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Thin films of organic polymer composites with inorganic aerogels as dielectric materials: polymer chain orientation and properties

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Summary
High temperature poly(*p*-phenylene biphenyltetracarboximide) nanocomposite films with inorganic particulates, which are applicable to the fabrication of microelectronic devices, were prepared from the poly(amic acid) and silica aerogels with a size of ca. 150 nm in diameter by solution blending and subsequent conventional polyimide film formation process. The structure and properties were measured. By the composite formation, the optical and dielectric properties were improved due to the low dielectric constant characteristic of silica aerogels, whereas the interfacial stress and thermal expansion coefficient were significantly degraded by a large disturbance in the polymer chain in-plane orientation caused by silica aerogels despite of their low thermal expansivity. This indicates that in the rigid type of polymer composites with inorganic particulates, the orientation of polymer chains still plays a critical role on the physical properties.

Introduction
Fully aromatic polyimides are extensively used in the fabrication of microelectronic devices, such as semiconductors and multichip modules as interdielectric and passivation layers owing to their excellent mechanical properties and chemical resistance in addition to the exceptionally high temperature stability up to 450°C.[1,2] Considering of properties of dielectric layer materials, lower dielectric constant and lower dissipation factor allow faster signal propagation with less attenuation, leading to the higher wiring density in devices, since the signal propagation speed is inversely proportional to the square root of dielectric constant.[1,3,4] Lower interfacial stress and higher interfacial adhesion strength can minimize mechanical failures, such as displacement, curling, warping, cracking and delamination at various interfaces (i.e., metal/polymer, ceramic/polymer, silicon wafer/ polymer and so on), consequently leading to the excellent reliability on devices.[1,3,4] Currently, the development of advanced microelectronic devices highly demands a new class of dielectric materials with a low dielectric constant, low interfacial stress, and high interfacial adhesion.

Silica aerogels, spherical hallow particulates, are known to exhibit a low dielectric constant and low thermal expansivity.[5-7] Utilizing these silica aerogels, aromatic polyimide

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composites in thin films, were prepared from poly(*p*-phenylene biphenyltetracarboxamic acid) precursor by solution blending in N-methyl-2-pyrrolidinone and followed by thermal imidization. Structure and properties of the polyimide/silica aerogel composites were characterized.

Experimental

Silica aerogels with a diameter of ca. 150 nm, which were prepared through sol-gel process followed by supercritical drying and high temperature sintering,[8] were added into poly(*p*-phenylene biphenyltetracarboxamic acid) (BPDA-PDA PAA) precursor (ca. 40K $\overline{M}_W$; 8.0 wt% solid content) solution in N-methyl-2-pyrrolidinone and well mixed with the aid of a thin rod type of ultrasonic probe. The precursor polymer/silica aerogel mixture solutions were spin-cast on precleaned silicon wafers of ca. 5.0" diameter, softbaked on a hot-plate at 85°C for 2 h, and followed by thermal imidization at 400°C for 1.5 h in an oven with a nitrogen gas flow. Here, the thermal imidization was performed through a four-step cure process: 150°C/30 min, 230°C/30 min, 300°C/30 min and 400° C/1.5 h with a ramping rate of 2.0 K/min between steps. After the completion of imidization, film samples were cooled with a rate of 1.0 K/min. In addition, pure poly(*p*-phenylene biphenyltetracarboximide) (BPDA-PDA) films were prepared from the poly(amic acid) in the same manner as the composite films were made. The thickness of films was measured using a Tencor alpha-stepper to be ca. 5.5 μm.

Phase-contrast micrographs of composite films were taken under crossed polarizations on an optical microscope (Carl Zeiss, Model Axioplan). Scanning electron micrographs for the cross-section of the films in the direction of thickness were additionally taken using a scanning electron microscope (SEM) (Philips, Model SEM-515). SEM specimens were prepared by molding of composite films with an epoxy glue followed by mechanical dicing with the aid of a blade.

