

Photoluminescence of Er^{3+} near $1.54 \mu\text{m}$ in Silicon-Rich Silicon Oxide Films

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Excitation of the intra- $4f$ -shell luminescence near $1.5 \mu\text{m}$ in silicon-rich silicon oxide is studied. Silicon-rich silicon oxide was produced by high dose implantation of Si^+ ions into SiO_2 layers grown on silicon. Erbium doping was also performed using implantation of Er^+ ions at an energy of 800 keV. An evidence is presented that transfer of energy from defects related to excess silicon in silica is the dominant mechanism of excitation of Er^{3+} for optical pumping in the UV-blue wavelength range. Si-nanocrystals created by annealing at 1100°C rather compete for excitation with erbium than transfer energy to Er^{3+} .

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1. Introduction

Erbium-doped semiconductors have been considered since many years as materials prospective for optoelectronic devices operating at $1.54 \mu\text{m}$, a basic wavelength for optical telecommunications. Er-doped silicon-based materials are particularly interesting for applications as potentially it should be possible to use the existing advanced VLSI silicon technology to produce optical components in all-silicon optoelectronic integrated circuits. However, application of bulk Si:Er in light emitters is difficult, because of a complex excitation mechanism of erbium involving charge carriers and excitons bound to shallow impurity levels [1], which results in efficient temperature quenching of Er luminescence [2].

It is well known that thermal quenching of photoluminescence (PL) of Er^{3+} is reduced in oxygen-doped wide band gap semiconductors [3]. Therefore, such semiconductors like amorphous-Si or silicon-rich silicon oxide (SRSO), which have

energy gaps wider than bulk silicon and contain high concentrations of oxygen are promising as hosts for erbium.

Some authors [4, 5] showed that strong and efficient Er^{3+} photoluminescence (PL) at room temperature can be obtained in SRSO containing Si-nanoclusters (nc-Si) embedded in an SiO_2 matrix. The PL intensity was by nearly two orders of magnitude higher than in silica, for which excitation of Er^{3+} ions can be done only resonantly. This observation was taken as proof of energy transfer from nc-Si, which absorb the pump light, to nearby erbium ions. However, other mechanisms cannot be excluded on the basis of experimental results presented so far [6].

In this work a new experimental evidence about energy transfer from defects and Si-nanocrystals to Er^{3+} ions in SRSO:Er is presented. In particular, it is shown that defects in SRSO are efficient sensitizers of Er^{3+} emission for optical excitation at wavelengths shorter than 700 nm.

2. Experiment

Layers of SiO_2 , 0.5 μm thick, thermally grown on (100) silicon wafers were implanted with Si^+ ions at three energies: 100, 150, and 200 keV and to doses of 3.0, 2.0, and $4.5 \times 10^{16} \text{ cm}^{-2}$, respectively, to produce a nearly flat $\approx 7\%$ excess concentration of Si. Some samples were implanted with 800 keV Er ions to a dose of 10^{15} cm^{-2} . The projected range of Er was 280 nm and straggling — 60 nm. It produced the maximum Er concentration of $\approx 10^{20} \text{ cm}^{-3}$. The samples were thermally annealed in nitrogen flow at different temperatures up to 1100°C. For luminescence measurements in the infrared a liquid nitrogen cooled Ge detector was used.

3. Results

We checked using transmission electron microscopy (TEM) that silicon nanocrystals were formed in SiO_2 layers as a result of annealing at 1100°C. The average size of nanocrystals was 1.5 nm, and the average distance between them was ≈ 4 nm. It gives an areal density of nc-Si of one nanocrystal per 17 square nanometers. Correspondingly, the volume density of nanocrystals is around $1.5 \times 10^{19} \text{ cm}^{-3}$.

Photoluminescence in the visible for SRSO samples annealed at different temperatures is presented in Fig. 1. Annealing at 1100°C results in a broad PL having its maximum at ≈ 760 nm. This emission is by many authors assigned to radiative recombination of excitons confined in Si-nanocrystals [4, 5, 7]. Some other authors believe that it comes from recombination of excitons at the interface between Si-nanocrystals and silicon oxide [6]. Broad PL bands observed for lower annealing temperatures are due to radiation defects.

