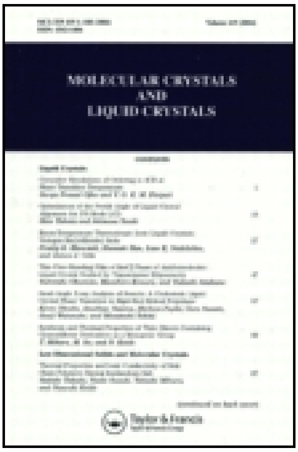

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Preparation and Physical Properties of Erbium-Doped Polymer Patterns by Micromolding in Capillaries for Optical Waveguide Amplifiers

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Preparation and Physical Properties of Erbium-Doped Polymer Patterns by Micromolding in Capillaries for Optical Waveguide Amplifiers

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Er^{3+}-doped precursor solutions were first prepared using 2,2,3,3,4,4,5,5-octafluoropentyl acrylate as a fluoromonomer, tetrahydrofurfuryl acrylate as a solubility enhancer, Ebecryl 220 as a cross-linking agent, Darocur 4265 as a radical photoinitiator and erbium(III) trifluoromethane sulfonate as an erbium source with various weight ratios. The crosslinked, patterned and erbium-doped fluoropolymer films were fabricated by micromolding in capillaries on glass substrates for planar optical amplifier applications. The fluoropolymer films acting as host materials for the Er^{3+} ions had excellent transmission properties (more than 90% over the visible and near-infrared regions), high thermal decomposition temperatures (greater than 300°C) and the ability to support high erbium complex concentrations (up to 10 wt% based on the polymer matrix). These results are sufficient for the films to be used in planar optical amplifier applications.

Keywords Erbium; fluoropolymer; micromolding in capillaries; planar optical amplifiers

Introduction

Optical waveguide amplifiers, such as erbium-doped waveguide amplifiers (EDWAs) and erbium-doped fiber amplifiers (EDFAs), are crucial for the development of optical communications technology [1]. EDWAs are attracting much attention because of the infrared emission properties of the Er^{3+} ion at approximately 1,550 nm and the potential of integration with several functionalities that are critical in integrated optical devices [2,3]. Currently, EDWA and EDFA technologies are commonly used in the optical communication system to compensate for signal losses, which include waveguide, coupling or intrinsic

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intensity losses [4–6]. To achieve greater gain per unit length in EDWAs, higher Er^{3+} ion concentrations than the typical range of 100 to 300 ppm used in EDFAs are required. 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 $^4I_{13/2}$ excited-state [7–10]. Consequently, the dispersion of Er^{3+} ions is an important factor in decreasing the concentration quenching and enhancing the pump efficiency. To reduce ion-ion interactions, Er^{3+} ions should be uniformly dispersed on a molecular level. Silica based inorganic matrices have been fabricated by high-temperature processes such as flame hydrolysis deposition and chemical vapor deposition, that may cause clustering of Er^{3+} ions. On the other hand, by using polymers as a host matrix for Er^{3+} ions, a very high doping level of Er^{3+} ions can be achieved without causing a significant ion-cluster effect, indicating that polymer matrices are useful host materials for Er^{3+} ions due to their good solubility and the processing temperature [11,12]. The use of polymeric hosts for the fabrication of optical waveguide amplifiers offers many advantages, including low fabrication costs, simplified processing steps and compatibility with various processing techniques for patterning. In addition, the various physical parameters—such as the refractive index, birefringence and thermal stability—can be easily controlled through blending and copolymerization, resulting in superior device performance [13,14]. However, when conventional polymers are used for waveguide fabrication, they tend to exhibit high optical propagation losses, particularly at 1,550 nm, which corresponds to the telecommunication wavelength, 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 [15,16].

In this study, the fabrication of cross-linked, patterned and Er^{3+}-doped fluoropolymer films by micromolding in capillaries (MIMIC), and their optical, thermal and dispersion properties were investigated. This study focuses on the fabrication of fluoropolymer film for application as the core material in optical waveguide amplifiers with the goal of achieving excellent optical clarity, thermal stability and chemical resistance to withstand typical fabrication processing and operation conditions.

