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# Flashlamp pumping of erbium-doped silicon nanoclusters†

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**We report recent results showing broad-band excitation of erbium ions implanted into thin films of silica containing silicon nanoclusters. Indirect excitation of the rare-earth ions is mediated by the nanoclusters, which are either grown in during plasma-enhanced chemical vapour deposition of the films, or are formed by implantation of thermally grown $SiO_2$ layers with $Si^+$ ions. We demonstrate efficient flashlamp pumping of the erbium 1535 μm photoluminescence band and discuss the device implications of this material. Copyright © 2001 John Wiley & Sons, Ltd.**

**Keywords: Si nanoclusters; energy exchange; erbium; photoluminescence; thin films**

## INTRODUCTION

Light emission from erbium-doped materials is at the heart of current optoelectronic telecommunications devices, as the intra-4*f* $Er^{3+}$ transition at 1.53 μm lies within one of the principal low-loss transmission windows of silica optical fibres. The continued success and growth of such technologies lies in the realization of full integration with existing silicon materials and processing. However, this integration of erbium emission with silicon electronics remains problematic, as erbium-doped bulk crystalline silicon suffers from very low luminescence quantum efficiency. Recently, erbium-doped nanoclustered or porous silicon has shown considerable promise, and there have been a number of studies, including those by this group, showing that an efficient exchange mechanism exists between the silicon host and rare-earth ion which transfers broad-band optical or electrical excitation into narrow-band emission at 1.53 μm.[1–8] Such materials exhibit efficient erbium luminescence and offer the advantages of ease of processing and convenient integration with current semiconductor manufacturing technology.

Current erbium-based optoelectronic devices typically employ erbium-doped silica fibres or waveguides configured in wavelength division multiplexing (WDM) geometries with a high-power laser diode pumping the 980 or 1480 nm $Er^{3+}$ absorption bands. Despite recent and continued reductions in the cost of such pump sources, the development of a broad-band pumpable erbium system, or perhaps a direct electrical injection device, would yield significant savings and constitute a major technological advance. The current emphasis in WDM technology is moving away from long-haul systems, which are dominated by the erbium-doped fibre amplifier (EDFA), towards smaller-scale local networks. Though the $10 000 unit cost of a laser-pumped EDFA makes little impact on the total budget of a transatlantic cable, such a cost becomes impractical on the scale of premises-based optical networks. The presence of an efficient coupling mechanism between erbium and a broad-band absorbing host suggests that broad-band pumped devices utilizing cheap sources are feasible. In this paper we demonstrate the existence of host-to-rare-earth coupling in silicon-

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rich silica and report, for the first time, broad-band white-light and flashlamp pumping of erbium-doped nanostructured material.

## EXPERIMENTAL

Samples were prepared by two methods, the first being plasma-enhanced chemical vapour deposition (PECVD). This method is more fully detailed elsewhere,[1,9,10] but briefly consisted of plasma dissociation of silane, nitrous oxide, and a volatile erbium organic chelate in a parallel-plate plasma chamber. Film stoichiometry was controlled by varying the relative flow rates of the silane and nitrous oxide gases, and by controlling both the temperature of the organic precursor and the flow rate of the carrier gas. Auger analysis of the deposited films showed them to be silicon-rich (15% excess silicon) and to contain 1 at. % erbium. Film thicknesses were in the range 1–3 μm. Previous work has demonstrated that careful selection of growth conditions produces films containing excess silicon in the form of nanoclusters, the sizes of which depend on growth parameters and post-process annealing. The presence of such clusters has been confirmed by transmission electron microscopy (TEM), and has been inferred from optical absorption and visible photoluminescence studies of silicon-rich silica.[1,9–11]

The second preparation method consisted of sequential ion implantation of high-quality thermally grown $SiO_2$ layers on silicon substrates with $Si^+$ and $Er^{3+}$ ions. Multiple implants of both silicon and erbium were used in order to obtain flat concentration profiles with depth. Again, this method is more thoroughly detailed elsewhere.[6] Care was taken to ensure that the erbium implants (peak concentration 0.5 at. % in each case) overlapped strongly with the silicon-rich region. In all cases, samples were annealed at 1050 °C in nitrogen for 8 h following the silicon implant; these annealing conditions are known to produce silicon nanocrystals.[6,9]

