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# $Er^{3+}$ excited state absorption and the low fraction of nanocluster-excitable $Er^{3+}$ in $SiO_x$

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Despite the observation by a number of groups of a strong luminescence sensitization effect of erbium ions by excitation exchange from silicon nanoclusters, there is considerable experimental evidence that the fraction of Er ions excited by Si-nc is actually very low for much of the material reported. In this work, we examine the evidence and point out that Er excited state absorption is the likely cause. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2227637]

In recent years, silicon nanocluster-sensitized Er-doped materials have generated great interest, as it has been demonstrated that silicon nanoclusters (Si-nc) can transfer their energy very effectively to the Er ions surrounding them. The attraction of this indirect excitation is twofold: (i) the excitation cross section of the Si-nc is at least four orders of magnitude greater than that of rare earths in silica and (ii) the broadband absorption spectrum of the Si-nc allows pumping with sources such as light-emitting diodes (LEDs). The latter would dramatically lower the cost of Er-doped amplifiers, and allow pumping geometries such as top-down nonguided pumping, which would enable easy integration of amplifiers in planar optical circuits. However, no lasing action has been achieved to date. Indeed, there is cumulating evidence that, for much of the material that has been reported, the fraction of Er ions that can be excited by Si-nc is actually very low—of the order of a few percent or less. Clearly, this issue will need to be understood and resolved in order for viable lasers and amplifiers to be realized from this material system.

There is now documented evidence from multiple groups, although it may not always have been explicitly recognized, that the fraction of Er ions that are excitable by Si-ncs is often quite low.[1,2] For example, for the data presented by Fujii *et al.*,[1] the Er photoluminescence (PL) for two samples with the same Er concentration, one of which contained Si-nc [silicon-rich oxide (SRO)] and the other without ($SiO_2$), was reported to differ by a factor of 30 under the same pumping conditions (see Fig. 1). It is straightforward to show by rate equation analysis that the Er excited state populations are given by

$$N_2^{SiO_2} = \frac{\sigma\tau P N_{Er}}{1+\sigma\tau P}, \quad N_2^{SRO} = \frac{k\tau n_b N_{Er}}{1+k\tau n_b}, \tag{1}$$

where $\sigma$ is the Er pump absorption cross section, $\tau$ the Er luminescence lifetime, $P$ the pump flux, $N_{Er}$ the Er ion concentration, $k$ the Si-nc to Er excitation transfer coefficient, and $n_b$ is the Si-nc excited state population.

At the maximum pump power reported (1.5 $W/cm^2$), the SRO sample is in the saturation regime while the $SiO_2$ sample is still in the linear regime; therefore the ratio of the number of excited Er ions in the two samples can be simply estimated as

$$\frac{N_2^{SRO}}{N_2^{SiO_2}} \cong \frac{1}{\sigma\tau P}. \tag{2}$$

Taking $\sigma_{488\ nm} \sim 10^{-20}\ cm^2$, $\tau = 10$ ms, and $P = 4 \times 10^{18}\ cm^2\ s^{-1}$ (corresponding to 1.5 $W/cm^2$), this yields an Er concentration ratio of 2000. As the experimentally observed PL ratio is only 30, this indicates that just 1.5% of the available Er ions in the SRO sample have been excited. This conclusion seems surprising considering that, for the volume fraction of Si-nc and Er concentration specified in the SRO sample, the majority of the Er ions would be expected to lie in the vicinity (within 1.5 nm, the interaction range for Si-nc-to-Er energy transfer[3]) of a Si-nc. Nonetheless, the small percentage inferred above is consistent with the findings of Wojdak *et al.*,[2] as they report a sublinear behavior beyond an excited Er population of $1.1 \times 10^{18}$ out of $2.2 \times 10^{20}\ cm^{-3}$, as estimated from their cw pumping data.

