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Simultaneous Determination of the Biaxial Relaxation Modulus and Thermal Expansion Coefficient of Rigid-Rod Polyimide Films Using a Bending-Beam Technique

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ABSTRACT: A bending-beam technique with the use of two different substrates, silicon and gallium arsenide, has been successfully employed to simultaneously determine the biaxial relaxation modulus, $E_f/(1 - \nu_f)$, and thermal expansion coefficient, α_f , of a rigid-rod-like polyimide film, PMDA-B (pyromellitic dianhydride-benzidine), coated on a substrate. As measured, the two properties, especially α_f , significantly increase with the increase of film thickness. At an observation temperature of 150 °C, for example, the obtained $E_f/(1 - \nu_f)$ increases from 6.0×10^9 to 8.7×10^9 N/m², and α_f from -0.33×10^{-6} to $+2.89 \times 10^{-6}$ /°C for thicknesses ranging from 10 to 35 μ m. The increase of the thermal expansion coefficient with respect to film thickness can be attributed to the decrease in the in-plane orientation of the film, according to an X-ray diffraction experiment. The increase of the biaxial relaxation modulus with respect to thickness may presumably be attributed to the decrease in the void size and/or void fraction in the film.

Introduction

Polyimides have drawn more and more attention for their importance in electronic packaging applications.¹⁻⁴ Generally speaking, they have relatively high glass-transition temperatures, high planarization, high processibility, low dielectric constants, and low thermal expansion coefficients. All these properties are crucial to device fabrication, performance, and/or reliability. However, several problems may arise from the stress in the polyimide film, when it is coated on other materials such as silicon, quartz, or glass substrate, due to mismatch in thermal expansion coefficients.⁵⁻⁷ The resulting stress, if too high, may cause serious bending, warpage, delamination, or cracking in a given layered structure or device composed of different materials.

Therefore, many studies have been focused on the measurement and/or analysis of stress in polyimide films coated on substrates.⁸⁻¹⁴ Among them, a few works have attempted to determine the elastic constant or thermal expansion coefficient of the films from the thermal stress data using a single substrate. However, the approach is not easy, regardless the correctness of its result. Using the thermal stress result to determine the thermal expansion coefficient of a given film, one must first know its biaxial relaxation modulus, or vice versa. This is usually obtained by separately measuring its relaxation modulus and Poisson's ratio. As known, neither two measurements is simple, if not impossible. Especially when the film is fragile, the measurements would become nearly impossible. Even if the film is not fragile, determination of its relaxation modulus requires its tensile testing, for example, performed at an infinitely low straining rate, if a conventional tensile tester is employed. In practice, this is an extremely difficult task.

It might seem easier using the thermal stress data to determine the biaxially relaxation modulus. This first requires an accurate measurement of the corresponding thermal expansion coefficient. As known, however, the resolution of conventional thermal mechanical analyzers is about 5×10^{-6} /°C, too poor for low thermal expansion polyimides. Some dilatometers have much better resolution, but demand "rigid" samples. Polyimide films are too weak or soft to stand vertically to be measured, unless

they are rolled up. Since most low thermal expansion, rigid polyimide films are relatively fragile, they cannot be rolled up for the above purpose. It can be seen that it is also not very easy to accurately determine the thermal expansion coefficient of a given low thermal expansion polyimide film using conventional methods.

Furthermore, it has been found that a given polyimide film coated on a substrate, such as silicon or quartz, exhibits a relaxation modulus significantly smaller than its elastic modulus.¹³ The difference should result from stress relaxation, which may account for the marked discrepancy found between the Young's modulus and thermal expansion coefficient of the polyimide film calculated from the thermal stress data and measured by typical methods.¹⁰ In order to have a sound prediction of the thermal stress that a polyimide film may exhibit when coated on any given substrate during thermal cycling, it definitely requires an appropriate method to accurately determine its relaxation modulus and thermal expansion coefficient.

For the above purpose, a bending-beam technique, which has been extensively used in the measurement of stress in various thin films deposited on substrates,^{9,12-18} has been employed. This is done by measuring the thermal stresses in the same polyimide films separately deposited on two different substrates.¹⁵ The substrates used must have thermal expansion coefficients significantly different from each other, and one substrate must have a thermal expansion coefficient near that of the film to be measured.

