Structural and compositional study of Erbium-doped silicon nanocrystals by HAADF, EELS and HRTEM techniques in an aberration corrected STEM

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Abstract: Er-doped SiO2 and Si nano-crystals (NCs) embedded in a SiO2 matrix were produced by ion beam implantation of Si (100) substrates. After annealing Er ions agglomerate in different positions with different compositional properties in samples with and without Si implants. HAADF and EELS show that in the sample with Si implants the Si and Er distribution is identical and within a band of ~110nm width ~75nm below the SiO2 surface whereas in the sample with no excess Si, Er forms on average much larger, amorphous aggregates, presumably an Er-oxide, in the SiO2 matrix with tendency to move towards the surface of the SiO2 layer.

1. Introduction
SiO2, doped with moderate concentrations of Er is currently used in Si-based optical amplifiers [1, 2]. As Er has a low absorption cross section highly doped structures could be a solution but Er clustering is a major problem with high Er concentrations. To overcome this problem, Er-doped silica containing Si-NCs have been introduced as a promising candidate [3-5]. The broad continuous absorption band of the Si-NCs together with the possibility of using cheap LEDs instead of laser excitation, the larger excitation cross section of Er-sensitized Si-NCs compared to pure silica (~ 10^-16 cm^2) [6] besides the improvement in the emission cross section of the sensitized Er ions (emission at 1.54 µm) [7] are advantages of this structure compared with Er-doped SiO2 in absence of Si-NCs. In this structure Er ions absorb excitonic energy of optically excited Si-NCs and emit at 1.54 µm via intra-band transitions of the 4f shell, ^{I_132}f_{132} \rightarrow ^{I_132}f_{132}.

To improve the excitation rate at 1.54 µm an understanding of the position of Er and Si-NCs with respect to each other as well as of the Er content in the structure in order to reach an optimal
concentration with the highest excitable fraction of Er is quite important. In previous work, implantation of Er ions into Si-NCs embedded in SiO$_2$ led to an amorphous Si structure evidenced by EFTEM, nevertheless these amorphous Si clusters were able to sensitize Er ions[8]. In photoluminescence measurements it has been shown that excitable Er ions were located in the surrounding SiO$_2$ with maximally 1-2 ions per nanocrystal [9]. In a recent EFTEM/ HAADF study involving Er concentrations larger than 1x10$^{19}$ cm$^{-3}$, Er-rich clusters, 5-10 nm in size, were observed separate from the Si-NCs [10]. In the mentioned work it was claimed that Er segregation is independent of Si-NCs density.

In this report we have applied a variety of microscopic techniques to investigate the structure of Er-doped Si-NCs in a SiO$_2$ matrix. High-angle annular dark field (HAADF), electron energy loss (EEL) spectrum imaging, energy-filtered TEM (EFTEM), conventional dark field (DF) and bright field (BF) TEM and high-resolution TEM (HRTEM) were carried out to understand the compositional and structural properties in the most direct and accurate way available.

2. Experimental

HRTEM and DF diffraction contrast images and EFTEM maps (produced by passing electrons through the filter, which have lost 29 eV corresponding to the Er O$_{2,3}$ absorption edge) were acquired with a Tecnai FEGTEM microscope operating at 300 kV and the sample aligned with the <110> zone axes of the Si parallel to the electron beam. HRSTEM BF and HAADF images were acquired with an aberration corrected STEM at Daresbury Laboratories (SuperSTEM, the first UK Cs corrected cold field emission STEM, which employs a Nion Mark II quadrupole-octupole corrector[11]) operating at 100 keV. In this instrument Z-contrast lattice images with 1Å resolution can be obtained. The equipment includes a UHV Gatan Enfina system, with which EEL spectrum images (SI’s) can be obtained.

In order to study Er-implant related microstructure and composition two kinds of samples grown on silicon substrates, with similar SiO$_2$ thickness and composition, were compared; these consisted of (1) solely Er-doped SiO$_2$, and (2) of Er-containing Si-NCs in SiO$_2$; in the latter case a beam of 85 keV Si ions to a dose of 8x10$^{16}$ at/cm$^2$ was first targeted at a 700-nm thick SiO$_2$ layer grown on the top of a Si (1 0 0) substrate, and then Er-ion implantation was carried out with a beam of 320 keV and a dose of 3x10$^{15}$ at/cm$^2$. Post implantation the samples were annealed at 1100°C in an N$_2$ ambient for 1 hour in order to form the Si-NCs. The Er concentration peak in the samples was 3x10$^{20}$ cm$^{-3}$, the silicon peak concentration 8x10$^{21}$ cm$^{-3}$.

3. Results and Discussion

Figures 1 a)-c) show DF diffraction contrast images of sample (2) under various reflections. The NCs appear crystalline, of the same density and size as revealed in the HAADF image (acquired in the Daresbury SuperSTEM) in figure 1d). The lower magnification HAADF image in figure 1e) shows the entire 110 nm wide band of Er-doped Si-NCs at ~75 nm depth below the surface of the SiO$_2$. The HAADF image at higher magnification (figure 1d) shows 1-4 nm diameter structures with a density of 3.3x10$^{17}$ cm$^{-3}$. The green rectangle in the image represents the area from which a spectrum image has been taken.

In order to evaluate the composition of the structure, EELS was performed. Figure 2 shows the intensity maps of the Er-N$_{4,5}$ and Si-L$_{2,3}$ absorption edges obtained from an EEL spectrum image [12] besides a simultaneously acquired HAADF image of the green-framed area shown in figure 1. The Er signal was extracted following a suitable power law background fitting very close to the onset of the Er-N$_{4,5}$ Edge at about 165 eV. The contrast of the maps is presented on the greyscale with white/bright signifying high and black/dark low concentration of the mapped materials. As can be seen from the maps there is an obvious correlation between the Si and Er distribution within the structure showing that Er is likely to accumulate within and around the Si-NCs after the annealing stage.
There is no significant Er-clustering within the SiO$_2$ away from the Si-NCs, suggesting there is no formation of separate Er$_2$O$_3$ particles in the presence of Si-NCs. Sample (1) with a similar concentration of Er but without implanted Si was investigated by conventional TEM and EFTEM. TEM revealed that implanted Er ions agglomerate in Er rich clusters with amorphous structure in a band near to and extending up to ~170 nm below the surface of SiO$_2$ as shown in figure 3. This is
different from the band extending only to ~75nm into the SiO$_2$ as observed in the sample (2) with Si-NCs. This proves that Er segregation is not independent of the Si-NC concentration as claimed in recent research [10] and is strongly correlated with the Si concentration. It may suggest that silicon ions or NCs act as agglomeration centres for Er ions.

4. Conclusion
When Er is co-implanted with Si and annealed, HAADF and EELS show that the Si and Er distribution is identical. The conventional DF images as well as HREM lattice images (not shown) strongly suggest that the aggregates are crystalline, thus constituting Er-rich Si-NCs. In the absence of Si, Er forms on average much larger, amorphous aggregates, presumably an Er-oxide, in the SiO$_2$ matrix.

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