

Excitation of Tm^{3+} by resonant energy transfer from Si nanocrystals

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Photoluminescence (PL) properties and PL decay dynamics of SiO_2 films containing Si nanocrystals (nc-Si) and Tm^{3+} were studied. The samples exhibited a broad PL at around 1.5 eV due to the recombination of excitons in nc-Si, and rather sharp PL at 1.58, 0.84, and 0.69 eV corresponding to the intra-4*f* shell transitions of Tm^{3+} . The correlation between the intensities of nc-Si and Tm^{3+} related PL was studied as a function of the Tm concentration, the size of nc-Si, and the temperature. It was found that the intensity of Tm^{3+} related PL depends strongly on the size of nc-Si. At low temperatures, the spectral shape of nc-Si PL was strongly modified by doping Tm. From analysis of the modified spectral shape, a resonant energy transfer from nc-Si to Tm^{3+} is discussed. © 2002 American Institute of Physics. [DOI: 10.1063/1.1503860]

I. INTRODUCTION

Recently, it has been demonstrated that 4*f* shells of rare-earth ions, e.g., Er^{3+} , Yb^{3+} , Nd^{3+} , and Tm^{3+} , can be efficiently excited by energy transfer from Si nanocrystals (nc-Si), i.e., excitation light is absorbed by nc-Si, and excitons generated in nc-Si recombine with the transferred energy to rare-earth ions. In particular, efficient luminescence at 0.81 eV (1.54 μm) from the system containing nc-Si and Er (the Er/nc-Si system) has attracted much interest.¹⁻⁹ The efficient 0.81 eV luminescence opens up the possibility of realizing silicon/silica-based planar optical amplifiers which can be integrated with existing semiconductor and fiber telecommunication technology.

The excitation mechanism of Er in Er/nc-Si systems has been studied in detail^{1,2,5,8} and direct spectroscopic evidence of the energy transfer has been obtained.³ Furthermore, energy transfer rates are experimentally determined as a function of the nc-Si size. It has been demonstrated that the smaller the size of the particles, the higher the energy transfer rate.³ In contrast to Er/nc-Si systems the detailed mechanism of the interaction between nc-Si and other rare-earth ions is not well understood, although enhancement of the intra-4*f* shell photoluminescence (PL) has been demonstrated.

Among several rare-earth ions which are reported to interact strongly with nc-Si, in this work, we adopted Tm and studied its interaction with nc-Si in silica glasses, because Tm doped glasses have attracted a lot of attention as potential materials for future near-infrared light sources and amplifiers.¹⁰⁻¹⁴ The enhancement of Tm^{3+} -luminescence efficiency by adding nc-Si would provide new perspectives on the development of silica based infrared lasers and amplifiers. This enhancement of the intra-4*f* shell PL of Tm^{3+} by

interaction with nc-Si was demonstrated for the first time, we believe, by Franzó *et al.*⁴ However, in their work, the size dependence of the luminescence properties was not studied. Since the quantum confinement effects of excitons in nc-Si are considered to play an important role in the interaction,⁴ the properties of energy transfer should depend strongly on the size of nc-Si. By analyzing size dependence, valuable information on the mechanism of energy transfer can be obtained. Furthermore, in the previous work, no spectroscopic evidence of the energy transfer was obtained.

In this work, the PL properties of SiO_2 films containing nc-Si and Tm^{3+} are studied in a wide spectral range from 0.45 to 1.9 eV. A comprehensive study of a wide spectral range is essential to understand the energy transfer mechanism, because Tm^{3+} exhibits several PL bands in the near-infrared to visible regions, and thus the intensity ratio may change, depending on experimental parameters. We show the correlation of the nc-Si PL and Tm^{3+} PL as a function of the Tm concentration, nc-Si size, and temperature. A result much different from that reported by Franzó *et al.* was observed in the temperature dependence of PL intensity. We also give spectroscopic evidence of resonant energy transfer from nc-Si to Tm^{3+} .

