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High Refractive-Index Thin Films Derived from Organic-inorganic Hybrid Materials

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Development of high refractive-index ($n_D > 2.0$) materials is needed for micro-optical devices to accomplish their optical performances. In this study, thin films of $n_D > 2.0$ were fabricated by heating the organic-inorganic hybrid films. The hybrid films of 0.1–1.0 μm in thickness were prepared on glass substrates by the dip-coating technique at room temperature, using titanium tetra-n-butoxide (TTBu), diphenyldimethoxysilane (DPhDMS), phenyltriethoxysilane (PTES) and 3-glycidoxypropyltrimethoxysilane (GPTMS) as starting materials. Refractive indices and thickness of the films were measured by the optical interference method. Refractive indices increased with increasing the TTBu content, and $n_D = 1.74$ was attained in the film of 80TTBu–10DPhDMS–10PTES composition. Subsequently, the films of 80TTBu–20(DPhDMS–PTES–GPTMS) compositions were heated up to 600°C under oxygen atmosphere, the transparent and amorphous films of $n_D = 2.45 \pm 0.1$ was achieved. Refractive indices of the hybrid films can be controlled from 1.52 to 1.74 by choosing the composition, and from 1.70 to 2.5 by selecting the heating temperatures.

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Key-words : High refractive-Index, Sol-Gel, Thin film

1. Introduction

In recent years, there has been a growing interest in the optical cavity effect called “morphology dependent resonances (MDR)” in a spherical particle of micrometer size. Due to its ultrafast response time¹⁾ and high quality factor Q ,²⁾ the MDR in microsphere is considered to have a potential for the use of opt-opt switching devices. The Q factor depends on sphere’s diameter and relative refractive index $n_r = (n_{\text{sphere}}/n_{\text{medium}})$,³⁾ thus high n_r , nearly over 1.5, is inevitable to accomplish the spherical optical cavity structure. From a practical point of view, the microspheres should be coated with clad materials of lowindex materials (e.g. solvent or plastics of $n_{\text{medium}} = 1.3$ –1.4). Hence, $n_{\text{sphere}} > 2.0$ is needed to satisfy the requirement of high n_r .

We have been interested in organic-inorganic hybrid materials for such high refractive-index microsphere, because they can combine the advantages of both inorganic-glasses (high refractive-index and stability against the high power laser) and organic-polymers (high process-ability and low temperature processing). Furthermore, hybrid materials also bring us the advantage that we can apply the vibrating orifice technique, which we already developed for fabricating the microspheres of highly controlled shape and diameter.⁴⁾

Much work has been reported on high refractive-index hybrid materials, and especially, titania-silica based hybrid materials were widely investigated: B. Wang prepared triethoxysilane-capped polymertitania hybrid materials of $n_D = 1.60$ –1.80;⁵⁾ C. C. Chang synthesized aminoalkoxysilane-capped pyromellitic dianhydride-titania hybrid materials of $n_D = 1.65$ –1.80.⁶⁾

Based on these studies, we also chose the titania-silica systems and used titanium tetra-n-butoxide (TTBu), diphenyldimethoxysilane (DPhDMS), phenyltriethoxysilane (PTES) and 3-glycidoxypropyltrimethoxysilane (GPTMS) as starting materials. In our works the microspheres of $n_D = 1.70$ –1.72 were prepared at room temperature, and $n_D = 2.25$ was achieved by heating them at 450°C.⁷⁾ High refractive index microspheres applicable to the practical use was extremely important. In addition, it possesses great significance that we developed the fabrication technique for transparent materials of high refractive index $n_D > 2.0$ using conventional metal-

alkoxides. Generally, it is not so easy to synthesize such high refractive-index materials. Hence, if we can make a different shaped high-index materials, such as film, fiber and bulk, wide application areas will open i.e., optical waveguides, ring resonator, two-dimensional photonic crystal structure, and so on.

In this paper, we report on the fabrication of high refractive index films derived from similar hybrid materials used for the high-index microspheres.

2. Experimental

2-1. Sample preparation

The processing steps for preparing films are shown in **Fig. 1**. The compositions of the films in the TTBu–DPhDMS–GPTMS system and 80TTBu–20(DPhDMS–PTES–GPTMS) system along with the refractive indices are shown in **Fig. 2**.

