Thermally stable optical characteristics of sol-gel hybrid material films

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Thermo-optic (TO) coefficients for transverse-electric and transverse-magnetic polarized light (dn_{TE}/dT and dn_{TM}/dT, respectively) were measured for sol-gel-derived, new organic-inorganic hybrid materials. The absolute values of dn_{TE}/dT are comparable to those of dn_{TM}/dT, indicating low anisotropy (dn_{TE}/dT-dn_{TM}/dT) in the TO coefficients. The low anisotropy is evidenced by the very small polarization dependence of the refractive index ($n_{TE}-n_{TM}$). The high stability of these materials is consistent with a high glass transition temperature ($T_g > 150$ °C), and evidenced by an absence of hysteresis in the refractive index and in film thickness during temperature cycling between 30 and 150 °C. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2186111]

The change in refractive index of a material in relation to the temperature is known as the thermo-optic (TO) effect. A number of studies have directly measured the thermal properties of glasses and polymers. Optical switching has also been explored. The use of temperature for tunability concerns mainly filters and lasers. Tuning through the thermo-optic effect was already applied to planar waveguide devices and lasers.[1,2] The tuning of the desired optical wavelength can be achieved by varying the refractive indices of the optical layers using controlled temperature. In the case of lasers the thermal tuning method bases on the idea that the optical length of diode lasers varies with the temperature of the laser chip. Recently, sol-gel-derived, organic-inorganic hybrid materials have attracted considerable attention because of their potential use in optical waveguide devices.[3,4] In particular, the TO effect of sol-gel-derived, organic-inorganic hybrid materials has been the subject of some investigation.[5,6]

Several important properties of optical materials for tuning applications using the TO effect—including thermal hysteresis and thermo-optic anisotropy—are yet to be rigorously evaluated. Thermal hysteresis affects the tuning characteristic of optical devices during the heating and cooling cycle.[7] In this case, large dn/dT and negligibly small anisotropy (polarization dependence) are highly desirable. Polarization dependence in dn/dT will mainly cause polarization dependence in the properties of optical components.[8,9] To fabricate active waveguide circuits using the TO effect, the anisotropy of waveguide materials should be quantitatively examined and carefully controlled. This letter analyzes the high temperature characteristics of new organic-inorganic hybrid materials (hybrimers). It is the first time we measured the polarization dependence of thermo-optic coefficients for sol-gel material between 30 and 150 °C and examine the hysteresis in the refractive index and film thickness during temperature cycling.

Two organic-inorganic, methacrylic hybrimers used in this study were produced using the nonhydrolytic sol-gel process. The first material is a methacrylic hybrimer (hybrimer I). The second is a fluorinated methacrylic hybrimer (hybrimer II), characterized by the presence of fluorine functionality and a methacrylic polymerizable group.

Diphenylsilanediol (DPSD), composed of silanol groups, can react with the alkoxy group of organo alkoxysilane to form a siloxane bond. The alkoxysilane consists of perfluoro-alkylsilane (PFAS) and 3-(trimethoxysilyl)propyl methacrylate (MPTMS). Methacrylic and fluorinated methacrylic polysiloxane resin can be synthesized through a polycondensation reaction between the silanol groups of DPSD and the methoxy groups of MPTMS or PFAS. To fabricate a thin film optical waveguide, the methacrylic hybrimer and the fluorinated methacrylic hybrimer were spin coated on silicon substrates, which had a 2 μm thermally grown SiO_2 layer on their surface. The refractive index of the sol-gel films was higher than that of SiO_2 ($n=1.44$) and, therefore, the hybrimer films guided light as a slab waveguide. The films were cured by UV light (365 nm, 860 mJ/cm^2) in a N_2 atmosphere. Finally, the films were cured thermally at 170 °C for 3 h. More details on the material synthesis can be found in a previous publication.[10]

A prism coupler (Metricon, 2010), equipped with a temperature-control apparatus, was used to make refractive index measurements at elevated temperatures. A HeNe laser ($\lambda=633$ nm) was used to excite TE or TM polarization in the hybrimer films. Variations in the refractive index of the films were measured over the temperature range 30–150 °C. An

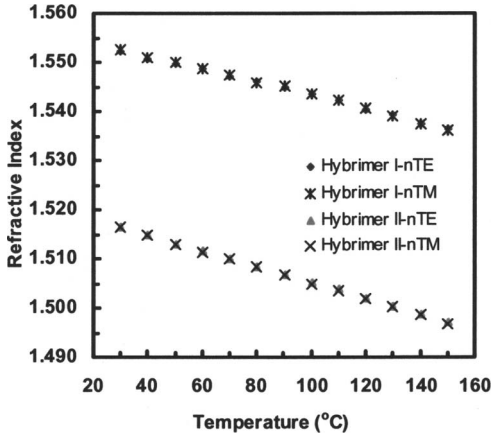

FIG. 1. Temperature dependence of refractive index of the hybrimer films for both TE and TM polarization.

