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Measurement of Thermo-Optic Coefficients in Sol-Gel Hybrid Glass Films

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Abstract. Thermo-optic coefficients (TOC) of inorganic-organic hybrid glass (HYBRIMER) films prepared by sol-gel process of organoalkylsilanes were measured using the prism coupler equipped with auto-controlled hot stage. The spin coated HYBRIMER films composing of silica and methacrylate networks were fabricated for the measurement. Their TOCs are negative and as high as the order of 10^{-4}, which are comparable to those of optical polymers. It was found that composition of the films, formation of organic network and addition of other elements in the HYBRIMER affect TOCs of the films.

Keywords: thermo-optic coefficient, inorganic-organic hybrid glass, HYBRIMER, optical waveguide

1. Introduction

Thermo-optics (TO) represents temperature dependence of refractive index (dn/dT) which can be used in optical switches or optical cross-connects [1, 2]. Those optical devices play a key function in communication network because of their control over the optical path [3]. Current materials used for thermo-optic switches are silica and optical polymers. The main advantages of silica-based TO switch are their easier fiber connection and lower optical loss [4]. However, it typically requires high switching power about 0.4–0.5 W and exhibits long response time in the order of msec due to the low TOC of silica. On the other hand, the polymer-based TO switch consumes less power but here thermal stability is a major issue of practical application [5]. Recently, inorganic-organic hybrid materials (which will be called HYBRIMER) composing of silica and organic or polymer have begun to receive attention for application of TO switch in integrated optics [6]. Because the performance of the HYBRIMER TO switch is comparable to that of polymer one, it is expected that the TOC of the HYBRIMER is as high as that of polymer. However, there have been no reports on the thermo-optic coefficient measurement of the inorganic-organic hybrid material systems. In this study, the thermo-optic properties of HYBRIMER films were investigated depending on their composition and molecular structure.

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2. Experimental Procedure

HYBRIMERs were fabricated using methacryloxypropyltrimethoxysilane (MPTMS) and tetramethylorthosilicate (TMOS). 0.1 N HCl was used as a catalyst and prehydrolysis of MPTMS was performed because of the difference of reaction rate between precursors. The films were fabricated by spin coating onto silicon wafers and their average thickness was about 4 μm. For the observation of polymerization effects, the 2,2-dimethoxy-2-phenylacetophenone (Benzildimetylketal, BDK) serving as the photoinitiator was added to the solution. Also, perfluoroalkylsilane (PFAS) was added to investigate the variation of thermo-optics caused by fluorine addition to HYBRIMERs. Refractive indexes of the films and their profiles across the film depth depending on temperature were measured by a prism coupler.

3. Results and Discussion

Figure 1 shows the prism coupler equipped with auto-controlled hot stage to measure refractive index of the

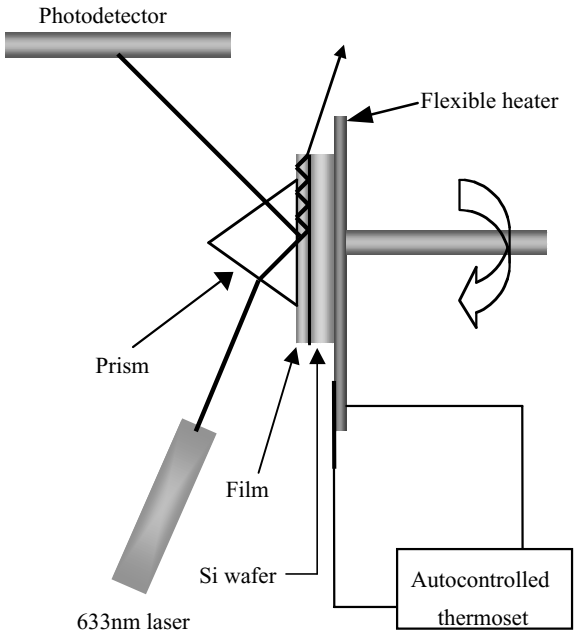

Figure 1. Prism coupler equipped with auto-controlled hot stage for measurement of thermo-optic coefficients of the films.

films as a function of temperature. For higher temperature, the flexible heater which is thin enough not to affect the optical coupling between the prism and the film was used. Temperature variation across the film depth and in the prism was neglected. In order to validate the reliability of the method, the refractive index of polymethylmethacrylate (PMMA) film depending on temperature was measured. Figure 2 shows the variation in refractive index of PMMA film with