Starting materials, DPhDMS, PTES and GPTMS were dissolved in tetrahydrofuran (THF) and hydrolyzed in aqueous HCl solution of pH 2 at room temperature for 3 days. After the reaction, the TTBu dissolved in isopropanol was titrated into the solution. Small amount of H₂O diluted with isopropanol was subsequently titrated slowly into the solution to accelerate the hydrolysis. In order to avoid inhomogeneity caused by high-rate chemical reaction, the solutions were held at 3°C. The TTBu/H₂O was chosen in the molar ratio 1 : 1, which was just the half amount of H₂O to complete the hydrolysis of TTBu. The resultant solution was stirred for 1 day at room temperature for aging.

Conventional slide glasses and fused silica glass plates were used as substrates. Before coating process, the substrates were cleaned ultrasonically in acetone, and their backside were masked by a conventional plastic tape to prevent backside coating. Films of 0.1–1.0 μm thicknesses were prepared on the glass substrates by the dip-coating technique. Nitrogen gas was flowed into the dip-coating chamber to avoid forming micrometer-sized cellular pattern on the film surface as reported in detail previously.⁸⁾ The samples were allowed to dry at 30°C for 1 day and they also used for the subsequent heating procedures.

For increasing the refractive index, the films of 80TTBu–20 (DPhDMS–PTES–GPTMS) were heated with a heating rate

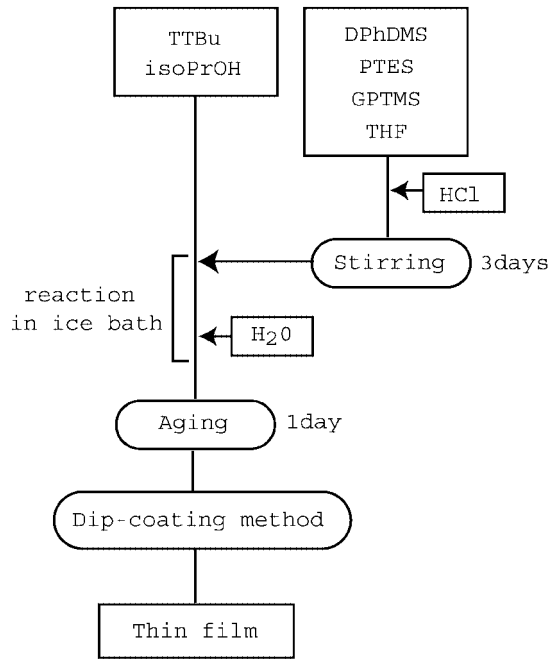


Fig. 1. Processing procedures for inorganic-organic hybrid thin films.

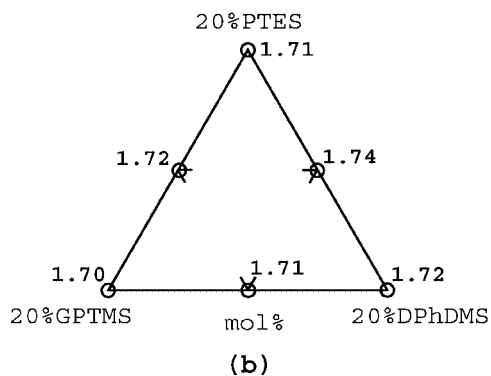
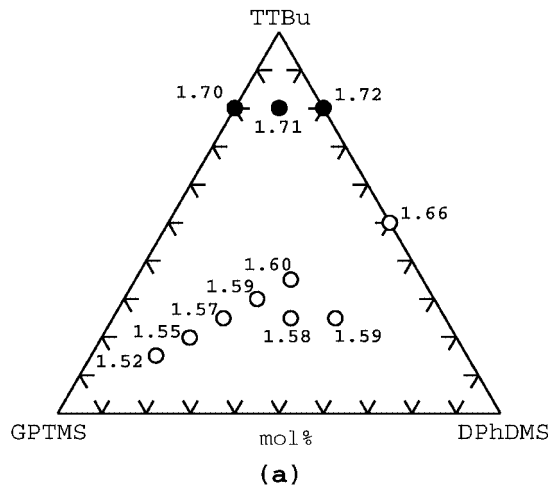


Fig. 2. Composition of inorganic-organic hybrid thin films. (a) TTbu-DPhDMS-GPTMS system and (b) 80TTbu-20(DPhDMS-PTES-GPTMS) system. Numerical values show refractive index n_D of the films.

of $10^\circ\text{C}/\text{h}$ up to a certain temperature of $200\text{--}600^\circ\text{C}$ and kept for 2 h in an electric resistance furnace under oxygen atmosphere.

