

Evidence of energy coupling between Si nanocrystals and Er³⁺ in ion-implanted silica thin films

C. E. Chryssou,^{a)} A. J. Kenyon, T. S. Iwayama,^{b)} and C. W. Pitt
*Department of Electronic and Electrical Engineering, University College London, Torrington Place,
 London WC1E 7JE, United Kingdom*

D. E. Hole
School of Engineering, University of Sussex, Falmer, Brighton BN1 9QH, United Kingdom

(Received 24 May 1999; accepted for publication 4 August 1999)

Silica thin films containing Si nanocrystals and Er³⁺ were prepared by ion implantation. Excess Si concentrations ranged from 5% to 15%; Er³⁺ concentration for all samples was 0.5%. Samples exhibited photoluminescence at 742 nm (attributed to Si nanocrystals), 654 nm (defects due to Er³⁺ implantation), and at 1.53 μm (intra-4f transitions). Photoluminescence intensity at 1.53 μm increased ten times by incorporating Si nanocrystals. Strong, broad photoluminescence at 1.53 μm was observed for λ_{Pump} away from Er³⁺ absorption peaks, implying energy transfer from Si nanocrystals. Erbium fluorescence lifetime decreased from 4 ms to 1 ms when excess Si increased from 5% to 15%, suggesting that at high Si content Er³⁺ ions are primarily situated inside Si nanocrystals. © 1999 American Institute of Physics. [S0003-6951(99)04040-1]

Recently, room-temperature light emission from porous Si,¹ Si-rich silica thin films,² and Si nanocrystals (nc-Si) in silica matrices³ has been demonstrated. Nanometer-sized Si particles exhibit unique electrical and optical properties not observed in bulk material. Er³⁺-doped Si has also attracted interest for its applications in silicon optoelectronics. Er³⁺ is attractive because its 1.53 μm emission coincides with the low attenuation region of silica optical fibers and Er³⁺-doped Si has received much attention.^{4,5} Energy coupling between Si nanoclusters and Er³⁺ was first demonstrated in Er³⁺-doped Si-rich silica thin films produced by plasma-enhanced chemical vapor deposition⁶ and was recently demonstrated in cosputtered Er³⁺-doped silica thin films;⁷ a similar effect is also seen in chalcogenide glasses.⁸ This is potentially important since it may relax requirements on the Er³⁺ pump source and lead to broadband pumped optical devices.

In this study we demonstrate energy coupling between nc-Si and Er³⁺ ions in ion-implanted silica thin films. Ion implantation is a promising technique for producing Si nanocrystals⁹ and also incorporating Er³⁺ into thin films.¹⁰

Samples were prepared by implanting Si⁺ into thermally oxidized Si (oxide thickness around 300 nm). Six implantation energies were used between 25 and 200 keV: peak excess Si concentrations were between 5 and 15 at. % (ion doses ranged from 1.0×10^{16} to 2.0×10^{17} ions/cm²). Depth profiles of implanted Si ions were calculated using TRIM¹¹ as a first approximation, and are shown in Fig. 1. Samples were subsequently annealed at 1050 °C in a flowing N₂ atmosphere for 8 h to form Si nanocrystals.⁹ Transmission electron microscopy analysis of annealed samples showed uni-

form nc-Si distribution (nanocrystal sizes ranged between 1 and 4 nm).

The annealed samples were implanted with Er³⁺. Implantation energies ranged between 80 and 380 keV and the peak Er³⁺ concentration was 0.5 at. % (ion doses ranged between 7.5×10^{14} and 2.4×10^{15} ions/cm²). The calculated depth profile of Er³⁺ is shown in Fig. 1. It is apparent that most of the incorporated Er³⁺ sees a nanocrystal environment. Er³⁺ implanted samples were not annealed in the present experiment. Prior to Er³⁺ implantation the samples exhibited luminescence only at about 1.7 eV due to nc-Si, as published in Ref. 9. Photoluminescence (PL) intensities and peak energies were strongly affected by the excess Si concentration; the 1.7 eV peak shifted to lower energies with increasing concentrations of excess Si atoms.⁹

Room-temperature PL from samples was studied using an Ar⁺ laser, a single grating monochromator, and standard lock-in techniques. An InGaAs photodiode and a photomultiplier tube were used to detect infrared and visible spectra, respectively. Spectral response of the detection system was calibrated using a tungsten white light source. For fluores-

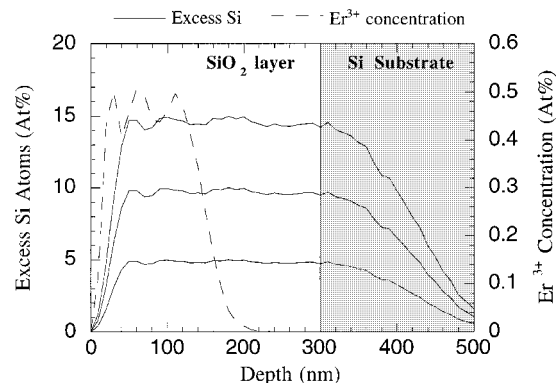


FIG. 1. Predicted plot of concentration profiles, calculated using TRIM, for ion-implanted Si and Er in silica using a range of implantation energies.