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TABLE I. Film thickness d, birefringence Δn, thermo-optic coefficients dn/dT, and thermal expansion coefficient β of hybrimer films formed on Si substrates at a wavelength of 633 nm. $n_{av}^2=(2n_{TE}^2+n_{TM}^2)/3$, $\Delta n=n_{TE}-n_{TM}$, and $\Delta(dn/dT)=dn_{TE}/dT-dn_{TM}/dT$.

Material	d (μm)	Δn	dn_{TE}/dT (ppm/K)	dn_{TM}/dT (ppm/K)	dn_{av}/dT (ppm/K)	$\Delta(dn/dT)$ (ppm/K)	β (ppm/K)
Sol-gel: hybrimer I	4.6	$<10^{-4}$	−133	−132	−124	−1	208
Sol-gel: hybrimer II	4.6	$<10^{-4}$	−155	−154	−154	−1	261
Polyimide: 6FDA/ODA[a]	5.1	0.0065	−71	−46	−62	−24	···
Polyimide: PMDA/ODA[a]	9.1	0.0686	−104	−72	−94	−32	···
Polyimide: 6FDA/TFDB[a]	10.7	0.0067	−63	−50	−59	−13	···

[a]Ref. 13.

accurate measurement of a sample's refractive index requires an accurate knowledge of prism refractive index versus temperature. The refractive index of the coupling prism (gallium gadolinium garnet) was calculated at each temperature using the values of $n=1.9646$ at 25 °C and $dn/dT=1.93\times10^{-5}/°C$ at 633 nm.[11] More details on the measurement technique can be found in a previous publication.[12]

The temperature dependence of refractive index of the hybrimer thin-film waveguides (for the two polarization cases TE and TM) is plotted in Fig. 1. The variation of refractive index with temperature is linear. No phase transition occurs within the measurement temperature range in both films, suggesting a glass transition temperature (T_g) above 150 °C. The refractive index of the film decreases with increasing temperature (i.e., $dn/dT<0$), indicating a volumetric expansion of the film and a consequent lowering of its density. This conclusion is consistent with the results in Fig. 4, which shows the thickness of film increases with increasing temperature. The slope, dn/dT, for TE and TM modes calculated from the measured values are presented in Table I. The absolute values of dn_{TE}/dT are comparable to those of dn_{TM}/dT, indicating low anisotropy (dn_{TE}/dT $-dn_{TM}/dT$) in the TO coefficients. This anisotropy is much smaller than one tenth of that of fluorinated and aromatic polyimide films currently used in optical applications.[13] The temperature dependence of birefringence for the hybrimer I and hybrimer II films is shown in Fig. 2. The variation of birefringence is within the measurement error of the machine. The samples exhibit very low birefringence ($<10^{-4}$ over 30–150 °C), supporting the reported low anisotropy values reported in Table I. This low birefringence is advantageous to make polarization independent devices. In the case of the three-dimensional waveguide the polarization dependence of the structure can be higher due to the geometrical consideration and processing. The matching of the mode indices is a good approach to obtain polarization independent devices. The waveguide birefringence can also be controlled by properly designing the waveguides and optimizing the fabrication process.[9,14,15] As can be seen in Fig. 2, this low birefringence is independent of the measurement temperature, probably due to an absence of residual stress in the films following film deposition. The refractive index of hybrimer II is smaller than that of hybrimer I. The addition of fluorine in the hybrimer decreases the refractive index and increases the TO coefficient of the material,[16,17] but does not affect the birefringence or the thermo-optic anisotropy. Theoretically, dn/dT is related to the refractive index n and the volume expansion coefficient β as follows:

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

Large dn/dT is achieved by high n or large β. Hybrimer I does not exhibit large dn/dT despite the large n. The small dn/dT for hybrimer I, compared with hybrimer II, is a result of a small volume expansion coefficient. The volume expansion coefficients for the hybrimers obtained from the inverse of the Lorentz-Lorenz relation[18] are presented in Table I.