2-2. Characterization

The refractive index of thin films was measured by the optical interference method. The interference on the measured spectrum is a function of the thickness and the refractive index of the film d , n_1 , and the refractive index of the substrate n_2 . The maximum and the minimum values of reflectance, R_{\max} , R_{\min} , are as follows:

$$R_{\max} = \left(\frac{n_1^2 - n_0 n_2}{n_1^2 + n_0 n_2} \right)^2 \quad (1),$$

$$R_{\min} = \left(\frac{n_2 - n_0}{n_2 + n_0} \right)^2 \quad (2),$$

where $n_0 < n_1 > n_2$.

The wavelengths λ_{2m} and λ_{2m+1} , at which the reflectance shows $R = R_{\max}$ or $R = R_{\min}$, are determined by the interference order $2m$, $2m+1$:

$$2m = \frac{4n_1 d}{\lambda_{2m}},$$

$$2m+1 = \frac{4n_1 d}{\lambda_{2m+1}} \quad (3).$$

Refractive index of the thin films n_1 was calculated by eq. (1) and eq. (2), and the thicknesses d was estimated by eq. (3).

Optical reflectance of samples R was measured by a conventional ultraviolet-visible spectrometer (Jasco, UV-610) using an aluminum mirror as the reference. A 60° prism (BK7 glass) was placed on the rear of the substrate to prevent the backside reflection. Methylbenzoate was used as index matching oil between the substrate and the prism. The indices were determined by comparing the theoretical spectrum with the experimental curves.

Thermal properties of the hybrid samples were measured by the differential thermal analysis and thermo gravimetric analysis (DTA-TG, Rigaku denki Co, Model TG8120) from 30°C to 1000°C in O_2 atmosphere at a heating rate of $2^\circ\text{C}/\text{min}$. Microscopic Raman-scattering spectroscopy (Jasco, Model NRS-2100) was measured to obtain the structural change in heating process. Excitation wavelength was 514.5 nm of CW-Ar⁺ ion laser (20 mW), and spectral resolution was 10 cm^{-1} . X-ray diffraction pattern was also measured in $2\theta = 5\text{--}70^\circ$ by using Cu-K α radiation.

3. Results and discussion

Refractive indices of the thin films prepared at room temperature in the TTbu-DPhDMS-GPTMS system are shown in Fig. 2(a). The indices in the 80TTbu-20(DPhDMS-PTES-GPTMS) system are also shown in Fig. 2(b). The refractive index increased with increasing the TTbu and DPhDMS content, and $n_D = 1.72$ was achieved in the composition of 80TTbu-20DPhDMS.

In the $x(\text{TTbu-DPhDMS}) - (100-x)\text{GPTMS}$ ($x = 15\text{--}30$) and the 25TTbu-75(DPhDMS-GPTMS) composition, an additive relation was obtained as follows

$$n = x \cdot n_{\text{TTbu}} + y \cdot n_{\text{DPhDMS}} + z \cdot n_{\text{GPTMS}} \quad (4),$$

$$x + y + z = 1$$

where $n_{\text{TTbu}} = 1.82$, $n_{\text{DPhDMS}} = 1.56$, $n_{\text{GPTMS}} = 1.46$. In 80TTbu-20(DPhDMS-GPTMS) film, indicated as closed circles in Fig. 2(a), the n_D of experimental value is slightly smaller than n_D from eq. (4), because the amount of remained butyl group was not negligible in the network. High-index

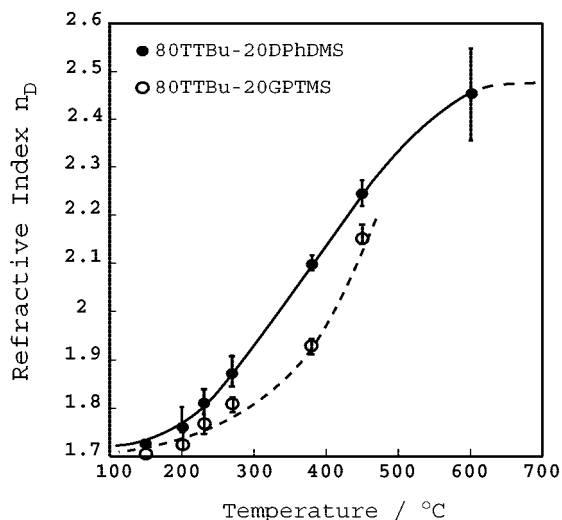


Fig. 3. Change in the refractive indices n_D by heating. Initial composition is 80TTBu-20(DPhDMS-PTES-GPTMS).