Theoretical Section

The thermal stress existing in a film deposited on a substrate is a function of thermal mismatch between the film and the substrate. It can be expressed as¹⁸

$$\sigma_{t,1} = \frac{E_f}{1 - \nu_f} \int_{T_i}^{T_f} (\alpha_1 - \alpha_f) dT \quad (1a)$$

$$\sigma_{t,2} = \frac{E_f}{1 - \nu_f} \int_{T_i}^{T_f} (\alpha_2 - \alpha_f) dT \quad (1b)$$

where $\sigma_{t,i}$ ($i = 1, 2$) is the thermal stress in the film coated on an i th substrate. $E_f/(1 - \nu_f)$ is the biaxial relaxation

modulus of the film. α_i and α_f are the thermal expansion coefficients of the i th substrate and the film, respectively. T_i and T_f are the initial and final temperatures.

By measuring the stress in the film at various temperatures, one can establish a stress-temperature curve, from which one can obtain the slope of the curve at any given temperature within the range investigated.

$$\frac{d\sigma_{t,1}}{dT} = \frac{E_f}{1-\nu_f}(\alpha_1 - \alpha_f) \quad (2a)$$

$$\frac{d\sigma_{t,2}}{dT} = \frac{E_f}{1-\nu_f}(\alpha_2 - \alpha_f) \quad (2b)$$

After a simple manipulation of these two equations, one can readily calculate the biaxial modulus and thermal expansion coefficient of the film according to the following equations

$$\frac{E_f}{1-\nu_f} = \frac{d\sigma_{t,2}/dT - d\sigma_{t,1}/dT}{\alpha_2 - \alpha_1} \quad (3a)$$

$$\alpha_f = \frac{C\alpha_2 - \alpha_1}{C - 1} \quad (3b)$$

where the arbitrary constant C is defined as

$$C \equiv \frac{d\sigma_{t,1}/dT}{d\sigma_{t,2}/dT}$$

Basically speaking, the accuracy of this method strongly depends on the difference between the two thermal mismatches, $\alpha_1 - \alpha_f$ and $\alpha_2 - \alpha_f$. As can be seen in eq 2a and 2b, if the two substrates have thermal expansion coefficients too close to each other, the two corresponding stress-temperature slopes, $d\sigma_{t,1}/dT$ and $d\sigma_{t,2}/dT$, would consequently be too close to distinguish, regardless of whether the film has high or low thermal expansion characteristics. Some small experimental inaccuracy in the measurement may give rise to a serious error in the calculation results according to eq 3a and 3b. Similarly, such a double-substrate approach will not work if the given film has a thermal expansion coefficient very different from those of the two substrates used. This, however, also depends on machine resolution and sample-to-sample reproducibility.

Experimental Section

Materials. The starting materials used in this study were pyromellitic dianhydride (PMDA) and diamines: 4,4'-oxydianiline (ODA) and benzidine (B). The solvent used is *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 Polyamic Acids. Homopolymers of PMDA-ODA and PMDA-B polyamic acids were prepared as follows: in a four-neck flask, dissolving diamine, ODA, or B, in NMP. When the diamine was completely dissolved, dianhydride PMDA of equal molar amount was added gradually.¹⁹ The reaction proceeded for 8 h with stirring. The entire process was done in a nitrogen atmosphere. The resulting solutions have a solid content of 14 wt %. The molecular structures of the resulting polyimide are shown in Figure 1.

Imidization. All the samples, before being clamped on the bending-beam apparatus for stress measurement, were prepared by spin-casting the resulting polyamic acid solutions on the desired substrates and prebaking them at 80 °C for 30 min. The resulting samples were then imidized by heating to 350 °C at a

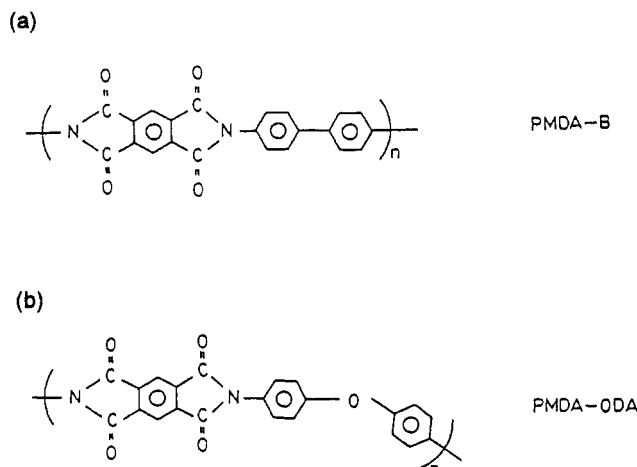


Figure 1. Molecular structures of the studied aromatic polyimides: (a) rigid-rod-like polyimide PMDA-B and (b) semiflexible polyimide PMDA-ODA.

