Efficient Energy Transfer between Si Nanostructures and Er Located at a Controlled Distance

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ABSTRACT: Systematic studies of the relaxation processes in nm-thick Er-doped SiO2/nc-Si multilayers have been conducted using cw photoluminescence and time-resolved photoluminescence. The size of the Si nanocrystals is determined by thickness of the Si layer. The distance between the Si nanocrystals and the Er ions in the SiO2 layers is fixed between 0 and 2.2 nm. An efficient energy transfer from amorphous and crystalline Si nanostructures to Er is observed and leads to a strong Er photoluminescence at 1535 nm, which increases as the Si layer thickness decreases. The fast Er photoluminescence (μs lifetime) results from energy transfer from α-Si nanostructures and the slow Er emission (ms lifetime) is caused by energy transfer from confined states in nc-Si. The transfer time was estimated to be 20 ± 5 ns by a direct time-resolved photoluminescence experiment. A model is proposed to explain these results.

KEYWORDS: Er-doped SiO2/Si multilayers, Si nanostructures, 1535 nm Er emission, energy transfer, time-resolved photoluminescence, silicon photonics

The element Er and its oxides play a very important role as an active material for optoelectronic applications, such as sources based on Er-doped silicon structures. Some of the candidates to attain this goal include different types of materials such as Er:Si/Si, Er:Si-rich SiO2/SiO2, Er:SiO/SiO2, Er:SiN/Si, or SiO2 layers doped with Er by implantation, or Er and ErY silicates fabricated by RF magnetron sputtering. Recently, we reported on efficient photo- and electroluminescence from Er-doped SiO2/nc-Si multilayers. Despite an impressive amount of this research, the efficiency of these light sources remains low.

Here, we report cw photoluminescence (PL) studies and time-resolved (TR) PL measurements. Previous studies on Er doped nc-Si/SiO2 superlattices have shown neither strong room temperature luminescence of the Si nanocrystals nor efficient Er emission at 1535 nm. The multilayers examined here are different from the samples described in earlier studies in several aspects. The Si nanocrystals are located in well-defined planes as they are formed by annealing of thin amorphous Si (α-Si) layers.  The thickness of the α-Si layers determines the nanocrystal size and thus the characteristics of the Si-related emission in the 740–800 nm spectral window. The maximum distance between any Si nanocrystal and any Er ion is 2.2 nm, which is half of the thickness of the SiO2 layers or less.

When Er is incorporated into the SiO2 layers, the Si-related PL intensity decreases and the 1535 nm Er linked PL intensity increases as a result of energy transfer from the photoexcited Si nanocrystals and amorphous Si nanostructures to Er. The nature of the energy transfer in Er doped structures is still a matter of some uncertainty. Dexter energy transfer and Förster energy transfer from nc-Si to Er ions are the two possible mechanisms. The most crucial parameter in these processes is the distance between the Si nanocrystals and the Er located in the adjacent SiO2 layers. Our multilayer structures...
offer two advantages: the size of the Si nanostructures is tightly controlled and the distance between the nc-Si and the Er ions can be quantified.10–12

In this work, we present strong, room temperature Er photoluminescence at 1535 nm from Er-doped SiO2/nc-Si multilayers and discusses its origin via the analysis of the visible and infrared PL lifetimes. Two PL decay times (fast and slow) are identified both at 740 nm from Si nanostructures and at 1535 nm from Er. We interpret the fast Er photoluminescence (μs lifetime) as due to energy transfer from a-Si nanostructures and the slow Er emission (ms lifetime) as caused by energy transfer from confined states in nc-Si. The energy transfer time from Si nanostructures to Er in SiO2 is measured, in a direct experiment, to be 20 ± 5 ns.

EXPERIMENTAL SECTION

Multilayer samples were prepared using a multigun (Si, SiO2, Er) magnetron sputtering system (ATC 2200, AJA International). Reference SiO2/nc-Si (no Er) and Er-doped SiO2/nc-Si multilayers were prepared. The multilayers were produced by the sequential deposition of layers of amorphous silicon and layers of SiO2 co-sputtered with Er on a Si(100) substrate. The Er concentration measured by Secondary Ion Mass Spectrometry was estimated to be 2 × 1020 atoms/cm3. Crystallization of the a-Si layers was achieved by furnace annealing at 1050 °C in Ar for 1 h.9,11,12,16 The thickness of the individual a-Si layers was 1.9, 2.1, and 2.3 nm, and that of the SiO2 layers was fixed at 4.5 nm. The accuracy of the average thickness was estimated to be ±3.6% and ±2.5% for the Si and SiO2 layers, respectively, using the deposition rates for Si and SiO2 layers determined from spectroscopic ellipsometry as well as from TEM pictures and the deviation of the layer uniformity from the manufacture web site.17 Figure 1 presents a sketch of the structures under study. Note that at these thicknesses, the conversion from a-Si into nc-Si is not complete and some a-Si remains in the Si layers after annealing.12,13,16,18 A representative TEM picture of the SiO2/nc-Si multilayer structure was shown in our earlier works.15,16

