1.54 μm photoluminescence of Er^{3+} doped into SiO$_2$ films containing Si nanocrystals: Evidence for energy transfer from Si nanocrystals to Er^{3+}

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SiO$_2$ films containing Si nanocrystals (nc-Si) and Er were prepared and their photoluminescence (PL) properties were studied. The samples exhibited luminescence peaks at 0.81 and 1.54 μm, which could be assigned to the electron-hole recombination in nc-Si and the intra-4f transition in Er^{3+}, respectively. Correlation between the intensities of the two luminescence peaks was studied as functions of Er concentration and excitation power. The present results clearly demonstrate that excitation of Er^{3+} occurs through the recombination of photogenerated carriers spatially confined in nc-Si and the subsequent energy transfer to Er^{3+}. © *1997 American Institute of Physics.*
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Er-doped Si has been recently attracting much interest because of its potential application in Si-based optoelectronic devices. The Er ions incorporated in Si in their 3+ state produce light emission from the intra-4f transition ($^4I_{13/2}$ to $^4I_{15/2}$) at around 1.54 μm, which corresponds to the absorption minimum in silica-based glass fibers.[1–3] Interest has also been focused on Er-doped porous Si, which emits strong 1.54 μm luminescence even at room temperature and exhibits very weak temperature quenching of the luminescence.[4–7] It is often suggested that, in porous Si, excitation of Er^{3+} occurs through the recombination of photogenerated carriers confined in Si nanocrystals (nc-Si) and subsequent energy transfer to Er^{3+} in or near the nc-Si.[5–7]

If the Er^{3+} is excited by the energy transfer from nc-Si, the 1.54 μm luminescence and the visible or near-infrared luminescence due to the band-to-band transition in nc-Si should correlate to each other depending on the number of active Er^{3+}, excitation energy and power, and temperature. However, despite the numerous research, detailed studies on these dependencies have so far not been carried out, and the energy transfer has not been clearly evidenced. The purpose of this work is to study the correlation between the two luminescence bands and demonstrate the energy transfer from nc-Si to Er^{3+}.

To study the above dependencies of the two luminescence bands, the stable nc-Si with well-defined size and shape as well as chemical composition is indispensable. For this purpose, porous Si is not appropriate, because of its instability, complexity in its structure and chemical composition, and resulting ambiguity in the origin of the luminescence. In this work, we employed SiO$_2$ films containing nc-Si, instead of porous Si, as a host of Er^{3+}. We have recently succeeded in preparing spherical nc-Si with good crystallinity as small as 2.7–5.5 nm in diameter dispersed in SiO$_2$ thin films.[8–10] We demonstrated that these samples show a luminescence peak in a near-infrared (NIR) region (about 0.8 μm) and the peak exhibits a blue shift with decreasing the size. From the observed size dependence, we could attribute the NIR peak to the recombination of electron-hole pairs in the nc-Si.[10–12] In this work, we added Er in the samples and studied the luminescence properties as functions of Er concentration and excitation power. We will demonstrate that two peaks corresponding to the recombination of electron-hole pairs in nc-Si and the intra-4f transition in Er^{3+} can be observed simultaneously, and a clear correlation between the intensities of the two peaks can be observed. We will show that the observed correlation provides clear evidence for the energy transfer from nc-Si to Er^{3+}.

Samples were prepared by a rf cosputtering method. In our previous studies,[8–10] we demonstrated that nc-Si embedded in SiO$_2$ films can be obtained by cosputtering Si and SiO$_2$ and postannealing at 1100 °C or higher. In this work, in an attempt to dope Er in the films, Er$_2$O$_3$ pellets were added for the cosputtering. In actual sputtering procedures, small pieces of Si chips 5×15 mm^2 in size and Er$_2$O$_3$ pellets 10 mm in diameter were placed on a SiO$_2$ target (10 cm in diameter) and they were cosputtered. The films of 1 μm in thickness were deposited onto fused quartz plates. After the deposition, the samples were annealed in a N$_2$ ambient for 30 min at 1100 °C. In this method, the size of nc-Si can be controlled by changing the number of Si chips during the cosputtering and the annealing temperature. Er concentration (C_{Er}) can also be controlled by changing the number of Er$_2$O$_3$ pellets during the cosputtering. The C_{Er} was determined by electron-probe microanalysis [JCXA-733 (JEOL)]. The size of nc-Si was determined by high-resolution transmission electron microscopic observation [JEM-2010 (JEOL)]. Photoluminescence (PL) spectra were measured using a HR-320 (Jobin Yvon) monochromater and an EO-817L (North Coast) Ge detector. The excitation sources were six lines of an Ar-ion laser with a power density of less than 1.5 W/cm^2. Spectral responses of the detection systems were

