Functionalized Polynorbornene Dielectric Polymers: Adhesion and Mechanical Properties

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ABSTRACT: Within the microelectronics industry, there is an ongoing trend toward miniaturization coupled with higher performance. High glass-transition temperature polynorbornenes exhibit many of the key performance criteria necessary for these demanding applications. However, homopolynorbornene exhibits poor adhesion to common substrate materials, including silicon, silicon dioxide, aluminum, gold, and copper. In addition, this homopolymer is extremely brittle, yielding less than 1% elongation-to-break values. To address these issues, the homopolymer was functionalized to improve adhesive and mechanical properties. Attaching triethoxysilyl groups to the polymer backbone substantially improved the adhesion, but at the cost of increasing the dielectric constant because of the polarity of the functional group. Alkyl groups were also added to the backbone, which decreased the rigidity of the system, and resulted in significantly higher elongation-to-break values and a decrease in residual stress. The addition of an alkyl group slightly decreased the dielectric constant of the polymer as a result of an increase in molar volume. The coefficient of thermal expansion and modulus are also reported for the polynorbornene functionalized with triethoxysilyl groups using a multiple substrate approach. © 1999 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 37: 3003–3010, 1999

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INTRODUCTION

Within the microelectronics industry, there is an ongoing trend toward miniaturization coupled with higher performance. Low dielectric constant interlevel dielectrics have been identified in the National Technology Roadmap for Semiconductors[1] as being critical to the realization of high performance interconnections. Dielectric constant targets[1] for the interlevel metal insulator were set at 4.1 in 1997, and are anticipated to drop to 2.5 in 2001. In an effort to reduce the permittivity of interlevel dielectrics, new organic films are being developed. In addition to a low dielectric constant, these films must meet all the performance characteristics for integrated circuits or electronic packages, which include good adhesion to a variety of films and substrates, thermal stability, high elongation-to-break values, and low stress.[2]

BFGoodrich has developed cyclic olefin-based Avatrel™ dielectric polymers that exhibit many of the key performance criteria required for these demanding electronic applications. The basic

building block material of Avatrel™ is shown in Figure 1. This polymer family, based principally on polynorbornene (PNB) derivatives, is produced via a novel transition metal catalyzed polymerization. The catalyst provides the ability to tightly control the polymerization of bulky cyclic monomers to form saturated polymers with high glass-transition temperature (T_g), low dielectric constant, and low moisture absorption.[3]

However, other properties of pure, nonfunctionalized PNB were not acceptable for the films used as interlevel dielectrics. During the development of PNB as an interlevel dielectric, two objectives were defined. First, improvement in adhesion to silicon dioxide and aluminum was required. Second, the elongation-to-break values of the homopolymer was not sufficient for microelectronic thin film applications. Two different types of functional groups[4,5] have been investigated to improve the adhesion and mechanical properties. Alkoxysilyl-substituted norbornene was investigated to address the adhesion issue. Silane coupling agents are frequently used to improve adhesion between materials and, thus, triethoxysilyl groups were incorporated into the polymer chain.[6] This improvement in adhesion occurs through the hydrolysis of the alkoxy groups, which can then undergo a condensation reaction of the hydroxyl groups with the surface of the metal or oxide to form a Si–O–M bond, where "M" represents the substrate surface. The silane also has the ability to react with other hydrolyzed silane groups to form a Si–O–Si bond resulting in a crosslinked film.

The second type of functionalized monomeric unit studied was alkyl-substituted norbornene. Polynorbornene homopolymer has an elongation-to-break values of less than 1%. The addition of a flexible alkyl chain to the backbone was anticipated to plasticize the polymer, resulting in an improvement in the elongation-to-break values of the polymer system.

In this study, the effect of the composition and concentration of the above-mentioned two functional groups on the critical performance properties of PNB as an interlevel dielectric has been investigated.