II. EXPERIMENT

SiO_2 films containing nc-Si and Tm were prepared by a cosputtering method similar to that used to prepare SiO_2 films containing nc-Si and Er.^{1,2} Small pieces of Si chips and Tm_2O_3 pellets were placed on a SiO_2 sputtering target and they were simultaneously sputtered in an Ar gas atmosphere. After deposition, in order to grow nc-Si, samples were annealed in a N_2 gas atmosphere for 30 min at temperatures higher than 1100 °C. In this work, the average size of nc-Si (d_{Si}) was changed from 2.7 to 3.5 nm and the Tm concentration was changed from 0.17 to 1.41 at. %. PL spectra were measured by a single grating monochromator. In the spectral

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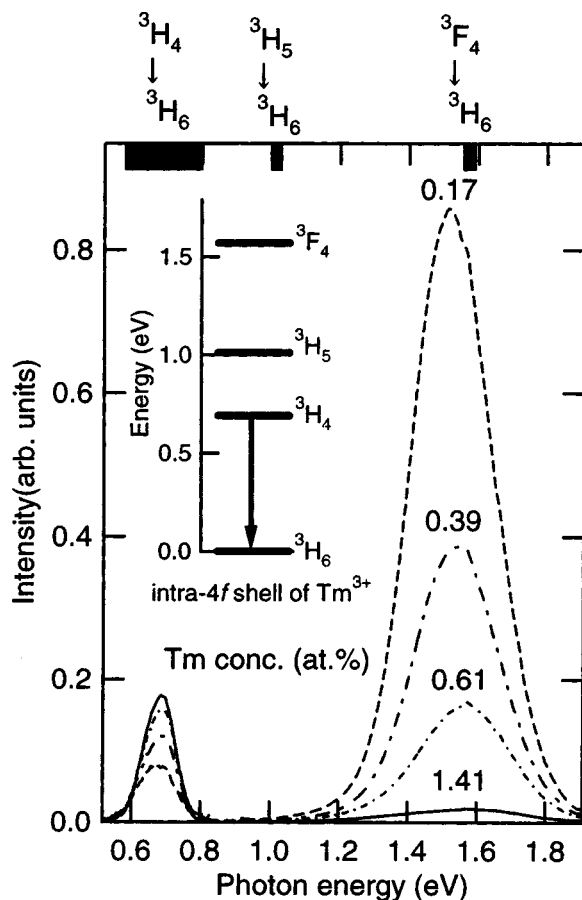


FIG. 1. PL spectra of SiO_2 films containing nc-Si and Tm. The size of nc-Si is about 2.7 nm and the Tm concentration is changed from 0.17 to 1.41 at. %. The inset shows the energy diagram of the intra-4*f* shell of Tm^{3+} .

range between 0.45 and 0.80 eV, a liquid nitrogen cooled InSb photodiode (Hamamatsu) was used as a detector, and in the spectral range between 0.80 and 1.90 eV, a liquid nitrogen cooled Ge photodiode (North Coast) was used. The excitation source was a 514.5 nm line of an Ar-ion laser. For all spectra, the spectral response of the detection system was corrected by a reference spectrum of a standard tungsten lamp. For the time response measurements, a 532.0 nm line of a Nd:yttrium-aluminum-garnet laser was used as an excitation source. The pulse width was 5 ns and the repetition frequency was 20 Hz. The decay curves were measured with a photon counting system that consisted of a photomultiplier with an InP/InGaAs photocathode, a high speed amplifier (1.2 ns rise/fall time) (SR445, Stanford Research Systems), and a multichannel scaler (SR430, Stanford Research Systems). The time resolution of the whole system was about 80 ns.

III. RESULTS AND DISCUSSION

A. Dependence of PL spectra on the Tm concentration

Figure 1 shows the room temperature PL spectra as a function of the Tm concentration. The size of nc-Si is fixed at 2.7 nm and the Tm concentration is changed from 0.17 to 1.41 at. %. The inset shows an energy diagram of the 4*f* shell of Tm^{3+} . We can see two peaks in all the spectra. The high-