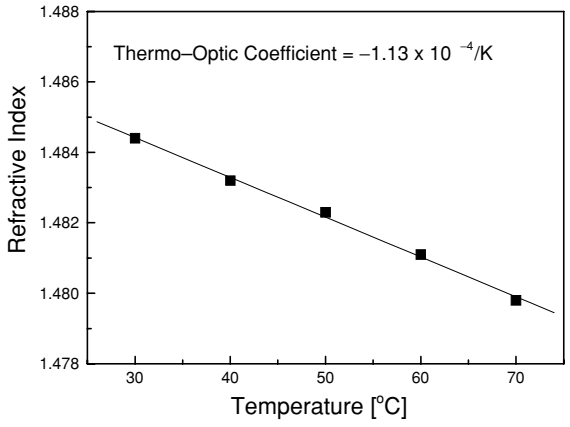

Figure 2. Variation in refractive index at TE 633 nm of PMMA film depending on temperature.

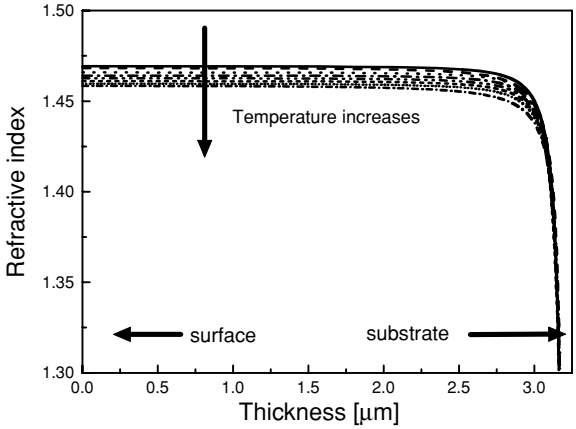

Figure 3. Film depth profile of refractive index at TE 633 nm of HYBRIMER films (MPTMS:TMOS = 1:1) with temperature ($30^{\circ}\mathrm{C} < T < 100^{\circ}\mathrm{C}$).

temperature. The refractive index variation with temperature is linear and the thermo-optic coefficient (-1.13×10^{-4}) calculated by the slope is very close to the value reported in the literature (-1.2×10^{-4}) [7, 8]. Figure 3 shows that the refractive index of HYBRIMER film is almost constant across the film depth at whole temperature, illustrating that the temperature gradient in the films is negligible. Thus, the method using the prism coupler equipped with auto-controlled hot stage can provide a reliable measurement of TOC of the films.

Figure 4 shows the variation in refractive index of HYBRIMER films prepared by MPTMS and TMOS precursors for various compositions depending on

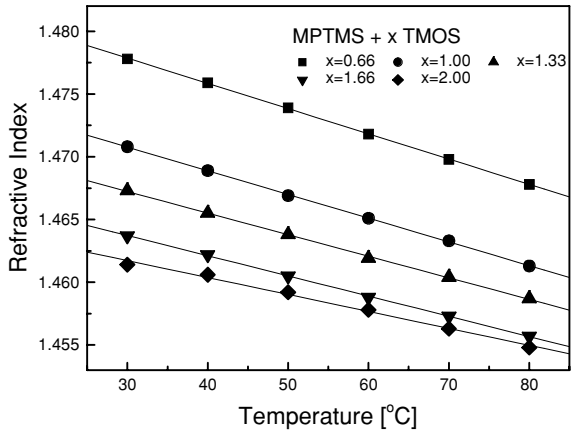

Figure 4. Variation in refractive index at TE 633 nm of HYBRIMER films with various compositions depending on temperature.

temperature. For all the compositions, the refractive index variation with temperature is linear whose slope can give TOC of the films. As the TMOS/MPTMS ratio in the precursor solution increases, the refractive indexes and TOCs decrease. The decrease in refractive index is due to the lower refractive index of silica than that of the organosilane containing methacrylate group. The decrease in TOC, the range from -2.0×10^{-4} (TMOS/MPTMS = 0.66) to -1.3×10^{-4} (TMOS/MPTMS = 2.00), results from the increase in the amount of silica which has a positive TOC of about 10×10^{-6}. TOCs of the films are negative and as high as the order of 10^{-4} which are comparable to those of optical polymers [9]. According to Prod'homme theory [10], the factors that decide TOC are density and electronic polarizability change with temperature.

