

## Luminescent properties of Er and Si co-implanted silicates

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### Abstract

An extensive research for optical active materials at 1540 nm is currently being carried out, on the steam of the strong need for optoelectronic devices which can be integrated with the mainstream Si technology. The formation of silica films doped with Er and Si clusters has been shown as one of the promising approaches. We explored the emission properties of different silicate glasses co-implanted with silicon and Er ions to various doses. As starting materials we used soda-lime and aluminium silicates, glasses which show a larger optical bandwidth than silica at 1540 nm. A Si multi-implantation scheme has been adopted for a planar profile. The best conditions to precipitate Si and activate the Er atoms have been investigated. Optimal annealing temperatures have been found around 500 °C, depending on the particular composition of the original glass substrate. The structural analysis of the resulting structures ensures that the best emission properties are the ones for which a phase separation between the implanted Si and the matrix occurs, even without the formation of crystalline aggregates. A comprehensive study of the emission properties is given as a function of the matrix characteristics, Si and Er content, excitation wavelength and power density. It is shown an increase of the emission enhancement of the Er atoms due to the presence of Si cluster when increasing the excitation power. Modelling of the interaction between the absorbing Si nanoprecipitates and the emitting Er atoms has been carried out, in order to estimate the relevant physical parameters which describe the PL process.

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### 1. Introduction

Recent spectacular advances towards the realization of a silicon-based photonic technology have come from the investigations of composite erbium/silicon systems in SiO<sub>2</sub> oxides. The enhancement of the erbium emission at 1.54 μm by co-doping silica with Si nanoparticles have been largely explored [1–7], leading to the demonstration of optical gain in waveguide structures where erbium-doped silicon-rich SiO<sub>2</sub> constitutes the active media [8–10]. The main advantages of such an active

medium are: (i) more than three orders of magnitude increase of Er effective excitation cross-section; (ii) the possibility to excite the Si nanoparticles in the visible spectrum with a non-coherent source, which transfer rapidly their energy to a nearby Er; (iii) the possibility to perform the optical excitation from topside or side-ways instead of coaxially, simplifying and making cheaper the design of the optical pumping scheme. Furthermore, it has been recently demonstrated the possibility to excite electrically such a system [11], opening the way to an electrically driven optical amplifier or laser. The use of other complex silicate glasses as a host is possible and desirable. The advantages rely on the increased Er solubility and the wider infrared optical bandwidth in these glasses which translates into the possibility to multiplex more channels in the third window of optical

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fiber communication. Although some reports exist in literature about varying the composition of the active material by choosing other compound silicate glasses [12,13], none of them explore the Er emission properties once a Si excess is added to the original glass.

In this contribution we explore the possibility to extend the mechanism of energy transfer from Si nanoparticles to Er in other glass matrices, in principle more suitable for optical amplification in the infrared window around  $1.54\ \mu\text{m}$ . The two kinds of silicates that we have investigated offer the advantages of a much larger erbium solubility and a wider emission bandwidth with respect to silica. We also prove that energy transfer occurs with high efficiency in those glasses in a similar way than in silica and so these results provide an open route to improve even further the gain figures and waveguide characteristics of photonic devices based on the erbium/nanosilicon system.

## 2. Experimental

Three kinds of glasses have been used as starting material: pure fused silica wafers, soda-lime silicate and Al-silicate wafers (all of them provided by Corning). We have chosen to get two Si excess values (low-high) of 5% or 15% inside the silicate matrices in a flat profile. For this, multiple  $\text{Si}^+$  ion implantations have been performed. The ion energies and relative doses were chosen to give rise to a “box-like” Si super-saturation down to a depth of  $0.4\ \mu\text{m}$ . Afterwards the samples were annealed for 15 min at  $350^\circ\text{C}$  (soda-lime and Al-silicate) or  $950^\circ\text{C}$  (silica) in a rapid-thermal process furnace with controlled  $\text{N}_2$  flow. This step was intended to provide a first stage of Si precipitation. The annealing temperature of the compound glasses was chosen to scale with the glass transition temperature in the same way that  $950^\circ\text{C}$  scales with the silica one.