Experimental

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) and tetrahydrofurfuryl acrylate (THFA) were purchased from Aldrich Chem. Co. (USA) as host polymer sources. Erbium(III) trifluoromethane sulfonate (ErTFMS) was obtained from Aldrich Chem. Co. (USA) as an erbium source. Ebecryl 210 (aromatic urethane diacrylate oligomer), Ebecryl 204 (aromatic urethane triacrylate oligomer), and Ebecryl 220 (hexafunctional aromatic urethane acrylate oligomer) were purchased from UCB Chem. Co.(Belgium) for use as cross-linking agents. 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 500°C and operating at a scan speed of 10°C/min in a N_2 atmosphere. To evaluate the dispersion of Er^{3+} ions in the samples, an Electron

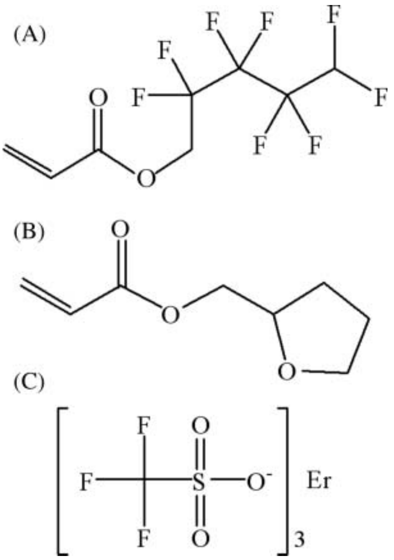

Figure 1. Structures of (a) OFPA, (b) THFA and (c) ErTFMS.

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 composition was performed over an area of approximately 70 × 70 μm^2 by monitoring the intensity of the characteristic X-rays.

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

The precursor solutions were prepared with OFPA, THFA and multifunctional urethane acrylate oligomers (Ebecryl 210, 204 and 220) in various compositions, as shown in Table 1. The ratio of OFPA and THFA was changed from 0 to 100 wt% to optimize the composition. The Er^{3+}-doped precursor solutions were also prepared by the addition of ErTFMS into the

Table 1. Precursor solution compositions

			Multifunctional urethane acrylate oligomer (g)		
Sample no.	OFPA (g)	THFA (g)	Ebecryl 210 (difunctional oligomer)	Ebecryl 204 (trifunctional oligomer)	Ebecryl 220 (hexafunctional oligomer)
F1	5.5	4.0			
F2	6.5	3.0			
F3	7.5	2.0			
F4	8.5	1.0			
F5	7.5	2.0	0.5		
F6	7.5	2.0		0.5	
F7	7.5	2.0			0.5

Table 2. Er^{3+}-doped precursor solution compositions

Sample no.	OFPA (g)	THFA (g)	Ebecryl 220 (g)	ErFTMS[a] (g)	Darocur 4265[b] (g)
E1	7.5	2.0	0.5	0.5	0.01
E2	7.5	2.0	0.5	1.0	0.01
E3	7.5	2.0	0.5	1.5	0.01

[a] 5 ∼ 15 wt% based on (OFPA + THFA + Ebecryl 220) content.
[b] 1 wt% based on (OFPA + THFA + Ebecryl 220) content.

optimized precursor solution, and the amount of ErTFMS was changed from 5 to 15 wt% based on the overall polymer matrix precursors (i.e., OFPA, THFA and oligomer) as shown in Table 2. In summary, ErTFMS was added to THFA under strong mechanical stirring, and after dissolving ErTFMS in THFA, OFPA, Ebecryl 220, 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 precursor and Er^{3+}-doped precursor solutions, respectively, by irradiation with UV light.

