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Spectrally resolved energy transfer from excitons in Si nanocrystals to Er ions

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The energy transfer from Si nanocrystals (Si-nc's) to Er ions was studied spectroscopically. At low temperatures, inhomogeneously broadened photoluminescence bands of Si-nc's were partially quenched and some dips were observed. A comparison of the quenched spectra with a photoluminescence excitation spectrum revealed that the dips are due to the resonant energy transfer from excitons in Si-nc's to Er ions. For the energy transfer to the $^4I_{11/2}$ state of Er ions, two dips, one very clear and the other indistinctive, were observed, while to the $^4I_{9/2}$ state, two dips with comparable depth were observed. Modification of the band structure of Si-nc's by the quantum size effects is responsible for the different dip structures, depending on to which states the energy transfer is made.

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I. INTRODUCTION

Si nanocrystals (Si-nc's) are promising materials as a photosensitizer for substances with small oscillator strength such as molecular oxygen[1–3] (MO) and rare-earth (RE) ions.[4–10] By placing Si-nc's in close proximity to these substances, their optical excitation cross section is strongly enhanced due to efficient energy transfer from Si-nc's. Furthermore, excitation by white light becomes possible because of a broad absorption band of Si-nc's covering the whole visible range.

The mechanism of energy transfer from Si-nc's to MO has been studied for porous Si, which consists of networks of Si-nc's. Porous Si in vacuum shows an inhomogeneously broadened featureless photoluminescence (PL) band even at liquid He temperature due to size and shape distributions of Si-nc's. By adsorbing MO, the broad PL band is partially quenched, and periodic dips with the period of 63 meV appear in the inhomogeneously broadened PL band. The dip is the deepest at 1.63 eV, which coincides with the energy separation between the second excited $^1\Sigma$ and ground $^3\Sigma$ state of MO ($^3\Sigma$-$^1\Sigma$), indicating that Si-nc's with the band-gap energy of 1.63 eV transfer their excitation energy resonantly to MO. Si-nc's having other band-gap energies have to emit phonons to satisfy the energy conservation rule during the energy transfer process. This results in periodic features in the PL spectra, the period of which corresponds to the energy of maximum density of phonon states of bulk Si (63 meV). Magneto-optical spectroscopy reveals that the mechanism of the energy transfer is a triplet-triplet annihilation-type electron exchange process.[2]

Compared to MO, the mechanism of energy transfer to RE ions was less elucidated. Among several RE ions being reported to be sensitized by Si-nc's, Er ions have been studied most intensively because of their possible application in optical telecommunication fields.[11–14] In our previous paper, we studied the mechanism of energy transfer by analyzing time transient of PL from Er after pulsed excitation of Si-nc's sensitizer.[15,16] The analysis revealed that two energy transfer processes, i.e., fast and slow processes, work simultaneously. The energy transfer time of the fast process is less than 100 ns, while that of the slow one is several tenths of a microsecond. The contribution of the fast process among the total energy transfer process increases, e.g., from 55% to 77% in the previous samples,[16] with increasing the size of Si-nc's, suggesting that the fast process is essentially the same as that reported for Er-doped bulk Si crystals., i.e., excited excitons are trapped to Er-related trap centers and the recombination energy of excitons are transferred to Er ions by an Auger-like process.[17–19] On the other hand, the slow energy transfer process is considered to be due to the Förster-type[20] Coulombic interaction between excitons in Si-nc's and Er ions staying apart from Si-nc's, because the energy transfer rate showed strong dependence on the radiative recombination rate of excitons.[16] The direct interaction between excitons and Er ions should manifest itself as dips in inhomogeneously broadened PL bands of Si-nc's as has been observed in the case of exciton-MO interactions. In fact, we observed small features in PL bands of Si-nc's in SiO_2 films containing Er ions and Si-nc's.[15] Similar features were also reported for Er-doped Si-nc's/SiO_2 superlattices.[21] However, the observed features were indistinctive and some of them could be recognized only after taking derivatives. The obscurity of the features prevents a detailed analysis of the energy transfer mechanism, and the meaning of the features is still controversial.

