



Modification of Thermo-Optic Characteristics of Sol-Gel Inorganic-Organic Hybrid Materials

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Abstract. The effect of the inorganic oxide network on the variation of thermo-optic characteristics (dn/dT) in inorganic-organic hybrid material prepared through the sol-gel process was investigated. The dn/dT values were negative for all samples, and decreased in magnitude with the increasing concentration of the inorganic oxide or heterometallic oxide network. The dn/dT also became less negative with the increase in the degree of inorganic condensation in sol-gel reaction. A negative dn/dT value is consistent with thermal expansion of the material, and it is believed that the value of the dn/dT in our inorganic-organic hybrid materials was principally sensitive to variations in expansion term.

Keywords: sol-gel, hybrid material, HYBRIMER, thermo-optic coefficient, waveguide

1. Introduction

Thermo-optic effect in a material is defined as the change in the refractive index as a function of temperature change (dn/dT) [1]. The thermo-optic characteristics of dielectric optical materials such as silica and optical polymer are an important consideration in their application to waveguide devices. The temperature dependence of lightwave devices such as arrayed waveguide grating (AWG), resonators, and Mach-Zehnder-type narrow band filters is a serious and outstanding problem in the dense wavelength division multiplexing (DWDM) system [2]. This feature is mostly due to the temperature dependence of the optical path length. To eliminate this undesirable feature, Kokubun et al. investigated the athermal waveguide (hybrid waveguide structure consisting of silica core and polymer overcladding) using the dn/dT characteristics of materials. In other words, athermal waveguide can be made by modification of overcladding layer because overcladding layer affects both the refractive index and the dn/dT of core layer [3]. However, the dn/dT of an op-

tical polymer is normally a higher negative than the dn/dT value that satisfies the athermal condition.

Recently, a sol-gel derived inorganic-organic hybrid material (HYBRIMER) composed of silica and organic structure has been attracting attention as a promising waveguide material that may be used to replace silica and polymer [4]. A previous study reported a novel and straightforward technique for measuring dn/dT for HYBRIMER films using a prism coupler equipped with a hot stage [5]. The dn/dT value of the HYBRIMER was found to be easily and widely controlled by changing its organic modifier structure [6].

In this study, the effect of the inorganic network variation on the value of the dn/dT in the HYBRIMER was investigated for application to the athermal waveguide. Based on the results, the manipulation of the inorganic network in the HYBRIMER was proposed as a method for controlling the dn/dT .

2. Experimental Procedure

To observe the effect of an inorganic network on the value of the dn/dT of the HYBRIMER, a range

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of precursors were used to manufacture various HYBRIMER solutions. To determine the variation in the dn/dT depending on the heterometallic oxide formation in the HYBRIMER, dimethyldiethoxysilane (DMDES, $\text{Si}(\text{OC}_2\text{H}_5)_2(\text{CH}_3)_2$) was mixed with tetramethylorthosilicate (TMOS, $\text{Si}(\text{OCH}_3)_4$) and zirconium *n*-propoxide (ZPO, $\text{Zr}(\text{OC}_3\text{H}_7)_4$). As a first step, DMDES was prehydrolyzed for 3 h in 0.75 equivalent water to the amount of alkoxy group with 0.1N HCl. Subsequently, TMOS and ZPO were added to the prehydrolyzed solutions, and the mixtures were stirred for another hour. The mixed solutions were reacted with additional water to enhance the hydrolysis, and condensation was then allowed to occur for 12 h. The total amount of water was equal to 1.5 times the equivalent amount of alkoxy group in the solution. To investigate the effect of the degree of the inorganic network on the value of the dn/dT in the HYBRIMER, phenyltrimethoxysilane (PhTMS, $\text{C}_6\text{H}_5\text{Si}(\text{OCH}_3)_3$) and TMOS were used as precursors. In this process, PhTMS was first prehydrolyzed, with TMOS later added to the solution. The procedure mentioned earlier was then followed once more. Finally, Aluminium acetylacetonate ($\text{Al}(\text{acac})_3$, $(\text{CH}_3\text{COCH}=\text{COCH}_3)_3\text{Al}$) serving as the catalyst of inorganic condensation was added to the solution, and the mixtures were stirred for 1 h. TMOS and silica sol solutions were mixed with 3-methacryloyloxypropyltrimethoxysilane (MPTMS, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$) and prepared the same way to determine the probable effect of these variations of inorganic network on the value of the dn/dT .

The prepared solutions were spin-coated onto silicon substrate at 2000 rpm for 30 s, and the resultant films were heat treated at 150°C for 12 h. The prism coupler equipped with an autocontrolled hot stage was used to measure the dn/dT of the HYBRIMER film. A He-Ne laser of 632.8 nm TE mode was used as the light source. Additional details on the measurement technique may be found in previous publications.