MIMIC to Fabricate Er^{3+}-doped Fluoropolymer Patterns

MIMIC is a convenient technique for generating patterned microstructures of organic polymers on the surfaces of solid substrates [17]. Figure 2 shows the MIMIC 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 placed on a substrate to make conformal contact with that surface. As a result, a network of channels was formed between the PDMS mold and the substrate. The Er^{3+}-doped precursor solution was then placed at the open ends of the network of channels. The Er^{3+}-doped precursor solution spontaneously filled the channels by capillary action. The Er^{3+}-doped fluoropolymer pattern was then fabricated by UV exposure (10 mW/cm^2 at 360 nm) for 200 seconds, and the PDMS mold was removed. A network of Er^{3+}-doped fluoropolymer remained on the substrate surface.

Results and Discussion

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

In the Er^{3+}-doped planar waveguide amplifier, 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 (1,550 nm) of Er^{3+} ions. However, ErTFMS was not dissolved directly into the fluoromonomer (OFPA), though it had a good solubility in THFA. For the formation of patterned microstructures from precursor solution by the MIMIC process, the precursor solution should have low viscosity ($<$300 cP) and should not contain certain organic solvents that swell the PDMS mold. Thus,

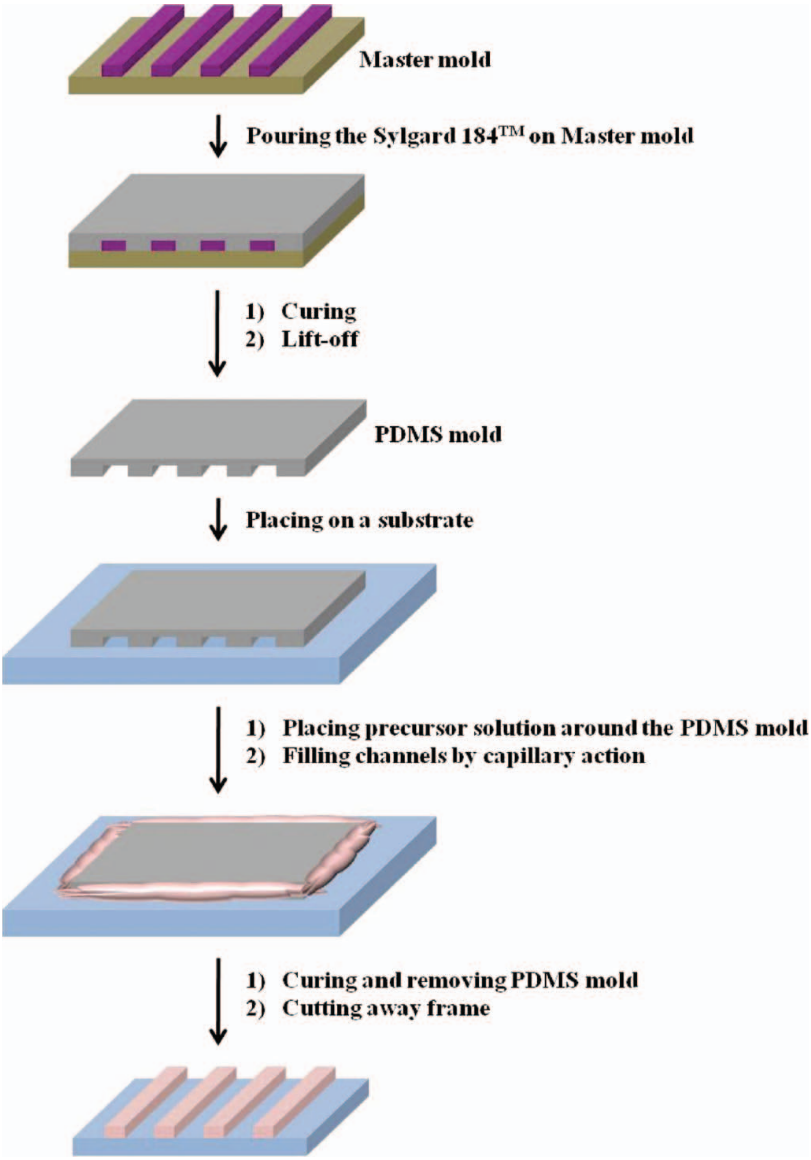

Figure 2. MIMIC process sequence using PDMS mold.

