Journal of Luminescence 132 (2012) 3103–3112

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Rate equation modelling of erbium luminescence dynamics in erbium-doped silicon-rich-silicon-oxide

Miraj Shah [a,*], Maciej Wojdak [a], Anthony J. Kenyon [a], Matthew P. Halsall [b], Hang Li [b], Iain F. Crowe [b]

[a] Department of Electronic & Electrical Engineering, UCL, Torrington Place, London WC1E 7JE, United Kingdom
[b] Photon Science Institute and School of Electrical & Electronic Engineering, University of Manchester, Sackville St Building, Manchester M13 9PL, United Kingdom

ARTICLE INFO

Available online 1 March 2012

Keywords:
Erbium cluster
Si-nanocrystal
Rate equations
Lifetimes
Ion–ion interactions
Energy migration

ABSTRACT

Erbium doped silicon-rich silica offers broad band and very efficient excitation of erbium photoluminescence (PL) due to a sensitization effect attributed to silicon nanocrystals (Si-nc), which grow during thermal treatment. PL decay lifetime measurements of sensitised Er^{3+} ions are usually reported to be stretched or multi exponential, very different to those that are directly excited, which usually show a single exponential decay component.

In this paper, we report on SiO_2 thin films doped with Si-nc's and erbium. Time resolved PL measurements reveal two distinct 1.54 μm Er decay components; a fast microsecond component, and a relatively long lifetime component (10 ms). We also study the structural properties of these samples through TEM measurements, and reveal the formation of Er clusters. We propose that these Er clusters are responsible for the fast μs decay component, and we develop rate equation models that reproduce the experimental transient observations, and can explain some of the reported transient behaviour in previously published literature.

1. Introduction

Over the past decade, erbium doped Si-nanocrystals (Si-nc) have attracted a great deal of attention, due to the enhanced emission from erbium sensitised through Si-nc's [1]. The 1.54 μm emission line of erbium is ideal for telecommunication purposes as it lies within the minimum propagation loss for silica fibres. Also, the broad absorption band of Si-ncs allows broadband excitation of erbium, enabling the realisation of an efficient broadband top pumped EDWA. Yet, to date, achieving gain from this material has proven to be a notoriously difficult task. This is, in part, due to the low excitable Er fraction sensitised through Si-ncs. Processes such as excited state absorption, Auger back-transfer, or defect-induced non-radiative paths have all been offered as possible explanations for this low fraction.

Given that there are claims of an enhanced excitation rate, [2,3] and of a distance dependence on excitation of Er ions through Si-ncs, [4] another set of processes that deserve attention are ion–ion interactions. Up-conversion between two Er ions is a well-known effect in existing Er doped amplifiers, and its effect is likely to increase with higher excitation rates. Forms of up-conversion include (i) Pair-induced quenching [5], resulting in the loss of 1 out of every 2 excited Er ions, and (ii) Energy migration, which extends the overall sensitization distance of Er ions [6].

Er decay lifetime measurements are indicative of such processes. Up-conversion effects usually result in a stretched, or multi, exponential decay component. In fact, for the Er doped Si-nc material, there have been many reports of a fast μs fast-decay component, in addition to the usual slow ms scaled decay. The origin of the fast decay component is still under debate through different interpretations: energy back-transfer to carriers confined in Si-nc [7], deep trap centres [8], recombination at defect centres in SiO2 or SiO2/Si-nc interfaces [9].

Recent reports on this material have also shown evidence that the Er ions are not uniformly distributed in the matrix; instead, they agglomerate and form clusters [10]. Even though erbium aggregation has been reported to cause quenching, in some cases, enhanced emission has been reported from these clusters [11].

In this work, the luminescence decay dynamics of Er doped Si-nc samples containing Er clusters are measured experimentally and modelled through rate equations. Strong ion–ion interactions that can be expected to occur in Er clusters result in a microsecond decay component, similar to that observed for our samples and amongst various other groups. We propose that the fast and slow components are a result of ion–ion interactions between Er ions in Er clusters. The cluster size dependence, the clustered fraction of the material, and the fraction of the cluster that is sensitised by the Si-nc will be studied through rate equation

* Corresponding author. Tel.: +44 20 7679 2162/32162.
E-mail address: m.shah@ee.ucl.ac.uk (M. Shah).

0022-2313/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2012.02.002

analysis, and the results discussed. We find that the random nature of the fast component (in terms of amplitude and rate) can be explained through the interactions in Er rich clusters.

2. Experimental

SiO_x:Er thin films were grown by PECVD on ⟨1 0 0⟩ silicon wafers, using N_2O, 5% SiH_4 diluted in N_2, and $Er(thd)_3$ precursor evaporated in a bubbler and carried by Ar gas as precursors. Three samples were grown by PECVD with different flow rates of silane, in order to obtain different levels of Si excess. The flow rates of diluted silane (5% of SiH_4 in N_2) were 30, 50, and 80 sccm for samples S1, S2, and S3, respectively. The other deposition conditions were kept the same: flow rate of N_2O (10 sccm), flow rate of $Er(thd)_3$:Ar (50 sccm), substrate temperature (300 °C) and deposition time (3 h). Subsequently, the samples were annealed at 1100 °C for 1.5 h in flowing Ar gas.