One of the possible reasons for the obscurity of the features is that the crystallinity of Si-nc's is not perfect, and PL spectra are determined not only by size distribution but also by the energy of defect states. If PL arises mainly from defect states, even when Si-nc's with a particular size transfer energy resonantly to Er ions, the PL spectra will be quenched totally and dips will be very shallow and ill-defined. Therefore, improving the crystallinity of Si-nc's is indispensable to observe distinct features and to discuss the mechanism of energy transfer.

In this paper, we have succeeded in preparing Si-nc's that show pronounced spectral dips by carefully controlling sample preparation conditions. The PL spectra of these samples are measured as a function of temperature and excitation power.

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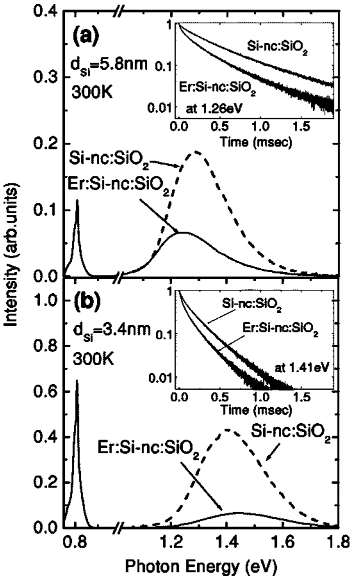

FIG. 1. PL spectra of Er:Si-nc:SiO$_2$ and Si-nc:SiO$_2$ at room temperature. The average sizes of Si-nc's are (a) 5.8 and (b) 3.4 nm. A sharp peak at 0.81 eV is due to the intra-4f shell transition ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) of Er ions, and the broad one to the recombination of excitons confined in Si-nc's. In the insets, decay curves of PL from Si-nc's with and without Er doping are shown.

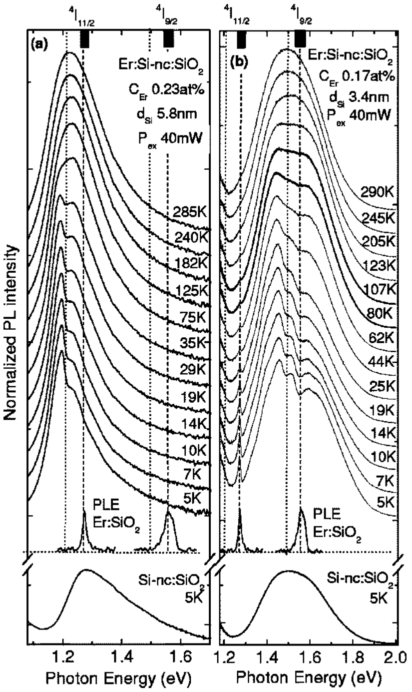

FIG. 2. Temperature dependence of the PL spectra of Er:Si-nc:SiO$_2$ (upper part). The average sizes of Si-nc's are (a) 5.8 and (b) 3.4 nm. The PL spectra of Si-nc:SiO$_2$ are shown in the lower part and the PLE spectrum of Er:SiO$_2$ is shown in the middle part. Vertical dashed lines are drawn to the energies of $^4I_{15/2} \rightarrow {}^4I_{11/2}$ and $^4I_{15/2} \rightarrow {}^4I_{9/2}$ transitions of 4f shell of Er ions. Vertical dotted lines are drawn 57 meV below these energies.

II. EXPERIMENTAL DETAILS

Er and Si-nc's codoped SiO$_2$ (Er:Si-nc:SiO$_2$) were prepared by a cosputtering method. Details of the preparation procedures are described in our previous papers.[6,7] Si, SiO$_2$, and Er$_2$O$_3$ were simultaneously sputterdeposited in argon (Ar) gas, and the deposited films (about 2 μm in thickness) were annealed in a nitrogen (N$_2$) gas (99.999%) atmosphere for 30 min at temperatures above 1200 °C. Si-nc's were grown in films of the mixture of SiO$_2$ and Er$_2$O$_3$ during the annealing. In this method, the size of Si-nc's can be controlled by changing the concentration of excess Si in films or changing the annealing temperature. Therefore, to realize a particular size distribution, different combinations of annealing temperature and Si concentration are possible. In the present paper, we choose a higher annealing temperature (above 1200 °C) and a lower Si concentration than those used in previous work.[6,7]