we adopted THFA as a solubility enhancer instead of using organic solvents. The weight ratio of OFPA:THFA was changed from 5.5:4.0 to 8.5:1.0 to determine the optimum composition of the homogeneous Er^{3+}-doped precursor solution, as shown in Table 1 (F1∼F4). When more than 80 wt% of OFPA was contained in the precursor solution, the homogenous Er^{3+}-doped precursor solution was not obtained by aggregation due to the low solubility of ErTFMS in OFPA. The F3 composition had lower THFA content, and therefore lower C-H bond content than the F1 and F2 compositions, indicating that the fluoropolymer film fabricated from the F3 composition minimized the optical loss from the C-H bond vibrational absorption overtone in the near infrared region [19].

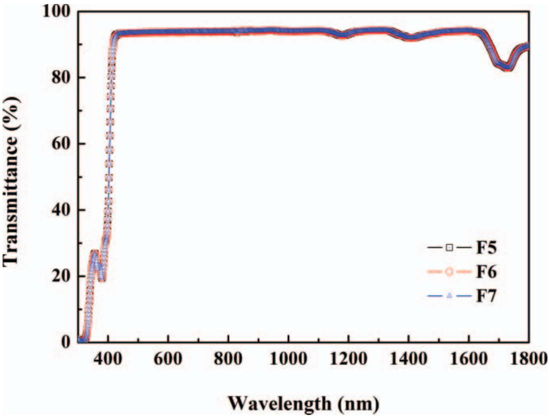

Figure 3. Transmission spectra of fluoropolymer films.

For pattern formation and high thermal stability, multifunctional urethane acrylate oligomers were added as crosslinking agent to the F3 composition to give compositions F5, F6 and F7. 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 number of acrylate functional groups in the crosslinking agent 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 (F5∼F7). Figure 3 shows the transmission spectra of the fluoropolymer films having a thickness of 50 μm, without ErTFMS, with various compositions (F5∼F7). The transmittances at 1,550 nm, which is the wavelength used in optical communication systems, were greater than 90%, 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 90%. 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 (F5∼F7). The fluoropolymer films had good thermal stabilities up to 300°C (10 wt.% loss). While there was no change in the transmittances with increasing acrylate functional groups, the thermal decomposition temperature gradually increased from 314 to 328°C due to higher crosslinking density. The fluoropolymer film prepared from the F7 composition had excellent optical and thermal properties, which made it sufficient for use in optical devices. The fluoropolymer film fabricated from F7 also had a very low birefringence at 1,550 nm. The reflective index and birefringence at 1,550 nm were 1.4353 and 5×10^{-4}, respectively. From the above results, F7 was selected as the optimum composition for the Er^{3+}-doped precursor solutions.

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 planar optical 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 ErTFMS to the previously optimized precursor solution (F7). To evaluate the

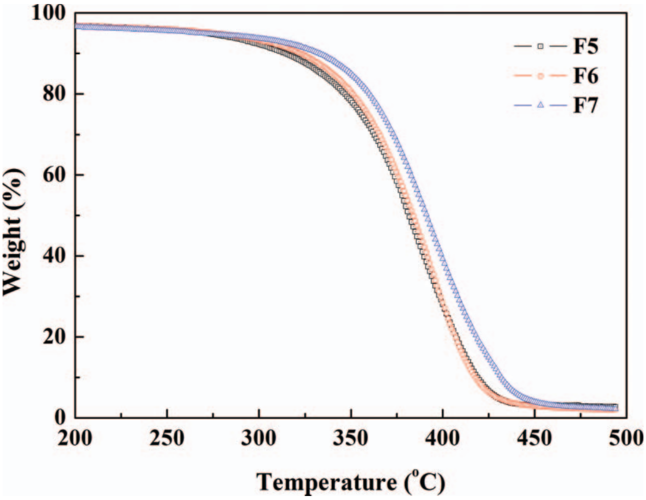

Figure 4. TGA thermograms of fluoropolymer films.

