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LETTER TO THE EDITOR

Optical properties of PECVD erbium-doped silicon-rich silica: evidence for energy transfer between silicon microclusters and erbium ions

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Abstract. We report the fabrication by PECVD of silicon-rich erbium-doped silica films that exhibit both 1535 nm fluorescence and visible photoluminescence. Fluorescence spectra are presented along with absorption spectra that display a strong band edge in the blue, which we ascribe to the presence of Si microclusters. We are unable to observe characteristic Er^{3+} absorption bands and propose that excitation of the rare earth is via an energy transfer process from Si microclusters.

A technologically important area in which there has recently been substantial interest is that of rare-earth-doped optical materials. Such materials offer the opportunity to fabricate a wide range of lasers, optical amplifiers, filters and other optical devices. Of particular interest is the Er^{3+} ion, as this species exhibits strong fluorescence at 1535 nm, a convenient wavelength within the low-loss window for SiO_2 -based fibres. The optical activity of this ion has been investigated in a wide range of host materials [1].

There is also currently a great deal of interest in the optical properties of microcrystalline and porous Si [2–6], principally due to the technological implications for fabrication of visible-light-emitting devices. Although much of the work in this area concentrates on the generation of light by quantum-size structures on Si substrates, there has recently been interest in the optical properties of Si clusters dispersed in an SiO_2 matrix [2, 3, 7]. The SiO_2 host has the advantages when compared to porous Si of greater stability and strength and superior optical properties. Typically, such a material exhibits room-temperature visible photoluminescence and a strong blue shift of the Si absorption edge up to energies as high as 2.5 eV. There is some dispute as to the source of the optical properties of microcrystalline Si, but there is now an appreciable body of evidence that the production of nanometre-size Si structures results in a quantum confinement of electrons; the resultant change in the band gap and consequent shift in absorption edge may then be attributed principally to the physical dimensions of the Si clusters [5, 6]. To date there have been only a limited number of studies of Si-rich SiO_2 , but this does appear to be an area of growing interest. Previous work has employed ion implantation and RF sputtering to incorporate the Si clusters. Plasma-enhanced chemical vapour deposition (PECVD) is an alternative low-temperature technique capable of accurately controlling the stoichiometry and growth conditions of the film. This allows high-quality SiO_2 to be grown easily with a well defined Si content.

In this letter we report the production of microclusters of Si within SiO_2 thin films by PECVD. The films studied also contain around 1 at.% Er, the purpose being to investigate

the effect of introducing a technologically useful optically active species into the strongly blue-absorbing Si/SiO₂ matrix. We observe room-temperature fluorescence due to the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ Er³⁺ transition of the Er³⁺ ion even when the films are pumped at wavelengths away from characteristic Er absorption bands. We also observe room-temperature visible photoluminescence, which we ascribe to the presence of Si microclusters in the SiO₂ matrix.

The films studied were produced by PECVD of Er-doped SiO₂ on Si substrates. The technique has been more fully described previously [8]. For all the samples studied here, the film thickness was approximately 2–3 μm and the Er concentration 1 at.% as measured by secondary-ion mass spectrometry (SIMS). Three samples were studied in this case: one as grown (sample 1), one annealed at 900 °C for 90 min (sample 2) and the third annealed at 1200 °C for 90 min (sample 3). All annealing was carried out in an N₂ atmosphere.

The experimental arrangement for measuring fluorescence spectra was as follows. A Coherent Innova 100 Ar ion laser provided pump radiation at any one of four discrete wavelengths in the blue/green region of the optical spectrum: 457 nm, 476 nm, 488 nm and 514.5 nm. The maximum power available varied from 450 mW at 457 nm to just over 3 W at 514.5 nm, and the beam diameter at the sample was around 4 mm. A prism placed just after the laser source served to filter residual plasma lines. The sample was positioned such that the thin film faced the laser at Brewster's angle to the pump beam. A collection lens focused the fluorescence through the slits of the monochromator (Bentham M300). Detection was by either an InGaAs or an Si photodiode connected to a current pre-amplifier (Bentham 286) and lock-in amplifier (Brookdeal 9503-SC). Both the detection system and monochromator were computer controlled.

For the measurement of absorption spectra, the thin film was removed from the Si substrate and placed onto a glass blank. A white light source (Bentham IL1A) was focused onto the sample, and collection of transmitted light remained as before. Two spectra were taken for each sample: one of a glass blank as a reference, and one of the sample itself. These were combined to produce the absorption spectrum.

Figure 1 illustrates the near-infra-red fluorescence spectrum obtained for sample 2 (annealed at 900 °C) when pumped using 514.5 nm radiation. The spectrum is characteristic of the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ Er³⁺ transition of the Er³⁺ ion. The other two samples exhibited similar spectra.