Wide-angle X-ray diffraction (WAXD) measurements were conducted at room temperature in both reflection and transmission geometry using a horizontal X-ray diffractometer (Model M18XHF, MAC Science) with a 18 kW rotating anode X-ray generator. The CuK_{α} radiation source was operated at 50 kV and 100 mA. One-half degree defining and scatter slits were employed together with two receiving slits of 0.15° and 0.3°. All measurements were carried out in θ/2θ mode. The 2θ scan data were collected at 0.02° intervals over the range of 3° - 60° and the scan speed was 0.4° (2θ)/min. The measured WAXD data were corrected for background runs.

Refractive indices of composite films were measured in air ambient using a prism coupler (Model 2010, Metricon) equipped with a diode laser light source of 830 nm wavelength and controlled by a personal computer (see the schematic diagram of prism coupler in Fig.1). The refractive index of films was measured in transverse electric (TE:

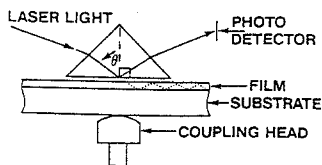

Fig.1. Schematic diagram of prism coupler.

n_{TE} = n_{xy}, refractive index in the film plane) and transverse magnetic (TM: n_{TM} = n_z, refractive index in the direction of film thickness) mode by choosing the appropriate polarization of the incident laser beam as described elsewhere.[9-12] All measurements were performed using a cubic zirconia prism of n_{TE} = n_{TM} = 2.1488 at 830 nm. When a film with a refractive index (n) is intimately contacted to a prism with a refractive index (n_p), laser light directed onto the base of the prism is normally totally reflected at the prism base. However, at certain discrete values of the incident angle θ, so-called mode angles, light will tunnel across the air gap into the film and enter into a guided optical propagation mode, causing a sharp drop in the intensity of light reaching the detector (see Fig.1). A computer-driven rotary table varies the incident angle θ, sensing each of the film propagation modes. The experimentally determined mode angles θ define $n_{eff} = n_p \sin\theta = n \sin\theta_f$ where n_{eff} and θ_f are the effective refractive index and the incident angle of light in the film plane, respectively. A computer program was used to numerically calculate the refractive index of the film n that was determined by all the possible pairs of TE mode angles for a given film thickness. This film thickness was then iterated until the difference between the calculated n's was minimized. The final n (namely, n_{TE}) and thickness in the TE mode were used to calculate n (that is, n_{TM}) from the TM mode. Dielectric constants of composite films were estimated from the measured refractive indices using the Maxwell equation, $\varepsilon = n^2$. The birefringence (Δ) of the film, which is defined as $\Delta = n_{TE} - n_{TM}$,[12] was estimated from the refractive indices measured.

For interfacial stress measurements, curvatures of silicon wafers without and with composite films were measured using a He-Ne laser based film stress analyzer (Flexus, Model 2-300) equipped with a hotstage and controlled by a personal computer (see Fig.2). Variations in the curvature of silicon wafers with composite films were monitored as a function of temperature during heating up to 400°C and subsequent cooling under a nitrogen gas flow. The rates of ramping and cooling were 2.0 K/min, respectively. The interfacial stress (σ_F) of films was calculated from the radii of the wafer curvatures measured before and after the film deposition using the following equation:[12-14]

$$\sigma_F = \frac{1}{6}\frac{E_S\, t_S^2}{(1-\nu_S)\; t_F}\left(\frac{1}{R_F} - \frac{1}{R_\infty}\right) \qquad (1)$$

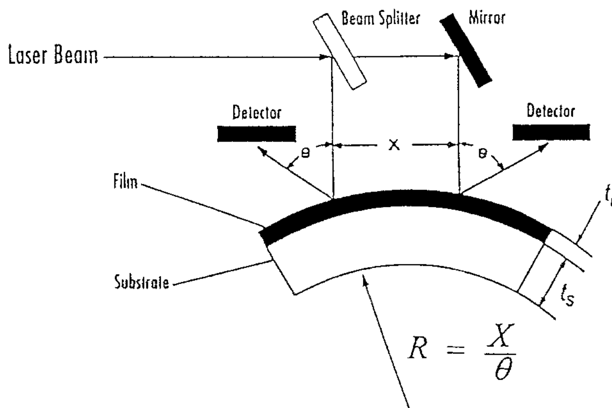

Fig.2. Schematic diagram of interfacial stress analyzer.

