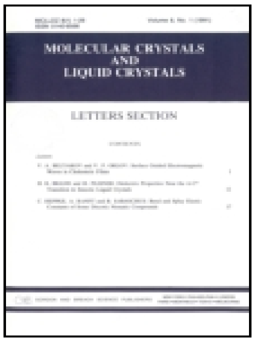

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Preparation and Characterization of Thermally Stable Silicon-Containing Fluoropolymer Matrix for Application to Erbium-Doped Waveguide Amplifiers

WOOK HYUN KIM,[1] YOON SOO HAN,[2,*] MINGYANG MA,[3]
AND YOUNGHWAN KWON[3,**]

[1]Energy Research Division, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, Korea
[2]Department of Advanced Materials and Chemical Engineering, Catholic University of Daegu, Gyeongbuk, Korea
[3]Department of Chemical Engineering, Daegu University, Gyeongbuk, Korea

This study focuses on the fabrication of fluoropolymer films as erbium(Er^{3+}) host material with a goal of achieving sufficient thermal stability, optical clarity in the optical communication region and a chemical resistance to withstand typical fabrication processing and operation conditions. To satisfy the demands mentioned above, acrylo-polyhedral oligomeric silsesquioxane as heat-resistance improver, 2,2,3,3,4,4,5,5-octafluoropentyl acrylate as fluorinated acrylic monomer, tetrahydrofurfuryl acrylate as solubility enhancer, 3-(trimethoxysilyl)propyl methacrylate as both a silane coupling agent and another heat-resistance improver and Darocur 4265 as photoinitiator were used. Various compositions were evaluated to obtain high quantity of Er^{3+} ions in the polymer matrix, high thermal stability and high transparency.

Keywords erbium; fluoropolymer; soft lithography; optical waveguide amplifiers

1. Introduction

In the past few years, erbium(Er^{3+})-doped waveguide amplifiers (EDWAs) are attracting much attention because of the infrared emission properties of the Er^{3+} ions at a wavelength around 1,550 nm resulting from its $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition, a standard wavelength used in optical communication systems, and the potential of integration with several functionalities that are critical in integrated optical devices. [1–3] EDWAs are commonly used in the optical communication system to compensate for signal losses, which include waveguide, coupling or intrinsic intensity losses. [4–6] The concentration of Er^{3+} ion in EDWAs should be approximately 10 to 20 times higher than that in Er^{3+}-doped fiber amplifiers (EDFAs)

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[*] Address correspondence to Yoon Soo Han, Department of Advanced Materials and Chemical Engineering, Catholic University of Daegu, 13-13 Hayang-ro, Hayang-eup, Gyeongsan-si, Gyeongbuk 712-702, Korea. E-mail: yshancu@cu.ac.kr

[**] Address correspondence to Younghwan Kwon, Department of Chemical Engineering, Daegu University, 201 Daegudae-ro, Gyeongsan-si, Gyeongbuk 712-714, Korea. E-mail: y_kwon@daegu.ac.kr

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to achieve high optical gain. [7] However, at higher (>300 ppm) Er^{3+} ion concentrations, energy transfer processes, such as upconversion or energy migration, occur, decreasing the luminescence quantum efficiency of the $[^4]I_{13/2}$ excited-state. [8] To obtain high gain EDWAs, Er^{3+} ions should not only have highly efficient 1,550 nm emission but also good dispersibility in polymer matrices on a molecular level. [9–11] In terms of waveguide materials and fabrication processes, polymers have many advantages, such as low fabrication costs, simplified processing steps and compatibility with various processing techniques for patterning. [12,13] In addition, the various optical parameters such as the refractive index and birefringence can be easily controlled through blending and copolymerization, leading to superior device performance. [14,15] However, when conventional polymers are used for waveguide fabrication, they have tended to exhibit high optical propagation losses, particularly at 1,550 nm because of the vibrational states of the O—H and C—H bonds. Such loss processes can be minimized by replacing of the hydrogen atoms with heavier atoms through deuteration or fluorination of the polymer host material, causing the frequencies of the relevant vibrational overtones to shift. [16]

