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Excitation of Er^{3+} emission in Er, Yb codoped thin silica films

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Abstract

Effects of Yb codoping on photoluminescence of Er^{3+} ions at room temperature in SiO_2 films thermally grown on silicon are investigated. We demonstrate that for an excitation wavelength of 488 nm Yb ions act as efficient sensitizers of the ${}^4I_{13/2}$–${}^4I_{15/2}$ emission of Er^{3+} ions. We have found that for the fixed dose of Yb the Er^{3+} intensity is directly proportional to the Er concentration. Models of the mechanisms responsible for sensitization are discussed. It is shown that the Yb/Er concentration ratio of 0.5–2 is optimum for the dopant densities of $2–4\times10^{20}$ cm^{-3}.

Keywords: Amorphous materials; Optical properties; Luminescence

1. Introduction

The realization of an all Si-based integrated optoelectronic devices is so appealing that much effort has been made in order to improve luminescence efficiency in silicon [1]. One of the most promising ideas is doping of Si and Si-based materials with luminescent impurities like rare earth ions. Among them Er deserves special attention since the ${}^4I_{13/2}$–${}^4I_{15/2}$ transition of Er^{3+} near 1.54 μm matches the minimum losses of silica based fibers used in optical communications. However, in spite of tremendous progress in Si:Er light emitting devices, since the first observation of 1.54 μm emission from Si:Er by Ennen et al., [2] practical use of these devices is still some way off, in part due to the low room temperature efficiency in crystalline Si. It seems that a consensus has been reached now that high doping of Si with oxygen is necessary to reduce temperature quenching of the Er^{3+} emission [3,4].

A strong demand also exists for Er doped active silicon-based planar optical devices, such as waveguides, amplifiers, and lasers integrated on a single chip. These inherently small size devices require high Er-concentrations, which involve cooperative interactions such as upconversion that may lead to substantial losses of excitation energy [5,6].

An important issue for optimization of the PL efficiency is a proper choice of the pump wavelength. Excitation at 980 nm with semiconductor laser diodes is considered to be an excellent way of pumping Er-doped fiber amplifiers [5,7]. However, in the case of short lasers and optical amplifiers the relatively low absorption of Er^{3+} ions at 980 nm is a serious limitation. This can be overcome by codoping with Yb [8,9], and making use of the at least an order of magnitude higher absorption cross section of Yb^{3+} at this wavelength [5]. In effect, the dominant excitation mechanism of Er ions is transfer of energy from the Yb^{3+}–${}^2F_{5/2}$ to the Er^{3+}–${}^4I_{11/2}$ state followed by de-excitation to the ${}^4I_{13/2}$ metastable state. In addition to the large absorption cross-section at 980 nm no upconversion between Yb^{3+} ions takes place as Yb^{3+} is a two-level only system.

Emission efficiency can also be enhanced by pumping the Er^{3+} ions in the green spectral range, as the absorption coefficient of Er^{3+} for example at 520 nm is ~20 times higher than at 980 nm [7], that directly leads to an order of magnitude improvement in the efficiency of Er-doped fibre lasers [10]. Moreover, we showed recently that at low temperatures the ${}^4I_{13/2}$–${}^4I_{15/2}$ photoluminescence (PL) of Er^{3+} at 1.54 μm in SiO_2 thermally grown on Si can be enhanced by Yb codoping not only for pump wavelengths within the range of 960–990 nm, but also using the 514 nm line of an Ar laser [11]. The latter observation suggests the existence of a sensitization mechanism of Er^{3+} by Yb^{3+} ions for excitation in the green spectral range.

In this paper the results of our studies on sensitization of the Er^{3+} emission in SiO_2 thermally grown on Si by Yb

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codoping are summarized. One of the aims of this work is the determination of the useful Er and Yb doping levels in SiO_2/Si for different excitation conditions in the visible and infrared wavelengths ranges.

