

Optical excitation of Er ions with 1.5 μm luminescence via the luminescent state in Si nanocrystallites embedded in SiO_2 matrices

Tetsuya Makimura,^{a)} Keiichi Kondo, Hiroshi Uematsu, Changqing Li, and Kouichi Murakami

Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

(Received 27 June 2003; accepted 30 October 2003)

Optical excitation bands have been investigated for Er-doped SiO_2 films, including Si nanocrystallites as sensitizers. The Er-doped films with photoluminescence at 1.5 μm were fabricated using a laser ablation technique. It is found that the major continuous portion of the excitation bands for Er ions completely coincides with that of Si nanocrystallites at room temperature. Thus, it has been demonstrated that the second indirect absorption band of Si nanocrystallites can be used for efficient excitation of Er ions. The photoluminescence spectroscopy revealed that Er ions are possibly excited from the ground state $^4I_{15/2}$ to the first excited state $^4I_{13/2}$ by the energy transfer from the singlet excitons in Si nanocrystallites. © 2003 American Institute of Physics. [DOI: 10.1063/1.1636247]

Er-doped Si crystals emit light at 1.5 μm and can be applied to optoelectronic devices compatible to Si-based large scale integrated circuit technology.¹⁻⁴ However, thermal quenching, observed at room temperature, presents one of the most crucial problems for applications.⁵ Nanostructuring has been investigated for the prevention of this thermal quenching.⁶⁻¹² In addition, Si nanocrystallites have advantages of (a) large absorption cross sections (10^{-16} – 10^{-14} cm^2 , depending on excitation energy)¹³ compared to Er ions (10^{-21} cm^2);¹⁴ (b) continuous absorption bands;¹⁵ (c) a high concentration of active Er ions (2×10^{20} cm^{-3})¹⁶ compared to those in Si crystals (1.3×10^{18} cm^{-3});⁴ and (d) long-lived excitation source^{17,18} compared to Er decay time.¹⁹ Therefore, Er-doped SiO_2 films, including Si nanocrystallites (nc-Si/ SiO_2) as sensitizers, can be also applied to compact optical amplifiers at 1.5 μm , pumped by laser diodes or flash lamps.

Many researchers have proposed energy transfer from optically excited Si nanocrystallites to Er ions.^{7-12,20,21} Kenyon *et al.*²⁰ fabricated Si-rich Er-doped silica films and found that Er luminescence at 1.5 μm is obtained even when the excitation wavelength is away from characteristic absorption bands of Er ions. Hence, they proposed an energy transfer from Si nanocrystallites. Fujii *et al.* reported that Er photoluminescence (PL) increases with Er concentration, while the PL of Si nanocrystallites decreases.¹⁰ Although they reported excitation efficiencies at wavelengths of Ar^+ laser lines, it was difficult to deduce excitation bands. Wu *et al.* reported PL excitation (PLE) spectra of Er ions implanted into porous silicon.⁹ They, however, reported a broad PLE band without any meaningful structure. Zhao *et al.* reported PLE spectrum for Er-doped Si nanocrystallites, having a size of 10 nm. The nanocrystallites were too large to have a quantum confinement effect, and direct excitation of Er ions dominated.²¹ For practical applications, it is neces-

sary to investigate optimum excitation bands as well as energy transfer processes.

Si nanocrystallites have the following characteristic features. (a) PL intensity increases as temperature increases from cryogenic to room temperature (RT) at an excited power density higher than 250 mW/cm^2 .¹⁷ The increase is explained by thermal activation of excitons in the lowest triplet state, which is optically inactive, to the luminescent singlet state.^{17,22} (b) Optical absorption occurs via an indirect transition as observed in indirect semiconductors.¹⁵ The fundamental absorption gap $E_{\Gamma-\Delta}$ is the energy difference between the $\Gamma_{25'}$ point in the valence band and the Δ_1 points in the conduction band. Above $E_{\Gamma-\Delta}$, the PLE intensity (I_{PLE}) follows a $\sqrt{I_{\text{PLE}}\hbar\omega} \propto \hbar\omega - E_{\Gamma-\Delta}$ law, where $\hbar\omega$ is photon energy of excitation light. Note that quantum efficiency can be assumed to be independent of $\hbar\omega$. Below the direct gap energy $E_{\Gamma-\Gamma}$, another indirect PLE band is observed. The indirect gap $E_{\Gamma-L}$ is attributed to transition from the $\Gamma_{25'}$ point to the L_1 points. The bandgaps $E_{\Gamma-\Delta}$, $E_{\Gamma-L}$, and $E_{\Gamma-\Gamma}$ shift to higher energies due to the quantum confinement effect, depending on size.

