Rare earth silicates as gain media for silicon photonics

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Erₓ₂₋ₓSiO₅ and ErₓYbₓ₋ₓ₋ₓSiO₅ crystalline thin films were investigated to apply to the high-gain media for silicon photonics. In addition to the sol–gel method, the directed self-assembly approach, using layer-by-layer deposition techniques, was also introduced to improve the crystallinity. The relaxation processes in Er ions were discussed to clarify the contribution of the energy transfer and cooperative upconversion. After optimization of the Er content, a Si photonic crystal slot ErₓY₂₋ₓSiO₅ waveguide amplifier was fabricated, and a 30 dB/cm modal gain was demonstrated. This achievement demonstrates the potential for compact and high optical gain devices on Si chips.

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1. INTRODUCTION

Silicon photonics have developed rapidly, and their achievements are attracting much attention for realizing the optical interconnection in computing systems [1–3]. Nowadays, with the development of the wavelength division multiplexing technologies, the success of Si photonics has stimulated a great deal of interest in photonic integration, which can provide many signal-processing functions to work together with LSI on silicon chips [1–7]. Taking the photonic integration into consideration, it is urgent to develop integrated optical amplifiers on the Si platform. This is because optical signal processing devices, i.e., modulators and switches, are passive components without optical gain, resulting in signal decrease at each step in the signal processes. Erbium-doped fiber amplifiers (EDFAs) have been used frequently as regenerative amplifiers in optical communication systems [8,9]. Thus, the C band corresponding to the intra-4f transition in Er ions is a suitable wavelength range for silicon photonics to combine with photonic networks. Therefore, waveguide amplifiers based on Er are expected to be one of the candidates for the integrated amplifier.

Silicon-based materials doped with Er have been discussed from the point of view of the device applications for Si photonics in previous reports [10–15]. A simple two-level model is used for studying the optical gain for convenience. When the incident light travels through a gain medium, the optical gain G is given by

\[ G \text{ [dB]} = 4.34(\sigma_{\text{em}}N_1 - \sigma_{\text{abs}}N_0)\Gamma L, \]  

where \( N_0 \) and \( N_1 \) are the populations of the ground and excited states, respectively. \( \sigma_{\text{em}} \) and \( \sigma_{\text{abs}} \) are the emission and absorption cross-sections of Er ions, \( L \) and \( \Gamma \) are the waveguide length and the optical confinement factor of the waveguide, respectively. According to the consideration of the Einstein B coefficient, \( \sigma_{\text{em}} \) is almost the same as \( \sigma_{\text{abs}} \). From Eq. (1), the optical gain is determined by the product of the Er concentration and the waveguide length. In order to achieve enough gain on the Si photonics chip with a centimeter scale, an extremely high Er concentration as compared with that in EDFAs is needed because of the approximate three orders of magnitude difference in the waveguide length. For this reason, we have proposed the use of Er silicates as a new light source material for the compact waveguide amplifiers [16]. This crystalline system can contain up to \( 1.6 \times 10^{22} \text{ cm}^{-3} \) Er atoms as a constituent element, and is expected to be studied for developing waveguide amplifiers with enough optical gain at a length less than 1 cm [16].

Resonant energy transfer processes between rare earth ions have been frequently discussed to explain the luminescence decay in such highly rare-earth-doped materials [17–21]. A chain of energy transfer processes among Er ions gives rise to nonradiative relaxation of excited Er ions such as concentration quenching and upconversion. The crystalline nature of the Er silicates can suppress the defect formation and the Er segregation which cause the concentration quenching. However, the concentration-quenching behavior has been observed in ErₓY₂₋ₓSiO₅ crystalline systems at high Er concentrations [10–13]. We have investigated the contribution of energy transfer among Er ions to the nonradiative relaxation processes in ErₓY₂₋ₓSiO₅ (\( x \leq 2 \)) crystallites by changing the Er concentration [22].

In this work, the optical excitation and relaxation processes of the Er silicates are reviewed from the point of view of a high optical gain media in silicon photonics. As the material synthesizes, the sol–gel, pulsed laser deposition (PLD) and radical-assisted sputtering (RAS) are shown. In the former, ordered Er silicates crystallites are obtained by self-organization. In contrast, the latter two are a directed self-assembly (DSA) approach using layer-by-layer deposition, which is expected to give more highly-ordered crystallinity. The relaxation processes caused by the Förster energy transfer are discussed to clarify the contribution of the energy transfer. Finally, the Si photonic crystal slot (PhC–S) ErₓY₂₋ₓSiO₅ waveguide and the gain characteristics are demonstrated.
2. PREPARATION OF ERBIUM SILICATE CRYSTALLINE THIN FILMS

A. Sol–Gel Method

The sol–gel method was performed using sol solutions mixed with Er–O, Y–O, and Si–O precursors prepared by Kojundo Chemical Laboratory [15]. The composition of Er$_x$Y$_{2-x}$SiO$_5$ can be well controlled by changing the molar ratio of the precursors, which is checked by Rutherford back-scattering. After spin-coating of the solutions, the samples were dried in dry air at 120°C for 30 min, and then baked in Ar at 500°C for 30 min. This process was repeated several times to obtain a film thickness enough for the characteristics (30–50 nm/cycle). Finally, they were annealed at 1200°C for 30 min in Ar atmosphere for crystallization.

