

Photoluminescence of mesoporous silica films impregnated with an erbium complex

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Transparent mesoporous silica films were prepared by sol-gel spin coating on silicon wafers at room temperature. An erbium complex, erbium tris 8-hydroxyquinoline (ErQ), was homogeneously impregnated into the pores of the mesoporous silica films, and its concentration was easily controlled by using a solution immersing technique. The ErQ-impregnated mesoporous silica films show a room-temperature photoluminescence at 1.5 μm .

Erbium-doped material films have received growing interest over the last decade due to their multiple applications such as use in integrated lasers or amplifiers for telecommunications.¹ Since planar optical amplifiers have a smaller interaction length with respect to erbium-doped fiber amplifiers, higher erbium concentration is required to obtain a sufficient optical gain. However, high doping levels of erbium quench the fluorescence emission and reduce the performance of the amplifier. Especially, the clustering of Er^{3+} ions is a main obstacle preventing concentration quenching because a silica-based inorganic matrix is fabricated by high-temperature processes such as flame hydrolysis deposition and chemical vapor deposition.² To reduce concentration quenching, erbium ions should disperse uniformly on a molecular level. When Er^{3+} ions are surrounded by bulky organic ligands, the average minimum distance between Er^{3+} ions increases due to the steric hindrance. Thus, introduction of an erbium complex can be a solution to reducing concentration quenching. Er complex is generally used with a polymer matrix because of its solubility and the processing temperature. There have been several reports concerning room-temperature photoluminescence in polymer/Er complex systems.^{3,4} However, the polymer matrix is largely composed of a linear CH chain and thus large CH quenching can occur. Therefore, a general polymer matrix is not suitable to the incorporation of an Er complex. Theoretically, the most effective method for uniform dispersion is the periodic arrangement of erbium ions in a matrix when high doping levels of Er^{3+} ions are required. Thus, we selected mesoporous materials as the host matrix. Mesoporous materials were developed for constructing a periodic pore structure, which has pores of a few nanometers in size.⁵ They can also be made of various inorganic components, such as silica and alumina, which have low optical losses.

Recently, mesoporous materials were used for encapsulating organic dyes to prevent aggregation of the dye molecules.⁶ Impregnation of Er complex into mesoporous silica has some advantages over incorporation of Er complex in the matrix. First, the mesoporous silica has a periodic pore distribution such that the impregnated Er ions are expected to be uniformly dispersed. Moreover, the absorption cross section can increase compared to Er^{3+} ion by doping Er complex into a low loss silica matrix.⁷ Although the mesoporous film is fabricated through a high-temperature process, there is no temperature restriction to impregnate Er complex because it can be impregnated by a solution immersing technique after the complete fabrication of the mesoporous silica film. Thus, it would be interesting to measure photoluminescence of a mesoporous silica film impregnated by Er complex because a large absorption cross section, low-loss characteristic, and homogeneous distribution of Er^{3+} ions are expected. However, there have been no reports on the impregnation of Er complex into mesoporous films to find the photoluminescence in the films. In this study, we impregnate Er complex into mesoporous silica film, and then measure the photoluminescence for 1.5 μm amplification.

Transparent mesoporous sol-gel thin films were prepared as follows. Tetramethylorthosilicate (TMOS, Aldrich, 98%) (Milwaukee, WI) was hydrolyzed under acidic conditions (hydrochloric acid, HCl, J.T. Baker, Phillipsburg, NJ, 36.5–38%), and then methanol (CH_3OH , Merck, Whitehouse Station, NJ, 99.8%) was added into the hydrolyzed TMOS at room temperature. Finally, surfactant (cetyltrimethylammonium chloride, CTACl, Aldrich, 25%) was added so that the final reactant molar ratios were 1–3 TMOS:8–16 H_2O :0.09–0.11 HCl:18–30 CH_3OH :0.2–0.8 surfactant. The mixture was allowed to react for a further 24 h at room temperature.

The reaction mixture after the silicate oligomerization was concentrated by evaporation of the solvent using a rotary evaporator with vacuum at 40 °C. The mixture solution was dripped onto a spinning silicon wafer substrate at a spinning rate of 5000 rpm. The films were obtained upon complete evaporation of the solvent in a drying oven at 60 °C. The films were calcined in air at 300–670 °C for 12 h, at a rate of 1 °C/min.