The PL properties of Er ions should be affected by those of Si nanocrystallites if Er atoms are excited via Si nanocrystallites. For practical applications, photoexcitation beyond the second gap $E_{\Gamma-L}$ will be important because the oscillator strength is about five times as large as that of the $\Gamma_{25'} - \Delta_1$ transition.¹⁵ In a previous paper, we reported an increase in Er PL intensity with increasing temperature in Er-doped nc-Si/ SiO_2 films fabricated using a laser ablation technique.¹² We proposed that Er atoms are excited via the luminescent singlet state of Si nanocrystallites.

In the present letter, we have investigated the optical excitation, via Si nanocrystallites, of Er ions doped in nc-Si/ SiO_2 films. We fabricated the Er-doped nc-Si/ SiO_2 films using a laser ablation technique, and performed PL spectroscopy and PLE spectroscopy for both Er ions and Si nanocrystallites. We report optical excitation bands of the Er-doped films in a region which includes the $\Gamma_{25'} - L_1$ transition region. Furthermore, we have investigated the energy

^{a)}Electronic mail: makimura@ims.tsukuba.ac.jp

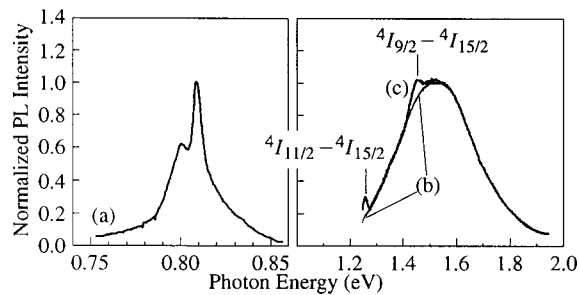


FIG. 1. PL spectra of (a) Er ions, and (b) and (c) Si nanocrystallites. The spectra (b) and (c) were measured under photoexcitation at 2.48 and 2.39 eV, respectively.

transfer by comparing the PL properties of Er ions with those of Si nanocrystallites. The detailed excitation path is suggested by PL spectra taken under excitation at photon energies, both at resonance and off-resonance with the direct excitation of Er ions.

An Er-doped SiO_2 film with precipitated Si nanocrystallites was fabricated using a laser ablation technique.¹² First, to deposit an Er thin film on a Si substrate, an Er metal target was laser ablated in a vacuum chamber by 1200 shots of 532 nm Nd:YAG laser light with a pulse duration of 7 ns at ~ 100 J/cm². Next, the Si target, covered with the Er thin film, was laser ablated in O_2 gas at 40 mTorr to deposit an Er-dispersed SiO_x (SiO_x :Er) film. Finally, the SiO_x :Er film was annealed at 900 °C in an Ar gas flow for 30 min. to precipitate Si nanocrystallites in a SiO_2 film. The precipitation was confirmed using a transmission electron microscope. Wu *et al.* also reported the precipitation by annealing at temperatures of 600–1000 °C.²³ For comparison, an Er-doped SiO_2 film without Si nanocrystallites was similarly prepared, but in O_2 gas at 150 mTorr. The composition of SiO_x :Er films was measured using Rutherford backscattering spectroscopy.

The PL of Er ions and Si nanocrystallites was observed under photoexcitation with either (a) optical parametric oscillator (OPO) light with a pulse duration of 7 ns at a repetition rate of 10 Hz or (b) cw He-Cd laser light at 325 nm. The PL in the near-infrared region was detected using an InGaAs photodiode (Hamamatsu, G8605-25), and amplified using an operation amplifier (Analog Devices, AD549). The visible PL was detected using a Si photodiode array.