The transmission electron microscopy (TEM) photograph of a sample prepared by the sol–gel method (hereafter, sol–gel sample) shows the formation of nanocrystallites with a grain size of about 30 nm [22]. The crystallite has a layered structure with a 0.86 nm period peculiar to Er monosilicate (Er$_2$SiO$_5$) crystals. The X-ray diffraction (XRD) patterns of the Er$_x$Y$_{2-x}$SiO$_5$ show almost the same crystalline structure as that of Er$_2$SiO$_5$ for various Er contents ($x$) [15]. The grain size estimated from the XRD results using Scherrer’s equation is in good agreement with the grain size obtained from the TEM observation. Figure 1 shows the Er-related photoluminescence (PL) of $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition at 17 K for $x = 0.5$ (sol–gel, thickness $\sim 600$ nm). The eight PL fine peaks corresponding to the Stark splitting of the ground state ($^4I_{15/2}$) of the 4f-electron of the Er$^{3+}$ ion are clearly observed as in the Er$_2$SiO$_5$ crystallites. Note that the fine structure is independent of Er content $x$. This result suggests that there is no change of the local environment of Er$^{3+}$ ions in the Er$_x$Y$_{2-x}$SiO$_5$ system. Figure 2 shows the TEM image of the sol–gel sample at about 100 nm thickness, and reveals a highly oriented layered structure due to self-assembly caused by the phase separation during the crystallization process [23]. Note that the thickness of the sol–gel sample in Fig. 2 is too thin to make a waveguide device. However, when the thickness is increased above $\sim 100$ nm, the structure is found to deteriorate. The thicker crystalline films also show segregation of the metals and densification of the crystallites frequently after the crystallization. In the next section, the DSA approach to overcome these problems is presented.

![Fig. 2. TEM image of highly oriented Er$_2$SiO$_5$ crystal.](image)

B. DSA Approach Using Layer-by-Layer Deposition Techniques

The layered structure of the sol–gel Er$_x$Y$_{2-x}$SiO$_5$ samples is caused by the self-assembly process. However, due to the presence of multiple nucleations everywhere in the preform, the grain size is limited below $\sim 50$ nm. In order to obtain a highly oriented crystalline thin film with large grain sizes, we have proposed a DSA approach using layer-by-layer deposition technique in which Er, Y, Si, and O are stacked in the atomic scale to form a preform similar to the crystalline arrangement of Er$_x$Y$_{2-x}$SiO$_5$ [24–26].

PLD was used as the layer-by-layer deposition technique. Fourth harmonic generation of a Q-switched YAG laser ($\lambda = 266$ nm; repetition frequency, 10 Hz; power, 30 mJ/shot) was used for the ablation. PLD was performed at room temperature in oxygen atmosphere of $10^{-3}$ Pa. The back pressure was less than $10^{-5}$ Pa. Metal pieces of Si, Er, and Y were arranged on a rotatable target holder. The target holder was rotated at such a speed that one cycle deposited a group of Er–O, Y–O, and Si–O layers having 0.86 nm thickness with the (Er + Y)/Si ratio of 2:1. PLD was carried out for 100 cycles to form about a 90 nm thick preform on a Si (100) substrate. The samples were then annealed in Ar at 1230°C by rapid thermal annealing (RTA) for 1 min.

Figure 3 shows the XRD patterns of Er$_x$Y$_{2-x}$SiO$_5$ crystalline thin films prepared by PLD (hereafter, PLD sample). The films exhibit intense diffraction peaks at 10.32°, 20.35°, and 31.23°, corresponding to the (100), (200), and (300) diffraction peaks of Er$_2$SiO$_5$ [24]. The (400) and (500) diffraction peaks are too weak to be observed clearly. This result indicates that the crystalline structure of the Er$_2$SiO$_5$ monosilicates is kept even though a large amount of Er is replaced with Y. This is because Y$^{3+}$ and Er$^{3+}$ ions have nearly the same radius (Er, 1.57 Å; Y, 1.62 Å). Note that the strong peak at 33° is the (200) diffraction peak of the silicon substrate. The fact that only the (n00) diffraction peaks appear in the XRD patterns shows that the film is highly oriented and that the crystallization proceeds effectively in the short period during RTA owing to the layered arrangements of the preform. Note that the grain size of the PLD sample is estimated to be about 100 nm from the XRD peak width by Scherrer’s equation. The size may be limited by the film thickness, and the thicker film can be the large grain size. The PL fine structure of the PLD sample is quite the same as that of the sol–gel sample (Fig. 1, below). Although the PLD film thickness is about 7 times as thin as the sol–gel film.

![Fig. 1. PL spectra of Er$_x$Y$_{2-x}$SiO$_5$ crystalline thin films prepared by sol–gel and PLD methods at 17 K.](image)
thickness, the PL intensity of the PLD film is comparable to that of the sol–gel film. The PL intensity improvement is due to reduction of the nonradiative relaxation process, which is described in Section 3.C.

The DSA approach was also utilized to fabricate Er$_x$Yb$_{2-x}$SiO$_5$ thin films in order to evaluate the sensitization effect of Yb$^{3+}$ for the optical excitation of Er$^{3+}$ ions. A part of the Y target metal was replaced with an Yb metal piece. Figure 4 compares the XRD pattern of Er$_x$Yb$_{2-x}$SiO$_5$ ($x = 0.33$, $y = 0.33$) thin films with that of Er$_x$SiO$_5$ ($x = 0.33$). The XRD patterns are also the same as those of the Er$_x$SiO$_5$ crystal, indicating the formation of the highly oriented crystalline structure. Introduction of Yb$^{3+}$ has almost no effects on the structure of the films. Note that the small diffraction peaks from erbium oxide at 29.32° and 29.73° are observed, probably due to imperfection of the crystallization. The demonstration of the highly oriented Er$_x$Yb$_{2-x}$SiO$_5$ crystalline thin film indicates that the DSA approach using PLD has a big advantage for the advanced material research.