The thermal stability of the material was determined by measuring the hysteresis in the refractive index and in the film thickness during heating and cooling cycles between 30 and 150 °C. Figure 3 shows the variation of average refractive index during temperature cycling for both materials. The average refractive index (n_{av}) was calculated using the equa-

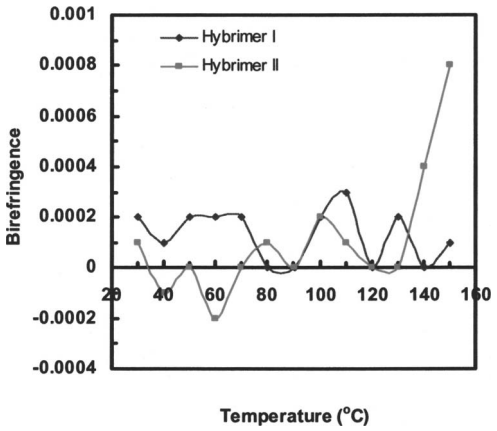

FIG. 2. Temperature dependence of the birefringence ($\Delta n=n_{TE}-n_{TM}$) for the hybrimer films.

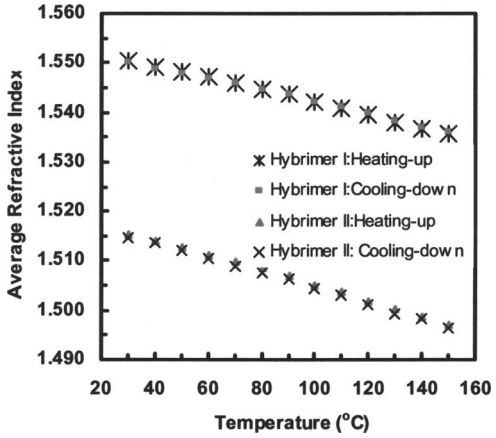

FIG. 3. Temperature dependence of the average refractive index (n_{av}) for the hybrimer films on heating and cooling cycles.

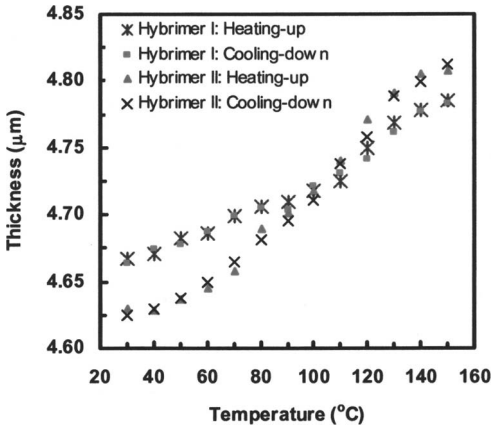

FIG. 4. Temperature dependence of the thickness for the hybrimer films on heating and cooling cycles.

tion, $n_{av}^2=(2n_{TE}^2+n_{TM}^2)/3$. The two sets of data for each material (Fig. 3) are in good agreement indicating that there is no hysteresis in the refractive index. The hysteresis of optical materials can arise for several reasons. In sol-gel silica thin films, it has been attributed to the unrelaxed strain during the heating and cooling cycle.[7] Anisotropically expanding materials undergo extensive microcracking during cooling due to thermal strain,[19] crystallization, and phase transition.[20] In our case, the cycling mechanism does not introduce any physical strain in the hybrimer films. Also of note is the absence of hysteresis in the film thickness, as shown in Fig. 4. The absence of hysteresis is desirable in optical device applications.

The optical properties measured for both hybrimers are listed in Table I. For comparison, we presented the same parameters measured for polyimide, which is typically used in optical applications.[13,21] The hybrimers used here exhibit very low birefringence, negligible TO anisotropy and high TO coefficients. The high thermal stability is consistent with a high glass transition temperature and an absence of hysteresis during temperature cycling. Tuning of the optical parameters of the hybrimer film—such as refractive index, TO coefficient, and thermal expansion coefficient—is achieved without altering the film's anisotropy. Since the thermo-optic coefficients of the materials are negative, they are excellent for the athermalization of interferometric components like arrayed waveguide gratings. The high thermo-optic coefficient of these materials also makes them useful for thermo-optic switches and variable optical attenuators.

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