Excitation of intra-4*f* shell luminescence of Yb^{3+} by energy transfer from Si nanocrystals

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SiO_2 films containing Si nanocrystals (nc-Si) and Yb were prepared and their photoluminescence (PL) properties were studied. For the sample containing nc-Si with an average diameter of 3.1 nm, a weak peak ($\sim$1.26 eV) attributable to the intra-4*f* shell transition of Yb^{3+} could be observed at the low-energy side of a broad peak ($\sim$1.4 eV) of nc-Si. The intensity of the 1.26 eV peak was found to depend strongly on the size of nc-Si and increase rapidly with decreasing size. The temperature dependence of the PL spectra was studied. It was found that the degree of temperature quenching of the 1.26 eV peak depends on the size of the nc-Si and becomes small as the size decreases. These results suggest that the band-gap widening of nc-Si due to the quantum size effects is essential to efficiently excite Yb^{3+} by nc-Si. © *1998 American Institute of Physics.* [S0003-6951(98)01047-X]

It is well known that rare-earth ions incorporated into semiconductor hosts in their 3+ states emit light from the intra-4*f* shell transition.[1–8] Er-doped Si has been most widely studied, because the emission band of Er^{3+} [1.54 μm (0.81 eV)] corresponds to the absorption minimum in silica-based glass fibers.[1–4] However, the 0.81 eV luminescence of Er-doped Si often exhibits very large temperature quenching and thus the room temperature luminescence efficiency is rather low. One of the causes of the low luminescence efficiency is the large probability of the phonon-assisted back transfer of energy from Er^{3+} to the host Si at high temperatures.[1]

The probability of back transfer is considered to depend on the band gap of the host materials and decreases as the band gap increases.[1] Since the band gap of Si nanocrystals (nc-Si), as small as several nanometers, is much larger than that of bulk-Si crystal,[9–13] nc-Si may efficiently excite Er^{3+}. In our previous work, we have studied in detail the nc-Si mediated excitation mechanism of Er^{3+}.[14,15] We have found that the intensity of the 0.81 eV photoluminescence (PL) depends strongly on the size of the incorporated nc-Si and increases about two orders of magnitude as the size decreases from 3.8 to 2.7 nm. Our data demonstrated that two major features of the quantum size effects of nc-Si, i.e., the band-gap widening and the increase in the PL efficiency with decreasing size, contribute to the improvement of the room-temperature PL efficiency of Er^{3+}.[15]

This work is an extension of our previous studies.[14,15] In order to further clarify the nc-Si mediated excitation process of rare-earth ions, we have studied PL properties of SiO_2 films containing nc-Si and Yb. An energy level scheme of Yb^{3+} 4*f* shell is very simple with only one excited state ($^2F_{5/2}$) at about 1.26 eV from the ground state ($^2F_{7/2}$).[8] Since the $^2F_{5/2}-{}^2F_{7/2}$ split is larger than the band gap of a bulk-Si crystal (1.12 eV), Yb^{3+} cannot be excited by the energy transfer from a bulk-Si crystal. By reducing the size of the host Si from the bulk to a few nanometers, the band gap changes continuously from 1.12 eV to above 1.5 eV,[9,10] and for the nc-Si with a band gap of larger than 1.26 eV, excitation of Yb^{3+} may become possible. Therefore, from the size-dependent PL studies, we can systematically study PL properties of rare-earth ions as a function of the band gap of a host.