Photoluminescence experiments were conducted using a standard tungsten–halogen bulb to excite the samples, care being taken to eliminate any 1.5 μm output from the bulb using a low-pass filter. A series of high-pass and band-pass filters was inserted between the source and sample in order to remove selectively different wavelength regions corresponding to strong erbium ion absorption lines. In this way, only indirect excitation channels were selected.

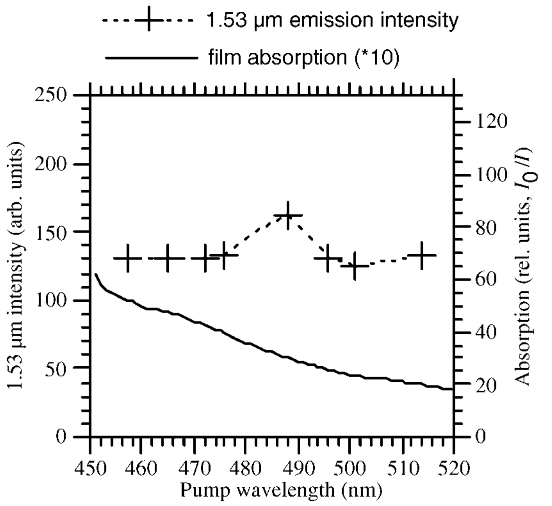

**Figure 1** PLE spectrum of erbium-doped silicon-rich silica film. Also shown is an absorption spectrum of the film.

Photoluminescence excitation (PLE) spectra were taken for all samples using an argon-ion laser, a scanning monochromator and an InGaAs photodiode. Spectra were obtained by tuning the argon-ion laser to each of the available lines in turn and monitoring the output from the samples at 1.53 μm. Care was taken to maintain the same laser power at each wavelength.

Absorption spectra of selected PECVD-grown

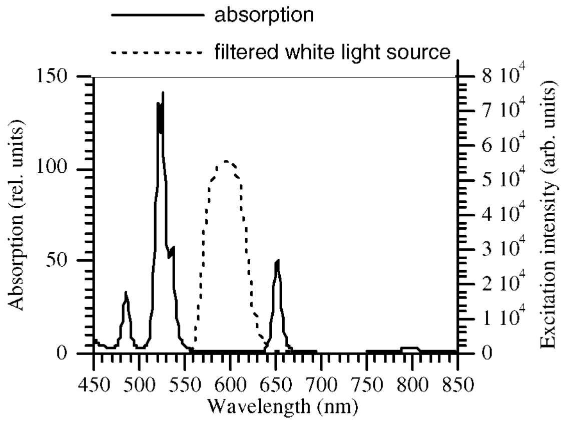

**Figure 2** Emission spectrum of the filtered white-light source used to pump the silicon-rich samples (dotted line). The solid line is an absorption spectrum of an erbium-doped silica fibre, included to show positions and magnitudes of erbium absorption bands in this region.

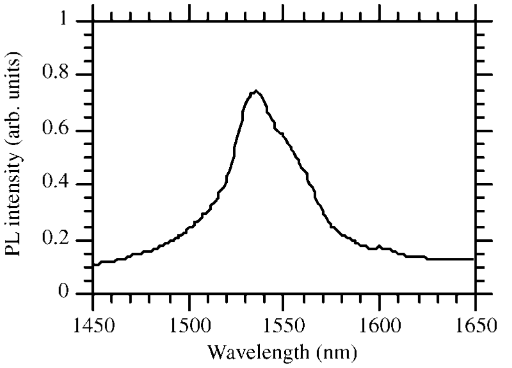

**Figure 3** Emission spectrum of erbium-doped sample pumped using the filtered white-light source shown in Fig. 2.

samples were taken after removing the films from the silicon substrate. For comparison and identification of the principal erbium absorption lines, an absorption spectrum was also measured for a reference erbium-doped silica fibre.