Low thermal stability of polymeric hosts is another limitation on their application to Er^{3+}-doped waveguide amplifiers. Polyhedral oligomeric silsesquioxane (POSS) is an organic–inorganic hybrid material. This class of silicon compounds has the empirical formula $RSiO_{1.5}$, where R denotes an organic substituent. The incorporation of POSS units into polymer matrix by chemical bonding improves the polymer properties such as thermal stability, oxidation resistance, surface hardening and mechanical properties. [17]

In this study, we fabricated fluorinated polymer films as Er^{3+} host material with a goal of achieving sufficient thermal stability, optical clarity and a chemical resistance to withstand typical fabrication processing. For this reason, precursor solutions containing an acrylo-POSS as a heat-resistance improver were prepared in various compositions, and their thermal and optical properties were investigated.

2. Experimental Details

Materials and Analytical Instruments

Figure 1 shows the structures of chemicals used for the Er^{3+}-doped fluoropolymer films. 2,2,3,3,4,4,5,5-Octafluoropentyl acrylate (OFPA) as fluorinated acrylic monomer, tetrahydrofurfuryl acrylate (THFA) as solubility enhancer and 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) as both silane coupling agent and heat-resistance improver were purchased from Aldrich Chem. Co. (USA). Acrylo-polysilsesquioxane (Acrylo-POSS) as both crosslinker and heat-resistance improver was purchased from Hybrid Plastics™ (USA). Erbium(III) trifluoromethane sulfonate (ErTFMS) was obtained from Aldrich Chem. Co. (USA) as an erbium source. Darocur 4265 was obtained from CIBA Specialty Chemicals (Switzerland) as radical photoinitiator. All reagents were used without further purification.

UV-visible-NIR absorption and transmission spectra of the samples were obtained from a UV-Vis-NIR spectrometer (PerkinElmer Lambda 750, USA) at 1-nm intervals. Absorption and transmission data were evaluated using PerkinElmer's UV WinLab software. The thermal stability was measured using a Thermo Gravimetric Analysis (Perkin Elmer TGA-7, USA) apparatus in the region of 30 to 650°C and operating at a scan speed of 10°C/min in a N_2 atmosphere. To evaluate the dispersion of Er ions in polymer matrices, an Electron Probe Micro Analyzer (EPMA; Shimadzu EPMA-1600, Japan) was used with a spot size of 1 μm and an acceleration voltage of 15 kV. The quantitative mapping of the elemental

