Selective modification of the Er$^{3+}$ $4I_{11/2}$ branching ratio by energy transfer to Eu$^{3+}$

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We present an investigation of Er$^{3+}$ photoluminescence in Y$_2$O$_3$ waveguides codoped with Eu$^{3+}$. As a function of europium concentration we observe an increase in decay rate of the erbium $4I_{11/2}$ energy level and an increase of the ratio of photoluminescence emission from the $4I_{13/2}$ and $4I_{11/2}$ states. Using a rate equation model, we show that this is due to an energy transfer from the $4I_{11/2} \rightarrow 4I_{13/2}$ transition in erbium to europium. This increases the branching ratio of the $4I_{11/2}$ state towards the $4I_{13/2}$ state and results in a higher steady state population of the first excited state of erbium. Absolute intensity enhancement of the $4I_{13/2}$ emission is obtained for europium concentrations between 0.1 and 0.3 at. %. In addition, the photoluminescence due to upconversion processes originating from the $4I_{11/2}$ state is reduced. Using such state-selective energy transfer the efficiency of erbium doped waveguide amplifiers can be increased. © 2000 American Institute of Physics. [S0021-8979(00)01321-9]

I. INTRODUCTION

Erbium-doped optical amplifiers operate at 1540 nm by stimulated emission from the $4I_{13/2}$ state in Er$^{3+}$. The standard in telecommunications to excite this energy level is via the second excited state $4I_{11/2}$ using 980 nm radiation (cf. Fig. 1). An important ingredient in this pumping scheme is the nonradiative transition between the $4I_{11/2}$ and $4I_{13/2}$ states. Its rate depends on the host material. Incidentally, the most promising materials for erbium doped waveguide amplifiers possess low phonon energies, and therefore small nonradiative transition rates. This is a severe problem, since it gives rise to a significant steady state population of the $4I_{11/2}$ level. As a result, a considerable fraction of Er$^{3+}$ is not available for stimulated emission from the $4I_{13/2}$ state. Moreover, when the $4I_{11/2}$ population is high, excited state absorption and cooperative upconversion processes lead to unwanted excitation of even higher lying energy levels. For these reasons it is desirable to increase the transition rate between the $4I_{11/2}$ and $4I_{13/2}$ energy levels without affecting the optimized properties of the $4I_{13/2}$ state itself. This will make the excitation stored in the $4I_{11/2}$ state available for amplification of 1540 nm radiation, and in the process will also significantly reduce the probability of cooperative upconversion and excited state absorption from the $4I_{11/2}$ state.

One way to enhance the transition rate from the second to the first excited state is engineering the crystal field of the host matrix at the position of the erbium ions. A simpler and newer approach, while leaving the well-established properties of existing waveguide materials unchanged, consists of selectively stimulating the transition between second and first excited state of Er$^{3+}$ by resonant energy transfer to a suitable codopant. Hereby the energy difference between the relevant states of the erbium is transferred to the codopant.

Mainly Ce$^{3+}$ has been investigated as codopant so far, while Eu$^{3+}$ and Tb$^{3+}$ have been suggested.

In this article we describe codoping of Er$^{3+}$:Y$_2$O$_3$ with Ce$^{3+}$. Yttrium oxide has already proven its suitability for optical amplification in waveguides, thanks to its high refractive index which provides both a high erbium emission cross section and the possibility of integration on a small area. We investigate the energy transfer by studying the erbium photoluminescence intensities and decay rates as a function of europium concentration, and establish a model based on rate equations which reproduces the data. Finally we show that the green upconversion emission of erbium in a planar waveguide is significantly reduced upon codoping with Eu$^{3+}$.

II. EXPERIMENT

The samples used in this study were prepared by sputter deposition of Y$_2$O$_3$ on a 3-μm-thick thermally grown silicon oxide buffer layer. Since Y$_2$O$_3$ has a higher index of refraction (1.7 at 1500 nm) than SiO$_2$, this structure acts as a planar waveguide. The films are 800 nm thick as determined using Rutherford backscattering spectrometry (RBS). They were doped with erbium by ion implantation at a series of energies between 200 and 500 keV to obtain a flat concentration profile ranging from 30 to 100 nm below the surface. Subsequently europium was implanted into the sample, creating a flat concentration profile that overlaps the erbium doped region completely. By implanting only part of the sample with europium we kept an on-wafer reference of only erbium doped Y$_2$O$_3$. In this way variations in luminescent properties caused by slight differences of quality and treatment between samples can be taken into account. Exact concentrations were determined by RBS analysis and amount to 0.19 at. % erbium and to 0.024, 0.048, 0.12, 0.24, and 0.48.

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at. % europium. After implantation, the samples were heat treated at 700 °C for 30 min in a rapid thermal annealer under oxygen flow.

