thickness, based on the same thickness range. This may be attributed to the fact that the imide structure of PMDA–PDA is less rigid than that of PMDA–B, according to their molecular structures and the measured TECs. The dependence of film orientation on thickness becomes more marked as the film rigidity increases, as previously revealed.[17]

Effect of Thickness on Relaxation Modulus. The calculated relaxation modulus of the film for PMDA–PDA is shown in Figure 4. Its relaxation modulus, in lieu of biaxial relaxation modulus, is presented in order to compare with any other result obtained using conventional methods. A Poisson's ratio of 0.47 was assumed in the calculation. The modulus, however, significantly increases with the increase of thickness at all the different observation temperatures, no matter whether being in terms of relaxation modulus or biaxial relaxation modulus. At 150 °C, for example, it increases from 7.8 to 8.6 × 10^9 N/m² for thickness increasing from 10 to 16 μm. Thicker polyimide films have generally exhibited a lower in-plane

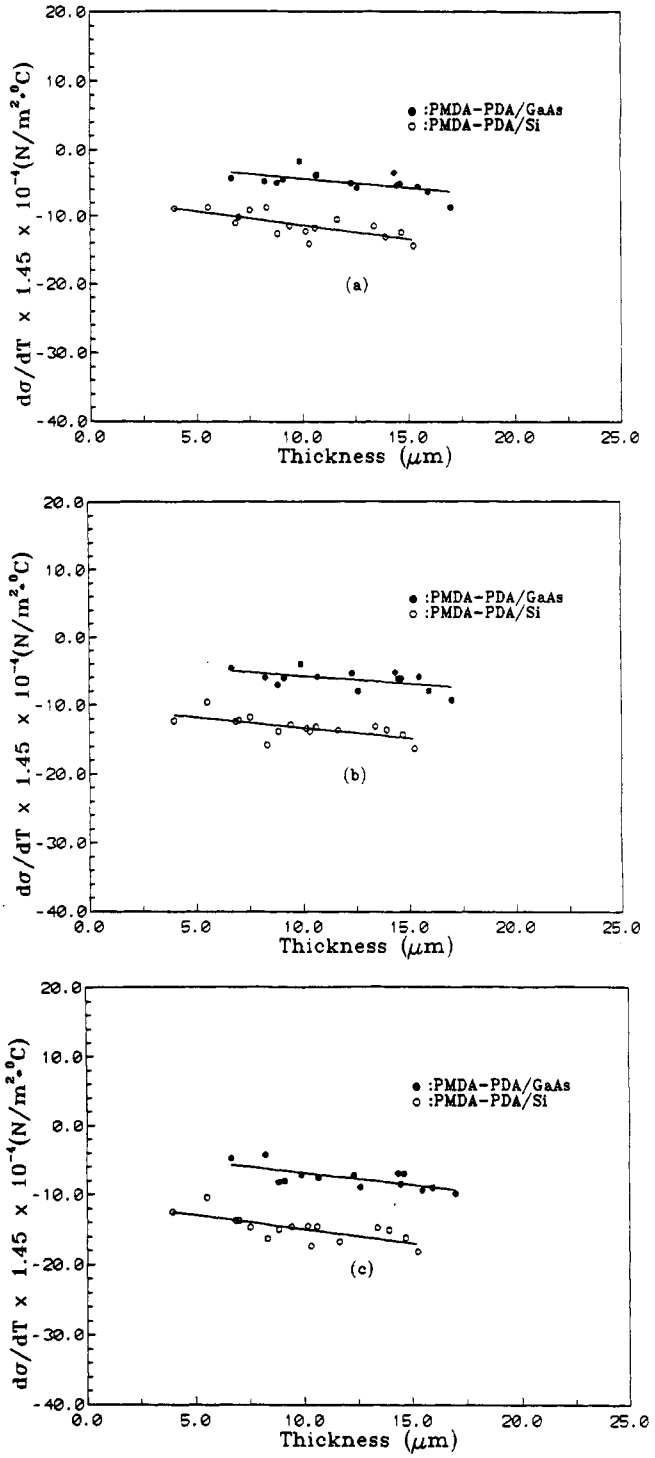

Figure 2. Calculated slopes of the stress variation curves for the PMDA-PDA films with different thicknesses on Si and GaAs substrates at three different observation temperatures: (a) 150 °C, (b) 200 °C, and (c) 250 °C.