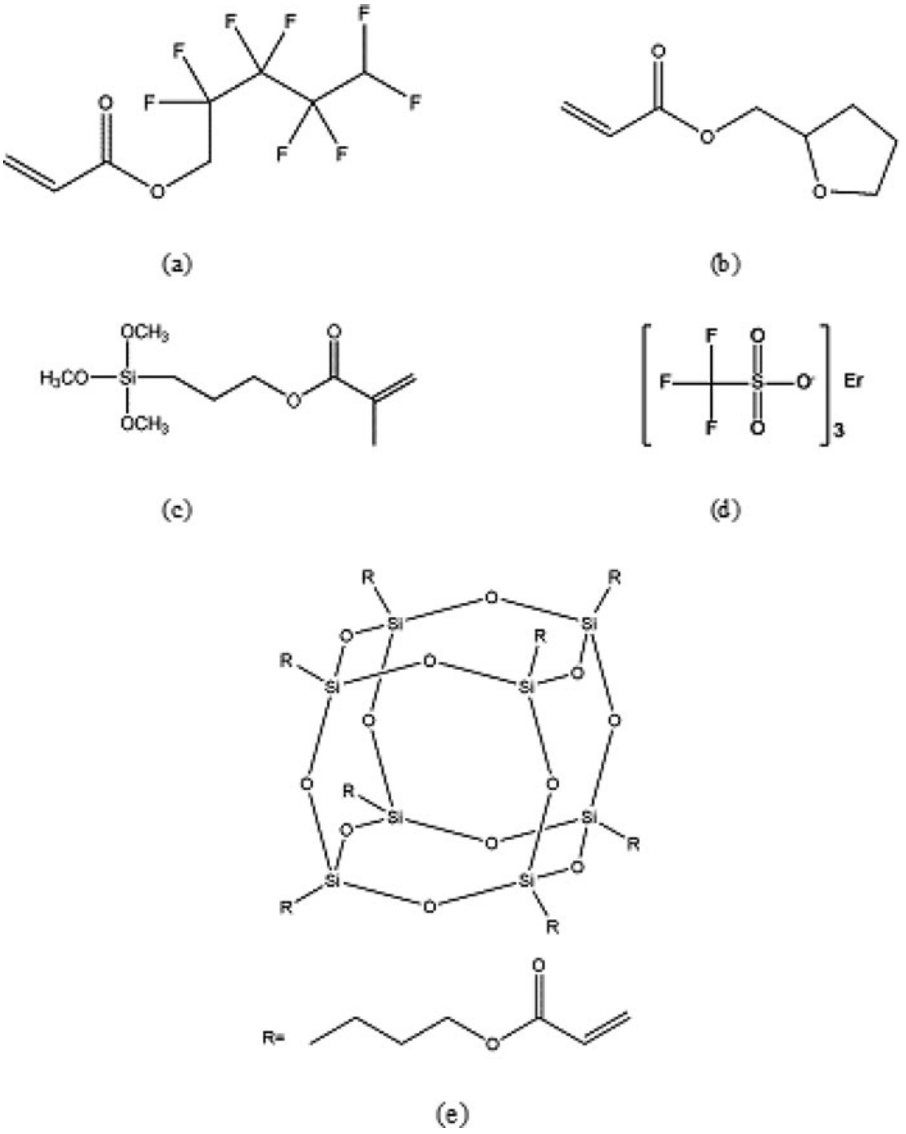

Figure 1. Structures of (a) OFPA, (b) THFA (c) TMSPMA (d) ErTFMS and (e) Acrylo-POSS.

composition was performed over an area of approximately 100 μm^2 by monitoring the intensity of the characteristic X-rays.

Preparation of Precursor Solutions and Er^{3+}-doped Precursor Solutions

The undoped precursor solutions were prepared with OFPA, THFA, TMSPMA and acrylo-POSS in various compositions, as shown in Table 1. The contents of OFPA and acrylo-POSS were changed from 45 to 75 wt% and 0 to 30 wt%, respectively, to optimize the composition. The Er^{3+}-doped precursor solutions were also prepared by the addition of ErTFMS into the optimized undoped precursor solution, in which the amount of ErTFMS fixed with

Table 1. Compositions of Er^{3+}-doped and undoped precursor solution

Sample No.	OFPA (g)	THFA (g)	TMSPMA (g)	Acrylo-POSS (g)	ErFTMS[a] (g)	Darocur 4265[b] (g)
P0	7.5	2.0	0.5	0.0	—	0.1
P1	6.5	2.0	0.5	1.0	—	0.1
P2	5.5	2.0	0.5	2.0	—	0.1
P3	4.5	2.0	0.5	3.0	—	0.1
P4	5.5	2.0	0.5	2.0	0.5	0.1

[a] 5 wt% based on (OFPA + THFA + TMSPMA + Acrylo-POSS) content.
[b] 1 wt% based on (OFPA + THFA + Ebecryl 220) content.

5 wt% based on the overall polymer matrix precursors (i.e., OFPA, THFA, TMSPMA, and acrylo-POSS). In summary, ErTFMS was added to THFA under strong mechanical stirring, and after dissolving ErTFMS in THFA. Then OFPA, TMSPMA, acrylo-POSS and Darocur 4265 were added to the solution, which was stirred for 24 hours to obtain a homogeneous Er^{3+}-doped precursor solution. The fluoropolymer and Er^{3+}-doped fluoropolymer films were prepared from the undoped and Er^{3+}-doped precursor solutions, respectively, by irradiation with UV light in N_2 atmosphere.

