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Fabrication and Optical Properties of Erbium-Doped Polymer Films

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The crosslinked, fluorinated, patterned and erbium (Er^{3+}*) doped polymer films were fabricated by UV-curing after a simple spin-coating.* Er^{3+}*-doped solutions containing Irgacure 819 used as a radical-type photoinitiator were prepared using erbium (III) trifluoromethane sulfonate as an erbium source, 2,2,3,3,4,4,5,5-octafluoropentyl acrylate as a fluorinated monomer, trimethylolpropane triacrylate and Ebecyl 810 resin as a crosslinking agent with various weight ratios. The fluorinated polymer films fabricated in this study showed the excellent transmission property more than 80% over visible and NIR region, and high thermal decomposition temperature about 310°C sufficient for optical device applications. From these results, the* Er^{3+}*-doped polymer films developed in this study could be applied to optical telecommunication devices.*

Keywords Amplifiers; erbium; fluorinated monomer; fluorinated polymer; optical telecommunication device; UV curing

Introduction

In the last decade, rare earth doped materials have received much attention because of their potential applications for displays [1], X-ray imaging [2], lasers [3], and optical amplifiers [4,5]. Among all the rare-earth ions, erbium (Er^{3+}) ion is the most interest dopant because of its intra-4f transition $^4I_{13/2}$–$^4I_{15/2}$ near 1530 nm which corresponds to the silica-based low-loss window [6]. The loss of silica fiber has two low-loss windows. One is between 1200 and 1350 nm by overtones of the hydroxyl absorption. Second is around 1450~1600 nm by Rayleigh scattering and infrared absorption due to the Si-O bond. The 1500 nm window is the wavelength

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region of the optical telecommunication [7]. For these reasons, there has been intense interest in utilizing erbium-doped materials for gain elements and sources in the optical telecommunication system. Erbium-doped waveguide amplifier (EDWA) and erbium-doped fiber amplifier (EDFA) technologies are commonly used in the optical telecommunication system to compensate for signal losses. The Er^{3+} content in the material for EDWA is normally maintained at higher concentration compared with a fiber.

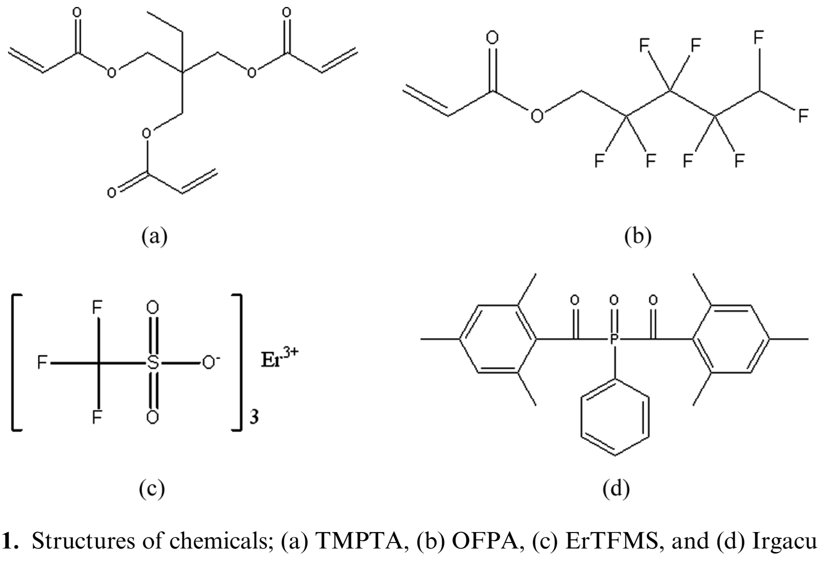
In recent years, polymers for EDWA applications have attracted significant attention as a waveguide material [8–10] because of their many advantages such as their low costs, high packaging density, and simple processing steps. Unfortunately, the excited state of Er^{3+} can be quenched by the vibronic coupling with high energy C–H bond (fundamental 2960 cm^{-1}) and O–H bond (fundamental 3400 cm^{-1}) stretching vibrations in its neighboring sites [11]. For this reason the fluorinated polymers represent a class of promising candidate materials [9]. As a result, much of the recent research into polymers for optical devices has focused on replacing hydrogen with fluorine [12].

This study focuses on the fabrication of fluorinated polymer films with a goal of achieving optical clarity in the optical telecommunication, sufficient thermal stability and a chemical resistance to withstand typical fabrication processing and operation conditions. To satisfy the demands mentioned above, fluorinated acrylate monomers were used. A cross-linked polymer system was employed to increase thermal stability and chemical resistance, and to fabricate patterned films necessary for application to optical amplifier.