Subsequent Er implantation was performed at 200 keV, which enabled to adjust the Er profile right at the center of the Si supersaturation. With ion doses ranging from  $1 \times 10^{14}\ \text{cm}^{-2}$  to  $2.7 \times 10^{15}\ \text{cm}^{-2}$ , the resulting Er peak concentration varies from  $2 \times 10^{19}\ \text{cm}^{-3}$  to  $6 \times 10^{20}\ \text{cm}^{-3}$ .

Post-implantation annealing was performed in order to remove the implantation damage and to activate the Er atoms. While the annealing time was kept at 15 min, the temperature was varied around the value used for the first thermal process, from  $850^\circ\text{C}$  to  $1000^\circ\text{C}$  for fused silica samples and from  $350^\circ\text{C}$  to  $600^\circ\text{C}$  for the two other glasses. Such an isochronal experiment was intended to find the best tuning of annealing conditions for maximizing the photoluminescence at  $1.54\ \mu\text{m}$ .

Systematic photoluminescence (PL) measurements were performed in all samples by using the He–Cd laser

line at 325 nm with power around 10 mW on the sample. Alternatively, we used an Ar laser with excitation at 365, 488 or 476 nm with a wider range of power in order to perform a detailed study of the response of the material as a function of the photon flux for resonant and non-resonant lines. The luminescent emission was analysed in backscattering mode by a 0.6 m monochromator and detected with a Ge detector. Great care has been taken to calibrate the system and to measure the incident power on the sample and the laser spot size.

## 3. Results and discussion

The emission enhancement of Er atoms due to the energy transfer from excitons generated in the Si nanoparticles has been successfully found in all the processed glasses including the multicomponent ones. As an illustrative example, we show in Fig. 1 the emission spectra of the three different matrices for the same and for two different Er content with the amounts of Si excess. The use of the pump radiation at 325 nm (non-resonant line) ensures that Er atoms are excited only through the silicon clusters, as suggested by the negligible response of the samples implanted only with Er ions (no Si excess). An additional evidence of the role of the silicon clusters in the absorbing and transfer process originates from the monotonic increase of the PL at  $1.54\ \mu\text{m}$  when the excitation energy is shifted towards the ultraviolet, while

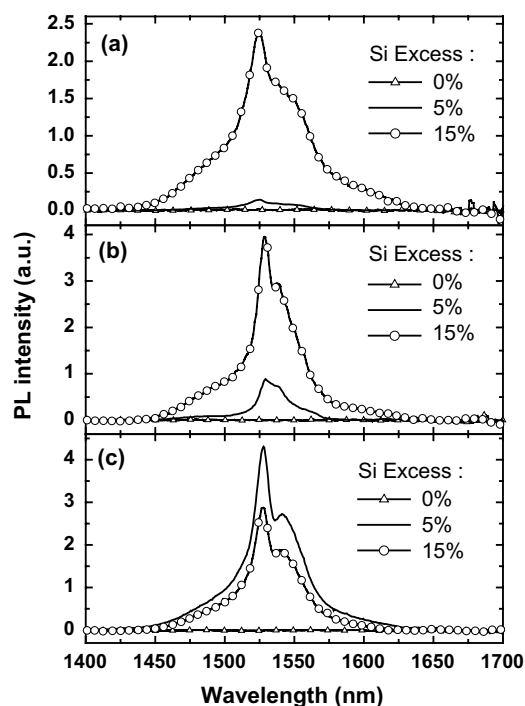


Fig. 1. PL spectra from co-implanted glass wafers excited with non-resonant line at 325 nm: (a) Al-silicate; (b) soda-lime; (c) fused silica.

keeping fixed the incident photon flux (not shown); this evolution reflects the increase of the absorption cross-section of the Si nanoparticles when increasing the energy of the radiation [14].

An additional interesting feature which is apparent in Fig. 1 is the clear dependence of the PL intensity on the silicon content in the Er-rich layer. Such dependence clearly looks like a function of the host glass: while for the fused silica a small Si amount is more effective in enhancing the Er emission, the opposite is true for the other two compound glasses. This trend can be drawn irrespective of the Er concentration in the sample in the whole range explored in this work, from  $2 \times 10^{19} \text{ cm}^{-3}$  up to  $6 \times 10^{20} \text{ cm}^{-3}$ .