Soft Imprint Lithography to Fabricate Er^{3+}-doped Fluoropolymer Patterns

Soft imprint lithography is a convenient technique for generating patterned microstructures of organic polymers on the surfaces of solid substrates. Figure 2 shows the soft imprint lithography process applied in this study to form micro-pattern of the Er^{3+}-doped fluoropolymer. First, we fabricated the polydimethylsiloxane (PDMS) mold by pouring a commercial silicon elastomer (Sylgard 184™, Dow Corning, USA) onto a master mold and then curing at 80°C for 4 hours to achieve an organometallic crosslinking reaction. The PDMS mold was then peeled from the master mold and cut prior to use. For Er^{3+}-doped fluoropolymer pattern using soft imprint lithography, a small drop of Er^{3+}-doped precursor solution was placed on a substrate. The PDMS mold was then brought into contact with the drop, and then pressure was applied during UV exposure (10 mW/cm^2 at 360 nm) for 200s. The PDMS mold was then peeled from the substrate leaving the cured Er^{3+}-doped fluoropolymer pattern.

3. Result and Discussion

Optimized Composition of the Er^{3+}-doped Precursor Solutions

In EDWAs, the low optical absorption of guided light in the Er^{3+} host materials is an important parameter. In polymers, optical absorption is caused by both molecular electronic excited states and by fundamental and overtone vibrations of molecular bonds. To achieve sufficient amplification, the signal loss from this absorption must be minimized. [18] Thus, we adopted the fluoropolymer system to minimize unwanted absorption by the polymer matrix at the emission wavelength (1550 nm) of Er^{3+} ions. However, ErTFMS was not dissolved directly into the fluoromonomer (OFPA), though it had a good solubility in THFA. Thus, we adopted THFA as a solubility enhancer and its ratio was fixed at 20 wt%

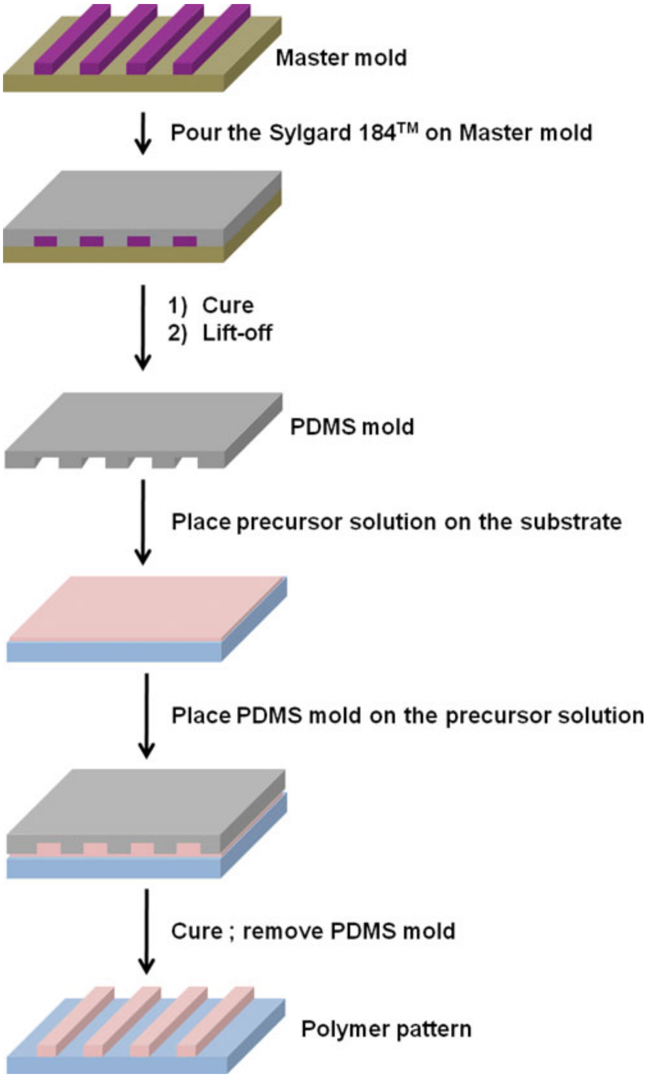

Figure 2. Soft imprint lithography process sequence using PDMS mold.