The DSA approach using PLD produced a lot of fruitful results, including the improvement of the emission properties described below. However metal clusters are frequently observed in the PLD films, and they cause great scattering loss in the waveguide devices. Therefore, further improvement of the layer-by-layer process is necessary to achieve high quality for the waveguide devices. Next, we attempted to introduce RAS into the device fabrication process [26]. Details of the RAS equipment are described in Ref. [27]. The RAS technique uses a high-speed rotatable drum as a substrate holder, and a radical source and metal targets are arranged independently around the drum. Controlling the drum rotation and sputtering conditions, it is possible to repeat metal-sputtering and oxidation processes alternatively with layer-by-layer accuracy. Therefore, RAS is suitable for the DSA process to form layered crystalline films such as Er$_x$Y$_{2-x}$SiO$_5$ and their device applications.

Figure 5 shows the XRD pattern of Er$_x$Y$_{2-x}$SiO$_5$ crystalline thin films at the crystallization temperature of 1200°C and 1250°C. The XRD patterns indicate the same crystalline structure as the Er$_x$Y$_{2-x}$SiO$_5$ layered crystal. Closed circles indicate each diffraction peak of Er$_2$SiO$_5$ crystal. Both samples show orientation to the (100) direction, but it is relatively low. The rare earth oxide (RE$_2$O$_3$) peak intensity around 29° remarkably increased. It is necessary to further optimize the RAS process and the crystallization conditions. However, the good surface morphology is well preserved in the whole surface area after the crystallization process, which is the big advantage for the waveguide device applications. In Section 4.A, the...
low scattering loss in the Er$_2$-$x$SiO$_5$ crystalline waveguide fabricated by the DSA approach using RAS is demonstrated.

3. PL EMISSION AND RELAXATION PROCESSES WITH FÖRSTER ENERGY TRANSFER

A. Basis of Förster energy transfer

The energy transfer between rare earth ions originates from the Förster energy transfer [28]. The excitation energy in each donor is transferred to the nearest neighbor donor, moving a distance $\delta$, which corresponds to the third square of the donor concentration $N$ ($\delta$ is $N^{-1/2}$). Assuming a dipole–dipole transition at the distance $\delta$, the energy transfer rate $\omega_T$ is given by

$$\omega_T = \omega_0 \left( \frac{R_0}{\delta} \right)^6 = \omega_0 R_0^6 N^2 = CN^2,$$

where $\omega_0 = (\tau_0)^{-1}$ and $R_0$ are the intrinsic decay rate (inverse of the intrinsic decay time) of the donor and the critical transfer distance for the coupling, respectively. $C = \omega_0 R_0^6$ is defined as the energy transfer constant for the dipole–dipole transition in the literature, and is independent of $N$ [17,18]. The reported value of $R_0$ is about 2 nm, and seems to be almost independent of the ion pair [18,19]. The donor density corresponding to the distance $R_0$ is $1.25 \times 10^{20}$ cm$^{-3}$, around which the concentration quenching begins to occur. Due to the sequential energy transfer, a part of the excitation energy reaches to the quenching centers before radiative relaxation [20]. Therefore, control of the energy transfer is needed in the materials doped highly with Er. In this chapter, the Er-related emission and relaxation processes based on the Förster energy transfer mechanism are discussed.

B. PL Emission and the Energy Transfer Dynamics

PL measurements were performed to evaluate the luminescence properties of Er$_x$Y$_{2-x}$SiO$_5$ and Er$_x$Yb$_y$Y$_{2-x-y}$SiO$_5$ ($x = 0.33, y = 0.33$) PLD thin films. Laser diodes (LDs) of different wavelengths were used as the excitation light source. The wavelength of the pumping light was adjusted by control of the operation temperature of LDs, and the power density was 30 mW/mm$^2$. The PL emissions were monitored with a 32 cm monochromator with a liquid-nitrogen-cooled Ge detector, and recorded with a lock-in amplifier. The decay time was measured by a time-gated photon counting method using an electrically cooled InGaAs photomultiplier.

Figure 6 shows the PL spectra of Er$_x$Y$_{2-x}$SiO$_5$ and Er$_x$Yb$_y$Y$_{2-x-y}$SiO$_5$ PLD thin films, both having the same Er content ($x = 0.33, y = 0.33$) and the same thickness (100 nm) at room temperature. The excitation wavelength is 654 nm, which corresponds to the $^4I_{11/2} \rightarrow ^4F_{9/2}$ transitions of Er$^{3+}$ ion. Both of the PL spectra exhibit the fine structure typical of the Er$_2$SiO$_5$ crystal. The measured lifetimes for Er$_x$Y$_{2-x}$SiO$_5$ and Er$_x$Yb$_y$Y$_{2-x-y}$SiO$_5$ samples were 250 and 410 $\mu$s, respectively. In Fig. 6(a), it can be noticed that the emission corresponding to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er$^{3+}$ ($\lambda = 1529$ nm) is weaker for Er$_x$Yb$_y$Y$_{2-x-y}$SiO$_5$ than for Er$_x$Y$_{2-x}$SiO$_5$. Figure 6(b) shows the PL spectra in the range of 950–1100 nm. Both thin films exhibit emission in this range, but the fine structure and the intensity are very different from each other. For the Er$_x$Y$_{2-x}$SiO$_5$ thin film, weak and broad emission peaks are observed, corresponding to the transition between the $^4I_{11/2}$ and $^4I_{15/2}$ levels of Er$^{3+}$ ion. For Er$_x$Yb$_y$Y$_{2-x-y}$SiO$_5$ thin film, a sharp and intense emission at 975 nm and a small peak at 1030 nm, which correspond to the transitions between $^2F_{9/2}$ and $^2F_{7/2}$ of the Yb$^{3+}$ ion, respectively, are observed, even though 654 nm excitation is off-resonant for the Yb 4f-electron transition. These phenomena indicate a strong energetic coupling between Er$^{3+}$ and Yb$^{3+}$.