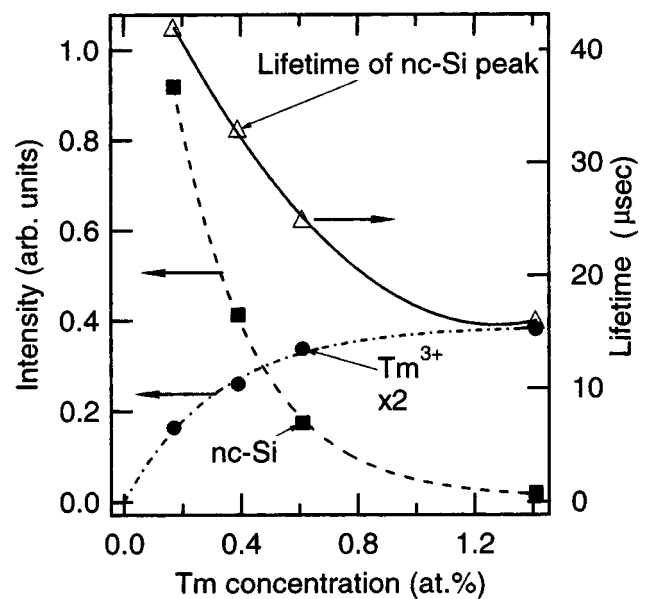


FIG. 2. Intensities of the Tm^{3+} related peak (0.69 eV) and the nc-Si related peak as a function of the Tm concentration. The lifetime which was measured at the maximum of the nc-Si PL is also shown. The lines are to guide the eye.

energy broad PL corresponds to the recombination of excitons confined in nc-Si (nc-Si PL),^{1,2,15} while the low-energy one (0.69 eV) corresponds to the intra-4*f* shell transition of Tm^{3+} (${}^3\text{H}_4$ to ${}^3\text{H}_6$) (Tm^{3+} PL).^{10,11} As the Tm concentration increases, the intensity of the Tm^{3+} PL peak increases, whereas that of nc-Si PL decreases. In Fig. 2, the intensities of the two peaks are plotted as a function of the Tm concentration. We can see that the intensity of nc-Si PL decreases rapidly with an increase in Tm concentration, while that of Tm^{3+} PL increases gradually and is saturated in the high Tm concentration range. The intensity of the Tm^{3+} PL peak is almost saturated at around 0.6 at. % (92% of its saturation value).

Figure 3 shows the Tm concentration dependence of the PL decay curves detected at the maximum of nc-Si PL in Fig. 1. The decay curves are nonexponential. The PL lifetime becomes shorter as the Tm concentration increases. The decay curves are fitted well by the modified exponential function, which is generally used to analyze the decay curves of porous-Si and nc-Si.^{6,16} The lifetime determined from fitting for the sample with the smallest Tm concentration is about 42 μs , while that with the largest Tm concentration is about 16 μs . The lifetimes obtained are shown in Fig. 2. In our previous work on Er-doped nc-Si, the lifetime of nc-Si decreased with an increase in Er concentration. However, in other PL studies of similar Er-doped samples, it has been reported that the lifetime of nc-Si was independent of the Er concentration.^{4,8} The reason for these contradictory results is not clear at present.

In the case of Tm-doped SiO_2 that does not contain nc-Si, the Tm^{3+} PL peak is too weak to detect because of the very low absorption coefficient of Tm^{3+} at the excitation wavelength (476.5 nm). Therefore, observation of intense Tm^{3+} PL implies that Tm^{3+} is excited by energy transfer from nc-Si, i.e., excitation light is absorbed by nc-Si and

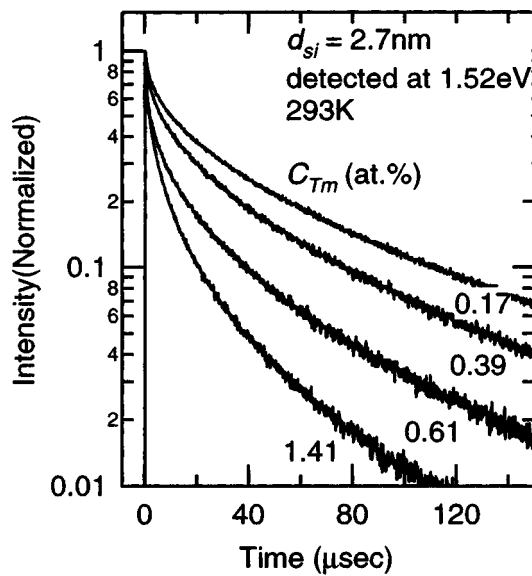


FIG. 3. Tm concentration dependence of the PL decay curves detected at the maximum of nc-Si PL shown in Fig. 1.

excitons generated in nc-Si recombine with the energy transferred to Tm^{3+} . Evidence of the energy transfer can be obtained from PL excitation spectra. Although not shown here, the excitation spectra of Tm^{3+} PL was very broad in spite of its discrete electronic states and was very similar to that of nc-Si PL. A similar result has already been reported by Franzó *et al.* The quenching and the shortening of the lifetime of nc-Si PL with an increase in Tm concentration, shown in Figs. 1–3, indicate that energy transfer is mediated by photogenerated excitons, i.e., it is not due to the absorption of light emitted by nc-Si. The energy transfer process from nc-Si to Tm^{3+} is the preferred nonradiative recombination process.

