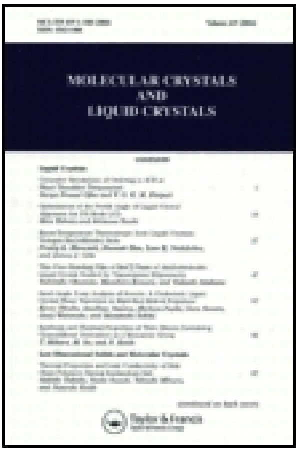

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Fabrication and Characterization of Erbium-Doped Polymer Patterns by Lift-Off Process for Planar Optical Amplifiers

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Erbium-doped aqueous polymer solutions were prepared using polyvinylpyrrolidone as a host polymer, potassium persulfate as a thermal cross-linking agent, erbium (III) trifluoromethane sulfonate as an erbium source, ethylene glycol as an antifoaming agent and DISPERBYK-180 as a dispersing agent with various weight ratios. The cross-linked, patterned and Er^{3+}-doped polymer films were fabricated using the solutions by a lift-off process for application to planar optical amplifiers. The polymer films fabricated in this study showed excellent transmission of more than 90% over the visible and NIR regions, a high thermal decomposition temperature of about 380°C and high Er^{3+} concentration up to 20 wt.% based on a polymer matrix without aggregation, making this material sufficient for planar optical amplifiers.

Keywords erbium; polyvinylpyrrolidone; lift-off process; planar optical amplifiers

Introduction

In the last decade, rare earth (RE)-doped materials have received much attention because of their potential applications for light-emitting diodes,[1–3] lasers devices[4,5] and optical amplifiers.[6–10] Among the RE ions, the erbium (Er^{3+}) ion is the most interest dopant and is used as an optically active element in waveguide amplifiers because of its intra-4*f* transition, which emits at around 1.54-μm wavelength for applications in optical communication systems.[11,12] Nowadays, erbium-doped waveguide amplifier (EDWA) and erbium-doped fiber amplifier (EDFA) technologies are commonly used in the optical communication system to compensate for signal loss such as the waveguide, coupling or intrinsic intensity losses.[13–15] Whereas EDWA is used for access and home network applications, EDFA is usually used for long-distance optical communication and networking systems because of its non-compatibility with integrated optical devices. The Er^{3+} content within the EDWA host material should normally be maintained at higher concentrations to obtain a high optical gain in small, short devices compared with an EDFA.[16] However, high Er^{3+} concentration

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may be detrimental because of ion-ion interaction phenomena such as up-conversion or cross-relaxation processes, which might reduce pump efficiency and gain performances.[17,18] Consequently, the dispersion of Er^{3+} is an important factor in decreasing the concentration quenching and enhancing pump efficiency. To reduce ion-ion interaction, Er^{3+} should be uniformly dispersed on a molecular level. A silica based inorganic matrix has been fabricated by high-temperature processes such as flame hydrolysis deposition and chemical vapor deposition, which could cause clustering of Er^{3+} ions. On the other hand, by using polymers as a host matrix of Er^{3+}, a very high doping level of Er^{3+} can be achieved without causing a significant ion-cluster effect, indicating that polymer matrix is useful for host materials of Er complex due to its good solubility and the processing temperature.[19, 20] In addition to above merits, polymers have also attracted significant attention as host material for Er^{3+} because of their low cost, high packaging density and simple processing steps on a wide range of substrates. Polymers can easily control various optical parameters such as refractive index, birefringence and thermal stability.[21,22] Thus, Er^{3+}-doped polymers have been extensively studied in recent years.

Cross-linked, patterned and Er^{3+}-doped polymer films were fabricated using the lift-off process, and their optical, thermal and dispersion properties were investigated. This study focuses on the fabrication of polymer film for application to optical communication systems with the goal of achieving excellent optical clarity, thermal stability and chemical resistance to withstand typical fabrication processing and operation conditions. To achieve dispersion of Er^{3+} sufficient for planar optical amplifiers, additives were introduced into Er^{3+}-doped polymer solutions, and their roles were investigated.