For photoluminescence measurements we exploited the planar waveguide geometry of the samples. The 488 nm emission line of an Ar + laser was mechanically chopped and then butt coupled into the waveguide via an optical fiber. Photoluminescence emission was collected perpendicular to the waveguide by a multimode fiber with 800 μm core diameter. The signal was dispersed in a 96 cm monochromator. The Er 3+ emission at 700 °C for 30 min in a rapid thermal annealer under oxygen flow.

The 488 nm radiation leaving the planar waveguide at the output end served to trigger lock-in amplifier, oscilloscope, and multichannel scaler. In that way variations of the chopping speed will not have an influence on the accuracy of the measurements.

To obtain a good measure for the intensity ratio of the emission originating from the 4 I 13/2 and 4 I 11/2 levels, spectra were taken of the corresponding lines around 1538 and 980 nm with the cooled germanium detector, taking care not to change the experimental settings. After correction for the detector response, the total intensity in each line was determined by integrating over the spectra.

In order for the analysis presented in this article to be correct, it is important to perform all measurements in a regime where no saturation of the emission signal due to high pump power takes place. Therefore the pump power dependence of the emission line intensity was monitored before each measurement, and the excitation power adjusted to a value within its region of linearity.

III. RESULTS AND DISCUSSION

A. Rate equation model

Figure 1 shows the mechanism we investigated to accelerate the decay rate of the second excited state of Er 3+ . The rates W 1 , W 20 , and W 21 are defined as transition rates of the excited states of Er 3+ in Y 2 O 3 when no codoping with europium has taken place: W 1 is the total decay rate from the 4 I 13/2 level, and is the sum of a radiative rate W 1r and a nonradiative rate W 1nr . W 21 is the transition rate between the 4 I 11/2 and 4 I 13/2 states. It consists as well of a nonradiative and a radiative part, this distinction is however unnecessary for the model. W 20 is the transition rate from the 4 I 11/2 state to the ground state and is taken to be purely radiative. The total decay rate of the 4 I 11/2 state is given by W 2 = W 21 + W 20 , in the absence of Eu 3+ . The coupling of the 4 I 11/2 → 4 I 13/2 transition with the Eu 3+ ion is described by the rate constant C 2 . We assume that an excited Eu 3+ ion relaxes nonradiatively and fast to its ground state via the 7 F j ladder. This is a reasonable conjecture since the energy level spacings of the 7 F j multiplet of Eu 3+ in Y 2 O 3 can be bridged by two phonons or less of the Y 2 O 3 host (highest phonon density of states at 400 cm −1 ).

This idealized model is complicated by undesirable interactions, which are not depicted in Fig. 1. Important are interactions especially of the 4 I 13/2 state of Er 3+ with Eu 3+ (e.g., phonon-assisted energy transfer) or with defects originating from the europium concentration. These constitute additional decay channels for the 4 I 13/2 state. We take this into account by an interaction rate S 1 , which may depend on europium concentration. The rate equations for the population of the excited erbium levels thus have the following form:

\[
\frac{dN_2}{dt} = R_2 - W_2 N_2 - C_2 N_4 N_2,
\]

\[
\frac{dN_1}{dt} = R_1 - W_1 N_1 + W_2 N_2 + C_2 N_4 N_2 - S_1 N_1.
\]

The symbols R 1 and R 2 signify the excitation rate per unit volume into the first and second excited states of Er 3+ , respectively. Here we take into account that in the experiments Er 3+ is initially excited into the 4 F 7/2 state, from which the two lowest levels are fed according to some branching ratio. It is assumed that no excitation-induced saturation of the Er 3+ occurs, and that the population of the Er 3+ energy levels is small enough to neglect nonlinear processes such as...
cooperative upconversion. $N_q$ represents the concentration of Eu$^{3+}$. We assume that only an insignificant part of the Eu$^{3+}$ is excited at any time.

The fraction of the population of the $^4I_{11/2}$ state that is de-excited via energy transfer to Eu$^{3+}$, so to speak the branching ratio of the energy transfer, is determined by the ratio of the energy transfer rate and the total decay rate of the Er$^{3+}^4I_{11/2}$ state at a given Eu$^{3+}$ concentration

$$Q_2 = \frac{C_2 N_q}{W_2 + C_2 N_q}.$$  \hspace{1cm} (2)

Similarly, we can write the fraction of the population of the $^4I_{13/2}$ level that is quenched by the presence of Eu$^{3+}$ or defects caused by the europium implantation as

$$Q_1 = \frac{S_1}{W_1 + S_1}.$$  \hspace{1cm} (3)

The branching ratios $Q_1$ and $Q_2$ are experimentally accessible via decay rate measurements, as will be shown in the next section. They do not depend on erbium concentration. We would like to draw attention to the differences in definition between $Q_1$ and $Q_2$. The interaction that quenches the first excited state of erbium ($S_1$) may depend on $N_q$ in an unspecified way, while we assume a dependence of $Q_2$ on $N_q$ given by an energy transfer towards europium. In this way we include the possibility that the reduction in luminescence efficiency of the first excited state is caused by defects from the europium implantation, which are not annealed out during the heat treatment. On the other hand the model stays sufficiently precise with respect to the energy transfer from the Er$^{3+}^4I_{11/2}$ level to Eu$^{3+}$ to be tested by experiment.