^{a)} Author to whom correspondence should be addressed. Electronic mail: cchryssou@ee.ucl.ac.uk

^{b)} Permanent address: Department of Materials Science, Aichi University of Education, Igaya-cho, Kariya-shi, Aichi 448-8542, Japan.

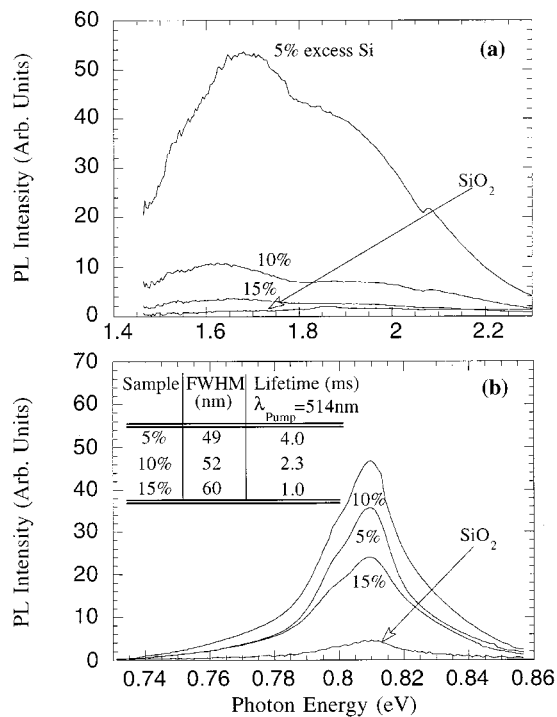


FIG. 2. Room-temperature PL spectra of Er^{3+} -doped silica samples with and without nc-Si using the 476.5 nm line of an Ar^+ laser as the excitation wavelength. The nc-Si samples prior to Er implantation were thermally annealed at 1050 °C for 8 h in a flowing N_2 atmosphere.

cence lifetime measurements, the lock-in amplifier was replaced with a digital oscilloscope which displayed fluorescence decay traces.

Figure 2 shows PL spectra from the Er^{3+} -doped silica thin films both with and without nc-Si, pumping the samples at 476 nm. After Er^{3+} implantation there is evidence of two PL peaks [Fig. 2(a)]; the first at around 1.9–2 eV can be attributed to implantation-induced defects in silica^{2,12,13} (caused by the incorporation of Er^{3+}) and does not shift with Si concentration, while the nc-Si peak at 1.7 eV changes peak energy as the Si concentration varies. Although related to implantation damage, the intensity of the 2 eV peak is clearly very sensitive to the Si content of the matrix. It appears that the inclusion of a small excess of Si facilitates the production of luminescent defects on further implantation.

Figure 2(b) shows near-IR Er^{3+} PL spectra, pumped at 476.5 nm. The emission peak at $\lambda=1.53 \mu\text{m}$ corresponds to the intra- $4f$ ($^4I_{13/2} \rightarrow ^4I_{15/2}$) transition. Figure 2(b) illustrates the effect of incorporating nc-Si in silica. PL from Er^{3+} -doped silica films containing nc-Si (10% excess Si) is ten times larger than that from a stoichiometric silica thin film implanted with the same Er^{3+} concentration. The full width at half maximum (FWHM) of the emission spectra is relatively broad: as high as 60 nm for the 15% Si sample [inset of Fig. 2(b)]. The spectral shape of the Er^{3+} emission does not change appreciably for up to 10% excess Si, suggesting that up to this concentration the Er^{3+} ions are primarily situated at the interface between nc-Si and the silica matrix. However, a significant increase of the FWHM is observed for the sample with 15% Si. We postulate that this is due to an increase in the number of Er^{3+} ions in nanocrystals. This argument is strengthened by the fact that the Er^{3+} fluorescence lifetime for this sample is 1 ms, compared to 4

