Optical gain in Er-doped SiO₂–TiO₂ waveguides fabricated by the sol–gel technique

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Abstract

The sol–gel technique is a highly flexible technique for fabrication of oxide glasses, and various researchers have previously reported fluorescence studies of Er-doped sol–gel films and monoliths. Here we report the fabrication of Er-doped strip-loaded sol–gel silicate waveguides, using a silica–titania–alumina host composition, and Er concentrations up to \( \approx 1.1 \times 10^{20} \text{ Er}^{3+}/\text{cm}^3 \), for possible application in integrated optic waveguide amplifiers. We have obtained high fluorescence lifetimes (> 8 ms), propagation loss values of 0.6–0.75 dB/cm at 1330 nm, and favourable fluorescence spectral shape. Relative gain levels up to 1 dB/cm were obtained. These results indicate that about half the Er ions effectively contribute to gain, suggesting segregation of the remaining ions in crystallites or clusters of some kind. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The silica-on-silicon (SOS) format for integrated optics is increasingly favoured for a variety of functions in optical communication systems. Fabrication technologies based on flame hydrolysis deposition (FHD) [1] and plasma-enhanced chemical vapour deposition (PECVD) [2] are now highly developed and in early stages of commercialisation. Most reported components use passive materials, but rare-earth-doped waveguides for lasers and optical amplifiers have also been demonstrated. Erbium-doped waveguide amplifiers, in particular, offer potential advantages over fibre amplifiers in cost and level of integration.

For erbium-doped integrated optical amplifiers, much higher doping levels than in the fibre equivalents are required due to the greatly reduced path
length. These levels must be achieved without loss of homogeneity, in order to keep scattering losses low and to limit Er ion–ion interactions, such as cooperative upconversion, which reduce gain [3]. Essentially two approaches have been taken, as a result of the low solubility of Er ions in silica: the use of moderate doping levels and relatively long path lengths (tens of centimeters), and the use of high doping levels in alternative host glass compositions.

Taking the former approach, and using FHD, Hattori et al. [4] demonstrated 12 dB net gain using 100 mW pump power, in a 47-cm-long silica-based waveguide monolithically integrated with a pump/signal combining coupler. The Er doping level was 0.45 wt.% (approximately $4 \times 10^{20}$ Er$^{3+}$/cm$^3$), and the core/cladding index difference was 1.2%. Since FHD and PECVD are limited in possible compositions, the alternative host glass approach typically requires a different fabrication route. For example, Nykolak et al. [5] used RF magnetron sputtering to deposit soda–lime waveguides doped with $4 \times 10^{20}$ Er$^{3+}$/cm$^3$, and achieved 15 dB gain with 280 mW pump power in a 4.5-cm amplifier. Yan et al. [6] also used sputtering to deposit a phosphate glass waveguide doped with $5.3 \times 10^{20}$ Er$^{3+}$/cm$^3$ and achieved 4.1 dB gain with 66 mW pump power in a 1-cm-long guide. In these latter cases there is significant mode mismatch between the waveguides and fibre, which must be considered when comparing to the results of [4]. Significant disadvantages of the nonsilicate exist: sputter rates are slow, and environmental sensitivity and low melting temperature hamper the processing of the active layer, and the deposition of the cladding layer, respectively.

An alternative route to SOS components is the sol–gel technique [7], in which oxide particles are formed in solution from metal–organic precursors followed by spin or dip-coating and firing to produce a glass film. Composition of these layers can be easily and widely varied, and in principle, molecular homogeneity as well as high density can be achieved at well below melt temperatures. This suggests advantages over FHD and PECVD in terms of host glass composition for amplifiers.