Flashlamp pumping experiments were carried out using a standard camera flashgun (Chinon Auto S-280), which produced a peak output power density at the sample of 88 mW $\mathrm{cm}^{-2}$ in a 250 μs pulse. The infra-red portion of the flashgun output was filtered out to separate the excitation from the 1.53 μm erbium emission. The output from the thin films was measured at 1535, 1450 and 1350 nm in order to confirm that the measured luminescence was characteristic of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ $\mathrm{Er}^{3+}$ transition at 1.53 μm.

## RESULTS

Figure 1 shows a PLE spectrum of an erbium-doped silicon-rich silica film deposited by PECVD (erbium concentration: 1 at. %). The peak at 488 nm demonstrates that there is some direct excitation of erbium, but luminescence is also seen when the sample is pumped at wavelengths away from erbium absorption bands. A comparison of the PLE signals at 488 and 465 nm indicates that excitation at 488 nm is approximately 75% indirect, 25% direct. In contrast, stoichiometric silica films doped with similar concentrations of erbium did not exhibit luminescence from indirect excitation and only showed 1.53 μm emission when pumped directly. Also shown is the absorption spectrum of the erbium-doped film over this range of wavelengths. Its distinctive feature is a monotonic band-edge absorption across much of the visible region; no erbium absorption lines can be seen, despite the observation of characteristic erbium luminescence from these films. The strong band-edge absorption thus appears to dominate the spectrum and 'swamp' the erbium absorption bands.

Figure 2 shows the emission spectrum of the filtered white-light source used in the broad-band pumping experiments. This illustrates the effect of the filters used to remove wavelengths corresponding to the erbium absorption lines around 380, 490, 520, and 650 nm. Superimposed is an absorption spectrum taken of a reference erbium-doped silica fibre, included to show the positions and intensities of the erbium absorption bands. The erbium

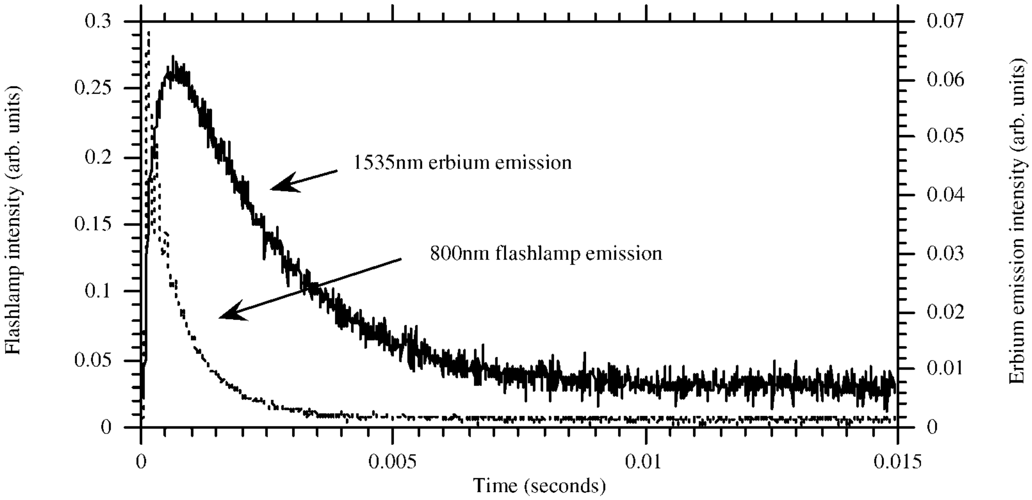

**Figure 4** Time evolution of erbium emission from PECVD-produced thin film pumped using camera flashgun (solid line). Also shown is the output from the flash at 800 nm (dotted line).