This preparation condition results in higher crystallinity of Si-nc's. The annealing temperature dependence of the crystallinity has been demonstrated by Iacona *et al.* by energy-filtered transmission electron microscopy.[22] They showed that in low-temperature annealed samples, e.g., ~1150 °C, substantial amounts of amorphous clusters remain, and the fraction of amorphous clusters decreases with increasing annealing temperature. In conventional PL spectroscopy excited by blue light, the difference in crystallinity does not appear clearly. However, the difference can be seen when the energy of excitation light is in the PL spectral band, and a small portion of particles in size distribution are excited. Under this resonant excitation condition, if the crystallinity is perfect, the PL spectra of Si-nc's show clear features corresponding to the emission and absorption of momentum-conserving phonons during the creation and recombination of excitons.[24] If defects are introduced in or on the surface of nanocrystals, the features become ill-defined.[23] In the present high-temperature annealing condition, the PL features are more pronounced than those of the samples annealed at lower temperatures, implying that the number of defective nanocrystals are reduced and the majority of excitons recombine radiatively without the participation of surface or defect-related recombination centers.

We have prepared samples with two different size distributions with the average sizes of about 3.4 and 5.8 nm. These sizes are chosen so that PL peak energies coincide with the excitation energies of the $^4I_{11/2}$ and $^4I_{9/2}$ states of Er ions. Er was doped rather heavily (0.2 at %) to make sure that all Si-nc's interact with Er ions.

PL spectra were measured using a single monochromator equipped with a Si charge-coupled device (detection energy 1.2–2.5 eV) or an InGaAs near-infrared diode array (detection energy 0.7–1.8 eV). The excitation source for taking the spectra was the 488-nm line of an Ar-ion laser. For all the spectra, the spectral response of the detection system was corrected by the reference spectrum of a standard tungsten lamp. In order to measure the PL excitation (PLE) spectra, an optical parametric oscillator (OPO) pumped by the third harmonic of a Nd:YAG laser and a liquid-nitrogen-cooled Ge photodiode were used as an excitation source and a detector, respectively. A continuous-flow-type He cryostat was used to take the temperature dependence of PL spectra.

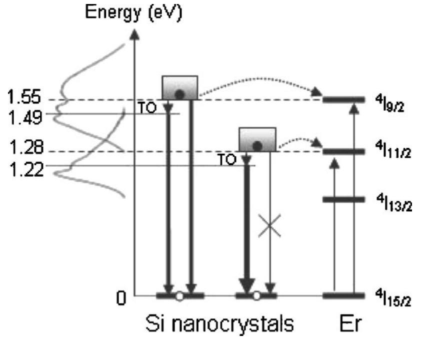

FIG. 3. Schematic illustration of an energy-level diagram of Si-nc's and Er ions. Si-nc's with the band-gap energies of 1.55 and 1.28 eV can resonantly excite Er ions to the $^4I_{9/2}$ and $^4I_{11/2}$ states, respectively. The luminescence energies of these nc-Si are one TO(Δ) phonon energy below or correspond to $^4I_{9/2}$ or $^4I_{11/2}$ states, resulting in dips in the positions shown in the figure.

III. RESULTS AND DISCUSSION

PL spectra of Er:Si-nc:SiO$_2$ and Si-nc's doped SiO$_2$ (Si-nc:SiO$_2$) at room temperature are shown in Fig. 1. The average sizes of Si-nc's are 5.8 and 3.4 nm for Figs. 1(a) and 1(b), respectively. A sharp peak at 0.81 eV corresponds to the intra-4f shell transition ($^4I_{13/2}$-$^4I_{15/2}$) of Er ions (Er PL), while the broad one arises from the recombination of excitons confined in Si-nc's (Si-nc PL), the intensity of which is decreased by Er doping. The quenching of the exciton PL by Er doping is accompanied by the shortening of lifetime, as can be seen in the insets of Fig. 1. The shortening of the lifetime is the evidence that nonradiative recombination due to energy transfer competes with radiative recombination of excitons. Although the PL lifetime of Si-nc's is reported not to be affected by Er doping in some of the literature,[8,12] in the present work the shortening is observed for all the samples.

