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Photoluminescence of Sol–Gel Hybrid Films Doped with Erbium Tris 8-Hydroxyquinoline

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Abstract. Erbium tris 8-hydroxyquinoline (ErQ) was successfully incorporated into the sol–gel hybrid material (HYBRIMER) synthesized by using methyltriethoxysilane, vinyltriethoxysilane, and phenyltrimethoxysilane even though it has poor solubility in general organic solvent. The composition and microstructure of the HYBRIMER film doped with ErQ was analyzed using Rutherford backscattering method and scanning electron microscope. The refractive index of the HYBRIMER film was also investigated with ErQ concentration. The HYBRIMER film doped with ErQ showed a clear photoluminescence (PL) at 1.5 μm. PL intensity increased with ErQ concentration without concentration quenching until Er/Si ratio reached 5 at%.

Keywords: sol–gel, HYBRIMER, erbium complex, photoluminescence

1. Introduction

Planar-type optical amplifier has been developed for the complete building of the ultra-high speed network. Especially, erbium-doped material films have received extensive attention due to their application for planar optical amplifiers [1, 2]. Since planar optical amplifiers have a smaller interaction length with respect to erbium-doped fiber amplifier (EDFA), higher erbium concentration is required to obtain a sufficient optical gain. The high concentration of Er^{3+} ions restricts the performance of planar optical waveguide due to concentration quenching [3]. The concentration quenching is originated from the low solubility of Er^{3+} ions on both inorganic and organic matrix which is inherent nature of rare-earth elements [4]. Recently, there have been many studies on polymer materials doped with erbium complex that can increase its solubility in organic materials [5]. Moreover, when Er^{3+} ions are encapsulated by bulky organic ligands, the average minimum distance between ions increases due to the steric hindrance. However, the polymer materials doped with Er complex show poor optical and thermal properties because they are largely composed of linear C—H groups. Sol–gel derived inorganic—organic hybrid materials (HYBRIMERs) have been widely studied with a view to their use as passive optical waveguide devices because of their good optical characteristics and relatively high thermal stability compared with polymer materials [6]. Therefore, the HYBRIMER can be a potential candidate for the application of planar optical amplifiers. We have already reported the HYBRIMER doped with erbium tris 8-hydroxyquinoline(ErQ) which shows a room-temperature photoluminescence (PL) at 1.5 μm through indirect excitation [7]. However, its luminescence properties with ErQ concentration should be investigated to obtain more intense PL. In the present study, therefore, we prepared HYBRIMER films doped with ErQ, and examined the refractive index and luminescence properties depending on erbium concentration in the HYBRIMER.

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2. Experimental Procedure

The HYBRIMER was prepared using various organoalkoxysilane such as methyltriethoxysilane (MTES, $CH_3Si(OC_2H_5)_3$), vinyltriethoxysilane (VTES, $H_2C{=}CHSi(OC_2H_5)_3$), and phenyltrimethoxysilane (PhTMS, $C_6H_5Si(OCH_3)_3$) as sol–gel precursors. MTES, VTES, and PhTMS were hydrolyzed with 3 equivalent of H_2O in the presence of 0.05 M HCl as a catalyst. The hydrolyzed solution was mixed with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (DIAMO) to enhance the silica condensation. Erbium tris-8 hydroxyquinoline (ErQ) was selected as an erbium precursor because it showed a room-temperature PL at 1.5 μm. However, since ErQ showed very low solubility in organic solvent, we dissolved it in ethanolic HCl to obtain homogeneous solution. Benzyldimethylketal (BDK) was added to the mixed solution for the polymerization of vinyl group. The prepared solution was then dripped onto silica grown silicon wafer substrate spinning 1000 rpm. The HYBRIMER films were obtained after UV illumination for 1 hr and heat-treatment at 150°C for 5 hrs.

Film composition was investigated by Rutherford backscattering spectrometry (RBS) using 2 MeV He^+ ions at a backscattering angle of 165°. For infrared PL spectrum, 477-nm line of Ar^+ ion laser was chosen because it does not coincide with any of the resonant excitation bands of Er^{3+}, thus giving a good feasibility of a broadband excitation source. The pump power was 200 mW. PL radiation was detected with a monochromator (Digikrom DK240) and a thermo-electrically cooled InGaAs *p-i-n* photo diode (Hamamatsu G5832-23). A low noise current preamplifier (Stanford Research SR570) and lockin amplifier (EG&G 5210) were used for PL signal amplification.

