

Modification of the Er³⁺ radiative lifetime from proximity to silicon nanoclusters in silicon-rich silicon oxide

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Abstract: The lifetime of Er³⁺ in silicon-rich silicon oxide has been reported with quite widely varying values ranging from 9 ms to 2 ms. In this work, we consider the direct impact of silicon nanoclusters on the erbium radiative lifetime, and show that it is a function of the silicon nanocluster size, and also the erbium proximity to the nanocluster.

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OCIS codes: (310.6860) Thin films, optical properties; (160.5690) Rare earth doped materials

References and links

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1. Introduction

In recent years, silicon nanocluster-sensitized Er-doped materials have sparked considerable interest, since it has been demonstrated that silicon nanoclusters (Si-nc) can transfer their energy quite effectively to the surrounding Er ions [1]. This indirect excitation of Er via the silicon is attractive as it leverages the absorption cross section of the Si nanocluster, which is 3 to 4 orders of magnitude greater than that of the Er ion. The broadband absorption spectra of the Si-nc also potentially allows pumping with sources such as light emitting diodes [2] instead of lasers, which would dramatically lower the cost of Er-doped amplifiers.

A considerable amount of work has been expended on fabricating and characterizing this material, but the radiative lifetime of Er^{3+} expected for this material system remains less than clear. Reports of measured Er lifetimes in this material differ widely from almost 9 ms [3] down to 3 ms and lower [4,5]. There is often an implicit assumption that a long lifetime (~ 10 ms), particularly if it is well described by a single exponential decay of the photoluminescence, is an indicator of 'good' material, and by default, short lifetimes suggest the presence of undesirable nonradiative decay processes. However, the presence of silicon nanoclusters renders this material inhomogeneous, and the impact of these nanoclusters, even though they are but a few nm in size, on the erbium radiative behavior should be taken into account. The radiative lifetime of the emitting species is a key parameter in assessing device potential, and a better understanding of the factors that determine it in this material would be useful, especially in the optimization of the material.

2. Analysis

To understand the impact of the silicon nanoclusters on erbium emission, we first review the simple but well-known case of the change in erbium radiative lifetime due to its proximity to a plane dielectric interface [6]. The modification to the radiative decay can be readily obtained from calculating the change in the local density of optical states (LDOS) brought about by the interface, via Fermi's golden rule, or classically by considering the scattered field \mathbf{E}^S from the interface on the emitter. For a silicon plane interface, there is a 4-fold enhancement to the radiative decay very close to the silicon surface, with the effect falling off rapidly with distance (Fig. 1). However, it is the erbium very close to the silicon interface that we are particularly interested in here, since it is only the erbium ions < 2 nm away that can be excited via the silicon [7].

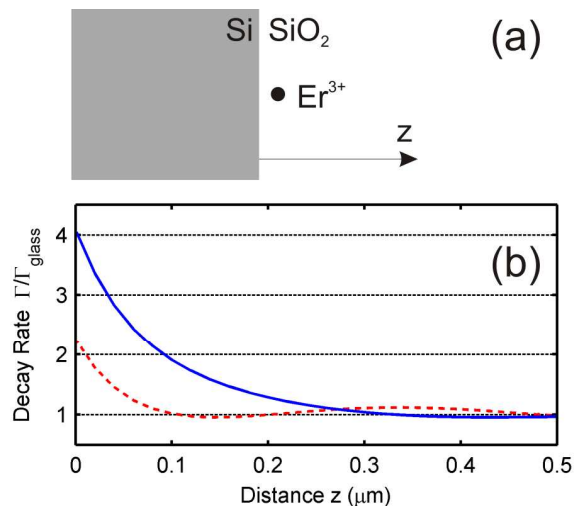


Fig. 1. Enhancement in the radiative decay rate of an emitter located in silica, close to a (semi-infinite) silicon plane, for polarizations orthogonal (solid line) and parallel (dotted line) to the interface.

For a spherical interface, the enhancement to the radiative decay rate γ for a dipole \mathbf{d} near a spherical particle has been analytically calculated by Chew [8] and experimentally verified for spheres of sizes down to 100 nm [9]. The radiative enhancement factor can be expressed as

$$\frac{\gamma}{\gamma_0} = 1 + \frac{3}{2k^3} \text{Im} \frac{\mathbf{d} \cdot \mathbf{E}^S}{|\mathbf{d}|^2} \quad (1)$$

where k is the wave number and γ_0 is the unperturbed decay rate.

