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Exciton–erbium coupling and the excitation dynamics of Er^{3+} in erbium-doped silicon-rich silicon oxide

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The exciton–erbium coupling and the excitation dynamics of Er^{3+} in erbium-doped silicon-rich silicon oxide are investigated using time-resolved measurements of Er^{3+} luminescence. The dependence of the Er^{3+} luminescence on the pump power and duration indicates that the exciton–erbium coupling is dominant over carrier–exciton coupling. The results further support the idea that the luminescent Er^{3+} ions are not in the Si nanoclusters but in the interface region surrounding the nanoclusters. © 2001 American Institute of Physics. [DOI: 10.1063/1.1369150]

Since the report by Ennen,¹ Er-doped silicon has been investigated by many researchers with the hope of developing it as the enabling material for realization of silicon-based optoelectronics. Much of the initial research was focused on Er doping of bulk Si. However, despite some success, the luminescence efficiencies, especially at high-temperature and excitation powers, have remained too low to be practical.

Recently, however, it was shown by several researchers that by using silicon-rich silicon oxide (SRSO), which consists of Si nanoclusters embedded in a SiO_2 matrix, strong and efficient Er^{3+} luminescence at room temperature can be obtained.^{2–5} While the exact details are not yet clear, an excitation mechanism similar to that of Er in bulk Si is often used for Er in SRSO. As shown schematically in Fig. 1, incoming photons generate carriers in the nanoclusters which then form an exciton [indicated by the arrow labeled (a)]. As the carriers recombine, they Auger excite the Er^{3+} ions [indicated by the arrow labeled (c)]. Despite the intermediate steps, this carrier-mediated excitation mechanism can be very efficient, with internal quantum efficiencies greater than 10%.^{5,6} Furthermore, because the optical capture cross section of Si nanoclusters are much larger than that of the Er^{3+} levels, the effective excitation cross section of Er in SRSO can be up to 10^6 times greater than that of Er in SiO_2 , where only direct optical absorption is possible.⁵ Finally, because the incoming photons only have to generate carriers, a low-cost broadband light source can be used instead of a laser, potentially paving the way for developing low-cost, silicon-based optical devices such as waveguide amplifiers.

However, such a direct transfer of the model from bulk Si to SRSO presents several difficulties because SRSO, unlike bulk Si, is a heterogeneous mixture of nanoclusters and SiO_2 with carriers that are confined within the nanoclusters. Thus, it may be expected that many different carrier–exciton and exciton–erbium couplings are possible, and that the ones dominant in SRSO may be different from those in bulk Si. As coupling with excitons is a crucial step in determining Er^{3+} luminescence, more understanding of this mechanism is needed for further improvements in the Er^{3+} luminescence and developments of possible devices.

In this letter, we investigate the carrier–exciton and exciton–erbium coupling by measuring the time-resolved Er^{3+} luminescence. We find that exciton–erbium coupling is dominant over carrier–exciton coupling. The results are consistent with the suggestion that luminescent Er ions are not inside the Si nanoclusters, but in the SiO_2 matrix near the nanoclusters.

Er-doped SRSO thin films were deposited on a *p*-type [100] wafer by the electron-cyclotron-resonance plasma-enhanced vapor-deposition method with concurrent sputtering of the Er target and a subsequent rapid thermal anneal for 5 min at 950 °C. This recipe was shown to result in optimum Er^{3+} luminescence.⁷ The Si content (C_{Si}) of films was 41 or 35 at. %, and the erbium content and film thickness were ~ 0.1 at. % and $\sim 1 \mu\text{m}$, respectively. All measurements were done at room temperature using the 488 nm line of an Ar-ion laser, 1/4 m monochromator, and employing the lock-in technique. Infrared and visible photoluminescence (PL) spectra were detected with InGaAs and Si photodetector, respectively, and all spectra were corrected for the system response. Time-resolved Er^{3+} PL traces were measured using a digitizing oscilloscope.