EXPERIMENTAL PROCEDURES

In order to investigate the effect of polymer composition on the properties of the films, various compositions of the polymers were produced. Tri-
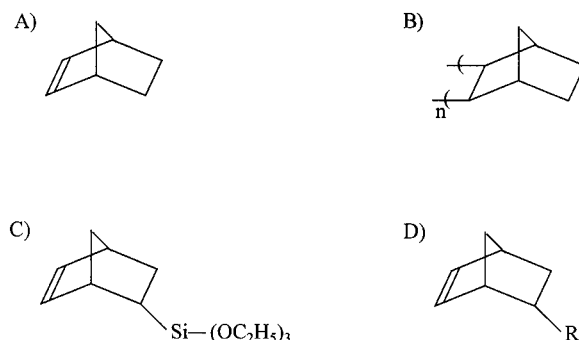
Figure 1. Polymer structure. (A) Norbornene monomer. (B) Polynorbornene. (C) Triethoxysilylnorbornene (TESNB). (D) Alkyl-substituted norbornene where R can be equal to $-CH_2CH_3$ (EthNB), $-(CH_2)_3CH_3$ (BuNB), or $-(CH_2)_5CH_3$ (HexNB).

ethoxysilylnorbornene (TESNB) was copolymerized with norbornene and alkyl-substituted norbornene in various ratios to investigate the improvement in adhesive and mechanical properties. The alkyl-substituted norbornenes were ethylnorbornene (EthNB), butylnorbornene (BuNB), and hexylnorbornene (HexNB). The polymer compositions are presented on a mol % basis of the norbornene monomers. For example, 90/10 BuNB/TESNB refers to 90 mol % of the monomeric units being BuNB and 10 mol % of the monomeric units being TESNB. The structures of polynorbornene and the attached side groups are shown in Figure 1.

All polymers tested in this study possessed a similar molecular weight. The weight-average molecular weight (M_w) of the polymers used in this study varied from approximately 190,000–240,000 with a polydispersity of approximately 3. The mechanical properties of these polymers have been found to be independent of molecular weight, at weight-average molecular weights exceeding 150,000.

Polymer solutions were obtained by dissolving the solid in mesitylene. Thin polymer films ($\sim$2–10 μm) were deposited onto the substrates by spin coating. The films were soft-baked for 10 min at 95°C and then heated in a nitrogen-purged tube furnace at a ramp of 5°C/min to 300°C and held for 1 h. Film thicknesses were measured using a Metricon 2010 Prism Coupler. The thickness is used in the calculation of the permittivity and loss. Metals were deposited onto the substrates and onto the polymer films using DC sputtering.

Parallel plate capacitors were fabricated using standard photolithographic processing with a

metal wet etch. The capacitance and conductance of each capacitor were measured at a frequency of 10 kHz and an input voltage of 1 V using a Hewlett Packard 4263A LCR meter. Twenty capacitors of two different sizes, approximately 11.7 mm and 8.6 mm, were measured on each wafer. The diameters of each capacitor were measured using a calibrated slide under a microscope. The relative permittivity, ε', and relative loss factor, ε'', were calculated based upon the measured values of capacitance, C, conductance, G, film thickness, t, and capacitor area, A, using eqs 1 and 2,

$$C = \frac{\varepsilon' \varepsilon_0 A}{t} \qquad (1)$$

$$R = \frac{1}{G} = \frac{t}{\omega A \varepsilon'' \varepsilon_0} \qquad (2)$$

where ε'' is the relative loss factor, ε_0 is the permittivity of free space (8.85×10^{-14} Farads/cm), and ω is the measurement frequency. A frequency of 10 kHz was used for all the electrical property characterization performed in this study. Fringing of the electrical field was minimized by using film thicknesses that were much less than the size of the plate. A total error of 3.5% (1σ) in the measurement of the relative permittivity is based upon a 2% error in each of the measurements of the capacitance, the film thickness, and the capacitor area.

The adhesion of the films to a variety of substrates was tested using the tape test, which is documented in ASTM D3359-95a.[7] In this test, the polymer film was crosshatched with a diamond scribe in a grid-like fashion. The specified tape was applied to the surface of the film. The tape is then pulled off, exerting a normal force on the film. Films that adhered were then immersed in boiling water for 2 h and retested. If no delamination of the polymer squares from the substrate occurred, the polymer passed the adhesion test. The films were examined prior to and after testing using an optical microscope. Adhesion data reported in this article were reproduced at least two times.

In addition to film adhesion, the crazing of polymer films was also observed under different solvent conditions, which simulated those used in the photolithographic processing (i.e., acetone, methanol, and isopropanol). Typically, the samples were exposed briefly (<10 s) to the solvent. After exposure, the films were observed both vi-

sually and with the aid of an optical microscope to detect the presence of crazes in the polymer.