The schematic diagram of the energy levels in the Er$^{3+}$ and Yb$^{3+}$ co-doping system and the energy transfer processes are shown in the inset of Fig. 6(b). The 654.5 nm laser excitation brings only Er$^{3+}$ 4f$^1$-electrons to its $^4F_{9/2}$ state. The electrons relax rapidly from this state to the $^4I_{11/2}$ and $^4I_{13/2}$ levels, and the populations of these two levels give rise to the emissions at 1.53 $\mu$m and 980 nm, respectively. In the presence of Yb, the 654.5 nm laser excites Er$^{3+}$ ions from the ground state to the $^4F_{9/2}$ state, which then relax to the $^4I_{11/2}$ and $^4I_{13/2}$ levels. A part of the electron energy at the $^4I_{11/2}$ level transfers to the $^2F_{5/2}$ state of Yb$^{3+}$ ions by the cross-relaxation process, $^4I_{11/2} \rightarrow ^4I_{13/2} \rightarrow ^2F_{7/2} \rightarrow ^2F_{5/2}$ (Yb$^{3+}$), resulting in the weaker emission at 1.53 $\mu$m (Er$^{3+}$:$^4I_{13/2} \rightarrow ^4I_{15/2}$) and the intense luminescence at 975 nm (Yb$^{3+}$:$^2F_{5/2} \rightarrow ^2F_{7/2}$).

On the other hand, the off-resonance excitation for the Er$^{3+}$ ion at 940 nm gives a strong Er-related emission from the Er$_x$Yb$_y$Y$_{2-x-y}$SiO$_5$ thin film. It is indicated that the excitation path is the inverted cross-relaxation process: $^2F_{7/2} \leftrightarrow ^2F_{5/2}$ (Yb$^{3+}$):$^4I_{11/2} \leftrightarrow ^4I_{15/2}$ (Er$^{3+}$) via relaxation in the
$^{2}F_{5/2}$ state of Yb$^{3+}$ ion. The excitation wavelength was varied at around 975 nm of the Er$_3$Yb$_3$Y$_{2-x}$SiO$_5$ sample in order to precisely observe the energy transfer between Er$^{3+}$ and Yb$^{3+}$ ions. Figure 7 shows the PL intensity ratio of Er$_3$Yb$_3$Y$_{2-x}$SiO$_5$ and Er$_3$Y$_{2-x}$SiO$_5$ at 1.53 μm as a function of the excitation wavelength. The PL excitation (PLE) spectrum indicates the excitation peak at 975 nm with the PL intensity enhancement of 3.2 in the presence of Yb. Note that there is no change in the fine structure of the PL spectrum between the two samples [Fig. 6(a)]. Because the measured lifetimes for Er$_3$Yb$_3$Y$_{2-x}$SiO$_5$ and Er$_3$Y$_{2-x}$SiO$_5$ samples are 410 and 260 μs respectively, the contribution from increase of the fluorescence efficiency is 1.6 times. Accordingly, the sensitization effect to the Er$^{3+}$ ion excitation is 2 times.

In general, it is considered that the absorption cross-section of Yb$^{3+}$ at the wavelength of 975 nm is about one order of magnitude higher than that of Er$^{3+}$ [29]. This wavelength is in good agreement with the PLE peak wavelength, as shown in Fig. 7. The energy transfer due to the cross-relaxation from Yb$^{3+}$ to Er$^{3+}$ ions results in the increased 1.53 μm PL intensity at the excitation wavelength of 975 nm. The Er$_3$Yb$_3$Y$_{2-x}$SiO$_5$ crystalline system is especially favorable for this sensitization effect, because the distance between Er$^{3+}$ and Yb$^{3+}$ ions is very close, resulting in the effective energy transfer. The effective sensitization of Er$^{3+}$ by Yb$^{3+}$ in the Er$_3$Yb$_3$Y$_{2-x}$SiO$_5$ thin film, taking advantage of the high absorption cross-section of Yb$^{3+}$', offers a potential material for a compact optical waveguide amplifier on the silicon substrate with a lower threshold and an increased optical gain.

PL intensity enhancement of ErYb silicates has been reported, and the sensitization effect and the reduction of the self-quenching have been discussed [30–32]. In comparison to the ErYb silicate system, the Er$_3$Yb$_3$Y$_{2-x}$SiO$_5$ system can control the two effects separately by changing the contents x and y. The content of Er x was reduced to 0.33 to suppress the self-quenching of the Er$^{3+}$ ion. When a part of Y$^{3+}$ ions is replaced by Yb$^{3+}$ ions up to y = 0.33, the neighboring Er$^{3+}$ and Yb$^{3+}$ ions should be joined preferentially and effectively. If y > 0.33, the excess Yb$^{3+}$ ions exist and are coupled with each other. Consequently, the excitation energy relaxes in the Yb$^{3+}$ ion without the energy transfer to the Er$^{3+}$ ion, and the excitation efficiency decreases. The contents of Er and Yb have not been optimized yet, but we consider that the contents x and y used here are relatively reasonable.

