Interaction between Er ions and shallow impurities in Si nanocrystals within SiO2

Imakita, Kenji
Yamaguchi, Yasuhiro
Fujii, Minoru
Hayashi, Shinji

Interaction between Er ions and shallow impurities in Si nanocrystals within SiO_2

Kenji Imakita, Minoru Fujii,* Yasuhiro Yamaguchi, and Shinji Hayashi
Department of Electrical and Electronics Engineering, Faculty of Engineering, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan
(Received 12 July 2004; revised manuscript received 1 September 2004; published 31 March 2005)

The interaction between Er^{3+} and shallow impurities in Si nanocrystals (nc-Si) is studied for SiO_2 films containing Er and nc-Si ($Er:nc\text{-}Si:SiO_2$). The luminescence property of Er^{3+} is strongly modified by shallow impurities in nc-Si. The formation of excess carriers in nc-Si by P or B doping results in the quenching of infrared photoluminescence (PL) of Er^{3+} and the shortening of the lifetime. When P and B are doped simultaneously and carriers are compensated, the intensity and the lifetime are recovered. It is shown that the mechanism of the interaction is Auger de-excitation of excited Er^{3+} with the interaction of electrons or holes in nc-Si. The estimated Auger coefficient is found to be two orders of magnitude smaller than that of Er doped bulk Si at low temperatures where carriers are bound to donor or acceptor ions, and four orders of magnitude smaller than that at room temperature. This small Auger coefficient makes nc-Si immune from the impurity Auger de-excitation process compared to Er doped bulk Si and is considered to be responsible for temperature independent efficient PL of $Er:nc\text{-}Si:SiO_2$ systems.

DOI: 10.1103/PhysRevB.71.115440 PACS number(s): 78.67.Bf, 73.22.−f, 78.55.−m

I. INTRODUCTION

Si nanocrystals (nc-Si) act as an efficient photosensitizer for Er ions (Er^{3+}).[1–4] The excitation cross section of Er^{3+} in SiO_2 ($Er:SiO_2$) is enhanced by more than four orders of magnitude if nc-Si are simultaneously doped ($Er:nc\text{-}Si:SiO_2$).[5–8] The enhanced excitation cross section is due to indirect excitation of Er^{3+} by the energy transfer from nc-Si. Since the absorption band of nc-Si covers the whole visible range, Er^{3+} can be excited by white light. The luminescence from Er^{3+} in this system exhibits almost no temperature quenching. Due to these remarkable features this system is considered to be a key component to realize planar waveguide-type compact optical amplifier operating at 1.54 μm.[9]

Detailed experimental and theoretical studies have been carried out to elucidate the mechanism of energy exchange between nc-Si and Er^{3+}.[5–8,10,11] In previous papers,[10,11] we studied the photoluminescence (PL) transient of Er^{3+} after pulsed excitation of nc-Si hosts and found that the intensity continues to rise after finishing excitation. The rising part contains valuable information about the energy exchange mechanism. The analysis of the rising part revealed that there are two different energy transfer processes occurring simultaneously, i.e., fast and slow processes, and the ratio of the fast to slow processes changes, depending on the size of nc-Si and Er concentration. From the size dependence of the energy transfer time, the fast process was assigned to be a trap-mediated process; an excited electron is trapped to Er^{3+} related center in the band gap, the recombination energy of a bound exciton is transferred to Er^{3+} by Auger-like process, and Er^{3+} is excited to the first excited state.[11] This process is essentially the same as that in Er doped bulk Si crystals (Er:bulk-Si).[12–14] On the other hand, the slow process is a characteristic one occurring only in nanocrystalline systems. This is probably the Förster[15] type Coulombic interaction between free excitons in nc-Si and Er^{3+}. Although the ratio of slow to fast processes increased with decreasing the size of nc-Si, the fast process was always the dominant energy transfer process in all the samples studied.

This conclusion seems to contradict the fact that luminescence properties of $Er:nc\text{-}Si:SiO_2$ are much different from those of Er:bulk-Si. Especially, the degree of temperature quenching of PL is much different; PL from $Er:nc\text{-}Si:SiO_2$ is almost insensitive to temperature, while that from Er:bulk-Si shows very strong temperature quenching. As the origin of the strong temperature quenching of Er:bulk-Si, two major de-excitation processes are considered.[16,17] The first one is an energy back-transfer process [Fig. 1(a)]. Since the lifetime of excited state of Er^{3+} is very long, the reverse energy transfer process can compete with spontaneous emission; excited Er^{3+} relaxes by exciting an electron to the trap level in the band gap of host Si. If the electron is thermally activated to the conduction band, luminescence from Er^{3+} is lost. This process becomes more significant at higher temperatures, resulting in very strong temperature quenching. The other de-excitation process is Auger de-excitation of excited Er^{3+} with energy transfer to free carriers in host Si [Fig. 1(b)]. The Auger coefficient of this process is determined to be $C_A = 5 \times 10^{-13}$ cm^3 s^{-1} for both free electrons and free holes.[16,18] When free carriers are frozen and the donor and acceptor levels are occupied at low temperatures, the inter-

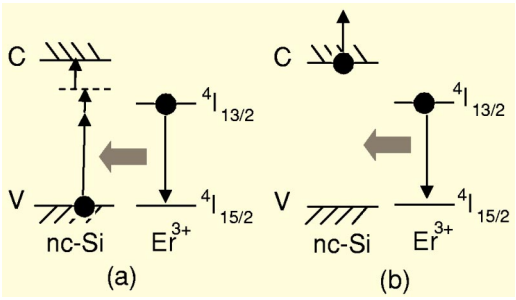

FIG. 1. Schematic representations of two possible nonradiative de-excitation processes for Er^{3+} bulk Si: (a) energy back transfer and (b) Auger deexcitation with free electrons.

action is made between Er^{3+} and electrons (or holes) bound to shallow donors (acceptors). The efficiency of this process is two orders of magnitude smaller than that of the Auger de-excitation with free carriers.[16,18] Therefore, the efficiency of the Auger de-excitation is also strongly enhanced at higher temperatures.