The elongation-to-yield and the elongation-to-break measurements (ETB) were performed following the ASTM D1708 procedure. The test was performed at 23°C and 50% relative humidity. The crosshead speed was 0.20 in./min.

The glass-transition temperature (T_g) data were collected using samples cut (nominally 50 mm long, 7 mm wide) from solvent cast sheets (nominally 0.2 mm thick). A dynamic mechanical spectrum was measured using a Rheometrics RSA II. The strain amplitude was fixed at 0.05% and the strain rate was fixed at 6.28 rad/s. The temperature ramp was set to 3°C/min, with data taken every 30 s. The temperature range was −150°C to 400°C in a nitrogen-purged atmosphere. The peak in the tan δ, which accompanied the abrupt change in modulus associated with the departure of glassy behavior, was reported as the glass-transition temperature for these materials.

The residual stress (σ) of polynorbornene film on a substrate was measured using a Tencor Instruments Flexus 2320 wafer curvature unit. The stress was calculated using the Stoney equation, which was developed assuming the presence of an infinitely thin film on a thick substrate,[8–10]

$$\sigma = \left(\frac{E}{1 - \nu} \right)_{\text{substrate}} \frac{h^2}{6Rt} \qquad (3)$$

where h is the substrate thickness, $E/1$-ν is the substrate biaxial modulus (1.805×10^{11} Pa for $\langle 100 \rangle$ silicon), R is the average radius of curvature, and t is the film thickness. The average radius of curvature was determined by knowing the initial curvature of the bare substrate (R_1) and the radius of curvature of the substrate after deposition and processing of the polymer film (R_2):

$$\frac{1}{R} = \frac{1}{R_2} - \frac{1}{R_1} \qquad (4)$$

The silicon substrate thickness ranged from 400–550 μm and was measured using calipers and a Logitech CG10 Contact Gauge.

In addition to room temperature residual stress, the wafer curvature technique can also be used to calculate both the linear coefficient of thermal expansion (CTE) and the biaxial modulus of the film as a function of temperature using the following equation:[11]

Table I. Tape Test Results and Crazing Observations for Functionalized Polynorbornenes and Other Commercially Available Dielectric Films

Polymer	SiO$_2$	Al	Au	Ag	Cu	Al*	Au*	Cu*	Crazing
100 NB	X	X							severe
75/25 NB/TESNB	$\checkmark$	$\checkmark$							none
80/20 NB/TESNB	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\triangledown$	$\checkmark$	$\checkmark$	$\triangledown$	none
96/4 NB/TESNB	$\checkmark$	$\checkmark$							light
93/7 NB/TESNB	$\checkmark$	$\checkmark$	$\checkmark$						light
92/8 NB/TESNB	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\triangledown$	$\checkmark$	$\checkmark$	$\triangledown$	light**
78/22 BuNB/TESNB	$\checkmark$	$\checkmark$				$\checkmark$			none
89/11 BuNB/TESNB	$\checkmark$	$\checkmark$				$\checkmark$			none
94/6 BuNB/TESNB	$\checkmark$	$\checkmark$				$\checkmark$			none
97/3 BuNB/TESNB	$\checkmark$	$\checkmark$				$\checkmark$			none
99/1 BuNB/TESNB	$\checkmark$	$\checkmark$	$\checkmark$			$\checkmark$			none
DuPont PI2540		X							
Dow CY3022-57		X					X		

A check mark indicates passing the tape test; an "X" indicates failure of the tape test; $\triangledown$ indicates variable results; a blank indicates that the test was not performed.
* Metal deposited on polymer film.
** Crazing was marginal and, in some instances, was not observed.

$$\frac{d\sigma}{dT} = \left(\frac{E}{1 - \nu} \right)_{\text{film}} (\alpha_{\text{substrate}} - \alpha_{\text{film}}) \qquad (5)$$

The slope of the stress–temperature curve ($d\sigma/dT$) can be generated using the Flexus and the CTE of the substrate ($\alpha_{\text{substrate}}$) is known. Using the above equation, the biaxial modulus ($E/1-\nu$) and the CTE of the film (α_{film}) can be calculated if the stress–temperature curve is measured for at least two different substrates. These experiments were performed on silicon, gallium arsenide, and aluminum. The modulus and CTE of each substrate as a function of temperature were obtained from the CINDAS Database.[12]

