Study of erbium-doped silicon nanocrystals in silica

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Abstract: Er-doped SiO$_2$ and Er-doped Si-NCs embedded in a SiO$_2$ matrix were produced by Er and/or Si ion beam implantation of a Si (100) substrate. The composition and distribution of implanted Er varies in samples either with or without Si implants. HAADF and EELS detail in samples with Si implants, the Si and Er distribution is identical, and within a band of ~110 nm width at ~75 nm below the SiO$_2$ surface. Intense PL emission at 1.54 µm confirms formation of ErSi$_2$, for the majority of aggregates, is unlikely. The present investigation details most Si-NCs are surrounded by Er$_2$O$_3$, or possess this phase within.

1. Introduction

The incorporation of the Er$^{3+}$ ion in silica makes optical amplification through sharp and temperature-stable radiative transitions at ~1.54 µm possible [1]. SiO$_2$, doped with erbium, is currently used in silicon-based optical amplifiers [2-3]. The low absorption cross section of erbium ions in this structure leads to low gain and the necessity of pumping with expensive lasers. To improve the optical gain of intraband transitions originating from the 4f shell, erbium-doped silica, containing silicon nanocrystals (Si-NCs), have been suggested as a promising candidate [4-5]. The internalisation of Si-NCs increases the absorption cross section ≈10$^4$ times. The larger excitation cross section of erbium sensitised Si-NCs compared to pure silica [6], the broad continuous absorption band of the Si-NCs, the enhanced emission cross section of the sensitized erbium ions [7], as well as the possibility of using cheap LEDs as pumping source, represent numerous advantages of this structure compared with erbium-doped SiO$_2$ in absence of Si-NCs.

In previous work, erbium-implanted Si-NCs embedded in to a silica matrix, resulted in an amorphous silicon structure evidenced by energy-filtered transmission electron microscopy (EFTEM), nevertheless, these amorphous silicon clusters were able to sensitize erbium ions [8]. In a recent study, authors employed EFTEM and high-angle-annular-dark-field (HAADF) imaging to characterise samples with erbium concentrations greater than ~10$^{19}$ cm$^{-3}$, observing erbium-rich clusters ≈5-10 nm in size, separated from the Si-NCs [9]. In our more recent study [10], we investigated highly erbium-doped silica and Si-NCs, within a dedicated aberration-corrected scanning transmission electron microscope (STEM). We demonstrated co-implantation of erbium and silicon leads to a band of nanostructures in a silica matrix, whereas implantation of erbium without silicon leads to large amorphous erbium-rich clusters, presumably Er$_2$O$_3$; owing to the tendency of erbium migrate to towards the surface of the
silica layer. We further detailed that silicon ions might act as agglomeration centres for erbium ions. Present electron energy loss spectroscopy (EELS) elemental maps confirm that strong correlation between the position of silicon and erbium exists. We also address the composition of erbium in the structure.

2. Experimental

Two types of samples, (1) exclusively erbium-doped SiO$_2$, or; (2) erbium-containing Si-NCs in SiO$_2$, were grown on a silicon substrate, with a similar SiO$_2$ thickness and composition, in order to investigate erbium-implanted microstructure and composition. In the latter, a beam of 85 keV silicon ions providing a dose of $8 \times 10^{16}$ at/cm$^2$ was targeted at a 700 nm thick SiO$_2$ layer, grown on the top of a Si (1 0 0) substrate. Erbium ion implantation was then performed using a beam of 320 keV and a dose of $3 \times 10^{15}$ at/cm$^2$. Post implantation, the samples were annealed at 1100$^\circ$C in a N$_2$ atmosphere for 1 hour, in order to form Si-NCs. The erbium and silicon concentration peaks in the samples were $3 \times 10^{20}$ cm$^{-3}$ and $8 \times 10^{21}$ cm$^{-3}$, respectively. The growth conditions and implantation parameters for the sample type (1) were similar to those for sample type (2), except there was no silicon implantation.