Thin-film x-ray diffraction (XRD) patterns of mesoporous silica thin films indicate that a mesoporous structure can be formed on the substrate as a transparent film by a spin-coating method. Thin-film XRD patterns of as-synthesized and calcined films are shown in Fig. 1. Well-defined XRD patterns show a prominent peak at 2.0–4.0° 2 θ and some broad peaks in a 2 θ range of 4.0–7.0° characteristic of a hexagonal structure, which is similar to that from MCM-41 materials.⁸ The unit cell parameter (a_o) for a hexagonal structure is calculated from $2d(100)/3^{1/2}$ from $d(100)$ which is obtained from the 2 θ value of the first peak in the thin-film XRD pattern from $d(100) = \lambda/2\sin\theta$, where $\lambda = 0.15417$ nm for the Cu K α line.^{9,10} The unit cell parameter a_o is equal to the internal pore diameter plus one pore wall thickness. As-synthesized film shows $d(100)$ spacing of 4.3 nm and a unit cell parameter of 5.0 nm. The integrity of the mesoporous structures is retained even after complete decomposition of the organic structure directing agents

by calcination at 550 °C in flowing air for 12 h. The thin-film XRD pattern of the calcined mesoporous film is similar and exhibits a single broad diffraction peak corresponding to $d(100)$ spacing of 2.6 nm and a unit cell parameter of 3.0 nm. The broadening of the $d(100)$ peak on calcination suggests less order after calcination. The $d(100)$ peaks shift about 1.7 nm for calcined film in comparison with as-synthesized film. Therefore, we can obtain condensed mesoporous silica film to impregnate Er complex.

Among the several Er complexes, erbium tris 8-hydroxyquinoline (ErQ, Gelest Inc., Tullytown, PA) is selected due to its bulky aromatic ligands. ErQ is synthesized for the application of organic light-emitting diodes and shows a photoluminescence at room temperature.¹¹ Thus, ErQ is a suitable Er complex to impregnate into the mesoporous silica films. However, it shows very low solubility in general organic solvent and hence it should be dissolved in acidic solution. Impregnation of the ErQ into mesoporous film was performed by immersing the mesoporous film in an ErQ solution. For impregnation, ErQ was dissolved in 0.5 N ethanolic HCl, and then the film was put into the ErQ dissolved solution. The concentration of ErQ/ethanol solution could not exceed 0.015 N due to the low solubility of ErQ. The solutions were stirred by using an ultrasonic cleaner (BRANSONIC 2210, Danbury, CT) for more homogeneous impregnation of ErQ into the pores of a few nanometer size. After the impregnation, the surface of the film was cleaned by ethanol. The residual ethanol of the impregnated film was removed by flowing nitrogen gas over the sample for 30 min and then the film was dried at 200 °C for 1 h on a hot plate.

The impregnation of ErQ into the mesoporous silica films is confirmed by N₂-sorption measurement. The mesoporous silica films show a typical nitrogen adsorption and desorption isotherm (type IV), as shown in Fig. 2(a). Brunauer–Emmett–Teller analyses of the sorption isotherms indicate that the mesoporous silica film with impregnated ErQ reduces the surface area from 920 to 725 m²g⁻¹ and the average pore diameter from 2.1 to 2.0 nm. The reduction of the surface area and pore diameter results from the adsorption of ErQ molecules on the internal surface of the pores in the mesoporous film, as shown in Fig. 3. Therefore, it is confirmed that ErQ is well incorporated into the pore of the mesoporous silica film.

Erbium depth profiles and film composition were investigated by Rutherford backscattering spectrometry (RBS) using 2 MeV He⁺ ions at a backscattering angle of 165°. Figure 4 shows typical RBS spectra of the mesoporous silica film impregnated with ErQ. Surface channel for each element was indicated by arrow. It is known that the impregnated Er ions are homogeneously distributed in depth from the nearly flat backscattering yield of Er, as shown in Fig. 4. Film compositions and

