

## Measurement of the thermo-optic coefficients in sol-gel derived inorganic–organic hybrid material films

Eun-Seok Kang, Tae-Ho Lee, and Byeong-Soo Bae<sup>a)</sup>

Laboratory of Optical Materials and Coating (LOMC), Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea

(Received 29 April 2002; accepted for publication 25 June 2002)

Thermo-optic coefficients ( $dn/dT$ ) of inorganic–organic hybrid material films prepared by sol-gel process of organoalkylsilanes are measured using the prism coupler equipped with autocontrolled hot stage. In order to validate the reliability of this method,  $dn/dT$  of polymethylmethacrylate film is measured.  $dn/dT$  of inorganic–organic hybrid material films are negative and as high as the order of  $10^{-4}$ , which are comparable to those of optical polymers. Their  $dn/dT$  increase with increasing organic content in the film and mainly depend on their thermal expansion. © 2002 American Institute of Physics. [DOI: 10.1063/1.1501448]

Thermo-optic effect in the materials is defined as a change in refractive index as a function of temperature change ( $dn/dT$ ). It can be used in fabrication of digital optical switch, Mach–Zehnder interferometer type optical switch and optical cross-connect.<sup>1,2</sup> Those optical devices play a key function in communication network because of their control over the optical path by changing the temperature.<sup>3</sup> Although many electro-optic devices have been well known for their fast reaction rate, their polarization change has always been a problem. That's the reason why thermo-optic devices have become of great interest in the application areas because of their advantage of polarization-insensitive characteristics.<sup>4</sup> The most widely quoted theory of thermo-optic effect in the materials is that of Prod'homme.<sup>5</sup> According to his theory, the factors that decide  $dn/dT$  are density and electronic polarizability change with temperature:

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

where  $\Phi$  is the temperature coefficient of the electronic polarizability, and  $\beta$  is the thermal expansion coefficient. When the electronic polarizability term is dominant, the refractive index becomes positive and increases with temperature. On the other hand,  $dn/dT$  becomes negative and decreases with increasing temperature when thermal expansion term is dominant. In general,  $dn/dT$  of inorganic glasses are decided by the competition between  $\Phi$  and  $\beta$ . However, in the case of optical polymers,  $dn/dT$  exclusively depends on thermal expansion term because their  $\beta$  are always much higher than their  $\Phi$ . This is the reason why most optical polymers have a negative  $dn/dT$ . Also, according to Lorentz–Lorentz relation in optical polymer, the function  $(n^2+2)/(n^2-1)$ , which is proportional to the specific volume, appears linear in the various temperature ranges where no phase transition occurs.<sup>6</sup> Therefore the thermal expansion coefficient can be directly obtained as  $\beta = a/b$  from the experimental form of

$$f_{LL} = \frac{n^2+2}{n^2-1} = aT + b. \quad (2)$$

Currently, optical waveguides for fabrication of thermo-optic switches have used the materials of silica and optical polymers. The main advantages of silica-based thermo-optic switch are their easier fiber connection, lower optical loss, and better thermal stability.<sup>7</sup> However, it typically requires high switching power of about 0.4~0.5 W and exhibits long response time in the order of ms because silica has a low  $dn/dT$  of about  $10^{-5}/^\circ\text{C}$ . The polymer-based thermo-optic switch overcomes the high switching power of silica-based one due to its higher  $dn/dT$  of about  $-10^{-4}/^\circ\text{C}$ , but then, its thermal stability is another major drawback of practical application.<sup>4</sup> Recently, sol-gel derived inorganic–organic hybrid materials (which will be called HYBRIMER in this study) composed of silica and organic or polymer have begun to receive attention for application of thermo-optic switch in integrated optics.<sup>8</sup> Because the performance of the HYBRIMER thermo-optic switch has been known to be comparable to that of polymer one, it is expected that  $dn/dT$  of the HYBRIMER is as high as that of polymer. It will be interested to measure  $dn/dT$  of HYBRIMER because inorganic materials usually have positive  $dn/dT$  while organic materials have negative values. However, there have been no reports on the  $dn/dT$  measurement of the inorganic–organic hybrid material systems. In this study, we propose an easy  $dn/dT$  measurement method of films using a prism coupler and measured  $dn/dT$  of the HYBRIMER films.