based on the overall polymer matrix precursors for uniform dissolution of ErTFMS. When less than 20 wt% of THFA was contained in the precursor solution, the homogenous Er^{3+}-doped precursor solution was not obtained by aggregation of ErTFMS. For pattern formation and high thermal stability, multifunctional acrylo-POSS were added as heat-resistance improver. The ratio of OFPA and acrylo-POSS were changed from 45 to 75 wt% and 0 to 30 wt%, respectively, to determine the optimum composition of the homogeneous Er^{3+}-doped precursor solution, as shown in Table 1 (P0 ∼ P3). However, in case of polymer film fabricated form P3 composition, film cracking was occurred during UV exposure due to its high crosslingking density. The P2 composition had higher OFPA content, and therefore higher C—F bond content than the P0 and P1 compositions, indicating that the

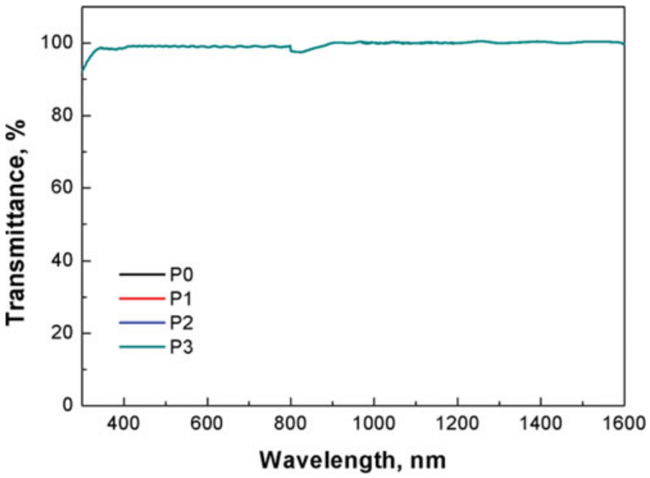

Figure 3. Transmission spectra of fluoropolymer films.

fluoropolymer film fabricated from the P2 composition minimized the optical loss from the C—H bond vibrational absorption overtone in the near infrared region. [19]

The optical transparency and thermal stability of the polymer matrix are important parameters for practical optical device applications. Optical devices are used inside and outside of buildings, so the thermal decomposition temperature of the host materials must be high enough to resist deformation. [20] To evaluate the effect of the crosslinking density on the optical transparency and thermal stability of the films, we measured the transmittance and thermal decomposition temperature of the fluoropolymer films fabricated with the compositions shown in Table 1. Figure 3 shows the transmission spectra of the fluoropolymer films having a thickness of 10 μm, without ErTFMS, with various compositions (P0 $\sim$ P3). The transmittances at 1,550 nm, which is the wavelength used in optical communication systems, were greater than 98%, indicating that the optical propagation loss was minimized. The transmittances at the wavelengths of the pumping light sources (488, 980, and 1,480 nm) used in the optical amplifiers were also greater than 97%. This result indicates that the loss of pump power by the host materials can be also minimized.

Figure 4 shows the TGA thermograms of fluoropolymer films with various compositions (P0 $\sim$ P3). The thermal decomposition temperature of the fluoropolymer film fabricated P2 composition defined as the 10% weight loss temperature at a heating rate of 10°C/min, was 349°C in nitrogen. While there was no change in the transmittances with increasing of acrylo-POSS content, the thermal decomposition temperature gradually increased from 333 to 360°C due to higher crosslinking density. The fluoropolymer film prepared from the P2 composition had excellent optical and thermal properties, which made it sufficient for use in optical devices. From the above results, P2 was selected as the optimum composition for the Er^{3+}-doped precursor solutions.