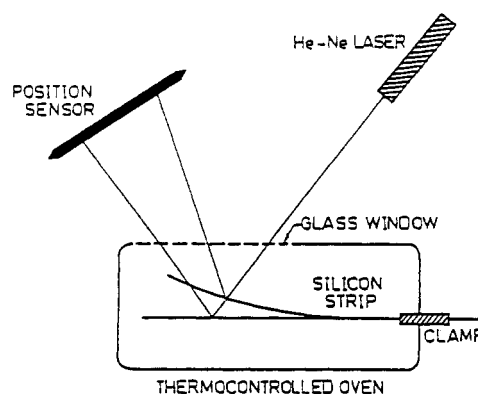


Figure 2. Schematic diagram of the experimental setup for the measurement of stress in the polyimide film coated on a substrate using a bending-beam apparatus.

ramp rate of 3.5 °C/min and kept at 350 °C for 30 min. After imidization, the film thickness of each sample was calculated by measuring its weight, width, and length, by knowing its density.

Bending-Beam Experiment. Figure 2 shows schematically the experimental setup of a bending-beam apparatus used for the film stress measurements. After the sample was mounted on a clamp, a thermocontrolled oven with an optical window to admit laser light was enclosed. While ramping up, the deflection positions of the reflected laser beam from the silicon strip were recorded. According to the geometry of the experimental setup, the bending curvature variation of the specimen at various temperatures could be calculated from the change in the deflection position. Likewise, variation in the thermal stress in the film could be readily calculated from the obtained bending curvature change according to eq 4, deduced from a stress analysis model

$$\sigma_{t,i} = \frac{1}{6} \frac{E_i}{1-\nu_i} \frac{d_i^3}{(d_i + d_f)} \left(\frac{1}{R} - \frac{1}{R_0} \right) \quad (4)$$

for multilayer structures, presented in ref 20, where R and R_0 are the bending curvature radii at any given observation temperature and at any chosen reference temperature, respectively. $E_i/(1-\nu_i)$ is the biaxial elastic modulus of the i th substrate. d_i and d_f are the thicknesses of the i th substrate and the film, respectively.

X-ray Diffraction Experiment. X-ray diffraction experiments were done using a Rigaku wide-angle X-ray diffractometer with a nickel-filtered $\text{Cu K}\alpha_1$ radiation. Its power setting was at 30 kV and 20 mA. For out-of-plane diffraction, the films were so arranged that the film plane was perpendicular to the plane formed by the incident and reflected X-ray beams. Details regarding X-ray sample preparation and the arrangement of X-ray diffraction experiment can be referred to in the paper.²¹

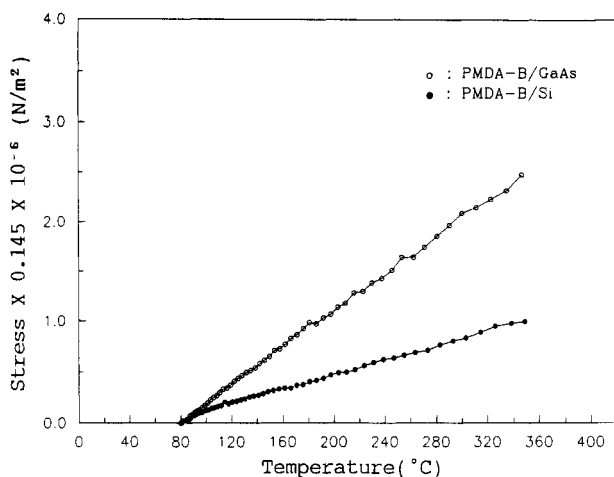


Figure 3. Variation of thermal stress, with respect to temperature, in the films of PMDA-B coated on GaAs and Si substrates.