SiO_2 films containing nc-Si and Yb were prepared by the same method used in our previous work for SiO_2 films containing nc-Si and Er.[14,15] Small pieces of Si chips 5 $\times$15 mm^2 in size and Yb_2O_3 pellets 10 mm in diameter were placed on a SiO_2 sputtering target (10 cm in diameter) and they were cosputtered in Ar gas atmosphere. Films of about 1 μm in thickness were deposited onto fused quartz plates. After the deposition, in order to grow nc-Si, samples were annealed in an atmosphere of N_2 gas 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. Yb concentration (C_{Yb}) can also be controlled by changing the number of Yb_2O_3 pellets during the cosputtering. The C_{Yb} and the volume fraction of nc-Si in films were determined by electron-probe microanalyses [JXA-8900 (JEOL)]. The size of nc-Si was determined by cross-sectional high-resolution transmission electron microscopic (HRTEM) observations [JEM-2010 (JEOL)]. In this work, C_{Yb} was fixed to about 0.16 at. %, while the average diameter of nc-Si (d_{Si}) was changed from 2.4 to 3.1 nm.

Photoluminescence spectra were measured using a HR-320 (Jobin Yvon) monochromator and an EO-817L (North Coast) Ge detector. The excitation source was a 457.9 nm line of an Ar-ion laser with a power density of less than 1.5 W/cm^2. The spectral response of the detection system was corrected by reference spectra of a standard tungsten lamp. The temperature dependence of PL spectra was measured from 20 to 300 K in a continuous-flow He cryostat [Optistat (Oxford Instruments)].

Figure 1 shows the room-temperature PL spectra of SiO_2

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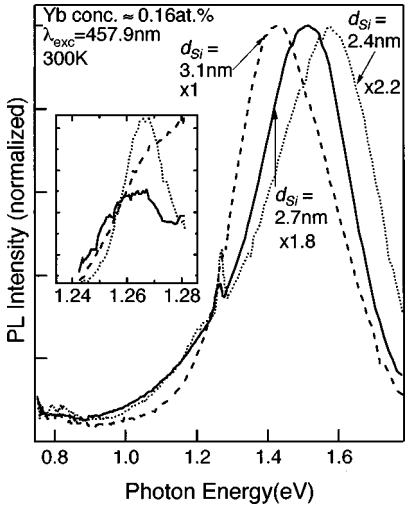

FIG. 1. Room-temperature PL spectra of SiO_2 films containing nc-Si and Yb. Inset is an expansion of the region between 1.235 and 1.285 eV. The size of nc-Si is varied from 2.4 to 3.1 nm, while Yb concentration and film thickness are fixed at about 0.16 at. % and 1.2 μm, respectively. For comparison purposes, the spectra are normalized at their maximum intensity.

films containing nc-Si and Yb as a function of d_{Si}. The inset is an expansion of the region between 1.235 and 1.285 eV. For comparison purposes, the spectra are normalized at their maximum intensity. In Fig. 1, we can see two peaks. The broad one around 1.5 eV corresponds to the radiative recombination of electron–hole pairs in nc-Si.[9,10] This peak exhibits a clear blueshift with decreasing the size due to quantum size effects. The relative intensity of this peak is shown in Fig. 1 (a larger value corresponds to a larger PL intensity). The intensities are corrected by the amount of nc-Si contained in the samples (f) by dividing the observed intensities by f. We can see that the band-edge PL becomes intense as the size decreases.[9,10] At the low-energy tail of the peak, a weak peak is observed around 1.26 eV. This peak can be assigned to the intra-4f shell transition of Yb^{3+} ($^2F_{5/2}-^2F_{7/2}$). The intensity of the 1.26 eV peak becomes large as the size of nc-Si is decreased (as the band-edge-related peak of nc-Si shifts to higher energies), although Yb concentration is nearly the same for all the samples. We have also studied samples containing nc-Si with $d_{\mathrm{Si}}>3.1$ nm. However, the 1.26 eV peak could not be observed for these samples.