The fact that Er:nc-Si:SiO_2 shows very small temperature quenching suggests that these de-excitation processes are inefficient. The asymmetry between efficient excitation and inefficient de-excitation is thus the origin of the characteristic luminescence properties. The reason for the small de-excitation efficiency can qualitatively be explained as follows. The de-excitation by back transfer is completed by two consecutive processes, i.e., the excitation of an electron to an Er-related level and the thermalization of the electron to the conduction band [see Fig. 1(a)]. The Er-related-defect level is considered to be not strongly affected by the size of nc-Si because a localized state is usually not strongly modified by quantum size effects.[19–21] On the other hand, the conduction band edge goes up with decreasing the size. As a result, the energy necessary to release an electron from the level becomes larger, making the thermalization of an electron inefficient even at room temperature. The other de-excitation process, i.e., the Auger de-excitation shown in Fig. 1(b), is possible only when free or bound carriers exist in host materials. This process is thus expected to be prohibited if shallow impurities do not exist in nc-Si. In Er:nc-Si:SiO_2 systems studied so far, shallow impurities are not intentionally doped, resulting in the absence of the de-excitation process. However, if doped nc-Si are used as a photosensitizer, it is highly plausible that excited Er^{3+} has interaction with shallow impurities. A detailed study on the interaction provides additional information on the mechanism of energy exchange and is crucial in fully understanding the differences and similarities between Er:bulk-Si and Er:nc-Si:SiO_2 systems. The study also provides vital information on the interaction between excited Er^{3+} and photogenerated carriers in nc-Si. The knowledge on the interaction is indispensable to discuss whether or not multiple Er^{3+} can be excited by a single nanocrystal.

In this work, we have studied the interaction between excited Er^{3+} and shallow impurities in nc-Si by controlling P and/or B concentration in nc-Si systematically. We will demonstrate that PL properties of Er^{3+} are strongly modified by shallow impurities in nc-Si and discuss the mechanism of the interaction.

II. EXPERIMENTAL PROCEDURE

Films containing Er and shallow-impurity-doped nc-Si were prepared by a cosputtering method.[22–24] Si, Er_2O_3, SiO_2, borosilicate glass (BSG), and/or phosphosilicate glass (PSG) were simultaneously sputter-deposited in Ar gas on a quartz or a Si substrate. The thickness of films was about 1 μm. P (B) concentration in films was controlled by changing the areal ratio of P_2O_5 (B_2O_3) in sputtering targets. The average concentration of P_2O_5 in a whole film was determined by an electron probe microanalysis, and that of B_2O_3 by the intensity ratio of Si-O and B-O vibration signals in infrared (IR) absorption spectroscopy.[24,25] Er concentration was fixed to be about 0.02 at. %.

After the deposition, films were annealed in N_2 gas (99.999%) atmosphere for 30 min at 1150 °C. By annealing, nc-Si were grown in films of the mixture of SiO_2, Er_2O_3, B_2O_3, and/or P_2O_5. During the growth of nc-Si, P, and/or B were incorporated and activated in nc-Si. Growth of single-crystalline nc-Si in glass matrices was confirmed by transmission electron microscopic observations.[24,26] The average size of nc-Si in pure SiO_2 was about 4 nm in diameter. At low P and B concentration, the size of nc-Si was almost independent of impurity concentration, while at high concentration (e.g., >1 mol%), the average size became slightly larger than that of nc-Si in pure SiO_2 with the same Si concentration. This is because glass matrices are softened by P and B doping, resulting in longer diffusion length of Si atoms during annealing, which makes particles slightly larger.[24]

The evidences that P and/or B are doped into substitutional sites of nc-Si and are electrically active have been obtained from IR absorption spectroscopy[22] and electron spin resonance (ESR) spectroscopy.[23] In IR absorption spectra, when P (B) was doped, broad absorption due to free-carrier (or confined-carrier) absorption, i.e., intraconduction (valence) band transitions of electrons (holes), was observed, and it became stronger with increasing impurity concentration.[22] On the other hand, the absorption became very weak if nearly the same amount of P and B was doped simultaneously, meaning that carriers were compensated. In ESR spectra, a broad signal that can be assigned to free carriers was observed by P doping, and at low temperatures, hyperfine splitting of the signal due to the interaction of electron spin with the P nuclear spin was observed.[23] The observed hyperfine splitting was much larger than that of a P donor in bulk Si, being the direct evidence that P donor wave function was squeezed by quantum-confinement effects.

