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The mechanism of energy transfer from Si nanocrystals to Er ions in SiO_2

Different mechanisms depending on Er concentration

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Abstract. The mechanism of energy transfer from silicon nanocrystals (Si-nc's) to erbium (Er) ions is studied by analyzing time transient of Er photoluminescence at 1.54 μm. It is shown that two different energy transfer mechanisms, i.e., fast and slow, exist in SiO_2 films containing Si-nc's and Er ions, and that the ratio of slow to fast processes depends on size of Si-nc's and Er concentration. A quantitative analysis reveals that Er ions located within about 1.5 nm from the surface of Si-nc's are excited by the fast process, and those located within about 2.5 nm by the slow process if no Er ions exist within 1.5 nm from the surface. Er ions staying outside these regions cannot be sensitized by Si-nc's.

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Silicon nanocrystals (Si-nc's) act as an efficient photosensitizer for erbium (Er) ions [1–15]. The presence of Si-nc's in Er-doped SiO_2 enhances the effective absorption cross-section of Er ions by more than four orders of magnitude in the visible range [6–8,15]. In addition, the luminescence from Er ions in this system shows almost no temperature quenching. Due to these remarkable features, this system is considered to be a key component to realize a planar waveguide type compact optical amplifier operating at 1.54 μm.

Since photo-sensitization of Er by Si-nc was first reported in 1994 [3], great efforts have been devoted to understanding the mechanism of the energy transfer [7–13]. Strong coupling of Er ions and excitons in Si-nc's and resultant fast energy transfer (faster than 1 μs) have been considered to be responsible for intense luminescence of Er ions [7–13]. However, in our previous work, we found that, in addition to the fast energy transfer process, slow process, whose energy transfer time was estimated to be several tenths of a μs, occurred simultaneously [13]. Moreover, the ratio of fast to slow processes was found to increase with increasing the size of Si-nc's [13]. This size dependence suggests that the mechanism of the fast process is essentially the same as that in Er-doped bulk-Si; an excited electron is trapped to Er related center in the bandgap, and then the recombination energy of a bound exciton is transferred to Er ions by an Auger-like process. On the other hand, the slow process is a characteristic process occurring only in Er and Si-nc codoped SiO_2. This is probably the Förester type Coulombic interaction between Er ions and Si-nc's because the energy transfer rate depends linearly on the oscillator strength of Si-nc's [13].

In this work, we study the ratio of slow to fast processes as a function of Er concentration. We will demonstrate that the ratio depends strongly on Er concentration, and will establish a model which explain the ratio as a function of Er concentration and size of Si-nc's consistently.

SiO_2 films containing Si-nc's and Er ions were prepared by a co-sputtering method. Details of the preparation procedures are described in our previous papers [4,5]. Si, SiO_2 and Er_2O_3 were simultaneously sputter-deposited in argon (Ar) gas, and the deposited films (about 1 μm in thickness) were annealed in a nitrogen (N_2) gas (99.999%) atmosphere for 30 min at temperatures between 1100 and 1250 °C. Si-nc's were grown in films of the mixture of SiO_2 and Er_2O_3 during the annealing. In this method, the size of Si-nc's can be controlled by annealing temperatures. The average size of Si-nc's was estimated by cross-sectional transmission electron microscopic (TEM) observations. In this work, the average size of Si-nc's (d_{Si}) was changed from 3.5 to 5.1 nm in diameter. The concentration of Er ions in whole films (C_{Er}) was changed from 1×10^{18} to 1×10^{19} cm^{-3}, and that of excess Si was fixed to 4×10^{22} cm^{-3}. In this Er concentration range, Er-Er interaction is negligibly small. For the photoluminescene (PL) time response measurements, a 532.0 nm line

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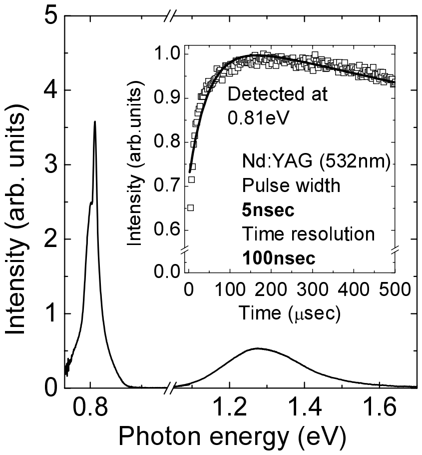

