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Fabrication and Characteristics of Sol-Gel Derived Fluorinated Hybrid Material Films

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Abstract. Fluorinated inorganic-organic hybrid materials (HYBRIMER) were successfully prepared from fluoroalkylsilanes (FASs) containing fluoro-alkyl functions and methacryloxypropyltrimethoxysilane (MPTMS) through a sol-gel process. The influence of concentration and fluoro-alkyl chain lengths of FASs on the physical characteristics of the fluorinated HYBRIMER films was examined. Larger fluorine contents lowered the refractive index within a range, which was closely dependent on the fluoro-alkyl chain lengths of FASs. Thermo-optic coefficients (TOC) were negative values, and the values grew with increasing fluorine contents and fluoro-alkyl chain lengths. Also, the thermal stability is enhanced by addition of fluorine in the HYBRIMER.

Keywords: sol-gel, hybrid material, fluoroalkylsilane, HYBRIMER, thermo-optic coefficient, thermal stability

1. Introduction

Sol-gel derived inorganic-organic hybrid materials (HYBRIMER) have attracted much attention in recent years as potential candidates for optical applications and have been much examined especially for application to waveguide devices [1–4]. Normally, the HYBRIMER made through the sol-gel technique for application to optical devices requires control of optical parameters, especially with regard to refractive index and thermo-optic coefficients defined as the temperature dependence of refractive index. Thus, many efforts have been concentrated on controlling optical parameters. In particular, the fluorine incorporation has received much attention because fluorine adds the unique characteristics such as low refractive index, low surface energy and lowering absorption loss [3]. Moreover, the introduction of fluorine into the HYBRIMER is expected to affect these optical properties in a technologically desirable direction, i.e., control of optical parameters such as refractive index, absorption loss, and thermo-optic coefficients [5, 6]. However, adding fluorine to the HYBRIMER was a very hard process, and the range of addition also was limited due to the low solubility of fluorine. To overcome these problems, methacryloxypropyltrimethoxysilane (MPTMS) is used with fluoroalkylsilanes (FASs) with fluoro-alkyl chain. This system exhibits good fluorine solubility and versatility in processing.

In this study, fluorinated HYBRIMER was fabricated using variable concentration and fluoro-alkyl chain lengths of fluoroalkylsilanes (FASs) through a sol-gel process. The study also examined the tunability and stability of fluorinated HYBRIMER. After obtaining a stable fluorinated HYBRIMER, the dependence of the different contents and chain lengths of FASs on optical properties was examined. In addition, the influence of FASs contents on thermal properties was investigated.

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2. Experimental Procedure

Fluorinated HYBRIMERS were synthesized using methacryloxypropyltrimethoxysilane (MPTMS) and fluoroalkylsilanes (FASs) as precursors. Three different kinds of fluoroalkylsilanes ($CF_3(CF_2)_nCH_2CH_2$ $Si(OR)_3$, $n = 0, 5, 7$) were used depending on fluoroalkyl chain length. These three FASs were designated as FAS-3, FAS-13, and FAS-17. MPTMS and FASs were mixed with water in the presence of 0.01 N hydrochloric acid (HCl), which acted as a catalyst for the sol-gel reaction. The total amount of water is 1.5 equivalents of total alkoxides in the solution. After stirring for 24 h at room temperature, the totally transparent filtered solution was coated on Si substrate using the spin-coating method. Spin-coating at 3000 rpm for 30s yielded an approximate 6–7 μm thickness of the films. The coated film was then thermally cured at 150°C for 10 h. Variations in refractive indexes and thermo-optics caused by adding FASs were measured by a prism coupler at wavelength of 633 nm. Thermal stability was examined with measuring thermal decomposition by thermogravimetric analysis (TGA).

3. Results and Discussion

Figure 1 shows the variation in the refractive index of fluorinated HYBRIMER films with varying FASs contents depending on fluoro-alkyl chain lengths (FAS-3, FAS-13, FAS-17) that were measured using a prism coupler. The respective variations in the refractive index were linear, and their slopes could be calculated by the fitting. Also, their slopes were very dependent on fluoro-alkyl chain lengths. Normally, the dependence of the refractive index on the density and the electronic polarization are determined using the Lorentz-Lorenz relation [7]. Adding fluorine to HYBRIMER lowered the density as well as the electronic polarization since fluorine has large electro-negativity and large free volume. As the fluoro-alkyl chain length of FASs increased, the rate of the refractive index reduction increased due to the low electronic polarization and large volume of fluorine. Thus, these decreases in the refractive index were caused by the increase of the fluorine contents and fluoro-alkyl chain lengths in FASs. As shown in Fig. 1, refractive indexes of fluorinated HYBRIMER could only be controlled widely and easily by changing fluorine contents and fluoro-alkyl chain lengths.