Figure 1 shows PL spectra of a nc-Si/ SiO_2 film with an Er concentration of 5×10^{20} cm⁻³, in the near-infrared region (a) and in the visible region (b) and (c). Each spectrum is normalized to its maximum intensity. Spectrum (a) was recorded at RT under photoexcitation using a He-Cd laser at 2.4 mW/cm². The peak energy of 0.809 eV and the spectral shape are characteristic of the intra-4*f* transitions of Er ions from the first excited state $^4I_{13/2}$ to the ground state $^4I_{15/2}$. Spectra (b) and (c) were recorded under photoexcitation by OPO light, detuned (at 2.48 eV) and tuned to Er direct excitation from the ground state $^4I_{15/2}$ to the excited state $^2H_{11/2}$ (at 2.39 eV), respectively, at ~ 25 W/cm² at 6 K. The peak energy and the bandwidth are characteristic of Si nanocrystallites. The size of the Si nanocrystallites prepared in 40 mTorr O_2 gas is estimated to be 3 nm by the PL peak energy.¹⁸ It is remarkable that Er intra-4*f* transitions of $^4I_{9/2} - ^4I_{15/2}$ at 1.46 eV and $^4I_{11/2} - ^4I_{15/2}$ at 1.27 eV were

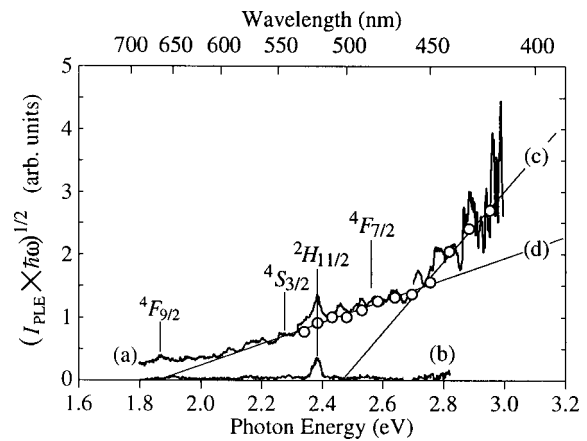


FIG. 2. PL excitation spectra of Si nanocrystallites (open circles) and Er ions doped in SiO_2 films (a) with and (b) without Si nanocrystallites. Straight lines (c) and (d) indicate $\Gamma_{25'} - \Delta_1$ and $\Gamma_{25'} - L_1$ absorption, respectively, in Si nanocrystallites.

observed for photoexcitation only by OPO light tuned to the resonant excitation at 2.39 eV.

Figure 2 shows PLE spectra of SiO_2 films with an Er concentration of 5×10^{20} cm⁻³ (a) with and (b) without Si nanocrystallites. The spectra were recorded at RT by monitoring Er PL intensity at 0.809 eV under photoexcitation by OPO light at ~ 10 mW/cm². For both films, narrow excitation bands were observed, as indicated by the markers, although not all of them are identified. The narrow bands correspond to direct excitations of the 4*f* system of Er ions in the ground state $^4I_{15/2}$. In the Er-doped SiO_2 film, only the direct excitation bands of Er ions were observed. In addition, continuous bands were observed for the Er-doped nc-Si/ SiO_2 film, as indicated by the straight lines (c) and (d).

The open circles in Fig. 2 show a PLE spectrum of Si nanocrystallites monitored at 1.6 eV. The PLE intensity is normalized so that correlation with the Er PLE is clearly seen. The normalization coefficient includes a ratio of optically active Er ions to Si nanocrystallites as well as each quantum efficiency. As indicated by straight lines (c) and (d), the continuous part follows the indirect transition laws $\sqrt{I_{\text{PLE}}} \times \hbar\omega \propto \hbar\omega - E_{\Gamma-\Delta}$ and $\sqrt{I_{\text{PLE}}} \times \hbar\omega \propto \hbar\omega - E_{\Gamma-L}$, respectively. The obtained gaps $E_{\Gamma-\Delta} = 1.86$ eV and $E_{\Gamma-L} = 2.46$ eV are in good agreement with reported gaps for a detection energy of 1.6 eV.¹⁵

We found that the continuous PLE bands of Er ions are completely identical to those of Si nanocrystallites. Therefore, it is evident that Er ions are excited via excitons in the luminescent singlet states in Si nanocrystallites. It should be emphasized that Er ions are efficiently excited via Si nanocrystallites by light with a photon energy beyond the $\Gamma_{25'} - L_1$ gap.