Results and Discussion

Figure 3 shows the variations of thermal stress with respect to temperature in the films of PMDA-B coated on Si and GaAs substrates. It should be noted that the thermal stresses shown here are on a relative basis. As seen, the thermal stress in the film coated on either Si or GaAs substrate increases with the increase of temperature, indicating that its thermal expansion coefficient must be smaller than that of either one of the substrates. The thermal expansion coefficients of the Si and GaAs substrates measured at various temperatures using a dilatometer are listed in Table I. Since the imide structure of PMDA-B is rigid-rod-like, as shown in Figure 1, it should naturally have relatively low thermal expansion characteristics. Here, the thicknesses of the films coated on the Si and GaAs substrates are 16.9 and 16.1 μm , respectively.

Contrary to the above PMDA-B films, the film of PMDA-ODA coated on the Si or GaAs substrate has exhibited a negative slope in the thermal stress-temperature curve; i.e. its thermal stress decreases with the increase of temperature, as shown in Figure 4. Apparently, the film must have a thermal expansion coefficient greater than that of either of the substrates. The thicknesses of the films of PMDA-ODA coated on the Si and GaAs substrates are both 18.1 μm .

As also noted, the slope of the thermal stress-temperature curve for either polyimide varies with the variation of film thickness, especially for the rigid-rod polyimide PMDA-B. Similar phenomena have been observed for the films composed of a different rigid-rod polyimide, as reported in ref 14. Figures 5 and 6 show the calculated slopes of the thermal stress-temperature curves for the films of PMDA-B and PMDA-ODA, respectively, with various thicknesses at 150, 200, and 250 $^{\circ}\text{C}$. Below 100 $^{\circ}\text{C}$, these films would take up moisture and swell, and the resulting data would deviate from their thermal stress-temperature curves. Since the slopes are a function of film thickness, calculation of the biaxial relaxation modulus and thermal expansion coefficient of a polyimide coating must be based on data from films with the same thicknesses. This is done by using data calculated from the best fitting curve of first order of the experimental data based on the same thickness. The obtained thermal expansion coefficients and biaxial relaxation moduli of the films of PMDA-B with different thicknesses at three different temperatures are shown in Figures 7 and 8, respectively.

As seen in Figure 7, at 150 $^{\circ}\text{C}$, for example, the thermal expansion coefficient of the film of PMDA-B varies from

-0.33×10^{-6} to $+2.89 \times 10^{-6}/^{\circ}\text{C}$ when its thickness increases from 10 to 35 μm . This polyimide has a thermal expansion coefficient even smaller than that of the silicon substrate, except when it is thicker than 30 μm . The observed low thermal expansion characteristics of the film of PMDA-B can be attributed to its highly symmetric, rigid-rod-like imide structure. Furthermore, the calculated thermal expansion coefficient apparently increases with the increase of thickness. This coincides with the result reported in the previous study,¹⁴ wherein, however, for the calculation of the thermal expansion coefficient, the relaxation modulus of the polyimide film has been assumed to be independent of film thickness. According to the study, the increase of the thermal expansion coefficient with respect to film thickness can be attributed to the fact that the in-plane orientation of the polyimide film decreases when its thickness increases. To confirm this thought, an X-ray diffraction experiment has been performed. The resulting out-of-plane diffraction patterns of the films of PMDA-B with various thicknesses are shown in Figure 9. The peak at $2\theta = 20.9^{\circ}$ corresponds to the ordering of the intermolecular spacing of imide chains in the films.^{22,23} When the thickness of the film increases, its diffraction intensity decreases. This means that less and less imide chains have been preferably aligned in the direction parallel to the plane of the film when the thickness increases. Consequently, the in-plane orientation of the film decreases with the increase of thickness. As known, a film with a poorer in-plane orientation will exhibit a higher thermal expansion characteristic in the film plane direction.