Figure 2 illustrates a fluorescence spectrum obtained from sample 2 under 476 nm excitation. Comparison of this with figure 1 shows that the spectrum obtained is once again due to the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ Er³⁺ transition.

The films appeared red in colour; a typical absorption spectrum is shown in figure 3. There is clearly an absorption band edge at around 510 nm whilst the characteristic absorption bands of the Er ion are too weak to be detected.

Figure 4 shows a visible photoluminescence spectrum of sample 2 pumped at 457 nm. There is a weak broad band centred around 550 nm. This is not a wavelength at which Er³⁺ fluorescence would be expected in a SiO₂ matrix.

SIMS analysis of the unannealed film shows the composition to be (in at.%) O 56%, oxygenated Si 22%, elemental Si 14%, N 5%, C 2%, Er 1%.

Figure 5 shows a plot of integrated fluorescence intensity of the 1535 nm band of sample 2 as a function of pump wavelength normalized to the intensity at 514.5 nm excitation. At each wavelength the pump laser power was held at 200 mW in order to provide a true comparison. Also shown is the corresponding plot for a reference Er-doped SiO₂ fibre.

The absorption spectra of these Si-rich samples exhibit strong absorption band edges

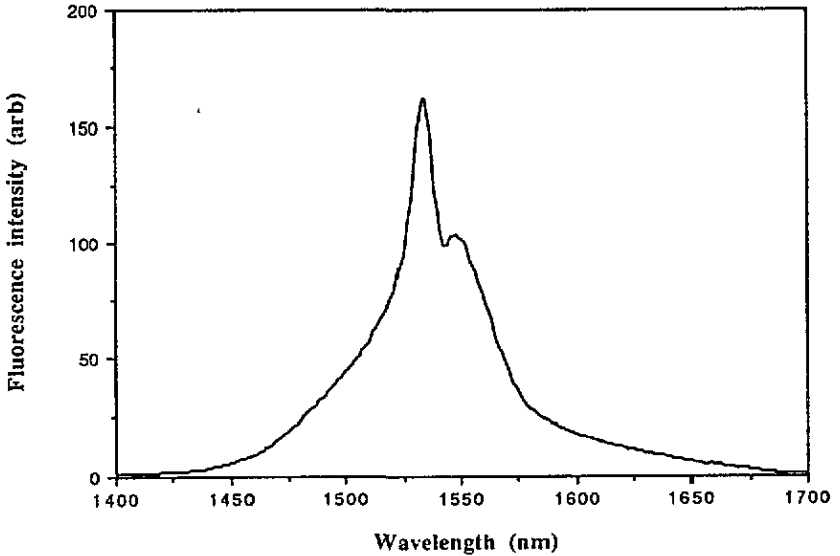


Figure 1. A fluorescence spectrum of Er-implanted Si-rich SiO₂; excitation wavelength = 514.5 nm. The film was annealed under N₂ at 900°C.

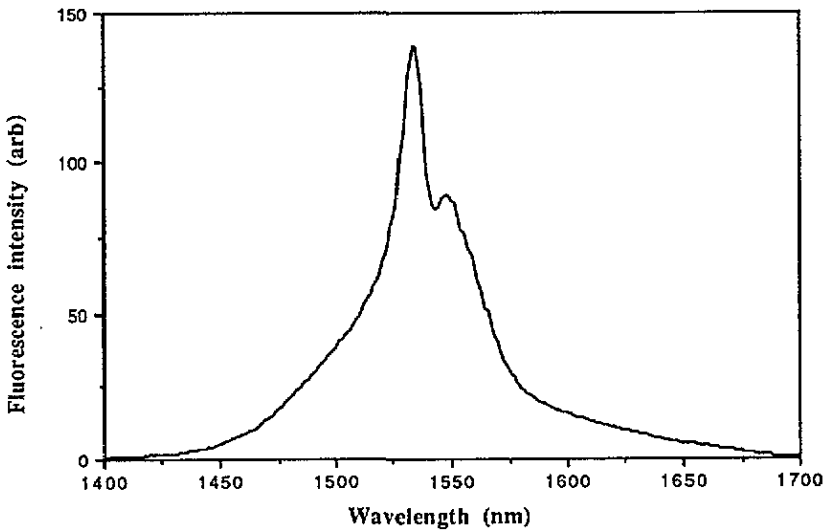


Figure 2. A fluorescence spectrum of Er-implanted Si-rich SiO₂; excitation wavelength = 476 nm. The film was annealed under N₂ at 900°C.