Figure 2 shows the visible and infrared PL spectra of the Er-doped SRSO films. For the PL measurements, hydrogenation was performed at 700 °C for 1 h in forming gas (90% N_2 and 10% H_2) to reduce the PL from defects. Broad luminescence from 0.6 to 1.1 μm , typical of Si nanoclusters, and

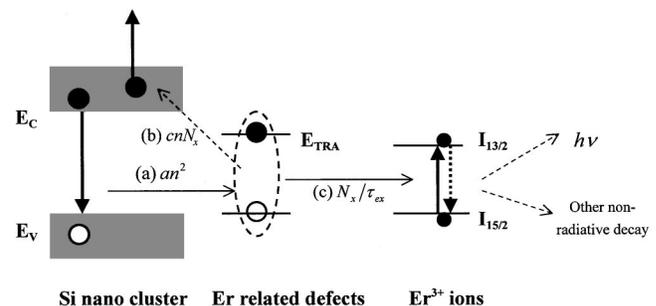


FIG. 1. Excitation process of Er^{3+} ions in Er-doped SRSO by mediated carriers. (a) Free carriers are trapped Er-related defects and (b) these electron–hole pairs can be deexcited by Auger excitation of free carriers or (c) can excite Er^{3+} ions.

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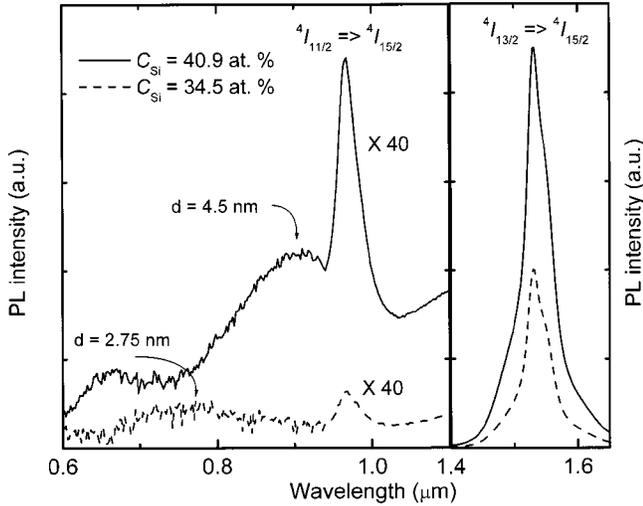


FIG. 2. Photoluminescence spectra from hydrogenated Er-doped SRSO films at room temperature. Broad 0.6–1.1 μm , sharp 0.98, and 1.54 μm luminescence bands are contributed to exciton recombination of Si nanocrystal, Er^{3+} $4f$ transition, and Er^{3+} $4f$ transition, respectively.

sharp peaks due to the $^4I_{11/2} \rightarrow ^4I_{15/2}$ and $^4I_{13/2} \rightarrow ^4I_{15/2}$ intra- $4f$ transition of Er^{3+} can be observed. Based on the published results relating the cluster PL peak position with cluster size,⁸ the average diameters of the Si clusters are estimated to be ~ 3 and ~ 5 nm for samples with C_{Si} of 35 at. % and C_{Si} of 41 at. %, respectively, implying a nanocluster density of $\sim 3 \times 10^{18} \text{ cm}^{-3}$ for both films. Note that the 1.54 μm Er^{3+} luminescence is stronger than the nanocluster luminescence by two orders of magnitude, implying a very efficient energy transfer from the Si nanoclusters to Er^{3+} ions.

To investigate the excitation dynamics, we monitored the Er^{3+} PL intensity as a function of time as the pump beam is turned on and quickly turned off. The total width of the pump pulse, Δt , and the pump power p were varied, but the total pump energy ($E = p\Delta t$) was maintained at 50 μJ . From the time-resolved measurements, we have deduced the value $I(\Delta t)$, the Er^{3+} PL intensity at the end of the excitation pulse, and $U(\Delta t)$, the total luminescent energy measured during the excitation pulse.

To analyze the data, we can set up a rate equation for the density of excitons and the number of excited Er^{3+} ions as

$$\frac{dN_x}{dt} = an^2 - cnN_x - \frac{N_x}{\tau_{\text{ex}}}, \quad (1)$$

and

$$\frac{dN_{\text{Er}}^*}{dt} = \frac{N_x}{\tau_{\text{ex}}} - N_{\text{Er}}^*W, \quad (2)$$

respectively. In Eqs. (1) and (2), N_x , n , and N_{Er}^* are the number of excitons, the number of free carriers, and the total number of excitable Er^{3+} ions, respectively, and a , τ_{ex} , W , and c are exciton generating coefficient by free carriers, excitation lifetime from exciton to Er^{3+} ions, decay rate of excited Er^{3+} ions, and Auger excitation rate of free carriers by excitons, respectively. This rate equation is a simplified form of that suggested by Palm *et al.*⁹ In simplifying, we assumed that only a small fraction of Er^{3+} ions are excited. This assumption was confirmed by observing that the Er^{3+}