Although the existence of electrically active shallow impurities in nc-Si can be evidenced by IR absorption and ESR studies, the number of active dopants or excess carriers in each nanocrystal cannot simply be estimated even if the average P or B concentration in a whole film is known, because solubility of dopants is different between nc-Si and SiO_2, and they may precipitate at interface regions. However, considering the small size of nanocrystals, the number of carriers should be very small even when impurity concentration is very high, e.g., impurity concentration of 1×10^{20} cm^{-3} corresponds to in average 3.2 impurities per a nanocrystal 4 nm in diameter.

PL spectra were measured by using a single grating monochromator and an InGaAs near-infrared diode array. The spectral response of the detection system was calibrated with the aid of a reference spectrum of a standard tungsten lamp. For the time transient measurements, a 510 nm line of an optical parametric oscillator (OPO) pumped by the third harmonic of a Nd:YAG laser was used as an excitation source (pulse energy 0.5 mJ/cm^2, pulse width 5 nsec, and repetition frequency 20 Hz). In this wavelength, Er^{3+} is not directly excited. This means that only Er^{3+} having interaction with nc-Si can be excited by the energy transfer, and that not interacting with nc-Si is not excited. Emitted light was de-

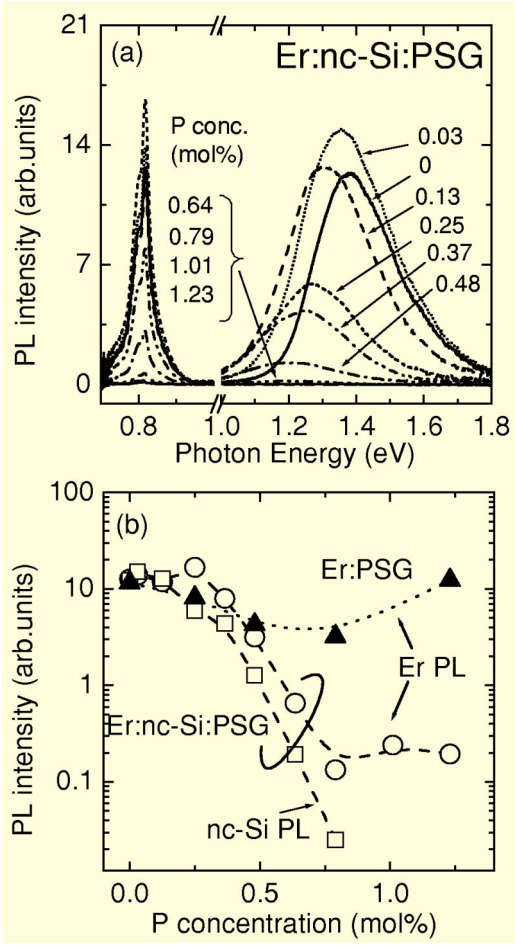

FIG. 2. (a) PL spectra of Er:nc-Si:PSG with different P concentration. A broadband centered at around 1.4 eV is due to recombination of excitons in nc-Si, and a sharp one at 0.81 eV arises from intra-4*f* shell transition of Er^{3+}. (b) P concentration dependence of PL peak intensities of Er^{3+} (○) and nc-Si (□) in Er:nc-Si:PSG, and that of Er^{3+} in Er:PSG (▲).

tected by a near-infrared photomultiplier (5509-72, Hamamatsu) and decay curves were recorded by a multichannel scaler. All measurements were carried out at room temperature.

As references, we studied PL properties of Er-doped PSG (Er:PSG) and Er-doped BSG (Er:BSG) prepared by the same procedure as that used for the other samples. Er^{3+} in these samples cannot be excited by 510 nm light. We, therefore, employed 521 nm light to excite Er^{3+} for the samples not containing nc-Si.

III. RESULTS AND DISCUSSION

A. P or B doping

Figure 2(a) shows PL spectra of nc-Si and Er doped PSG (Er:nc-Si:PSG) with different P concentration. Peaks are observed at around 1.4 and 0.81 eV. The 1.4 eV peak is assigned to the recombination of excitons confined in nc-Si, and the 0.81 eV one to the intra-4*f* shell transition of Er^{3+} (Er-PL). In Fig. 2(b), PL intensities of nc-Si and Er^{3+} are

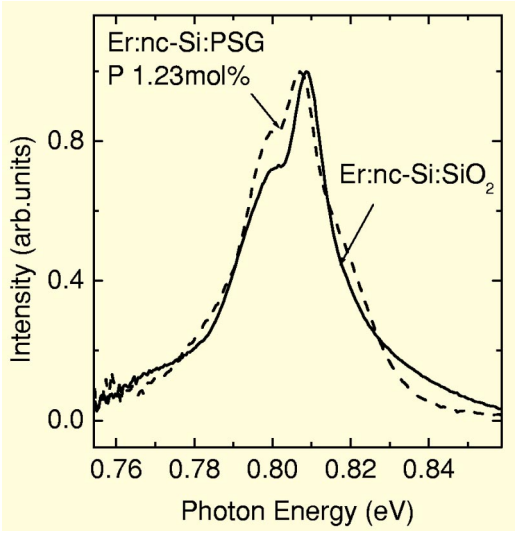

FIG. 3. PL spectra of Er^{3+} in Er:nc-Si:SiO_2 (solid curve) and in Er:nc-Si:PSG (P concentration of 1.23 mol %) (dashed curve).

plotted as a function of P concentration. The PL intensity of nc-Si (□) first increases slightly with increasing P concentration and then decreases monotonously. In the present Er concentration, nc-Si not interacting with Er^{3+} remain in a film, and the PL arises mainly from these nc-Si, because strong interaction with Er^{3+} efficiently quenches the PL. Therefore, the observed P concentration dependence can be explained by the same model proposed for nc-Si in PSG without Er^{3+} doping (nc-Si:PSG).[22,23] Low-concentration doping results in inactivation of dangling-bond defects at Si-SiO_2 interfaces, while heavy doping results in the formation of excess electrons in nc-Si, which quenches exciton luminescence by an impurity Auger process.

