

# Fine structure in the Er-related emission spectrum from Er–Si–O matrices at room temperature under carrier mediated excitation

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## Abstract

Er–Si–O crystalline matrices (ESO) have been synthesized by coating the Si surface with an ErCl/ethanol solution, followed by a two-step annealing process, first in oxygen and second in argon. Fine structures of the Er<sup>3+</sup>-related photoluminescence (PL) spectrum (line width less than 4 meV) have been observed at room temperature. The PL fine structures indicate Stark splitting of the 4f-electron energy levels in erbium ions. The PL excitation spectrum at room temperature shows the carrier-mediated excitation of Er ions. These results suggest that ESO are of a stable and homogeneous structure in semiconducting silicon matrix and are optically very active. The local environment of erbium ions is discussed from the Stark splitting.

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## 1. Introduction

Optical waveguide amplifiers with centimeter length scale need high erbium concentrations of atomic percent range in order to achieve high optical gain. The Er<sup>3+</sup>-related emission is very sensitive to detrimental interactions with the surrounding matrix. The very low solubility of erbium inside the silica matrix enhances the

tendency of erbium clustering, which nearly totally quenches the photoluminescence (PL) emission [1]. In contrast single crystalline Y<sub>2</sub>SiO<sub>5</sub> makes high erbium doping of more than 10% possible, because Er atom substitutes for Y site [2]. As a result, the Er<sup>3+</sup>-related spectra from the homogeneous media behave as fine structures.

In order to realize Si-based optoelectronic integrations [3,4], erbium doping into silicon and related materials has been tried to obtain Er<sup>3+</sup>-related intense emission at room temperature. The validity of oxygen incorporation to enhance Er<sup>3+</sup>-related emission and improve the thermal quenching [2–9], in achieving a stimulated emission at 1540 nm from erbium and oxygen co-doped

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nanocrystalline silicon at room temperature has been demonstrated [10].

In this paper, we report the  $\text{Er}^{3+}$ -related PL spectrum fine structure coming from Er–Si–O crystalline matrices (ESO) at room temperature. In addition to the line width narrowing, the local environment of  $\text{Er}^{3+}$  ion from Stark splitting which appears in the PL spectrum fine structure is also discussed. Note that the excitation process is due to energy transfer to the 4f-electron in  $\text{Er}^{3+}$  ion via recombination of electron–hole (e–h) pairs generated in certain host material.

## 2. Experimental

A single crystal Czochralski-grown n-type silicon (100) wafer (P-doped, resistivity:  $5\ \Omega\text{cm}$ ) etched in a 5% HF solution was used. ESO on Si surface are formed by a spin-coating process (3000 rpm for 1 min) with an  $\text{ErCl}_3$ /ethanol solution, followed by a two-step annealing process: rapid thermal oxidization (RTO) and annealing (RTA) processes. Total amount of Er on a planar Si surface after the coating process was estimated to be about  $3 \times 10^{15}\ \text{cm}^{-2}$  by a Rutherford back-scattering spectrometry (RBS). The combined thermal process with RTO and RTA (RTOA) was performed continuously with a short interval by using a rapid thermal annealing system using a halogen lamp, and by switching off the ambient flow gases between oxygen for RTO and argon for RTA with atmospheric pressure. RTO and RTA processes were carried out typically at  $900^\circ\text{C}$  for 4 min and at  $1200^\circ\text{C}$  for 3 min, respectively. SEM-EDX analysis reveals Er–Si–O island formation and high Er concentration more than 10%. Details of the formation processes are described elsewhere [11].

Photoluminescence (PL) measurements were performed by using 6 single lines of an argon ion laser. The excitation lights were chopped by an acoustic optical modulator, and the cw PL signal was processed by a lock-in technique. Signal processing of the PL time response was performed by a digital storage oscilloscope. The PL emissions were monitored through a 98 cm monochromator by a liquid  $\text{N}_2$ -cooled Ge p–i–n detector.