Experimental

Materials

Figure 1 shows the structures of chemicals used to fabricate the Er^{3+}-doped polymer films. Erbium(III) trifluoromethane sulfonate (ErTFMS) as an Er^{3+} source, 2,2,3,3,4,4,5,5-octafluoropentyl acrylate (OFPA) as a fluorinated monomer and



(a) (b)

(c) (d)

Figure 1. Structures of chemicals; (a) TMPTA, (b) OFPA, (c) ErTFMS, and (d) Irgacure 819.

Table 1. Composition of solvent-free pre-polymer solutions (a) and Er^{3+}-doped solutions (b)

Sample No.	OFPA (g)	TMPTA (g)	Ebecryl 810 (g)	Irgacure 819[a] (g)
		(a)		
S1	0.40	0.35	0.25	0.016
S2	0.50	0.30	0.20	0.020
S3	0.60	0.25	0.15	0.024
S4	0.70	0.20	0.10	0.028
S5	0.80	0.15	0.50	0.032

Sample No.	OFPA (g)	TMPTA (g)	Ebecryl 810 (g)	ErTFMS[b] (g)	Irgacure 819[a] (g)
			(b)		
E1	0.70	0.20	0.10	0.05	0.028
E2	0.70	0.20	0.10	0.10	0.028
E3	0.70	0.20	0.10	0.15	0.028
E4	0.70	0.20	0.10	0.20	0.028

[a] 4 wt% of OFPA content.
[b] 5 through 20 wt% of pre-polymer (OFPA + TMPTA + Ebecryl 810) content.

1,1,1-trymethylol propanetriacrylate (TMPTA) as a cross-lingking agent were purchased from Aldrich Chem. Co. Ebecryl 810 resin was purchased from UCB Chemicals. Bis acyl phosphine (Irgacure 819) used as a radical-type photoinitiator was purchased from Ciba Specialty Chemicals. All reagents were used without further purification.

Fabrication of Er^{3+}-doped Polymer Films

The solvent-free pre-polymer solutions were prepared with OFPA, TMPTA, Ebecryl 810 resin and Igacure 819 with various compositions. The amount of OFPA was changed from 40 to 80 wt% (Table 1(a)). First, OFPA and TMPTA were added into Ebecryl 810 resin under strong mechanical stirring, and then Irgacure 819 (4 wt% of the fluorinated monomer content) as a photoinitiator was dissolved in the mixtures. Then the mixtures were stirred for 24 hours to obtain the homogeneous pre-polymer solutions. Finally, Er^{3+}-doped solutions were prepared by dissolving ErTFMS in the pre-polymer solutions with stirring for 30 min at 50°C. The amount of ErTFMS was changed from 5 to 20 wt% of the pre-polymer content (Table 1(b)). The patterned pre-polymer films and Er^{3+}-doped polymer films were prepared from the pre-polymer solutions and Er^{3+}-doped solutions, respectively, by photolithographic process.

Measurements

UV-visible-NIR absorption and transmission spectra of the samples were obtained from PerkinElmer Lambda 750 UV-Vis-NIR spectrometer. Absorption and transmission data were evaluated by using PerkinElmer's UV WinLab software. Data interval was 1.00 nm and scans were taken with a slit width of 2 nm both of the

NIR and UV–visible region. FT-IR spectra of the samples were obtained from Thermo Scientific Nicolet 380 FT-IR spectrometer. FT-IR transmittance data were evaluated by using OMNIC Lite software. Data interval was 2.00 cm^{-1}. The thermal stability has been measured with a Perkin Elmer TGA-7 apparatus at the region of 30 to 500°C operating at a scan speed of 10°C/min in N_2 atmosphere. To evaluate the dispersion property of Er^{3+} ions in the samples, EPMA (Electron Probe Micro Analyzer) was used. The EPMA (Shimadzu EPMA-1600) was operated at a spot size of 1 μm and an acceleration voltage of 15 kV. Quantitative mapping of the elemental composition was performed over an area of approximately 50 μm^2 by monitoring the intensity of characteristic X-rays.