The PL spectra of Er^{3+} near 1.5 μm are shown in Fig. 2. An increase in the Er^{3+} PL intensity in comparison with silica implanted only with Er was observed

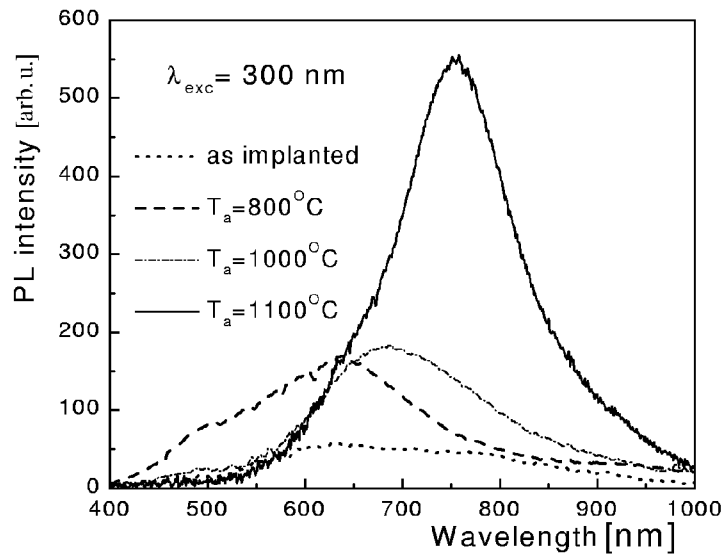


Fig. 1. PL spectra in SRSO samples annealed at different temperatures.

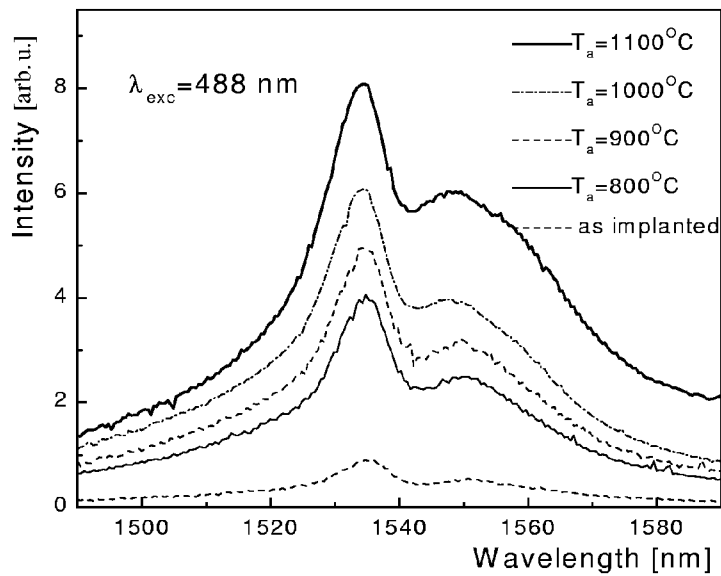


Fig. 2. PL of Er^{3+} in SRSO after thermal annealing.

already in as-implanted samples. Then the intensity was consecutively enhanced after each annealing. It seems, however, that enhancement of the PL intensity is not correlated with the formation of nc-Si. In fact, the PL is strongest in nanocrys-

talline samples, but it is only 25–30% more intense than in samples without nc-Si annealed at 1000°C. This observation suggests that all defects absorbing the pump light in the visible and UV may act as sensitizers of Er emission.

We were particularly interested in the possibility of excitation with pump wavelengths near 750 nm corresponding to the emission assigned to nc-Si. For this purpose photoluminescence excitation (PLE) spectra of Er^{3+} excited within the range of 720–850 nm were measured and the results are shown in Fig. 3. Resonant excitation of Er ions to the $^4I_{9/2}$ state is the dominant process now. Moreover, in nanocrystalline samples the emission is weakest. On the basis of this observation we conclude that nanocrystals and defects responsible for the red emission centred near 760 nm do not participate in energy transfer to erbium. Just the opposite — it seems they compete with Er ions for excitation energy.