Figure 1 shows a schematic diagram of the prism coupler<sup>9</sup> equipped with autocontrolled hot stage to measure the refractive index of films as a function of temperature. The flexible heater, which is thin enough not to affect the optical coupling between the prism and the film was used to elevate sample temperature. The film-type thermocouple was attached to sample surface and temperature variation in the prism was neglected over the range of measurement (30~100 °C). Refractive index variation due to film thickness change with temperature can be neglected because it is possible to calculate thickness and refractive index independently using a prism coupler. A He-Ne laser of 632.8 nm

<sup>a)</sup>Electronic mail: bsbae@mail.kaist.ac.kr

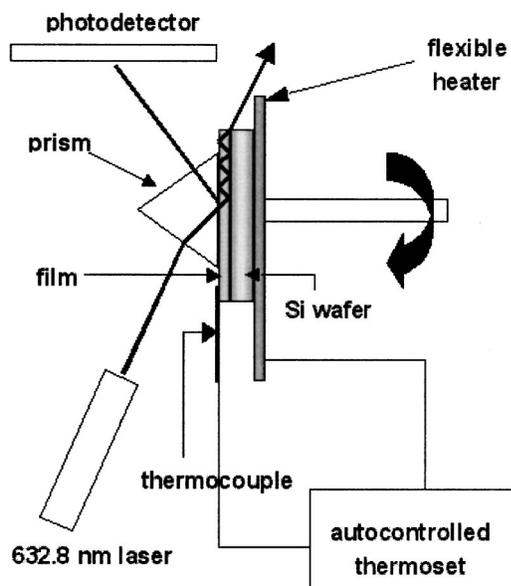


FIG. 1. Apparatus for measuring thermo-optic coefficients of the films.

wavelength was used as the light source. In order to validate the reliability of this method, the refractive index of polymethylmethacrylate (PMMA) film depending on temperature was measured. For preparing PMMA film, tetrahydrofuran was used as a solvent of PMMA powder (average  $M_w \sim 350\,000$ ) and the solution was spin coated onto silicon substrate. Figure 2 shows the variation of refractive index and  $f_{LL}$  of PMMA film with temperature. The measurements were carried out over the range  $30\sim 70^\circ\text{C}$  because the transition temperature of PMMA is about  $90^\circ\text{C}$ . The refractive index variation with temperature increase is linear and the  $dn/dT$  calculated by the slope ( $-1.13 \times 10^{-4}/^\circ\text{C}$ ) is very close to the value reported in the literature ( $-1.20 \times 10^{-4}/^\circ\text{C}$ ).<sup>10,11</sup> We also obtained the thermal expansion coefficient ( $2.02 \times 10^{-4}/^\circ\text{C}$ ) of PMMA film from the variations of Eq. (2) ( $f_{LL} = 3.47 + 7.01 \times 10^{-4}T$ ). This value is very close to the reported ones ( $2.20\sim 2.70 \times 10^{-4}/^\circ\text{C}$ ) of PMMA. Although we evaluated the values of the film-type PMMA, they are in good agreement with the common values of PMMA bulk with small error range. In order to observe the temperature variation in the film thickness, we measured

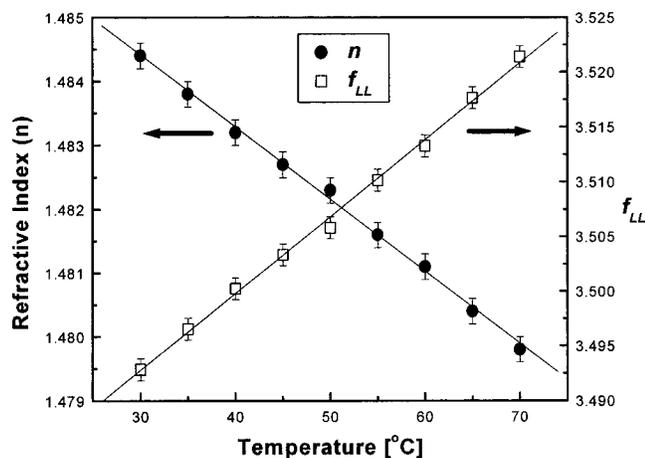


FIG. 2. Variation of refractive index and  $f_{LL} = (n^2 + 2)/(n^2 - 1)$  of the PMMA film as a function of temperature.