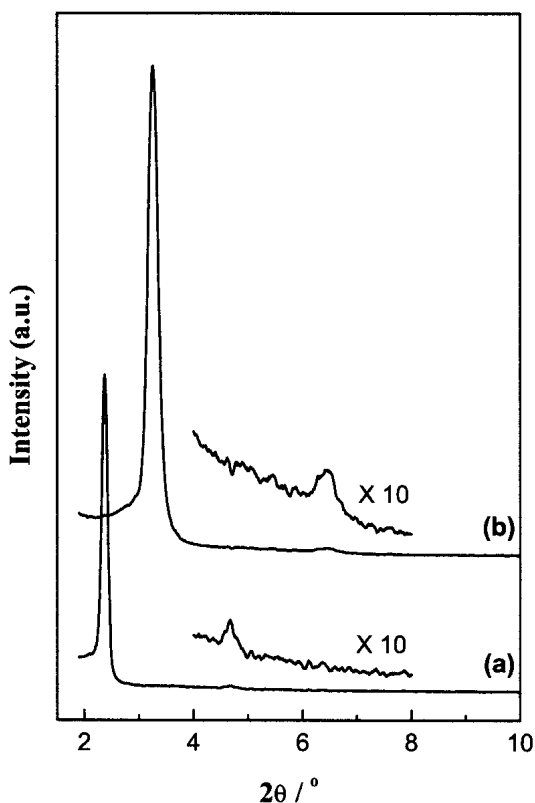


FIG. 1. XRD patterns of (a) as-synthesized and (b) calcined mesoporous silica films.

Er atomic densities are calculated using RBS data and listed in Table I. The atomic ratio of ErQ molecule is considered for the simulation of the carbon and nitrogen contents.

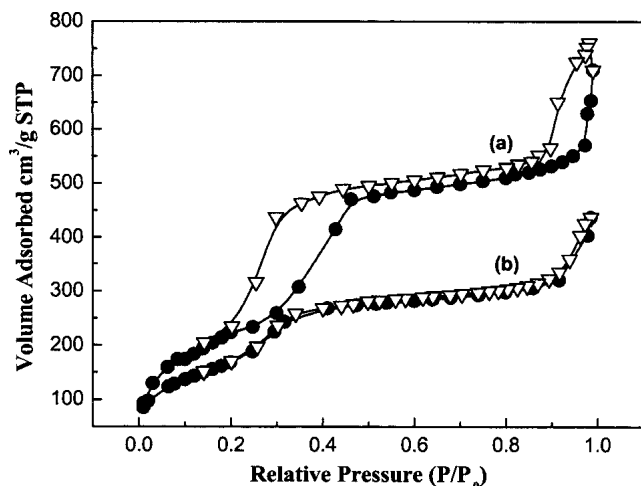


FIG. 2. N_2 adsorption curve of mesoporous silica films (a) before and (b) after impregnation of ErQ. Circles and triangles indicate adsorption and desorption, respectively.

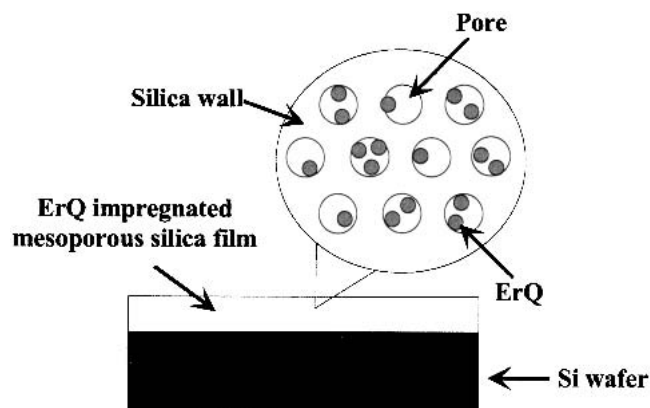


FIG. 3. Scheme of ErQ impregnated mesoporous silica film.

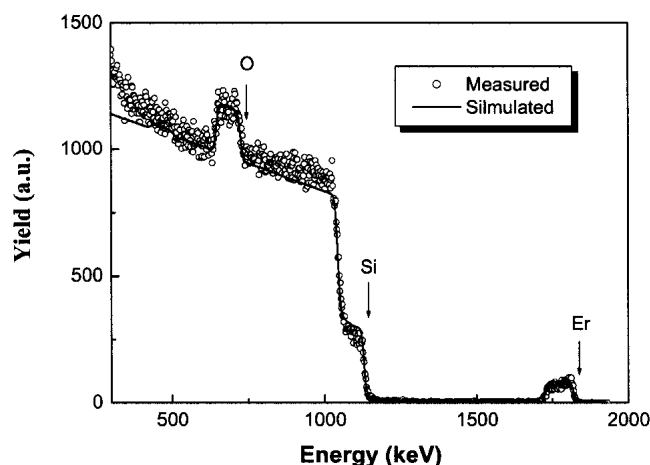


FIG. 4. Typical RBS spectra of the mesoporous silica film impregnated with ErQ.

Figure 5 shows the photoluminescence spectra of mesoporous silica films with impregnated ErQ. For the infrared photoluminescence spectrum of ErQ into the mesoporous silica films, a 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 photoluminescence spectra show two peaks near 1510 and 1530 nm due to the different surroundings of Er^{3+} ions. As the concentration of ErQ increases, higher luminescence is observed.