$$\frac{dn}{dT} = f(n)(\Phi - \beta) \tag{1}$$

where Φ is the temperature coefficient of the electronic polarizability, β is the volume expansion coefficient, and $f(n)$ is defined as

$$f(n) = \frac{(n^2 - 1)(n^2 + 2)}{6n} \tag{2}$$

If the electronic polarizability term is dominant, the refractive index increases with temperature. On the other hand, TOC is negative when thermal expansion term is dominant. For organic polymers, it is known that TOC exclusively depends on its volume expansion term. This is the reason why most optical polymers have a negative TOC. Therefore, it can be thought that the thermo-optic characteristic of the HYBRIMER exhibits the same behavior as that of polymer because TOCs of HYBRIMER films are also highly negative. This can be confirmed by studying the effect of methacrylate group polymerization in HYBRIMER films on the variation in TOC. It is known that TOC of higher molecular polymer is generally less than that of lower molecular one because the cross-linking reduces the thermal expansion considerably [2, 5]. From the FT-IR spectroscopy, formation of organic network by photo-polymerization in the HYBRIMER is confirmed by the result that absorbence of 1719 cm^{-1} C=O peak in methacrylate group remains constant while that of 1638 cm^{-1} C=C peak relatively decreases as shown in Fig. 5. TOCs of the HYBRIMER films decrease with the degree of

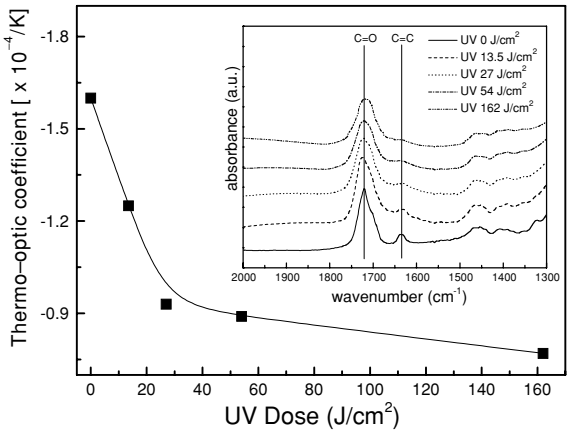

Figure 5. Variation in thermo-optic coefficients at TE 633 nm of HYBRIMER films (MPTMS:TMOS = 1:1) with photo-polymerization initiated by BDK. Inset shows the change in FT-IR spectra with UV illumination.

photo-polymerization. Moreover, fluorine addition in the HYBRIMER by using PFAS as a precursor gradually increases TOC of the films as shown in Fig. 6. As fluorine is well known for its role of increasing thermal expansion of glass, variation in TOC of HYBRIMER films may be related with the change in thermal expansion coefficient of the film [11]. Namely, the HYBRIMER containing more unreacted organic and fluorine can make higher TOC of the films due to its higher thermal expansion. Thermal expansion of HYBRIMER films and their relationship with TOC of HYBRIMER films will be discussed in other publications.

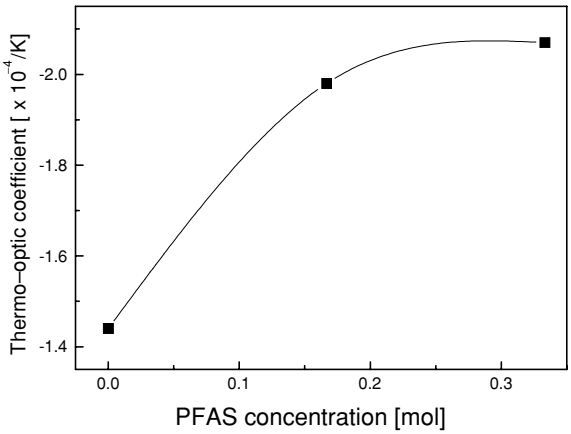

Figure 6. Variation in thermo-optic coefficient at TE 633 nm of HYBRIMER films (MPTMS:TMOS = 1:1) with PFAS concentration in precursor solution.

4. Conclusion

TOC of the HYBRIMER films composing of silica and methacrylate group were measured using the prism coupler equipped with hot stage. Their TOCs are negative and are the order of 10^{-4} which are comparable to those of optical polymers. TOCs of the films increase with increasing organic components in HYBRIMER. Formation of an organic network by photo-polymerization reduces TOC in the same way as polymers do. Also, addition of fluorine in the HYBRIMER gradually increases TOCs of the films. The dependence of composition and molecular structure on TOCs of the HYBRIMER films may be mainly affected by the variation in thermal expansion of the films.

Acknowledgments

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