The spectral resolution in all PL measurements was assessed as ∼5 nm (1/4 m Oriel monochromator 257). Cw photoluminescence spectra were carried out at room temperature using the Ar+- laser line at 514.5 nm, which is off resonance with Er3+.19,20 PL spectra were recorded at room temperature using a two-dimensional multichannel digital lock-in amplifier (Model 5263, EG&G Princeton Applied Research) with lock-in time constants of 1.9 and 2.3 ms for fast and slow PL, respectively. The collected data were stored and analyzed using software written in Matlab (Mathworks). Photoluminescence spectra were carried out at room temperature using the Ar+ laser line at 514.5 nm, which is off resonance with the Er3+ photoluminescence (1.54 μm) but on resonance with Er3+ absorption bands (1.53 μm and 1.55 μm). A representative TEM picture of the Er-doped SiO2/nc-Si multilayer structure is shown in Figure 1, which presents a sketch of the structures under study.

RESULTS

Photoluminescence spectra from a reference and an Er doped SiO2/nc-Si multilayer are presented in Figures 2 and 3. In the spectra from the Er-free (reference) samples, the broad PL spectra, centered at ∼780 nm blue shifts as the Si layer thickness decreases (Figure 2). This result is in general agreement with the PL maxima shift reported earlier.8,16,18,21 Such broad PL is the outcome of emission from Si nanocrystallites, from the embedding a-Si matrix and from the interface between the two as well.22,26,27 Deconvolution of these spectra was done with two Gaussian distributions with a maximum at ∼740 nm linked to a-Si24,25 and another maximum that varied from ∼780 to ∼800 nm, depending on the nc-Si size from 1.9 to 2.3 nm (Figure 2). Note the total photoluminescence signal from a-Si nanostructures is very similar for both sizes: the difference in intensity for samples with Si layers of 1.9 and 2.3 nm is less than 5%. Theory shows that the a-Si energy gap increases significantly only for slabs thinner than 1.2 nm. For a-Si slabs with thicknesses between 1.9–2.3 nm, the change of energy gap was calculated to be 0.01–0.03 eV.24,26,27 Since the localization length of carriers in a-Si, estimated to be 0.6–1 nm,28–30 is less than the a-Si thickness, no quantum confinement effects on the PL peak energy are expected for our structures. From the nc-Si structures, the total PL intensity increases with decreasing nc-Si size, as expected from theory.31

In contrast, when the SiO2 layers are doped with Er, the PL spectra show no measurable blue shift when the thickness of the Si layer decreases. The peak at ∼740 nm, characteristic for amorphous Si nanostructures24,25 (Figure 3). We attribute the PL as a result of transitions between strongly localized states in a-Si24–26

More importantly, unlike the reference spectra, the thinnest Si layer (1.9 nm) yields the weakest ∼740 nm PL intensity and the strongest Er-related infrared PL intensity at 1535 nm (see Figure 3). The simultaneous increase in Er-related PL and decrease in PL from Si nanostructures demonstrates clear evidence of energy transfer from Si nanostructures to Er in the adjacent SiO2 layers.

Time-resolved photoluminescence (TR PL) collected at 740 nm from both reference and Er-doped multilayers is shown in Figure 4a as a function of the Si layer thickness. The PL decay spectra are the results of radiative and nonradiative transitions in amorphous and nanocrystalline components. All spectra have been fitted as the sum of two exponentials:

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I = I_{fast} \exp(-t/\tau_{fast}) + I_{slow} \exp(-t/\tau_{slow})
\]

known in the literature as the “fast” and “slow” PL decay channels.14,32 Figure 4b,c show the fast and slow lifetimes as a function of the Si layer thickness, which determines the nanocrystal diameter. No Si nanocrystal size (layer thickness) dependence is observed in the reference samples, whereas both lifetimes decrease rapidly with decreasing nc-Si size in the Er-doped specimens (see Figures 4b,c).

For the reference samples the fast and slow decay times are 3.7 and 34 μs, respectively. These values are in a good agreement with the lifetimes observed from a-Si (of the order of few μs) and from radiative transitions in nc-Si (tens of μs).32–35 Hence, we attribute the fast lifetime to a-Si nanostructures and the slow decay to nc-Si.