In Figs. 2(a) and 2(b), the PL spectra of Er:Si-nc:SiO$_2$ are shown as a function of temperature. In order to compare the spectral shape, all the spectra are normalized at maximum intensity. At the bottom of these figures, the PL spectra of Si-nc:SiO$_2$ at 5 K are shown. Without Er doping, the spectra are broad and featureless. In contrast, small features start to appear on the spectra of Er:Si-nc:SiO$_2$ below 80 K, and clear dips can be seen at 5 K. It is interesting to note that only one dip (at around 1.22 eV) is observed in Fig. 2(a), while two dips with nearly identical depths (at around 1.49 and 1.55 eV) are observed in Fig. 2(b). A small peak at 1.27 eV at low temperatures in Fig. 2(b) is the emission of Er ions from the second excited state ($^4I_{11/2} \rightarrow {}^4I_{15/2}$).

In order to investigate the origin of these dips, PLE spectra of Er PL at 0.81 eV are measured for Er-doped SiO$_2$ (Er:SiO$_2$) (Fig. 2). We can see two peaks corresponding to the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ and $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transitions of Er ions. The energy positions of the $^4I_{11/2}$ and $^4I_{9/2}$ states with respect to the ground $^4I_{15/2}$ state are shown with the vertical dashed lines and the labels at the top of the figures. We can see that the positions of PLE peaks roughly coincide with those of dips. This coincidence suggests that the dips are due to the energy transfer from excitons in Si-nc's to Er ions. It should be stressed here that the dips are caused by nonradiative energy transfer, i.e., the exchange of near-field light, but not by the reabsorption of PL from Si-nc's by Er ions. The absorption cross section of Er ions is very small, and in the present samples, absorption due to the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ and $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transitions is not detectable by conventional absorption spectroscopy.

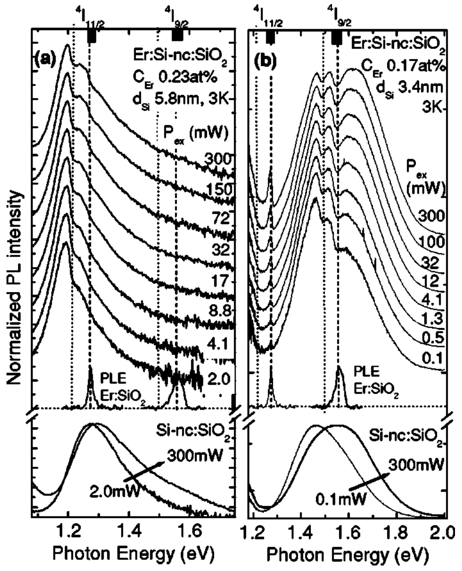

FIG. 4. Excitation power dependence of PL spectra of Er:Si-nc:SiO$_2$ (upper part). The average sizes of Si-nc's are (a) 5.8 and (b) 3.4 nm. PL spectra of Si-nc:SiO$_2$ excited by two different powers are shown in the lower part and the PLE spectrum of Er:SiO$_2$ is shown in the middle part. Vertical dashed lines are drawn to the energies of $^4I_{15/2} \rightarrow {}^4I_{11/2}$ and $^4I_{15/2} \rightarrow {}^4I_{9/2}$ transitions of 4f shell of Er ions. Vertical dotted lines are drawn 57 meV below these energies.

It is interesting to note that in Fig. 2(a), the spectral dip does not coincide perfectly with the $^4I_{11/2}$ state. It exists at about 57 meV below the $^4I_{11/2}$ state. On the other hand, in Fig. 2(b), the higher-energy dip coincides perfectly with the $^4I_{9/2}$ state, while the lower-energy one again stays at 57 meV below the $^4I_{9/2}$ state. The vertical dotted lines are drawn 57 meV below the $^4I_{9/2}$ and $^4I_{11/2}$ states. The reason that dips appear at 57 meV below the $^4I_{11/2}$ and $^4I_{9/2}$ states can be explained by considering the fact that Si-nc's inherit the indirect band-gap nature of bulk Si crystals. In bulk Si, the conduction band bottom is located in the vicinity of the X points of the Brillouin zone (Δ minima), and thus emission or absorption of momentum-conserving phonons are required for the optical transition. Usually, the TO phonon-assisted transition is the most dominant and the PL maximum appears at 57 meV (=TO phonon energy at Δ minima) below the band gap. Similarly in Si-nc's, TO phonon-assisted transition is reported to be the dominant recombination path in the present size range.[24]