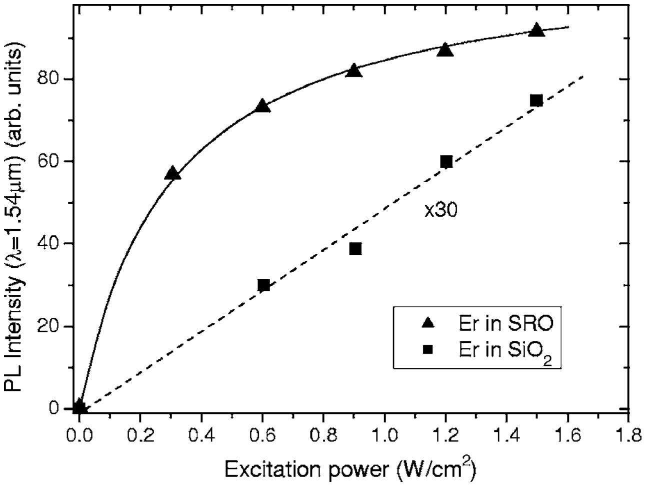

FIG. 1. Er PL data for Er-doped SRO and Er-doped $SiO_2$ extracted from Ref. 1. The PL intensity differed by only a factor of 30 at maximum pump power, in contrast to an expected ratio of 2000 if all the Er ions in the SRO sample had been excited.

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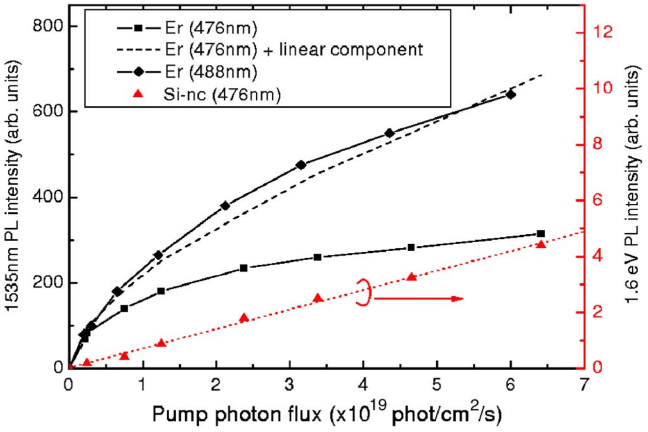

FIG. 2. (Color online) Left axis: Er PL behavior for 476 and 488 nm optical pumping. The dashed line is the PL curve under 476 nm pumping with a linear component added on to it. Right axis: Si-nc PL intensity at 1.6 eV. The sample contains 7 at. % excess Si and 1 at. % Er.

In fact, the small fraction of Er ions that is excited by the Si-nc is related to a previous debate on whether a Si nanocrystal can excite more than one Er ion.[4,5] Initial evidence seemed to suggest that each Si nanocrystal could only excite one Er ion, leading to various hypotheses such as Auger deexcitation and pair-induced quenching to account for this limit.[4] It is now becoming clear though that multiple Er ions (as many as 20) can be excited if the pump power is increased sufficiently—by 10–100 times beyond the saturation power.[2] More recently, the framing of this problem has become complicated by findings that strong Er PL can be sensitized not just with Si nanocrystals, but also by an amorphous silicon network in which no distinct Si nanocrystals exist.[6]

To date, no compelling explanation has been able to account satisfactorily for all these observations in a consistent manner. For example, a plausible explanation that most (over 90%) of the Er ions in the material may be optically inactive or quenched, and therefore nonluminescent, appears at odds with the ability of these ions to be excited at high power, after the initial Er PL saturation has occurred. Furthermore, the Er ions that are not excited by the Si-nc can nonetheless be excited by direct resonant optical excitation, which provides further proof that these Er ions are optically active, though not susceptible to excitation exchange from Si-ncs. Figure 2 shows the Er PL for a sample grown at UCL by plasma-enhanced chemical vapor deposition,[7] under 476 nm (nonresonant) and 488 nm (resonant) pumping. We see that the Er PL under 488 nm pumping is almost twice as strong as with 476 nm pumping at maximum pump power, suggesting that the Er ions excited directly by the optical pump are equal in number to those excited by the Si-nc. This is supported by the dashed curve, which we have constructed simply by adding a linear contribution to the Er PL curve under 476 nm pumping (the numbers of Er ions excited directly by the 488 nm pump should increase linearly with pump power at these power levels). From these curves, we can also estimate the fraction of Er ions excited by Si-nc as the Er PL saturates: it comes out to just 0.7%—similar to the samples studied by Fujii *et al.*[1] and Wojdak *et al.*[2]

The low fraction of Er ions excitable by Si-ncs is clearly a pressing issue with crucial device implications, especially since the unexcited Er ions still exhibit their characteristic absorption, and will contribute to a large loss.[4] In a recent paper, we pointed out the existence of Er excited state absorption (ESA) occurring in this material system.[8] We propose here that ESA is the primary cause for the low fraction of Er ions excited by the Si-nc.

