Controlling Er–Tm interaction in Er and Tm codoped silicon-rich silicon oxide using nanometer-scale spatial separation for efficient, broadband infrared luminescence

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The effect of nanometer-scale spatial separation between Er3+ and Tm3+ ions in Er and Tm codoped silicon-rich silicon oxide (SRSO) films is investigated. Er and Tm codoped SRSO films, which consist of nanocluster Si (nc-Si) embedded inside SiO2 matrix, were fabricated with electron cyclotron resonance-plasma enhanced chemical vapor deposition of SiH4 and O2 with concurrent sputtering of Er and Tm metal targets. Spatial separation between Er3+ and Tm3+ ions was achieved by depositing alternating layers of Er- and Tm-doped layers of varying thickness while keeping the total film thickness the same. The films display broadband infrared photoluminescence (PL) from 1.5 to 2.0 μm under a single source excitation due to simultaneous excitation of Er3+ and Tm3+ ions by nc-Si. Increasing the layer thickness from 0 to 72 nm increases the Er3+ PL intensity nearly 50-fold while the Tm3+ PL intensity is unaffected. The data are well-explained by a model assuming a dipole–dipole interaction between excited Er3+ and Tm3+ ions, and suggest that by nanoscale engineering, efficient, ultrabroadband infrared luminescence can be obtained in an optically homogeneous material using a single light source. © 2004 American Institute of Physics. [DOI: 10.1063/1.1812578]
excitation of Er\(^{3+}\) is still dominated by nc-Si. PL spectra were measured at room temperature using either a standard or a long wavelength enhanced InGaAs PIN photodiode, a grating monochromator, and the standard lock-in technique. All spectra are corrected for the system response. Time resolved PL decay traces were recorded using a mechanical chopper and a digitizing oscilloscope. The system response was 180 \(\mu\)s.

Figure 2 shows the PL spectra of SRSO films with alternating Er- and Tm-doped layers. Also shown is for comparison is the PL spectrum from the film codoped homogeneously with Er and Tm. We observe a broad luminescence peak from 1.5 to 2.0 \(\mu\)m due to superposition of \(4I_{13/2}\) \(-4I_{15/2}\) Er\(^{3+}\) peak at 1.54 \(\mu\)m and \(4F_{4}\) \(-4H_{6}\) Tm\(^{3+}\) peak at 1.78 \(\mu\)m. However, the Er\(^{3+}\) peak from the homogeneously doped film is extremely small compared to that of Tm\(^{3+}\). Separating Er and Tm into 2 nm thin layers results in more than tenfold increase in the Er\(^{3+}\) PL intensity. Further increasing the layer thickness to 72 nm results in additional fourfold increase in the Er\(^{3+}\) PL intensity such that it is about 50 times greater than that from the homogeneously doped film. However, the Tm\(^{3+}\) PL intensity is completely unaffected in all cases. The dependence of Er\(^{3+}\) and Tm\(^{3+}\) PL intensity on the layer thickness is summarized in the inset.

Figure 3 shows time resolved PL decay traces at \(\lambda = 1.54 \mu m\). For comparison, the decay trace of a SRSO film doped with Er only is also shown. The Er-only film shows a single-exponential decay with a luminescence lifetime of \(~5.1\) \(\mu\)m. On the other hand, Er and Tm codoped films show nonexponential decay with a fast initial decay followed by a slow tail. As \(d\) increases, the fast initial decay is reduced, and the PL decay trace approaches that of the Er-only film. It should be noted, however, that the observed PL decay trace at 1.54 \(\mu\)m contains the contribution from the Tm\(^{3+}\) luminescence as well. Thus, we deconvoluted the effective 1.54 \(\mu\)m Er\(^{3+}\) PL lifetimes as follows. First, the Tm\(^{3+}\) PL decay at 1.78 \(\mu\)m was measured, and confirmed to show a single exponential decay behavior with a decay time of \(~400 \mu\)s from all films, in agreement with previous results (data not shown).\(^{10}\) Second, the PL decay trace at 1.54 \(\mu\)m was integrated to obtain an effective luminescence lifetime. Finally, the Tm\(^{3+}\) effective lifetime, scaled by the relative Tm\(^{3+}\) PL intensity, was subtracted to obtain the effective Er\(^{3+}\) luminescence lifetime. We find that the effective Er\(^{3+}\) luminescence lifetime increases from 1.8 to 4.9 \(\mu\)m as \(d\) is increased from 2 to 72 nm, as is shown in the inset.