in the visible region of the spectrum, which cannot be ascribed to the presence of Er ions. Moreover, it appears that the characteristic absorption bands of the rare-earth ion at 450 nm, 490 nm, 520 nm, 635 nm and 980 nm are very much weaker than the band edge. In addition, the photoluminescence spectrum of sample 2 exhibits a weak band in the visible, centred around 550 nm. It can reasonably be assumed that this is not due to the presence of Er. Visible luminescence in this region has been noted due to transitions from the $^4S_{3/2}$

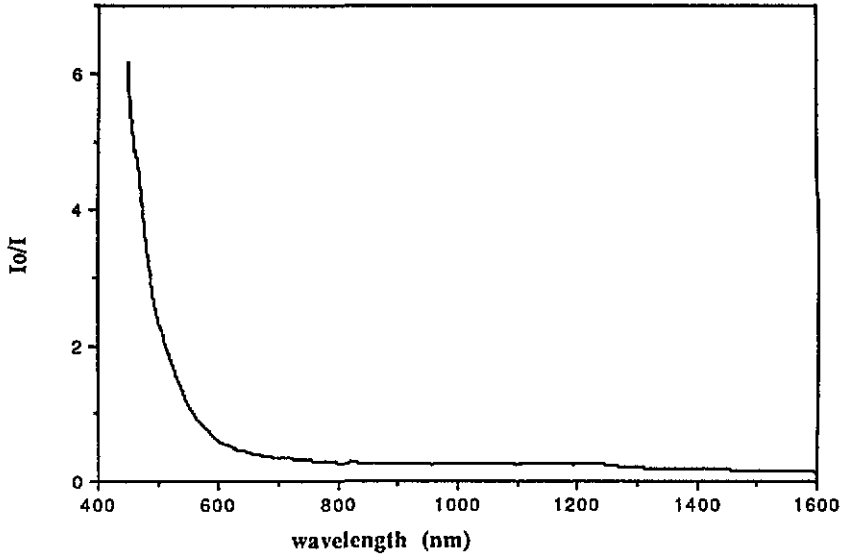


Figure 3. An absorption spectrum of Er-implanted Si-rich SiO_2 . The film was annealed under N_2 at 900°C .

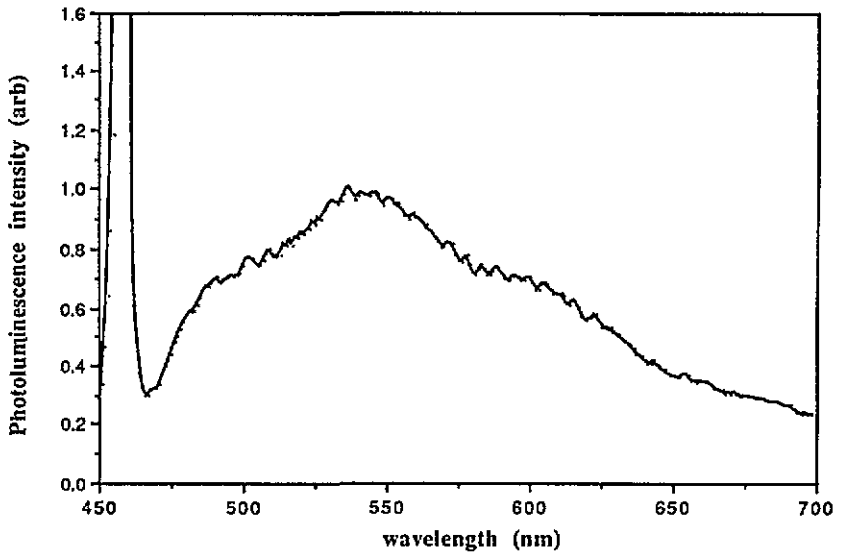


Figure 4. A visible photoluminescence spectrum of Er-implanted Si-rich SiO_2 ; excitation wavelength = 457 nm . The film was annealed under N_2 at 900°C .

level in low-phonon glasses when pumped at 1480 nm via an up-conversion process [10]. However, to our knowledge it has never been observed in SiO_2 glasses. Therefore it seems more probable that some other species within the film is causing both the absorption band edge and the visible photoluminescence. Comparison of our data with recent results on Si-rich SiO_2 strongly suggests that microclusters of Si may be responsible. There is a striking agreement between our visible photoluminescence data and that reported elsewhere [3, 7]