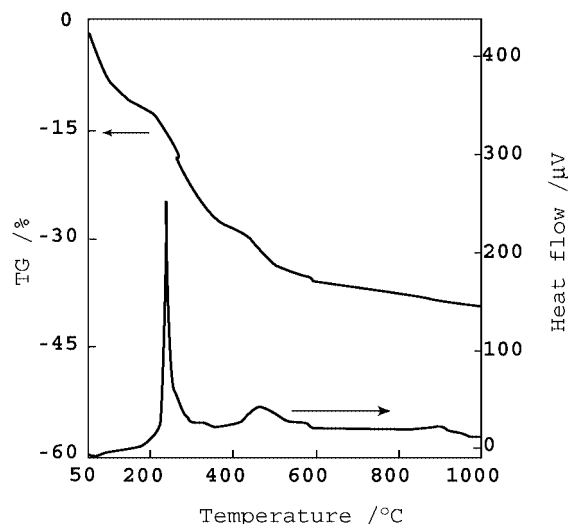


Fig. 5. DTA-TG traces of the 80TTBu-20DPhDMS sample. Heating rate was 2°C/min.

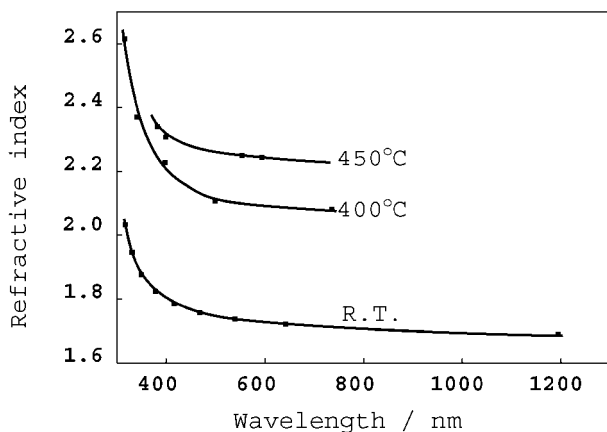


Fig. 4. Refractive index dispersion of the films prepared at room temperature (R. T.) and after heating at 400°C and 450°C.

sample was prepared in the 80TTBu-10DPhDMS-10PTES composition by replacing the DPhDMS with PTES, as shown in Fig. 2(b).

In Fig. 3, the refractive index change of 80TTBu-20(DPhDMS-PTES-GPTMS) is shown against heating temperature. The refractive index increased dramatically above 200°C, and $n_D = 2.45 \pm 0.1$ were achieved in 80TTBu-20DPhDMS after heating at 600°C. Refractive index dispersion of the films after heating at 400°C and 450°C in the wavelength region of 300–1200 nm is shown in Fig. 4. The refractive index of the film after 450°C heating is above 2.0 in the wavelengths from visible to near-infrared region, which will be useful in wide application areas such as an optical fiber communication. Such high indices after 400–600°C heating were not surprising because the indices of TiO₂ (anatase) and TiO₂ (rutile) are known as high as $n_D = 2.493$ –2.554 and $n_D = 2.616$ –2.903.⁹⁾ The heating evolved solvents and fired the organic groups from hybrid matrix, followed by the densification, and then resulted in $n_D > 2.0$. Figure 5 shows the DTA-TG result. Weight loss below 200°C was due to the evolving solvents and H₂O. The exothermic peak due to firing the organic groups from hybrid matrix was observed at 250°C

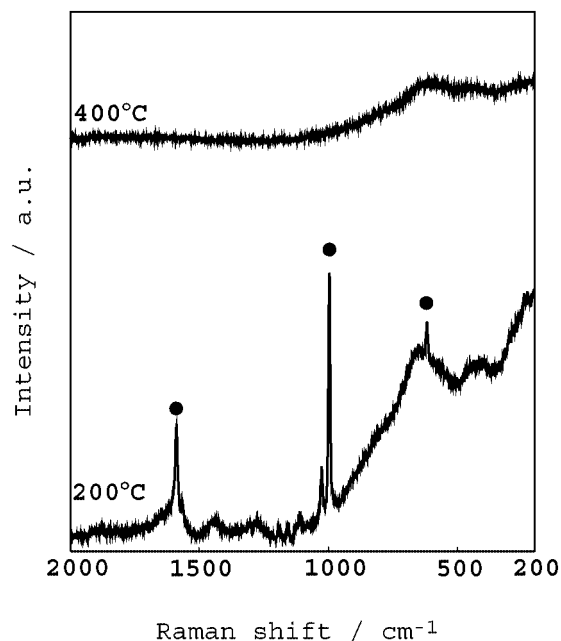


Fig. 6. Raman scattering spectra of the 80TTBu-20DPhDMS thin films after heating at 200°C and 400°C.