## 3. Results

Fig. 1 shows the Er-related PL spectra from ESO, observed under the 476.5 nm excitations at room temperature. A sharp intense peak at  $1.529\ \mu\text{m}$  (photon energy of 0.811 eV) with a line width of less than 7 nm (4.0 meV) are observed at room temperature. A fine structure in the PL spectrum can be seen, which is caused by Stark splitting due to the crystalline-field under the specific local environment. Details will be discussed in the next section.

PL peak intensities at  $1.53\ \mu\text{m}$  plotted as a function of excitation wavelengths using six single-lines of the Ar ion laser is also shown in the inset. The 488.0 nm excitation corresponds to the  $\text{Er}^{3+}$  transition  ${}^4\text{I}_{15/2} \rightarrow {}^4\text{F}_{7/2}$ , resulting in the intense emission. However, the off-resonant excitations to the  $\text{Er}^{3+}$  absorption lines are still efficient. This result indicates the existence of indirect excitation processes through energy transfer from e–h pairs generated in certain host material [7,8]. The PL spectra for each excitation condition, corresponding to the predominantly direct and the indirect excitations, are of quite the same shape. The agreement with the fine structures between the direct and the indirect excitations means that both the PL peak emissions come from the same kind of  $\text{Er}^{3+}$  ions. This indicates a possibility of controlling the excited states both electrically and optically.

Fig. 2 shows the Er-related PL intensity and the lifetime at  $1.53\ \mu\text{m}$  plotted as a function of temperature. The PL spectra measured at various temperatures are also shown in the inset. The excitation wavelength is 476.5 nm, corresponding to the e–h pair mediated excitation. The Er-related PL intensity decreases by one-fifth from 20 to 290 K, but the spectrum structure is independent of temperature. In contrast, the lifetime is independent of temperature, and is about 200  $\mu\text{s}$  which is relatively short compared to Er-doped semiconductors. The short lifetime is possibly due to concentration quenching. These results indicate that the temperature quenching of the PL intensity is caused by decreasing of the excitation efficiency, which may be due to thermal enhancement of the non-radiative recombination of e–h pairs.

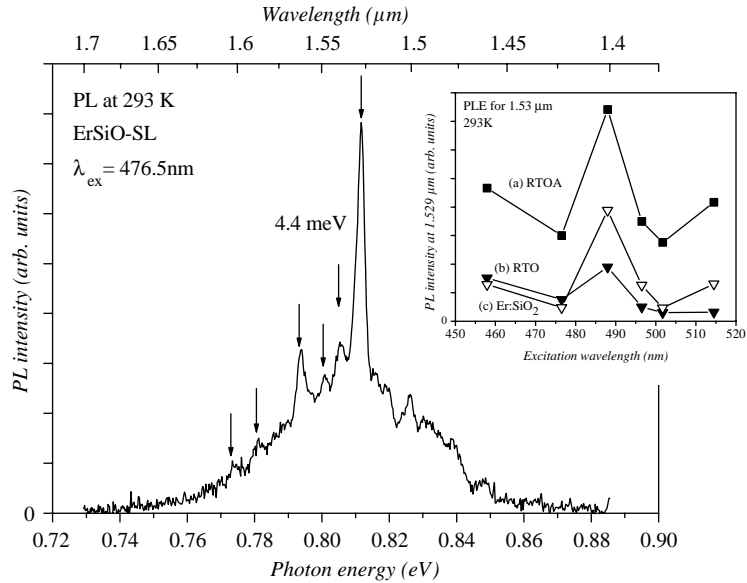


Fig. 1. Room temperature PL spectrum fine structure from ESO excited by 476.5 nm lines of an argon ion laser. A full-width at half-maximum of the main peak at 1529 nm is less than 4.0 meV, and arrows indicate Stark splitting of the ground state ( $^4I_{15/2}$ ) of Er ion. PLE spectra of RTOA (a), RTO (b), and Er:SiO<sub>2</sub> (c) are shown in the inset. The Er-related emission intensity at 1.53 μm is plotted as a function of the excitation wavelength, which is used as six single lines of an argon ion laser. All data were taken at room temperature at a constant pump power of 100 mW.

