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

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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. Those optical devices play a key function in communication network because of their control over the optical path by changing the temperature. 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. The most widely quoted theory of thermo-optic effect in the materials is that of Prod’homme. According to his theory, the factors that decide dn/dT are density and electronic polarizability change with temperature:

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

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. Therefore the thermal expansion coefficient can be directly obtained as \( \beta = ab/ \) from the experimental form of

\[ f_{11} = \frac{n^2 + 2}{n^2 - 1} = aT + b. \]  

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. 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}/°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}/°C, but then, its thermal stability is another major drawback of practical application. 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. 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 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

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close to the value reported in the literature (the temperature variation in the film thickness, we measured of PMMA bulk with small error range. In order to observe PMMA, they are in good agreement with the common values PMMA. Although we evaluated the values of the film-type transitions of Eq. ~2.20 and the 10,11 We also obtained the thermal expansion coefficient (~2.02 × 10⁻⁴/°C) of PMMA film from the variations of Eq. (2) (f_LL = 3.47 + 7.01 × 10⁻⁴T). This value is very close to the reported ones (~2.0 to ~2.70 × 10⁻⁴/°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 the refractive index profiles across the depth of ~5 μm PMMA and ~3 μm 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 tetramethyldisiloxane (TMOS). First, MPTMS was prehydrolyzed at 60 °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 alkoxydes 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 °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 °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.12 Their values increase from ~1.35 × 10⁻⁴/°C (MPTMS/TMOS = 0.5) to ~1.94 × 10⁻⁴/°C (MPTMS/TMOS = 1), and saturate about ~2.0 × 10⁻⁴/°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 × 10⁻⁴/°C (0 J/cm²) to ~0.89 × 10⁻⁴/°C (54 J/cm²). 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.2,4 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-type HYBRIMER,

![FIG. 1. Apparatus for measuring thermo-optic coefficients of the films.](image1)

![FIG. 2. Variation of refractive index and f_LL=(n²+2)/(n²-1) of the PMMA film as a function of temperature.](image2)
type HYBRIMER, we dried the solutions at 60 °C for several days and obtained their gels. The rod-shaped samples were made with cutting those gels and then heat-treated at 180 °C for 12 h. Finally, we can obtain the HYBRIMER rods with about 30 × 5 × 0.5 mm³ dimension. The TMA measurements were carried out over the range 30 ~ 150 °C with 5 °C/min heating rate at N₂ atmosphere. The rod length variation with temperature is perfectly linear for all compositions, and the linear thermal expansion coefficient (α) can be calculated from the slope. We assumed that the volumetric thermal expansion coefficient is approximately three times the linear thermal expansion coefficient 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 (n²−1)(n²+2)/6n which are used to calculate 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 (β = 3α) while 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.

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<table>
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<th>TABLE I. Linear thermal expansion coefficient (α), Volumetric thermal expansion coefficient (β) and (n²−1)(n²+2)/6n of the HYBRIMER.</th>
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<tr>
<td>MPTMS</td>
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<td>TMOS</td>
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β = 3α.

Refraction index at 30 °C is used.

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.