In the particular case of the nanocluster (modelled here as a dielectric nanosphere much smaller in dimension than the emission wavelength), Eq. (1) can be simplified further from the work of Klimov [10]; the erbium spontaneous emission lifetime in the vicinity of a nanocluster can be written as

$$\frac{\tau_{SRSO}}{\tau_0} = \left| 1 + \frac{2(\varepsilon - 1)}{\varepsilon + 2} \left(\frac{a}{r} \right)^3 \right|^{-2} + O((ka)^2) \quad (2)$$

where τ_{SRSO} is the lifetime of the Er ions in the silicon rich oxide that are coupled to the Si nanoclusters, τ_0 the unperturbed Er lifetime (in the absence of the nanocluster), ε is the ratio of the permittivity of the sphere to that of the surrounding bulk medium, r the distance of the ion from the center of the nanocluster, and a the radius of the nanocluster. Eq. (2) holds for Er polarization in the radial direction which is more strongly coupled, see Fig. 1, and will therefore be predominantly observed in fluorescence experiments. We point out that the underlying basis here for the lifetime shortening is essentially the same as that for the well-known Purcell effect [11]. Although the Purcell effect is commonly associated with a cavity-induced lifetime modification, it is basically the change to the density of optical states (from the presence of the cavity) that causes the change to the spontaneous emission lifetime. Close proximity to a dielectric interface will also modify the local density of optical states, and the result is a corresponding change to the spontaneous emission rate.

Fig. 2 shows the predicted behavior of the erbium radiative lifetime in the vicinity of a silicon nanocluster, for nanocluster diameters ranging from 0.5 nm to 6 nm (with nanosphere sizes of just a few nm, the term $O((ka)^2)$ in Eq. (2) can be neglected). We assume τ_0 to be 10 ms for this calculation; we will examine this assumption in more detail later in the discussion.

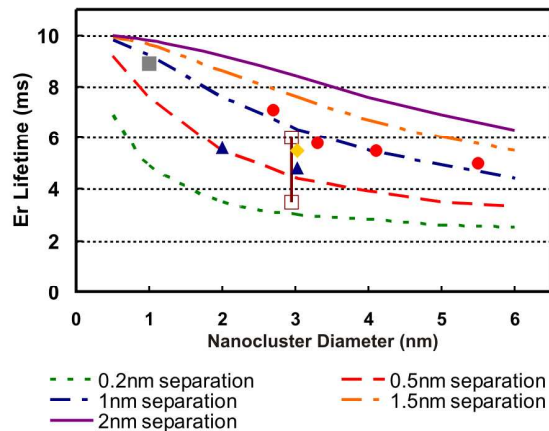


Fig. 2. Er lifetime as a function of Si nanocluster size, and for a range of distances from the nanoclusters. The curves are calculated from Eqn 1, and the experimental data points from the reports of 5 different groups: ● Watanabe et al. [15]; ▲ Gourbilleau et al. [13]; □ Franzo et al. [4]; ◆ Forcales et al. [14]; ■ Han et al. [3]

We see that the erbium lifetime decreases to half its unperturbed value when the erbium is near a nanocluster 3 nm or greater in size. The lifetime also depends on the distance of the erbium from the nanocluster, which we have plotted for distances 0.2 nm to 2 nm from the surface of the nanoclusters. The closer the erbium is to the nanocluster, and the larger the nanocluster, the shorter will be its radiative decay time.

3. Comparison with experimental results reported in the literature

It is useful to compare the calculated lifetimes with some of the measured lifetimes previously reported in the literature. We focus on those reports which contain sufficiently complete data that we can reliably correlate the measured erbium photoluminescence (PL) decay behavior with the nanocluster size. The experimental data shown in Fig. 2, from 5 independent groups [3,4,12,13,14], show reasonable agreement with the predicted lifetimes.

Perhaps most interesting is the data from Watanabe et al. [12], where the erbium showed near-single exponential decay, and the lifetimes were documented as a function of 4 different nanocluster sizes. The authors had speculated on the possibility that the lifetime was a function of nanocluster size, but were unsure that it might also have just been an artifact of the fabrication process. In fact, we find the 4 data points follow one of the theoretical curves quite closely. That the 4 data points follow one curve rather than cut across the curves suggests that the erbium ions tend to favor a particular distance from the nanoclusters, rather than assume a random distribution. The two erbium lifetimes from Gourbilleau et al. [13] also support this behaviour.