Figure 2 shows the variation in the refractive index of fluorinated HYBRIMER (MPTMS: FAS-17) film with varying FAS-17 contents depending on temperature. For all the compositions, refractive index variations with temperature were linear, and their thermo-optic coefficients ($-1.39 \times 10^{-4} - -2.1 \times 10^{-4}$) could be calculated by the slope. As FAS-17 contents increased, the refractive index depending on the temperature increased negatively. Figure 3 shows the variation in the refractive index of fluorinated HYBRIMER films (MPTMS: FAS-17, FAS-13, FAS-3 = 7:3) with varying fluoro-alkyl chain lengths depending

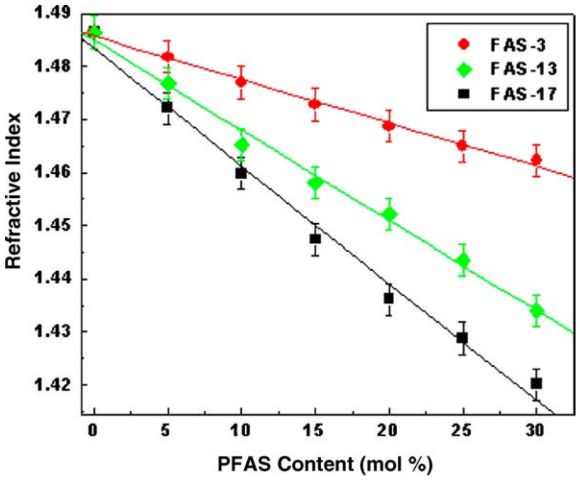

Figure 1. Variation in refractive index at 633 nm of fluorinated HYBRIMER films (MPTMS:FAS-17, FAS-13, FAS-3) with various compositions and fluoro-alkyl chain lengths of FASs.

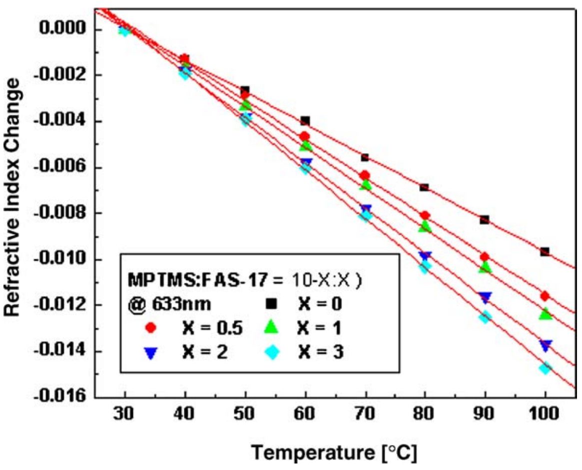

Figure 2. Variation in refractive index at 633 nm of fluorinated HYBRIMER films (MPTMS:FAS-17) with various FASs compositions depending on temperature.

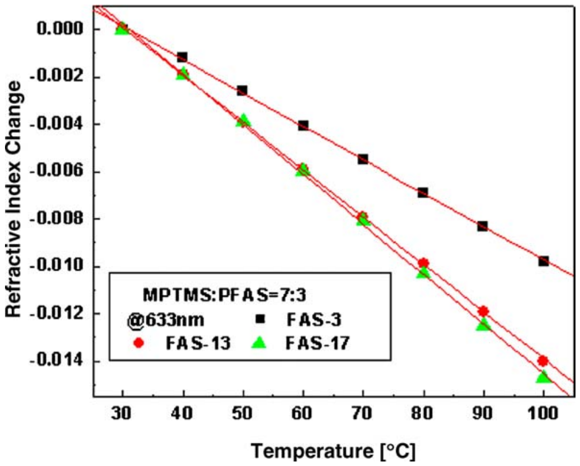

Figure 3. Variation in refractive index at 633 nm of fluorinated HYBRIMER films (MPTMS:FAS-17, FAS-13, FAS-3 = 7:3) with various fluoro-alkyl chain lengths of FASs depending on temperature.