along with the weight loss more than 10%, and slightly small loss continued with increasing temperature up to 450°C. Raman-scattering spectra of the films after heating at 200°C and 400°C were shown in Fig. 6. The peaks at 600 cm⁻¹, 1000 cm⁻¹ and 1600 cm⁻¹ due to phenyl group observed in the 200°C samples disappeared after heating at 400°C. The 80TTBu-20DPhDMS film changed to oxides (80TiO₂-20SiO₂) by heating. The film thickness of 80TTBu-20DPhDMS is plotted against heating temperature in Fig. 7. The thickness was about 450 nm before heat treatment, and was about 150 nm after 450°C heating. Decrease of the film thickness and the TG curve suggests that the film matrix was densified by heating because its volume decreased more than 50% after 400°C heating, while the weight loss was only 30%. After heating under 600°C, no peak was observed in the XRD pattern of the films as

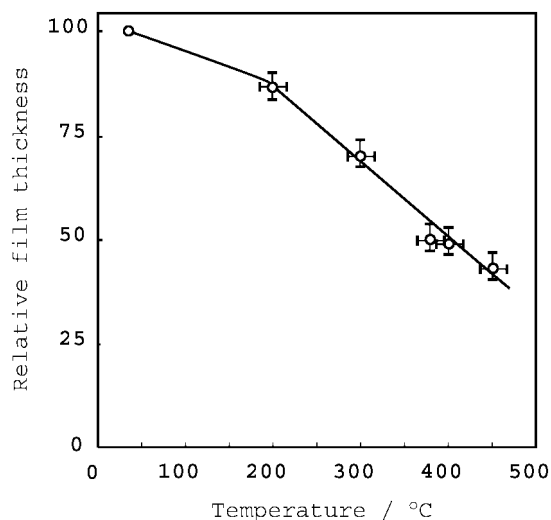


Fig. 7. Change in the film-thickness by heating. Initial composition of the sample is 80TTBu-20DPhDMS.

shown in Fig. 8, those samples of $n_D=2.5$ still remained in amorphous state. The samples after 1000°C heating shows some peaks attributed to rutile and anatase structure, indicated as open and closed circle in Fig. 8, therefore the heating at 1000°C caused the crystallization of the matrix.

The indices of all the samples in the 80TTBu-20(DPhDMS-PTES-GPTMS) system were remarkably similar to that of the 80TTBu-20DPhDMS film. Thus, the 80TTBu-20(DPhDMS-PTES-GPTMS) samples changed into oxides by heating above 400°C. The differences in increase rates of n_D by heating between 80TTBu-20DPhDMS and 80TTBu-20GPTMS, as shown in Fig. 3, seems to be caused by the thermo plasticity of hybrid materials involving phenyl groups.¹⁰⁾

High refractive-index films of $n_D > 2.0$ have been realized, but unfortunately the thickness of the films is limited to several hundreds of nanometers by cracks on their surface during the heating process. Improvement in the film shrinkage or formation of a certain cushion layer between the films and substrates will be necessary.

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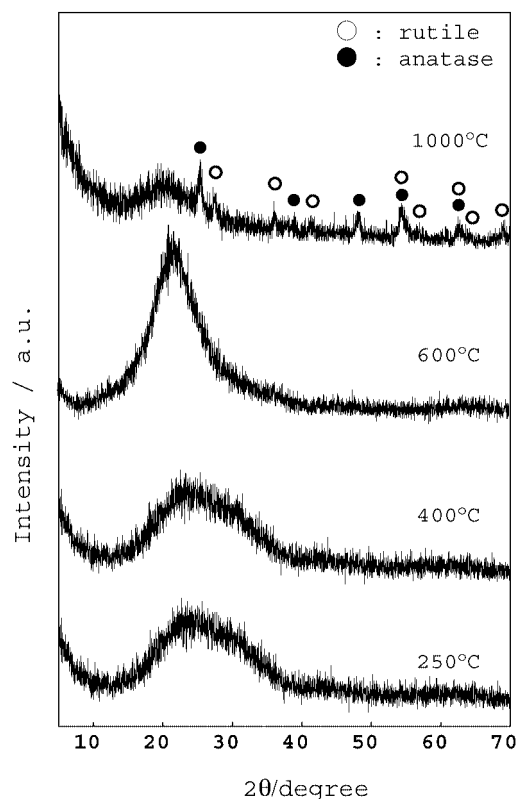


Fig. 8. XRD patterns of 80TTBu-20DPhDMS samples after heating at 250°C, 400°C, 600°C and 1000°C.

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