High-Efficiency Erbium Ion Luminescence in Silicon Nanocrystal Systems


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Abstract—The photoluminescence spectra and kinetics of both erbium-doped and undoped multilayer structures of quasi-ordered silicon nanocrystals in a silicon dioxide matrix were studied. It was shown that the optical excitation energy of silicon nanocrystals 2–3 nm in size can be practically completely transferred to Er$^{3+}$ ions in the oxide surrounding the nanocrystals, with its subsequent radiation at 1.5 µm. Possible reasons for the high excitation efficiency of the Er$^{3+}$ ions are discussed, and the conclusion is drawn that the Förster mechanism is dominant in the energy transfer processes occurring in these structures. © 2004 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

Considerable attention has been focused in recent years on Er$^{3+}$ ion luminescence in crystalline and amorphous silicon (see, e.g., [1, 2]). This interest stems from the need to develop silicon devices capable of emitting light efficiently at a wavelength of 1.54 µm (the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transitions in the inner 4f shell of the Er$^{3+}$ ion), which corresponds to the maximum transparency of fiber communication lines. The development of such optoelectronic devices is hindered, however, by a number of still unsolved problems. For instance, if crystalline silicon (c-Si) is used as a matrix for Er$^{3+}$, strong thermal quenching of the erbium luminescence is observed, which is caused by the nonradiative Er$^{3+}$ ion deexcitation originating from the energy transfer back to the matrix [3]. As a result, the room-temperature luminescence quantum efficiency of c-Si : Er samples turns out to be very low. The 1.5-µm photoluminescence (PL) and electroluminescence of erbium-doped amorphous hydrogenated silicon (a-Si : H : Er) features a fairly weak temperature dependence [4]. Furthermore, analysis of the PL kinetics in a-Si : H : Er suggests that the energy of the electron–hole pairs is transferred to Er$^{3+}$ ions in fairly short (submicrosecond-scale) times, which accounts for the high efficiency of their excitation [5–7]. Because, however, of the existence of various nonradiative energy-loss channels, the erbium luminescence intensity in a-Si : H : Er is still not high enough to make this material promising for application in light-emitting devices.

A promising approach to combating these difficulties could be the use of erbium-doped silicon nanocrystals (nc-Si) embedded in an insulating matrix [8–11]. It should be pointed out that, although the wavelength of the erbium luminescence is practically independent of the nature of the matrix because of the “operating” Er$^{3+}$ 4f shell being screened by the outer electronic shells, the ion excitation efficiency can be controlled by properly varying the properties of the matrix, for instance, the width of its band gap, and/or the density of electronic states of the defects and impurities contained in the matrix [1, 3]. This can be readily reached in nc-Si structures, because the band gap of nanocrystals can be varied within broad limits by properly varying their dimensions [12, 13]. Furthermore, in Si nanocrystals one can simultaneously attain both a good carrier localization in small space regions near the Er atoms and fairly long (hundreds of microseconds) lifetimes of the electronic excitation [12, 13]. In this case, the energy released in recombinaction of a photoexcited electron–hole pair can be efficiently transferred to the Er$^{3+}$ ion. Indeed, samples of erbium-doped nc-Si in a SiO$_2$ matrix exhibit an intense and stable Er$^{3+}$ ion PL even at room temperature [9, 10]. Note that the efficiency of the PL and its lifetime depend strongly on the technique by which the nc-Si/SiO$_2$ structures were prepared, as well as on the size of the Si nanocrystals [9]. This suggests that layers of quasi-ordered silicon nanocrystals in nc-Si/SiO$_2$ superlattices, which permit easy tailoring of the nanocrystals to desired sizes, could have application potential [11].

This report deals with a comparative study of the PL spectra and kinetics of multilayered nc-Si/SiO$_2$ structures, both erbium-doped and not containing this impurity, which makes it possible to judge the efficiency of electronic excitation energy transfer from silicon nanocrystals to the Er$^{3+}$ ions in such structures.
2. SAMPLES AND EXPERIMENTAL TECHNIQUES

The nc-Si/SiO\(_2\) structures studied here were prepared by successive deposition of SiO and SiO\(_2\) layers on a c-Si substrate by reactive sputtering [10, 11]. The SiO layers were 2 and 3 nm thick in samples A and B, respectively. The structures consisted of 40–50 pairs of layers for a total thickness of 200–300 nm. The samples were thermally annealed at a temperature of 1100 °C in a nitrogen environment for 60 min to produce layers of closely packed Si nanocrystals separated by SiO\(_2\) layers [11]. As follows from electron microscopy and x-ray diffraction measurements, the nanocrystal size was 2–0.5 and 3.5–0.5 nm in samples A and B, respectively. After the annealing, 300-keV Er\(^{3+}\) ions were implanted in part of the structures to a dose of 5 \(\cdot\) 10\(^{14}\) cm\(^{-2}\). After the implantation, the samples were thermally annealed at 950 °C for 5 min.