2. Experimental

Wafers of SiO_2/Si (thicknesses of SiO_2 layers were 0.5 μm) were implanted at room temperature (RT) with Er^+ ions at 800 keV and doses $\Phi_{Er}=5\times10^{14}$–4×10^{15} cm^{-2}. The projected range R_p, and straggling, ΔR_p, were 230 nm and 48 nm, respectively, as calculated using the TRIM code [12]. The maximum Er concentration $[Er]_m$ for the dose of 4×10^{15} cm^{-2} was 3.2×10^{20} cm^{-3}. Quarters of each wafer were coimplanted with 835 keV Yb^+ ions (the dose range as above) to match the Er profile.

Some other samples were implanted with a dose of 2×10^{15} cm^{-2} of 250 keV Er^+ ions. The R_p and ΔR_p values were 87.3 and 19.1 nm, respectively, and the peak Er concentration was 4×10^{20} cm^{-3}. Coimplantation with 260 keV Yb^+ ions to create overlapping profiles of the RE dopants was also done. The maximum Yb dose was 2×10^{16} cm^{-2} which produced a peak concentration of 4×10^{21} Yb cm^{-3}. All implanted samples were thermally annealed at 800°C, for 30 min in a nitrogen gas flow.

Photoluminescence (PL) measurements were performed at RT. Luminescence was excited with the 488 or 514 nm lines of an Ar laser chopped at low frequency, and detected with a liquid-nitrogen cooled Ge detector. Photoluminescence excitation (PLE) spectra were measured at RT with the detection wavelength set to 1535.0 nm at the maximum of the $4f$–$4f$ PL band of Er^{3+}.

3. Results

The PL spectra for samples implanted with a dose of 2×10^{15} cm^{-2} of 800 keV Er^+ ions and coimplanted at different fluences Φ_{Yb} of Yb are presented in Fig. 1. It is clearly seen that the Er emission increases markedly with the increasing dose of Yb and for the highest dose of 2×10^{15} cm^{-2} it is enhanced by a factor of fifteen.

The increase of the PL intensity due to Yb codoping was observed for all doses of Er and Yb. In Fig. 2 the PL intensity as a function of Er dose for fixed Yb contents is shown. It is seen that the PL intensity is proportional to Φ_{Er} and a slope efficiency increases with the increasing fluence Φ_{Yb}. In Fig. 2 two additional points corresponding to the Er/Yb doses of $4\times10^{15}/4\times10^{15}$ cm^{-2} and $2\times10^{15}/4\times10^{15}$ cm^{-2}, denoted with an asterisk and a cross, respectively, are also marked. The most intense PL was observed in samples implanted with the highest doses of 4×10^{15} cm^{-2} for each ion (an asterisk in Fig. 2). It seems that $\Phi_{Yb}=4\times10^{15}$ cm^{-2} is above the optimum value, as for $\Phi_{Er}=4\times10^{15}$ cm^{-2} the PL intensity increases by 6% only after increasing the Φ_{Yb} from 2×10^{15} cm^{-2} to 4×10^{15} cm^{-2}.

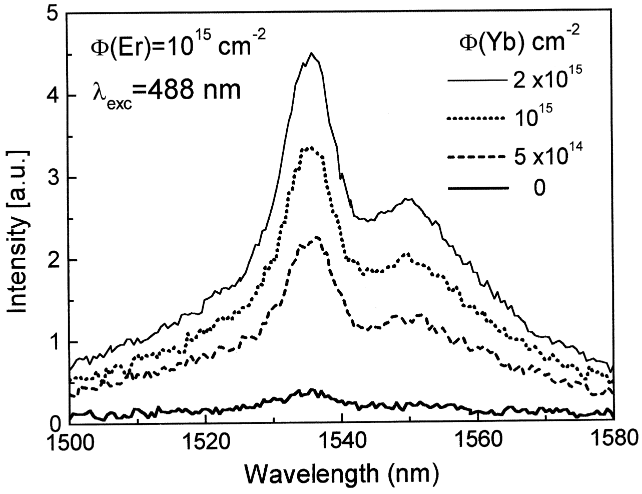

Fig. 1. PL spectra of Er^{3+} at 300 K in Er+Yb-implanted SiO_2/Si excited at 488 nm. The Er dose is fixed to 1.0×10^{15} cm^{-2} for all samples.