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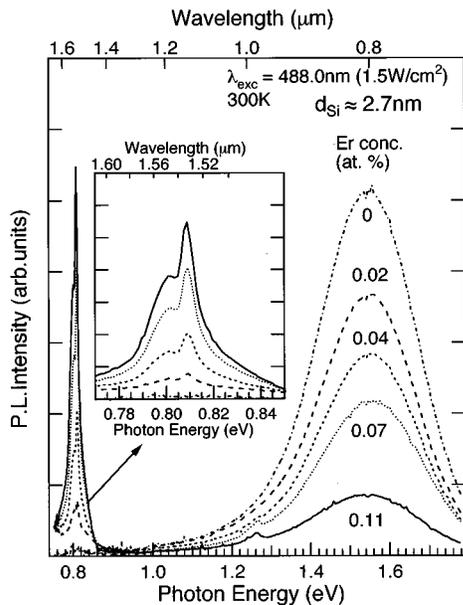
FIG. 1. PL spectra of SiO$_2$ films containing nc-Si and Er. Inset is an expansion of the region between 1.46 and 1.61 μm.

corrected by reference spectra of a standard tungsten lamp. All the measurements were made at room temperature.

Figure 1 shows the dependence of PL spectra on C_{Er}(at.%) for SiO$_2$ films containing nc-Si about 2.7 nm in diameter (volume fraction of the nc-Si is about 5%). Inset is an expansion of the region between 1.46 and 1.61 μm. For the sample not containing Er, we can see only one peak at about 0.81 μm. From previous PL studies for nc-Si,[10] this peak can be assigned to the recombination of electron-hole pairs in nc-Si. As the C_{Er} increases, the intensity of the peak decreases rapidly. It should be noted here that, in spite of the drastic change in the intensity, the peak position is not affected by the C_{Er}. In our previous paper, we demonstrated that the PL peak of nc-Si is size sensitive and shifts from 0.87 to 0.80 μm as the size decreases from 3.8 to 2.7 nm.[10] Therefore, the size of the nc-Si is not affected by the C_{Er} and is considered to be almost identical for all the samples (about 2.7 nm).

For the samples containing Er, we can see another peak at 1.54 μm, corresponding to the intra-4f transition of Er^{3+} ($^4I_{13/2}$ to $^4I_{15/2}$).[2] In contrast to the 0.81 μm peak, this peak becomes intense as C_{Er} increases. Figure 2 compares the intensities of the two peaks as a function of C_{Er}. In spite of the very small amount of Er, the intensities of the two peaks change drastically with C_{Er}. We can see that the 1.54 μm peak becomes strong with increasing C_{Er}, while the 0.81 μm peak decreases rapidly.

Although not shown here, the intensity of the 1.54 μm peak in Fig. 2 is more than 50 times stronger than those of SiO$_2$ films not containing nc-Si and containing the same amount of Er. This suggests that nc-Si enhances the 1.54 μm luminescence of Er^{3+}. If the energy transfer from nc-Si to Er^{3+} is assumed, the results of Figs. 1 and 2 can be explained as follows. First, the excitation light is absorbed mainly by nc-Si and the electron-hole pairs are generated in the nanocrystals. A part of the recombination energies of the electron-hole pairs are then transferred to Er^{3+}. The amount
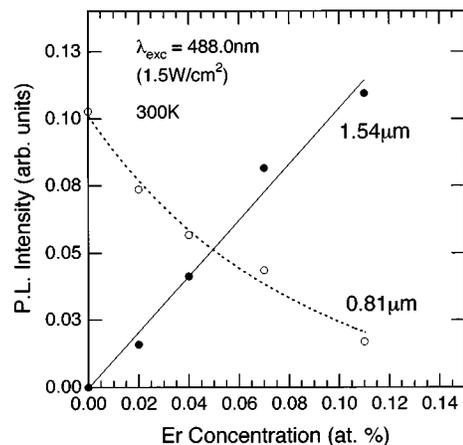
FIG. 2. Intensities of 0.81 and 1.54 μm peaks as a function of Er concentration. The lines are drawn to guide the eye.

of the energy transferred to Er^{3+} increases as C_{Er} increases. This results in the growth of the 1.54 μm peak and the quenching of the 0.81 μm peak with increasing C_{Er}.