The results of Figs. 2 and 3 are in agreement with our previous report that excited Er\(^{3+}\) and Tm\(^{3+}\) ions interact via a cooperative-upconversion process in which an excited Er\(^{3+}\) atom decays nonradiatively by resonantly exciting an excited Tm\(^{3+}\) ion from the \(3F_{4}\) to the \(3H_{4}\) state. The increase in the Er\(^{3+}\) with increasing layer thickness therefore indicates that the Tm\(^{3+}\)-induced quenching of Er\(^{3+}\) luminescence can be suppressed by spatial separation between Er\(^{3+}\) and Tm\(^{3+}\), consistent with previous reports that such interaction between RE ions can be described by resonant dipole–dipole transition.\(^{11,12}\)

Therefore, we model the energy transfer rate \(a\) between Er\(^{3+}\) ions at depth of \(x\) and Tm\(^{3+}\) ions at depth of \(y\) as \(a = k/(x-y)^9\), where \(k\) is a proportionality factor [see Fig. 4]. Experimentally, however, we can only observe the average interaction. Since the RE ions are confined within their respective layers, we calculate average Er–Tm energy transfer rate, \(a_{ave}\), as a function of \(d\) by integrating for each layers and then summing over all doped layers as

\[
a_{ave}(d) = k \frac{\sum_{n=1}^{m} \sum_{l=1}^{m} \int_{2l-1}^{2l} \int_{2n-1}^{2n} \int_{2n-1}^{2n} \frac{1}{(x-y)^9} dxdy}{\sum_{n=1}^{m} \sum_{l=1}^{m} \int_{2l-1}^{2l} \int_{2n-1}^{2n} \int_{2n-1}^{2n} dx dy},
\]

where \(l\) and \(n\) is layer index for Er and Tm doped layer, and \(m\) is total number of each RE doped layer \([m = d_{tot}/(2d)]\). In the inset shows deconvoluted Er\(^{3+}\) and Tm\(^{3+}\) PL intensity. Dotted lines are a guide for the eyes.
order to avoid divergence of integral at \( x = y \), we need to assume a lower limit of integration, \( 2\varepsilon \), representing the minimum distance between RE ions. The value of 0.1 nm for \( \varepsilon \) was found to lead to best results, and was used. It was confirmed, however, that the value of \( \varepsilon \) did not significantly affect the result as long as \( \varepsilon \ll d \).

Equation (1) was then solved analytically with a help from a computation program, and used to simulate the \( d \) dependence of the \( \text{Er}^{3+} \) PL intensity and luminescence lifetime. Previously,\(^{10} \) we have shown that given an \( \text{Er}-\text{Tm} \) energy transfer rate \( a \), the \( \text{Er}^{3+} \) PL intensity can be written as

\[
I_{\text{Er}}(d) = bN_0 \frac{g}{g + 1/\tau_{\text{Er}} + a} W_R, \tag{2}
\]

where \( b, N_0, g, \tau_{\text{Er}} \), and \( W_R \) are a proportional factor, the total number of optically active \( \text{Er}^{3+} \) ions, \( \text{Er}^{3+} \) excitation rate, \( \text{Er}^{3+} \) PL lifetime without coupling with \( \text{Tm}^{3+} \), and radiative \( \text{Er}^{3+} \) decay rate, respectively, while the effective 1.54 \( \mu\text{m} \) \( \text{Er}^{3+} \) PL decay lifetime can be written as

\[
\tau_{\text{Er}}(d) = \int_0^\infty \exp \left\{ -\frac{t}{\tau_{\text{Er}}} + a\tau_{\text{Tm}} \left[ 1 - \exp \left( -\frac{t}{\tau_{\text{Tm}}} \right) \right] \right\} \, dt. \tag{3}
\]