### C. Diffusion-Limited Relaxation in the Er Silicate Crystallites

The crystalline nature of the rare earth silicates can suppress the formation of defects and Er segregation, which causes concentration quenching [20]. However, the quenching behavior has still been observed in Er$_3$Y$_{2-x}$SiO$_5$ crystalline systems for high Er content. The PL decay rates of the sol–gel and PLD samples were plotted as a function of Er concentration N, as shown in Fig. 8. The PL decay rate is almost proportional to the Er concentration, and then the PL efficiencies of both processes behave in a similar manner as the decay time quenching. Note that the PL decay rate is about one order of magnitude larger in the sol–gel samples than in the PLD samples. This may be explained by the grain size difference. The grain size of the sol–gel samples is around 30 nm, which is about 3 times as small as those of the PLD samples (~100 nm) [24]. It has been considered that the excitation energy migrates in the Er network owing to the resonant energy transfer, and then a part of the excitation energy is quenched at the grain boundaries [22]. Here, the relaxation processes based on the Förster energy transfer are described.

In order to deal statistically with the energy migration, a diffusion coefficient D for the excited state is introduced [17,18]. According to the microscopic diffusion theory [22,23], the diffusion coefficient D based on the energy transfer is given by

$$D = a \tau_0 \delta^2 = CN^{4/3},$$

where $a \tau_0 = CN^2$ is the energy transfer rate, δ is the distance between the nearest neighbor Er$^{3+}$ ions, and N is the concentration of Er$^{3+}$ ions. Here, we assume an energy migration under a weak excitation, and therefore N is almost equal to the Er concentration. If the grain radius $r_g$ is comparable to the free diffusion length $L_0 = (D\tau_0)^{1/2}$, the relaxation should be limited by the nonradiative relaxation at the grain boundaries. We consider a spherical model where only the grain boundary is the quenching center, as shown in Fig. 2 [22]. Assuming a radial distribution of the excited Er$^{3+}$ ions under a uniform excitation, the average distance from the excited Er$^{3+}$ ions to the grain boundary corresponds to the diffusion length of the excited state ($L_D$), and is given by $r_g/4$, which is the mean distance weighted by the number of Er$^{3+}$ ions. Consequently, ($L_D$) is limited by the grain size. At this limit, the decay time due to the diffusion $\tau_D$ is given by

![Fig. 7. PL intensity ratio of Er$_3$Yb$_3$Y$_{2-x}$SiO$_5$ and Er$_3$Y$_{2-x}$SiO$_5$ crystalline thin films at 1.53 μm, as a function of the excitation wavelength. The dashed lines show PL spectra of both samples for comparison.](image1.png)

![Fig. 8. 1.53 μm emission decay rate as a function of the Er concentration. The solid lines show the fitting curves by Eq. (2).](image2.png)
$\tau_f^1 = (L_D)^{-2} = CN^{1/3}(L_D)^{-2}$.  

Therefore, the fluorescence lifetime $\tau_f^1$ in the diffusion-limited relaxation (DLR) process is expressed by

$$\tau_f^1 = \tau_0^1 + \tau_D^1 \approx \tau_0^1 (1 + 16R_0^2N^{1/3}r_g^2).$$

The fitting curves obtained using Eq. (5) are drawn with solid lines on Fig. 8. These curves are plotted using the intrinsic decay rate of $\omega_0 = 300$ s$^{-1}$, and the energy transfer constants of $C = 3.5 \times 10^{-8}$ cm$^6$ s$^{-1}$ for the sol-gel samples ($2r_g = 30$ nm) and $C = 2.6 \times 10^{-8}$ cm$^6$ s$^{-1}$ for the PLD samples ($2r_g = 100$ nm). These correspond to the critical transfer lengths of $R_0 = 2.2$ nm for the sol-gel samples and $R_0 = 2.1$ nm for the PLD samples. These values are in good agreement with the previous reports [18,19].

D. Cooperative Upconversion

DLR owing to the Förster energy transfer is suppressed in large crystallites with lower Er concentrations, as described previously. The energy transfer also causes the cooperative upconversion (CUC) in the Er silicate system under high-power excitation. CUC leads the transitions of the excited Er ions to higher energy levels, and consequently the emission efficiency at the 1.5 µm band is reduced.

Figure 10 shows the CUC emission spectra of an Er0.5Y1.5SiO5 crystalline waveguide prepared by the sol-gel method. Optical pumping is performed through a lensed fiber using a 1.48 µm LD light source, which corresponds to a transition from the ground state ($^4I_{13/2}$) to the first excited state ($^4I_{15/2}$). The intense emission at 550 nm corresponding to the transition from $^4S_{3/2}$ to $^4I_{15/2}$ in Er$^{3+}$ ions is clearly observed. The energy diagram and CUC energy transfer process model are shown in Fig. 11. The 550 nm CUC emission process requires three excited Er$^{3+}$ ions which are located close together.

Figure 12 shows the logarithmic plots of the CUC luminescence intensities at 550 nm as a function of the excitation power. The slopes corresponding to the exponent of the excitation power are $k = 1.74$ for the RAS and $k = 1.87$ for the sol-gel samples, respectively. This is due to the three-body effect, but the slopes are less than three. The slope is critically dependent on the upconversion coefficient $C_{up}$. According to the CUC model shown in Fig. 11, the CUC processes are expressed by simultaneous rate equations as follows:

$$\frac{dN_0}{dt} = \phi_p \sigma_{abs}N_0 + \omega_{21}N_2 + \omega_{23}N_3 - \omega_f N_1 - 2C_{up}N_1^2 - C_{up}N_1N_2,$$

$$\frac{dN_1}{dt} = C_{up}N_1^2 - \omega_2N_2 - C_{up}N_1N_2,$$

$$\frac{dN_2}{dt} = C_{up}N_1N_2 - \omega_3N_3,$$

$$\frac{dN_3}{dt} = N_{Er} - N_0 + N_1 + N_2 + N_3.$$

where $N_0$, $N_1$, $N_2$, $N_3$, and $N_{Er}$ are the populations of Er ions corresponding to the $^4I_{15/2}$, $^4I_{13/2}$, $^4I_{9/2}$, and $^4S_{3/2}$ states and the total Er density, respectively, and $\phi_p$ is the pumping efficiency at the 1.5 µm band. 