Experimental

Materials and Analytical Instruments

Figure 1 shows the structures of chemicals used for the Er^{3+}-doped polymer films. Poly vinylpyrrolidone (PVP), potassium persulfate (KPS), erbium (III) trifluoromethane sulfonate (ErTFMS), and ethylene glycol (EG) were purchased from Aldrich Chem. Co.(USA) for use as a host polymer, a thermal cross-linking agent, an erbium source, and an antifoaming agent, respectively. DISPERBYK-180 was purchased from BYK Chemie (Germany) for use as a dispersing agent. 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). Absorption and transmission data were evaluated using PerkinElmer's UV WinLab software. The data

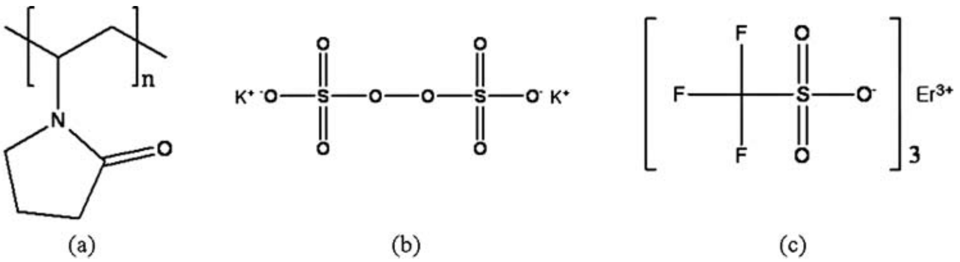

Figure 1. Structures of (a) PVP, (b) KPS and (c) ErTFMS.

interval was 1.00 nm, and scans were taken with a slit width of 2 nm in both the NIR and UV–visible region. 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+} in the samples, an Electron Probe Micro Analyzer (EPMA) was used. The 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 50 μm^2 by monitoring the intensity of characteristic X-rays.

Preparation of the PVP Solutions and Er^{3+}-Doped PVP Solutions

The PVP solutions were prepared using PVP, KPS and distilled water with various compositions as shown in Table 1 (a). The weight ratio of PVP:KPS was changed from 8.5:1.0 to 6.5:3.0. The PVP as a binding polymer was first dissolved into the distilled water under strong mechanical stirring, and then the mixture was stirred for 4 hours to obtain a homogeneous aqueous solution. After dissolving PVP in distilled water, KPS, a thermal cross-linking agent, was added into the solution with stirring for 30 min. When 3.0 g of KPS was added into the PVP solution, the homogenous polymer solution could not be obtained due to its low solubility. The Er^{3+}-doped PVP solutions were prepared by addition of ErTFMS into the PVP solutions with stirring for 30 min, and the amount of ErTFMS was changed from 5 to 20 wt.% by the polymer matrix of the PVP solutions. To investigate the effects of the antifoaming and dispersing agent, Er^{3+}-doped PVP solutions were prepared from the composition listed in Table 1 (b). The cross-linked PVP (cPVP) films

Table 1. The compositions of (a) PVP solutions and (b) Er^{3+}-doped PVP solutions.

(a)

Sample No.	PVP (g)	KPS (g)	Distilled water (g)
S0	9.5	0	30.0
S1	8.5	1.0	30.0
S2	8.0	1.5	30.0
S3	7.5	2.0	30.0
S4	7.0	2.5	30.0
S5	6.5	3.0	30.0

(b)

					Additives	
Sample No.	PVP (g)	KPS (g)	ErTFMS (g)	Distilled water (g)	EG (g)	DISPERBYK-180 (g)
E1	7.0	2.5	2.0	30.0	–	–
E2	7.0	2.5	2.0	30.0	0.4	–
E3	7.0	2.5	2.0	30.0	0.4	0.1

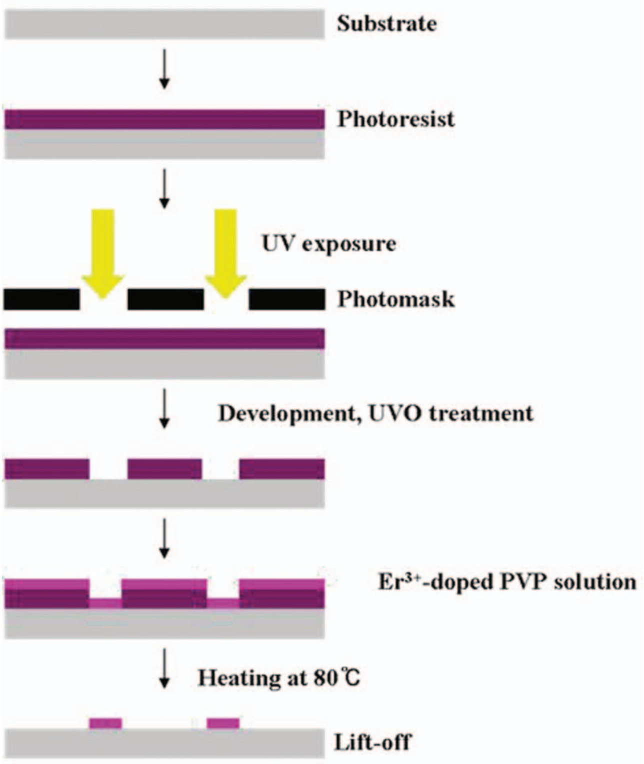

Figure 2. Lift-off process sequence using positive photoresist.