It is noted here that the degree of quenching of nc-Si PL is much larger than that of the gain of the Tm^{3+} PL intensity. In particular, the intensity of the Tm^{3+} PL peak is not proportional to the Tm concentration and is saturated. As a result, the energy conversion efficiency which represents the ratio of the degree of quenching of nc-Si PL to that of the gain of the Tm^{3+} PL intensity is very small particularly in the high Tm concentration range. Two mechanisms can be considered to be the origin of the small energy conversion efficiency. The first one is the concentration quenching of Tm^{3+} PL due to the relatively high Tm concentration. Excited Tm^{3+} is relaxed by transferring energy to a neighboring Tm^{3+} and finally it is nonradiatively relaxed by meeting a nonradiative recombination center in the matrix. During the energy transfer process, it is not known whether the energy transfer efficiency is high or not. Another mechanism is the generation of defects in or at the surface of nc-Si by heavy Tm doping. The photogenerated excitons recombine nonradiatively in nc-Si before energy transfer occurs. At present, it is not clear which mechanism is the main cause of the small energy conversion efficiency. It is worth noting that in our previous work on Er- and nc-Si-doped SiO_2 films, the total intensity of nc-Si and Er^{3+} PL was about 80% of the PL

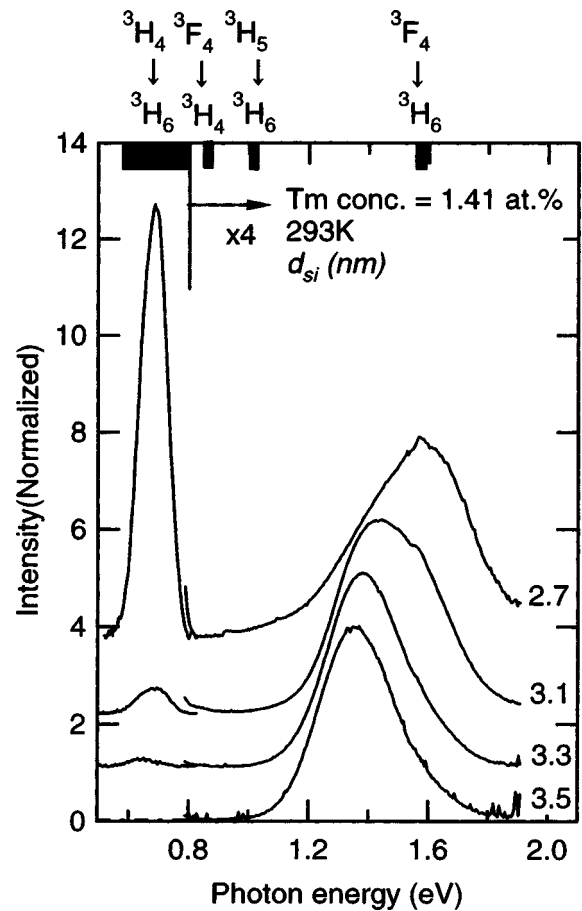


FIG. 4. PL spectra at room temperature as a function of the size of nc-Si diameter. The Tm concentration was fixed at 1.41 at. %. The PL spectra are normalized at the maximum of the nc-Si PL. The energy positions of the first (3H_4), second (3H_5), and third (3F_4) excited states measured from the ground state (3H_6) are shown.

intensity of nc-Si in SiO_2 that did not contain Er, i.e., the energy conversion efficiency was around 80%.¹⁷