To examine the effect of mesoporous silica wall on the concentration quenching, the maximal photoluminescence intensities are also plotted as a function of the obtained Er atomic density. As shown in Fig. 6, there is a linear relationship between photoluminescence intensity and Er atomic density. This concentration dependency implies that ErQ is effectively separated by the mesoporous silica wall, which reduces concentration quenching. Thus, the content of Er complex incorporated into mesoporous films can be controlled by changing the concentration of Er complex solution while maintaining the homogeneous distribution of Er complex. Moreover, the bandwidth at half-maximum is about 68 nm. This is a wide bandwidth compared with those of other Er-doped

TABLE I. Film compositions and Er atomic densities of the mesoporous silica films impregnated with ErQ

ErQ concentration in ethanol solution (N)	Film composition except hydrogen (at.%)					Er/Si ratio	Er atomic density (cm^{-3})
	Si	O	N	C	Er		
1.5×10^{-3}	28.8	58.6	1.2	11.0	0.4	0.012	1.8×10^{20}
0.7×10^{-2}	21.2	44.3	3.6	29.8	1.1	0.052	0.8×10^{21}
1.5×10^{-2}	14.8	30.1	5.8	47.5	1.8	0.12	1.8×10^{21}

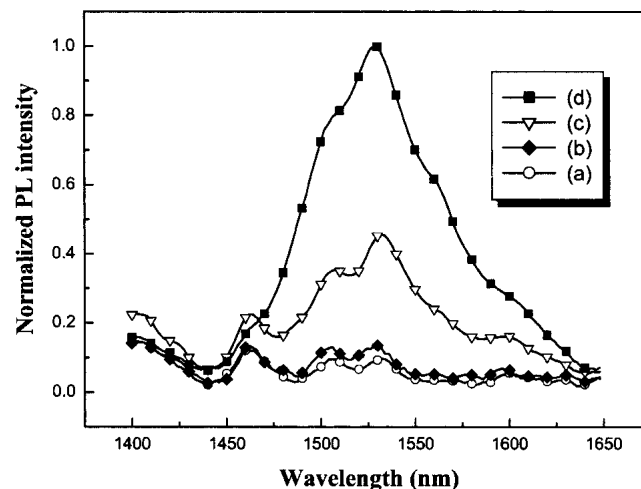


FIG. 5. Photoluminescence spectra of mesoporous silica films immersed in (a) 0, (b) 1.5×10^{-3} , (c) 0.7×10^{-2} , and (d) 1.5×10^{-2} N ErQ/ethanol solution, respectively.

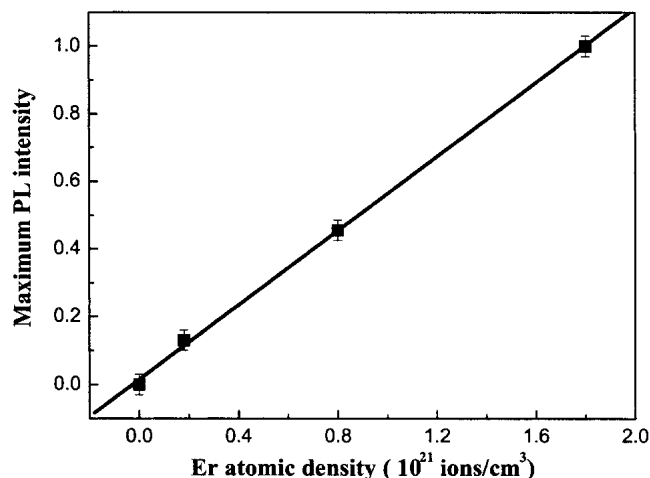


FIG. 6. Maximum PL intensities of the mesoporous silica films impregnated with ErQ as a function of the impregnated Er atomic density.

materials.¹² The wide bandwidth can be obtained by emitting from Er atoms in different local environments. Such a broad spectrum enables a wide gain bandwidth for optical amplification. Therefore, it is considered that the mesoporous silica film is a good matrix for homogeneous impregnation by a rare-earth complex.

In conclusion, we have prepared transparent mesoporous silica films using a sol-gel spin coating method. Er complex is homogeneously impregnated into the mesoporous silica film by an immersing technique and its concentration can be easily controlled by changing the concentration of Er complex solution. The ErQ impregnated mesoporous silica film shows a room-temperature

photoluminescence at 1.5 μm . Therefore, the Er complex impregnated mesoporous silica films can be applied to develop planar optical amplifiers.

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