Figure 2 shows the temperature dependence of the PL spectra for the sample with $d_{\mathrm{Si}}\approx 2.4$ nm. At room temperature, we can see peaks at around 1.26 and 1.6 eV. As the temperature decreases, the 1.6 eV peak shifts monotonously to higher energies. The degree of the high-energy shift was nearly the same as that of the band gap of the bulk-Si crystal [about 45 meV (300–20 K)].[10] The intensity of the 1.6 eV peak first increases and then decreases. The intensity at 20 K is comparable to that at 293 K. Although the reason for the characteristic temperature dependence of the PL intensity is not clear, a similar temperature dependence has commonly been observed for nc-Si in SiO_2 matrices.[10] At 20 K, the 1.6 eV peak is very broad with a long tail at the low-energy side. The origin of the tail is considered to be the recombination of carriers trapped at P_b centers at the interfaces between nc-Si and SiO_2 matrices.[10,16,17] In contrast to the 1.6 eV peak, the

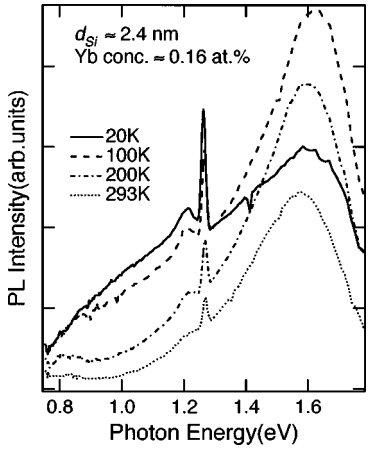

FIG. 2. Temperature dependence of the PL spectra for the sample with $d_{\mathrm{Si}}=2.4$ nm and $C_{\mathrm{Yb}}=0.16$ at. %.

1.26 eV peak of Yb^{3+} increases monotonously with decreasing the temperature. The small peak appearing at low temperatures at around 1.2 eV is due to the crystal field splitting of the $^2F_{5/2}$ and $^2F_{7/2}$ bands.[8] Figure 3 shows the intensity of the 1.26 eV peak as a function of a temperature for the samples with $d_{\mathrm{Si}}\approx 2.4$, 2.7 and 3.1 nm. The intensities are normalized at 20 K. We can find that the degree of temperature quenching of the PL depends strongly on the size of nc-Si. The sample with $d_{\mathrm{Si}}\approx 3.1$ nm exhibits the largest temperature quenching, and as the size decreases, the quenching becomes small.

Until now, PL properties of Yb^{3+} have intensively been studied for Yb-doped InP.[5–8] Yb forms an acceptor-like electron trap level at 30 meV below the bottom of the conduction band.[5] Electron–hole pairs generated by visible light excitation are captured by this trap and form a bound exciton. The recombination energy of the bound exciton is subsequently transferred to Yb^{3+} and excites the intra-4f shell. At relatively high temperatures, the reverse process of the energy transfer is also possible. The excited 4f shell relaxes nonradiatively, transferring its energy to the host by producing electron–hole pairs (back transfer). Since the back transfer is

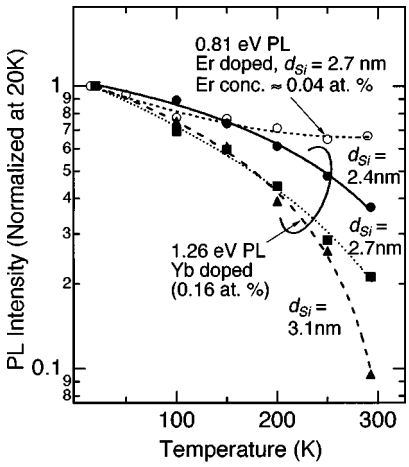

FIG. 3. Intensity of the intra-4f shell PL of Yb as a function of temperature for the samples with $d_{\mathrm{Si}}=2.4$, 2.7 and 3.1 nm. For comparison purposes, the intensity of the intra-4f shell PL of Er is also shown as a function of a temperature ($d_{\mathrm{Si}}=2.7$ nm). The curves are drawn to guide the eye.

a phonon-assisted process, the probability becomes large as the temperature is increased.[5]

In the present experiments, no PL signal was detected for the sample not containing nc-Si (Yb-doped SiO_2). Since Yb^{3+} has only one excited state ($^2F_{5/2}$) in the near-infrared region, to excite Yb^{3+} by visible light, energy transfer from a host material is indispensable. The 1.26 eV PL of Yb^{3+} shown in Fig. 1 is thus considered to be excited by the energy transfer from nc-Si by a process similar to that of Yb-doped InP, although we have at present no definite idea about a Yb-related trap center.