Fig. 1. PL spectrum of SiO_2 thin film containing Er ions and Si-nc's. In the inset, PL time transient at 0.81 eV just after 5 ns pulsed excitation is shown. The open squares are experimental results, and the solid curve is a result of model fitting.

of a Nd:YAG laser was used as the excitation source. The pulse width was 5 ns and the repetition frequency was 20 Hz. A multi-channel scalar was used in obtaining decay curves. The overall time resolution of the system was better than 100 ns.

A typical room temperature PL spectrum of a SiO_2 thin film containing Si-nc's and Er ions is shown in Figure 1. Strong emission can be observed at around 1.3 eV and 0.81 eV. The 1.3 eV peak is assigned to the recombination of excitons confined in Si-nc's, and the 0.81 eV one to the intra-$4f$ shell transitions of Er ions [4,5].

The inset of Figure 1 shows PL time transient of Er at 0.81 eV. We can see that the PL intensity of Er rises fast until reaching about 65% of the maximum intensity, and then starts to rise slowly. This two step rising of the intensity means that there are two energy transfer processes, i.e., fast and slow processes. The observed PL time transient is fitted by a model taking into account two energy transfer processes having different energy transfer rates. The solid curve in the inset is the result of fitting. From the fitting, the ratio of slow to fast processes is estimated. The model to estimate the ratio is described in detail in our previous paper [13].

The ratio of slow to fast processes estimated from the fitting is shown in Figure 2 as a function of size of Si-nc's (a) and Er concentration (b). The ratio depends both on the size and Er concentration. The observed dependences are considered to arise from different average distance between Si-nc's and Er ions, because the fast process requires considerably small separation between Er ions and Si-nc's, while the slow one can occur even if the separation is relatively large.

In order to analyze quantitatively, we introduce a simple model in which Er ions are categorized into three groups depending on the location relative to Si-nc's. We consider three spherical fields around a Si-nc in a cubic as shown in the inset of Figure 2b. Er ions located in the first field (region (I)) which is the closest to Si-nc are excited by the fast process, and those in the second field (region (II)) by the slow process. Er ions located outside the second field (region (III)) do not interact with Si-nc. Here, the volume of the cubic (V_{cubic}) was determined to be the reciprocal of the concentration of Si-nc's, which was estimated from excess Si concentration and average size of Si-nc's. The number of Er ions in the cubic (N_{Er}) was obtained from Er concentration.

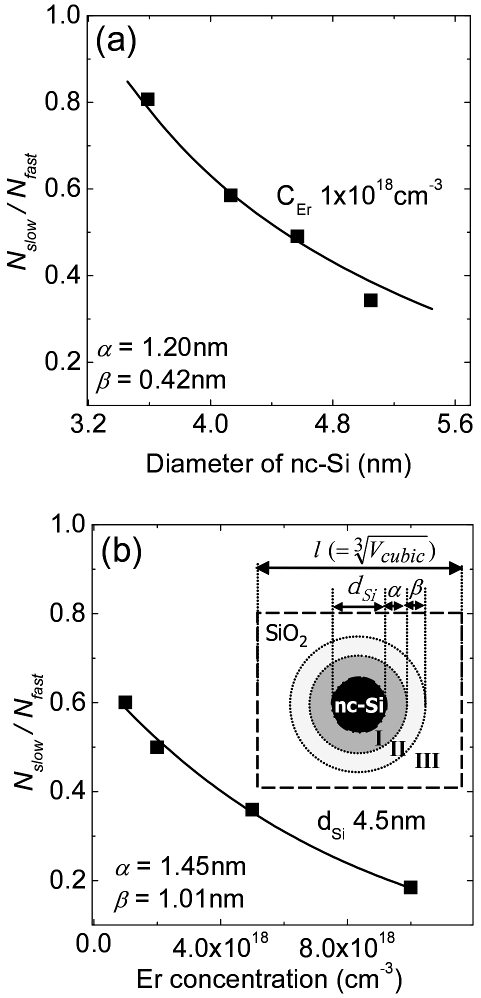

Fig. 2. The ratio of slow to fast processes as a function of Si-nc's size (a) and Er concentration (b). Filled squares are experimental results, and solid curves are results of model fitting. In the model, three spherical fields around a Si-nc are considered (the inset of (b)).

