Erbium environments in erbium-silicon/silica light emitting nanostructures

R J Kashtiban1, U Bangert1*, I F Crowe2, M P Halsall2
1School of Materials, The University of Manchester, Manchester, M1 7HS, UK
2School of Electrical and Electronic Engineering, The University of Manchester, Manchester M60 1QD, UK

E-mail: ursel.bangert@manchester.ac.uk

Abstract. Co-doping of SiO$_2$ with Si and Er to achieve silica fibre amplifiers has resulted in encouraging levels of light emission, much above those of Er-only doped SiO$_2$. However, different fabrication methods, i.e., co-implantation and sequential implantation of Er and Si, has led to several factors difference in light levels. This paper looks into the reasons for these differences by establishing structure and local stoichiometry of the created entities via analytical transmission electron microscopy. In both cases Si-nanocrystals (NCs) have formed in the SiO$_2$ matrix. In the former case Er-ions are co-located with/inegrated within the NCs, in the latter case NCs and Er are separate. By assessing the NCs’ internal and interfacial structure with the surrounding material, we attempt to identify chemical/structural Er-phases/defects and their effect on the sensitising efficiency in the Er:Si-NCs system; high resolution phase contrast- and high angle dark field imaging as well as nano-scale spatially resolved electron energy core loss- and plasmon-spectroscopy carried out in an aberration corrected dedicated STEM lend valuable support to these studies.

1. Introduction

Si based light sources for Si-integrated technologies (Si-photonics) are a long and much aspired goal, but previous attempts concerned with Er doping of Si (Si:Er laser) and also of SiO$_2$ (optical fibre amplifiers [1,2]), have poor or insufficient outcomes due to the low absorption cross section of erbium ions in this structure. To improve the optical gain of intraband transitions originating from the 4f shell, erbium-doped silica containing silicon nanocrystals (Si-NCs) has been suggested [3,4]. The internalisation of Si-NCs increases the absorption cross section by ~10$^4$ times [5,6] and the light emission by ~3 orders of magnitude; the broad continuous absorption band of the Si-NCs allows furthermore use of cheap LEDs as pumping source, making this structure advantageous over the erbium-doped SiO$_2$ alone. There are various ways of forming the Er-doped Si-NC/Si-oxide structure. In this contribution we compare two fabrication methods, (i) co-implantation and (ii) sequential implantation of Er and Si, the latter method improving the light emission by several factors over the former.

To find the reasons for these differences one needs to address the chemical/structural environment of the Er-ions on the atomic scale in correlation with photoluminescence. In a recent study [7] we investigated highly erbium-doped silica and Si-NCs obtained via method (i) in a dedicated aberration-corrected STEM...
corrected scanning transmission electron microscope (STEM). We demonstrated that co-implantation of erbium and silicon leads to a band of Si-NCs in a silica matrix, where Er is co-located with the NCs, whereas implantation of erbium without silicon leads to large amorphous erbium-rich clusters, presumably Er$_2$O$_3$. We suggested that silicon ions might act as agglomeration centres for erbium ions. Here we go further in investigating the detailed Er-environment to better understand the bonding and chemical compound of the Er that gives rise to the improvement.

2. Experimental

Erbium-containing Si-NCs in method (i) were grown by targeting a beam of 85 keV silicon ions providing a dose of 8x10$^{16}$ at/cm$^2$ together with an Er-ion beam of 320 keV and a dose of 3x10$^{15}$ at/cm$^2$ onto a 700 nm thick SiO$_2$ layer, grown by thermal oxidation of a Si (1 0 0) substrate. Post implantation, the samples were annealed at 1100°C in a N$_2$ atmosphere for 1 hour, in order to form Si-NCs. The erbium and silicon peak concentrations in the samples were 3x10$^{20}$ cm$^{-3}$ and 8x10$^{21}$ cm$^{-3}$, respectively. In method (ii) Er was first implanted into a Si-substrate, which was oxidized and subsequently Si-implanted and annealed. Samples (i) and (ii) were compared with only-Er implanted oxides; respective implantation parameters were the same in all samples.

An aberration corrected STEM, at the SuperSTEM Laboratory Daresbury, fitted with a Nion Mark II quadrupole-octupole corrector [8] operating at 100keV was employed to acquire high resolution phase contrast (HRTEM), bright field (BF) and high angle annular dark field (HAADF) images as well as EEL spectrum images (SIs) [9]. 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 with energy dispersions of 0.05-0.7 eV/channel, depending on the required energy regime, and achieving energy resolutions down to 0.3 eV.

