Anisotropy in thermo-optic coefficients of polyimide films formed on Si substrates

ARTICLE *in* APPLIED PHYSICS LETTERS · DECEMBER 2003

Impact Factor: 3.3 · DOI: 10.1063/1.1631744

Shinji Ando
Tokyo Institute of Technology

Anisotropies in Thermo-Optic Coefficients of Polyimide Films Formed on Si Substrates

<u>Yoshiharu TERUI</u>, Shinji ANDO
Department of Organic and Polymeric Materials, Tokyo Institute of Technology
Ookayama 2-12-1-S1-21, Meguro-ku, Tokyo, 152-8552, Japan

Abstract

Thermo-optic coefficients for TE- and TM-polarized lights (dn_{TE}/dT and dn_{TM}/dT; temperature gradient of refractive index) were measured for seven kinds of aromatic polyimide (PI) films formed on Si Substrates. The values of dn/dT for average refractive indices (dn_{av}/dT) are in a range of –52 to –87 ppm/K, and the absolute values of dn_{TE}/dT are significantly larger than those for dn_{TM}/dT for all PI films. As predicted from the temperature derivative of the Lorenz-Lorenz equation, the amorphous PI films with high n_{av} exhibit large $|dn_{av}/dT|$. On the other hand, significant polarization dependences of dn/dT, which are observed as the temperature gradients of birefringence ($d(\Delta n)/dT$), was observed even for the PI films having very small Δn, although a large Δn should cause a large $d(\Delta n)/dT$ according to the temperature derivative of the Vuks equation. The significant $d(\Delta n)/dT$ observed for the PI films with small Δn is originated from the large residual stress (~50 MPa) induced on the films derived from the mismatch in thermal expansion between the PI and Si substrate. Since residual stress on the films decreases as temperature increases, the stress birefringence should exhibit temperature dependence, which causes significant polarization dependence in dn/dT.

Introduction

Aromatic polyimides (PIs) have been widely used as microelectronics and opt-electronics materials because of their excellent properties such as high thermal stability, good processability, and resistance for organic solvents. Furthermore, fluorinated PIs (FPIs) exhibit low water sorption and high transparency in visible to near-IR regions, hence, FPIs are very important candidates for waveguide material. Our group has employed them for waveguide components such as thin-film waveplate[1] and polarizers.[2] One of the most important characteristics of polymeric material is large negative thermo-optic (TO) effect (temperature dependence of refractive index). The large TO effect of polymeric materials should contribute to the high-speed response and small driving energy of waveguide circuits such as optical switches or attenuators. These devices must endure extensive temperature changes, thus FPIs are good candidate as TO waveguide materials.

Since the waveguide devices are generally formed on Si substrates, values of dn/dT for films on Si substrates should be precisely designed for such devices. According to the temperature derivative of the Lorentz-Lorenz equation;

$$\frac{dn}{dT} = -\frac{(n^2-1)(n^2+2)}{6n}\beta \qquad (1)$$

(β; CTE, coefficient of thermal volume expansion), $|dn/dT|$ becomes large with a large β and a high refractive index n. Since PI films frequently exhibit in-plane / out-of-plane anisotropy in their properties, the polarization dependence in dn/dT may exists in PI films. In the present study, the values of dn/dT and their polarization dependence are measured for PI films formed on Si substrates. Furthermore, the origin of the polarization dependence in dn/dT was investigated in the light of residual stress and polarization dependence of refractive indices.

Experimental

Precursor of PIs, poly(amic acid) (PAA) solutions were prepared by addition polymerization of equimoler amounts of dianhydrides and diamines in *N,N*-dimethylacetamide. PI films were prepared by thermal imidization of PAA solutions spin-coated on 3-inch Si substrates coated by adhesion promoter. The spin-coated PAA solutions were dried at 70°C for 30 min, heated to 350°C with a heating rate of 5°C/min, and kept for 1 h under nitrogen flow for thermal imidization. The molecular structures of the resultant PIs are shown in Fig. 1.

A prism coupler (Metricon, PC-2000), equipped with a home-built temperature-control apparatus, was used for refractive index measurements at elevated temperatures (35 – 85°C). All measurements were performed at a wavelength of 1320 nm in dried atmosphere (~20%RH).

Residual stress of PI films on Si substrates was evaluated from a curvature of substrate measured by a DekTak-3 profilometer (Stanford Nanofab.).