B. Dependence of PL spectra on the size of nc-Si

Figure 4 shows PL spectra at room temperature for samples containing different size nc-Si. The intensity scale above 0.8 eV is expanded by a factor of 4. The Tm concentration is fixed at 1.41 at. %. The spectra are normalized at the maximum intensities of nc-Si PL. The energy position of the first (3H_4), second (3H_5), and third (3F_4) excited states of Tm^{3+} measured from the ground state (3H_6) are shown at the top of Fig. 4. As the size of nc-Si decreases from 3.5 to 2.7 nm the nc-Si PL peak shifts from 1.35 eV to 1.60 eV. For samples with average nc-Si sizes of 2.7 and 3.1 nm, a small peak can be observed at 1.58 eV. This peak corresponds to the 3F_4 to 3H_6 transition in Tm^{3+} . Figure 5 shows the intensity ratio of Tm^{3+} and nc-Si PL peaks (I_{Tm}/I_{Si}) as a function of the peak energy of nc-Si PL. The inset shows an energy diagram of the intra-4f shell of Tm^{3+} . Figure 5 clearly shows that I_{Tm}/I_{Si} depends strongly on the peak energy of nc-Si PL, i.e., the size of nc-Si. I_{Tm}/I_{Si} increases

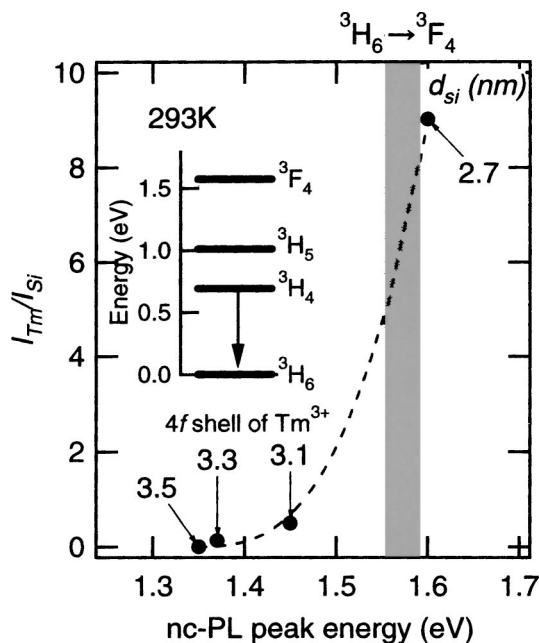


FIG. 5. Intensity ratio of the Tm related and the nc-Si related peaks ($I_{\text{Tm}}/I_{\text{Si}}$) as a function of the peak energy of nc-Si PL. The line is to guide the eye.

with an increase in the PL peak energy of nc-Si. In particular, the ratio increases dramatically as the nc-Si PL peak approaches 1.6 eV.

As shown in Fig. 5, the energy separation between the ground state and the third excited state of Tm^{3+} is around 1.58 eV. Therefore, the steep incline of the $I_{\text{Tm}}/I_{\text{Si}}$ ratio at around 1.58 eV indicates that energy is transferred to the third excited state of Tm^{3+} . For the sample with average diameter of 2.7 nm, the PL peak energy is at around 1.6 eV. Therefore, the majority of particles in the size distribution can contribute to energy transfer to the third excited state. On the other hand, for samples with average diameters of larger than 3.1 nm, only a small portion of particles in the size distribution interacts with the third excited state, resulting in a small $I_{\text{Tm}}/I_{\text{Si}}$ ratio.

It is noted here that, in our previous work on Er-doped nc-Si, the intensity ratio of Er^{3+} to nc-Si PL peaks ($I_{\text{Er}}/I_{\text{Si}}$) increased by a factor of ~ 4 in a relatively wide range between 1.2 and 1.6 eV.³ In contrast to this, $I_{\text{Tm}}/I_{\text{Si}}$ dramatically increases by a factor of ~ 18 in a narrower range between 1.45 and 1.6 eV. This indicates that the dramatic increase of $I_{\text{Tm}}/I_{\text{Si}}$ cannot simply be explained by the size dependence of nc-Si. Excitation of the third excited state of Tm^{3+} plays an important role in the energy transfer process.