The fitting curves obtained using Eq. (6) are drawn with solid lines on Fig. 12. These curves are plotted using the intrinsic decay rate of $\omega_0 = 300$ s$^{-1}$, and the energy transfer constants of $C_{up} = 1 \times 10^{-17}$ cm$^6$ s$^{-1}$. 

Fig. 9. Schematic diagram of the spherical grain model. Density plots show distribution of the excited Er ions at the steady state.

Fig. 10. CUC emission spectra of the sol-gel sample. The energy diagram and CUC energy transfer process are also shown.

Fig. 11. CUC process modeling of the Er$_x$Y$_{2-x}$SiO$_5$ crystal.

Fig. 12. CUC emission intensity as a function of excitation power. The solid line is a calculation result using the rate equation [Eq. (6)] with $C_{up} = 1 \times 10^{-17}$ cm$^6$ s$^{-1}$. 

[Figure captions and diagrams are omitted for brevity.]
Table 1. Parameters Used in the Rate Equation Modeling of the Er$_2$Y$_2$SiO$_5$ Crystal

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\omega$ (s$^{-1}$)</th>
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<tbody>
<tr>
<td>$^4S_{3/2} \rightarrow ^4I_{13/2}$</td>
<td>$\omega_3$ $2.5 \times 10^7$</td>
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<tr>
<td>$^4S_{3/2} \rightarrow ^4I_{13/2}$</td>
<td>$\omega_3$ $2.8 \times 10^7$</td>
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<tr>
<td>$^4I_{15/2} \rightarrow ^4I_{13/2}$</td>
<td>$\omega_2$ $1.4 \times 10^7$</td>
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<tr>
<td>$^4I_{15/2} \rightarrow ^4I_{13/2}$</td>
<td>$\omega_2$ $7.2 \times 10^6$</td>
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<tr>
<td>$^4I_{15/2} \rightarrow ^4I_{13/2}$</td>
<td>$\omega_1$ $300$ this work</td>
</tr>
</tbody>
</table>

Photon flux. $\omega_0$ and $\omega_3$ are the total relaxation rates from the $^4I_{15/2}$ and $^4S_{3/2}$ states. $\omega_2$ and $\omega_1$ are the transition rates associated with the transitions $^4I_{15/2} \rightarrow ^4I_{13/2}$ and $^4S_{3/2} \rightarrow ^4I_{13/2}$.

The parameters used in this calculation are summarized in Table 1. Moreover the DLR decay given by Eq. (2) was used as the fluorescence decay rate $\omega_0$ ($= \tau_0^{-1}$), where we put $\tau_0^{-1} = \omega_1$ and $N = N_0$ because of the strong excitation. The luminescence intensity at 550 nm is proportional to the population $N_3$. The pumping power dependence of $N_3$ was calculated as a function of $C_{wp}$. As shown in Fig. 12, the excitation power dependence of the experimental CUC emission intensity at 550 nm is well reproduced by the calculated $N_3$ (solid lines) for $C_{wp} = 1 \times 10^{-17}$ cm$^2$ s$^{-1}$.

The upconversion coefficients at various Er concentrations reported in the literatures [13,29,34–37] are plotted together with the present results in Fig. 13. It is found that the upconversion coefficient is proportional to the Er concentration with the fitting coefficient of $5 \times 10^{-38}$ cm$^6$ s$^{-1}$. This coefficient corresponds to the energy transfer constant in CUC expected from the Förster energy transfer, and is a little smaller than the energy transfer constant $C$ obtained from the DLR process analysis. The energy transfer constant should be proportional to an overlap integral of the energy spectra between the donor and accepter. It is speculated that an overlap of the transition energy spectra between the donor (Er$^{3+}$:I$_{13/2}$ $\rightarrow$ I$_{15/2}$) and accepter (Er$^{3+}$:I$_{13/2}$ $\rightarrow$ I$_{15/2}$) in the CUC process becomes smaller than that of the cross-relaxation process (Er$^{3+}$:I$_{13/2}$ $\rightarrow$ I$_{15/2}$).

4. CHARACTERIZATION OF Er$_x$Y$_2$-xSiO$_5$ WAVEGUIDES

A. Cross-Section and Scattering Loss

In this section, light propagation in Er$_x$Y$_2$-xSiO$_5$ waveguides is characterized. In order to couple an Er$_x$Y$_2$-xSiO$_5$ waveguide with a Si wire waveguide, we have proposed an Er$_x$Y$_2$-xSiO$_5$ waveguide structure with a buried Si guide layer as shown in Fig. 14. The fabrication process is as follows. After a thick SiO$_2$ layer was formed on a Si (100) substrate, Si stripes of 4 $\mu$m width and about 30 nm thickness were formed on the SiO$_2$/Si substrate by Si evaporation. Then, an Er$_x$Y$_2$-xSiO$_5$ crystalline thin film was formed on the prepared substrates by the sol-gel method or RAS. The thickness of the Er$_x$Y$_2$-xSiO$_5$ film was about 250–500 nm, and the corresponding optical confinement factor was estimated to be 0.54–0.71. Optical pumping was performed using a 1.48 $\mu$m light source with output power of 20 mW through a lensed fiber.