orientation and might have a smaller elastic constant, as previously revealed.[17] The thicker polyimide films of PMDA-PDA studied here have, on the contrary, exhibited a larger relaxation modulus. This phenomenon is in accordance with that observed for the films of PMDA-B and may presumably be attributed to the presence of voids in the films.[3,18] The thicker films may have contained, on average, a smaller fraction of voids and/or voids with a smaller size. Stress relaxation behavior would, as a result, be lessened and a higher relaxation modulus would be resultant in these thicker films.

Furthermore, thicker polyimide films cured on substrates seem to exhibit a higher degree of cross-linking, as revealed in a previous study.[19] The presence of cross-link

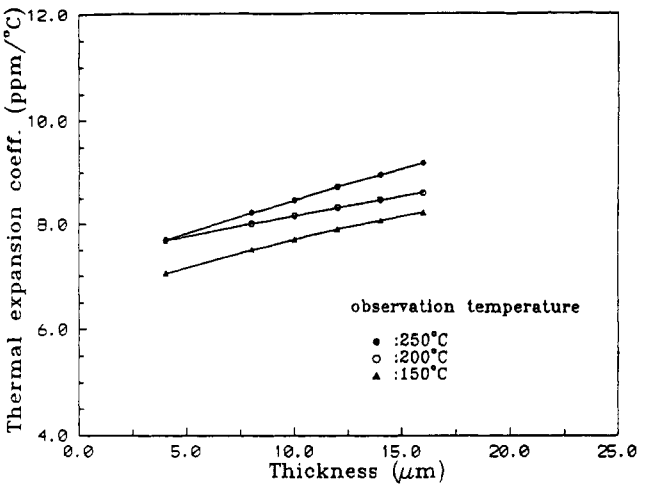

Figure 3. Calculated thermal expansion coefficients of the PMDA-PDA films with different thicknesses at three different observation temperatures.

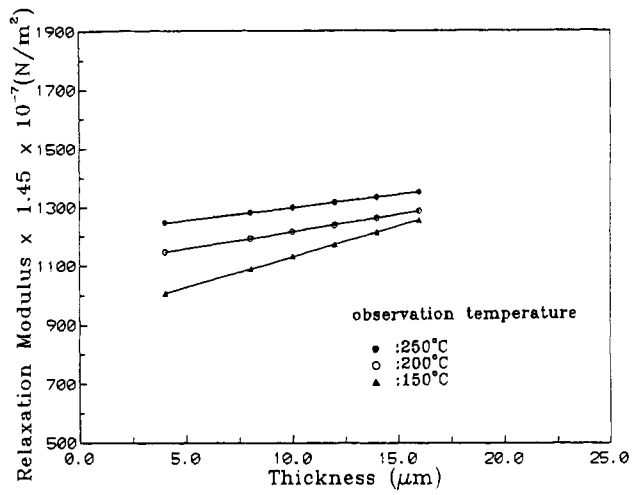

Figure 4. Calculated relaxation moduli of the PMDA-PDA films with different thicknesses at three different observation temperatures.

is known to significantly enhance the mechanical characteristics of a given polymer film, especially when the film is under stress and stress relaxation is present. The thicker films would then exhibit a higher relaxation modulus, as observed.