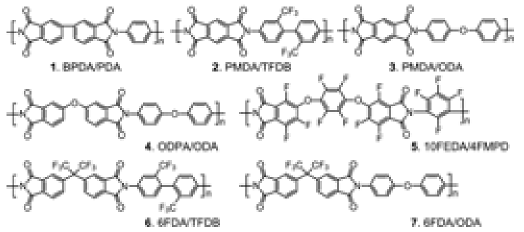

Fig. 1 Molecular structures of polyimides used in this study.

Results

As expected from Eq. 1, the PI films with large n_{av}, which give large $(n_{av}^2 - 1)(n_{av}^2 + 2)/6n_{av}$, exhibit large $|dn_{av}/dT|$ as shown in Fig. 2. However, PI **1** (BPDA/PDA) does not exhibit large dn_{av}/dT despite the large n_{av}. The small dn_{av}/dT for PI **1** film can be attributed to the small volume expansion coefficient β, which originates from the semi-crystalline nature.

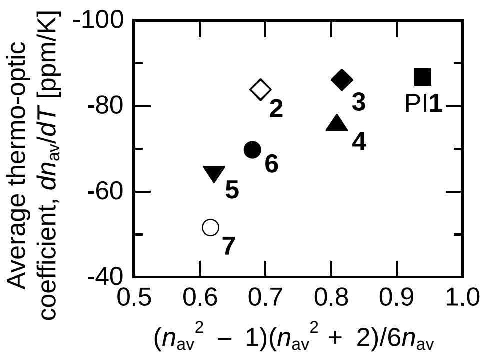

Fig. 2 Relationship between the average refractive index n_{av} and the average thermo-optic coefficient dn_{av}/dT.

As shown in Fig. 3, the absolute values of dn_{TE}/dT (TE : polarization parallel to the film plane) are significantly larger than those of dn_{TM}/dT (perpendicular to the film plane) for all PI films, which represents that the in-plane/out-of-plane birefringence (Δn; $n_{TE} - n_{TM}$) decreases as temperature increases. Moreover, no distinct relationships are observed between Δn and the anisotropy in dn/dT ($d(\Delta n)/dT$; $dn_{TE}/dT - dn_{TM}/dT$). In particular, the films of PI **4**–**7**, which are now used in waveguide and opto-electronics circuits, exhibit significant anisotropies despite the very small Δn. This result suggests that PI-based waveguide circuits utilizing TO effects may exhibit significant polarization dependence.

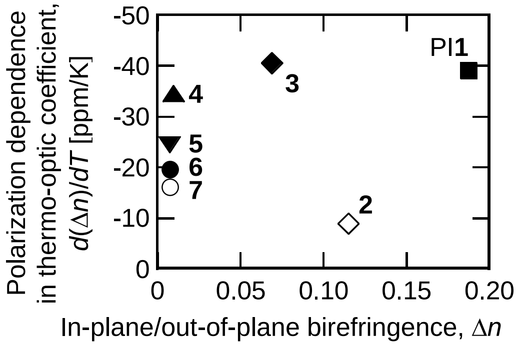

Fig. 3 Comparison between the in-plane/out-of-plane birefringence Δn and the polarization dependence in thermo-optic coefficient $d(\Delta n)/dT$.

Large values of $d(\Delta n)/dT$ for the films of PI **4**–**7** can be caused by the large residual stress induced by CTE (coefficient of thermal expansion) mismatch between substrates and PI films. According to the previous study,[3] residual stress on PI films decreases as temperature increases, which provides temperature dependence of stress birefringence. Since the residual stress in the films of PI **4**–**7** is very large (~50 MPa), the temperature dependence of stress birefringence should be significantly large. Hence, the temperature dependence of Δn becomes negative even for the PI films exhibiting small Δn.

Conclusions

The values of dn_{av}/dT for amorphous PI films formed on Si substrates are in a range of –52 to –87 ppm/K, and the amorphous PI films with high n_{av} exhibit large $|dn_{av}/dT|$. In contrast, the absolute values of dn_{TE}/dT are larger than those of dn_{TM}/dT even for the PI films with very small Δn (PI **4**–**7**). The polarization dependence of dn/dT for those PIs is mainly originated from the temperature dependence of stress birefringence.

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