In Fig. 3 the PL spectra excited with the 514 nm line for different ion energies, but with a constant dose of Er are compared. Samples doped with Er only differ in that their peak concentrations are 4×10^{20} cm^{-3} and 1.6×10^{20} cm^{-3} for 250 and 800 keV, respectively. Nevertheless, the PL intensities are the same. We have also found that in medium energy (250 keV) implanted samples there was no enhancement of the PL intensity due to the high Yb codoping, in spite of the fact that this effect existed at 10 K [11].

A weak luminescence near 1 μm originating in the $^2F_{5/2}$–$^2F_{7/2}$ transitions of Yb^{3+} was observed in samples doped only with Yb. In Er+Yb doped samples the PL of

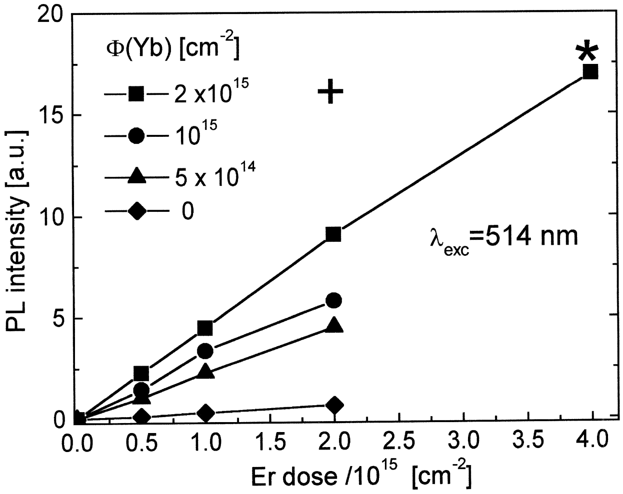

Fig. 2. Er dose dependence of the PL intensity of Er^{3+} in SiO_2/Si for fixed doses of Yb. An asterisk and a cross denote Er/Yb implant doses of $4\times10^{15}/4\times10^{15}$ cm^{-2} and $2\times10^{15}/4\times10^{15}$ cm^{-2}, respectively.

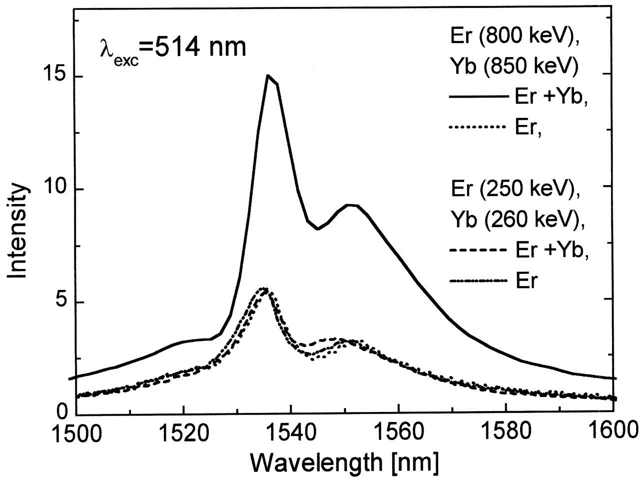

Fig. 3. Luminescence of Er^{3+} excited at 514 nm in SiO_2/Si implanted at high (800 keV) and medium (250 keV) energies. $\Phi_{Er}=2\times10^{15}$ cm^{-2} in all samples, $\Phi_{Yb}=2\times10^{15}$ cm^{-2} at 850 keV, and 2×10^{16} cm^{-2} at 260 keV.