3. Results and Discussion

To examine ErQ concentration effect on PL, ErQ was incorporated into the HYBRIMER solution with different concentrations. The used Er/Si ratios were 0.56, 2.5, and 5 at%, respectively. When Er/Si ratio exceeded 5 at%, homogeneous solution could not be obtained due to the immiscibility of ErQ in the HYBRIMER solution. Film composition was investigated to confirm the exact Er content in the HYBRIMER film by RBS measurement. Figure 1 shows typical RBS spectra of the HYBRIMER film doped with ErQ. Surface channel for each element was indicated by arrow. It is known that the incorporated ErQ molecules are homogeneously distributed in depth from the nearly flat backscattering yield of erbium, as shown in Fig. 1. Er/Si ratio of the HYBRIMER films doped with ErQ was calculated using RBS data, and listed in Table 1. As shown in Table 1, the difference of Er/Si ratio between in the actual HYBRIMER solution and in the measured film was negligible. It is considered that the compositions are maintained during film fabrication process. Thus, Er^{3+} concentration can be easily controlled by adjusting the ratio of starting precursors. When Er/Si ratio is 5 at%, Er atomic density is as high as order of 10^{20} ions/cm^3. In practice, concentrations of 10^{20}–$10^{21}Er^{3+}$ ions/cm^3 are required to achieve a reasonable gain over a length of a few centimeters [1].

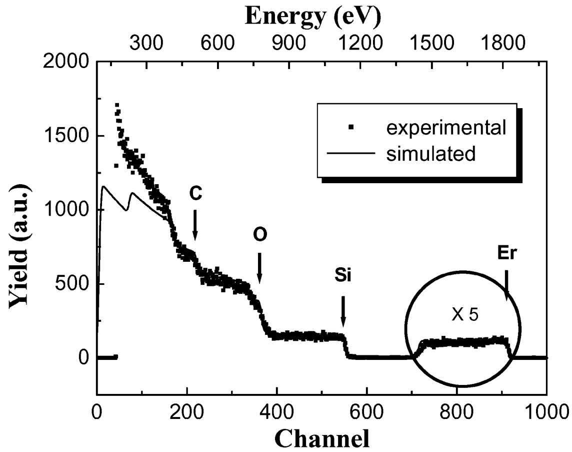

Figure 1. Typical RBS curve of the HYBRIMER film doped with ErQ. Erbium related spectra were magnified for clarity.

The erbium complex with bulky organic ligand can prevent inorganic condensation, which causes the inhomogeneous morphology of the film. The inhomogeneous morphology can increase the scattering loss of waveguide devices. Thus, the cross-section of the HYBRIMER film doped with ErQ on 2-μm silica grown wafer was shown in Fig. 2. The film has smooth

Table 1. Er/Si ratio and relative Er areal density of the HYBRIMER film doped with ErQ from RBS measurement.

Sample number	Er/Si ratio (calculated)	Er/Si ratio (measured)	Relative Er areal density
1	0.56 at%	0.54 at%	0.063
2	2.5 at%	2.31 at%	0.279
3	5 at%	5.43 at%	0.569

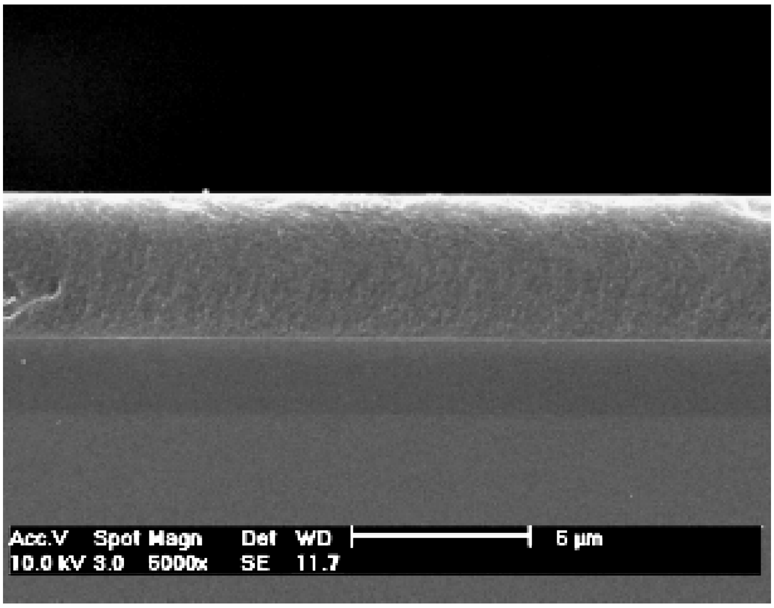

Figure 2. SEM image of cross-section of the HYBRIMER film doped with ErQ.

morphology and its thickness is nearly 4 μm. Thus, it is known that homogeneous optical quality film to be used in optical waveguides is prepared using the HYBRIMER solution doped with ErQ.

The refractive index is one of the important factors for the design of optical devices. Thus, the refractive index of the HYBRIMER film doped with ErQ was examined by using prism coupling technique. As shown in Fig. 3, the refractive index increases with ErQ concentration due to the aromatic rings with high electronic polarizability in ErQ. The refractive index of HYBRIMER films varies from 1.497 to 1.525 depending on ErQ concentration, which makes it possible to create high refractive index difference. A high index contrast gives a strong confinement of the light beam in the waveguide core and relatively sharp bends are then possible. The latter is of importance for planar optical amplifier to design long structures yet on a small area [8].