Moutonnet et al. [8] prepared silica gels doped with Er and Yb, and observed up-conversion fluorescence in Er-doped samples. Holmes et al. [9] demonstrated Er-doped buried channel silica waveguides prepared by sol–gel spin coating, with 1.2 mol% Er$_2$O$_3$ and background insertion losses below 5 dB. Orignac et al. [10] doped a sol–gel silica–titania planar (slab) waveguide with 1 at.% Er, and measured a fluorescence lifetime for the $^4I_{13/2}$ metastable energy level of 1.78 ms. Benatsu and Bouazaoui [12] and Benatsu et al. [13] have reported fluorescence studies of Er-doped sol–gel films (slab waveguides) deposited by dip-coating. In TiO$_2$ films they measure fluorescence lifetimes of 4.9 ms at 0.1% Er$^{3+}$ ($= 3 \times 10^{19}$ Er$^{3+}$/cm$^3$), dropping to 2.3 ms at 1% Er$^{3+}$ [11]. In SiO$_2$–GeO$_2$ films they obtain 6.5 ms lifetime for 0.25% Er ($= 5 \times 10^{19}$ Er$^{3+}$/cm$^3$) [12]. Propagation losses at 633 nm wavelength were 4 and 2 dB/cm in the two materials, respectively. More recently the same group reported low losses (0.2 dB/cm) in Er-doped alumino-silicate films [13]. Martucci et al. [14] prepared Er-doped planar waveguides in sol–gel germania–silica–alumina, obtaining losses of 2 dB/cm at 633 nm, lifetimes of 5.5 ms at low Er concentration, and quenching concentration of about 1 at.%.

2. Experimental

The large shrinkage stresses inherent in the deposition of inorganic sol–gel films limit the thickness attainable without mechanical failure to typically < 1 μm, unless high annealing temperatures are employed. We have used a technique of iterative spin-coating and annealing developed by Holmes et al [15]. This technique has later been elaborated by Symms et al. [16] to produce low-loss passive waveguides, using reactive-ion etching (RIE), reflow and burial of the higher refractive index core material. In this work we have adopted a different approach, in which a strip load is etched into a lower index cladding layer. This has two advantages. Firstly, it avoids the development of etching and reflow processes for the Er-doped active layer, and hence speeds the development cycle and allows a wider range of active materials to be investigated. Secondly, since there is no reflow of the active layer, compositions can be used that would crystallise, or phase separate, if raised to reflow temperature. This allows us to investigate whether the molecular-scale...
homogeneity obtained in the sol can be retained in the fully consolidated glass layers. The waveguide format is illustrated in Fig. 1.

We have used silica–titania as the host glass, in order to obtain a large index difference between the guiding and buffer/cladding layers. High index differences lead to strong confinement of the mode fields, which can lower the required pump-power levels, although in the current geometry the strong confinement is in the vertical direction only. The cost of pump sources, which is roughly proportional to output power, is a major component of amplifier cost. Titania doping gives large index differences at relatively low doping levels, but TiO₂ has a strong tendency to segregate and crystallise, which has limited its use in optical fibre. In sol–gel, it has the additional disadvantage of a much higher hydrolysis rate of the precursors than for those of silica. We have used the common technique of prehydrolysis of the silicon alkoxide to compensate for this, so that heterometallic Si–O–Ti species are formed. However, we believe that excess water which is absorbed during spin coating, because of the high surface-to-volume ratio and the strong convection currents inherent to the spinning process, can cause the hydrolysis of these heterometallic species, after which the titania segregates. Previously we have overcome this problem by reduction of relative humidity during spin coating, and have shown that low-loss passive waveguides (0.3 dB/cm at 1330 nm) can be fabricated with this material in the strip-loaded geometry [17]. Thus the same low-humidity coating approach was used in this work.

Fig. 1. Cross-sectional structure of strip-loaded waveguide configuration.

Heat-treatment temperatures must be sufficient to eliminate any porosity accessible to atmospheric water if a stable material is to be obtained; however, this does not guarantee elimination of OH groups, and in Ref. [17] we showed that the use of aluminium oxide as a codopant was effective in reducing OH concentration. This is important to avoid the associated absorption band at 1.4 µm wavelength, as well as the quenching of Er ion fluorescence and the consequent reduction of quantum efficiency.