ESA occurs when a nanocluster transfers its energy to an excited Er ion, elevating it from the $^4I_{13/2}$ to the $^2H_{11/2}$ or $^4S_{3/2}$ levels. The excited erbium ion then rapidly decays back to the $^4I_{13/2}$ level, and the net result is just an energy loss. To understand the impact of ESA on the fraction of Er ions excited, let us consider the situation in which there are multiple Er ions surrounding each nanocrystal. Even if all these ions are within the excitation range of the Si-nc, the Si-nc will predominantly transfer its energy to the nearest Er ion due to the short-range nature of the Si-nc-Er interaction, which falls off rapidly with distance.[3] Because the lifetimes of the $^2H_{11/2}$ or $^4S_{3/2}$ levels are much shorter than that of the $^4I_{13/2}$ level, any further transfer of energy from the Si-nc—preferentially to the same ion—will result in a cycling of the Er ion between the $^4I_{13/2}$ and $^2H_{11/2}$ or $^4S_{3/2}$ levels.

To study this effect, we have run simulations of various Si-nc and Er populations, based on rate equation analyses assuming each nanocluster is surrounded by a set of Er ions, which are located randomly. Although the exact nature of the interaction between the Si-nc and the Er ions is still under debate (whether it is a dipole-dipole or Auger interaction), we assume (without much loss of generality to the argument here) a dipole-dipole interaction process. The energy transfer probability then diminishes as the sixth power of the Si-nc-Er separation distance. The separation distance is taken from the Er ion to the surface of the nanocluster, rather than to the core, because the surface states have been shown to play a crucial role in the emission process at 800 nm.[9,10] The minimum distance of Er ions to a nanocluster was set to 0.16 nm, the length of the Si–O bond. Back-transfer and Auger processes from the Er to the Si-nc were neglected, as it has been experimentally shown that they are unlikely to occur for this material.[11] For simplicity, and in keeping with results from our previous analysis of ESA in this system,[8] the ESA coupling coefficient is taken to be comparable (equal) to the Si-nc-Er ground state coupling coefficient. We performed the calculations with ESA present, and without ESA for comparison.

We first consider the case similar to that studied by Wojdak *et al.*,[2] in which there were 220 Er ions per nanocluster. Using the parameters specified in that paper, we calculated the ratio of excited Er ions and nanoclusters versus pump photon flux. In that paper, the excited population was measured experimentally, enabling us to compare our results with the measurements. The result is shown in Fig. 3(a).

The saturation behavior of the Er is markedly different when ESA is present. At very low flux, the excited Er population grows linearly. When the excited population reaches ~0.5%, the behavior becomes sublinear. This threshold population corresponds to the situation of one excited Er per nanocluster, and shows that it is considerably more difficult to excite the second nearest Er ion. This effect does not occur if ESA is absent (dashed line). Considering the simplicity of the model (which neglects concentration quenching or upconversion effects), and the fact that the only free parameter is the Si-nc-Er coupling constant, there is very good qualitative agreement with the experimental behavior observed in