Results and Discussion

Photolithographic Properties of Pre-Polymer Solutions

It is important to fabricate an Er^{3+}-doped polymer pattern on a substrate to apply to optical amplifier. First of all, we investigated photolithographic properties of pre-polymer solutions, and the resulting process conditions are as follows. The solvent-free pre-polymer solution (Table 1) was spin-coated on an ultrasonically cleaned glass substrate at 1,200 rpm for 30 sec, and then covered with PET film to avoid oxygen inhibition. In order to undergo photo-induced polymerization and cross-linking reaction, the coated sample was exposed to ultraviolet (UV) light of 10 mW/cm^2 at 365 nm for 20 sec through a photomask with $10 \times 10\,mm^2$ of exposure area. After UV exposure, the film was developed with isopropyl alcohol, and then dried to give 100 μm of film thickness. Due to the low viscosity of the composition, **S5**, the thickness uniformity of the patterned film was not good. On the other hand, the uniform film thickness was obtained from the compositions of **S1** through **S4** after photolithographic process. Therefore, **S4** was selected as a composition for fabrication of Er^{3+}-doped solutions because of its highest fluorine content. Thus, the Er^{3+}-doped polymer pattern could be also prepared using the composition containing erbium ion by a similar process above-mentioned. The patterned Er^{3+}-doped polymer film prepared using the composition, **E3**, by photolithography is illustrated in Figure 2.

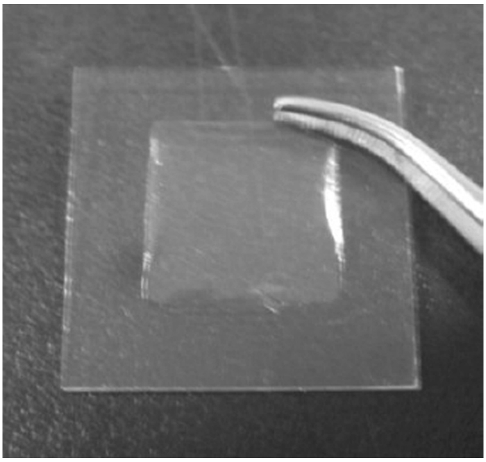


Figure 2. Photograph of patterned pre-polymer film by photolithography.

Optical and Thermal Properties of Pre-Polymer Films

Figure 3 shows the transmission spectra of fluorinated polymer films, without Er^{3+}, prepared with various compositions as a function of wavelength from 350 to 1600 nm at room temperature. The transmission intensity values at the 1530 nm as an optical telecommunication region were higher than 80%. These results mean that the fluorinated polymer films fabricated in this study show the excellent transmission property. In other words, this indicates that the transmission loss can be minimized. Beside the transmission intensity values at the region (488 nm, 980 nm and 1480 nm) of pumping laser sources in the optical amplifier were also more than 80%.

Figure 4 shows the FT-IR spectra of fluorinated polymer films as a function of wavenumber from 400 to 4000 cm^{-1}. C–F stretching was observed at around 1200 cm^{-1} in the low region and aliphatic C–H stretching was observed at around 3000 cm^{-1} in the high region. As shown in Figure 4, the transmittance value at the 3000 cm^{-1} region decreased with decreasing the amount of other compounds which have C–H bond. These results indicate that the loss of quenching from the vibronic coupling with high energy C–H bond can be minimized by increasing the amount of fluorinated acrylate monomer.

The thermal stability of the polymer matrix for practical application to optical communication devices is a critical issue. Table 2 shows the thermal decomposition temperature of fluorinated polymer films. The thermal decomposition temperature defined as 5% weight loss temperature was about 310°C. This means that there is no mass loss by the decomposition process at temperatures below 300°C. It is concluded that the thermal stability of our fluorinated polymer films is excellent and sufficient for optical device applications demanding high thermal resistance.

Optical Properties of Er^{3+}-doped Polymer Films

Figure 5 shows the absorption spectra of Er^{3+}-doped solution and Er^{3+}-doped polymer film as a function of wavelength from 350 to 1600 nm at room temperature.

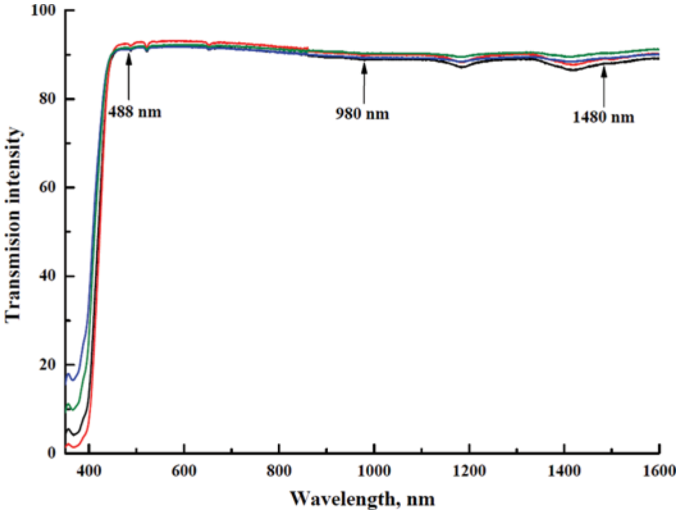


Figure 3. Transmission spectra of fluorinated polymer films (black line: FS1, red line: FS2, blue line: FS3, and green line: FS4).