Similarly, at the other studied temperatures, such as 200 and 250 $^{\circ}\text{C}$, the thermal expansion coefficient of the PMDA-B film consistently increases when its thickness increases, as demonstrated in Figure 7. On the basis of the same thickness, the calculated thermal expansion coefficient increases with the increase of observation temperature throughout the entire thickness range. This phenomenon is typical. However, it is interesting to see that when the film is relatively thin, such as 10 μm , it exhibits a negative thermal expansion coefficient at 150 or 200 $^{\circ}\text{C}$. This result is not unusual if one recalls the negative thermal expansion behavior frequently observed in polymeric fibers or rubbers, stretched to a certain extent, in the stretching direction. As mentioned previously, polyimide films obtained by curing on a substrate, without exception, exhibit an in-plane orientation. The in-plane orientation would become much more significant if the films are composed of rigid-rod-like polyimides, as shown in ref 14. As also shown in that paper, the dependency of the in-plane orientation on film thickness is very pronounced in rigid-rod-like polyimides. Coupling with its low thermal expansion nature, the effect of orientation and its dependency on thickness may be used to reveal why the film of PMDA-B has exhibited a negative thermal expansion coefficient.

However, it is really surprising to see that the calculated biaxial relaxation modulus of the film of PMDA-B significantly increases with the increase of thickness at all the different observation temperatures, as shown in Figure 8. At 150 $^{\circ}\text{C}$, for example, the biaxial relaxation modulus increases from 6.0×10^9 to $8.7 \times 10^9 \text{ N/m}^2$ for thicknesses increasing from 10 to 35 μm . As revealed previously, the thicker films have a lower in-plane orientation. Generally speaking, a film with a lower in-plane orientation should have a smaller elastic constant. However, contrary to the typical phenomenon, the thicker polyimide films of PMDA-B have exhibited lower relaxation moduli. Such

Table I
Thermal Expansion Coefficients (α) of (100) Silicon and (100) Gallium Arsenide Substrates at Various Temperature Ranges ($^{\circ}\text{C}$) Measured by Using a Dilatometer

	$\alpha/(10^{-6}^{\circ}\text{C}^{-1})$							
	50–100 $^{\circ}\text{C}$	100–150 $^{\circ}\text{C}$	150–200 $^{\circ}\text{C}$	200–250 $^{\circ}\text{C}$	250–300 $^{\circ}\text{C}$	300–350 $^{\circ}\text{C}$	350–400 $^{\circ}\text{C}$	400–450 $^{\circ}\text{C}$
GaAs(100)	5.5	5.5	5.6	5.7	5.7	6.1	6.1	6.2
Si(100)	2.2	2.2	2.3	2.4	2.9	3.3	3.4	3.4

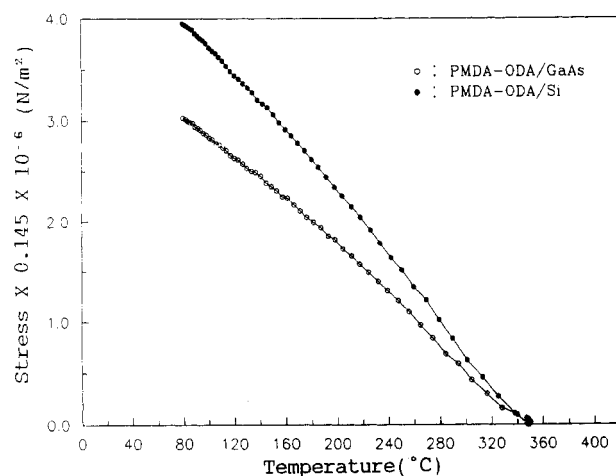


Figure 4. Variation of thermal stress, with respect to temperature, in the films of PMDA-ODA coated on GaAs and Si substrates.

a unexpected or "anomalous" phenomenon may presumably be attributed to the presence of voids in the films. As shown in the study by Russell,²⁴ due to solvent evaporation and water evolution during curing, polyimide films would contain voids, whose sizes may range from 5 to 15 nm in radius. The voids trapped in a film would cause stress concentration, which would in turn result in stress relaxation and give rise to a smaller relaxation modulus. The above results seem to imply that the thicker films may have contained, on average, a smaller fraction of voids and/or voids with a smaller size on average. It is known that for any given film obtained by solution casting, its polymer chains on or near the surface would solidify much faster than those beneath upon drying. Consequently, larger voids or a higher void content could result in the surface, where solvent evaporation would be much more vigorous, especially when the film is dried at a relatively high temperature. Away from the surface, void content should decrease and/or void size should be smaller. When a thicker coating layer is applied, the fraction or average size of the voids in the film would become smaller. As a result, stress relaxation behavior would become lessened and the resulting relaxation modulus would become higher when the film thickness increases. Nevertheless, further experiments examining the dependence of void size or fraction on thickness are definitely needed to verify the above postulation.