The ratio of the emission intensities from the $^4I_{13/2}$ and $^4I_{11/2}$ levels can serve as an independent way to test the model. Substituting $Q_1$ and $Q_2$ into the rate Eq. (1) at steady state, and writing the intensities as $I_1 = W_{1r} \cdot h \nu_1 \cdot N_1$ and $I_2 = W_{20} \cdot h \nu_2 \cdot N_2$ for the emission from the first and second excited states of Er$^{3+}$, respectively, the intensity ratio is given by the expression

$$\frac{I_1}{I_2} = \frac{1 - Q_1 Q_1^0}{1 - Q_2 Q_2^0} \cdot \frac{W_{1r}}{W_1} \cdot \frac{Q_2 (1 - Q_1)}{1 - Q_2} \cdot \frac{\nu_1}{\nu_2}.$$  \hspace{1cm} (4)

$I_1$ and $I_2$ are the emission intensities from the first and second excited states of erbium, respectively, in the presence of europium, $\nu_1$ and $\nu_2$ the corresponding emission frequencies, $h$ Planck’s constant, and $Q_1^0/Q_2^0$ the intensity ratio of the two emission lines in the limit of zero Eu$^{3+}$ concentration. The first term on the right of Eq. (4) describes the change in intensity ratio due to the depopulation of the two levels, while the second term takes into account the feeding of the first excited state from the second via the energy transfer to Eu$^{3+}$.

Along the same line of reasoning, an absolute increase in emission intensity $I_1$ is achieved when

$$Q_2 > \frac{Q_1 Q_1^0}{1 - Q_1 Q_1^0} \cdot \frac{W_{1r}}{W_1} \cdot \frac{\nu_1}{\nu_2}.$$  \hspace{1cm} (5)

Let us stress that in the ideal case of $S_1 = 0$ ($Q_1 = 0$) the analysis presented here is greatly simplified. The quenching of the first excited state is very likely linked to the ion implantation, and can be reduced to zero using other doping methods (compare, e.g., Ref. 3).

B. Experimental results

Figure 2 shows the emission spectrum of the sample doped with 0.19 at. % erbium and 0.44 at. % europium in the visible and near infrared region, when excited at 488 nm. Emission lines of both Er$^{3+}$ and Eu$^{3+}$ can be identified, confirming the triply charged state of the ions in the matrix. The weaker emission of Eu$^{3+}$ as compared to Er$^{3+}$ is due to the small excitation cross section of Eu$^{3+}$ at 488 nm. Figure 3 compares decay traces at 981 nm originating from the Er$^{3+}^4I_{11/2}$ level in Y$_2$O$_3$ with and without addition of 0.24 at. % europium. The decay is single exponential in the sample without europium, with a decay rate of 471 s$^{-1}$. Upon addition of europium, the decay becomes faster, the decay rate increases to 947 s$^{-1}$, and the decay becomes non-single ex-
potential. By evaluating decay rates from curves taken at 981 and 1538 nm, we obtain experimental values for the fraction of the population de-excited via a channel induced by the europium

\[ Q_{N_q}^{N_q} = 1 - \frac{W_i^0}{W_i^{N_q}}. \]  

(6)

The index \( i \) labels the emission wavelength, the superscripts 0 and \( N_q \) refer to the europium concentration.

\( Q_{1538}^{N_q} \) can be identified directly with \( Q_1 \) as given in the previous section, since the definition of the latter does not explicitly state a dependence on \( N_q \). Conversely, if \( Q_{981}^{N_q} \) exhibits the functional form of \( Q_2 \), this is a clear indication that energy transfer towards \( \text{Er}^{3+} \) really takes place.

In Fig. 4 we show the values for \( Q_{1538}^{N_q} \) and \( Q_{981}^{N_q} \) as a function of europium concentration. \( Q_{981}^{N_q} \) increases monotonically and seems to saturate for high europium concentrations. \( Q_{1538}^{N_q} \), however, increases for low europium concentrations, and saturates for intermediate europium concentrations. At \( N_q = 0.44 \) at. \% we see another increase. Included in the figure are data calculated according to equation 4 with \( W_{1r} = 89 \) s\(^{-1}\) for the best fit. As a comparison, the total decay rate \( W_1 \) was measured to be 115.7 s\(^{-1}\) for the best fit. As a comparison, the total decay rate \( W_1 \) was measured to be 115.7 s\(^{-1}\).