In the present case, \( a \) must be replaced by \( a_{\text{ave}}(d) \), evaluated using Eq. (1). For numerical simulation, \( g \) was evaluated by subtracting the \( \text{Er}^{3+} \) PL decay rate from the \( \text{Er}^{3+} \) PL decay rate, and found to be 100 s\(^{-1} \) (data shown now). For \( \tau_{\text{Er}} \) and \( \tau_{\text{Tm}} \), the values of 5.1 ms and 400 ms obtained from Fig. 3 were used. Thus, the only adjustable fitting parameters for both Eqs. (2) and (3) were \( k \) and \( bN_0 \).

The result of fitting Eqs. (2) and (3) to the measured \( d \) dependence of \( \text{Er}^{3+} \) PL intensity and lifetimes are shown in Figs. 4(b) and 4(c), respectively. The symbols are experimental data, and the solid line is the result of the fit. The value of \( k \) used for fit was 0.26 nm\(^6\) s\(^{-1} \). The resulting calculated values of \( a_{\text{ave}}(d) \) used in the fits are given in the inset of Fig. 4(c). We obtain good fits to both sets of data using a single set of values for \( k \) and \( bN_0 \), indicating the validity of the resonant dipole–dipole interaction model between \( \text{Er}^{3+} \) and \( \text{Tm}^{3+} \), and confirming that by separating the \( \text{Er}^{3+} \) and \( \text{Tm}^{3+} \) ions in nm-thin layers, the energy transfer rate \( a \) can be reduced from \( \sim 5 \times 10^3 \) to 70 s\(^{-1} \) to increase the \( \text{Er}^{3+} \) PL efficiency. We note that the value of \( \sim 5 \times 10^3 \) for \( a \) is comparable to the value of \( \sim 2 \times 10^3 \) we reported previously for \( \text{Er} \)-\text{Tm} coimplanted film, demonstrating the universality of the model. The higher value obtained in the present study is also consistent with the higher \( \text{Tm}^{3+} \) concentration used in the present study.

Clearly, the \( \text{Er}^{3+} - \text{Tm}^{3+} \) interaction will decrease further with further increase in the layer thickness, up to the limit of a single \( \text{Er}^{3+} \) and \( \text{Tm}^{3+} \)-doped layer. Such a macroscopically inhomogeneous film, however, may be inappropriate for optical amplifier applications as it can lead to different mode profiles for \( \text{Er}^{3+} \) and \( \text{Tm}^{3+} \) bands, as well as require complicated pumping schemes to maintain pump uniformity across the amplification band. On the other hand, we note that at a layer thickness of 72 nm the \( \text{Er}^{3+} \) PL intensity reaches 81% of the maximum value possible without any interaction with \( \text{Tm}^{3+} \). Similarly, the value of \( \tau_{\text{Er}} \) for the film with \( d \) of 72 nm (4.9 ms) is very close to the value for \( \text{Tm} \) free \( \text{Er}^{3+} \)-doped SRSO film (5.1 ms), indicating near complete recovery of the \( \text{Er}^{3+} \) luminescence efficiency. Yet since 72 nm is still less than one-tenth of the signal wavelength, the entire film may still be described as being optically homogeneous.

In conclusion, we have investigated controlling the \( \text{Er}^{3+} - \text{Tm}^{3+} \) interaction in \( \text{Er}^{3+} \) and \( \text{Tm}^{3+} \)-doped silicon-rich silicon oxide via nm-scale spatial separation. We find that by separating \( \text{Er}^{3+} \) and \( \text{Tm}^{3+} \) into nm-thin layers, we can nearly completely suppress \( \text{Er}^{3+} - \text{Tm}^{3+} \) interaction while still maintaining optical homogeneity, thereby obtaining efficient rare earth luminescence across the entire 1.5–2.0 \( \mu\text{m} \) wavelength range. The data are well-explained by a model assuming a dipole–dipole interaction between excited \( \text{Er}^{3+} \) and \( \text{Tm}^{3+} \) ions, and suggest the possibility of developing compact, ultrawideband optical amplifier employing a single pump source.

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\begin{itemize}
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