Figure 3 shows PL intensity of (+) Er ions at 0.809 eV (I_{Er}) and (×) Si nanocrystallites at 1.55 eV (I_{Si}) at RT as a function of Er concentration. The PL measurements were performed at RT under photoexcitation by He-Cd laser light at ~ 300 mW/cm². PL intensity of Si nanocrystallites is normalized using a fitting parameter *k*. With increasing Er concentration, Er PL intensity increases, while PL intensity of Si nanocrystallites decreases in an inverse correlation. Total PL intensity ($= I_{\text{Er}} + kI_{\text{Si}}$), shown by circles (○), is constant at Er concentrations up to 1.5×10^{21} cm⁻³. Note that the con-

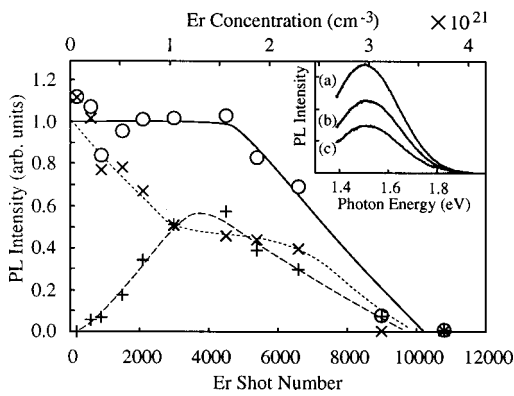


FIG. 3. PL intensity of Si nanocrystallites (\times) and Er ions ($+$) as a function of Er shot number. The total intensity (\circ) is constant up to 4500 shots. The lines are guides to the eye. The inset shows PL spectra of Si nanocrystallites for Er-doped nc-Si/SiO₂ films with Er shot number of (a) 200 shots, (b) 1500 shots, and (c) 3000 shots.

stant region appears only if the complete inverse correlation is valid, even though we include the parameter k . The inverse correlation in Fig. 3 further confirms the energy transfer via the luminescent singlet state of excitons in Si nanocrystallites to the Er ions.

As proposed by Kik *et al.*,²⁴ the obtained results are explained consistently, assuming that Si nanocrystallites connected to Er ions exhibit no visible PL because exciton energy is transferred to Er ions, while Si nanocrystallites not connected to Er ions exhibit visible PL.

The detailed excitation path is suggested by the difference between spectra (b) and (c) in Fig. 1. The photoexcitation at 2.39 eV (resonance) partially causes direct excitation of Er ions from the ground state $^4I_{15/2}$ to the excited state $^4H_{11/2}$. During de-excitation processes, light emission from the lower excited states $^4I_{9/2}$ and $^4I_{11/2}$ was observed. In contrast, neither $^4I_{9/2} - ^4I_{15/2}$ nor $^4I_{11/2} - ^4I_{15/2}$ transitions were observed under photoexcitation at 2.48 eV (off-resonance). These results rule out the energy transfer to the $^4I_{9/2}$ or $^4I_{11/2}$ state. Otherwise, light emission initiated from these states would be observed. Therefore, it is possible that Er ions are excited to the first excited state $^4I_{13/2}$ by energy transfer from the excitons in Si nanocrystallites. The Er light emission at 1.27 eV is more intense in films annealed at higher temperatures such as 1000 and 1100 °C. The result suggests that the energy transfer is governed by configurations such as (a) atoms neighboring Er ions and (b) the distance between Er ions and Si nanocrystallites.

Recently, Watanabe *et al.* reported dips in PL spectra of Si nanocrystallites.¹¹ They argued that the dips correspond to resonant excitation from Si nanocrystallites to the second or the third excited states in Er ions. If the resonant excitation dominated in our samples, PL spectra in the inset in Fig. 3 would be much deformed by the dips. However, we could not find any change in the shape, but rather in the integrated intensity of the spectra by Er doping. Consequently, we propose that dominant energy transfer occurs from the excitons in Si nanocrystallites to the $^4I_{13/2}$ state.

In conclusion, we have investigated optical excitation of Er ions doped in SiO₂ films, including precipitated Si nanoc-

rySTALLITES as sensitizers. The Er-doped films were fabricated by thermal annealing of Er-dispersed SiO_x films that were deposited by laser ablation of Si targets, covered with Er thin films, in O₂ gas. We found that PLE spectra of Er ions probed at 1.5 μm completely coincide with those of Si nanocrystallites at RT. In addition, PL intensity of Er ions is inversely correlated with that of Si nanocrystallites. Thus, it is evident that Er ions are excited via photogenerated singlet excitons in Si nanocrystallites. PL spectra suggests that Er ions are excited from the ground state $^4I_{15/2}$ to the first excited state $^4I_{13/2}$. It is claimed that the Er-doped films can be efficiently excited by light with photon energy beyond the second indirect gap of Si nanocrystallites at 2.7 eV.

The authors would like to thank Prof. K. Shima for Rutherford backscattering spectroscopy. This work was partially supported by Industrial Technology Research Grant Program in '03 from NEDO of Japan, University of Tsukuba Research Project, and Research Consortium for Synthetic Nano-Function Materials Project.