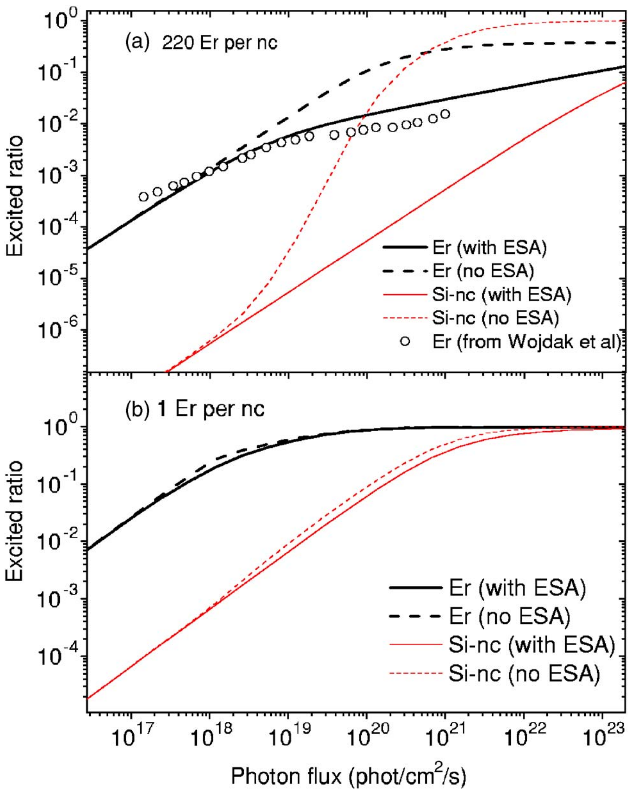

FIG. 3. (Color online) Excited population vs pump photon flux calculated from our model. (a) Considering the parameters extracted from Ref. 2 ([Si-nc]$=10^{18}$ cm$^{-3}$, [Er]$=2.2\times10^{20}$ cm$^{-3}$). The void circles represent the Er excited ratio extracted from Fig. 3(b) of the same paper. (b) Considering one Er per nanocluster, with a concentration of $10^{19}$ cm$^{-3}$.

Ref. 2, strongly suggesting that ESA is responsible for this sublinear, gradual saturation behavior.

The behavior of the Si-nc excited population is also interesting, and informative. If ESA is neglected, the Si-nc excited ratio increases nonlinearly when the Er begins to saturate, as depicted in Fig. 3(a). The physical basis behind this is simple: without ESA, saturation of the Er implies that energy transfer from the Si-nc to the Er effectively ceases, or slows to a very low rate constrained by the long (millisecond) Er lifetime. With this energy dissipation route terminated, the Si-nc excited population (and corresponding PL) must therefore increase. By contrast, with ESA occurring, the Si-nc excited ratio remains linear with pump power near the Er saturation point. Experimental evidence reported indicates that the Si-nc PL is quite linear with pump power as the Er PL saturates,[12] which is also confirmed in Fig. 2. This linear Si-nc PL behavior can be interpreted as further evidence of ESA occurring in the material.

Finally, we consider the situation where there is at most one Er ion per nanocluster. The material studied by Lee *et al.*[13] appears to correspond more closely to this situation. Their low Er concentration, together with the low annealing temperature and short annealing time, leads to a high quantity of small Si nanoclusters. For our calculations, we assume concentrations of $10^{19}$ cm$^{-3}$ for both Si nanoclusters and Er ions, and nanocluster sizes of 1 nm, which corresponds roughly to 1 at. % Si excess and 0.05 at. % Er concentration. The results are shown in Fig. 3(b).

In this case, the behavior of the system is quite similar whether ESA is present or absent. The entire erbium population can be saturated much more easily at lower pump powers because there is only one Er per Si-nc to excite. It is worth noting that the only report of optical gain has been with such material.[13] However, even though it is easier to achieve a population inversion in this case, ESA will still adversely impact the performance of the optical amplifier or laser, as it represents a constant drain of energy that increases the pump threshold and decreases the slope efficiency.

In conclusion, we have shown that the low fraction of Er ions excitable by Si-nc is mainly due to Er excited state absorption in the material. The evidence is manifested in the sublinear behavior of the Er PL signal with pump power, and also the *linear* behavior of the emission coming from the Si nanoclusters. Our model shows good agreement with the experimental behavior reported from multiple groups. Eliminating the excited state absorption, e.g., by further engineering the Si-nc band structure away from the 1.6 eV energy transition, should enable multiple Er ions to be readily excited, and at the same time eradicate a highly problematic energy dissipation mechanism. This should enable efficient optical amplifiers and lasers to be realizable in this highly promising material system.

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