In fact, it is relatively straightforward to calculate the initial decay lifetime expected for a random erbium distribution (we refer to an initial decay lifetime, because the decay behavior takes on a more noticeable multi-exponential character in this situation). Fig. 3 shows that, for a random distribution, the lifetimes should vary more rapidly with nanocluster size and erbium concentration. The reason is simple: with a higher density of randomly located erbium ions, the probability of finding an ion very close to the nanocluster surface increases. Since the nanocluster-erbium energy transfer is strongly distance-dependent, it is the nearest erbium to the nanocluster that will be excited, resulting in short decay times.

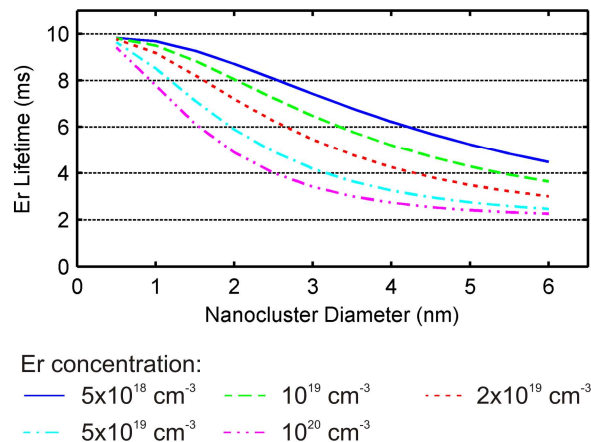


Fig. 3. Expected Er lifetime as a function of Si nanocluster size, assuming a randomly distributed Er population, and for different Er concentrations.

From Fig. 3, we would expect a range of lifetimes down to 3.5 ms for 3 nm size nanoclusters and erbium concentrations $\sim 10^{20} \text{ cm}^{-3}$, if the ions were indeed randomly distributed. It is useful that Watanabe et al. [12] observed that their erbium decay curve did not strongly depend on erbium concentration. That the erbium ions are not randomly sited in this material is perhaps not entirely surprising. It is well known that erbium has low solubility in silicon (hence it would prefer to avoid being in the nanoclusters themselves), and also low

solubility in high quality silica (thus also avoiding the SiO₂ regions far away from the nanoclusters); it is therefore not unreasonable to expect that the interfacial region near the nanoclusters contains sites that the erbium would prefer to be located. It is worth noting that Watanabe et al. [12] and Gourbilleau et al. [13] used different techniques for changing the nanocluster size - through changing the Si excess and hydrogen partial pressure respectively - during the fabrication of their films, while arriving at similar erbium behavior.

Of the 5 independent data sets used in this comparison, it is the earlier work by Franzo et al. [4] that shows a pronounced multi-exponential erbium PL decay with an initial short lifetime component of ~3 ms. As this behavior persisted from room temperature to 17 K with only a slight lengthening of the lifetime components, it is not unreasonable to assume that the behavior is still largely due to radiative decay. The multi-exponential behavior and short radiative lifetimes indicate that the erbium ions are randomly distributed in this particular film. This is consistent with the fabrication process for this material - ion implantation, which tends to place the ions randomly in the film, with only a short annealing time (5 min) following the erbium implant. Such a procedure would leave little opportunity for any substantive redistribution of the erbium ions to take place. We note that the peak erbium concentration in this film is high, $>10^{20}$ cm⁻³, and consistent with the 3.5 ms initial lifetime for 3 nm nanoclusters (Fig. 3). The implantation process also produces a significant variation of the erbium concentration across the thickness of the film, which should contribute to the multi-exponential decay behavior observed.

Finally, the calculations presented here could account for the long erbium lifetimes observed by Han et al. [3] which, at 8.9 ms, start to approach those seen in erbium doped optical fibers. Unlike the other groups, a low silicon excess and only one rapid thermal anneal (1000°C for 5 min) was used to precipitate the silicon in the film, leaving little opportunity for nanoclusters of substantial size to form. Although the size of the nanoclusters was not directly measured, the Si nanocluster PL spectrum is significantly flatter and broader than that recorded from 3 nm or even 2 nm sized silicon nanoclusters [12,13]. We note that while Han assumed the peak emission was at 720nm and thereby inferred nanocluster sizes of 2nm, the peak is actually very broad, and the maximum is closer to 680 nm. Luminescence at such wavelengths is likely to originate from nanoclusters significantly smaller than 2 nm. From Fig. 2 and Fig. 3, we see that for such sized nanoclusters, we would expect little modification to the erbium lifetime.