In the case of Er doped multilayers, both fast and slow lifetimes of the visible (740 nm) TR PL spectra are faster than those from the reference samples (Figure 4b,c). The values of
τ_{fast} and τ_{slow} and their dependence of nc-Si size are strikingly different compared to the reference samples. The fast decay time decreases from 3.6 to 1.7 μs and the slow decay time also decreases from 33 to 19 μs as the Si thickness decreases from 2.3 to 1.9 nm. This result in combination with the observation that a weaker visible cw PL is associated with a stronger Er emission reflects an additional nonradiative process present in the Er-doped multilayers. The most likely decay pathway is via transfer of energy from Si nanostructures (donor) to Er (activator). Additionally, the amplitude of the fast lifetime (due to a-Si) is approximately 40X stronger than that of the slow lifetime (due to nc-Si). This fact confirms the cw PL results where no noticeable contribution from nc-Si was observed (see Figure 3).

To complete our studies and to monitor the Er luminescence, infrared PL was collected at 1535 nm. Under 405 nm excitation, there is no PL signal detected at 1535 nm from the reference sample while a strong response from the Er-doped structure is observed (Figure 5a). Figure 5b presents TR PL spectra for two different Si layer thicknesses. The intensity of the Er luminescence is higher for the smallest Si nanocrystals, consistent with Figure 3. The decay consists of a fast initial decrease followed by an approximately exponential tail with a characteristic Er^{3+} decay time of the order of microseconds. A biexponential fit was also used to determine the IR PL lifetimes. The fast lifetimes at 1535 nm for the multilayers with 1.9 and 2.3 nm Si thickness were estimated as 24.6 and 29.4 μs, respectively (Figure 5b). This fast PL can be associated with indirectly excited Er^{3+} transitions. We link this emission to excitation via energy transfer from a-Si nanostructures. The slow IR decay time for both multilayers was estimated of the order of 3 ms, which is typical for Er^{3+} in a SiO_2 matrix.

TR PL spectra in the time window of 130 ns are shown in Figure 5c. The spike near t = 0 in the Er-free (reference) sample is the result of scattered light from the excitation beam. The rise time of the Er-doped spectrum, obtained after subtraction of the scattered light peak, is 20 ± 5 ns, which corresponds directly to the energy transfer time (in blue, Figure 5c). This time covers transfers from both amorphous and crystalline Si nanostructures. The time resolution in our experiment (±0.5 ns) and the noise in the data does not allow us to separate the transfer time of these two components. We observe no significant changes of the estimated transfer time for other Er-doped samples (Figure 5d).

**DISCUSSION**

Extensive studies of energy transfer mechanism in Er-doped, silicon-rich, SiO_2 films prepared by sputtering have been reported by Savchyn et al., Izeddin et al., and Pitanti et al. In these studies, Si nanocrystals were formed during annealing from excess Si atoms in a SiO_2 matrix. Savchyn et al. indicate that discrete luminescence centers (LCs) associated with excess-silicon related electronic defects in SiO_2 matrix are responsible for most of the indirect Er^{3+} excitation for all annealing temperatures, with a small
contribution due to Si nanocrystals formed at higher annealing temperatures (>1000 °C). Si nanocrystals of various sizes and Er ions are randomly distributed in the SiO2 matrix. Thus, the distance between nc-Si and Er, which determines the efficiency of the energy transfer, cannot be established precisely. There is no indication of amorphous Si phase in this system. These authors identify two distinct transfer times: fast (<80 ns) attributed to the Er3+ excitation via only LCs and slow (4−100 μs) due to the energy transfer mediated by emission from excited nc-Si. In our samples, the nanocrystal diameter is precisely controlled by the thickness of the a-Si layers, and there is no single Si atoms dissolved in the SiO2 matrix that could serve as LCs.

Izeddin et al.35,37 discuss temporal details of emission bands from Er3+ and nc-Si located in an SiO2 matrix. The PL spectrum from a reference sample shows two maxima. The first maximum at 775 nm is not sensitive to the nc-Si size and is attributed to recombination of carriers from higher electronic states in nc-Si. The peak of the second band near 850 nm depends on the nc-Si size and is attributed to excitonic PL in nc-Si. The decay time of this band, for a sample with an average nc-Si diameter of 3.1 nm was estimated as 20−50 μs.35 Their decay time is in very good agreement with that obtained from our reference multilayers. The time-resolved PL near 1.5 μm exhibits three regimes in the Er kinetics, which are explained as follows by these authors: a fast decay (<1 μs) caused by a fast energy transfer involving cooling of hot carriers via an Auger process and direct excitation of Er3+ ions to the first 4I13/2 energy level, a slow rise (1−10 μs) associated with the slow energy transfer between nc-Si and Er, and a slow decay (>10 μs) where Er3+ ions are excited via intraband transition of confined carriers in nc-Si.