The relaxation modulus being shown, by further examination of the above data, to be higher at the higher observation temperatures based on the same thickness is surprising. For the 8-μm-thick film, for example, the relaxation modulus increases from 7.5 to 8.8 × 10^9 N/m^2 for observation temperatures changing from 150 to 250 °C. This is contrary to what can be observed typically for most polymers. However, this is not at all unusual for rubbers or cross-linked polymers under a stretching condition. The force of contraction of a given rubber or elastomer being stretched to a certain level has been well-known to increase with the increase of temperature, for the contribution of entropy elasticity to the entire elasticity is dominant.[20] These polyimide films should be cross-linked, as just mentioned above. They have been biaxially stretched (or oriented) when being cured on the substrates. Polyimide films cured on substrates exhibiting an in-plane orientation have been reported in many studies.[17,21-23] Details can be referred to in this literature and will be omitted here. The relaxation moduli of these films would, as a result, increase with the increase of observation temperature as found.

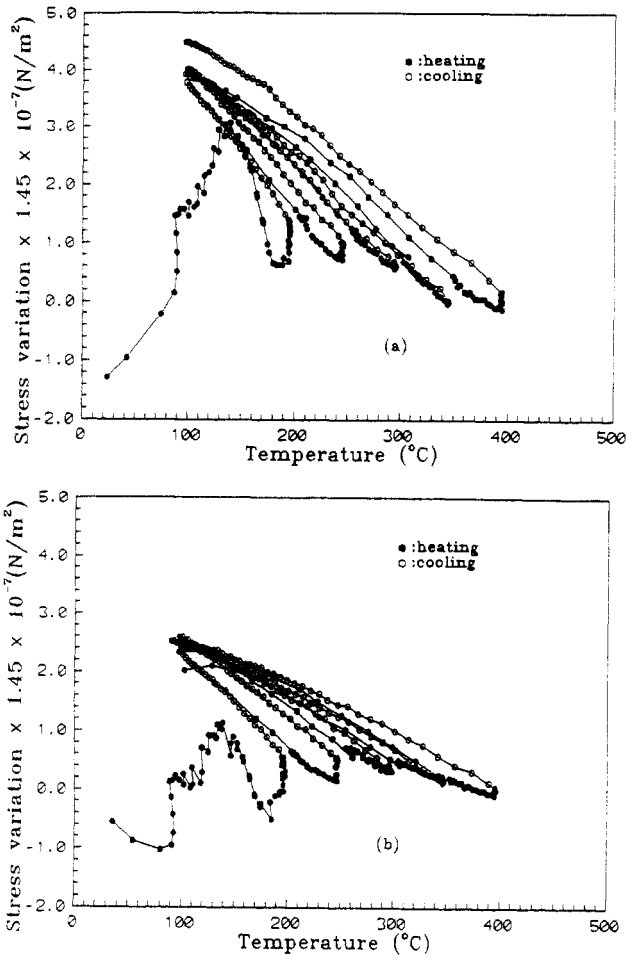

Figure 5. Stress variations with respect to observation temperature for the PMDA–PDA films, coated on (a) Si and (b) GaAs substrates, at five different curing temperatures. The thickness is 13.7 μm for the film on Si and 15.4 μm on GaAs.

Effect of Curing on Thermal Stress. The films were cured directly to 400 °C after prebaking in the above experiments. They should be fully imidized according to a previous Fourier transform infrared study,[14] wherein the film of PMDA–PDA has become nearly fully cured at 250 °C. The effect of curing on thermal stress, as well as TEC and relaxation modulus, however, needed to be examined. A separate batch of the films of PMDA–PDA were cured successively from 200 to 400 °C, and their thermal stress variations during cooling were measured in situ. The resulting curves of thermal stress variation for the PMDA–PDA films on Si and GaAs are respectively shown in Figure 5a,b. The thickness of the film is 13.7 μm for the former system and 15.4 μm for the latter one. The variation of thermal stress is seen to lessen for both systems with the increase of curing temperature. The drastic change in the variation of thermal stress, for curing temperatures changing from 200 to 250 °C, may mainly be attributed to the effect of imidization. The change above 250 °C may presumably be attributed to the fact that some intermolecular links (or called transimides) would convert to imides at elevated temperatures.[12,14] This is since the intermolecular links being formed at lower curing temperatures would undergo a chain scission reaction and convert to imides at an elevated temperature. These intermolecular links are thermodynamically unstable when compared with regular imide chains.