To complete the discussion, we examine the assumption of an unperturbed Er lifetime of 10 ms in our model. In fact, the value of the Er³⁺ radiative lifetime in the matrix surrounding the silicon nanoclusters is not known, but it is highly unlikely that the local environment around the erbium ions in the silicon-rich material is pure stoichiometric SiO₂. Therefore measurements of the corresponding Er lifetime in pure SiO₂ are indicative, but not directly applicable to our model. Miniscalco [15] cites a value of 14 ms for pure silicate glass, while Wojdak et al. [16] quoted a value of 11ms. Reports in the literature suggest that the environment close to silicon nanoclusters is likely to be sub-stoichiometric SiO_x, in which case the local refractive index will be higher than 1.46, and a shorter radiative lifetime should therefore be expected [16].

Given the above, we have assumed a radiative lifetime of 10 ms in Fig. 2 and Fig. 3 to illustrate the effect on radiative lifetime of the proximity of Er ions to silicon nanoclusters. We chose 10 ms as this is close to the maximum lifetime reported in the well-characterized material that we considered in our study (i.e. that from Han et al.), yet shorter than the 14 ms reported for stoichiometric SiO₂. The important point demonstrated here is that the proximity of silicon nanoclusters to Er ions causes a very significant *change* in the erbium radiative lifetime. To emphasize this, Fig. 4 shows the same calculation as Fig. 2 but assuming a pure SiO₂ Er environment (i.e. for a radiative lifetime in the matrix of 14 ms), demonstrating the same effect seen in Figs. 2 and 3 - namely a shortening of the radiative lifetime by a factor of 3x or more.

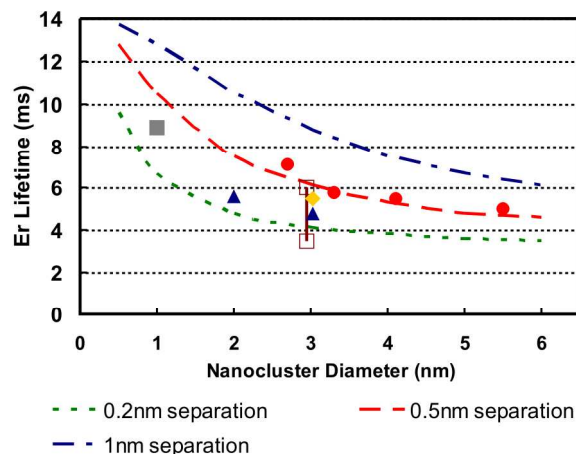


Fig. 4. Er lifetime as a function of Si nanocluster size, as in Fig 2, but assuming a pure silica matrix immediately outside the nanocluster. The curves are calculated from Eqn 1, and the experimental data points from the reports of 5 different groups: ● Watanabe et al. [15]; ▲ Gourbilleau et al. [13]; ◻ Franzo et al. [4]; ◆ Forcales et al. [14]; ■ Han et al. [3]

We note that the analyses applied here are for the case of erbium ions in the proximity of one nanocluster. Where the silicon nanocluster concentration is high ($>10^{19} \text{ cm}^{-3}$), it becomes increasingly likely that an erbium will be close to 2 or more nanoclusters. The calculation of the radiative enhancement in such a situation is beyond the scope of this work, e.g. it would depend on the particular location of each nanocluster with respect to the erbium ion; however, the enhancement will be greater in such configurations, resulting in even shorter radiative decay times.

4. Conclusion

The radiative lifetime of erbium ions is significantly modified in the presence of silicon nanoclusters, decreasing to half its unperturbed value even for nanoclusters just 3 nm in size. This effect is highly local, and substantial only when the erbium is very close to the nanoclusters, within 2 nm or less, but this is also the region that is of most interest when silicon is used as a sensitizer for another emitting species. Although non-radiative quenching processes can still be a factor, particularly where temperature-dependent lifetimes are observed, our results suggest that Er-doped silicon-rich silicon oxide exhibiting Er lifetimes shorter than those observed in conventional erbium-doped silica fibers should not necessarily be considered as being of poorer quality. Er lifetimes as short as 4 ms or even less can be purely radiative in this material system, and would have no negative impact in itself on the optical efficiency.

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