Below the P concentration of 0.79 mol %, the intensity of Er-PL shows similar behavior to that of nc-Si, while above 0.79 mol %, the intensity is slightly recovered. It should be stressed here that the observed strong P concentration dependence of the intensity below the P concentration of 0.79 mol % does not come from a modified local environment of Er^{3+} by P doping. This can be proved by studying P concentration dependence of PL from Er:PSG (▲ in Fig. 2). Without nc-Si, the variation of the intensity by P doping is much smaller. Furthermore, below the P concentration of 0.79 mol %, spectral shape of Er-PL is independent of P concentration. The observed strong quenching is thus due to the interaction between Er^{3+} and P in nc-Si.

Above the P concentration of 0.79 mol %, P concentration dependence of PL from Er^{3+} deviates from that from nc-Si, suggesting that the local environment of Er^{3+} is changed from that of low P concentration samples. In fact, above 0.79 mol %, the spectral shape of Er^{3+} is modified significantly as can be seen in Fig. 3. Although the effect of the local environment of Er^{3+} is interesting to study in detail, we will restrict our attention to the P concentration range of smaller than 0.79 mol % because the purpose of this work is to study the interaction between Er^{3+} and shallow impurities, and the change of the local environment makes the analysis of data more complicated.

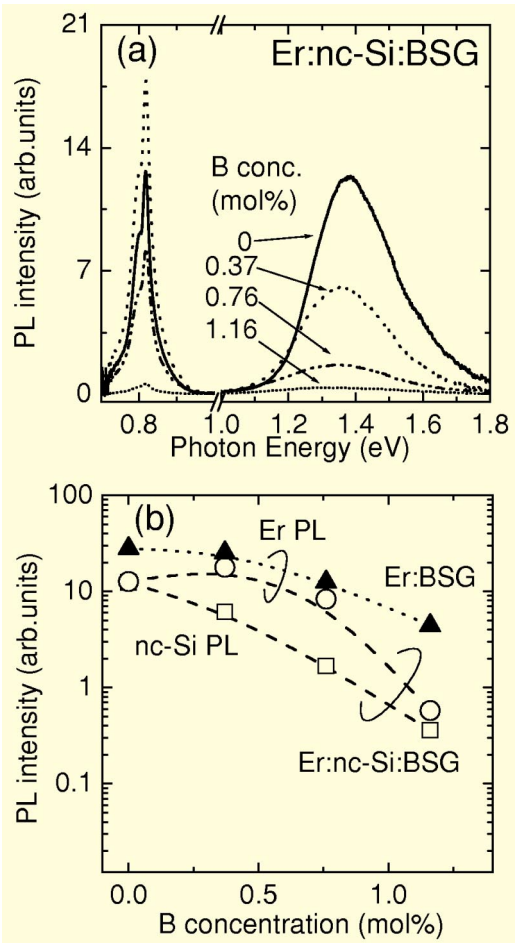

FIG. 4. (a) PL spectra of Er:nc-Si:BSG samples with different B concentration. (b) B concentration dependence of PL peak intensities of Er^{3+} (○) and nc-Si (□) in Er:nc-Si:BSG, and that of Er^{3+} in Er:BSG (▲).

Figure 4(a) shows PL spectra of nc-Si and Er^{3+} doped BSG (Er:nc-Si:BSG) with various B concentration. In contrast to the case of P doping, the change of spectral shape of Er-PL is not seen even at the highest B concentration. The PL intensities of nc-Si and Er^{3+} are plotted in Fig. 4(b) as a function of B concentration together with that of Er^{3+} in Er:BSG. We can see that the effect of B doping on the PL properties of nc-Si and Er^{3+} are qualitatively the same as that of P doping. This suggests that the mechanism of PL quenching by doping is within the first approximation independent of the polarity of doped carriers. In the following, we will discuss the mechanism mainly for P doped samples. The same discussion can be applied to B doped samples.

If excess carriers are supplied to nc-Si, then two quenching paths become active. The first one is Auger interaction within nc-Si; an exciton recombines nonradiatively by giving kinetic energy to an excess carrier [Fig. 5(a)]. If the rate of this process is comparable to or larger than that of energy transfer to Er^{3+}, then the energy transfer efficiency is suppressed. Therefore, PL efficiency of Er^{3+} interacting with doped nc-Si is smaller than that interacting with pure nc-Si. With increasing impurity concentration, the number of doped nc-Si increases, resulting in the quenching of Er-PL. This