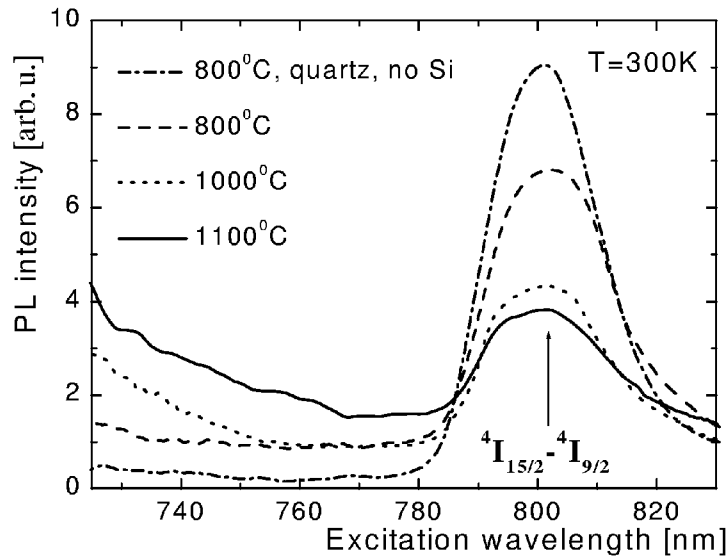


Fig. 3. PLE spectra of Er^{3+} emission at $1.54 \mu\text{m}$ excited using a Ti-sapphire laser.

Close similarities in the behaviour of PL in SRSO samples annealed at different temperatures suggest that structure of the emitting erbium centres in SRSO is most probably like in silica or quartz. If it is so, we may expect that the lifetime of Er emission is the same in all samples.

To support this assumption, time decay measurements were performed using resonant excitation of the $^4I_{11/2}$ level of Er^{3+} with a 980 nm line of a Ti-sapphire laser. The results are presented in Fig. 4. As can be seen, the decay is a single exponential function of time. The time decay is 6.5 milliseconds and is almost independent of annealing temperature. Temperature dependent measurements show only slight shortening of the decay time, which suggests that there is no back

transfer of energy from Er^{3+} to defects and the observed lifetime is most probably the radiative lifetime.

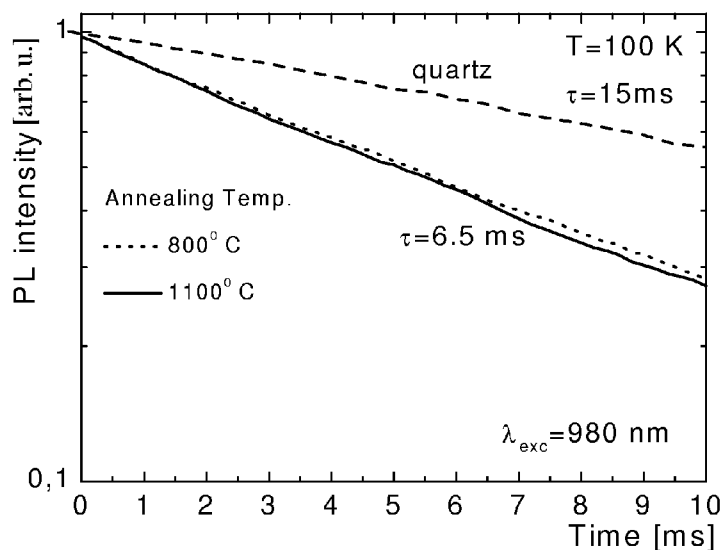


Fig. 4. Decay time of Er^{3+} emission at $1.54 \mu\text{m}$ excited resonantly at 980 nm .

4. Discussion

Two experimental facts: (a) close similarities in the excitation of Er^{3+} ions in SRSO samples annealed at different temperatures, and (b) the lifetime independent of annealing temperature suggest that the emitting Er ions are located in an SiO_2 -like environment. In this location they can be excited either resonantly by pumping to any of the excited multiplets or via energy transfer from defects. The latter mechanism is particularly efficient for excitation in the UV-blue range of wavelengths. This is because for these wavelengths the integrated absorption on defects and nanocrystals is order of magnitudes higher than for excited state of erbium. It seems that Er ions are located close to defects which ensures efficient energy transfer. On the other hand, absorption in the red is much lower than for Er^{3+} and, as a result, direct excitation processes dominate (Fig. 3).

We do not see any particular evidence that Si nanocrystals are involved in the excitation process or play other role than defects in sensitization of the Er^{3+} ions. It also seems that excitation via nc-Si/ SiO_2 interface states [6] can be excluded, because no enhancement of the PL of Er^{3+} above the intensity obtained for resonant excitation is observed for excitation near 750 nm . Moreover, a competitive character of absorption by these defects is clearly seen in Fig. 3.

5. Summary

An evidence is presented that Er ions and Si-nanocrystals compete for excitation in the wavelength range corresponding to the red emission related to the presence of nc-Si. Sensitization via defects is the dominant mechanism for energy transfer to Er ions. The measured decay time of Er³⁺ PL is the radiative lifetime.

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