Here, the subscripts F and S denote composite film and Si wafer substrate, respectively. The symbols E, ν, and t are Young's modulus, Poisson's ratio, and thickness of each layer material, respectively. R_F and R_∞ are the radii of the wafer with and without a composite film, respectively. For Si(100) wafers,[15] the biaxial modulus, $E_S/(1 - \nu_S)$ is 1.805 x 10^5 MPa.

In addition, thermal expansion coefficients in the plane of films were measured at a heating rate of 10.0 K/min under a nitrogen flow using a Perkin-Elmer thermomechanical analyzer (Model TMS-2). The gauge length was 7.5 mm and the width of film strips was 2.0 mm.

Results and Discussion

The degree of dispersion of silica aerogel particulates in the matrix of BPDA-PDA polyimide was examined by means of optical and scanning electron microscopy. Representative optical and scanning electron micrographs are shown in Fig.3. The micrographs show that silica aerogel particulates were reasonably well dispersed in the polyimide matrix.

Refractive indices of composite films were measured at a wavelength of 830 nm (namely, a frequency of 361.45 THz) by prism-coupling technique. The coupling patterns of BPDA-PDA/silica aerogel (73/27, w/w) composite film, which were measured in TE and TM modes, respectively, are shown in Fig.4. In-plane refractive index (n_{xy}) and film thickness, which were estimated from the coupling pattern in TE mode, were 1.7522 and 5.5 μm, respectively. Here, the film thickness obtained is in good agreement with that measured directly by an alpha-stepper. The coupling pattern in TM mode gave an out-of-plane refractive index (n_z) of 1.5976. From these refractive indices, the bulk refractive index $[\bar{n} = (2n_{xy} + n_z)/3]$ was estimated to be 1.7007. Using the Maxwell relation, dielectric constants were estimated from the refractive indices to be 3.070 (ε_{xy}) in the film plane, 2.552 (ε_z) in the out-of-plane, and 2.897 ($\bar{\varepsilon}$) in bulk. On the other hand, a pure

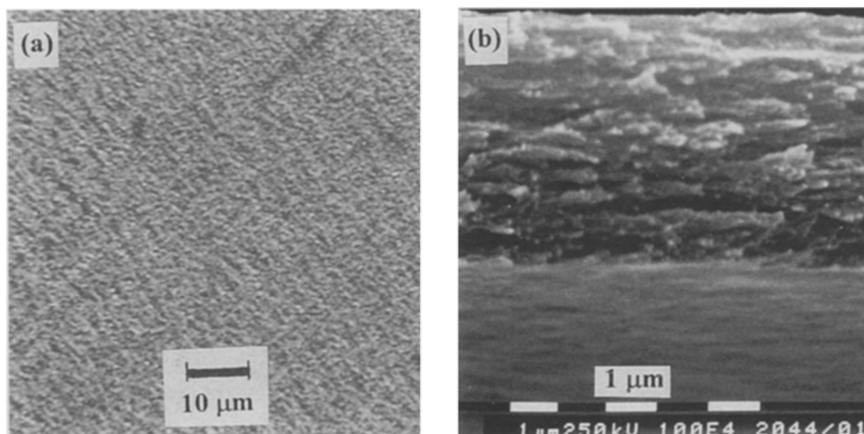

Fig.3. Optical and scanning electron micrographs of BPDA-PDA/silica aerogel (73/27, w/w) composite film with a thickness of 5.5 μm: (a) Optical micrograph taken in a magnification of 1,000X under crossed polarizations; (b) Scanning electron micrograph taken in a magnification of 10,000X.

BPDA-PDA polyimide film, which has the same thickness as the composite film does, showed n_{xy} = 1.8163, n_z = 1.5937, and $\bar{n}$ = 1.7421. The dielectric constants estimated were ε_{xy} = 3.299, ε_z = 2.540, and $\bar{\varepsilon}$ = 3.035. In comparison, the composite film with silica aerogels exhibited relatively low refractive indices and optical anisotropy, leading to the relatively low dielectric constants and dielectric anisotropy. Overall, the optical and dielectric properties of BPDA-PDA polyimide were improved by the composite formation with silica aerogels.