An aberration corrected STEM, at the SuperSTEM Laboratory Daresbury, fitted with a Nion Mark II quadrupole-octupole corrector[11] operating at 100 keV was employed to acquire HRTEM, Bright Field (BF) and High Angle Annular Dark Field (HAADF) images as well as EEL spectrum images (SIs) [12] with 0.2s/pixel exposure time, 0.7 eV/channel energy dispersion, the convergence angle of 24mrad and the collection semi-angle of <5mrad. The instrument allows Z-contrast lattice images with 1Å resolution to be obtained. An Ultra High Vacuum (UHV) Gatan Enfina system was used to obtain spectrum images.

3. Results and discussion

Figure 1(a) represents typical EEL spectra of a NC (red line) and of the oxide layer (green line), in which the Si L$_{2,3}$-, Er N$_{4,5}$- and O K-edges can be identified. The erbium peak is clear in the red line spectrum in (a), whereas there are no clear features consistent with the presence of erbium in the green line spectrum, which represents an area off the NCs in the oxide layer. The C K-edge was employed to calibrate EEL spectra. Figure 1(b) represents an HREM image of a NC of size $\approx 3.5$ nm (clear lattice fringes are existed). Figure 2(b-c) details elemental maps of the Er-N$_{4,5}$- and Si-L$_{2,3}$- edges, following a power law background fitting. There is a clear and strong correlation between the silicon and erbium distribution in the maps. No substantial erbium clusters within the SiO$_2$ exist apart from the Si-NCs, detailing no sign of formation of separate Er$_2$O$_3$ clusters in between the Si-NCs. Figure 1(d,e) represents the FWHM and energy of a Gaussian peak fitted to the onset peak of O-K edge. Rare earth oxides exhibit a split OK-edge structure and earlier onset, compared to a later onset and single peak characteristics of SiO$_2$[13].

Fitting a single Gaussian envelope leads to a larger FWHM, than for a Gaussian peak fitted to the single OK-edge peak of SiO$_2$. The fact that a larger FWHM and lower peak energy are spatially correlated with the Si-NCs indicates the presence of erbium oxide in/near the Si-NCs. HREM inspection shows the NCs are crystalline (not shown here); hence due to the strong evidence of co-location of Er, Si and O and the well known low solubility of Er in Si and high quality silica [14] the erbium oxide presumably forms a shell surrounding the Si-NCs. In contrast, the narrower Gaussian peak and blue-shifted energy, indicates the presence of SiO$_2$. 

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Figure 1 (a) Typical EEL spectrum on a NC (red) shown on (b), and on the SiO$_2$ layer (green) together with OK edge intensity multiplied by 10 (light green) within a SI with edges used to extract compositional maps of Si L$_{2,3}$, Er N$_{4,5}$ and OK intensities at ~99 eV, ~167-177 eV and ~532-542 eV respectively. (b) HREM image of a NC.

Figure 2 (a) HAADF image of erbium doped Si-NCs of the mapped area, (b) Si L$_{2,3}$ edge map (98-101 eV), (c) Er N$_{4,5}$ edge map (167-177 eV), following a suitable power low background fitting. (d) FWHM and, (e) energy of the Gaussian peak fitted to the O K-edge. Dashed circles and rectangles indicate correlations in quantities of the images. The contrast of the maps is presented on the colour-scale with white/bright signifying high and blue/dark low values of the respective quantity.

4. Conclusion
EELS and HAADF measurements detail erbium and silicon co-implantation leads to identical distributions of erbium and silicon. The dominant presence of SiO$_2$ within the matrix results
in direct oxygen elemental mapping, by employing the O K-edge of the expected \( \text{Er}_2\text{O}_3 \) phase, extremely difficult. Indirect investigations, using modifications of the O K-edge characteristics such as width and position arising from the presence of the rare earth oxides, demonstrate that the majority of erbium is in the form of \( \text{Er}_2\text{O}_3 \). This erbium is distributed identically with Si-NCs in the structure, but as no structural phases other than silicon can be detected in HREM. It must be concluded that the erbium oxide surrounds the Si-NCs.

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5. References

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