Yb^{3+} was practically undetected which confirms fast energy transfer from the Yb to Er centres.

In Fig. 4 the PLE spectra for the same samples as in Fig. 3 are compared. Now, the PL intensity in Er doped samples seems to depend on the concentration, as for 250 keV implantation it is 3 times lower than for 800 keV. It suggests that part of the excitation energy is lost, most probably due to cooperative processes or fast migration of energy between the Er^{3+} ions. The high dose of Yb (2×10^{16} cm^{-2}) causes some enhancement of the PL intensity for $\lambda_{exc}<981$ nm, but for longer wavelengths the effect is just the reverse and the PL is lower than in a sample implanted with Er only.

The spectra in Fig. 4 reveal also that the maximum absorption of Yb^{3+} at $\lambda_{exc}=976$ nm (1.270 eV) is shifted with respect to the absorption maximum of Er^{3+} at $\lambda_{exc}=982$ nm (1.262 eV) by 8 meV. It makes a search for the optimum Er and Yb doping more difficult, as this energy shift may impose some limitations on the number of Er sites that are accessible for excitation via energy transfer from the Yb^{3+} donors.

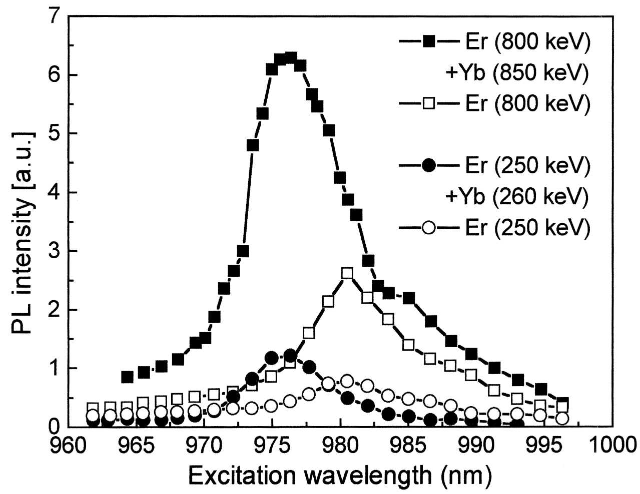

Fig. 4. Comparison of the PLE spectra for the same samples as in Fig. 3.

4. Discussion

The results of this work show clearly that Yb ions can be used to sensitize the emission of Er^{3+} in SiO_2/Si not only near 1 μm, but also in the blue–green visible range. The latter effect was not expected as there is no other excited Yb^{3+} state than the $^2F_{5/2}$ located ~1.27 eV above the ground state.

Explanation of the observed sensitization on the basis of the presented results does not seem straightforward as a few excitation mechanisms should be considered. The simplest explanation is based on an assumption that the Yb atoms form some complexes in SiO_2, which strongly absorb the blue–green light and mediate energy transfer from the pump laser beam to the Er^{3+} ions. Since neither the structure nor charge state (Yb^{2+} ?) of Yb in such complexes are known, a specific path of energy transfer from the excited Yb (Yb*) centre to the $^4I_{13/2}$ state of Er^{3+} can definitely not be determined and at least two possibilities should be considered:

1. The first stage of the process is intra-centre nonradiative relaxation of the excited Yb* complex, which brings the Yb^{3+} ion to its $^2F_{5/2}$ excited state. Excitation energy is then transferred to the Er^{3+}-$^4I_{11/2}$ state followed by relaxation to the $^4I_{13/2}$ emitting level. This mechanism does not require more pairing of Er and Yb ions than for pumping near 1 μm and in fact in samples implanted at 800 keV the enhancement of the PL intensity due to Yb codoping is similar for the two excitation wavelengths of 488 and 976 nm.
2. The second possibility is excitation of Er^{3+} via transfer of energy from the Yb* centre to one of the highly excited states of Er^{3+} (i.e. $^4F_{7/2}$ or $^4S_{3/2}$) followed by rapid non-radiative relaxation to the $^4I_{13/2}$ metastable state. The fact that sensitization is not observed in very highly doped Yb samples (Fig. 3) suggests that the pump energy absorbed by the Yb ions is not transferred to the Er^{3+} ions, most probably due to the fast energy migration within the Yb ion subsystem, which ends up in nonradiative recombination [5,10]. In effect, we conclude that the first proposed sensitization mechanism is the most likely.