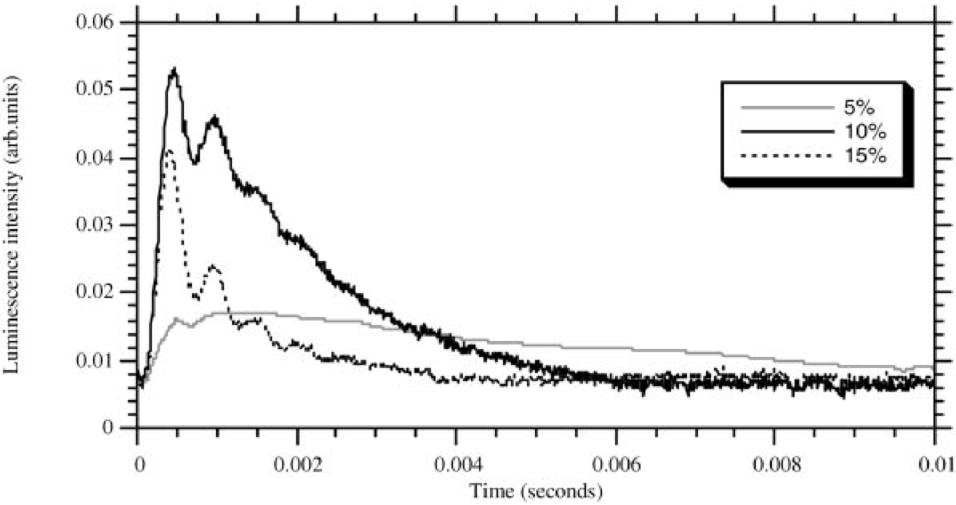

**Figure 5** Time evolution of flashgun-pumped 1.53 μm emission from the three erbium-implanted samples.

emission spectrum obtained using this combination of filters is given in Fig. 3. The range of excitation wavelengths used lies away from any of the characteristic erbium absorption bands, and hence the overlap between pump and absorption wavelengths is very small. In addition, the light source was not tightly focused on the sample and the power density at the sample surface was around 25 mW cm$^{-2}$.

Figure 4 shows the time evolution of the 1.5 μm signal from the same PECVD-deposited sample pumped using a standard photographic camera flashgun; also shown is the flash output at 800 nm. No emission signal was detected at wavelengths of 1350 and 1400 nm, indicating that the 1.5 μm signal originated from the optically active erbium in the film. The time resolution of the system, limited by the detection electronics, was of the order of 15 μs, and the decay time of the erbium luminescence (approximately 3 ms) matches that measured using laser excitation. The peak power density of the flashgun at the film was of the order of 88 mW cm$^{-2}$, and the power efficiency of the excitation process was estimated using the method detailed in Ref. 12 to be 0.1%.

Figure 5 shows the time evolution of flashgun-pumped 1.53 μm output from three erbium-doped samples created by ion implantation. Each sample was implanted with the same peak concentration of erbium, but the peak excess silicon concentration varied from 5 to 15 at. %. Clearly evident is a strong correlation between excess silicon content and luminescent output at 1.53 μm. The oscillations evident on the 5 and 10% traces are artefacts of the detection electronics.

Figure 6 shows photoluminescence spectra obtained using the 476 nm line of the argon-ion laser as pump source for the three implanted samples, and Fig. 7 shows the corresponding PLE spectra. Of particular note is the trend towards an increasingly flat PLE spectrum with increasing excess silicon content.

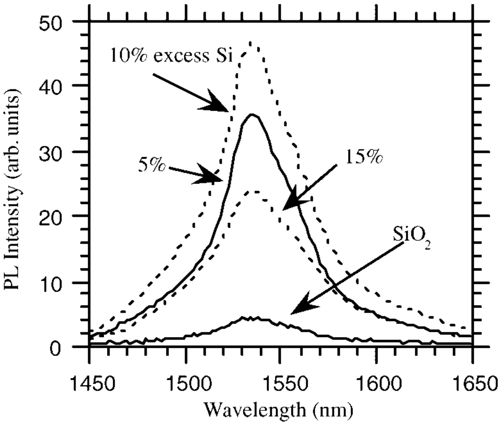

**Figure 6** Photoluminescence spectra of the three erbium-implanted samples. Laser pump wavelength 476 nm. Also included is a photoluminescence spectrum of stoichiometric silica implanted with the same concentration of erbium.