In order to simplify the problem, we make following assumptions. First, Er ions are not inside Si-nc's but on the surface or outside Si-nc's, because the solubility of Er ions in bulk-Si is very low (10^{14}–10^{16} cm^{-3}). Second, one Si-nc can excite at most one Er ion under 5 ns pulse excitation, because if two excitons are excited in a Si-nc, one of them recombines nonradiatively by Auger interaction between two excitons before transferring its energy to Er ions.

Under these assumptions, the requirement necessary for the fast process is the existence of at least one Er ion in region (I). Assuming that Er ions are uniformly dispersed in SiO_2, the ratio of Si-nc's contributing to the fast process with respect to all Si-nc's (N_{fast}) is given by,

$$N_{fast} = 1 - \left(\frac{V_2 + V_3}{V_1 + V_2 + V_3}\right)^{N_{\mathrm{Er}}}, \qquad (1)$$

where V_1, V_2, and V_3 are the volumes of regions (I), (II), and (III), respectively.

In a similar manner, the ratio of Si-nc's contributing to the slow process can be easily obtained. It should be noted here that if at least one Er ion exists in the region (I), the slow process is suppressed by the fast process. Thus the requirement necessary for the slow process is the existence of at least one Er ion in region (II) and no Er ion in region (I). Therefore, the ratio of Si-nc's contributing to the slow process (N_{slow}) is given by,

$$N_{slow} = \left(\frac{V_2 + V_3}{V_1 + V_2 + V_3}\right)^{N_{\mathrm{Er}}} - \left(\frac{V_3}{V_1 + V_2 + V_3}\right)^{N_{\mathrm{Er}}}. \qquad (2)$$

Thus, the ratio of slow to fast processes (N_{slow}/N_{fast}) can be written

$$\frac{N_{slow}}{N_{fast}} = \frac{(V_2 + V_3)^{N_{\mathrm{Er}}} - V_3^{N_{\mathrm{Er}}}}{(V_1 + V_2 + V_3)^{N_{\mathrm{Er}}} - (V_2 + V_3)^{N_{\mathrm{Er}}}}, \qquad (3)$$

where $V_1 = 4\pi\{(R+\alpha)^3 - R^3\}/3$, $V_2 = 4\pi\{(R+\alpha+\beta)^3 - (R+\alpha)^3\}/3$, and $V_3 = V_{cubic} - 4\pi(R+\alpha+\beta)^3/3$. α and β are the thickness of region (I) and (II), and R is the radius of Si-nc's ($= d_{\mathrm{Si}}/2$).

We tried to reproduce the observed data in Figure 2 by fitting them with the equation (3) by using α and β as fitting parameters. Results of the fittings are shown by solid curves. Both the size and the Er concentration dependences are well fitted by the model. α and β were estimated to be 1.45 nm and 1.01 nm from Figure 2a, and 1.20 nm and 0.42 nm from Figure 2b. The good reproduction of the observed results indicates that the model is qualitatively correct and the ratio of slow to fast processes is in principle determined by the average distance between Er ions and Si-nc's.

However, α and β estimated from Figures 2a and 2b do not coincide perfectly. This disagreement may come from oversimplification of the model. In particular, we don't take into account the effect of neighboring Si-nc's. This effect is crucial in discussing the size dependence of the ratio in Figure 2b, because in this case, the distance between Si-nc's changes depending on the size. Compared to the size dependence, the effect is smaller and the obtained parameters are more reliable for the Er concentration dependence in Figure 2a, because the distance is fixed.

In conclusion, we have succeeded in demonstrating that there are two different energy transfer processes in SiO_2 films containing Si-nc's and Er ions and the ratio of the two processes depends on the average distance between Si-nc's and Er ions. Our model could reproduce experimental results. However, quantitative agreements were not achieved. To explain all the results quantitatively, higher order effects such as nanocrystal–nanocrystal interaction, Er–second-neighboring-nanocrystal interaction, etc. should be taken into account.

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