Downloaded 18 Aug 2002 to 143.248.117.5. Redistribution subject to AIP license or copyright, see <http://ojps.aip.org/aplo/aplcr.jsp>

the refractive index profiles across the depth of  $\sim 5\ \mu\text{m}$  PMMA and  $\sim 3\ \mu\text{m}$  HYBRIMER films over the measurement temperature range. Those are almost the same at all the temperatures, indicating the temperature variation in the film thickness is negligible. Thus, this method using the prism coupler equipped with an autocontrolled hot stage can provide reliable measurements of  $dn/dT$  of the films.

The HYBRIMER were fabricated using the precursors of methacryloxypropyltrimethoxysilane (MPTMS) and tetramethylorthosilicate (TMOS). First, MPTMS was prehydrolyzed at  $60^\circ\text{C}$  for 1 h with 0.75 equivalent water in the present of 0.05 N HCl as catalyst because of the difference of reaction rate between precursors. Then, TMOS and additional water were added to the prehydrolyzed MPTMS solution and stirred to complete the hydrolysis and condensation at room temperature. The total amount of water was equal to the 1.5 equivalent of total alkoxides in the solution. The prepared solution was spin coated onto silicon substrates at 3000 rpm for 30 s and the coated films were heat treated at  $180^\circ\text{C}$  for 12 h.

For the observation of  $dn/dT$  variations depending on HYBRIMER composition, MPTMS/TMOS ratio in solution was controlled. The organic content in the films increases with increasing MPTMS/TMOS ratio due to the higher methacrylate group in MPTMS being confirmed by Fourier transform infrared spectra. As the MPTMS/TMOS ratio in the solution increases, the refractive indexes at  $30^\circ\text{C}$  gradually increase from 1.4616 (MPTMS/TMOS=0.5) to 1.4797 (MPTMS/TMOS=4). The increase in refractive index is due to higher refractive index of the MPTMS precursor containing methacrylate group than that of the TMOS precursor. For all the compositions, the refractive index change depending on temperature was linear whose slope can give  $dn/dT$  of the film. Their variation depending on composition is shown in Fig. 3(a).  $dn/dT$  of the HYBRIMER films are negative and as high as the order of  $10^{-4}$  which are comparable to those of optical polymers.<sup>12</sup> Their values increase from  $-1.35 \times 10^{-4}/^\circ\text{C}$  (MPTMS/TMOS=0.5) to  $-1.94 \times 10^{-4}/^\circ\text{C}$  (MPTMS/TMOS=1), and saturate about  $-2.0 \times 10^{-4}/^\circ\text{C}$  above MPTMS/TMOS=1. This means  $dn/dT$  of the HYBRIMER increases with growing their organic contents.

For the observation of polymerization effects in HYBRIMER films, 10 mol % 2,2-dimethoxy-2-phenylacetophenone serving as the photoinitiator was added to the solution (MPTMS/TMOS=1). The degree of photopolymerization of methacrylate group in the HYBRIMER can be controlled by the UV illumination time. As the degree of photo-polymerization increases,  $dn/dT$  of HYBRIMER films decrease from  $-1.94 \times 10^{-4}/^\circ\text{C}$  ( $0\ \text{J}/\text{cm}^2$ ) to  $-0.89 \times 10^{-4}/^\circ\text{C}$  ( $54\ \text{J}/\text{cm}^2$ ). It is known that  $dn/dT$  of higher molecular polymer network is generally less than that of lower molecular one because the cross-linking reduces the thermal expansion considerably.<sup>2,4</sup> Therefore, variation in  $dn/dT$  of the HYBRIMER may be related to changes in thermal expansion.