In Fig. 3, the energy diagram of Er and Si-nc's is depicted. Si-nc's with the band-gap energy of 1.28 eV transfer energy resonantly to Er ions. Since, without Er doping, these Si-nc's luminesce at 1.22 eV by emitting one TO(Δ) phonon, PL quenching appears at around 1.22 eV. Similarly, resonant energy transfer from Si-nc's having the band-gap energy of

1.55 eV to the $^4I_{9/2}$ state results in the quenching at 1.49 eV.

If Si-nc's are purely indirect band-gap semiconductors, dips should appear always at 57 meV below excited levels of Er ions. In fact, in Fig. 2(a), we can see only one dip at 57 meV below the $^4I_{11/2}$ state. This means that Si-nc's having the band-gap energy in this region hold the indirect-band-gap nature strongly. On the other hand, two dips with nearly identical depths can be seen in Fig. 2(b). The observation of the dip exactly at the energy of the $^4I_{9/2}$ state implies that the probability of a quasidirect nonphonon optical transition is not negligibly small and it can compete with the TO(Δ) phonon-assisted transition.

The transition from an indirect band gap to a quasidirect one is a result of the quantum size effect. The confinement of excitons in a space comparable to or smaller than the Bohr radius of bulk excitons leads to uncertainty of quasimomentum and breakdown of the momentum conservation rule. Although this effect has been well known and theoretically studied in detail,[25] direct observation of the effect is not straightforward because of inhomogeneous broadening of PL bands. In order to lift the inhomogeneous broadening and extract the information of size-selected Si-nc's, spectral narrowing techniques such as resonant PL and hole burning spectroscopy should be employed.[24,26,27] The dips observed in this work can be regarded as holes in hole burning spectroscopy and quenched spectral region provides information on size-selected Si-nc's. Therefore, the present approach, i.e., digging spectral holes by resonant energy transfer to discrete electronic states of an energy acceptor, offers a new tool to extract information of size-selected semiconductor nanocrystals in inhomogeneously broadened PL bands.

The dips in the inhomogeneously broadened PL band appear most clearly when the PL maximum exists at the energy of excited states of Er ions. However, it is not easy to tune sample preparation conditions to realize it. Fortunately, the fine tuning of the PL maximum is possible by controlling the excitation power. The PL lifetime of Si-nc's at low temperatures is in the microsecond range, and thus the condition of the formation of two excitons in a nanocrystal can easily be achieved at rather low excitation power. In a Si-nc having two excitons simultaneously, Auger interaction between them is so efficient that one of them recombines nonradiatively by giving kinetic energy to an electron or a hole of the other exciton, resulting in saturation of the PL intensity. This effect is more significant for larger Si-nc's because of longer exciton lifetimes. Therefore, at high excitation power, a lower-energy side of the PL bands saturates, resulting in a high-energy shift of the band.

In the lower part of Fig. 4, the PL spectra of Si-nc:SiO_2 excited by different powers are compared. The shape of the PL features changes depending on the excitation power. We can see that the dips are more pronounced with increasing excitation power. This is because the PL peak energy of Si-nc's approaches the excited states of Er ions at higher excitation powers. It is worth noting that, in Fig. 4(a), a very weak dip appears at the position of the $^4I_{11/2}$ state when the PL band shifts to higher energy and the slope of the envelope function at the position becomes smaller by high-power excitation. This suggests that the band structure of Si-nc's with the band-gap energy of 1.26 eV is not purely indirect but that a quasidirect transition is slightly allowed.

IV. CONCLUSION

We have shown that inhomogeneously broadened PL bands of Si-nc's are partially quenched due to resonant energy transfer to discrete electronic states of Er ions. The observation of clear dips is the evidence that there is a direct interaction between excitons in Si-nc's and Er ions. The analysis of the dips gives us valuable information for electronic structures of size-selected Si nanocrystals. Si nanocrystals with the band-gap energy of around 1.28 eV strongly hold the indirect band-gap nature of bulk Si crystals, while quasidirect nonphonon optical transition becomes possible in Si-nc's of the 1.55-eV band gap.

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