All the results below used a host glass prepared from a sol with nominal composition SiO₂:TiO₂:AlO₃ of 93:7:10. Phosphosilicate glass in the composition 90SiO₂:10Po₂₅, prepared as described in Ref. [18], was used for the buffer and cladding layers, which were deposited as 30 and 5 coatings, giving approximately 6 µm and 1.0 µm thickness, respectively. Deposition time per coating (dispense, spin, anneal, cool) is less than 3 min. The active layers consisted of 10 coatings, and were spun in an atmosphere-controlled chamber with relative humidity < 30%. Sol preparation for the active layer was as described in Ref. [17], with Er added to the sol as an ethanol solution of Er(NO₃)₃·9H₂O or ErCl₃·6H₂O. Ytterbium codoping was also used, Yb being added to the sol as a nitrate or chloride to match the Er precursor. This can provide a useful indirect pumping mechanism for highly doped, short Er-doped amplifiers [19].

Loading strips 6 µm wide were fabricated using conventional photolithography and reactive-ion etching, leaving a 0.4-µm-thick residual cladding height adjacent to the 1-µm-thick strips.

3. Results and discussion

In the results that follow, rare-earth concentration is defined using the molar ratios of the metal ions in the starting solutions, according to:

\[
\text{Si:Ti:Al:Yb:Er} = 93:7:10:0.125:x
\]

with \(x\) given in percent, i.e., as percent of Si + Ti molarity. Loss of volatile species during annealing may alter these ratios in the final films, and we do not have precise measurements of the final concentrations. If the ratios are maintained, then a nominal Er concentration of 0.5% (the highest used here), as
defined above, corresponds to \( \approx 1.1 \times 10^{20} \text{Er}^{3+}/\text{cm}^3 \), or 1.25 wt.% Er.

Background propagation losses were determined from insertion losses measured at 1330 nm wavelength, using standard single-mode communication fibre at the guide input, and a microscope objective at the output. For each guide, coupling loss at the fibre-guide interface was computed numerically using digital images of the mode fields, since approximate equations based on mode radii are not accurate for the strip-loaded guides, which are strongly asymmetric in the vertical direction. The resulting propagation losses are illustrated in Fig. 2. They are considerably higher than those obtained previously for the equivalent passive waveguides, but variations in the data do not allow the dependence of loss on Er concentration to be clearly determined. However, additional losses at 1535 nm (Fig. 3), derived from the depth of the spectral absorption peak, do show clear correlation to the Er concentration, and are in good quantitative agreement with, for example, Ref. [6], where \( 5.3 \times 10^{20} \text{Er}^{3+}/\text{cm}^3 \) gave an excess absorption peak of 8 dB/cm.

A typical absorption spectrum is given in Fig. 4, showing the strong pump absorption band around 980 nm, and the main \( ^5\text{I}_{15/2} \rightarrow ^3\text{I}_{13/2} \) band around 1550 nm; the loss peak at about 1400 nm characteristic of OH content is not seen. There is, however, a general increase in background absorption towards shorter wavelengths. The spectral shape of this background does not correspond to true Rayleigh scattering, but may nevertheless be the result of small scatterers, either in the bulk material or on the etched surface of the confining strip.

Fluorescence lifetimes are shown in Fig. 5. These are higher than previously reported for sol–gel host glasses (e.g., Refs. [10–12,14]), and show no significant variation with Er content. The high values suggest that strong quenching by OH impurities is not occurring. Faster decay components in the temporal response were not seen, but the possibility of quenching mechanisms faster than the measurement temporal response cannot be discounted, as discussed below.

The fluorescence spectra were measured, and examples are given in Figs. 6 and 7. The shape is typical of alumino-silicate host glasses, with good...
spectral width and flatness for amplification (≈ 1.7 dB variation between 1520 and 1560 nm). Pump powers noted are those in the launch fibre; due to coupling losses, pump power in the guides will be about 3 dB less. No change in spectral shape is observed with varying pump power, whereas there appears to be some reduction of the longer wavelength shoulder with increased erbium concentration. This shoulder is a typical feature of alumina codoping, and its reduction may be associated with an increased contribution to the fluorescence by ions less effectively shielded by an alumina solvation shell.