PL measurements were performed using a Bentham M300 single grating monochromator and a NIR-sensitive Hamamatsu photomultiplier (R5509-72). Time-resolved PL transients were recorded with a digital oscilloscope, and the laser was modulated with a Pockels cell. For indirect excitation of erbium luminescence a DPSS laser emitting at a wavelength of 473 nm was used. Direct excitation of erbium was obtained with a Spectra Diode Laboratories MOPA laser emitting at a wavelength of 980 nm.

Conventional bright field (BF) TEM imaging was carried out on Tecnai FEG-30 operating at 300 keV. The chemical composition of the three samples has also been obtained. An aberration corrected STEM, at the Super STEM Labratory Daresbury, fitted with a Nion Mark II quadrupole–octupole corrector operating at 100 keV was employed to acquire high resolution phase contrast (HRTEM), bright field (BF) and high angle annular dark field (HAADF). The instrument allows Z-contrast lattice images with 1 Å resolution to be obtained.

3. Experimental results

All three samples show strong erbium PL under direct excitation (980 nm). With indirect excitation (473 nm) very weak PL is observed, which increases with Si excess. The PL spectra obtained with both excitation methods are shown in Fig. 1. Note that, for indirect excitation, wider monochromator slits were used during the measurements because of the very weak PL intensity.

Decay transient data is shown in Fig. 2. Direct excitation of erbium leads to nearly single exponential decay characteristics with a long time constant of about 14 ms. This relatively long lifetime indicates a high quality matrix. For indirect excitation, the best fits are double exponential functions of the form $A\exp(-t/\tau_1)+B\exp(-t/\tau_2)$, with long components having time constants close to those observed with direct excitation (10 ms). This is among the longest lifetimes reported for similar materials. A fast component of the order of μs is also observable. A summary of the transient fits for both direct and in-direct excitation is shown in Table 1. No apparent correlation can be made for the random nature of the microsecond component. It is most prominent in S3 and S1, but hardly observable in S2.

Fig. 3 shows TEM images for samples S1, S2, and S3. We see evidence of Si-ncs in S2 and S3 ranging from a size of 2–5 nm, but none in S1, probably due to low Si excess contents, or the detection limit of the apparatus. Along with Si-ncs, erbium-rich agglomerates, or clusters, are also shown. The chemical compositions of these Er clusters have been studied through electron energy loss spectroscopy (EELS). At the high energy loss region, the EELS spectra reveal that a pre-peak before the main SiO_2 O–K edge peak appears in the Er cluster region, and indicates that these Er clusters are oxidised in SRSO film and likely to be Er_2O_3.

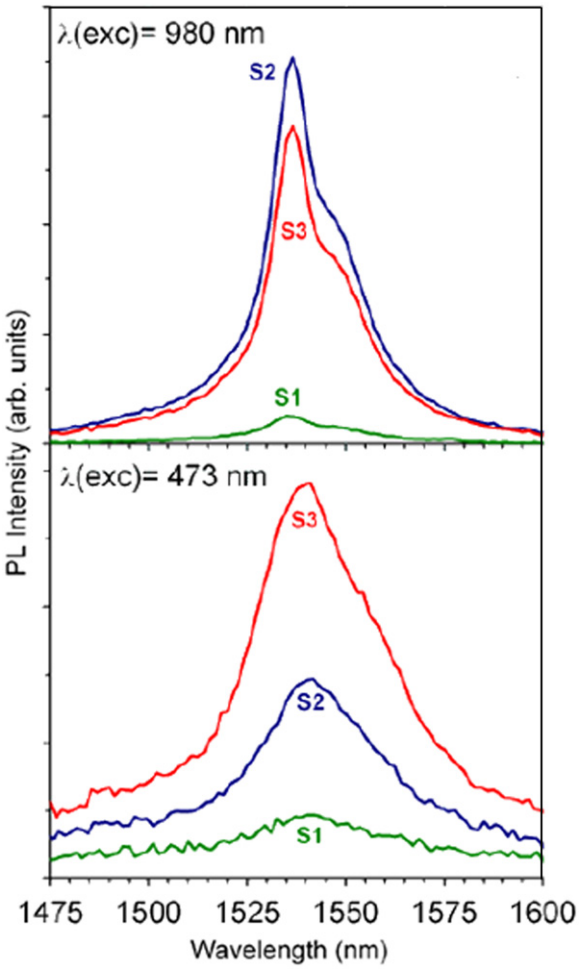

Fig. 1. Erbium PL spectra for both direct (top) and in-direct (bottom) excitation.

The size distribution of these clusters has also been obtained through HAADF measurements. Fig. 4 shows the size distribution for the erbium clusters for samples S1, S2, and S3. We see rather large clusters, particularly in S2 ($\approx$17 nm). In fact, if we look closer at the size distribution and the amplitude and rate of the fast component in Table 1, we see that a direct correlation can be made. For large clusters, the amplitude of the fast component is small and its rate is very fast. So, perhaps these clusters are responsible for the observed decay dynamics.

4. Theory/Modelling

We attempt to explain the observed transient results through rate equation modelling. Rate equations for erbium clusters in glass have been extensively studied [12] and show both fast and slow components. The fast component is a result of strong ion–ion interactions that can be expected to occur for erbium ions in Er-rich clusters. In this work, the fast component only becomes significant and observable for high pumping rates. Due to the 3–4 orders of magnitude increase in the effective excitation cross section through Si-ncs, we know that the pumping rate of erbium ions is also increased by a similar factor. This, together with the evidence of erbium clusters, suggests that the microsecond decay components are due to ion–ion interactions between erbium ions closely spaced in erbium rich clusters.