Figure 4 shows the PL spectra of the HYBRIMER films doped with ErQ. Each PL spectrum was normalized only by film thickness. As shown in Fig. 4, the HYBRIMER films doped with ErQ give clear PL spectra when they are excited using the 477-nm line of Ar^+ laser through indirect excitation, even though the 477-nm beam is not absorbed by Er^{3+} ions. The detailed excitation mechanism was reported elsewhere [7]. PL intensity increases with ErQ concentration, indicating that the active Er^{3+} fraction increases with ErQ concentration. However, when adjacent Er^{3+} ions interact each other, PL intensity is not proportional to Er concentration due to concentration quenching. The concentration quenching depends strongly on the microscopic distribution of Er^{3+} ions in the host material. Thus, it is expected that the concentration quenching can be reduced by using the erbium complex with bulky organic ligand encapsulated in the HYBRIMER matrix. Thus, it is necessary to investigate PL intensity per one Er^{3+} ion to confirm the concentration quenching effect at high doping levels. To estimate the PL intensity

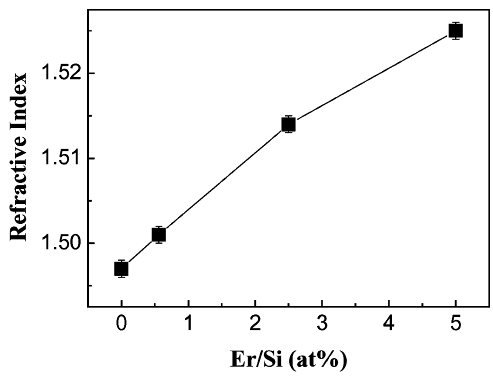

Figure 3. The refractive index of the HYBRIMER film depending on Er/Si ratio.

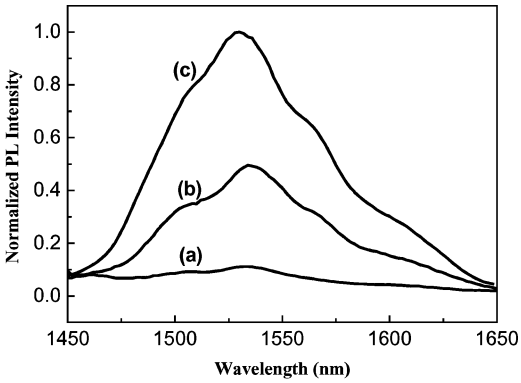

Figure 4. Photoluminescence spectra of the HYBRIMER film as a function of ErQ concentration. Er/Si ratios are (a) 0.56, (b) 2.5, and (c) 5 at%, respectively.

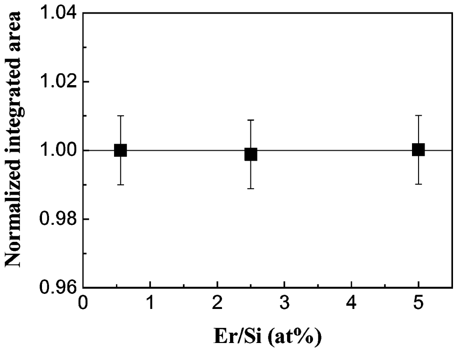

Figure 5. Normalized integrated area of the photoluminescence spectra in the HYBRIMER film doped with ErQ as a function of Er/Si ratio.

per one Er^{3+} ion, PL spectra should be normalized by film thickness and the real Er areal density since PL intensity is directly proportional to the Er concentration. However, we can obtain same result using relative areal deinsity instead of the real areal density because relative Er areal density is linearly proportional to the real areal density. Therefore, the PL spectra shown in Fig. 4 were normalized again by relative areal densities listed in Table 1, respectively. Figure 5 shows the normalized integrated area of the PL spectra that is proportional to intensity per one Er^{3+} ion. As shown in Fig. 5, no concentration quenching is found until Er/Si ratio reaches 5 at%, indicating that ErQ molecules are effectively separated in the HYBRIMER matrix to avoid the interaction between Er^{3+} ions. Thus, the HYBRIMER is a suitable matrix for the high concentration doping of erbium complex without concentration quenching.

4. Conclusions

We have successfully prepared the homogeneous HYBRIMER film doped with erbium complex using MTES, VTES, PhTMS, and ErQ. Erbium concentration can be easily controlled by adjusting the molar ratio of starting precursors. As ErQ concentration increased, intenser PL at 1.5 μm was obtained. The HYBRIMER film doped with ErQ does not show concentration quenching until Er/Si ratio reaches 5 at%, and its refractive index increases up to 1.525 with ErQ concentration. Therefore, the HYBRIMER doped with ErQ can be a good candidate material for the fabrication of planar optical amplifiers.

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