Contrary to PMDA-B, no reliable results could be obtained for the films of PMDA-ODA. This is because the films of PMDA-ODA have thermal expansion coefficients so much higher than those of the two substrates used. The resulting thermal mismatches between the films with different thicknesses and the silicon substrate have become nearly indistinguishable from those between the films and the gallium arsenide substrate within the machine resolution. When being compared with any rigid-rod polyimide, PMDA-ODA has a relatively high thermal expansion coefficient due to its "flexible" imide chain. As shown by Numata et al.,⁷ the thermal expansion coefficient of the film of PMDA-ODA cured biaxially fixed is $23.6 \times$

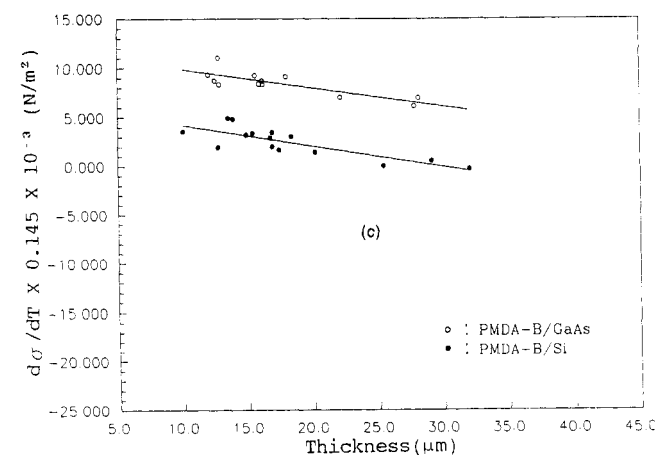
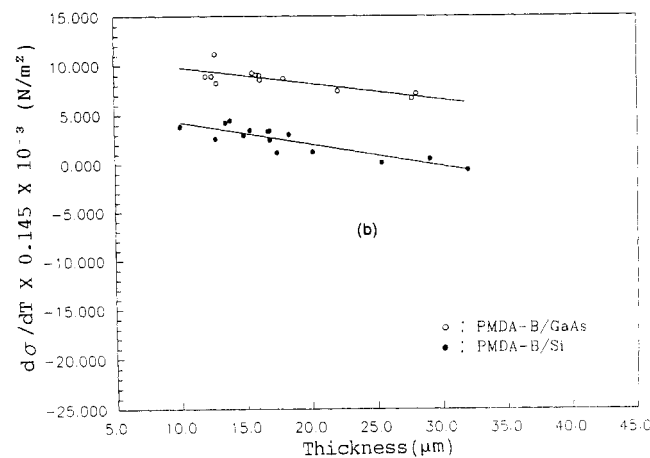
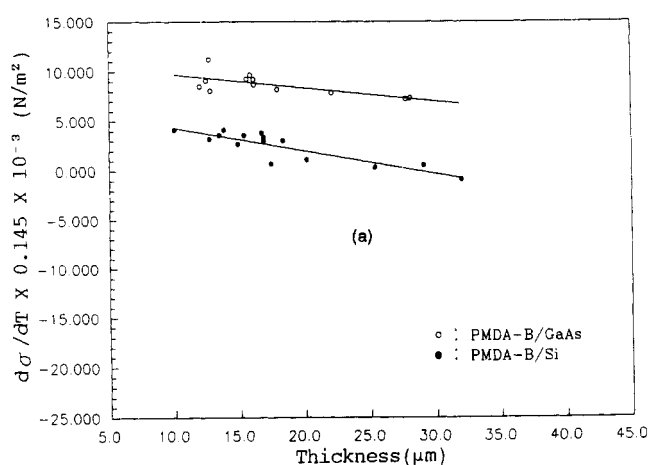


Figure 5. Calculated slopes of the thermal stress-temperature curves for the films of PMDA-B with various thicknesses coated on GaAs and Si substrates at three different observation temperatures: (a) 150, (b) 200, and (c) 250 $^{\circ}\text{C}$.