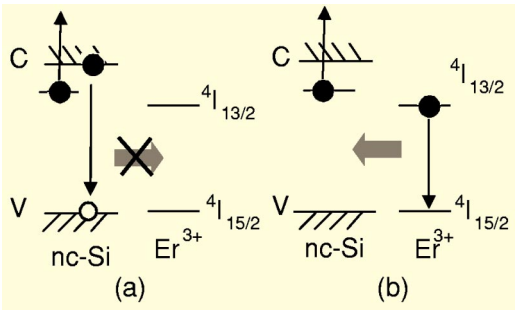

FIG. 5. Schematic representations of two possible mechanisms for the quenching of PL from Er^{3+}: (a) Auger recombination of an exciton within nc-Si with the interaction of an excess electron bound to a P donor and (b) Auger deexcitation of excited Er^{3+} with the interaction of an electron in nc-Si.

process does not affect the lifetime of the PL. The other mechanism of PL quenching is Auger de-excitation of excited Er^{3+} by giving energy to an excess carrier in nc-Si [Fig. 5(b)]. In this case, PL quenching is accompanied by the shortening of the lifetime. Therefore, these two processes can be distinguished by studying PL lifetime as a function of P(B) concentration.

Figures 6(a) and 6(b) show PL time transients of Er^{3+} for Er:nc-Si:PSG and Er:nc-Si:BSG, respectively. Without P (B) doping, the decay curve is nearly a single-exponential function with the lifetime of about 3.8 msec. By P (B) doping, the lifetime becomes shorter, and the decay curve deviates from a single-exponential function. The shortest lifetime observed is about 480 μsec for Er:nc-Si:PSG with the P con-

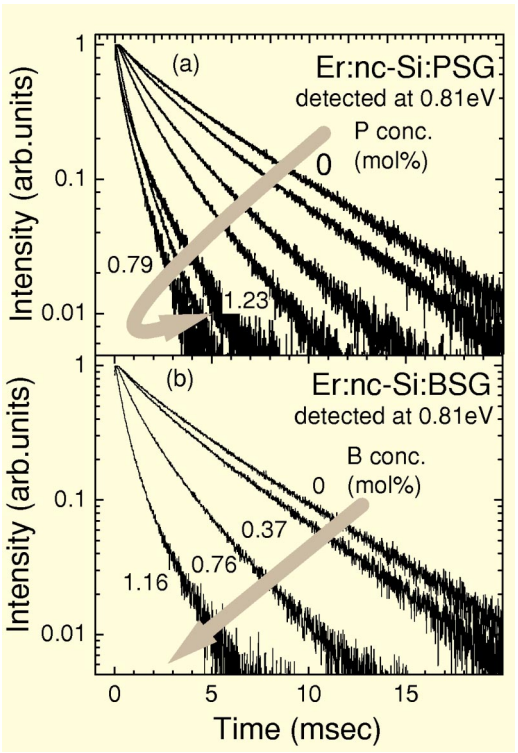

FIG. 6. PL time transient of Er^{3+} for (a) Er:nc-Si:PSG and (b) Er:nc-Si:BSG.

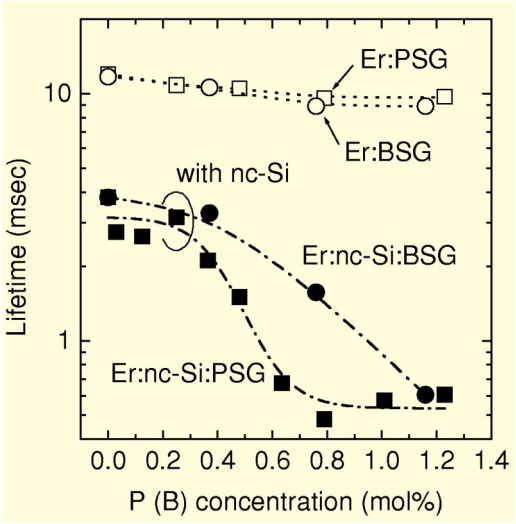

FIG. 7. PL lifetime of Er^{3+} as a function of P(B) concentration for Er:nc-Si:PSG (■), Er:nc-S:BSG (•), Er:PSG (□), and Er:BSG (○).

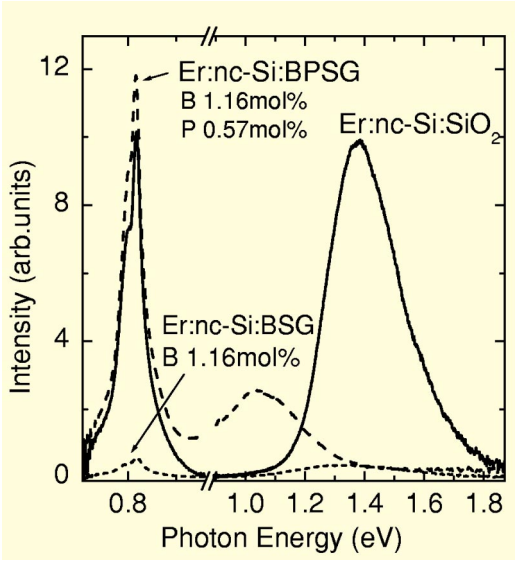

FIG. 8. (a) PL spectra of Er:nc-Si:SiO_2 (solid curve), Er:nc-Si:BSG (dotted curve), and Er:nc-Si:BPSG (dashed curve). B concentration in Er:nc-Si:BSG and Er:nc-Si:BPSG is the same.

centration of 0.79 mol %. In Fig. 7, the lifetime is plotted as a function of P (B) concentration together with the data obtained for Er:PSG and Er:BSG. The lifetime of Er-PL for Er:PSG (□) and Er:BSG (○) does not depend strongly on P and B concentrations. The observed shortening of lifetime in Er:nc-Si:PSG(BSG) is thus due to the interaction of excited Er^{3+} with shallow impurities in nc-Si.