dispersing property of Er^{3+} ions, an EPMA analysis was performed. Figure 5 shows the images obtained by quantitative mapping of the Er^{3+}-doped fluoropolymer films fabricated from the compositions given in Table 2. In the case of the films prepared from the E1 and E2 compositions, good dispersion of the Er^{3+} ions was observed as shown in Fig. 3(a). However, the Er^{3+}-doped fluoropolymer film prepared from the E3 composition contained ErTFMS aggregates [Fig. 3(b)] due to the excess ErTFMS. Considering the concentration quenching of Er^{3+} ions by aggregation, the optimum amount of ErTFMS was less than 10 wt% of the polymer matrix.

In an optical waveguide amplifier, Er^{3+} ions are incorporated in the core of an optical waveguide. Using an external laser, such as a 980 nm diode laser, the Er^{3+} is excited into one of its higher energy levels and then allowed to relax rapidly to the first excited state. An emission from the first excited state to the ground state is induced at 1,550 nm [22]. Figure 6 shows the absorption spectra of the Er^{3+}-doped precursor solution and the Er^{3+}-doped fluoropolymer film as a function of wavelength from 400 to 1100 nm at room temperature. In the Er^{3+}-doped fluoropolymer film, peaks related to the absorption of Er^{3+} around 490, 520, 650, 800 and 980 nm arising from the $^4F_{7/2}$, $^2H_{11/12}$, $^4F_{9/2}$, $^4I_{9/2}$ and $^4I_{11/2}$ transitions, respectively, were observed. Particularly the absorption at 980 nm, which is an ideal pump wavelength, was clearly observed from the $^4I_{11/2}$ transition.

Fabrication of the Er^{3+}-doped Fluoropolymer Pattern by MIMIC

It is important to fabricate the Er^{3+}-doped fluoropolymer patterns on a substrate for optical waveguide amplifiers. MIMIC, used in this study, is currently used to form patterned microstructures of polymeric materials due to its simplicity, economy, effectiveness with which the channels fill by capillary action, and fidelity in transferring the patterns from the mold to the polymeric structures. When patterning a polymer waveguide with the imprinting technique, a residual layer, a slab layer, is formed on the imprinted areas. Too thick layer of the slab causes a propagation loss due to power leakage to the slab guide, and is usually removed by an etching process [23]. By using MIMIC, this propagation loss can be minimized by removing the slab guide. In addition, the prevention of oxygen