The interfacial stress of films were measured on Si(100) wafers over 25 - 400°C under a nitrogen gas flow. Results are illustrated in Fig.5. For the 73/27 composite film, interfacial stress stayed at a level of 12.4 MPa over 350 - 400°C and almost linearly increased with decreasing temperature, finally reaching to 39.0 MPa at room temperature. In contrast, the pure BPDA-PDA film showed a quite different stress versus temperature behavior that the film stress almost linearly decreased with decreasing temperature from 12.4 MPa at 400°C to 4.5 MPa at room temperature. In general, the interfacial stress in a polymer is predominated by the thermal stress component rather than the intrinsic stress term.[16,17] Thermal stress is a primary function of the mismatch of thermal expansion coefficients between polymer film and substrate.[16,17] Therefore, the interfacial stress results indicate that thermal expansion coefficient is higher in the composite film than the BPDA-PDA film.

Thermal expansion coefficient was measured for both the composite film and the pure BPDA-PDA film. The thermal expansion coefficient averaged over 100 - 200°C was 16

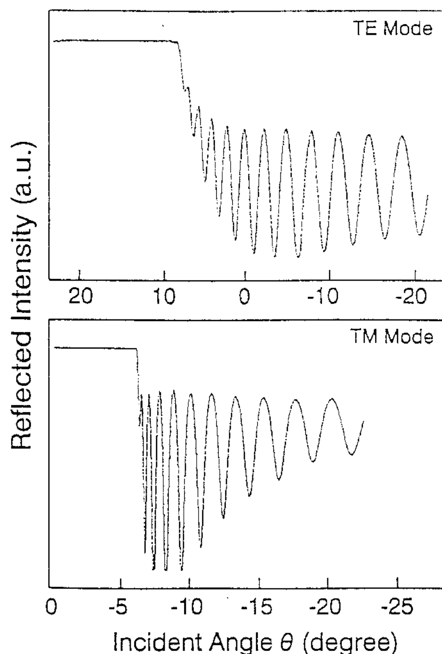

Fig.4. Intensity of reflected light as a function of incident angle θ obtained for BPDA-PDA/silica aerogel (73/27, w/w) composite film with a thickness of 5.5 μm on a silcon oxide/silicon wafer substrate: Top, reflected intensity scan in TE mode; Bottom, reflected intensity scan in TM mode.

ppm/°C for the composite film and 6 ppm/°C for the pure BPDA-PDA film. The thermal expansion coefficient of Si(100) wafers is known to be 3 ppm/°C.[16] Therefore, the mismatch of thermal expansion coefficients between the silicon substrate and film is much larger in the composite film than the pure BPDA-PDA film, consequently leading to the higher interfacial stress in the composite film.

These stress and thermal expansion behaviors in the composite film are abnormal and surprising. These behaviors are in contradiction to those of various common polymers in literature.[18] In general, the thermal expansion coefficient and film stress in conventional polymers are reduced by composite formations with inorganic particulates because of the significant contribution of a low thermal expansivity of the particulates added.[18]

The abnormal thermal expansion and stress behaviors observed in the silica aerogel composite may be related to the chain rigidity and orientation characteristics of BPDA-PDA polyimide. According to a previous study of Ree *et al.*,[3,12] the higher chain rigidity causes the higher chain in-plane orientation in thin films on substrates. BPDA-PDA polyimide with a relatively large Kuhn length (ca. 120 Å), which is a measure of chain rigidity,[12] is known to highly align in the film plane, resulting low thermal expansion coefficient and low film stress.[3,12] For the strong tendency of surface-induced chain in-plane orientation, BPDA-PDA molecules in the composite film may favorably aligned on the surface of spherical silica aerogel particulates as well as the surface of the silicon substrate, consequently leading to a large decrease in the overall molecular in-plane orientation. The decrease of molecular in-plane orientation in the composite film might cause the large increase in the thermal expansion coefficient, leading to the drastic increase in the film stress.