As discussed in the Introduction, the cross section of impurity Auger interaction in Er:bulk-Si is two orders of magnitude different depending on whether carriers are free or bound. In nc-Si, donors or accepters are considered to be not ionized even at room temperature because of the enhanced ionization energy by quantum size effects.[19–21] Therefore, Er^{3+} interacts with bound carriers in nc-Si, and thus the situation is similar to Er:bulk-Si at low temperatures. Unfortunately, theory of Auger de-excitation of impurities with bound carriers does not lead to a simple final formula, and thus a phenomenological treatment has been applied to quantitatively analyze the phenomena in Er:bulk-Si.[16] In the treatment, the effective Auger coefficient (C_A) is estimated from the relation, $1/\tau = 1/\tau_0 + C_A N_A$, where τ and τ_0 are the lifetime of Er^{3+} for the samples with and without impurity doping, and N_A the excess carrier concentration.[16] In the present samples, N_A cannot simply be estimated from average P or B concentration, because P or B are not expected to be uniformly distributed. However, rough estimation is possible. For example, for the Er:nc-Si:PSG sample with P concentration of 0.79 mol %, PL intensity of nc-Si is nearly completely quenched. This suggests that almost all nc-Si have at least one electrically active P atom. One P in a nanocrystal with 4 nm in diameter corresponds to the P concentration of 3×10^{19} cm^{-3}. Thus N_A should be larger than 3×10^{19} cm^{-3}. This estimation gives us the maximum possible value of C_A of 6.1×10^{-17} cm^3 s^{-1}. This value is two orders of magnitude smaller than that reported for Er^{3+} doped bulk Si for bound carriers.[16] Similar value is obtained for Er:nc-Si:BSG samples.

It is now clear that the shortening of PL lifetime by the impurity Auger process is the cause of observed quenching of Er-PL. However, the quenching cannot be fully explained by the mechanism. In the case of P doping, the intensity of Er-PL is decreased by two orders of magnitude, while the lifetime is shortened by one order of magnitude. This difference suggests that impurity Auger within nc-Si [Fig. 5(a)] competes with energy transfer to Er^{3+}, and is also responsible for the quenching. As mentioned in the introduction, there are two energy transfer processes, i.e., fast and slow processes. Among them, the slow process, the time scale of which is μsec range, is more strongly affected. In fact, the slow rising part of Er-PL after pulsed excitation disappears by P or B doping.

B. P and B doping

PL properties of simultaneously P and B doped samples (Er:nc-Si:BPSG) give us additional information on the interaction between Er^{3+} and shallow impurities. Figure 8 compares the PL spectra of Er^{3+} in Er:nc-Si:SiO_2, Er:nc-Si:BSG and Er:nc-Si:BPSG. B concentration in Er:nc-Si:BSG and Er:nc-Si:BPSG is the same (1.16 mol %). We can see that quenching of Er-PL by B doping is recovered by adding P to nearly the same intensity as that of Er:nc-Si:SiO_2. The recovery of the PL intensity is accompanied by the appearance of a broad peak below the bandgap of bulk Si. The low energy peak has been observed for B and P doped nc-Si without Er doping, and assigned to the optical transition between impurity states formed in the band gap of nc-Si by B and P doping.[24,27] The intensity of the impurity-related PL of Er:nc-Si:BPSG is much larger than that of Er:nc-Si:BSG due to the compensation of excess carriers in nc-Si.

The recovery of Er-PL by P doping can also be explained by carrier compensation. By compensation, both Auger recombination processes shown in Figs. 5(a) and 5(b), i.e., within nc-Si and between excited Er^{3+} and carriers in nc-Si, respectively, are suppressed. The suppression of the second

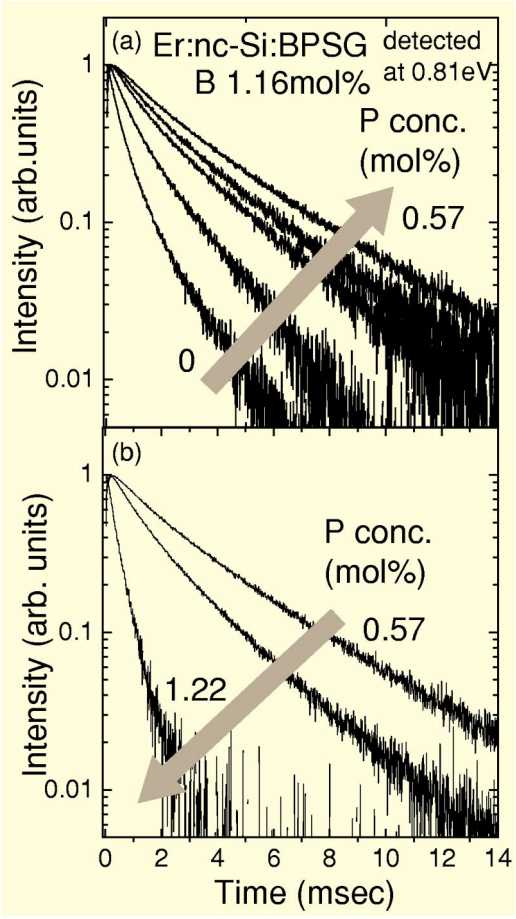

FIG. 9. PL time transient of Er^{3+} in Er:nc-Si:BPSG. B concentration is fixed to 1.16 mol %, and P concentration is changed (a) from 0 to 0.57 mol % and (b) from 0.57 to 1.22 mol %.