Effect of Curing on TEC. The effect of curing on thermal stress was learned here to vary with thickness by performing the above experiment on the films of PMDA–PDA with different thicknesses. The effect of curing on

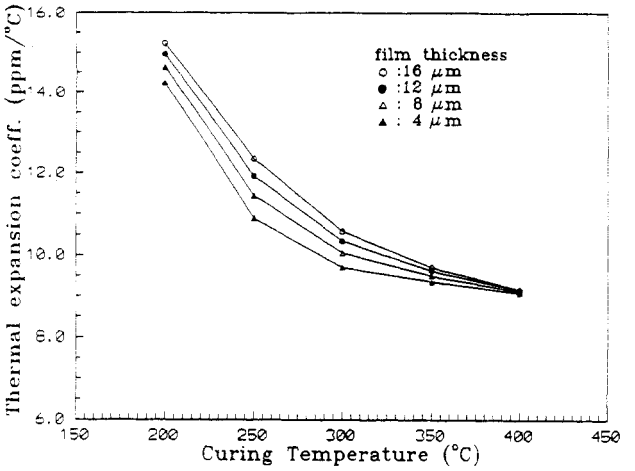

Figure 6. Effect of curing temperature on the thermal expansion coefficient of the PMDA–PDA films with four different thicknesses. The corresponding observation temperature is 175 °C.

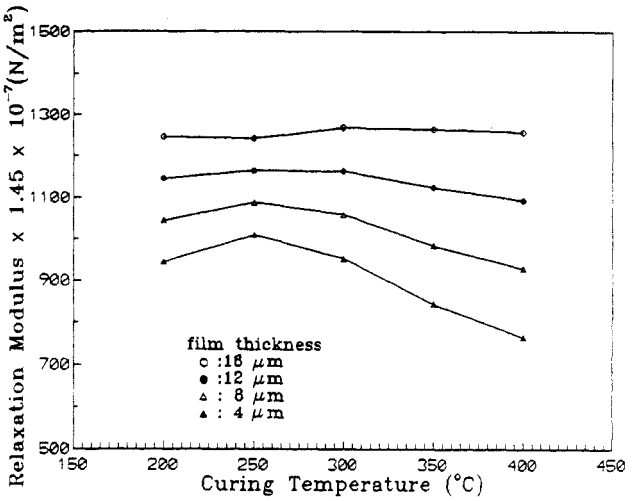

Figure 7. Effect of curing temperature on the relaxation moduli of the PMDA–PDA films with four different thicknesses. The corresponding observation temperature is 175 °C.

the TECs of PMDA–PDA films with different thicknesses is shown in Figure 6. The calculated TEC based on the same thickness obviously decreases with the increase of curing temperature. The decrease in TEC is most marked especially for curing temperatures increasing from 200 to 250 °C. The films were not completely cured at 200 °C, as mentioned previously. At 250 °C, the uncured amic acid chains, which are semiflexible and should have high thermal expansion characteristics, would convert to the imide counterparts, which are rigid and have low thermal expansion characteristics. This would then result in the film being a lower TEC, as observed. The TEC keeps decreasing at temperatures higher than 250 °C. This may also be attributed to the conversion of intermolecular links to their imide counterparts. This is because the links lack a structural symmetry and therefore can hardly form any coplanar, resonant structure. They are then much more likely to vibrate and expand when subjected to heat. They should consequently have higher thermal expansion characteristics.

Effect of Curing on Relaxation Modulus. Figure 7 shows the calculated relaxation moduli of the PMDA–PDA films with different thicknesses at five different curing temperatures. The relaxation modulus, based on the same curing temperature, increases unanimously with the increase of thickness for all the five different curing

temperatures. Restated, stress relaxation becomes less and less prominent when the film thickness increases. This is regardless of what the curing temperature is. The observation temperature used here is 175 °C.