on the temperature. As the fluoro-alkyl chain lengths of fluorinated HYBRIMER increased, TOCs increased negatively. In general, TOCs are dependent on volume expansion, and electronic polarization changes with temperature [8]. For inorganic silica, it is known that it has a positive TOC of about 10^{-6} dependent on their electronic polarization with temperature. On the other hand, TOCs of HYBRIMER are reportedly highly dependent on volume expansion [9] and are negative, as high as the order of 10^{-4}, and comparable to those of optical polymers [10]. As shown in Figs. 2 and 3, TOCs of the fluorinated HYBRIMER films were negative, as high as the order as 10^{-4} and the volume expansion term could be thought the dominant term of the increase in TOCs. Moreover, fluorine addition is well known for increasing thermal expansion of glass due to large free volume of fluorine [11]. Therefore, the increase in TOC in fluorinated HYBRIMER films can be regarded as an increase in thermal expansion due to the large free volume of fluorine obtained by increasing FASs contents and fluoro-alkyl chain lengths.

Figure 4(a) shows the dynamic thermogravimetric curves of fluorinated HYBRIMER and (b) the weight loss curves differentiated by temperature of the fluorinated HYBRIMER (MPTMS:FAS-17) with different FASs contents at a heating rate of 10°C min^{-1} under nitrogen. Their differentiated curves indicate the weight loss represents two types of decomposition at different temperature ranges as shown in Fig. 4(b). As FAS contents increased, thermal decomposition rate at lower temperature range decreased, whereas thermal decomposition rate at higher temperature range increased. Moreover, thermal decomposition temperature of fluorinated HYBRIMER increased since fluorocarbon bond is more thermally stable than the hydrocarbon bond. Therefore, fluorinated HYBRIMER with the largest FASs contents showed the highest thermal stability.

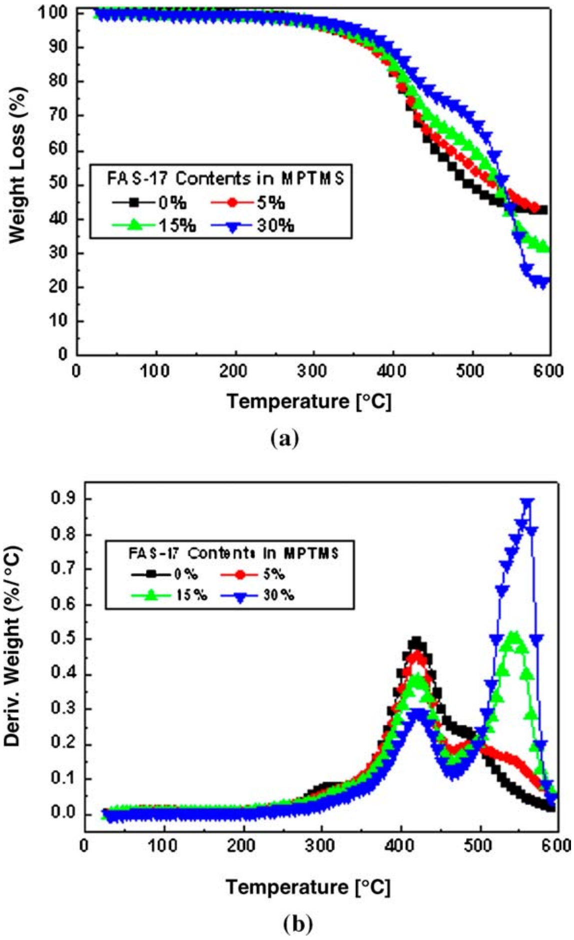

Figure 4. (a) Dynamic thermogravimetric curves and (b) the differential weight loss curves of the fluorinated HYBRIMER (MPTMS:FAS-17) with various FAS contents at a heating rate of 10°C min^{-1} under nitrogen.

4. Conclusion

Fluorinated HYBRIMER with varying contents and chain lengths of FASs was successfully made through a sol-gel process. Their refractive indexes linearly decreased due to the low electronic polarization and large volume of fluorine. As the concentration and chain lengths of FASs increased, their TOCs became negative in the order of 10^{-4}. TOCs of the films gradually increased with increasing FASs contents and fluoro-alkyl chain length. Fine-tuning of optical parameters such as refractive index and TOCs of fluorinated HYBRIMER films could be obtained by changing the contents and the chain lengths of FASs and the optimum optical parameters expected from the fitting. Additionally, adding FASs in fluorinated HYBRIMER increased the thermal decomposition temperature.

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