deexcitation process should manifest itself as recovering of the lifetime of PL. Figures 9(a) and 9(b) show the time transient of Er-PL in Er:nc-Si:BPSG. B concentration is fixed to 1.16 mol %, and P concentration is changed from 0 to 1.22 mol % [from 0 to 0.57 mol % in Fig. 9(a), and from 0.57 to 1.22 mol % in Fig. 9(b)]. The lifetime estimated from Fig. 9 is plotted in Fig. 10 as a function of P concentration together with the PL intensities of nc-Si and Er^{3+}. In Figs. 9(a) and 10, we can see that the lifetime of Er-PL, which is shortened by B doping, is drastically recovered by adding P. The longest lifetime observed is about 3 ms. This value is very close to that of Er:nc-Si:SiO_2 (3.8 ms), meaning that carriers in nc-Si are almost perfectly compensated and Auger de-excitation does not work. In fact, the PL intensities of both nc-Si and Er^{3+} are the maximum at this P concentration.

After passing through the longest lifetime point, further increase of P concentration results in shortening of lifetime, which is accompanied by the quenching of PL from nc-Si and Er^{3+} [Figs. 9(b) and 10]. Formation of excess electrons by further P doping realizes the same situation as that of Er:nc-Si:PSG.

In Fig. 10, the longest PL lifetime is obtained when B and P concentration in a whole film is 1.16 mol % and 0.57 mol %, respectively, indicating that carriers in nc-Si are

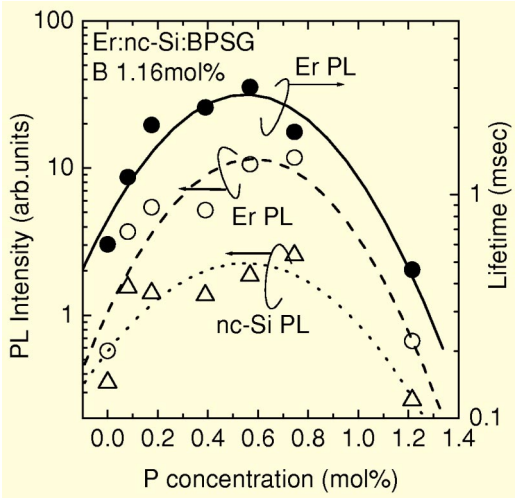

FIG. 10. The intensities of nc-Si (△) and Er (○) PL, and the lifetime of Er PL (•) as a function of P concentration for Er:nc-Si:BPSG. B concentration is fixed to 1.16 mol %.

perfectly compensated in this concentration. This result contradicts our previous results on PL from P and B codoped nc-Si.[27] In that case, PL from nc-Si was the strongest when B and P concentration in a whole film was nearly the same. Two mechanisms are considered as the origin of the discrepancy. The first one is that the distribution of B and P in a film is modified by Er doping, i.e., suppression of B doping in nc-Si or enhancement of P doping, resulting in carrier compensation in nc-Si when P concentration in a whole film is nearly the half of B concentration. The second possible model is that doped Er^{3+} acts as a donor and thus smaller amount of P is necessary for compensation. Donor behavior of Er^{3+} is well known in Er:bulk-Si, and compensation of the donor by B doping is demonstrated.[16] At present, we have no direct evidence to decide which mechanism is working.

IV. CONCLUSION

We have studied the interaction between shallow impurities in nc-Si and Er^{3+}. It was shown that shallow-impurity doping drastically decreases the efficiency of Er-PL. Two different Auger processes are responsible for quenching. Auger recombination of photoexcited excitons with the interaction of electrons or holes supplied by impurity doping competes with energy transfer to Er^{3+} and degrades energy transfer efficiency. Even if excitation of Er^{3+} by the energy transfer is successfully completed, radiative relaxation of Er^{3+} has to compete with Auger de-excitation with the interaction of electrons or holes in nc-Si, resulting in shortening of lifetime and degradation of the quantum efficiency. These effects are very similar to that observed for Er:bulk-Si, thus supporting our previous conclusion that the mechanism of the interaction between nc-Si and Er^{3+} is qualitatively the same as that of Er:bulk-Si.[11] However, there are some quantitative differences. The estimated Auger coefficient is found to be two orders of magnitude smaller than that of Er:bulk-Si at low temperatures, where carriers are bound to donor or acceptor ions, and four orders of magnitude smaller than

that at room temperature. This small Auger coefficient makes nc-Si immune from the impurity Auger de-excitation process compared to Er:bulk-Si and is considered to be one of the origins of temperature independent efficient PL of $Er:nc\text{-}Si:SiO_2$ systems.

We also studied the effects of carrier compensation on PL from Er^{3+} and demonstrated that perfectly compensated nc-Si does not degrade PL from Er^{3+}, although PL properties of nc-Si themselves are strongly modified. The recovery of luminescence properties by compensation is another evidence of the interaction between excited Er^{3+} and shallow impurities in nc-Si.