RESULTS AND DISCUSSION

Polynorbornene (PNB) homopolymer, without any adhesion promoting functional groups, does not adhere to silicon dioxide or aluminum. The delamination of these films was observed after 1.5 min in boiling water and during the photoresist processing. In addition to delamination, crazing of the film after heating and during photolithography was observed. The ease of film cracking is a qualitative measure of film toughness, whereas the elongation-to-break value provides a quantitative measure. Thus, the adhesion and mechanical properties of the polynorbornene homopoly-

mer were unacceptable. Alkoxysilyl functional groups have been recognized to improve adhesion between inorganic and organic materials through hydrolysis and condensation reactions with oxides and hydroxyls at the surface, and to improve the mechanical properties of composites. Thus, triethoxysilyl functional groups (TES) were used in varying concentrations (mole fraction of the functionalized monomer) to determine the minimum amount to obtain acceptable adhesion.

The tape test results for the NB/TESNB copolymers with 25, 20, 8, 7, and 4 mol % TESNB on a variety of substrates are shown in Table I along with crazing observations made on these films. No delamination was observed for the NB/TESNB films deposited on aluminum, silicon dioxide, gold, and silver substrates. In addition, good adhesion was also observed when aluminum and gold were deposited on top of the NB/TESNB films.

Adhesion of a polymer to gold or copper surfaces is typically difficult to achieve. To compare the adhesion performance of NB/TESNB to gold with other commercial polymer dielectrics, DuPont Polyimide Pyralin 2540 and Dow Cyclotene CY3022-57 were spin-coated onto oxidized silicon wafers, which had been sputtered with an adhesion layer of titanium and approximately 2400 Å of gold. The processing of the polymer was completed following the conditions recommended by each manufacturer, which included the use of ad-

Table II. Elongation-to-Break (ETB) Values and Glass-Transition Temperatures (T_g) of Functionalized Polynorbornenes

Polymer	Elongation-to-Yield (%)	Elongation-to-Break (%)	T_g (°C)
NB	—	0–2	380–390
90/10 NB/TESNB	7	8–10	355
80/20 NB/TESNB	12	15	355
BuNB/TESNB*	12	21	340
HexNB	17	52	265

* All compositions of BuNB/TESNB. No effect of TESNB concentration.

hesion promoters. The tape test was performed on each wafer. As shown in Table I, only the NB/TESNB could not be removed from the gold surface.

Copper is a complex surface because of its ease of oxidation and lack of an adherent oxide. The adhesion results for NB/TESNB on copper and copper on NB/TESNB were variable. Some samples clearly passed the tape test; however, some delaminations could be traced to copper oxidation.

Although the adhesion of NB/TESNB films to aluminum, silicon dioxide, gold, and silver substrates was sufficient, light crazing was observed for the 96/4 and 93/7 NB/TESNB films after exposure to acetone, methanol, and isopropanol, while no crazing was observed for the higher silane content films. It was concluded from the crazing results that at least 8% TESNB was necessary to reduce crazing of the film. It should be noted that all of these compositions were synthesized with similar molecular weights and were above the critical entanglement molecular weight. In addition, no reaction (and hence, no change in molecular weight) was observed for the polynorbornene systems under normal processing conditions.[13] Therefore, this reduction of crazing with an increase in TESNB content is a compositional effect rather than a molecular weight effect.

The elongation-to-yield and the elongation-to-break (ETB) values for the functionalized polynorbornenes were also measured as shown in Table II. The pure polynorbornene homopolymer is very brittle; as a result, the ETB of the film could not be measured. The addition of alkoxysilyl groups increased the ETB of the polymer to approximately 15% for 80/20 NB/TESNB. Because the TESNB is a more flexible molecule than NB, the addition of silyl groups appears to plasticize the films. This effect can also be observed by a decrease in the glass-transition temperature (T_g)

upon addition of TESNB into the polymer as shown in Table II. Significant improvements in the ETB were also observed by the addition of the alkyl side groups, as will be discussed later.