In contrast to the Er kinetics discussed in refs 35 and 37, we observe a double exponential Er PL decay and describe the fast PL (Er μs lifetime) as due to transfer from a-Si nanostructures and the slow PL (Er ms lifetime) as resulting from energy transfer from confined states in nc-Si.

In the report by Pitanti et al.,15 the transfer time for the 980 nm Er emission line in the Si-rich SiO2 system implanted with Er was estimated to be 36 ± 10 and 117 ± 30 ns for the case of a-Si nanoparticles and nc-Si, respectively. Our measured transfer time of 20 ns in the multilayers studied averages both a-Si nanostructures and nc-Si components. This time is much faster than that for the implanted samples with emission at 980 nm.35 Although the authors of ref 15 have also studied the 1535 nm Er emission by TR PL, they do not report the transfer time for this important Er emission wavelength.

To follow the origin of the Er strong luminescence from our samples, a model of energy transfer in the Er-doped multilayers is proposed in Figure 6. We consider cw excitation at 2.4 eV
and femtosecond pulsed excitation at 3.1 eV (process (1) in the Figure 6). The excited hot carriers relax very rapidly to the lowest energy states in the conduction and valence bands of a-Si and nc-Si structures (process (2) in Figure 6). In a-Si, the excited carriers thermalize down through the localized band tail states by phonon-assisted transitions.24,39,40 Energy transfer occurs from both types of Si nanostructures (processes (3) and (4) in Figure 6). The cw PL spectra (Figure 3) and the TR PL decay spectra at 740 nm (Figure 4a) from Er-doped samples reflect recombination of carriers to the ground state of a-Si mostly via radiative transitions and to the ground state of nc-Si mostly via non-radiative processes (process (5) in Figure 6). Finally, the Er emission at 1535 nm is observed (process (7) in Figure 6) as a result of the efficient Er energy transfer.

The distance between Si and Er atoms is the key parameter in determining the efficiency of the energy transfer.14,15 For the Dexter energy transfer mechanism, the distance between the sensitizer (nc-Si) and the activator (Er atom) needs to be 0−1 nm,41 while for the Förster mechanism it can range from 0−10 nm.42 In our samples, assuming a homogeneous Er distribution in the SiO2 layers, there is approximately one Er ion less than 2.2 nm (i.e., half of the SiO2 thickness) away from each Si nanocrystal in the SiO2 layers above and below. Nearly 50% of the Er atoms are so close (≤1 nm) to the nc-Si that overlap of the wave functions can occur, allowing Dexter energy transfer. Note that it has been shown in thicker Er-doped SiO2 structures (50 nm) cladled by Si layers33 that the Er concentration is inhomogeneous after annealing and that Er atoms move toward the SiO2/Si interface. If this is the case in our structures too, a higher concentration of Er near the nc-Si makes the Dexter process even more likely. As the nc-Si diameter increases, the electron and hole wave functions extend less in the SiO2 and the Dexter process becomes less dominant.

In all our multilayers the distance between nc-Si and Er ions covers the Förster energy transfer distance requirement between the sensitizer and the activator. If this process was responsible for the efficient Er emission at 1535 nm, no significant reduction of infrared PL should be observed with an increase of the Si nanocrystal size. From these considerations, we conclude that PL emission at 1535 nm occurs mainly due to the Dexter process. Our measured transfer time of 20 ns agrees well with theory.41

**CONCLUSION**

In this paper, we demonstrated strong emission at 1535 nm from Er-doped SiO2/nc-Si multilayers under Er-off-resonant excitation and discussed the relaxation dynamic of the visible and IR photoluminescence. Systematic studies of reference (SiO2/nc-Si) and Er-doped SiO2/nc-Si multilayers revealed that...
the fast and efficient Er emission at 1535 nm is due to effective energy transfer. The reduction in visible PL intensity and shortening of the visible PL lifetime for the Er doped samples are due to the energy transfer from Si nanostructures to Er ions. The key parameter in the transfer process, the distance between Si nanostructures and Er, is well controlled in our system. The fast (µs) Er lifetime is due to the transfer from a-Si nanostructures and the slow (ms) Er lifetime is caused by the energy transfer from confined states in nc-Si. The transfer process involves both nc-Si and a-Si nanostructures and results in fast and efficient indirect Er excitation. The transfer time was estimated to ~20 ns and is faster for 1535 nm than for 980 nm. The combination of having a short controllable distance between Er and Si nanostructures, one Er ion less than 2.2 nm away from each Si nanocrystal in the SiO₂ layers above and below, and confinement of light inside the SiO₂ layers in a waveguide configuration leads to effective energy transfer and elimination of free carrier absorption in Si nanocrystals, both of which are required for efficient Si-based light amplifiers and lasers.

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