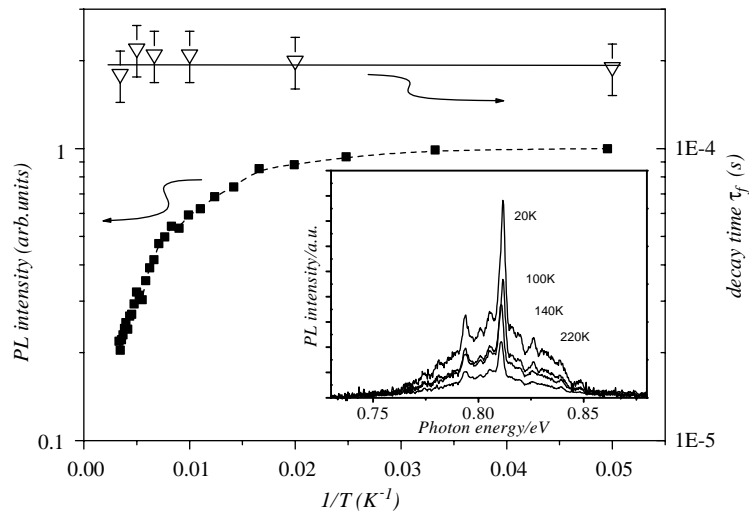


Fig. 2. Er<sup>3+</sup>-related PL intensity at 1.53 μm and the decay time plotted as a function of temperature. The PL spectra measured at various temperatures are also shown in the inset.

#### 4. Discussions

Let us discuss a few points about the line width-narrowing at room temperature. The room tem-

perature emissions have been reported for several Er-doped Si-related materials [3–10]. Almost all of them are fabricated by non-equilibrium thermal processes (i.e. ion implantation [3–5], sputtering [6]

and other deposition techniques [7–10]) and the luminescent centers are considered to be in an inhomogeneous medium. As a result, inhomogeneous broadening of the PL peak line width can occur in such samples synthesized under thermal non-equilibrium conditions. In this experiment, however, the whole fabrication processes are performed under thermal equilibrium on crystalline silicon. The narrow line width observed in the PL spectrum is comparable to homogeneous broadening in the Er-doped glasses, which is extracted from the inhomogeneous broadening emissions by special techniques as fluorescence line narrowing [12] or spectral gain hole burning [13]. Given the larger inhomogeneous broadening in glasses than crystals, it is more difficult to unequivocally measure and assign individual Stark levels. It is caused by its multiplicity of sites and environments due to the amorphous nature. The PL spectrum fine structure indicates that the emissions come from  $\text{Er}^{3+}$  in certain homogeneous medium. This suggests that ESO matrix has single crystalline quality. Although the Er concentration is high enough to cluster together, the

emission is still efficient. The investigations of the oxidation of thin Er and Si layers on  $\text{SiO}_2$  films have shown that it is more favorable to oxidize Er than Si [14]. It is considered that the Er–O complex is formed preferentially in the RTO process because of the lower decomposition temperature of  $\text{ErCl}_3$  (below  $800^\circ\text{C}$ ), and aligned in the following RTA process.

The PL spectrum fine structure is independent of temperature as shown in Fig. 2. Since, according to Boltzmann's law, only the lowest Stark-level in the excited state ( $^4\text{I}_{13/2}$ ) is populated at low temperature, the PL peaks correspond to transitions from the lowest Stark-level in the excited state to the Stark-levels in the ground state ( $^4\text{I}_{15/2}$ ). At room temperature, the occupation probabilities of the higher excited levels of  $^4\text{I}_{13/2}$  are high enough to contribute to the additional emission lines the so-called “hot lines”, but the higher energy tail of PL emission than the main peak at 1529 nm is suppressed even at room temperature. The decay time for the 1.53  $\mu\text{m}$  emission, corresponding to a lifetime of the first excited state, is relatively short to the other Er doped Si related

Table 1

Comparison among Stark level energies of the ground state ( $^4\text{I}_{15/2}$ ) of Er ion measured from different types of Er–Si–O related materials