In order to explore further the interaction between Er and nanostructured silicon, isochronal annealings experiments have been performed on the co-implanted wafers. The results have been reported in Fig. 2 as a function of the Er content. A significant dependence on the processing temperature has been found for both the Al-silicate and soda-lime glasses only for high Er content. The quite low melting temperature of such matrices (around  $700^\circ\text{C}$ ) does not enable a further increase of the thermal budget. A rather low post-implantation temperature, around  $350^\circ\text{C}$ , appears as the optimal value to maximize the PL enhancement in the

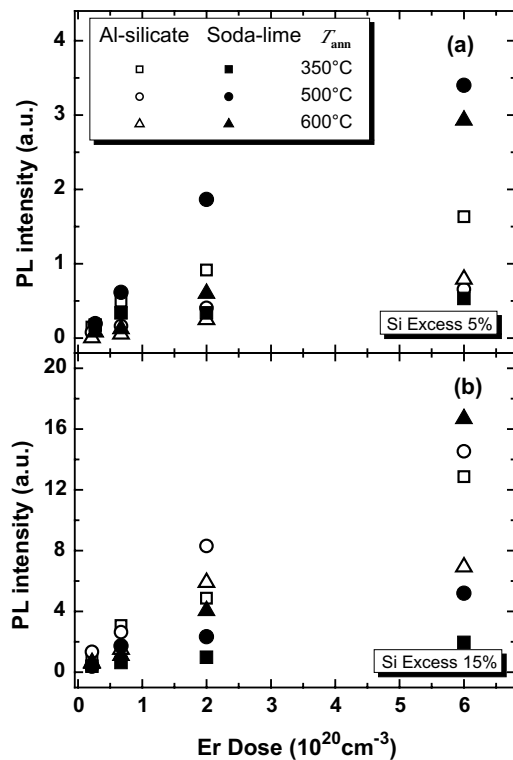


Fig. 2. Evolution of the PL signal at  $1.54\mu\text{m}$  with post-implantation annealing temperature for soda-lime and Al-silicates co-implanted with 5% (a) and 15% (b) Si excess.

case of Al-silicates, while it shifts to much higher temperature, quite close to the glass-transition temperature,  $500$  (5% Si excess)– $600^\circ\text{C}$  (15% Si excess) for soda-lime glasses. On the contrary, for the pure silica wafers annealed in the  $850$ – $1000^\circ\text{C}$  temperature range, a more marked dependence has been found (not shown). In this case the highest PL intensity is reached after annealing at  $850^\circ\text{C}$  and no variation of the optimum temperature have been observed when changing the Si excess from 5% to 15%.

To complete this study and find a suitable set of processing parameters to optimize the Er PL in these glasses, the dynamics of the energy transfer process have been investigated. For this purpose, the dependence of the Er emission as a function of the incident power has been studied for two different excitation lines, 365 and  $488\text{nm}$ . A typical result of this analysis is shown in Fig. 3, where the PL signal at  $1.54\mu\text{m}$  from co-implanted soda-lime wafers with different Er content have been collected as a function of the excitation photon flux  $\phi$ . Some interesting features can be observed, which are common to the whole set of investigated samples, irrespective of the glass substrate, silicon excess, and excitation line used:

- No PL saturation has been observed when pumping the system to very large photon fluxes, even in case of the lowest Er concentration. After an initial onset, a linear trend is observed in the whole investigated power range. Saturation mechanisms such as energy up-conversion [9,12], which could occur at large  $\phi$  and/or Er concentration can be discarded in the analysis of the curves.
- The PL intensity dependence on the pump power density is identical for all the Er concentrations, except for a normalizing factor. This observation implies that the mechanism of coupling between silicon clusters and Er atoms is the same, irrespective

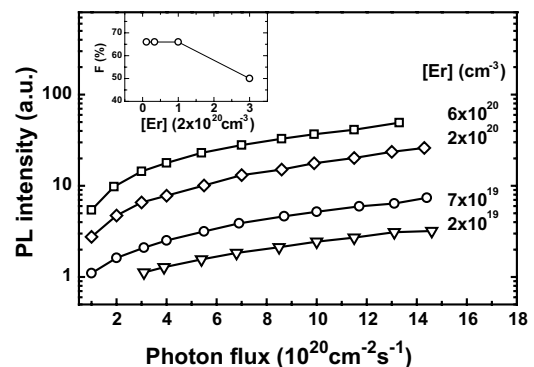


Fig. 3. PL emission at  $1.54\mu\text{m}$  as a function of the incident photon flux at  $365\text{nm}$  for Al-silicate glasses with 15% Si excess and different Er concentrations. The inset shows the estimated fraction of the active erbium concentration as a function of the total [Er].

of the Er content, while the only variation from sample to sample lie in the number of actively-coupled Er atoms.