3. Results and Discussion

3.1. Heterometallic Oxide Network

To investigate the effect of formation and concentration of the heterometallic oxide on the dn/dT in the HYBRIMER, the ratio of both TMOS/DMDES and ZPO/DMDES in the solution was varied. These materials were expected to have similar structures because

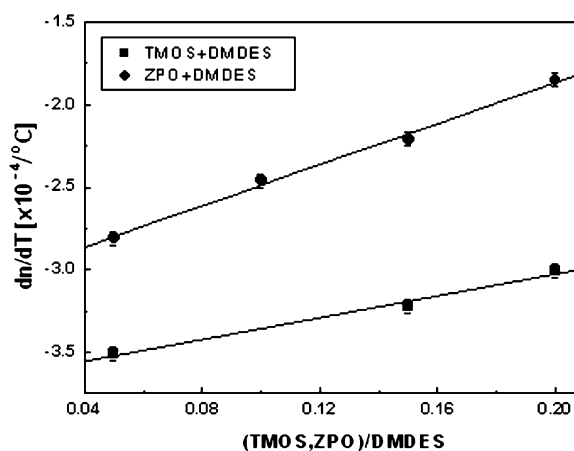


Figure 1. Temperature dependence of the refractive index of the HYBRIMER (TMOS/DMDES and ZPO/DMDES) as a function of solution composition.

both TMOS and ZPO have the same number of reaction group. However, ZPO/DMDES contains zirconium oxide in the silicon-based HYBRIMER, indicating the formation of heterometallic oxide. Figure 1 shows the variation of the dn/dT in the HYBRIMER as a function of the solution composition. The magnitudes of dn/dT of the HYBRIMER decreased as the concentration of both ZPO/DMDES and TMOS/DMDES increased. In the previous work, the origin of the dn/dT in HYBRIMER was examined and found to be in proportion to the negative thermal expansion term ($-\beta$) [5]. The decrease in magnitude is therefore due to the decrease in β . This is because the β of organic polymers is of the order of $10^{-4}/^\circ\text{C}$, and that of silica about $0.49 \times 10^{-6}/^\circ\text{C}$ [7, 8]. In addition, the change in the dn/dT of ZPO/DMDES was observed to be higher compared to TMOS/DMDES. These results suggest that the heterometallic oxide network effectively decreases the magnitude of the dn/dT in the HYBRIMER.

3.2. Inorganic Condensation Degree

To observe the dependence of the dn/dT on inorganic condensation in the HYBRIMER, its value in both TMOS/MPTMS and silica sol/MPTMS was studied. The degree of inorganic condensation in TMOS/MPTMS was expected to be lower compared to silica sol/MPTMS because the methacryl group in MPTMS sterically hinders the condensation of TMOS while silica sol has complete Si—O—Si bond at the precursor. The FT-IR absorbance spectroscopy

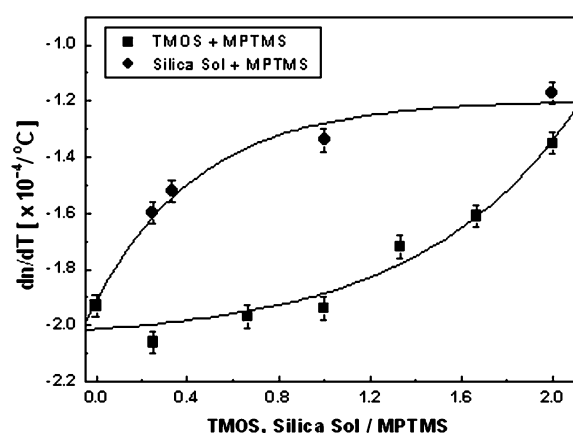


Figure 2. Variation in dn/dT of the HYBRIMER (silica sol/MPTMS and TMOS/MPTMS) as a function of solution composition.

confirmed the presence of more unreacted alkoxy group in TMOS/MPTMS compared to silica sol/MPTMS. Figure 2 shows the variation of the dn/dT in the HYBRIMER as a function of the solution composition. As mentioned earlier, the magnitude of the dn/dT decreases with the growth of the inorganic network in the HYBRIMER. The magnitudes of the dn/dT of the silica sol/MPTMS were found to be lower compared to the TMOS/MPTMS, indicating that the dn/dT becomes less negative when the inorganic condensation in HYBRIMER increases. Because not all the alkoxy groups have reacted, the inorganic condensation is reduced and therefore the thermal expansion coefficient is greater, contributing to the larger magnitude of the dn/dT in HYBRIMER. Thus, silica sol/MPTMS has less negative dn/dT values than TMOS/MPTMS.