	Si:Er <sup>a</sup> (FZ–Si) Er–Si <sub>12</sub> <sup>f</sup>	Si(O):Er <sup>a</sup> (CZ–Si) Er–O <sub>6</sub> <sup>f</sup>	Si:Er/O <sup>b</sup> (codoped) Er–O <sub>6</sub> <sup>g</sup>	Al–Ge Silica <sup>c</sup> —	Y <sub>2</sub> SiO <sub>5</sub> :10%Er <sup>d</sup> Er–O <sub>6</sub> <sup>h</sup>	This Paper	Er <sub>2</sub> O <sub>3</sub> <sup>e</sup> Er–O <sub>6</sub> <sup>i</sup>
$^4\text{I}_{15/2}$ (meV)					59.3		60.8, 62.6
	51.8				53.1		
	—	41.4			39.9	38.0	
	30.9	34.4	31.0	24.9–33.2	31.1	30.4	32.9
	19.5	15.3, 23.9	19.0	15.5–16.5	17.4	17.9	19.7
	9.8	8.7	9.5	6.3–7.3	12.4	10.8	9.3, 10.9
	—	4.3	(6.0)		5.8	6.3	4.7
	0	0	0	0	0	0	0

<sup>a</sup> Ref. [15].

<sup>b</sup> Ref. [16].

<sup>c</sup> Ref. [17].

<sup>d</sup> Ref. [2].

<sup>e</sup> Ref. [18].

<sup>f</sup> Ref. [20].

<sup>g</sup> Ref. [21].

<sup>h</sup> Ref. [2].

<sup>i</sup> Ref. [24].

The local environments for each material, expected from extended X-ray absorption fine structures (EXAFS), are also mentioned in the table.

materials, and independent of temperature. The short lifetime is probably responsible for the suppression of the hot lines at room temperature.

The PL spectrum fine structure makes it possible to identify Stark levels of the  $^4I_{15/2}$  manifold in  $Er^{3+}$  ions. Crystalline fields due to the local environment, especially the nearest neighboring atoms, determine the Stark splitting, so that the local environment of  $Er^{3+}$  ions can be identified from the Stark splitting. The emission peaks corresponding to Stark levels of the  $^4I_{15/2}$  manifold in  $Er^{3+}$  ions are indicated by arrows in Fig. 2. Comparison among Stark level energies of the  $^4I_{15/2}$  manifold measured in different types of Er–Si–O related materials (Er doped Si [15,16], silica [17] and crystalline  $Y_2SiO_5:Er$  [2]) and crystalline  $Er_2O_3$  [18] is made in Table 1. The expected local environments for each material are also shown in the table. The positions of the Stark levels vary with the host, and are comparable with those of the crystalline hosts. The Stark levels of ESO reported here are found to be close to their counterparts in the other hosts with a six-fold coordination around Er of the oxygen atoms. Especially, the splitting behavior is in good agreement with those of  $Y_2SiO_5:Er$  [2] and  $Er_2O_3$  [18] crystalline compounds. Doping Er into crystalline  $Y_2SiO_5$ , Er can substitute for Y site and Er–O octohedra ( $Er-O_6$ ) are assembled. The self-assembles of the Er–O octahedron in Er–Si–O systems have been reported frequently [2,19–24], and it is considered to be the true nature in such material systems. It is considered that ESO are similar to erbium silicates ( $Er_2SiO_5$ ,  $Er_2Si_2O_7$ ) in their crystalline structure. The Stark splitting of ESO can be attributed to a six-fold coordination  $Er-O_6$ .

## 5. Conclusion

Fine structures in the  $Er^{3+}$ -related room temperature PL spectra from ESO matrices have been reported. PLE measurements reveal the excitation mechanism, which is due to both the energy transfer from electron–hole pairs generated in the host material and the optical direct absorption of the  $Er^{3+}$  ions. The PL spectra show the fine

structure with a homogeneous linewidth (4 meV), and Stark splitting of 4f electron in  $Er^{3+}$  ions has been observed. These results suggest that ESO are of a stable and homogeneous structure in semi-conducting silicon matrix. From the Stark splitting, the local environment of optically active  $Er^{3+}$  ions in ESO is attributed to a six-fold coordination  $Er-O_6$ .

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