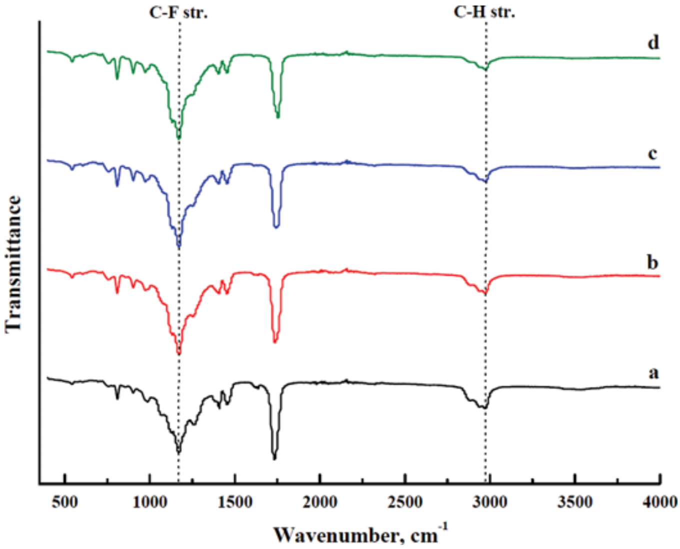


Figure 4. FT-IR spectra of fluorinated polymer films; (a) FS1, (b) FS2, (c) FS3, and (d) FS4.

Table 2. Thermal decomposition temperature of fluorinated polymer films

Sample No.	Decomposition temperature (°C)
FS1[a]	313.7
FS2[a]	310.8
FS3[a]	310.2
FS4[a]	311.9

[a] F means film, and Sx (x = 1 ~ 4) means the composition of the film in table1.