In order to investigate the variation of thermal expansion of the HYBRIMER depending on the composition, we fabricated the rod-type HYBRIMER samples and carried out a thermal mechanical analysis (TMA). For preparing the rod-

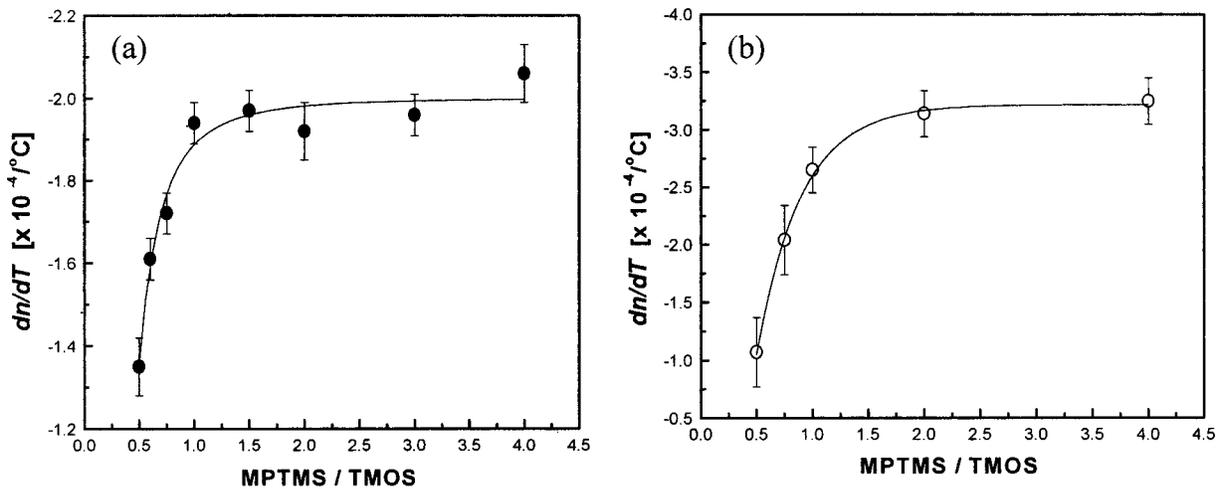


FIG. 3. Variation of (a) the measured  $dn/dT$  in the HYBRIMER films and (b) the calculated  $dn/dT$  in the HYBRIMER as a function of solution composition.

type HYBRIMER, we dried the solutions at  $60^{\circ}\text{C}$  for several days and obtained their gels. The rod-shaped samples were made with cutting those gels and then heat-treated at  $180^{\circ}\text{C}$  for 12 h. Finally, we can obtain the HYBRIMER rods with about  $30 \times 5 \times 0.5 \text{ mm}^3$  dimension. The TMA measurements were carried out over the range  $30 \sim 150^{\circ}\text{C}$  with  $5^{\circ}\text{C}/\text{min}$  heating rate at  $\text{N}_2$  atmosphere. The rod length variation with temperature is perfectly linear for all compositions, and the linear thermal expansion coefficient ( $\alpha$ ) can be calculated from the slope. We assumed that the volumetric thermal expansion coefficient is approximately three times the linear thermal expansion coefficient ( $\beta = 3\alpha$ ), and  $dn/dT$  of the HYBRIMER exclusively depend on the thermal expansion term. We neglect the temperature dependence term of the polarizability in Eq. (1) because  $dn/dT$  of the HYBRIMER films are highly negative and the thermo-optic characteristic of the HYBRIMER exhibits the same behavior as that of polymer. In these assumptions,  $dn/dT$  can be evaluated from Eq. (1). Table I shows the thermal expansion coefficients of the rod-type HYBRIMER and  $(n^2 - 1)(n^2 + 2)/6n$  which are used to calculate Eq. (1).  $dn/dT$  of the HYBRIMER obtained from the theoretical calculation is shown in Figure 3(b). There was slight difference between the calculated  $dn/dT$  and the measured ones. This result may be because we calculated  $dn/dT$  from the thermal expansion coefficient of the bulk-type samples and isotropic assumption ( $\beta = 3\alpha$ ) while

TABLE I. Linear thermal expansion coefficient ( $\alpha$ ), Volumetric thermal expansion coefficient ( $\beta$ ) and  $(n^2 - 1)(n^2 + 2)/6n$  of the HYBRIMER.