To investigate the effect of the degree of inorganic condensation in the HYBRIMER on the dn/dT , $\text{Al}(\text{acac})_3$ was added as the condensation catalyst to $\text{PhTMS}/\text{TMOS} = 1$ solution from 0 mol% to 5 mol% over the total silicon atom. Figure 3(a) shows the FT-IR absorbance spectra of the HYBRIMER films as a function of the amount of $\text{Al}(\text{acac})_3$. The bands 2948 cm^{-1} and 2849 cm^{-1} indicating the $-\text{CH}_3$ asymmetric stretching mode and $\text{Si}-\text{OCH}_3$ vibrational mode, respectively, decreased considerably with the increase in $\text{Al}(\text{acac})_3$ [9]. This change in the bands is due to the enhanced inorganic condensation degree caused by the catalytic effect. Thus, the degree of inorganic condensation for these HYBRIMER materials can be controlled by varying the amount of the condensation catalyst. Figure 3(b) shows the variation of the dn/dT in HYBRIMER as a function of the concen-

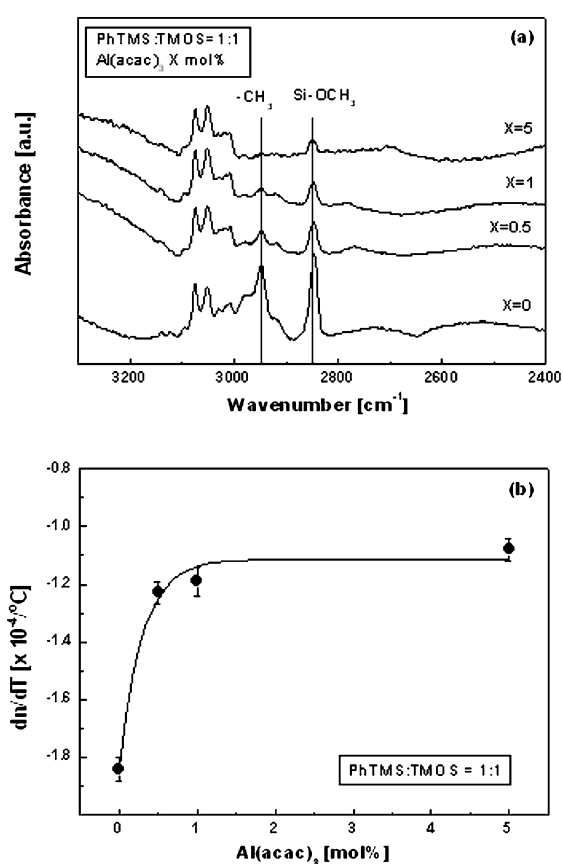


Figure 3. (a) The FT-IR absorbance spectra and (b) variation in dn/dT for the PhTMS/TMOS HYBRIMER films as a function of amount of $\text{Al}(\text{acac})_3$ in the solution.

tration of $\text{Al}(\text{acac})_3$. As $\text{Al}(\text{acac})_3$ in the solution increased, the dn/dT abruptly became less negative changing from $-1.84 \times 10^{-4}/^\circ\text{C}$ ($\text{Al}(\text{acac})_3$ 0 mol%) to $-1.23 \times 10^{-4}/^\circ\text{C}$ ($\text{Al}(\text{acac})_3$ 0.05 mol%), gradually to $-1.08 \times 10^{-4}/^\circ\text{C}$ ($\text{Al}(\text{acac})_3$ 5 mol%). This decrease in the magnitude of dn/dT resulted from the increase in the degree of inorganic condensation, which decreases β .

As a result, the variation of the dn/dT in the HYBRIMER as a function of the inorganic network may be explained mainly by the change in thermal expansion. The value of the dn/dT in HYBRIMER may therefore be easily controlled by modifying the inorganic network structure in the HYBRIMER.

4. Conclusion

The values of the dn/dT of the HYBRIMER prepared through the sol-gel process were measured. The zirconium oxide in the HYBRIMER was added by the

precursor in the solution, with the dn/dT becoming less negative as the zirconium oxide concentration increased. The silica sol and the inorganic condensation catalyst were used to control the degree of silica network formation in the HYBRIMER. The value of the dn/dT became less negative with the increase in the degree of inorganic condensation. The effect of variation in the inorganic network on the dn/dT of HYBRIMER was mainly caused by the material's thermal expansion term. Thus, their tunable values of the dn/dT make them applicable in thermo-optic device materials.

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