C. Temperature dependence

Figure 6 shows PL spectra of the sample with Tm concentration of 1.41 at. % at various temperatures. The intensity scale above 0.8 eV is expanded by a factor of 10. With a decrease in temperature, the spectral shape changes gradually. First, below 150 K, a new broad peak appears at around 1.0 eV. This peak is considered to be due to the recombination of excitons trapped at P_b centers at the interfaces between nc-Si and SiO_2 matrices.^{18,19} Second, a very weak

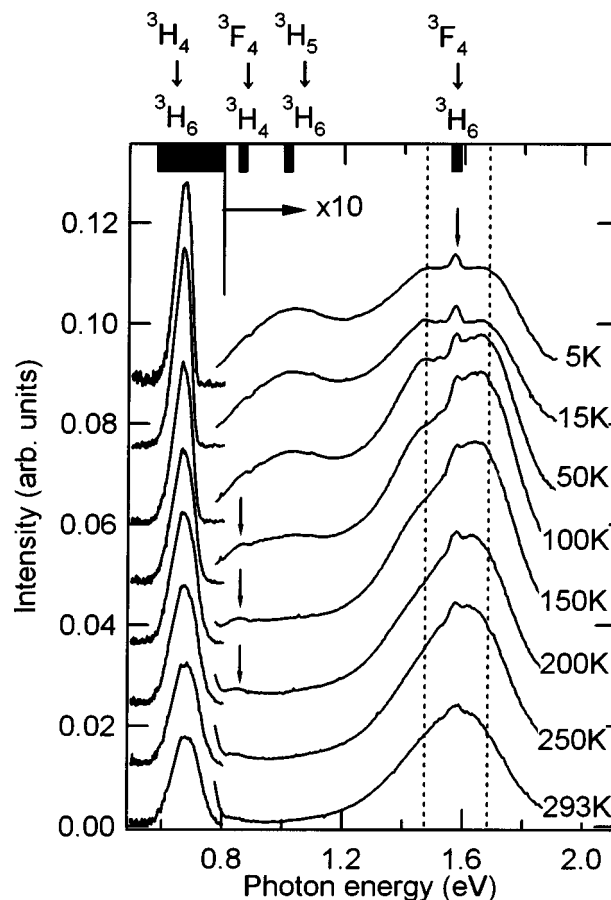


FIG. 6. PL spectra of the sample with Tm concentration = 1.41 at. % at various temperatures. Part of spectra at the higher-energy side above 0.8 eV is expanded by a factor of 10. Vertical lines are drawn at 1.48 and 1.68 eV.

peak appears at around 0.84 eV, indicated by arrows. Third, the 1.58 eV peak becomes more pronounced. The 0.84 and 1.58 eV peaks correspond to the intra-4f shell transitions of Tm^{3+} (3F_4 to 3H_4 and 3F_4 to 3H_6). Fourth, the 0.69 eV peak is shifted toward lower energy (0.69–0.67 eV) and becomes sharper. Finally, the spectral shape of nc-Si PL is strongly modified. At room temperature, the spectral shape is Gaussian like. At around 100 K, the lower energy side of the spectrum is strongly suppressed. At 5 K, both sides of the 1.58 eV PL are suppressed, and clear bends appear at around 1.48 and 1.68 eV. It should be noted here that without Tm doping, the spectral shape is almost independent of the temperature. Although not shown here, for samples of 3.1 and 3.3 nm, the suppression of nc-Si PL could be observed at the same energies at low temperatures.

The suppression of the spectrum at around the 3F_4 to 3H_6 transition PL of Tm^{3+} strongly suggests that the excitation energy of nc-Si for some particular sizes is resonantly transferred to Tm^{3+} before the spontaneous recombination of excitons occurs in nc-Si. To our knowledge, this is the first spectroscopic evidence of resonant energy transfer from nc-Si to Tm^{3+} .

If the energy transfer is made resonantly (without emitting phonons) or by emitting phonons, suppression should appear only at the high-energy side of the 1.58 eV peak. However, not only the higher-energy side, but also the lower-

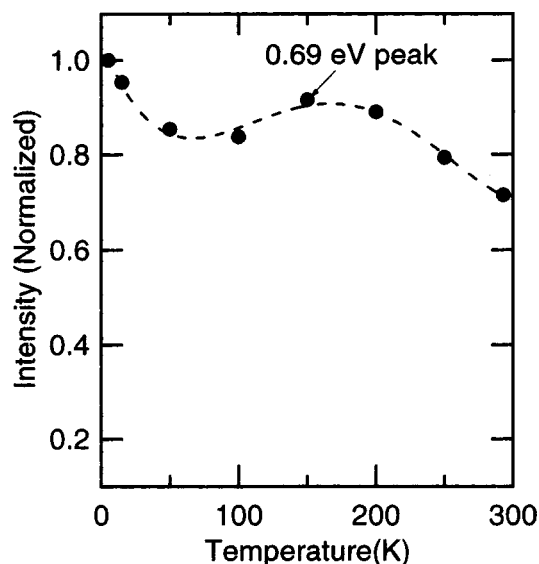


FIG. 7. Integrated intensities of the Tm^{3+} related peaks as a function of the temperature shown in Fig. 6. The intensity is normalized at 5 K. The dashed lines are to guide the eye.