The effect of curing temperature on relaxation modulus, however, seems to be complicated; i.e. it varies with the films with different thicknesses. For the thinnest film studied here, i.e. 4 μm, for example, the modulus first increases significantly when the curing temperature increases from 200 to 250 °C. It then starts decreasing at above 250 °C. These phenomena are also exhibited in those thicker films; they, however, become less and less prominent with the increase of thickness. The relaxation modulus for the thickest film studied, i.e. 16 μm, becomes nearly unvaried with respect to curing temperature.

The modulus of a given polyimide film should theoretically increase when more and more semirigid amic acid chains convert to rigid imide chains. The modulus should, as a result, increase with the increase of curing temperature. The degree of imidization of PMDA–PDA would change from 85 to 98% for a curing temperature changing from 200 to 250 °C.[14] This may be used in explaining why the moduli shown above increase with the increase of curing temperature from 200 to 250 °C. The decrease in modulus at above 250 °C may presumably be attributed to the conversion of inermolecular links to imides, as mentioned above. The links may actually be treated as cross-links and would consequently provide the film with a better mechanical resistance against stress relaxation. This would then result in a higher relaxation modulus. The relaxation modulus should drop, as observed when the conversion from intermolecular links to imides occurs at the elevated temperature. This may be used in explaining why the relaxation modulus became smaller and smaller as the curing temperature kept increasing at above 250 °C.

The reason the thickest film is nearly unaffected by varying the curing temperature can be seen as follows. Polyimide films cured on substrates exhibit cross-linking, as mentioned above. The extent of cross-linking increases with the increase of film thickness.[19] In other words, the thickest film studied here should have the highest degree of cross-linking. Cross-linking is thought to possibly become the major factor in affecting the relaxation modulus exhibited in the film when the degree of cross-linking exceeds a certain level. It is because the film would have a networking structure through the formation of interlinks and should have a comparatively high mechanical strength. When the film becomes thicker, its higher degree of cross-linking should give itself a stronger mechanical characteristics. It is very likely that when the thickness increases to a certain extent, the degree of cross-linking is so high that the mechanical strength of the networking structure, that comprises some uncured amic acid chains, is so high that it becomes comparable with that of the structure comprising pure imide chains. Therefore, the conversion of the residual, namely 13%, uncured amic acids to imides when the curing temperature is raised from 200 to 250 °C then has a weaker and weaker effect on the modulus as the thickness increases. The conversion of some interlinks to imides when the film is cured at above 250 °C would likewise have a lesser effect on the reduction of modulus for the thicker films. This may expalin why the relaxation modulus becomes less and less affected by the variation of curing temperature as the film thickness increases.

Conclusion

For the films of PMDA–PDA cured on Si and GaAs substrates at 400 °C, the corresponding thermal stresses, thermal expansion coefficients, and relaxation moduli increase with the increase of film thickness. The thicker films have exhibited a higher relaxation modulus since they may contain a smaller fraction of void content and have a higher degree of cross-linking. The increase of the relaxation modulus with respect to observation temperature may be attributed to the inherent characteristics of cross-linking and in-plane orientation of these films.

With the increase of curing temperature, the variation of thermal stress with respect to temperature becomes lessened and the thermal expansion coefficient decreases. For curing temperature changing from 200 to 250 °C, the decreases in the variation of thermal stress and thermal expansion coefficient and the increase in the relaxation modulus may mainly be attributed to the effect of a further imidization. Above 250 °C, the decreases in the variation of thermal stress, thermal expansion coefficient, and relaxation modulus with respect to curing temperature may presumably be attributed to the conversion of some intermolecular links to imides.

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Registry No. PDA/PMDA (copolymer), 25038-82-8; PDA/PMDA (SRU), 26099-65-0; Si, 7440-21-3; GaAs, 1303-00-0.