Top views of the Er$_x$Y$_2$-xSiO$_5$ ($x = 0.45$) waveguide taken by CCD were shown in the top of Fig. 15. The waveguide was fabricated by DSA using RAS. The CUC emission was observed at 150 $\mu$m along the waveguide from the input facet edge. This result indicates that the pumping light is confined in the waveguide. The green emission tail behaves as an exponential decay, as shown in the bottom of Fig. 15. We attempted to estimate the propagation loss of the pumping light from the decay profile of green emission in Er$_x$Y$_2$-xSiO$_5$ waveguides [16]. The pumping photon flux $\phi$ in the propagation is given by

$$\phi = \phi_0 \exp(-\alpha x),$$

where $\alpha$ and $\Gamma$ are the decay coefficient of the 1480 nm pumping light and the optical confinement factor, respectively. The green emission corresponds to the transition from the $^4S_{3/2}$ excited states to the ground state $^4I_{15/2}$ of Er$^{3+}$ ions and the intensity is proportional to the population $N_3$, as described above. According to the relation between the CUC luminescence intensity and excitation power as shown in Fig. 12, the CUC emission decay profile is given by

$$I_{\text{CUC}}^\text{green} \propto \phi^k = \phi_0^k \exp(-k\alpha x),$$

where $k$ is the slope of the logarithm plot in Fig. 12. The decay coefficient $\alpha$ was estimated from the CUC emission decay as a function of Er concentration and plotted in Fig. 16. The decay coefficient $\alpha$ consists of absorption and scattering losses, and is expressed by

$$\alpha = \sigma_{\text{abs}} N_{\text{Er}} + \alpha_s.$$
Here, the absorption coefficient \( \alpha_{\text{abs}} \) is a product of absorption cross-section \( \sigma_{\text{abs}} \) and Er concentration \( N_{\text{Er}} \) \( (\alpha_{\text{abs}} = \sigma_{\text{abs}} N_{\text{Er}}) \), and \( \alpha_s \) is the scattering loss.

From the linear approximation of the decay coefficient versus Er concentration obtained from a series of the sol–gel samples (black square in Fig. 16), \( \sigma_{\text{abs}} \) and \( \alpha_s \) were estimated to be \( 3.4 \times 10^{-20} \text{ cm}^2 \) and \( 131 \text{ cm}^{-1} \), respectively. The absorption cross-section is comparable to the previous report [12]. On the other hand, the scattering loss (intersection of \( \alpha \) at \( N_{\text{Er}} = 0 \)) is remarkably large, presumably due to the scattering at the grain boundaries of the Er\(_{2-x}\)SiO\(_5\) crystallites. In contrast, the waveguide fabricated using RAS shows a lower scattering loss than the sol–gel samples, and the scattering loss is \( 27 \text{ cm}^{-1} \) or less obtained from the parallel extrapolation (dashed line in Fig. 16) of the measured absorption loss data. This achievement is due to the improvement of the crystallinity. A remarkable reduction of the scattering loss has also been attained in a Si PhC–Si \( \text{Er}_{x}\text{Y}_{2-x}\text{SiO}_5 \) waveguide, as described in the next section.

**B. Si Photonic Crystal Slot Waveguide**

The photonic crystal (PhC) waveguide is known to show a strong optical confinement and “slow light” nature [38]. The Er\(_{2-x}\)SiO\(_5\) crystal has a lower refractive index (~1.8) than Si (3.45). We introduced a Si PhC–Si structure in the waveguide to obtain a strong confinement of the propagation light [39]. The top view of the PhC and a schematic of the cross-section of the PhC–Si waveguide is shown in Figs. 17(a) and 17(b). The triangle configuration of holes was applied to the PhC, and the hole diameter and the period are 675 and 1350 \( \text{nm} \). The photonic band gap (PBG) was designed using the Kronig–Penney model, with the effective refractive index determined by the layer thickness. PBG is tuned to the C band and the shorter wavelength edge is around 1.48 \( \mu\text{m} \).

The Si PhC–Si of 4 \( \mu\text{m} \) width and 500 \( \mu\text{m} \) length was formed on an SOI wafer using e-beam lithography and ICP dry etching. An SEM top view of the PhC after ICP is shown in Fig. 17(a). Next, the air gaps were filled with \( \text{Er}_{0.1}\text{Y}_{1.6}\text{SiO}_5 \) crystal (Er: \( 3.2 \times 10^{21} \text{ cm}^{-3} \)) using the sol–gel method mentioned in Section 2. The depth of the slot was 380 \( \text{nm} \). After crystallization, the SiO\(_2\) over cladding layer was deposited by PVD. The cross-sectional SEM photograph is shown in Fig. 17(c). It is confirmed that the Si PhC–Si is filled flat and smooth with \( \text{Er}_{0.4}\text{Y}_{1.6}\text{SiO}_5 \) crystal. This is an advantage of the sol–gel method. A slight shrinkage of the layer thickness at the waveguide region (the center part) can be seen in Fig. 17(c). This is caused by the densification due to the crystallization, but the influence is small. We consider that the direction of the densification is limited by the Si side wall in the slot.

Figure 18 shows top views of a Si PhC–Si \( \text{Er}_{0.4}\text{Y}_{1.6}\text{SiO}_5 \) waveguide. The C band ASE light source is incident from the...
cleaved facet through a lensed fiber (from the right side of the figure), and the light propagation along the waveguide was monitored. The bottom of Fig. 18 is the green emission caused by CUC. The long decay tail (deep into 250 µm from the edge) indicates a low scattering loss. The middle of Fig. 18 shows an infrared (IR) camera image taken at the same time. The IR light scattering from the Si PhC region is clearly seen. However, the scattering light from the waveguide region is extremely weak. These results suggest a good optical confinement in the Si PhC–S Er₄₋₅YₓSiO₅ waveguide. In addition, the segregation is not observed in the PhC–S region. The fine segregation is frequently observed in the sol solution. Then we speculate that the PhC structure acts as a filter for the fine segregation during spin coating, and the pure sol solution permeates into the PhC.