3. Results and Discussion

3.1. Er-compound determination from HAADF and core loss EELS.

In figure 1a) we show HAADF images of the sample acquired by method (i). Si-NCs (of ~3.5 nm average diameter) are positioned in a narrow band (indicated by orange dashed lines) around the implantation depth. The bright contrast of the NCs suggests co-location of Er and Si-NCs. We have previously proven this [7] by combined HAADF and EELS analysis. In figure 2 a), b) and c) we show that bright patches in the HAADF image and Si and Er signals extracted from EEL spectrum images (procedures are explained elsewhere [7,10]) have indeed identical distributions. We have encircled corresponding features across all panels in fig. 2 by same-colour dashed lines. Panels d) and e) in fig. 2 show results of studies of the O-edge fine structure: in contrast to the single peak of the O K-edge in SiO$_2$ (at ~538 eV), the rare earth oxide O K-edge has a double peak structure (peaks at ~533 and 538 eV; [11]), hence fitting a single Gaussian function to the O K-edge of an SI taken around Si-NCs would result in a broadening of the fitting function if Er was present as Er-oxide. Simultaneously the fit-peak maximum would shift towards lower energies. This is exactly what we observe in figs. 2 d) and e), which show the spatial distribution of the FWHM, and the peak position of the Gaussian fit, respectively. The O K-edge in locations of Si-NCs has an increased FWHM, as indicated by the yellow/orange colours and a lower peak energy value, as indicated by the black colours. Spatial coincidence of all the features in figure 2 has led us to conclude that an Er-oxide shell of some sort has formed around the Si-NCs.

Coming back to figure 1, we show HAADF images of the sample made by method (ii) in 1b) and of an Er-only implanted sample in 1c). Er is no longer co-located with Si-NCs in sample (ii); a number of large Er-clusters (~average size 15 nm) has formed throughout the oxide layer from the implantation depth right to the top of the sample, similar to the Er-rich clusters which are presumably Er$_2$O$_3$, in the Er-only implanted oxide in fig. 2c). Between large Er-rich clusters faint small-scale speckle can be seen in 1b), arising from a band of Si-NCs that has formed similarly to that in sample (i), fig. 1a). Figure 1d) shows an HRTEM image from an enlarged area in 1b), where atomic lattice
structure is visible in the NCs. Further enlargement of areas in between the NCs in fig. 1e) shows atomic size bright dots in HAADF, indicating atomically dispersed Er, either as single atoms or few-atom clusters, most likely representing Er-oxide molecules.

So importantly in sample (ii) we have two types of appearance of Er, aggregated in large separate clusters, and atomically dispersed around Si-NCs. We think that this is the clue to the high emission efficiency in this sample: in the finely dispersed form Er-ions are close enough to NCs to take part in the energy transfer and sensitisation process. Because Er is highly dispersed there is also less chance of back-transfer or self-excitation, as in the big clusters in the Er-only sample in fig. 1c).

However, an Er-oxide shell surrounding Si-NCs as in sample (i) should also warrant good energy transfer; furthermore ALL Er is consumed in this structure and no 2nd ‘waste’ Er-phase has formed, contrary to sample (ii). The question arises, why then the efficiency is lower in sample (i). This can be further clarified by finding out, where exactly the Er sits, and whether, due to the high fraction, some Er is incorporated within the NCs in sample (i), e.g., as an Er-silicide phase. This could not be decided
from atomic resolution HAADF or BF images, partly due to the fact that the features of interest are extremely small and furthermore embedded in an amorphous matrix.

3.2. Er-phase determination from low-loss EELS.

EEL spectra in the low loss regime can be treated and interpreted within the dielectric theory. If the loss function can be reliably extracted from EEL spectra, then the dielectric function can be extracted and, by using Kramers-Kronig (KK) relationships, $\varepsilon_1$ and $\varepsilon_2$ can be calculated. Much work has gone into separating the zero-loss energy peak from the loss spectrum [12]; furthermore deconvolution routines [13,14] have successfully been applied to improve the energy resolution in the spectra, so that access to losses down to 2 eV can be obtained.

The dielectric function of ErSi$_2$ is distinct, so if we could extract it from low loss spectra this would provide, maybe the only evidence possible as to whether such a phase exists. Employing the above procedures we have attempted KK analysis, but the outcome so far was inconclusive. Nonetheless, low-loss spectra of the plasmon region should give direct indication as to the materials’ phase. However, the contribution of the matrix surrounding the features, of which we want to determine the structural and chemical phase, is dominant in low loss spectra, and needs to be reduced. With the sample thickness lying in the single scattering regime it should be possible to subtract the SiO$_2$ matrix contribution, which can be estimated from knowledge of the size of the features of interest in relation to the sample thickness. Figure 3 shows difference spectra of the plasmon energy region obtained by subtracting an adequate proportion of a matrix spectrum. The arrowed colour circles in figure 1 indicate the regions from which low loss spectra were obtained.