Two lots of samples containing Si nanocrystals were prepared in this way: the starting nc-Si/SiO\(_2\) structures (samples A and B) and Er-doped nc-Si/SiO\(_2\) : Er structures (samples AE and BE). According to our estimates, the concentration of Er atoms in the AE and BE samples was approximately equal to that of Si nanocrystals, which, from TEM observations, was \(\sim 10^{19}\) cm\(^{-3}\) [11]. Besides the above structures, we also studied samples formed by implanting Er\(^{3+}\) ions of the above-mentioned energy and to the same dose into a uniform amorphous SiO\(_2\) film 250 nm thick, with its subsequent fast thermal annealing to remove implantation defects (CE samples).

A pulsed N\(_2\) laser (photon energy 3.68 eV, pulse duration 10 ns, pulse energy density 10 μJ/cm\(^2\), pulse repetition frequency 100 Hz) was employed to excite the PL. The PL spectra were recorded using a computerized spectrometer equipped with an InGaAs photodiode. The measured spectra were corrected for the spectral response of the system. The PL kinetics in the visible region of the spectrum was measured with a PM tube with a time constant of \(\sim 30\) ns complemented by an InGaAs photodiode with a time constant of \(\sim 1\) μs to cover the IR region. Because the sensitivity of the latter diode was not high enough, it was used in studies of the initial part of the kinetics only to measure the integrated PL intensity in the range 1.1–1.6 μm. The slow PL relaxation components were recorded using an InGaAs photodiode with a time constant of 0.5 ms. The spectral resolution in the measurement of the erbium PL kinetics was 4 nm.

Most of the studies of the PL spectra and kinetics were conducted in air at a temperature of 300 K. Several PL spectra were also measured in vacuum in the temperature range 10–450 K with the use of a DE-204N closed-cycle cryostat (Advanced Research Systems).

3. RESULTS AND DISCUSSION

Figure 1 shows PL spectra of samples A and B. The A structures containing Si nanocrystals with smaller average dimensions are seen to exhibit a blue-shifted PL spectrum. This shift is known [11, 12] to be usually associated with an increase in the band gap of nc-Si caused by the quantum-confinement effect. The PL spectra have a fairly large band width, with a FWHM of 0.35 eV for samples A and 0.3 eV for samples B.

Our measurements revealed a weak increase (by a factor 1.5–2) in the PL intensity of samples A and B with the temperature decreasing from 300 to 6 K. Such an increase indicates a good passivation of nonradiative recombination centers in the structures under study. Note that the PL external quantum efficiency of samples A at \(T = 10\) K was found to be \(\sim 1\)%.

As is evident from Fig. 2, erbium implantation results in a considerable suppression (by more than two
due to the intracenter time, the CE samples representing uniform structures with slightly larger nanocrystals. At the same time, the erbium band were also observed to occur in BE matrix [1, 2]. Quenching of the nc-Si PL and formation of a strong band near 0.81 eV (\(I_{13/2} \rightarrow I_{15/2}\) transitions, is always observed in Er\(^{3+}\) ions embedded in a solid matrix [1, 2]. Quenching of the nc-Si PL and formation of the erbium band were also observed to occur in BE structures with slightly larger nanocrystals. At the same time, the CE samples representing uniform \(a-SiO_2:Er\) layers exhibited an extremely low PL intensity in the vicinity of 0.8 eV. These samples primarily produced a weak band at 1.1 eV, which originates from interband radiative recombination in the \(c-Si\) substrate.

The band at 1.1 eV in the CE samples and the shoulder observed in the same spectral region in the A and AE samples are apparently due to the penetration of the pump radiation into the single-crystal silicon substrate as a result of the layers under study being partially transparent.