The room temperature residual stress was measured for the NB/TESNB polymers. The polymer compositions, film thicknesses, and room temperature residual stress are reported in Table III. These reported values are averaged over several samples; at these levels of stress, a reproducibility of ±15% is generally observed using the wafer curvature technique. As can be seen, an increase in silane content in the polymer results in a decrease in the residual stress. This can be explained by the higher rigidity of the system with decreasing silyl content, which support the plasticization hypothesis.

Although the incorporation of TESNB improved both the adhesive properties and mechanical properties, it had a detrimental effect on the dielectric constant. The through-plane dielectric constant was measured as a function of silyl concentration using parallel plate capacitors. The results of the dielectric constant measurements for the NB/TESNB polymers are shown in Table IV. The dielectric constant increased from 2.20 for the homopolymer to 2.53 and 2.67 for 90/10 NB/TESNB and 80/20 NB/TESNB, respectively. Triethoxysilyl is a more polar molecule compared with polynorbornene. Although the presence of alkoxysilane side chains improved the adhesion and reduced crazing in the polymer, the dielectric constant increased substantially. Therefore, a second functional group was investigated to improve the mechanical properties without increasing the dielectric constant.

It was found that the addition of an alkyl group to the polymer backbone would increase the flexibility of the polymer. In addition, because the alkyl groups are less polar than the alkoxysilyl groups, it was anticipated that the addition of

Table III.   Residual Stress and Film Thickness for Functionalized Polynorobrnenes

Wafer #	Polymer	$t \pm 1\sigma$ (μm)	Stress (MPa)
1	80/20 NB/TESNB	7.05 ± 0.15	31
1	80/20 NB/TESNB*	7.05 ± 0.15	31
2	90/10 NB/TESNB	5.87 ± 0.04	34
2	90/10 NB/TESNB*	5.87 ± 0.04	34
3	78/22 BuNB/TESNB	8.27 ± 0.04	19
4	89/11 BuNB/TESNB	7.88 ± 0.12	20
5	89/11 BuNB/TESNB**	9.60 ± 0.07	18
5	89/11 BuNB/TESNB***	9.42 ± 0.05	18
6	94/6 BuNB/TESNB	6.06 ± 0.03	20
7	94/6 BuNB/TESNB	5.39 ± 0.15	19
8	97/3 BuNB/TESNB	5.53 ± 0.04	21
9	99/1 BuNB/TESNB	2.54 ± 0.02	18
10	90/10 EthNB/TESNB	9.23 ± 0.02	27
11	90/10 HexNB/TESNB	6.82 ± 0.01	10

* Experiment performed twice on the same wafer.
** Wafer heated at 200°C for 1 h.
*** Wafer heated at 300°C for 1 h.

alkyl groups would not increase the dielectric constant. Hence, butylnorbornene (BuNB) and TESNB monomers were copolymerized in a variety of compositions (78/22, 89/11, 94/6, 97/3, and 99/1) to determine the optimum composition in terms of adhesion, mechanical, and electrical properties. These polymer solutions were spin-coated onto a variety of substrates. No delamination of the polymer or metal films was observed during adhesion testing, as was shown in Table I. In addition to the excellent adhesion results of the BuNB/TESNB films, no crazing was observed on any of the films indicating that the mechanical properties were improved with the addition of the alkyl group.

Table IV.   Dielectric Constants for Functionalized Polynorbornene

Polymer Composition	ε'
100 NB	2.20
80/20 NB/TESNB	2.67
90/10 NB/TESNB	2.53
78/22 BuNB/TESNB	2.58
89/11 BuNB/TESNB	2.48
94/6 BuNB/TESNB	2.42
97/3 BuNB/TESNB	2.39
99/1 BuNB/TESNB	2.31
90/10 EthNB/TESNB	2.45
90/10 HexNB/TESNB	2.43