Going from top to bottom through the spectra in figure 3, the purple, uppermost spectrum is from a region between NCs in sample (i) (purple-circled location in figure 1a), after subtraction of an Er-oxide spectrum (obtained from a large Er-cluster in the Er-only implanted sample). The subtraction should have eliminated the Er-oxide contribution, and indeed the purple spectrum shows the pure SiO$_2$ character by the interband transition at ~14 eV and the plasmon at ~23.5 eV. The second spectrum down (red) is from the Si-NC-containing oxide in sample (ii) (red-circled location in fig. 1b), after subtracting a portion of a pure Si-oxide spectrum. The remaining spectrum exhibits mostly Si-oxide characteristics; a small contribution of the Si-plasmon at ~17 eV is present resulting from the large scattering cross sections in the low loss region and proximity of Si-NCs. Significantly there is also an absorption feature from Er5d6s-> O3s and possibly Er4f->5d transitions at ~9 eV. The Er-oxide plasmon at ~15.7 eV, on the other hand, is absent. This confirms that there is atomically dispersed Er in the Si-oxide, as suggested by the HAADF investigations (figure 1b). The 3rd curve down (black) is
of a large Er\textsubscript{2}O\textsubscript{3} cluster (black-circled region in figure 1c), after subtraction of a Si-oxide spectrum, presenting a typical Er-oxide low loss spectrum with the \(-9\) eV interband transitions and the Er\textsubscript{2}O\textsubscript{3} plasmon [15].

The 4\textsuperscript{th} spectrum down (blue) is of a Si-NC in sample (i) (blue-circled region in figure 1a), after subtraction of an appropriately scaled Si-oxide spectrum, so should reflect the behaviour of an Er-oxide-surrounded Si-NC, and thus give the best evidence concerning a possible Er-silicide phase. The atomic Er-transitions at \(-9\) eV and the Si-plasmon at \(-17\) eV are present without evidence of a blue-shift typical for a silicide phase [16]. Importantly, there is also no Er-oxide plasmon, the presence of which would be expected, if the oxide surrounding the Si-NC consisted of a solid shell. So either the surrounding oxide shell shares a highly defective ‘interface’ with the Si-NC core, or constitutes an unconnected rather ‘dendritic’ Er-oxide network, or both. In any case the lower light efficiency of sample (i) combined with the lack of a plasmon point towards the existence of high numbers of defects at the Si-NC surface/interface with the Er-oxide, which cause significant non-radiative recombination.

The 5\textsuperscript{th} spectrum (turquoise) is of pure Si, showing the Si-plasmon at \(-17\) eV, the 6\textsuperscript{th} spectrum (orange) is of the oxide between Si-NCs in sample (i) (orange circle in fig. 1a), after subtraction of a pure SiO\textsubscript{2} spectrum, and the bottom spectrum (green) is the difference between two pure oxide spectra taken in regions near the green circle. Spectrum 6, not surprisingly, has reminiscent features of Er-oxide (at \(-9\) eV) and of Si (at 17 eV), and the bottom spectrum, again not surprisingly, shows just background noise.

4. Conclusions

Er-environments in SiO\textsubscript{2} matrices (for Er-doped silica fibre amplifiers), sensitised for achievement of enhanced light emission by incorporation of Si-NCs, were investigated by HAADF, HREM, core loss and valence band EELS. Samples, co-implanted with Er and Si before annealing to form Si-NC, gave several times less light emission than samples, which were sequentially implanted with Er (followed by thermal oxidation of Si) and then with Si (followed by annealing to form Si-NC). This was understood in terms of the core shell structures formed in the first case, where Si-NCs act as nucleation centres for Er, which precipitates in form of an Er-oxide shell around them, in contrast to

![Figure 3. Low EELS difference spectra, taken in locations indicated by the respective numbered arrows and circles (colour online) in figure 1. All curves are a result of a subtraction of a scaled matrix spectrum (either Er-oxide or SiO\textsubscript{2}) from the original, raw data. This matrix contribution was estimated from the portion that the matrix would occupy along the e-beam path in relation to the nanofeature of interest, and was derived from sample thickness and NC dimension. Curves in descending numbers (top to bottom): spectrum of the oxide around Er:SiNCs in sample (i) minus Er\textsubscript{2}O\textsubscript{3} spectrum from an Er-cluster in the Er-only implanted oxide (i.e., without NCs, purple online); spectrum of NC-containing Si-oxide in sample (ii) minus pure SiO\textsubscript{2} spectrum (red online); spectrum of Er\textsubscript{2}O\textsubscript{3} cluster in the Er-only implanted sample minus SiO\textsubscript{2} spectrum (black online); spectrum of an Er:SiNC in sample (i) minus SiO\textsubscript{2} spectrum (blue online); Si spectrum (turquoise online); spectrum of Si-oxide between NCs in sample (i) minus pure SiO\textsubscript{2} spectrum (orange online); difference of two pure SiO\textsubscript{2} spectra (green online).](image-url)
atomically dispersed Er in the SiO$_2$ matrix surrounding the Si-NCs in the second case. More specifically plasmon EELS results point to a highly defective Er-oxide shell and/or interface with the Si-NC giving rise to non-radiative recombination in the first structure, whereas in the second structure Er-ions are in close proximity but not directly connected to the Si-NCs. There is no indication of Er-silicide phases, which had been considered a possibility with the co-implantation.

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