and Er^{3+}-doped cPVP films were prepared from the PVP solutions and Er^{3+}-doped PVP solutions, respectively.

Lift-Off Process for Fabrication of Er^{3+}-Doped cPVP Films

Figure 2 shows the lift-off process applied in this study for patterning the Er^{3+}-doped cPVP films. First, we fabricated the micro-patterns with photosensitive polymer (AZ 7210 photoresist, AZ Electronic Materials Ltd., USA) using the conventional photolithographic process. Second, the surface of the patterned PR was modified by UV/ozone treatment for 30 min to enhance the adhesion between the surface of the PR pattern and the Er^{3+}-doped PVP solution. Next, the Er^{3+}-doped PVP solution was spin-coated on the patterned PR with an acceleration of 2000 rpm for 20 sec and cured at 80°C for 4 hours on a hot plate. Finally, the cured Er^{3+}-doped cPVP film on the PR pattern was eliminated by lift-off using organic solvent and then dried to give the pattern of the Er^{3+}-doped cPVP film.

Results and Discussion

Optimized Composition of the Er^{3+}-Doped PVP 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

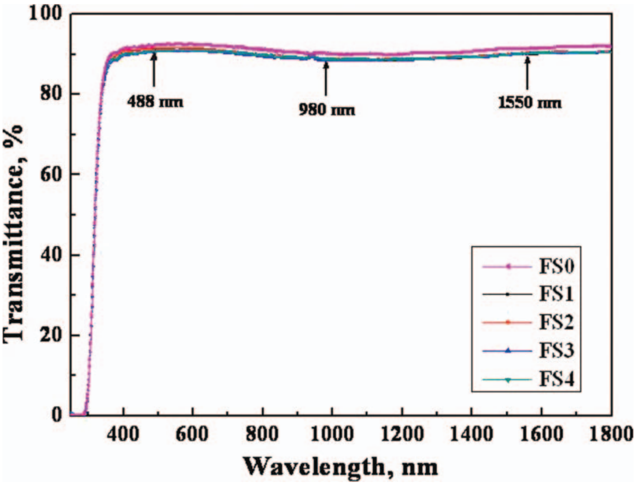

Figure 3. Transmission spectra of cPVP films (black line: FS1, red line: FS2, blue line: FS3, green line: FS4).

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 has to be minimized.[23] Another important parameter is the thermal stability of the polymer matrix for practical application to optical devices. 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.[24] We measured the transmittance and the thermal decomposition temperature of the cPVP films fabricated according to the compositions listed in Table 1 (a). Figure 3 shows the transmission spectra of the cPVP films, without Er^{3+}, prepared from various compositions (S0∼S4). The transmittances at 1,540 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 was also minimized.

Table 2 shows the thermal decomposition temperature of the cPVP films. The cPVP films had good thermal stabilities up to 380°C, at which point over 95% of their mass remained. From these data, we conclude that the thermal stability of the cPVP films is excellent and sufficient for optical device applications demanding high thermal resistance.

Table 2. Thermal decomposition temperatures of cPVP films.

Sample No.	Decomposition temperature (°C)
FS1[a]	380.46
FS2 [a]	385.29
FS3 [a]	385.62
FS4 [a]	383.12

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

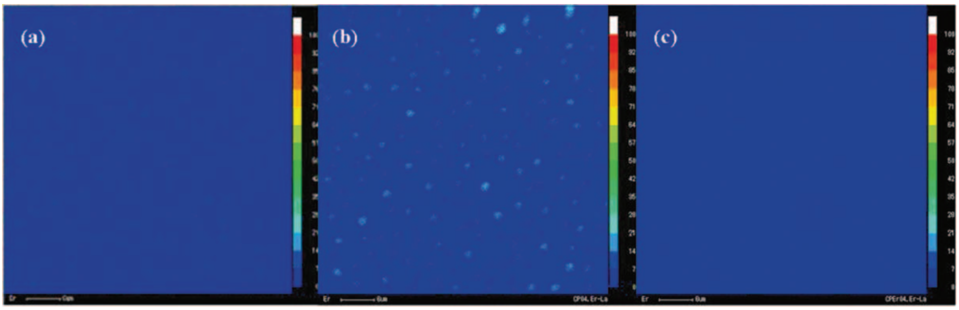

Figure 4. EPMA images by quantitative mapping of the Er^{3+}-doped cPVP films; (a) E1, (b) E2 and (c) E3.