$10^{-6}/^{\circ}\text{C}$, while those of the silicon and gallium arsenide substrates are 2.2×10^{-6} and $5.5 \times 10^{-6}/^{\circ}\text{C}$, respectively, at room temperature. In order to obtain an accurate measurement for high thermal expansion polyimides, such as PMDA-ODA, one of the substrates must be replaced

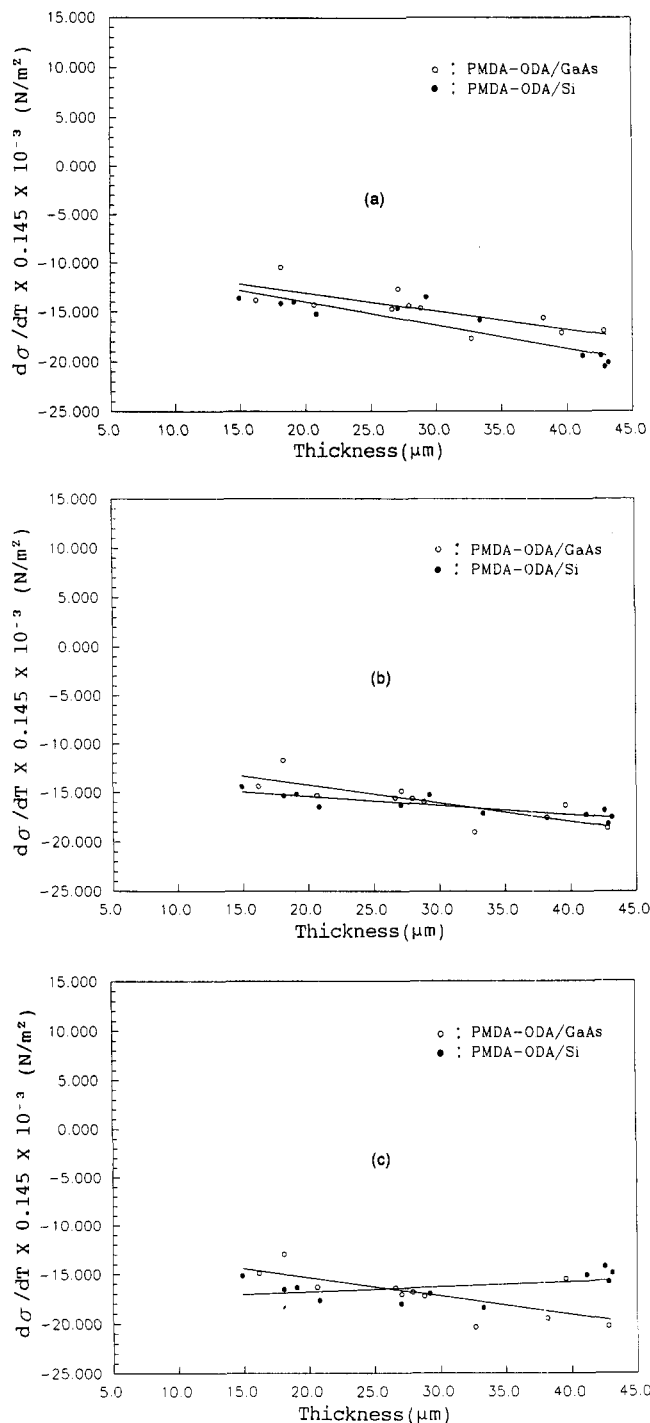


Figure 6. Calculated slopes of the thermal stress-temperature curves for the films of PMDA-ODA with various thicknesses coated on GaAs and Si substrates at three different observation temperatures: (a) 150, (b) 200, and (c) 250 $^\circ\text{C}$.

by another substrate with a comparatively high thermal expansion coefficient.

Summary

To conclude, it has been learned that the bending-beam apparatus is an effective tool in determining the biaxial relaxation moduli and thermal expansion coefficients of films of polyimides coated on substrates. Using silicon and gallium arsenide substrates in the technique, one can effectively determine the relaxation moduli and thermal expansion coefficients of the films of a rigid-rod-like polyimide with low thermal expansion characteristics. As observed, both the biaxial relaxation modulus and thermal