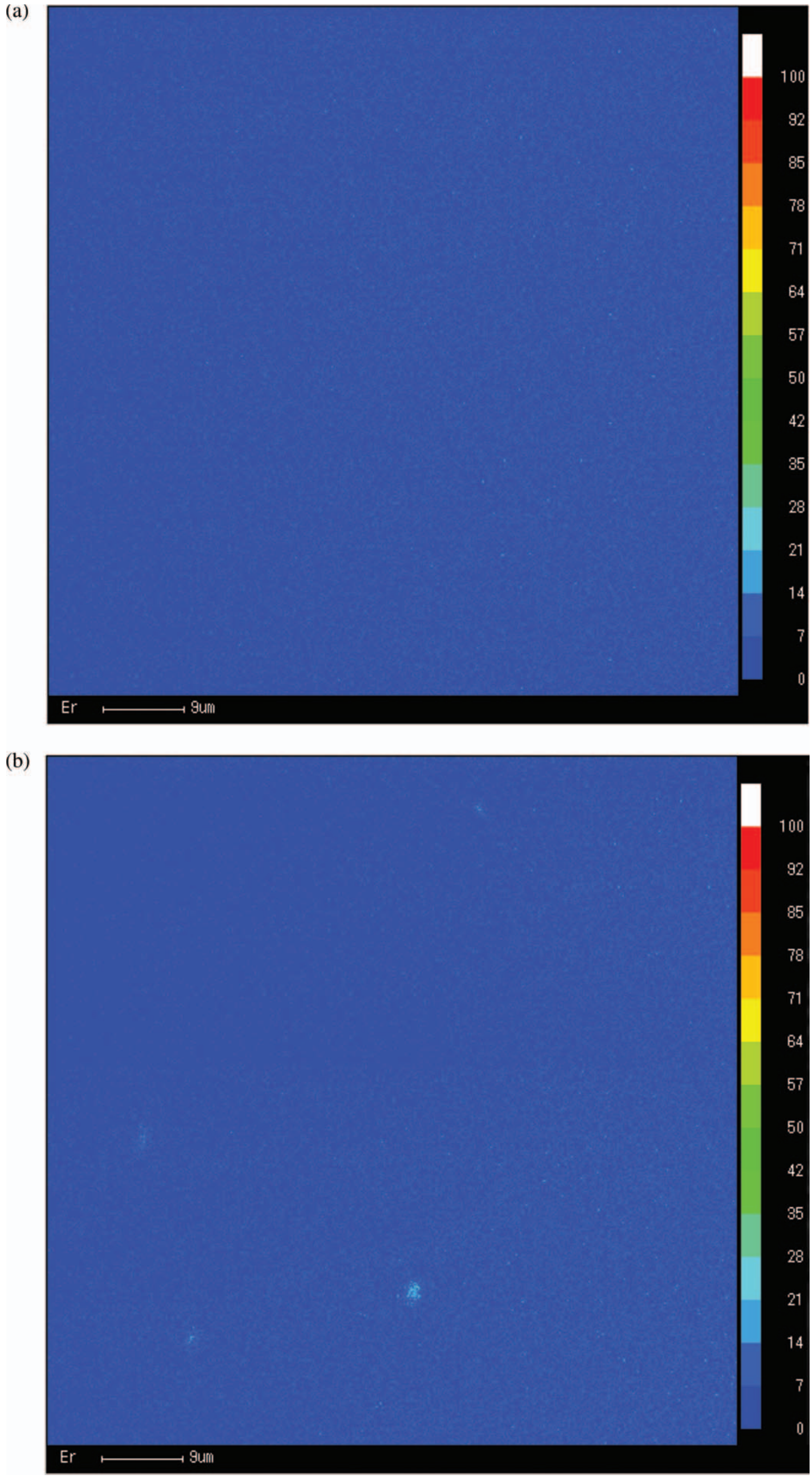

Figure 5. EPMA images by quantitative mapping of the Er^{3+}-doped fluoropolymer films: (a) E2 and (b) E3.

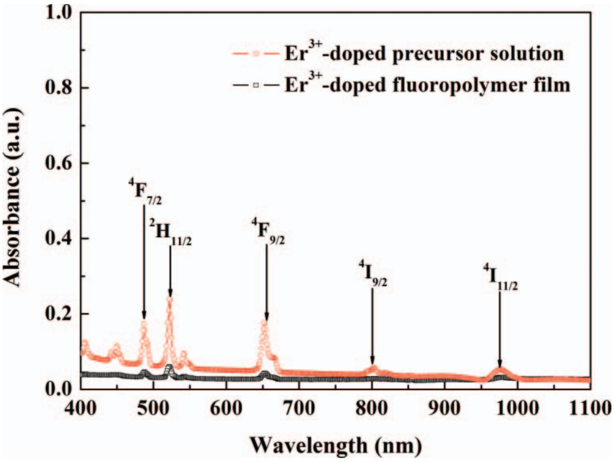

Figure 6. UV-Vis-NIR spectra of the Er^{3+}-doped precursor solution and the fluoropolymer film.