The sharp PL emission at 1.5 µm was confirmed from the edge of the Si PhC–S Er₄₋₅YₓSiO₅ waveguide. Furthermore, variable stripe length (VSL) measurement was performed to estimate the optical gain of the waveguide. A 980 nm LD with an emitter size of 1 x 100 µm was used as a pumping light source. Then we expanded the beam size to 10 times by microscope. The pumping light with a line-shaped pattern was irradiated along the waveguide, and the irradiation length was varied by moving a shade. The PL emission from the edge of the waveguide was collected with a lensed fiber, and monitored. The bottom of Fig. 18(b) is shown.

Fig. 19. (a) PL spectra and the edge emission intensity versus the pumping power. The excitation length dependence of the emission intensity is shown in Fig. 19(b). The PL emission from the waveguide was collected with a lensed fiber, and monitored. The bottom of Fig. 18(b) is shown.

The pumping light with a line-shaped pattern was irradiated along the waveguide, and the irradiation length was varied by moving a shade. The PL emission from the edge of the waveguide was collected with a lensed fiber, and monitored with an infrared camera. SEM observation indicates that Er₅₋₆SiO₅ in the slot shows no segregation of Er, and is smooth and homogeneous. We therefore assume that the scattering loss is negligibly low, and estimate the absorption cross-section of the Er ions to be 1.74 x 10⁻²⁰ cm² from the total propagation loss 35 cm⁻¹ and the confinement factor Γ = 0.63. This value is in good agreement with the result of CUC emission decay profile in Fig. 16.

As a function of the pumping power in Fig. 20, the optical gain increased with the pumping photon flux, and reaches 30 dB/cm at 4.4 x 10²² cm⁻² s⁻¹. The Er population inversion is estimated to be 3.2 x 10¹⁰ cm⁻³ from Eq. (1). Here, we assumed that the emission cross-section is the same as the obtained absorption cross-section from Fig. 16. The pumping light at 980 nm corresponds to the I₄₁₁/₂ → I₂₁₁/₂ transitions of Er³⁺ ion. The relaxation time at the second excited state I₄₁/₂ is 40 µs, estimated from the PL decay measurement. It is sufficiently fast in comparison with the decay time at the first excited state I₄₁/₂ to use the two-level approximation for deriving a fitting curve, which is shown as a reference in Fig. 20. The threshold photon flux ϕₜh is estimated to be 3.1 x 10¹⁰ cm⁻² s⁻¹ from the fitting curve. At the zero pump power, the total propagation loss is estimated to be 35 cm⁻¹ from Fig. 20. It is considered that the high gain obtained in the Er₅₋₆SiO₅ waveguide is due both to the high Er concentration and the homogeneous crystallinity. We speculate that the improvement of the crystallinity in the sol–gel method is due to the application of the modified surface of the Si PhC structure described previously.

SEM observation indicates that Er₅₋₆SiO₅ in the slot shows no segregation of Er, and is smooth and homogeneous. We therefore assume that the scattering loss is negligibly low, and estimate the absorption cross-section of the Er ions to be 1.74 x 10⁻²⁰ cm² from the total propagation loss 35 cm⁻¹ and the confinement factor Γ = 0.63. This value is in good agreement with the result of CUC emission decay profile in Fig. 16.
On the other hand, the threshold photon flux $\phi_{th}$ is relatively low. The threshold photon flux is determined by the lifetime of the excited state $^{1}I_{13/2}$ and the absorption cross-section. We considered that, first, the strong excitation reduces the ground state population, resulting in the reduction of DLR and that, second, the 980 nm excitation suppresses CUC because the high population of both the coexistence of $^{4}I_{11/2}$ and $^{4}I_{13/2}$ states under the strong excitation inhibits the direct coupling of $^{1}I_{13/2}$- $^{4}I_{13/2}$. In addition, as Suh et al. suggested, the homogeneous Er$_{x}$Y$_{2-x}$SiO$_{5}$ crystalline system can suppress the upconversion sufficiently due to uniform Er–Er distances even at high Er concentrations [13]. Therefore, the improvement of the lifetime of the 1.53 μm can be expected. Furthermore the slot waveguide structure plays a role of a defect in the photonic bandgap of Si PhC, and then the 1.53 μm light emitted from Er ions in Si PhC is concentrated into the slot. Consequently, the absorption cross-section increases effectively, and the threshold photon flux becomes lower.

5. CONCLUSIONS
Rare earth silicates, i.e., Er$_{x}$Y$_{2-x}$SiO$_{5}$ and Er$_{x}$Yb$_{2-x}$SiO$_{5}$, are reviewed from the point of view of the high optical gain media for silicon photonics. By introducing the DSA approach to the crystal preparation, highly oriented crystalline thin films were obtained, and a low scattering loss in Er$_{x}$Y$_{2-x}$SiO$_{5}$ crystalline waveguides was achieved. The relaxation processes caused by the Förster energy transfer were discussed, and the important parameters for designing the waveguide amplifier were estimated.

An Er$_{0.3}$Y$_{1.7}$SiO$_{5}$ waveguide slotted into Si PhC was demonstrated. Strong optical confinement for the C band is confirmed, and a 30 dB/cm optical gain was achieved, indicating a potential for compact and high optical gain devices on Si chips.

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