The data displayed in Fig. 2 indicate that Er\(^{3+}\) ions in the nc-Si/SiO\(_2\): Er structures under study are excited through the transfer of electron excitation energy from the Si nanocrystals. Recalling the relative magnitude of the PL intensities in samples A and AE, we can reasonably assume that the energy absorbed by the nanocrystals is largely transferred to the optically active Er\(^{3+}\) ions. The actual mechanism of energy transfer will be discussed in more detail below. We note, however, that a certain contribution to the residual nc-Si PL in samples AE and BE comes apparently from the nanocrystals that are so distant from Er\(^{3+}\) as to make their interaction with these ions inefficient. As is evident from a comparison of curves 1 and 2, the nc-Si PL band undergoes a change in its spectral shape after the implantation of Er\(^{3+}\) ions in the nc-Si/SiO\(_2\) structures. One clearly sees an enhancement of PL quenching by a few times with the photon energy increasing from 1.3 to 1.7 eV. This can be interpreted, in terms of the mechanism of inhomogeneous broadening of the nc-Si PL band, as indicating a more efficient energy transfer from smaller nanocrystals (i.e., nanocrystals with a larger band gap) [9]. In view of a possible contribution from homogeneous broadening associated with the electron–phonon coupling and polariton effects, this increase in PL quenching with increasing photon energy implies more efficient energy transfer from nonthermalized excitons (i.e., excitons residing in nonstationary or excited states).

Experiments showed that the erbium PL intensity in nc-Si/SiO\(_2\): Er structures increases noticeably with the temperature decreasing from 300 to 10 K (Fig. 3). At the same time, the band intensity integrated over the spectrum in the range 0.75–0.85 eV increases only by a factor of 1.5 (see inset to Fig. 3). Such an increase indicates a low efficiency of the competing nonradiative recombination channels, for instance, of the energy transfer from Er\(^{3+}\) back to the solid matrix or of the recombination at point defects, such as silicon dangling bonds.

Let us turn now to an analysis of the PL kinetics of silicon nanocrystals. As seen from Fig. 4, relaxation of the PL intensity \(I_{PL}(t)\) in undoped nc-Si/SiO\(_2\) structures following a laser pulse cannot be fitted by an exponential. Our analysis showed that the PL kinetics can be well approximated by an extended exponential,

\[
I_{PL}(t) = I_0 \exp \left\{ -\frac{t}{\tau_0} \right\}^\beta, \tag{1}
\]

where \(\tau_0\) is the average time and \(\beta\) is a parameter describing the deviation from exponential behavior.

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**Fig. 3.** PL spectra of sample BE measured in the Er\(^{3+}\) luminescence band at different temperatures. The inset shows the dependence of integrated erbium PL band intensity on reciprocal temperature.

**Fig. 4.** PL kinetics of samples A obtained at various photon energies: (1) 1.5, (2) 1.7, and (3) 1.9 eV. Symbols are experimental data and solid lines represent fitting by an extended exponential. The inset shows the spectral response of the PL relaxation times obtained by approximation for samples A (triangles) and AE (circles).
The PL with the kinetics described by Eq. (1) is usually observed in disordered solid-state systems characterized by a dispersion in the recombination times, for instance, in $a$-$Si : H$ [5, 6] and porous silicon [13]. The value of $\tau_0$ was established to increase from 4 to 25 $\mu$s with the photon energy decreasing from 2 to 1.5 eV (see inset to Fig. 4). Note that the parameter $\beta$ remains practically unchanged and is close to 0.5. This behavior of $\tau_0$ and $\beta$ was observed in both A and B samples. Moreover, both samples revealed the same (within the experimental error and fitting accuracy) spectral response of the quantities $\tau_0$ and $\beta$ at the same PL photon energy. At the same time, erbium-doped structures exhibit a decrease in $\tau_0$ by a factor of about 2–2.5, whereas the value of $\beta$ practically does not change. This effect was observed in samples with nanocrystals of both sizes.