Two possible quenching processes are often considered to explain the PL properties of rare-earth ions doped into semiconductor hosts. One is the dissociation of excitons bound to a rare-earth-related trap center before the energy is transferred to the rare-earth ions, and the other is the energy back transfer from rare-earth ions to a host. Since both quenching processes require the annihilation of phonons, they become more probable at high temperatures. A decision between these two possibilities is made through a study of PL decay dynamics. The dissociation process will not affect the PL lifetime, while the back transfer process will decrease both the PL intensity and lifetime. In the case of Yb-doped InP (Ref. 5) and Er-doped Si,[1] the temperature dependence of the PL lifetime has been studied in detail. It has been demonstrated that the back transfer process is the primary cause of the temperature quenching at high temperatures.

The band-edge-related PL of the present nc-Si appears at around 1.4–1.6 eV (Fig. 1). This value is very similar to that of InP ($\sim$1.4 eV). We thus assume that the back transfer process is also the dominant quenching process in the present samples. Under the assumption, the observed size and temperature dependences can be explained as follows. The probability of the back transfer depends on the band gap of a host, and decreases as the band gap increases, because the back transfer requires multiple phonons. In Fig. 1, we have shown that as the size of nc-Si decreases (as the band-edge-related PL shifts to higher energies), the 1.26 eV PL intensity increases. We believe that the enhancement of the 1.26 eV PL with decreasing the size is mainly caused by the reduction of the back transfer probability due to the band-gap widening. The suppression of the temperature quenching with decreasing the size shown in Fig. 3 can also be explained by the widening of the band gap of nc-Si.

In Fig. 3, we also show the temperature dependence of the 0.81 eV PL (intra-4f shell transition of Er^{3+}) intensity of a Er-doped sample with $d_{Si}\approx 2.7$ nm. We can see that the 0.81 eV peak exhibits very small temperature quenching. We have performed the same experiments for Er-doped samples with various sizes ($d_{Si}\approx 2.7-3.8$ nm). However, even with the largest size (3.8 nm), the temperature quenching was very small and no remarkable size dependence was observed on the degree of temperature quenching. The small temperature quenching is considered to be caused by the large energy difference between the band gap of nc-Si and the emission band of Er^{3+}.

As described above, the decay dynamics of PL should be studied to definitely determine the PL quenching process of the present samples. However, the decay dynamics of the 1.26 eV PL of Yb^{3+} for the present samples are difficult to measure, because the 1.26 eV PL is on the tail of the band-edge PL of nc-Si. In the case of Yb-doped InP, evidence for the back transfer is demonstrated from the PL decay dynamics of an InP host.[5] It was demonstrated that at temperatures above 100 K, a slow component appears in the decay curve of the band-edge PL. The appearance of the slow component suggests that free electrons and holes are generated by the energy back transfer from the excited Yb^{3+} to the InP host, and then the electrons and holes recombine and contribute to the band-edge PL. Similar studies seem to be useful in discussing the PL quenching process of the present samples.

In summary, we have studied PL properties of SiO_2 films containing nc-Si and Yb. By reducing the size of nc-Si to about 3.1 nm, we could successfully excite Yb^{3+} and observe a PL peak at around 1.26 eV ($^2F_{5/2}-^2F_{7/2}$ transition). The 1.26 eV PL intensity increased rapidly by further decreasing the size. The temperature dependence of the PL spectra was studied. It was found that the degree of the temperature quenching depends on the size of nc-Si and becomes small as the size decreases. These results clearly demonstrate that excitation of Yb^{3+} is made by the energy transfer from nc-Si. Furthermore, the band-gap widening of nc-Si due to the quantum size effects is essential to efficiently excite Yb^{3+} by nc-Si.

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