It is important to control the refractive indexes of the core and cladding materials for application to waveguide devices. Figure 5 shows the dependence of the refractive indexes for TE- and TM-mode polarization at 1,550 nm wavelength. The refractive index of the polymer was decreased linearly with increasing OFPA content. This result indicates that the refractive index of polymers can be controlled at 1,550 nm by combination of OFPA and THFA content. The birefringence ($\Delta n = n_{TE}$ - n_{TM}) was almost constant at low values of

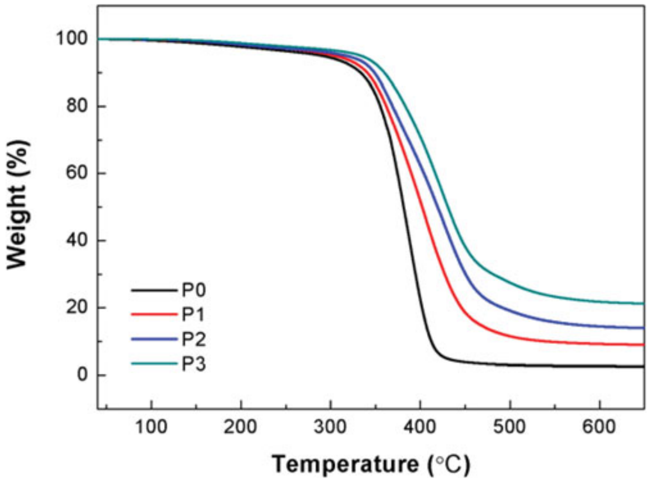

Figure 4. TGA thermograms of fluoropolymer films.

0.00004 ~ 0.00006. The high birefringence results in significant performance deterioration of the waveguides. The photonic component having the high birefringence shows a high polarization dependent loss (PDL).

In addition to the thermal stability and optical properties of the Er^{3+} host materials, the dispersion of Er^{3+} ions in the host film is also an important factor in optical waveguide amplifier applications. Rare earth ions tend to form clusters, and such aggregates quench the luminescence through the non-radiative decay channels from unwanted transitions by ion-ion interactions, etc. [21] The Er^{3+}-doped precursor solutions were prepared by the addition of 5 wt% ErTFMS to the previously optimized precursor solution (P2). To evaluate the dispersing property of Er^{3+} ions, an EPMA analysis was performed. Figure 6 shows

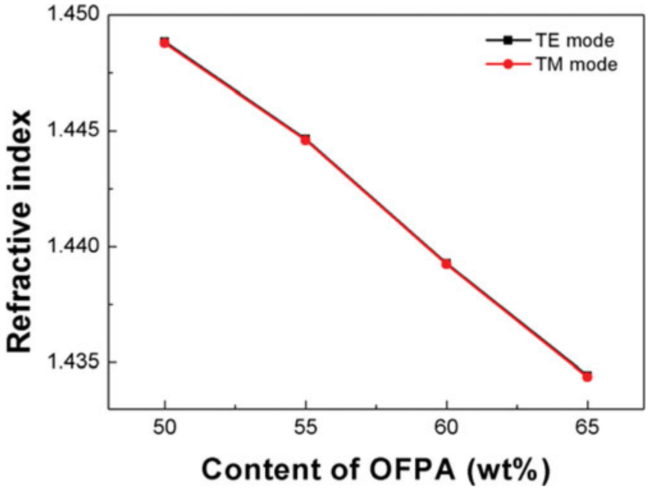

Figure 5. Dependence of refractive index on OFPA content of fluoropolymers for TE and TM polarizations at a wavelength of 1,550 nm.