inhibition is the key for acrylate-based free-radical polymerization. MIMIC 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 MIMIC. First, the PDMS mold was fabricated by the conventional method using a commercial silicon elastomer on a master mold. The ends of the PDMS mold were removed, and then the PDMS mold was placed on the surface of a pre-cleaned substrate. Then, the Er^{3+}-doped precursor solution was placed at the open ends of the channels, and the Er^{3+}-doped precursor solution spontaneously filled the channels by capillary action. The Er^{3+}-doped precursor solution

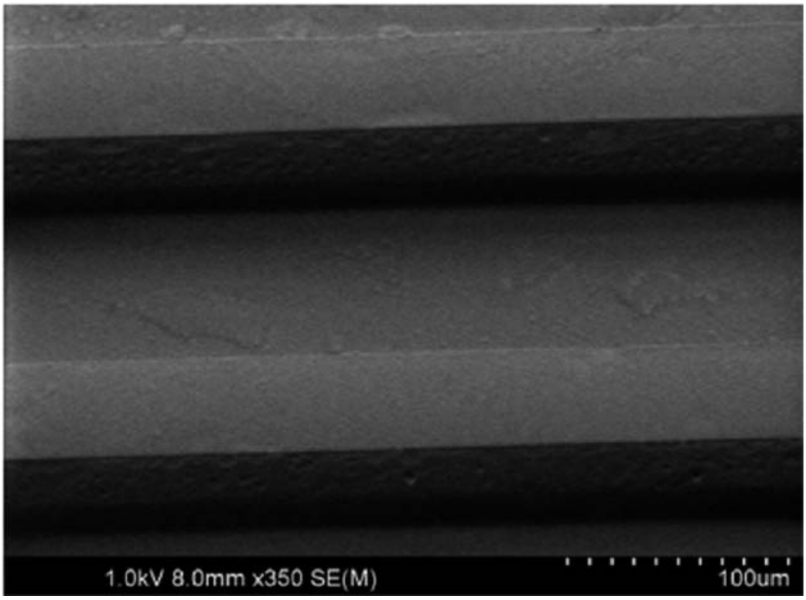

Figure 7. SEM image of a 50-μm-wide Er^{3+}-doped fluoropolymer pattern by MIMIC.

was then cured through the UV exposure (10 mW/cm^2 for 200 s). The PDMS mold was then removed, and a network of Er^{3+}-doped fluoropolymeric material remained on the substrate surface. Figure 7 shows an SEM image of the Er^{3+}-doped fluoropolymer pattern fabricated by MIMIC. However, the Er^{3+}-doped fluoropolymer patterns were partially separated from the substrate during the removal of the PDMS mold due to the low adhesion of the Er^{3+}-doped fluoropolymer patterns to the substrate. The fluoropolymers have many advantages, such as high thermal stability, chemical inertness, low surface tension and low dielectric constants, but their poor adhesion to other materials is a critical defect that affects some engineering aspects [24]. 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 trialkoxysilane forms self-assembled monolayers (SAMs) on the glass 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 eliminated the partial detachment of the fluoropolymer patterns by enhancing the adhesion between the substrate and the fluoropolymer patterns.

Conclusions

In summary, fluoropolymer films have been designed with high erbium complex content without aggregation and with good film-forming properties, high optical transparency at 1,550 nm and high thermal stability. By adjusting the Er^{3+}-doped precursor solution and the MIMIC process conditions, we successfully fabricated Er^{3+}-doped fluoropolymer patterns without ErTFMS aggregation up to 10 wt% based on the polymer matrix. This well-defined cross-linkable polymer has shown promise for optical device applications.

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References

[1] Lei, K.-L., Chow, C.-F., Tsang, K.-C., Lei, Elva, N. Y., Roy, V. A. L., Lam, Michael, H. W., Lee, C. S., Pun, E. Y. B., & Li, J. (2010). *J. Mater. Chem.*, *20*, 7526.

[2] van den Hoven, G. N., Koper, R. J. I. M., Polman, A., van Dam, C., van Uffelen, J. W. M., & Smit, M. K. (1996). *Appl. Phys. Lett.*, *68*, 1886.