The polymer chain in-plane orientation in films was examined by film birefringence measurements. Film birefringence ($\Delta = n_{xy} - n_z$), which is a measure of molecular in-plane orientation,[12] was estimated from the refractive indices to be 0.2324 for the pure BPDA-PDA film and 0.1691 for the composite film. This indicates that the high molecular in-plane orientation in the pure BPDA-PDA film was significantly disturbed in the composite film by the aerogel particulates added. The molecular in-plane orientation was further characterized by wide-angle x-ray diffraction. The results are presented in Fig.6. The

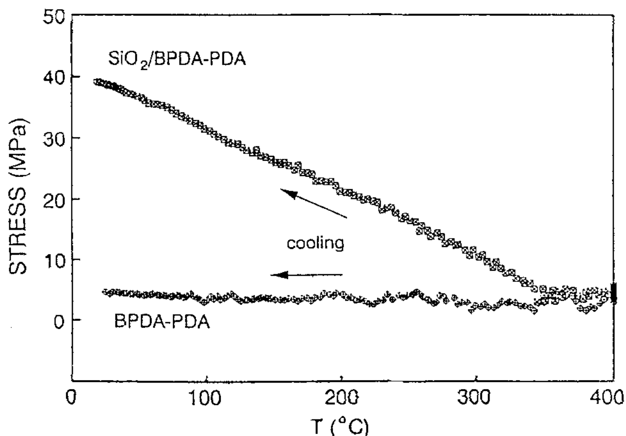

Fig.5. Interfacial stresses of pure BPDA-PDA polyimide and BPDA-PDA/silica aerogel (73/27, w/w) composite film in a thickness of 5.5 μm measured on Si(100) wafers as a function of temperature under a nitrogen gas flow.

WAXD reflection peaks in Fig.6 were assigned in accordance with the structural analysis result of Ree *et al.*[19] For the pure BPDA-PDA film, the multiple (00*l*) peaks, which are indicative of a high degree of chain order along the chain axis, appeared only in the transmission pattern in which the diffraction vector is in the film plane, but did not appear in the reflection pattern in which the diffraction vector is in the out-of-plane of film. This indicates that the polyimide chains in the pure BPDA-PDA film were almost completely aligned in the film plane. However, for the composite film the (00*l*) peaks appeared in both transmission and reflection pattern, apparently indicating the random orientation of polymer chains. However, except the (004) peak, the intensity of the higher ordered (00*l*) peaks were relatively stronger in the transmission than in the reflection. This indicates that the population of polymer chains aligned in the film plane still is slightly higher than that oriented in the out-of-plane, resulting in the relatively weakened birefringence.

Conclusions

For rigid type of polymers like BPDA-PDA, the thermal expansion and interfacial stress in thin films could not be reduced by the composite formation with silica aerogels having a low thermal expansivity. These properties still changed predominantly with the variation in the polymer chain orientation caused by silica aerogel particulates. However, the optical

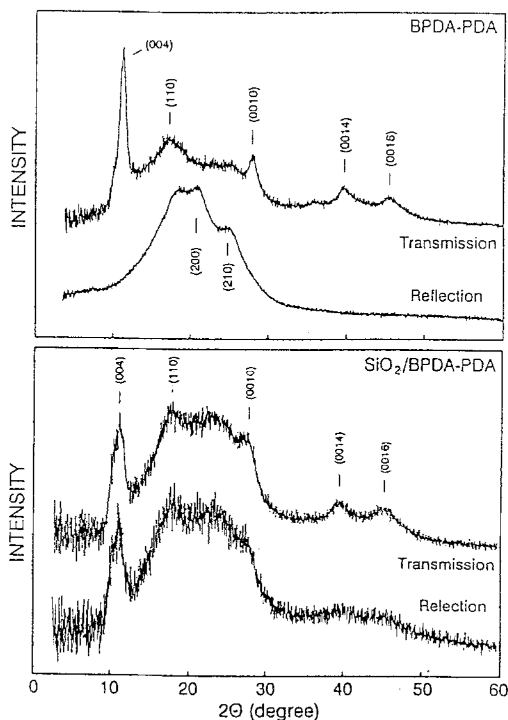

Fig.6. Wide-angle X-ray diffraction patterns of pure BPDA-PDA polyimide and BPDA-PDA/silica aerogel (73/27, w/w) composite film in a thickness of 5.5 5.5 μm measured in reflection and transmission geometry. CuK_α radiation source was used.

and dielectric properties was improved utilizing the low dielectric constant characteristics of silica aerogels.

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