The observation that Er$^{3+}$ implantation brings about quenching of the nc-Si PL intensity by two orders of magnitude (Fig. 2) while the relaxation times of the Er$^{3+}$ PL kinetics decrease only by one half compared to the times recorded for the undoped structures (Fig. 4) suggests the following explanation. It appears that the majority of Si nanocrystals in erbium-doped structures practically do not contribute to the luminescence in the range 1.2–1.9 eV. This may be due to the fact that such nanocrystals have completely transferred the energy to the Er$^{3+}$ ions, followed by luminescence at 0.81 eV. At the same time, the remaining nanocrystals (less than 1%) have shorter PL times because of the interaction with the Er$^{3+}$ ions. The times can also decrease, in principle, as a result of nonradiative recombination on the defects produced by the Er$^{3+}$ implantation. The absence of a noticeable thermal quenching of the PL in the samples under study suggests, however, that the concentration of such defects is low.

Figure 5 displays the PL relaxation kinetics of Er$^{3+}$ ions measured for two luminescence photon energies, 0.81 eV (i.e., at the band maximum) and 0.84 eV (at the short-wavelength side of the band). We readily see that the erbium PL is characterized by a practically exponential kinetics nearly independent of the photon energy. Approximation of the kinetics by Eq. (1) yields the average lifetime $\tau_0 = 3$ ms. Such large values of the relaxation time are typical of the intrinsic radiative lifetime of Er$^{3+}$ ions; for instance, in the case of $c$-$Si : Er$, they are observed only at liquid-helium temperature, where the deexcitation processes are suppressed [1, 2]. The initial part of the erbium PL kinetics measured with a microsecond-scale resolution is presented in the inset to Fig. 5. We readily see that the PL rise times of the Er$^{3+}$ ions do not exceed 1–2 $\mu$s, which is shorter than the nc-Si PL band relaxation times. This supports the above assumption of a high efficiency of energy transfer from nanocrystals to the Er$^{3+}$ ions.

Consider a possible mechanism of erbium PL excitation in nc-Si/SiO$_2$ : Er structures in more detail. In our opinion, the most probable process in the samples under study is direct energy transfer from excitons in a Si nanocrystal to Er$^{3+}$ ions, for instance, through the Förster mechanism [14]. The states excited in this process are the high-lying Er$^{3+}$ levels, which can be broadened substantially through electric-field fluctuations in the given solid matrix [1, 2]. Because the density of nanocrystals in the oxide matrix of the above structures is quite high (~$10^{19}$ cm$^{-3}$) and, hence, the nanocrystals are separated by barriers only 1- to 3-nm thick, this mechanism of energy transfer from nanocrystals to the ions present in the matrix appears reasonable. This process becomes still more probable in the cases where the Er$^{3+}$ ion is localized directly at the nanocrystal surface.

The increase in the energy transfer efficiency for nanocrystals of smaller size observed in our experiments may be accounted for by a larger relative penetration of the exciton wave function into the oxide barrier, which has a finite height. The experimental data can be readily interpreted if we assume that the time required for the energy to be transferred from an exciton to Er$^{3+}$ is shorter than the exciton thermalization time. Estimation of the energy transfer time from the exciton to the ion made from the measured PL kinetics yields a value not in excess of a few microseconds. On the other hand, it is known that the thermalization time of nonequilibrium carriers in semiconductor single crystals, which is determined by the electron–phonon interaction processes, is on the order of $10^{-12}–10^{-11}$ s [15]. Thermalization in a silicon nanocrystal can apparently be slowed down because of a decrease in the number of phonons, which is known to be proportional to $3(N–1)$, where $N$ is the number of atoms. Note that a decrease in the spin–lattice relaxation times by three to four orders of magnitude was observed to occur in porous silicon with small nanocrystals [16]. The assumption of the exciton thermalization being slowed down in silicon nanocrystals of a small size fits very
well with the increase in the energy transfer efficiency to the Er\(^{3+}\) ions observed to occur with decreasing nanocrystal size.

4. CONCLUSIONS

To sum up, we have studied the luminescent properties of nc-Si/SiO\(_2\) multilayer structures containing Er\(^{3+}\) ions. It was shown that the energy absorbed in Si nanocrystals can be transferred with a high efficiency to Er\(^{3+}\) ions, with its subsequent emission in the 1.5-\(\mu\)m region. We believe that the high efficiency of the erbium PL excitation can be potentially applied in the development of optical amplifiers and light-emitting devices in the 1.5-\(\mu\)m range. Further steps in optimizing the technology for preparing nc-Si/SiO\(_2\) : Er structures, for instance, by increasing the number of layers and the Er\(^{3+}\) ion concentration, should apparently favor an increase in the erbium PL efficiency.

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REFERENCES


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