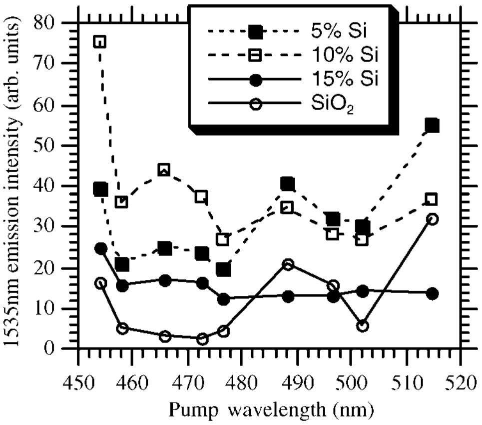

**Figure 7** PLE spectra of the three erbium-implanted samples. Also shown is a PLE spectrum of erbium-implanted stoichiometric silica, exhibiting no indirect excitation of the Er$^{3+}$ emission.

## DISCUSSION

The observation of clear erbium luminescence spectra in these samples using such low excitation levels pumping away from the rare-earth absorption lines strongly suggests the presence of a broad-band absorbing species and an efficient exchange mechanism. The samples studied here all exhibited a visible photoluminescence band around 1.6 eV, which we and other groups have attributed in previous work to radiative recombination of confined excitons within silicon nanoclusters,[10,11] along with a 2 eV band that has been assigned to non-bridging oxygen hole defects in the silica matrix.[10,13,14] Both of these bands are quenched by the presence of erbium: samples show luminescence at 1.6 and 2 eV, which is reduced by two orders of magnitude by implantation with erbium. Increasing the erbium concentration produces an associated decrease in the 1.6 and 2 eV bands that is not restored by annealing out implantation damage. We are therefore led to the conclusion that emission at 1.6/2 eV and erbium luminescence are competing processes. Auger analysis of the PECVD-produced films showed an excess silicon content of around 15 at.%, which we propose on the basis of the visible photoluminescence data to be in the form of silicon nanoclusters. The observation of the band-edge absorption in these films supports this contention. TEM studies of the implanted samples confirmed the presence of silicon nanocrystals with a mean size of around 3 nm.[9] We therefore conclude that absorption is via the silicon nanoclusters, which may de-excite either by excitonic or defect-related recombination, leading to emission at 1.6 or 2 eV, or else by transferring excitation to erbium ions. The nature of this exchange is unclear, but agrees qualitatively with similar observations published by this and other groups working on erbium-doped crystalline and porous silicon, silicon nanopowders, and chalcogenide glasses.[1–8,15,16] It is unlikely that the exchange proceeds via defect states, as there is a strong dependence of the strength of coupling on the excess silicon content of the films, and samples exhibiting very little defect luminescence also exhibit strong indirect excitation of the optically active erbium fraction. High concentrations of silicon lead to shorter erbium luminescent lifetimes and flatter PLE spectra, consistent with the assumption of an increased probability of interaction between nanoclusters and erbium ions. Annealing the samples at temperatures sufficient to remove defect luminescence (i.e. in excess of 600 °C) produces an enhancement of the erbium luminescence, implying that annealing serves to reduce defects acting as nonradiative recombination centres around erbium ions, and promotes coordination of erbium ions with oxygen. Annealing at temperatures higher than 900 °C reduces the intensity of the 1535 nm emission as erbium precipitates are formed. These results are consistent with results published by a number of other groups studying similar material.[5,7,17] For the case of erbium-doped silicon, the contention is that the exchange mechanism is carrier-mediated, whilst for chalcogenide glasses the mechanism is presumed to proceed via the host absorption bands followed by a resonant transfer to the luminescent ion, possibly via defect states.[15] Recent results from other groups looking at silicon nanopowders doped with erbium during the growth phase also indicate efficient excitation exchange between the silicon host and the rare-earth ion.[16] The efficiency of this process in our samples is surprisingly high, being of the order of 0.1% for resonant laser excitation. The observation that this efficiency is preserved for broad-band flashlamp pumping indicates that the predominant route for excitation of the optically active erbium is indirect.

