1.5 μm light emission of Er$^{3+}$ ions doped in SiO$_2$ films including Si nanocrystallites and in SiO$_x$ films

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Abstract. We have investigated the fabrication of two types of Er-doped silicon oxide films. The films were prepared by ablating a Si target covered with a thin Er metal layer, by Nd:YAG laser light at 50 mJ/pulse in 40 Torr O$_2$ gas. After depositing the Er-dispersed SiO$_x$ ($x \sim 1.4$) films, the films were annealed in Ar gas. We found that Er-doped films deposited at (a) 4 J/cm$^2$ and (b) 100 J/cm$^2$ have the optimum annealing temperatures of 600°C and 900°C, respectively. Furthermore, we found that Er-doped films deposited at 4 J/cm$^2$ exhibit much more intense light emission at 1.5 μm than those deposited at 100 J/cm$^2$. For the Er-doped films deposited at 100 J/cm$^2$, it is evident that electron-hole pairs are generated in Si nanocrystallites precipitated in a SiO$_2$ film and that recombination energy is transferred to Er$^{3+}$ ions that emit 1.5 μm light, via the lowest luminescent state in Si nanocrystallites.

1. Introduction
Si-based light emitters are required for efficient telecommunication devices and interconnections between chips. Since it turned out that 1.5 μm light emission of Er$^{3+}$ ions doped in crystalline Si quenches at room temperature, doping Er$^{3+}$ in nanostructured Si-based materials with wider band gaps has been extensively investigated. Some researchers reported an optimum temperature of 900°C, at which one can expect precipitation of Si nanocrystallites in SiO$_2$ matrices during annealing [1–3]. In contrast, other researchers reported Er-doped silicon-rich silicon oxide films, which has an optimum annealing temperature of 600°C [4–12]. For further investigation, it is important to compare two types of films fabricated under controlled conditions. In the present work, we have investigated fabrication method of two types of Er-doped films and optical properties of Er-doped silicon-based films.

2. Experimental
Er-doped Si-rich silicon oxide films were prepared by a laser ablation technique. First, for depositing Er thin films on Si targets, Er metal targets were ablated by Nd:YAG laser light at 532 nm with a pulse duration of 7 ns at 100 J/cm$^2$ in a vacuum chamber for 1200 shots. Next, the Si targets covered with the Er films were ablated in O$_2$ gas at 40 mTorr, at fluences of either 4 J/cm$^2$ and 100 J/cm$^2$, for depositing Er-dispersed SiO$_x$ films. The fluence was controlled by changing distance between the Si targets covered with Er films and the focal point of the Nd:YAG laser beam used for ablating the targets. The composition $x$ is $\sim 1.4$, which was measured by Rutherford backscattering spectroscopy. Finally, the Er-dispersed SiO$_x$ films were...
annealed in Ar gas for 30 minutes. Photoluminescence (PL) was observed under excitation with either a) optical parametric oscillator (OPO) light tuned from 400 nm to 700 nm with a pulse duration of 7 ns or b) cw He-Cd laser light at 325 nm or 442 nm. PL in visible and near infrared regions was detected using a Si photodiode array and an InGaAs diode, respectively.

3. Results and Discussion

Figure 1 shows PL spectra of an Er-doped Si-rich silicon oxide film in (a) a visible region and (b) a near infrared region. The film was fabricated by laser ablation of a Si target covered with an Er film at 100 J/cm² and annealing at 900°C. The PL in the infrared region is due to the transition from the first excited state $^4I_{13/2}$ to the ground state $^4I_{15/2}$ in Er$^{3+}$ ions. In the visible range, broad-banded PL is observed.