PL intensity did not deviate appreciably from the linear dependence upon pump power up to the highest pump power used, which was 100 mW. Based on published theoretical and experimental results,^{5,8} we also assumed that the exciton generation rate from free carriers is very fast, such that the exciton population saturates very quickly. Finally, we assume that, as is the case in bulk Si,^{9,10} that the free carriers are generated bimolecularly as $n^2 = \beta p$, where n , β , and p are the number of free carriers, the coefficient of free-carrier generation, and pump power, respectively.

Note that we include the possibility of carrier-mediated removal of excitons [indicated by the arrow labeled (b) in Fig. 1]. It is also possible for carriers to deexcite excited Er^{3+} . This effect will be discussed later.

From the above equations, we find

$$I(\Delta t) = N_{\text{Er}}^*(\Delta t)W_{\text{sp}} = \frac{N_x W_{\text{sp}}}{\tau_{\text{ex}} W} (1 - e^{-W\Delta t}), \quad (3)$$

and

$$U(\Delta t) = \int I dt = \frac{N_x W_{\text{sp}}}{\tau_{\text{ex}} W} \left\{ \Delta t - \frac{1}{W} (1 - e^{-W\Delta t}) \right\}, \quad (4)$$

where W_{sp} is the spontaneous radiative lifetime of Er^{3+} . As Eqs. (3) and (4) show, $I(\Delta t)$ and $U(\Delta t)$ are mainly dependent on N_x . As N_x is assumed to reach saturation very quickly, N_x can be easily estimated from Eq. (1) to be $an^2/(cn + 1/\tau_{\text{ex}})$. Now, if the exciton–erbium coupling is much stronger than carrier–exciton coupling, then

$$N_x(\Delta t) = \frac{a\beta E \tau_{\text{ex}}}{\Delta t}. \quad (5)$$

If, on the other hand, the carrier–exciton coupling is much stronger than the exciton–erbium coupling, then

$$N_x(\Delta t) = \frac{a}{c} \sqrt{\frac{\beta E}{\Delta t}}. \quad (6)$$

Figure 3 shows the experimental and simulated results of $I(\Delta t)$ and $U(\Delta t)$. The symbols are the experimental data and the lines are the simulated results of fitting using Eqs. (3) and (4). The inset shows an actual Er^{3+} luminescence trace and the quantity being measured. The results of fitting for N_x using Eq. (5) are shown by solid lines. The values of $a\beta E W_{\text{sp}}$ used for the fit are 0.2 and 0.05 for the film with C_{Si} of 41 and 35 at. %, respectively. The dotted lines are the results of the fit using Eq. (6). The values of $(aW_{\text{sp}}\sqrt{\beta E})/c\tau_{\text{ex}}$ used for the fit are 5 and 1 for the film with C_{Si} of 41 and 35 at. %, respectively. In fitting the data, the possibility of free-carrier-mediated deexcitation of excited Er^{3+} was included explicitly by measuring W during excitation using a two-beam setup⁶ and using that in fitting the data.

As shown in Fig. 3, an excellent fit to *both* sets of data using a *single* fitting parameter is obtained by assuming a strong exciton–Er coupling but a weak carrier–exciton coupling. On the other hand, the fit assuming a strong carrier–exciton coupling and weak exciton–erbium coupling is very poor, and even gives a completely different functional form for $I(\Delta t)$. Taken together, Fig. 3 indicates that in SRSO, exciton–erbium coupling dominates over carrier–exciton coupling.