An assumption about the existence of Yb centres absorbing strongly in the blue–green range of wavelengths allows us to explain qualitatively the observed dose dependencies of the PL intensity (Fig. 2). At such an assumption the contribution of the Er^{3+} ions excited directly by the absorption of light into the total PL intensity is small in comparison with the contribution due to the Yb^{3+} ions mediating energy transfer. Therefore, at fixed Yb contents the PL intensity is limited by the concentration of Er ions [Er], and is directly proportional to the [Er] up to 3.2×10^{20} cm^{-3} ($\Phi_{Er}=4\times10^{15}$ cm^{-2}). It also explains the fact that a small dose of Yb leads to a fast initial increase of the PL intensity of Er^{3+} (Fig. 2).

The results presented here also suggest that the Yb concentration of ~3.2×10^{20} cm^{-3} is above the upper limit for codoping at [Er] of ~$1.6–3\times10^{20}$ cm^{-3} (Fig. 2). Thus it seems that the proper Yb/Er ratio for the highest [Er] used in this work is 0.5–2.

In spite of the fact that the mechanism proposed above seems to explain the observed sensitization satisfactorily, other mechanisms should be mentioned. Johnson et al. [13] found that in BaY_2F_8:Er:Yb the lifetime of the excited $^4S_{3/2}$ state of Er^{3+} is much shorter than in BaF_2Y_8:Er. The authors explained this effect in terms of a cross-relaxation mechanism in which the Er^{3+} ion excited to its $^4S_{3/2}$ state in an Er–Yb pair relaxes according to the scheme:

$$|^4S_{3/2}, {}^2F_{7/2}\rangle \rightarrow |^4I_{13/2}, {}^2F_{5/2}\rangle + \Delta E,$$

(where ΔE is an energy dissipated by phonons).

This mechanism apparently results in sensitization of the Er^{3+} PL, as it involves the excited Yb^{3+} ions from which the energy is transferred back to the Er subsystem. However, this mechanism cannot easily explain the Yb dose dependence of the PL intensity (Fig. 2), in particular, the fast initial increase of the PL intensity for relatively low doping level, for which the distance between Yb and Er ions is quite large. It also seems that another mechanism, cooperative absorption of a single 2.5–2.6 eV quantum of energy by two Yb ions in an Yb–Yb pair (the energy difference of $^2F_{5/2}$–$^2F_{7/2}\cong1.27$ eV) is much less probable than the mechanism described in the beginning of this section, as it requires efficient Yb–Yb and Yb–Er pairing. Such pairing is not expected, because of the very low diffusivity of rare earth atoms in the solid phase in the presence of oxygen [14]. Moreover, the linear dependence of the PL intensity on Er dose indicates that cooperative processes mentioned above are inefficient for the concentrations of Er and Yb used in this work.

5. Summary

It is shown that codoping of SiO_2:Er/Si with Yb may enhance the PL intensity of Er^{3+} by more than an order of magnitude for a pump wavelength in the blue–green range. A tentative mechanism of sensitization has been proposed. It is suggested that some Yb complexes are formed that strongly absorb the pump light. The Er^{3+} are excited as a result of energy transfer from these complexes. Useful levels of Er and Yb in SiO_2 thermally grown on Si have been estimated. It has been shown that for Er concentrations of $2–4\times10^{20}$ cm^{-3} the optimum Yb/Er ratio is ~0.5–2.

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