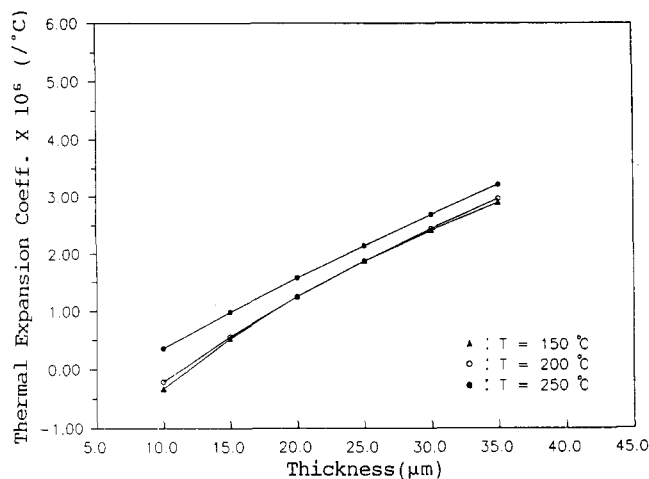


Figure 7. Obtained thermal expansion coefficients of the films of PMDA-B with different thicknesses at three different observation temperatures.

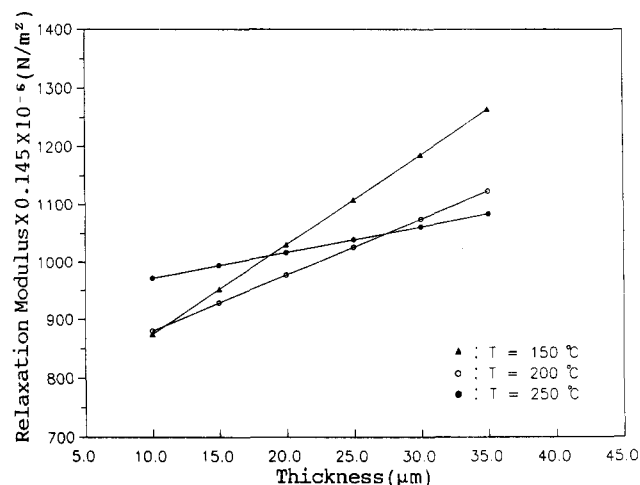


Figure 8. Obtained biaxial relaxation moduli of the films of PMDA-B with different thicknesses at three different observation temperatures.

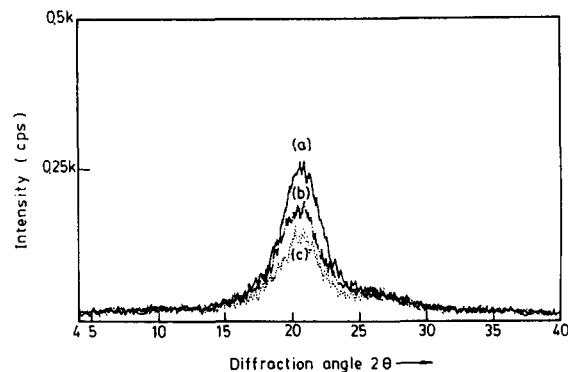


Figure 9. Resulting out-of-plane diffraction patterns of the films of PMDA-B with various thicknesses: (a) 5.5, (b) 12.7, and (c) 20.2 μm . The peak at $2\theta = 20.9^\circ$ corresponds to the ordering of the intermolecular spacing of imide chains in the films.

expansion coefficient of the film of PMDA-B obviously increase with the increase of film thickness. At an observation temperature of 150 $^\circ\text{C}$, for example, the biaxial relaxation modulus increases from 6.0×10^9 to $8.7 \times 10^9 \text{ N/m}^2$ and the thermal expansion coefficient increases from -0.33×10^{-6} to $2.89 \times 10^{-6}/^\circ\text{C}$ for thicknesses increasing from 10 to 35 μm . The negative thermal expansion coefficient may result from the low thermal expansion nature of the polyimide film due to its highly

rigid and symmetric chain structure and the effect of biaxial stretching upon curing. The increase of the thermal expansion coefficient with respect to film thickness can be attributed to the decrease in the in-plane orientation of the film. The increase of the biaxial relaxation modulus with respect to thickness may presumably be attributed to the decrease in the void size and/or void fraction in the film. Since the thermal expansion coefficient of the film of PMDA-ODA is much higher than those of the two substrates used, no reliable results could be obtained within machine resolution.

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Registry No. (PMDA)(B) (copolymer), 25668-07-9; (PMDA)-(B) (SRU), 25667-67-8; (PMDA)(ODA) (copolymer), 25038-81-7; (PMDA)(ODA) (SRU), 25036-53-7; GaAs, 1303-00-0; Si, 7440-21-3.