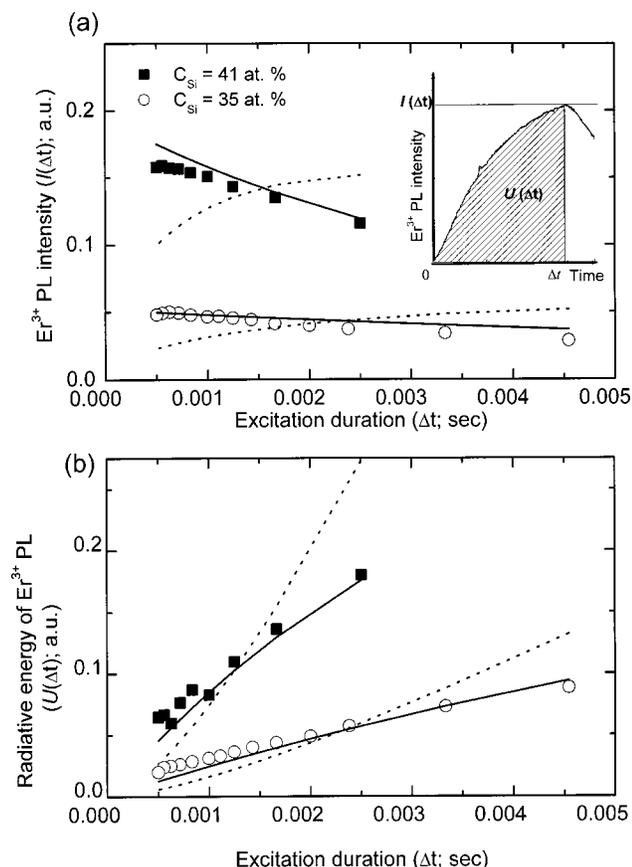


FIG. 3. Excitation duration (Δt) dependence of (a) Er³⁺ PL intensities and (b) the radiative energy of Er³⁺ PL at $t = \Delta t$, respectively. Symbols, solid lines, and dotted lines are results of experiment, simulated with Eq. (5), and simulated with Eq. (6), respectively. The inset shows a real-time trace of Er³⁺ luminescence and the quantity being measured.

The results presented are consistent with, and may be explained by, the recent suggestions that the dominant luminescent sites of Er³⁺ in SRSO are in interfacial region of the SiO₂ matrix rather than in the Si nanoclusters themselves.^{11,12} In such a case, as excitons localized near the Er³⁺ ions have the highest excitation efficiency,^{10,13} the excitons that excite Er in SRSO are likely to be those that are trapped in the interfacial region or have tunneled into the SiO₂ matrix to an Er-related site in SiO₂. Then, because both Er³⁺ ions and the excitons that excite them are physically separated from the carriers that are confined within the nanoclusters, they would indeed be coupled only weakly with the carriers in the Si nanoclusters, resulting in suppression of carrier-mediated deexcitation mechanisms and in increased luminescence efficiency of Er³⁺ luminescence. Indeed, we have shown recently that in a similar system of Er-doped Si/SiO₂ superlattices, the best Er³⁺ luminescence properties are obtained if Er is in the SiO₂ layers, and if the carriers are made to tunnel from the Si layers to the Er³⁺ ions.¹⁴

Moreover, using the values obtained from Fig. 3 and the published values for the optical absorption cross section of nanoclusters,¹⁵ it is possible to find the value of a if W_{sp} is known. If we take the value of W at 25 K to be W_{sp} , then we find that a is the same within $\sim 15\%$ for the samples. This is

in contrast to the exciton luminescence from Si nanoclusters, whose properties are known to be sensitively dependent upon the nanocluster size,⁸ but it is consistent with the above explanation that excitons that excite Er³⁺ ions are distinct from carriers inside nanoclusters (e.g., carriers that contribute to nanocluster luminescence).

These findings have important implications for recent efforts to directly self-assemble Si nanoclusters doped with Er. Our results indicate that rather than placing Er atoms *into* nanoclusters, Er atoms should be placed on the surface of the nanoclusters, or in the oxide shell surrounding the nanoclusters. Note also that Er is known to be a donor in Si.¹⁶ Having a donor atom inside a nm-sized cluster would represent a very high doping concentration, a condition known to lead to severe quenching of Er³⁺ luminescence.¹⁰ Furthermore, since we need to place as many Er ions as possible on the surface region of the Si nanoclusters, having a large surface-to-volume ratio would be preferable. In other words, given the same total Si content, having many very small Si nanoclusters would be better than having a smaller number of larger Si nanoclusters.

In conclusion, we have investigated exciton-mediated excitation dynamics of Er³⁺ in Er-doped SRSO. Exciton-erbium coupling was found to be dominant over carrier-exciton coupling. The results are consistent with, and support the interpretation that most of the Er are located in the oxide shell surrounding the Si nanoclusters.

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