Furthermore, the cPVP films prepared from the compositions of S1 to S4 had sufficient optical and thermal properties for optical device applications. The S4 composition had lower PVP content and therefore lower C-H bond content than those of S1, S2 and S3, indicating that the film fabricated from S4 can minimize the optical loss from the C-H bond vibrational absorption overtone in the near infrared region.[25] Moreover, the S1, S2 and S3 compositions showed poorer processability during the coating process because of their high viscosity. From the above results, S4 was selected for the Er^{3+}-doped PVP solutions.

In addition to the thermal stability and optical properties of the Er^{3+} host materials, the dispersion of Er^{3+} in the host film is an important factor in planar optical amplifier applications. RE ions tend to form clusters, and such aggregates quench the non-radiative decay channels and the luminescence from unwanted transitions by ion-ion interactions, among others.[26] The Er^{3+}-doped PVP solutions were prepared by the addition of ErTFMS into the previously optimized PVP solutions (S4). EPMA analysis was performed to evaluate Er^{3+} dispersion. Figure 4 shows the images obtained by quantitative mapping of the Er^{3+}-doped cPVP films fabricated from the compositions listed in Table 1 (b). As shown in Figure 4 (a), the EPMA image of a film formed from a formulation without additives [E1 in Table 1 (b)], such as antifoaming and dispersing agents, showed an aggregation of Er^{3+} and a stain due to a small bubble. Because of the incorporation of EG as antifoaming agent, the stains formed by bubbles were reduced as shown in Figure 4 (b), but severe aggregation of Er^{3+} was observed. This uneven dispersion of Er^{3+} in the film could be remedied by the introduction both antifoaming agents and the dispersing agent DISPERBYK-180 for aqueous solution, as illustrated in Fig. 4 (c).

In the planar optical amplifier, Er^{3+} is 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-lying energy levels and then relaxes rapidly into the first excited state. An emission from the first excited state to the ground state is induced at 1,540 nm.[27] Figure 5 shows the absorption spectra of the Er^{3+}-doped PVP solution and Er^{3+}-doped cPVP film as a function of wavelength from 300 to 1,100 nm at room temperature. As shown in Figure 5, an absorption band was observed from 300 to 400 nm, ascribable to the ErTFMS ligands. In the Er^{3+}-doped cPVP 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.

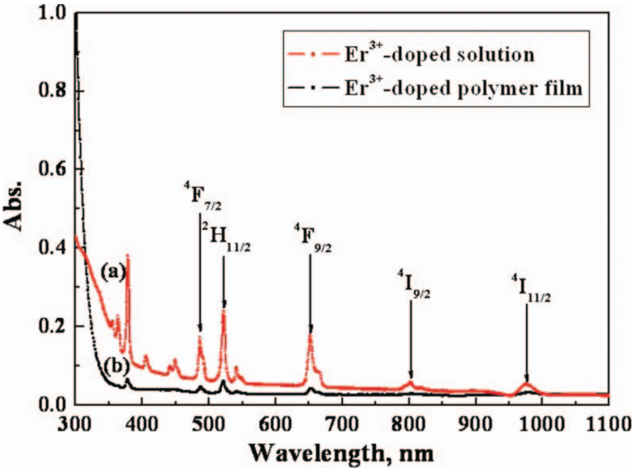

Figure 5. UV-Vis-NIR spectra of the Er^{3+}-doped PVP solution (a) and cPVP film (b).