[3] Snoeks, E., van den Hoven, G. N., Polman, A., Hendriksen, B., Diemeer, M. B. J., & Priolo, F. (1995). *J. Opt. Soc. Am. B*, *12*, 1468.

[4] Payne, F. P., & Lacey, J. P. R. (1994). *Opt. Quant. Electron.*, *26*, 977.

[5] Kowalczyk, T. C., Kosc, T., Singer, K. D., Cahill, P. A., Seager, C. H., Meinhardt, M. B., Beuhler, A. J., & Wargowski, D. A. (1994). *J. Appl. Phys.*, *76*, 2505.

[6] Snoeks, E., van den Hoven, G. N., & Polman, A. (1996). *IEEE J. Quanum. Electron.*, *32*, 1680.

[7] van den Hoven, G. N., Snoeks, E., Polman, A., van Dam, C., van Uffelen, J. W. M., & Smit, M. K. (1996). *J. Appl. Phys.*, *79*, 1258.

[8] Myslinski, P., Nguyen, D., & Chrostowski, J. (1997). *J. Lightwave Technol.*, *15*, 112.

[9] Auzel, F., & Goldner, P. (2001). *Opt. Mater.*, *16*, 93.

[10] Vallés, J. A., Lázaro, J. A., & Rebolledo, M. A. (2002). *IEEE J. Quantum Electron.*, *38*, 318.

[11] Park, O. H., Seo, S. Y., Jung, J. I., Bae, J. Y., & Bae, B. S. (2003). *J. Mater. Res.*, *18*, 1039.

[12] Kulishov, M., Grubsky, V., Schwartz, J., Daxhelet, X., & Plant, D. V. (2004). *IEEE J. Quanum. Electron.*, *40*, 1715.

[13] Jiang, J., Callender, C. L., Blanchetiere, C., Jacob, S., Noad, J. P., Ding, J., Qi, Y., & Day, M. (2006). *Opt. Mat.*, *28*, 189.

[14] Ma, H., Jen, A. K.-Y., & Danton, L. R. (2002). *Adv. Mater.*, *14*, 1339.

[15] Tan, R. H. C., Pearson, J. M., Zheng, Y., Wyatt, P. B., & Gillin, W. P. (2008). *Appl. Phys. Lett.*, *92*, 103303.

[16] Slooff, L. H., Polman, A., Klink, S. I., Hebbink, G. A., Grave, L., van Veggel, F. C. J. M., Reinhoudt, D. N., & Hofstraat, J. W. (2000). *Opt. Mat.*, *14*, 101.

[17] Xia, Y., Kim, E., & Whitesides, G. M. (1996). *Chem. Matter.*, *8*, 1558.

[18] Tamaki, K., Takase, H., Eriyama, Y., & Ukachi, T. (2003). *J. Photopolymer Sci. Tech.*, *16*, 639.

[19] Pitois, C., Hult, A., & Wiesmann, D. (2001). *J. Opt. Soc. Am. B*, *18*, 908.

[20] Slooff, L. H., Van Blaaderen, A., Polman, A., Hebbink, G. A., Klink, S. I., Van Veggel, F. C. J. M., Reinhoudt, D. N., & Hofstraar, J. W. (2002). *J. Appl. Phys.*, *91*, 3955.

[21] Miniscalco, W. (1991). *IEEE J. Lightwave Technol.*, *9*, 234.

[22] Laming, R. I., Poole, S. B., & Tarbox, E. J. (1988). *Opt. Lett.*, *13*, 1084.

[23] Wang, M., Hiltunen, J., Uusitalo, S., Puustinen, J., Lappalainen, J., Karioja, P., & Myllyla, R. (2011). *Microelectr. Engin.*, *88*, 175.

[24] Sprang, N., Theirich, D., & Engemann, J. (1998). *Surf. Coat. Technol.*, *98*, 865.