Small-signal gain measurements at 1532 nm were conducted using bidirectional pumping at 980 nm with pump power (in the launch fibres) of 60 mW (forward) and 100 mW (backward). The relative gain obtained is shown in Fig. 3. The high levels of pump power were used to ensure maximum inversion across the entire signal mode cross-section, but most of the gain is typically obtained with pump levels of about 40 mW, corresponding to ≈ 20 mW after fibre-to-guide coupling loss. The correlation with Er content is clear, but the levels are similar to, or less than, the additional 1535 nm absorption.

A very simple model suggests that if complete inversion is achieved, the relative gain can reach a maximum of twice the Er absorption at the signal wavelength for the unpumped guide here we neglect differences between emission and absorption cross-sections, $\sigma_e$ and $\sigma_s$, respectively. Measurements with shorter waveguides indicate that the measured gain is not significantly limited by insufficient pump power. We can postulate that the Er ions are effectively segregated into a population contributing to gain, and a population which cannot be inverted with reasonable pump levels. This could be because these latter ions are in close enough proximity to suffer from strong parasitic ion–ion interactions such as cooperative upconversion [20], and we refer to these ions as ‘clustered’, although the nature of their local environment is not known. Green upconversion fluorescence is clearly visible in these guides when pumped.

Internal gain is defined as the increase in signal power relative to the background loss, i.e., the relative gain minus the magnitude of the (unpumped) Er absorption peak. If the fraction of clustered ions is $k$, and these ions cannot contribute to gain, then the internal small-signal gain $G$ when the unclustered
ions are fully inverted (high pump power) can be approximated as [21]:

$$ G \ (\text{dB/cm}) = \frac{\sigma_r (1 - 2k) N_i}{10 \ln(10)} $$

(2)

where $N_i$ is the total Er ion concentration. Since the gain we have measured is similar to the Er absorption level, i.e., internal gain $G$ is close to zero, a value for $k$ of 0.5 is indicated. This fraction does not appear to vary strongly with Er concentration. This agrees with the observation that fluorescence lifetime also does not vary with concentration, indicating that the unclustered ions are below quenching concentration, and that during the gelation and sintering mechanisms, a consistent fraction of the Er ions are segregated in a different environment. One possibility for this environment is in nanocrystallites, which may occur more readily than in the passive host glass. Almeida and Vasconcelos [22] have reported the formation of Er$_2$Ti$_2$O$_7$ in Er-doped silica–titania glasses. Almeida and Vasconcelos [22] have reported the formation of Er$_2$Ti$_2$O$_7$ in Er-doped silica–titania glasses with high titanium content.

Nilsson et al. [23] have modelled the effects of pair- and cluster-induced quenching. They suggest that for a cluster of $n$ ions, rapid cross-relaxation allows one excited ion per cluster. Accordingly, the variable $k$ above should be interpreted not as the total fraction of ions in clusters, but as

$$ k = (n - 1) N_c / N_i, $$

(3)

where $N_c$ is the concentration of clusters. Thus the interpretation of $k = 0.5$ could correspond to half the ions in large clusters ($n \gg 1$), or all the ions in pairs ($n = 2$), or something in between.

4. Conclusions

A number of researchers have reported fluorescence studies of Er-doped sol–gel films and glasses. We have fabricated Er-doped strip-loaded sol–gel silicate waveguides, with concentrations up to $\approx 1.1 \times 10^{20}$ Er $^{3+}$/cm$^3$, and have demonstrated high fluorescence lifetimes ($> 8$ ms), reasonable propagation loss values, and relative gain up to 1 dB/cm. The results indicate that about 50% of ions effectively contribute to gain, suggesting segregation of the remaining ions in crystallites or clusters of some kind. Such segregation is also likely to increase propagation loss through scattering, and therefore is also suggested by the higher loss values obtained in relation to the passive waveguides. Further studies to investigate and overcome this problem are underway. If the segregation can be substantially reduced, Er-doped sol–gel glass films will be very promising for application in integrated optic amplifiers.

Acknowledgements

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