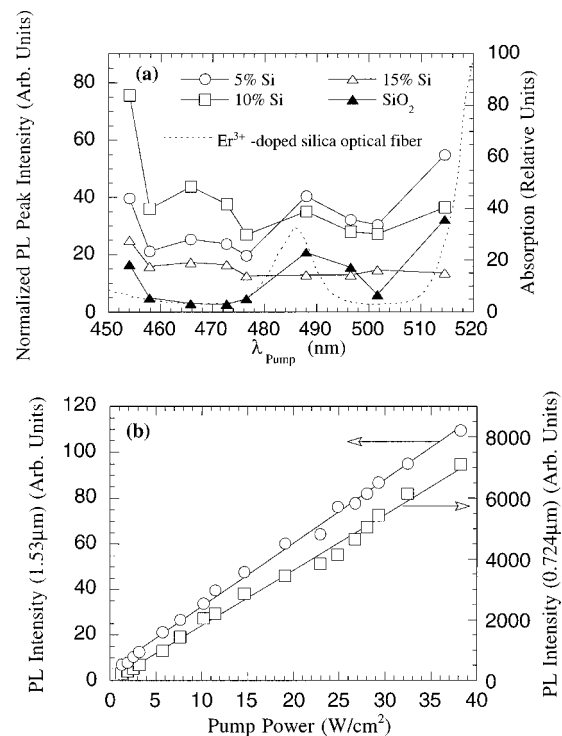


FIG. 3. (a) PLE spectra of Er^{3+} -doped silica samples with and without nc-Si. An absorption spectrum of an Er^{3+} -doped silica optical fiber is also shown for comparison. (b) PL intensities at 1530 and 724 nm as a function of pump power density for the silica sample with 5% excess Si. The sample was pumped using the 488 nm line of an Ar^+ laser.

ms for the sample containing 5% excess Si [inset of Fig. 2(b)]. It should be noted that the Er^{3+} lifetime in both amorphous and crystalline Si is far shorter than in silica.⁷ Moreover a significant decrease of the PL is evident for the 15% Si sample indicating that the Er^{3+} ions see a predominantly Si environment. The luminescence yield from erbium in Si is low, as coordination with oxygen is a necessary prerequisite for photoluminescence.¹⁰ We therefore speculate that for low concentrations of excess Si in silica enhanced Er^{3+} PL results from energy exchange between Si and Er. However, at higher concentrations, the proportion of Er^{3+} lying within Si clusters is sufficiently high that the PL yield is reduced.

Figure 3(a) shows PL excitation (PLE) spectra for the Er^{3+} -implanted silica samples. For comparison, we include an Er^{3+} absorption spectrum from a silica optical fiber. The agreement between the PLE spectrum of stoichiometric silica and the absorption spectrum of the fiber indicates direct excitation of Er^{3+} in stoichiometric silica. However, the samples containing nanocrystals demonstrate indirect pumping of Er^{3+} . This is most obvious for the sample containing 15% excess Si: the PLE spectrum is relatively flat, illustrating a more effective energy exchange than in the case of 5% or 10%. We postulate that in the samples with 5% and 10% excess Si the Er^{3+} is situated mainly within the silica and therefore excitation through direct absorption is significant. However, in the sample with 15% Si, the proportion of Er^{3+} associated with nanocrystals is much higher, indirect excitation predominates, and there is a reduction in PL yield. We propose the existence of three classes of Er^{3+} within the films: (i) optically active ions within silica which exhibit only direct excitation, (ii) optically active ions at the Si

nanocrystal–silica interface which exhibit both direct and indirect excitation, and (iii) nonoptically active ions within Si nanocrystals.

In contrast to other studies,^{7,14} PL intensities at 1.53 and 0.724 μm increased linearly with excitation power [Fig. 3(b)]. We do not see saturation of 1.53 μm PL even for power densities on the order of 40 W/cm^2 (this was apparent for all samples). Although Fujii *et al.*^{7,14} reported saturation at power levels of 0.3 W/cm^2 in similar material, their Er^{3+} concentration was 20 times less than ours, hence our PL is not limited by the availability of Er^{3+} ions in the same way as Fujii's.

In summary, we have studied the PL properties of ion-implanted Er^{3+} -doped silica containing nc-Si. We have demonstrated that the presence of nc-Si in silica thin films enhances the Er^{3+} PL by approximately an order of magnitude compared to stoichiometric silica. From PLE spectra of silica samples with a range of excess Si atoms we find that Er^{3+} can be excited indirectly through energy coupling with Si nanocrystals.

The authors would like to thank Professor P. D. Townsend of the University of Sussex for assistance with implantation. They also acknowledge financial support from

the Engineering and Physical Sciences Research Council (EPSRC).

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