It is worth commenting on the trends in 1.53 μm emission observed from the implanted samples. In the case both of laser and flashgun excitation there is a striking trend in photoluminescence output: the highest being from the sample containing 10% excess silicon, the lowest from that with 5% excess, and the 15% sample being intermediate. There are also significant differences in the photoluminescence lifetimes observed in these samples. The 15% excess silicon film exhibits a much shorter lifetime than either of the others. Our contention in a previous publication[6] concerned with laser excitation of these samples was that the change from 5 to 10% excess silicon represented an increase in number density and size of silicon nanoclusters (TEM studies support this) and, consequently, the mean separation between erbium ions in the silica matrix and silicon nanoclusters is smaller for the higher silicon content. However, there is also an associated increased probability that the implanted erbium sits within the silicon nanoclusters, rather than in the surrounding silica matrix. Coordination with oxygen is a prerequisite for efficient emission from $Er^{3+}$, and it is well known that erbium-doped bulk silicon is a very inefficient emitter at 1.5 μm. The results for the 15% excess silicon sample can therefore be explained by assuming that, at this concentration, a significant proportion of the erbium lies within the silicon nanoclusters, and hence the luminescence intensity is quenched with respect to that from the 10% sample.

The lifetime data may be explained similarly, as erbium in bulk silicon shows a much shorter observed luminescent lifetime of the metastable state (typically around 100 μs, limited by nonradiative recombination) than that in silica (generally in the range 2–10 ms, depending on the degree of rare-earth ion clustering).[2] Thus, postulating that increasing the excess silicon concentration increases the proportion of erbium ions within silicon nanoclusters, the observed reduction of measured lifetime is consistent with the optically active erbium ‘seeing’ an environment more like bulk silicon.[6] The long lifetime observed for the 5% excess silicon case is, therefore, governed primarily by the oxide matrix, and the much shorter value for the 15% sample comes from stronger nonradiative interactions between erbium ions and silicon within nanoclusters.[2] The role of clustering of the erbium ions as a contributing factor to the change in observed luminescent lifetime can be neglected, as all three samples were implanted with the same concentration of erbium and, consequently, any differences between them must be ascribed to differences in the concentration and/or size distribution of silicon nanoclusters. TEM studies are currently under way to investigate this further.

The trend towards a flat PLE spectrum for high excess silicon concentrations indicates the strong dependence of the transfer mechanism on the presence of silicon nanoclusters. This may also be because the host matrix is more closely approaching bulk silicon, in which case the excitation of the luminescent rare-earth ions is by the generation of carrier pairs in the semiconductor followed by recombination at rare-earth sites. Alternatively, this trend merely reflects the decreased mean separation between the luminescent ions and the silicon nanoclusters for high excess silicon concentrations. It is hoped that the more detailed TEM investigation under way will allow us to discriminate between these two effects.

## CONCLUSIONS

Even with the 350, 490, 520, and 650 nm bands removed from our white-light pump source, erbium emission from the thin film samples is strong enough to yield a clear spectrum. We have estimated that the power efficiency of this indirect excitation process is of the order of 0.1%, and we postulate an efficient excitation exchange mechanism between silicon nanoclusters and erbium ions. It is possible that the mechanism may be carrier-mediated or take the form of a resonant dipole–dipole interaction; the exact nature of the transfer is unclear, and work is under way within this group to investigate it more closely. In particular, the possible role of defects and the chemical environment of the erbium ions are being studied. However, we have used this effect to pump erbium-doped nanostructured samples using a low power, low cost source: a standard SLR camera flashgun. The efficiency of this process suggests that flashlamp-pumped erbium-doped optoelectronic components are feasible. This is particularly attractive for use in local networks and integrated systems in which the cost of the pump source is an important design factor.

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