The addition of flexible alkyl groups to the polymer also resulted in an increase in the elongation-to-break values and a decrease in the residual stress on a silicon wafer. In addition to varying concentration of BuNB, ethylnorbornene (EthNB) and hexylnorbornene (HexNB) were also polymerized with the norbornene monomer. At similar TESNB contents, the stress of the polymers decreases as the alkyl chain length increases (Table III). For instance, 90/10 NB/TESNB has a residual stress of 34 Mpa, whereas 90/10 EthNB/TESNB has a residual stress of 27 MPa, 89/11 BuNB/TESNB has a residual stress of 18 Mpa, and 90/10 HexNB/TESNB has a residual stress of 10 MPa. By decreasing the rigidity through internal plasticization, the stress of the film decreases substantially. ETB values increase from 8–10% (for 90/10 NB/TESNB) to 52% (for HexNB/TESNB), as the length is increased (Table II). This increase in ETB is accompanied by a decrease in the T_g. Thus, although the HexNB film had the lowest stress, the low T_g makes it undesirable in many dielectric applications because of its inability to withstand high temperature processing.

The dielectric constants for the alkyl and alkoxysilyl functionalized NB are shown in Table IV. For the BuNB/TESNB copolymer, the dielectric constant dropped as the content of alkyl functionalized monomers is increased (and the content of alkoxysilyl groups is decreased). This is a
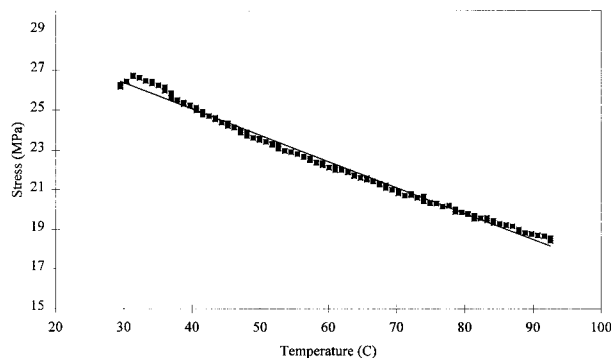
Figure 2. Stress as a function of temperature for 80/20 NB/TESNB.

result of the alkyl functional group being less polar than the alkoxysilyl functional group. In addition, the dielectric constant of the polymer decreases as the length of the alkyl functional group is increased. This is most likely a result of the increase in the molar volume of the system, which occurs as the alkyl chain length is increased.[12]

The BuNB films, which have low stresses, also appear to have the most desirable combination of properties for dielectric applications based on the adhesion, dielectric constant, ETB, and T_g results. Unlike the NB/TESNB films, the stresses for the BuNB films do not change significantly as a function of the TESNB content (Table III). The room temperature stress for all of the films is approximately 20 MPa. These results are also reflected in the ETB results, which do not show any increase with silyl content Table II. Thus, for the BuNB/TESNB polymers, the effect of the butyl group is more important than the silyl group in establishing the mechanical properties. Because the silyl content does not impact the mechanical properties, only the adhesion and permittivity are affected by the TESNB concentration. Thus, the silyl content of the film can be chosen without deleterious effect on the mechanical properties of the film.

In addition to the room temperature stress, the coefficient of thermal expansion (CTE) and modulus were measured for the 80/20 NB/TESNB film by measuring the stress–temperature behavior of the film on silicon, aluminum, and gallium arsenide. The bare aluminum substrate had a small change in radius of curvature with temperature and, thus, the radius of the uncoated substrate was measured as a function of temperature and was used to calculate the stress of the film at each temperature. The stress of the 80/20 NB/TESNB film on silicon as a function of temperature is shown in Figure 2. The substrate data, film thickness, slope (m), intercept (b), and regression coefficient for the stress–temperature data on the various substrates are shown in Table V. Using eq 3, regression was performed and the modulus and CTE were calculated. The CTE calculated for the 80/20 NB/TESNB film is 72 ± 14 ppm/°C and the biaxial modulus is 2.0 GPa $\pm$ 1.1 GPa. Assuming a Poisson ratio of 0.35, the Young's modulus calculated for this film is 1.3 ± 0.7 GPa. The residual stress of films on a bare wafer is low because of the low modulus; the CTE of the polymer is substantially higher than the CTE for silicon (2.87 ppm/°C), which results in a large CTE mismatch between the film and substrate.