- ¹S. Coffa, F. Priolo, G. Franzò, V. Bellani, A. Carnera, and C. Spinella, *Phys. Rev. B* **48**, 11782 (1993).
- ²H. Przybylinska, W. Jantsch, Y. Suprun-Belavitch, M. Stepikhova, L. Palmetshofer, G. Hendorfer, A. Kozanecki, R. J. Wilson, and B. J. Sealy, *Phys. Rev. B* **54**, 2532 (1996).
- ³J. Stimmer, A. Reittinger, J. F. Nützel, G. Abstreiter, H. Holzbrecher, and C. Buchal, *Appl. Phys. Lett.* **68**, 3290 (1996).
- ⁴D. J. Eaglesham, J. Michel, E. A. Fitzgerald, D. C. Jacobson, J. M. Poate, J. L. Benton, A. Polman, Y.-H. Xie, and L. C. Kimerling, *Appl. Phys. Lett.* **58**, 2797 (1991).
- ⁵S. Coffa, G. Franzò, F. Priolo, A. Polman, and R. Serna, *Phys. Rev. B* **49**, 16313 (1994).
- ⁶J. H. Shin, G. N. van den Hoven, and A. Polman, *Appl. Phys. Lett.* **66**, 2379 (1995).
- ⁷A. Dorofeev, E. Bachilo, V. Bondarenko, N. Gaponenko, N. Kazuchits, A. Leshok, G. Troyanova, N. Vorozov, V. Borisenko, H. Gnaser, *Thin Solid Films* **276**, 171 (1996).
- ⁸U. Hömmerich, F. Namavar, A. Cremins, and K. L. Bray, *Appl. Phys. Lett.* **68**, 1951 (1996).
- ⁹X. Wu, U. Hömmerich, F. Namavar, and A. M. Cremins-Costa, *Appl. Phys. Lett.* **69**, 1903 (1996).
- ¹⁰M. Fujii, M. Yoshida, S. Hayashi, and K. Yamamoto, *J. Appl. Phys.* **84**, 4525 (1998).
- ¹¹K. Watanabe, M. Fujii, and S. Hayashi, *J. Appl. Phys.* **90**, 4761 (2001).
- ¹²C. Li, K. Kondo, T. Makimura, and K. Murakami, *Jpn. J. Appl. Phys.* **42**, 3424 (2003).
- ¹³D. Kovalev, J. Dinner, H. Heckler, G. Polisski, N. Künzner, and F. Koch, *Phys. Rev. B* **61**, 4485 (2000).
- ¹⁴W. J. Miniscalco and R. S. Quimby, *Opt. Lett.* **16**, 258 (1991).
- ¹⁵M. Ben-Chorin, B. Averboukh, D. Kovalev, G. Polisski, and F. Koch, *Phys. Rev. Lett.* **77**, 763 (1996).
- ¹⁶F. Priolo, G. Franzò, D. Pacifici, V. Vinciguerra, F. Iacona, and A. Irrera, *J. Appl. Phys.* **89**, 264 (2001).
- ¹⁷D. Kovalev, H. Heckler, G. Polisski, and F. Koch, *Phys. Status Solidi B* **215**, 871 (1999).
- ¹⁸S. Takeoka, M. Fujii, and S. Hayashi, *Phys. Rev. B* **62**, 16820 (2000).
- ¹⁹G. Franzò, D. Pacifici, V. Vinciguerra, F. Priolo, and F. Iacona, *Appl. Phys. Lett.* **76**, 2167 (2000).
- ²⁰A. J. Kenyon, P. F. Trwoga, M. Federighi, and C. W. Pitt, *J. Phys.: Condens. Matter* **6**, L319 (1994).
- ²¹X. Zhao, H. Isshiki, Y. Aoyagi, T. Sugano, and S. Komuro, *Mater. Sci. Eng., B* **74**, 197 (2000).
- ²²M. L. Brongersma, P. G. Kik, A. Polman, K. S. Min, and H. A. Atwater, *Appl. Phys. Lett.* **76**, 351 (2000).
- ²³X. L. Wu, Y. F. Mei, G. G. Siu, K. L. Wong, K. Moulding, M. J. Stokes, C. L. Fu, and X. M. Bao, *Phys. Rev. Lett.* **86**, 3000 (2001).
- ²⁴P. G. Kik, M. L. Brongersma, and A. Polman, *Appl. Phys. Lett.* **76**, 2325 (2000).