It is clear from Fig. 4 that through the right choice of europium concentration, a substantial increase of the transition rate from the second to the first excited state of erbium can be induced at a low cost in lifetime of the first excited state itself.

For completeness let us state that we have also measured the change in decay rate of erbium energy levels in the visible region. A significant increase is observed only in the sample containing 0.44 at. \% europium. In this case, the 4\( ^{11/2} \) and 4\( ^{3/2} \) levels are the only ones affected, with \( Q_{563}^{N_q} \) and \( Q_{521}^{N_q} \) amounting to 0.2 at 0.1. This may be due to nonresonant energy transfer to the 5\( ^{1}D_{0,1} \) levels of \( \text{Eu}^{3+} \) (cf. Fig. 1).

The validity of the model can be independently checked by measuring the intensity ratio of the emission originating from the 4\( ^{11/2} \) and 4\( ^{13/2} \) levels. Figure 5 shows these measurements as a function of europium concentration. The intensity ratio increases from 0.57 without europium to 1.41 at 0.24 at. \% europium. A slightly lower value is observed at 0.44 at. \% europium. Included in the figure are data calculated according to Eq. (4), with the data of Fig. 4 as input. The measurement is once again reproduced well by the calculation. The only free parameter here is the radiative decay rate of the first excited state 4\( ^{13/2} \) level, which has been adjusted to 89 s\(^{-1}\) for the best fit. As a comparison, the total decay rate \( W_1 \) was measured to be 115.7 s\(^{-1}\).

To illustrate the effect of the increased branching ratio from the 4\( ^{11/2} \) to the 4\( ^{13/2} \) state, we have also plotted the calculated values for \( W_{1r} = 0 \). It is clear that for high europium concentrations the second term on the right-hand side of Eq. (4) contributes significantly to the intensity ratio. As stated earlier, this term represents the contribution caused by the additional feeding of the 4\( ^{11/2} \) level via the interaction between the 4\( ^{11/2} \) level and \( \text{Eu}^{3+} \). It is only this term that contains the adjustable parameter \( W_{1r} \). In case all europium-induced de-excitation of the 4\( ^{11/2} \) state were towards the ground state, this term would be zero this is equivalent to setting \( W_{1r} = 0 \). The values of the first term of Eq. (4), however, lie significantly lower than the measurement points,
The reduction of upconversion emission due to codoping with Eu$^{3+}$ can also find application in erbium-doped amplifiers pumped directly into the $^4I_{13/2}$ level, e.g., with 1480 nm light. In highly doped amplifiers, cooperative upconversion and excited state absorption from the $^4I_{13/2}$ state lead to a significant population of the $^4I_{11/2}$ level. The same mechanisms of gain reduction as described for 980 nm pumping come into effect, on a somewhat lesser scale. Even in such a system it is therefore desirable to increase the transition rate between the $^4I_{11/2}$ and $^4I_{13/2}$ states.

IV. CONCLUSION

The population in the first excited state of Er$^{3+}$ in an Y$_2$O$_3$ matrix under excitation at 980 nm can be increased by codoping with Eu$^{3+}$. This is due to a controlled resonant energy transfer from the second excited state of Er$^{3+}$ towards Eu$^{3+}$, reducing the population in that state in favor of the population in the first excited state. This process of selective increase of the decay rate of a certain energy level with control over the transition’s final state is especially useful for materials with low phonon energies.

We have been able to show that energy transfer between Er$^{3+}$ and Eu$^{3+}$ is responsible for the acceleration of the decay of the erbium’s second excited state in Y$_2$O$_3$ doped by ion implantation. By codoping with only 0.44 at. % europium we have achieved a 60% efficiency of the energy transfer in depopulating the second excited state. This is reflected in the emission intensities: the emission from the first excited state is significantly increased for europium concentrations above 0.1 at. %. The reduced population of the second excited state leads further to a decrease in green upconversion photoluminescence under 980 nm excitation. In this way an important loss channel in highly pumped optical amplifiers can be effectively closed.

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10 Actually the argument has to be revised slightly. Assuming an additional de-excitation channel proportional to $N_q$, leading from the $^4I_{13/2}$ level to the ground state, will change the dependencies on europium concentration of neither $Q_2$ nor the intensity ratio. The parameter arrived at in Fig. 5 then constitutes a lower limit for $W_{1r}$ rather than $W_{1r}$ itself. On the other hand, the measured lifetime of the $^4I_{13/2}$ state extrapolated to zero erbium concentration [96 s$^{-1}$ (Ref. 6)] provides an upper limit for $W_{1r}$. Since the radiative decay rate has not been determined independently, we have to conclude by pointing out that the limits to $W_{1r}$ do not allow for enough variation to jeopardize the statements made in the main text.