As a comparison, the Young's modulus data was obtained using Dynamic Mechanical Analysis (DMA) for the 80/20 NB/TESNB film. The trend in the moduli between 20 and 100°C is shown in Figure 3. The derivative of the polynomial fit in Figure 3 to the stress–temperature curve on silicon was used to calculate $d\sigma/dT$ from 30–90°C. Using a Poisson ratio of 0.35, the modulus data, and the $d\sigma/dT$ values, the CTE values were calculated for the film as a function of temperature using eq 3. The CTE result is shown in Figure 4. The CTE of the NB/TESNB film ranges from 92–60 ppm/°C and is similar to the result of 72 ppm/°C calculated using the wafer curvature method with multiple substrates. In addition, the Young's modulus measured on the bulk films,
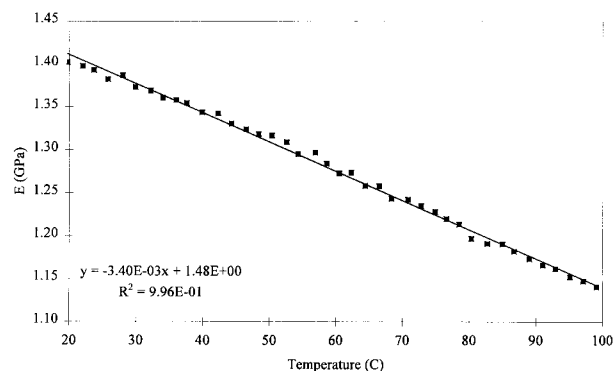
Table V. Substrate CTE, Film Thickness and Slope, Intercept, and Regression Coefficient for Silicon, Gallium Arsenide, and Aluminum Substrates Coated with 80/20 NB/TESNB

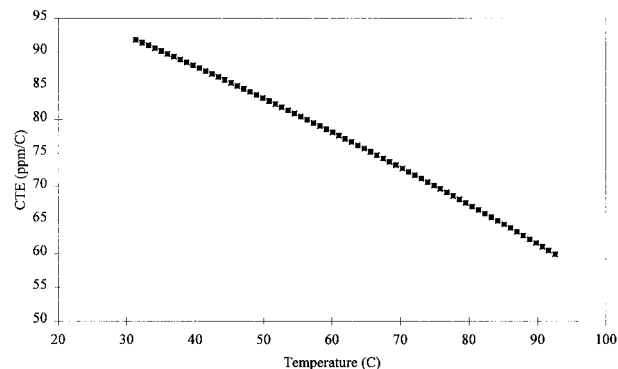| Substrate	CTE (ppm/°C)	$t \pm 1\sigma$ (μm)	$m \times 10^1$ (MPa/°C)	b (MPa)	R^2
Si	2.87	6.78 ± 0.04	−1.31	30.3	0.991
GaAs	5.9	6.73 ± 0.08	−1.47	37.7	0.992
Al	22.7	7.61 ± 0.02	−0.991	41.3	0.540

1.15–1.4 GPa, is similar to that calculated using the multiple substrate method. The correlation of these results indicates that the CTE and modulus values for the 80/20 NB/TESNB film obtained using the multiple substrate approach are in agreement with DMA results.

CONCLUSION

The copolymerization of triethoxysilylnorbornene with norbornene and alkyl norbornene substantially improves the adhesion of the films to many surfaces including aluminum, gold, and copper. Although the silyl groups improve the mechanical properties of the NB polymer at higher alkoxysilyl concentrations, as seen by decreased film stress, the low alkoxysilyl content films continue to demonstrate crazing, indicating poor mechanical properties. To improve the mechanical properties, the addition of an alkyl group to the norbornene polymer was necessary. This improvement in mechanical properties was observed both through an increase in the elongation-to-break values and a decrease in stress. An ethyl group increased the elongation-to-break measurement slightly. Significant improvements were observed with the addition of the butyl or hexyl groups. The low T_g of the hexyl groups limits its use as a dielectric film. Thus, the butyl group is the best option to improve the mechanical properties. Various compositions of BuNB/TESNB polymers demonstrated the ability of the silyl groups to provide adhesion even at TESNB concentrations as low as 1 mol %. No variation in mechanical properties was observed for the BuNB/TESNB

Figure 4. Coefficient of thermal expansion as a function of temperature for 80/20 NB/TESNB.

films with higher silyl content. Thus, a butylnorbornene polymer with low alkoxysilyl content (1–5 mol %) provides a film with the necessary adhesion and mechanical properties.

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Figure 3. Young's modulus as a function of temperature for 80/20 NB/TESNB measured on bulk films.