Since the intensity of the 1.54 μm peak in Fig. 2 depends nearly linearly on C_{Er}, the energy transfer is considered to be limited by the number of optically active Er^{3+} in the films (i.e., almost all optically active Er^{3+} is excited by the energy transfer). In this case, we can expect much different excitation power (P_{ex}) dependence between the two peaks. Since the amount of the energy transferred to Er^{3+} is limited by the number of Er^{3+} and is not proportional to P_{ex}, the intensity of the 1.54 μm peak will not depend linearly on P_{ex} but will be saturated at rather low P_{ex}, while that of the 0.81 μm peak will not be saturated. The saturated intensity of the 1.54 μm peak will depend on C_{Er}. Figure 3 shows the P_{ex} dependencies of the PL intensities for the sample with C_{Er} of 0.02 at.%. We can see that the intensity of the 1.54 μm peak shows very small P_{ex} dependence and is almost saturated, while that of the 0.81 μm peak increases monotonously. It should be noted here that the saturation was not observed for the samples not containing nc-Si. The results of Fig. 3 combined with Figs. 1 and 2 strongly sug-
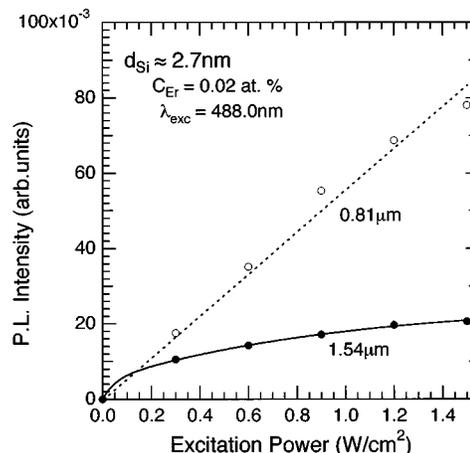
FIG. 3. Intensities of 0.81 and 1.54 μm peaks as a function of excitation power for the sample with the Er concentration of 0.02 at. %. The lines are drawn to guide the eye.
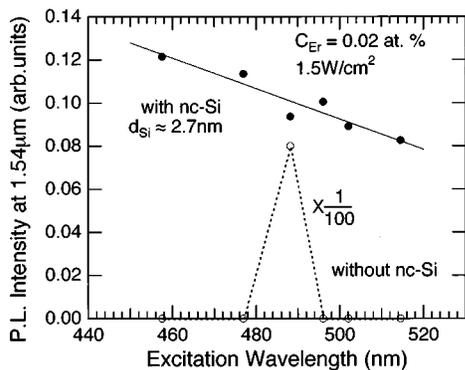
FIG. 4. Intensity of 1.54 μm peak as a function of excitation energy for samples containing nc-Si and not. The lines are drawn to guide the eye.

gest that the excitation of Er^{3+} occurs through the energy transfer from nc-Si.

To investigate the excitation mechanism of Er^{3+} further, we also studied the excitation energy (λ_{ex}) dependence of the 1.54 μm peak. Figure 4 compares the λ_{ex} dependence for the sample containing nc-Si with that not containing nc-Si. Since the intensity of the sample without nc-Si is very weak, a factor of 100 is multiplied. We can see the completely different λ_{ex} dependencies between the two samples. The sample not containing nc-Si exhibits a distinct peak at 488 nm, corresponding to the $^4I_{15/2}$ to $^4F_{7/2}$ transition of Er^{3+}.[2] It is noted that, in this power density (1.5 W/cm^2), no signal was detected with other λ_{ex}. On the other hand, the sample containing nc-Si shows no distinct structure, indicating that the excitation is not a direct absorption by Er^{3+}, but the absorption by nc-Si and the subsequent energy transfer to Er^{3+}.

In the above, we did not discuss whether the Er^{3+} responsible for the strong 1.54 μm luminescence is located inside or outside the nc-Si. Since the shape of the 1.54 μm peak is considered to depend on the local environment of Er,[4] we compared spectral shape of the samples containing nc-Si with that not containing nc-Si. Although the PL intensity becomes more than 50 times stronger by incorporating nc-Si, the spectral shape was almost identical for all the samples. This result and a relatively low solid solubility of Er in Si ($\sim 10^{18}$ /cm^3)[13] suggest that Er^{3+} responsible for the strong luminescence is around the interface region between nc-Si and SiO$_2$, although a few may exist in the nanocrystals.

In this letter, we restricted our discussion for nc-Si with only one average size (2.7 nm). We also studied the size dependence of the PL spectra and found that the PL intensity (1.54 μm) decreases with increasing the size of nc-Si. The results of the size and the temperature dependencies of the PL properties will be published elsewhere.

In summary, we have studied luminescence properties of SiO$_2$ films containing nc-Si and Er. Peaks attributable to nc-Si (0.81 μm) and Er^{3+} (1.54 μm) were observed simultaneously. Er concentration, excitation power, and excitation energy dependencies of the two peaks were studied. It was found that the 1.54 μm peak increases almost linearly with C_{Er}, while the 0.81 μm peak decreases rapidly. The 1.54 μm peak did not depend linearly on P_{ex} but was saturated at rather low P_{ex}. The λ_{ex} dependence of the 1.54 μm peak did not have any distinct structure corresponding to the direct transition in Er^{3+}. These results provide clear evidence for the energy transfer from nc-Si to Er^{3+}.

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