It is very plausible that Auger de-excitation of Er^{3+} with the interaction of carriers in nc-Si is not limited to the situation that the carriers are supplied by shallow impurity doping. The de-excitation may also be possible in $Er:nc\text{-}Si:SiO_2$ containing pure nc-Si if the second exciton is photogenerated in a nanocrystal when Er^{3+} is already excited by the energy transfer from the nanocrystal. The Auger interaction of the excited Er^{3+} with the photogenerated carrier may quench Er-PL, if the rate of this process is comparable to or larger than that of the energy transfer rate. If this process really works, then excitation of multiple Er^{3+} by a single nanocrystal becomes very inefficient and one nanocrystal can excite only one Er^{3+} during the lifetime of excited Er^{3+}. This conclusion is consistent with the result obtained by Kik *et al.*[8]

ACKNOWLEDGMENTS

This work is supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and, in part, by the Industrial Technology Research Grant Program in 2002 from the New Energy and Industrial Technology Development Organization (NEDO), Japan.

*Corresponding author. Electronic mail: fujii@eedept.kobe-u.ac.jp

[1] C. E. Chryssou, A. J. Kenyon, T. S. Iwayama, C. W. Pitt, and D. E. Hole, Appl. Phys. Lett. **75**, 2011 (1999).
[2] A. J. Kenyon, P. F. Trwoga, M. Federighi, and C. W. Pitt, J. Phys.: Condens. Matter **6**, L319 (1994).
[3] M. Fujii, M. Yoshida, Y. Kanzawa, S. Hayashi, and K. Yamamoto, Appl. Phys. Lett. **71**, 1198 (1997).
[4] M. Fujii, M. Yoshida, S. Hayashi, and K. Yamamoto, J. Appl. Phys. **84**, 4525 (1998).
[5] D. Pacifici, G. Franzo, F. Priolo, F. Iacona, and L. DalNegro, Phys. Rev. B **67**, 245301 (2003).
[6] F. Priolo, G. Franzò, D. Pacifici, V. Vinciguerra, F. Iacona, and A. Irrera, J. Appl. Phys. **89**, 264 (2001).
[7] A. J. Kenyon, C. E. Chryssou, C. W. Pitt, T. Shimizu-Iwayama, D. E. Hole, N. Sharma, and C. J. Humphreys, J. Appl. Phys. **91**, 367 (2002).
[8] P. G. Kik and A. Polman, J. Appl. Phys. **88**, 1992 (2000).
[9] J. H. Shin, S.-Y. Seo, S. Kim, and S. G. Bishop, Appl. Phys. Lett. **76**, 1999 (2000).
[10] K. Watanabe, M. Fujii, and S. Hayashi, J. Appl. Phys. **90**, 4761 (2001).
[11] M. Fujii, K. Imakita, K. Watanabe, and S. Hayashi, J. Appl. Phys. **95**, 272 (2004).
[12] M. S. Bresler, O. B. Gusev, B. P. Zakharchenya, and I. N. Yassievich, Phys. Solid State **38**, 813 (1996).
[13] M. Forcales, T. Gregorkiewicz, M. S. Bresler, O. B. Gusev, I. V. Bradley, and J-P. R. Wells, Phys. Rev. B **67**, 085303 (2003).
[14] M. Forcales, T. Gregorkiewicz, and M. S. Bresler, Phys. Rev. B **68**, 035213 (2003).
[15] T. Förster, Ann. Phys. **2**, 55 (1948).
[16] F. Priolo, G. Franzò, S. Coffa, and A. Carnera, Phys. Rev. B **57**, 4443 (1998).
[17] S. Coffa, G. Franzò, F. Priolo, A. Polman, and R. Serna, Phys. Rev. B **49**, 16 313 (1994).
[18] A. Suchocki and J. M. Langer, Phys. Rev. B **39**, 7905 (1989).
[19] C. Delerue, M. Lannoo, G. Allan, E. Martin, I. Mihalcescu, J. C. Vial, R. Romestain, F. Muller, and A. Bsiesy, Phys. Rev. Lett. **75**, 2228 (1995).
[20] C. Delerue, M. Lannoo, G. Allan, and E. Martin, Thin Solid Films **255**, 27 (1995).
[21] G. Allan, C. Delerue, M. Lannoo, and E. Martin, Phys. Rev. B **52**, 11 982 (1995).
[22] A. Mimura, M. Fujii, S. Hayashi, D. Kovalev, and F. Koch, Phys. Rev. B **62**, 12 625 (2000).
[23] M. Fujii, A. Mimura, S. Hayashi, Y. Yamamoto, and K. Murakami, Phys. Rev. Lett. **89**, 206805 (2002).
[24] M. Fujii, K. Toshikiyo, Y. Takase, Y. Yamaguchi, and S. Hayashi, J. Appl. Phys. **94**, 1990 (2003).
[25] A. S. Tenny, J. Electrochem. Soc. **118**, 1658 (1971).
[26] S. Takeoka, M. Fujii, and S. Hayashi, Phys. Rev. B **62**, 16 820 (2000).
[27] M. Fujii, Y. Yamaguchi, Y. Takase, K. Ninomiya, and S. Hayashi, Appl. Phys. Lett. **85**, 1158 (2004).