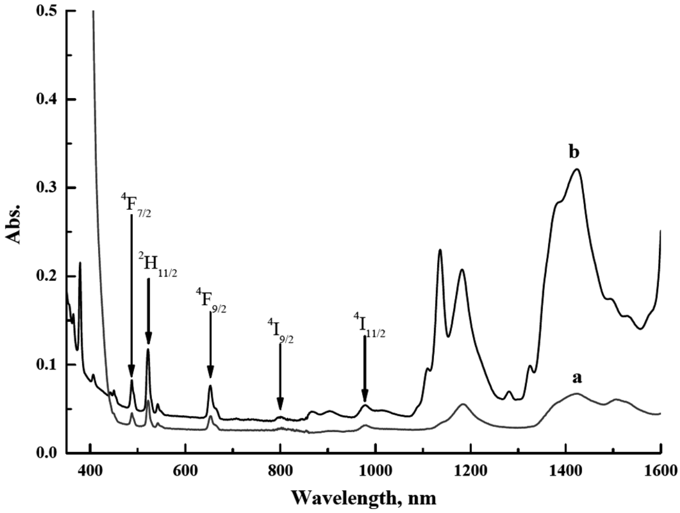


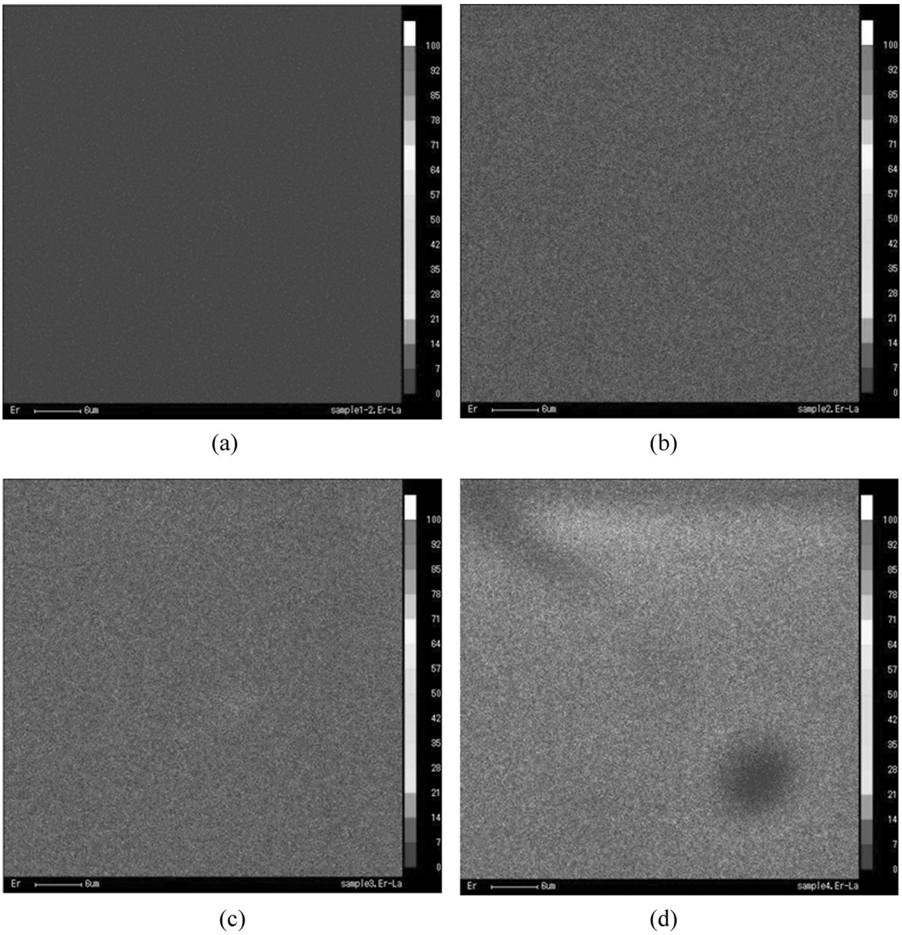
Figure 5. UV-Vis-NIR spectra of Er^{3+}-doped solution (a) and film (b).

Table 3. Relative wt% of Er^{3+} in Er^{3+}-doped polymer films obtained by EPMA

Sample No.	Point 1	Point 2	Point 3	Point 4	Point 5	Average	Standard deviation (σ)
FE1^a	1.213	1.171	1.198	1.190	1.231	1.2006	0.022766
FE2^a	2.342	2.027	2.858	2.484	2.491	2.4404	0.299764
FE3^a	3.112	3.486	3.275	3.414	3.639	3.3852	0.201362
FE4^a	4.127	2.443	3.452	1.707	0.502	2.4462	1.428554

^{a}F means film, and Ex ($x = 1 \sim 4$) means the composition of the film in Table 1.

As shown in Figure 5, an absorption band was observed from 300 to 400 nm that is ascribable to the ligands. The absorption intensity of the Er^{3+}-doped polymer film was much lower than that of Er^{3+}-doped solution. In the case of the Er^{3+}-doped polymer film, however, the important point to note was that the peaks related to the absorption of Er^{3+} around 490, 520, 650, 800 and 980 nm arising from the



(a) (b)

(c) (d)

Figure 6. EPMA images by quantitative mapping; (a) FE1, (b) FE2, (c) FE3, and (d) FE4.

$^4F_{7/2}$, $^2H_{11/12}$, $^4F_{9/2}$, $^4I_{9/2}$ and $^4I_{11/2}$ transitions, respectively, were observed like the Er^{3+}-doped solution.

Dispersion Property of Er^{3+} Ions in Er^{3+}-doped Polymer Films

In addition to the thermal stability and optical property of the polymer matrix, the dispersion of Er^{3+} ions in Er^{3+}-doped polymer film is an important factor to be considered. To evaluate a dispersion of Er^{3+} ions, EPMA analysis was performed. Table 3 shows the relative wt% of Er^{3+} of 5 points in Er^{3+}-doped polymer films and standard deviations (σ). Standard deviations, which mean the condition of dispersion of Er^{3+} ions, were very low in the case of **FE1, FE2** and **FE3**, as shown in Table 3. Figure 6 shows the images obtained by quantitative mapping. In the case of **FE1**, **FE2** and **FE3**, well-dispersion of Er^{3+} ions was observed, as shown in Figure 6(a), (b) and (c), respectively. However, standard deviation of **FE4** was very high and the degree of dispersion of Er^{3+} ions was deteriorated as shown in Figure 6(d). These results were due to the aggregation of Er^{3+} ions by adding the excess amount of ErTFMS. Considering the concentration quenching of Er^{3+} ions by aggregation, the optimum concentration of ErTFMS was about under 15 wt%.

Conclusions

In summary, Er^{3+}-doped polymer films were fabricated by UV curing after a simple spin-coating technique. The fluorinated polymer films have been designed and prepared to have a high density of Er^{3+}, good film-forming property and optical transparency at 1530 nm. In particular, the polymers could be cross-linked photochemically, yielding materials with good chemical resistance and high decomposition temperature. Well-defined photo-curing of the polymers has shown promise for direct photopatterning of optical devices.

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