energy side of the spectra is strongly suppressed. The suppression of the low-energy side can be explained by taking into account the indirect band-gap nature of nc-Si. As reported previously, the indirect-gap nature of bulk Si crystal is highly preserved in nc-Si even if its size is a few nanometer in diameter, i.e., radiative recombination of excitons in nc-Si requires the emission of momentum conserving phonons at Δ minima.²⁰ Since the transverse optical (TO) phonon energy at Δ minima is about 57 meV, nc-Si whose exciton recombination energy exactly coincides with the energy of the third excited state of Tm^{3+} (1.58 eV) shows PL at around 1.58 eV–57 meV if energy transfer does not occur. Therefore, the appearance of spectral suppression at the low-energy side of the 1.57 eV PL is direct evidence of resonant energy transfer from nc-Si to Tm^{3+} .

It is worth noting that the PL spectra of nc-Si become weak in the entire spectral range with an increase in Tm concentration, i.e., not only the spectral positions that satisfy the resonant energy transfer condition, but also other regions in broad PL bands of nc-Si are quenched. This indicates that there is a dominant nonresonant energy transfer process in addition to the resonant one. The energy conservation rule during energy transfer is satisfied by emitting various combinations of optical and acoustic phonons.

Figure 7 shows the integrated intensities of the 0.69 eV PL peak as a function of the temperature. The intensities of the 0.69 eV peak decrease slightly with an increase in temperature, although there is small fluctuation. The origin of the small fluctuation has not been identified. The cause of small temperature quenching is considered to be due to the small energy back transfer rate. In the present samples, excitation of Tm^{3+} is mainly to the third excited state due to the large band gap of nc-Si. Tm^{3+} excited to this higher state relaxes promptly to the lowest excited state (3H_4) before energy back transfer occurs. The probability of back transfer from the lowest excited state to nc-Si is negligibly small

even at room temperature due to the large energy mismatch. This may result in the rather small temperature quenching of the PL observed.

The observed temperature dependence of the PL intensity is qualitatively different from that reported by Franzó *et al.* for similar samples. In their report, the PL peak due to the transition from 3H_4 to 3H_6 states is at around 0.75 eV at room temperature. With a decrease in temperature, the PL intensity decreased and the PL disappeared below 100 K. The reason for this qualitative disagreement is not clear at present. One possible explanation is an artificial effect. Their data suggest that the measurement system does not have sensitivity below 0.72 eV. It might be that they measured only a high-energy tail of the spectrum. Since the 3H_4 to 3H_6 transition PL shifts toward lower energy and becomes sharp with a decrease in temperature, the signal intensity of the spectral region, where the measurement system has sensitivity, decreases with a decrease in temperature. This might have resulted in considerable underestimation of the PL intensity at low temperatures.

IV. CONCLUSION

The interaction between excitons in nc-Si and $4f$ -shell electrons in Tm^{3+} was studied by PL spectroscopy. We demonstrated that $4f$ -shell electrons in Tm^{3+} can be excited by energy transfer from nc-Si. The intensity of Tm^{3+} PL at 0.69 eV depended strongly on the size of nc-Si. As the PL energy of nc-Si approached the difference in energy between the third excited state and the ground state of Tm^{3+} (1.58 eV), the intensity of Tm^{3+} PL increased dramatically. This result indicates that the third excited state interacts more strongly with excitons confined in nc-Si than other energy states of Tm^{3+} . Tm^{3+} showed a very weak peak at around 1.58 eV in addition to the 0.75 eV peak. At low temperatures, broad PL spectra of nc-Si were suppressed at both sides of the 1.58 eV PL of Tm^{3+} . This suppression is spectroscopic evidence of resonant energy transfer from nc-Si to Tm^{3+} .

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