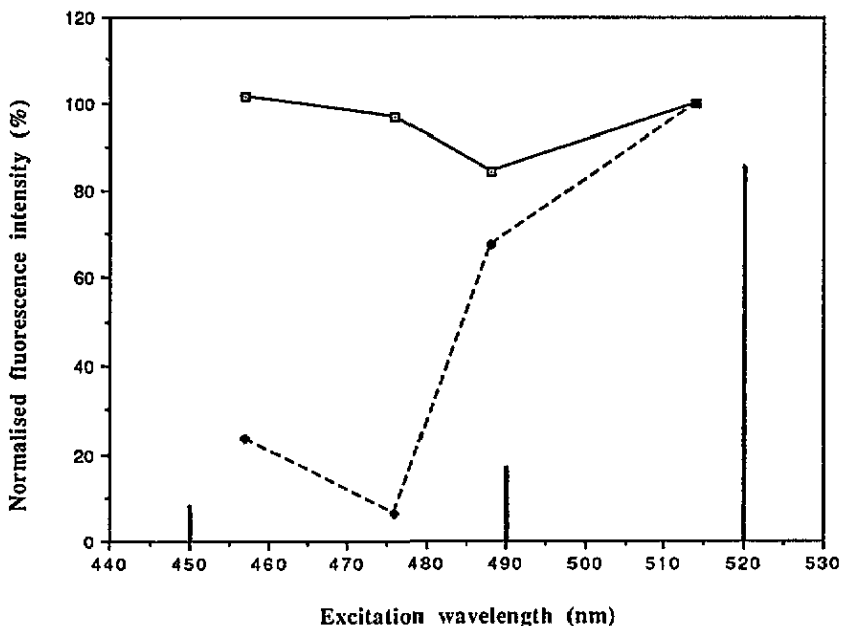


Figure 5. The integrated 1535 nm fluorescence intensity as a function of pump wavelength. The upper (solid) line is data from sample 2; the lower (dashed) line is data from a reference Er-doped SiO₂ fibre. The pump power in all cases was 200 mW. Intensities are normalized to the 514.5 nm excitation value. The positions of Er absorption bands are indicated by the vertical lines. The lengths of these lines correspond to the approximate absorption strengths given in [13].

for Si-rich SiO₂. The SIMS analysis of the films supports this conclusion by indicating the presence of a significant proportion of elemental Si.

PECVD, being a low-temperature process, is a likely candidate for production of Si microclusters when used to grow SiO₂ films in an O-deficient environment. The thermal mobility of the ions on the substrate will be sufficiently low so as to inhibit diffusion of species within the film, and hence Si clusters formed in the deposition process will persist. Preliminary results from another group working on PECVD growth of Si microclusters in SiO₂ support our conclusions [11].

Fluorescence spectra of the samples exhibit a strong band around 1535 nm characteristic of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ Er³⁺ transition. The Er present in the films is thus optically active, although we have not been able to observe any appreciable absorption due to the species. Moreover, it appears that it is possible to obtain fluorescence from Er³⁺ even when the pump wavelength is away from its characteristic absorption bands. Even more striking is the observation that the intensity of fluorescence remains largely unchanged with decreasing pump wavelength. Figure 5 illustrates the normalized integrated fluorescence intensity as a function of excitation wavelength for sample 2 and a reference Er-doped SiO₂ fibre. In the case of the fibre, the fluorescence intensity shows a good correlation with the absorption spectrum of Er in SiO₂ [12]. This is in marked contrast to the Si-rich sample, which exhibits a largely excitation-wavelength-independent fluorescence intensity.

The presence of Si microclusters can be inferred from the luminescence in the visible and from the band-edge effect in the absorption spectrum. The marked difference between the fluorescence in our samples and the reference fluorescence from the fibre cannot be

explained by a change in the Er absorption or emission cross-sections, for which there is no supporting evidence in the literature. However, if bands due to Si microclusters and excited levels of the Er ion overlap, it is possible that energy between 2.49 eV (500 nm) and 2.76 eV (450 nm) and beyond is absorbed by the Si microclusters and transferred non-radiatively to the excited states of the Er. The precise transfer mechanism is difficult to identify and is probably a combination of the mechanisms proposed in [13] as an explanation for Yb electroluminescence in indium phosphide.

In conclusion, we have produced by PECVD Si-rich SiO₂ thin films, which exhibit optical properties strikingly similar to those observed in Si⁺-implanted or sputtered SiO₂ films. Both absorption and photoluminescence spectra strongly suggest the presence of Si microclusters. In addition, doping the films with Er produces samples that exhibit characteristic 1535 nm fluorescence when excited at wavelengths away from Er absorption bands. Indeed, the fluorescence yield appears to be largely independent of the pump wavelength over the range studied. This contrasts with data presented for an Er-doped SiO₂ fibre and suggests some form of excitation transfer from the Si microclusters to the rare-earth ion. We are currently investigating further the properties of Si-rich SiO₂ and the nature of the transfer process.

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