In order to clarify the origin of the PL in the visible range, we measured photoluminescence excitation (PLE) spectra. Open circles in Fig. 2 shows PLE spectrum monitored at 780 nm. As shown by lines (a) and (b) in Fig. 2, the PLE spectrum can be fitted by two straight lines. The visible PL is assigned to Si nanocrystallites as follows. Si nanocrystallites have an indirect band structure same as that of a bulk Si crystal but band gap energies that are shifted to higher energies due to the quantum confinement effect [13]. The fundamental absorption gap
$E_{\Gamma-\Delta}$ is the energy difference between the $\Gamma_{25'}$ point in the valence band and the $\Delta_1$ points in the conduction band. Above the $E_{\Gamma-\Delta}$ gap, another indirect gap $E_{\Gamma-L}$ is observed due to an indirect transition from the $\Gamma_{25'}$ point to the $L_1$ points in the conduction bands. Above the gaps, $E_{\Gamma-\Delta}$ and $E_{\Gamma-L}$, PLE intensity $I_{\Gamma-\Delta}$ and $I_{\Gamma-L}$ follows laws $\sqrt{I_{\Gamma-\Delta}} = \hbar \omega - E_{\Gamma-\Delta}$ and $\sqrt{I_{\Gamma-L}} = \hbar \omega - E_{\Gamma-L}$, respectively. Above the indirect gaps, a direct gap $E_{\Gamma-\Gamma}$ is observed. The band gaps $E_{\Gamma-\Delta}$, $E_{\Gamma-L}$ and $E_{\Gamma-\Gamma}$ shift to higher energies due to the quantum confinement effect. They also reported that the PLE spectra coincide with optical absorption spectra. That is, photo-generated electron-hole pairs relax into the luminescent state at a constant rate, independent of excitation photon energy. Because the PLE spectra shown by open circles in Fig. 2 follows the law that Si nanocrystallites obeys, it is evident that visible PL shown in Fig. 1(a) is due to Si nanocrystallites precipitated in a SiO$_2$ film.

In order to investigate photo-excitation of Er$^{3+}$ ions, we measured PLE spectrum for Er$^{3+}$ ions. Closed circles in Fig. 2 shows PLE spectrum monitored at 1530 nm. It is found that PLE spectrum of Er$^{3+}$ ions coincide with that of Si nanocrystallites. Therefore, it is concluded that Er$^{3+}$ ions are excited via energy transfer from the luminescent state in Si nanocrystallites.

![Figure 3](image)

**Figure 3.** PL intensity of Er$^{3+}$ ions doped in Si-rich silicon oxide films deposited by laser ablation at (a) 4 J/cm$^2$ and (b) 100 J/cm$^2$.

Figure 3 shows PL intensity of Er$^{3+}$ ions in Si-rich silicon oxide films deposited by laser ablation of Er-coated Si targets at (a) 4 J/cm$^2$ and (b) 100 J/cm$^2$, as a function of annealing temperature after the deposition. We found optimum annealing temperatures of 600°C and 900°C for films deposited at 4 J/cm$^2$ and 100 J/cm$^2$, respectively. That is, there exist two distinct types of Er-doped films. As described above, one is a SiO$_2$ film that includes Si nanocrystallites and Er$^{3+}$ ions, which are fabricated by depositing at 100 J/cm$^2$ and annealed at 900°C. Because precipitation of Si nanocrystallites does not occur during annealing at low temperature such as 600°C, the other film, i.e., SiO$_x$ films deposited at 4 J/cm$^2$ and annealed 600°C, does not contain Si nanocrystallites. That is, the films deposited at 600°C are still SiO$_x$ films even after annealing. Because SiO$_2$ has a band gap wider than 8 eV and an Er$^{3+}$ ion has discrete, narrow and weak excitation bands, excitation light is possibly absorbed by electronic state in SiO$_x$ films and the absorbed energy is transferred to Er$^{3+}$ ions.

We should emphasize that we can fabricate the two types of Er-doped silicon-rich silicon oxide films by laser ablation, which has not been achieved by other methods so far. Changing kinetic energy of ablated species most possibly enables us to fabricate two kinds of Er-doped silicon-rich silicon oxide films. Because the kinetic energy strongly depends on the fluence, microscopic structure of the Er-doped SiO$_x$ films are most possibly governed by kinetic energy of depositing Si ions and Si neutrals ejected from Si targets. Using the laser ablation method, we found...
that Er-doped silicon-rich silicon oxide films fabricated by annealing at 600°C are suitable for silicon-based 1.5-μm light emitter. For further investigation, it is required to assign microscopic structures and energy transfer mechanism of the Er-doped films deposited at 4 J/cm² and annealed at 600°C.

4. Conclusion
We have investigated the fabrication of two types of Er-doped silicon oxide films. The films were prepared by ablating a Si target covered with a thin Er metal layer, by Nd:YAG laser light at 50 mJ/pulse in 40 Torr O₂ gas. After the deposition of the Er-dispersed SiOₓ (x ~ 1.4) films, the films were annealed in Ar gas. We found that Er-doped films deposited at (a) 4 J/cm² and (b) 100 J/cm² have the optimum annealing temperature of 600°C and 900°C, respectively. Furthermore, we found that Er-doped films deposited at 4 J/cm² exhibit much more intense light emission at 1.5 μm than those deposited at 100 J/cm². For the Er-doped films deposited at 100 J/cm², it is evident that electron-hole pairs are generated in Si nanocrystallites precipitated in a SiO₂ film and that recombination energy is transferred to Er³⁺ ions that emit 1.5 μm light.

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