MPTMS / TMOS	$\alpha$ ( $\times 10^{-4}/^{\circ}\text{C}$ )	$\beta^a$ ( $\times 10^{-4}/^{\circ}\text{C}$ )	$\frac{(n^2 - 1)(n^2 + 2)^b}{6n}$
0.5	0.66	1.98	0.5359
0.75	1.26	3.78	0.5389
1	1.64	4.92	0.5393
2	1.90	5.70	0.5515
4	1.93	5.79	0.5613

<sup>a</sup> $\beta = 3\alpha$ .

<sup>b</sup>Refractive index at  $30^{\circ}\text{C}$  is used.

$dn/dT$  of the film-type samples were measured. In spite of this difference, the calculated and the measured  $dn/dT$  show the same order of  $-10^{-4}$  and their variation tendencies are very similar. Their  $dn/dT$  highly increase with increasing organic contents below MPTMS/TMOS=1 and saturate above that ratio. Therefore, it can be thought that variation in thermal expansion of HYBRIMER mainly affects their  $dn/dT$ .

In conclusion,  $dn/dT$  of the films were measured easily using the prism coupler equipped with a hot stage. This method has potential for studying  $dn/dT$  of the optical waveguide films.  $dn/dT$  of HYBRIMER films which are composed of silica and methacrylate group are negative and the order of  $10^{-4}$ . Their high values of  $dn/dT$  make them possible in thermo-optic applications. The dependence of composition and organic cross-linking degree on  $dn/dT$  of HYBRIMER is mainly affected by the variation in thermal expansion.

This work has been supported from the Korea Science & Engineering Foundation (KOSEF, Grant No. R01-2000-000-00224-0) and by the Brain Korea 21 project.

- <sup>1</sup>H. Nishihara, M. Haruna, and T. Sahara, *Optical Integrated Circuits* (McGraw-Hill, New York, 1989), p. 124.
- <sup>2</sup>L. Eldada, K. M. T. Stengel, L. W. Shacklette, R. A. Norwood, C. Xu, C. Wu, and J. T. Yardley, *Proc. SPIE* **3006**, 344 (1997).
- <sup>3</sup>S. V. Kartalopoulos, *Introduction to DWDM Technology* (SPIE Bellingham, WA, 2000), p. 141.
- <sup>4</sup>J. Zhai, L. Qiu, J. Zhou, Y. Zhao, Y. Shen, Q. Ling, and M. Yang, *Adv. Mater. Opt. Electron.* **10**, 3 (2000).
- <sup>5</sup>L. Prod'homme, *Phys. Chem. Glasses* **4**, 119 (1960).
- <sup>6</sup>P. Michel, J. Duglas, J. M. Cariou, and L. Martin, *J. Macromol. Sci., Phys.* **25**, 379 (1986).
- <sup>7</sup>D. Bosc, N. Devoldere, M. Bonnel, J. L. Favennec, and D. Pavy, *Mater. Sci. Eng., B* **57**, 155 (1999).
- <sup>8</sup>O. S. Rosch, W. Bernhard, R. Muller-Fiedler, P. Dannberg, A. Brauer, R. Buestrich, and M. Popall, *Proc. SPIE* **3799**, 214 (1999).
- <sup>9</sup>R. Ulrich and R. Torge, *Appl. Opt.* **12**, 2901 (1973).
- <sup>10</sup>D. N. Nikogosyan, *Properties of Optical and Laser-Related Materials* (Wiley, New York, 1997), p. 390.
- <sup>11</sup>U. Bernini, P. Russo, M. Malinconico, E. Martuscelli, M. G. Volpe, and P. Mormile, *J. Mater. Sci.* **28**, 6399 (1993).
- <sup>12</sup>C. C. Lee and T. J. Su, *Appl. Opt.* **33**, 7016 (1994).