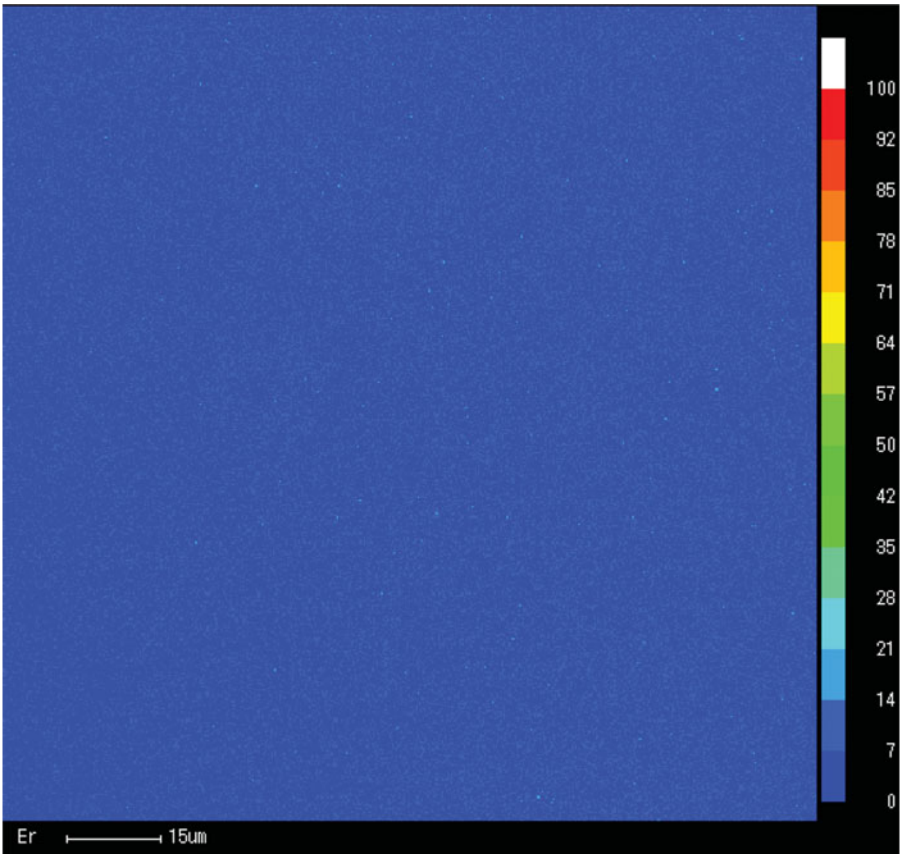

Figure 6. EPMA images by quantitative mapping of the Er^{3+}-doped fluoropolymer films.

the images obtained by quantitative mapping of the Er^{3+}-doped fluoropolymer film. Until 5 wt% of ErTFMS, good dispersion of the Er^{3+} ions was observed without aggregation.

Fabrication of the Er^{3+}-doped Fluoropolymer Pattern by Soft Imprint Lithography

Microfabrication of Er^{3+}-doped fluoropolymer has become important to application for optical waveguide amplifiers. Soft imprint lithography, a set of techniques for microfabrication of polymeric materials, is commonly used due to its simplicity, low energy consumption, low cost and fidelity in transferring the patterns from the mold to the polymeric structures. [22] In addition, the prevention of oxygen inhibition is the key for acrylate-based free-radical polymerization. Soft imprint lithography is a good method for eliminating the oxygen inhibition by covering the PDMS mold. We investigated the lithographic properties of Er^{3+}-doped precursor solutions by soft imprint lithography. The Er^{3+}-doped polymer patterns were fabricated with the process condition described in experimental section, and their pattern sharpness was observed. A surface treatment using ZAP 1020 (Chemoptics Inc., Korea), a trialkoxysilane with an acrylate functional group in 1-methoxy-2-propanol as an adhesion promoter, was introduced to enhance the adhesion between the substrate and the Er^{3+}-doped fluoropolymer pattern. Through heat treatment after spin-coating, the

Figure 7. Microscope image of a 5-μm-wide Er^{3+}-doped fluoropolymer pattern by soft imprint lithography.

trialkoxysilane forms self-assembled monolayers(SAMs) on the substrate surface. The adhesion of fluoropolymer to the substrate could be increased by coupling the acrylate functional group of the SAMs and other acrylate functional monomers of Er^{3+}-doped precursor solutions. The incorporation of an adhesion promoter prevents the partial detachment of the fluoropolymer patterns by enhancing the adhesion between the substrate and the fluoropolymer patterns. Figure 7 shows a microscope image of the Er^{3+}-doped fluoropolymer pattern fabricated by soft imprint lithography.

4. Conclusions

In summary, fluoropolymer films have been designed with high erbium complex content with good dispersion and film-forming properties, high optical transparency at 1,550 nm and high thermal stability. By adjusting the Er^{3+}-doped precursor solution and the soft imprint lithography process conditions, we successfully fabricated Er^{3+}-doped fluoropolymer patterns without ErTFMS aggregation up to 5 wt% based on the polymer matrix. This well-defined cross-linkable polymer has shown promise for optical device applications.

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