Fabrication of the Er^{3+}-Doped cPVP Film by Lift-Off Process

For applications to planar optical amplifiers, it is important to fabricate a pattern of the Er^{3+}-doped cPVP films on a substrate. We investigated the lithographic properties of Er^{3+}-doped PVP solutions by the lift-off process. The resulting process conditions are as follows. First, the positive PR was spin-coated and soft-baked. This process was repeated three times to give a thickness of 3.7 μm, sufficient for successful lift-off. With thicknesses less than 3.7 μm, the sharpness of the patterns of the Er^{3+}-doped cPVP film were reduced due to a polymer residue after the final lift-off process. Second, the Er^{3+}-doped PVP solution (E3) of Table 1 (b) did not coat on the surface of the patterned PR because of the strong hydrophobic nature of the PR pattern. To enhance the adhesion between the PR pattern and the Er^{3+}-doped PVP solution, the modification of the PR surface was performed by a UV/ozone treatment before coating the Er^{3+}-doped PVP solution. The UV/ozone treatment results in the enhancement of the hydrophilic nature of the PR surface.[28,29] Figure 6 shows the contact angle between the PR pattern and the Er^{3+}-doped PVP solution before and after UV/ozone treatment, which changed from 75.6° to 51.7°. Finally, the Er^{3+}-doped PVP solution was spin-coated on the PR pattern and thermally cured on a hot plate at 80°C for 4 hours by the mechanism shown in Figure 7. The cross-linking of PVP should decrease both solubility and swelling phenomena because of the increase in molecular weight. When

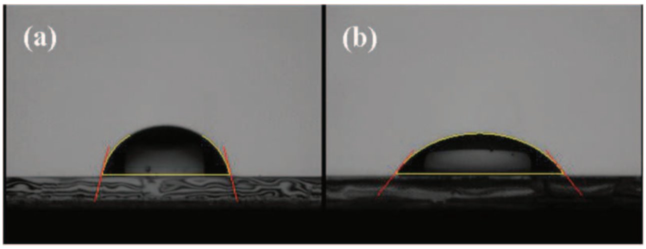

Figure 6. The contact angles of the Er^{3+}-doped PVP solution on the PR before (a) and after (b) UV/ozone treatment; (a) 75.6° and (b) 51.7°.

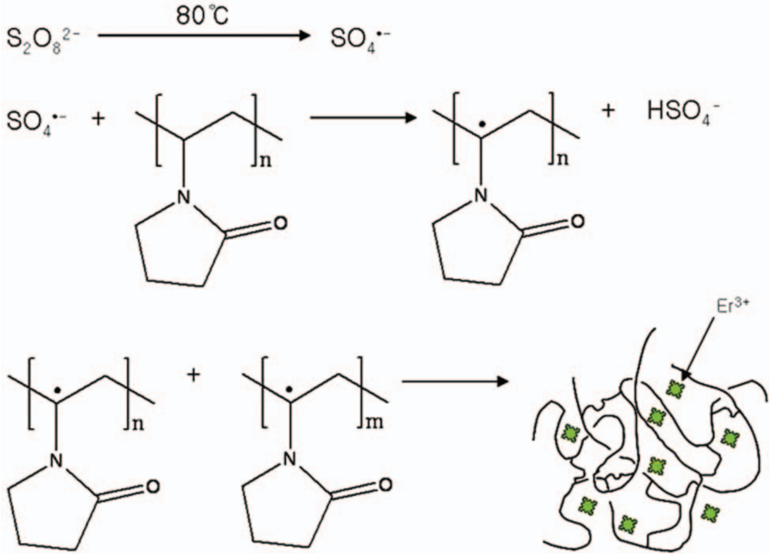

Figure 7. Cross-linking mechanism of poly vinylpyrrolidone (PVP).

using alcohol such as methanol, ethanol and isopropyl alcohol as lift-off solvents, cPVP film swelling phenomena were observed. However, by applying acetone as the lift-off solvent, the lift-off step was successfully completed without swelling because the cross-linked PVP did not dissolved in acetone.[30] Thus, the cured polymer film on the PR layer was eliminated by acetone and then dried to give 5-μm film thickness. The patterned Er^{3+}-doped cPVP film prepared from the E3 composition [Table 1 (b)] by the lift-off process is demonstrated in Figure 8.

Figure 8. Photograph of a 100-μm-wide Er^{3+}-doped cPVP film by lift-off process.

Conclusions

In summary, polymer films have been designed with high Er^{3+} content without aggregation, good film-forming properties, high optical transparency at 1,540 nm and high thermal stability. By adjusting the Er^{3+}-doped PVP solution and the lift-off process conditions, we successfully fabricated patterned Er^{3+}-doped cPVP films without Er^{3+} aggregation up to 20 wt.% based on the polymer matrix. This well-defined cross-linkable polymer has shown promise for application to optical devices.

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