- (c) At any fixed pump power, a direct proportionality between PL and Er concentration holds, at least up to  $[\text{Er}] = 2 \times 10^{20} \text{ cm}^{-3}$ . This is somehow expected because concentration quenching effects start to dominate right above this threshold [12]. By normalizing the data to the lowest Er dose, where quenching should be negligible, we can extrapolate the PL behaviour to higher doses. Thus, we can estimate the fraction of excitable Er atoms through Si clusters which stays close to 70% up to the threshold concentration, whereas it drops for larger values, reaching 50% at  $[\text{Er}] = 62 \times 10^{20} \text{ cm}^{-3}$  (see inset of Fig. 3).

The absence of saturation of the PL curves shown in Fig. 3 reflects the weak absorbance of the Si nanoparticles coupled to Er, even if the efficiency of the hybrid system is comparable for all the three matrices (see Fig. 1), and of course much larger than by pumping directly Er. Microstructural analysis provides additional information that complete the description of the results discussed above. By Raman experiments we found that the crystallization of the Si excess in the compound glasses does not take place if the annealing temperature is kept below  $650^\circ\text{C}$ . The onset for crystallization in pure silica samples is around  $1000^\circ\text{C}$ . Moreover, by means of Raman and X-ray photoelectron spectroscopy (XPS) measurements of the implanted layers, a quite high fraction of the Si excess is found in the form of amorphous Si aggregates, even in the as-implanted samples. Moreover, energy-filtered transmission electron microscopy (EFTEM) analysis has revealed the presence of Si clusters in pure silica and Al-silicates with an average size of 2.5 nm, whereas none of these has been observed in the similarly treated soda-lime wafers. Although this striking result deserves a more detailed analysis, which is under way, it appears that even amorphous Si clusters found to be efficient sensitizers as nanocrystals [15] are not necessary for an optimum sensitisation. This is due to the non observation of Si clusters in soda-lime wafers by EFTEM within the resolution limit (1 nm).

Temporal evolution of the PL de-excitation processes enables further insight on the coupling mechanism, providing useful parameters for the description of the system. In Fig. 4 typical PL relaxation transients with a decay time-constant in the range of 2–2.5 ms are shown for the highest Er dose, irrespective of the substrate composition, while larger values are obtained at lower Er concentrations (see inset in Fig. 4). The observed  $[\text{Er}]$ -dependence is quite similar to the one studied in Er-implanted stoichiometric glasses with the same com-

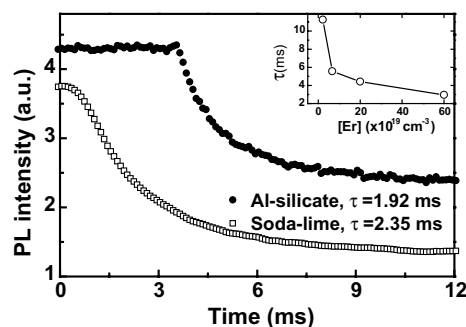


Fig. 4. PL decay transients for implanted glasses with 15% Si excess and  $[\text{Er}] = 6 \times 10^{20} \text{ cm}^{-3}$ ; excitation line was 488 nm at 1.7 mW. The inset shows the time-decay constant as a function of  $[\text{Er}]$  for the same kind of processed glass.

position, and it has been attributed to the well known concentration quenching effect [12].

#### 4. Conclusions

We investigated the optical properties of silicates codoped with Si and Er ions. The sensitizing action of Si clusters on the emission at  $1.54 \mu\text{m}$  has been demonstrated for glass matrices such as soda-lime and Al-silicates. The enhancement of the emission has been found similar to that from silica based wafers, being originated from the same kind of energy transfer process. The observed differences in optical behaviour of these glasses with respect to silica can be attributed to the more complex chemical environment around the active Er, and to the different Si clusterization occurring with the low thermal budget allowed by the glass matrices. While Si amorphous precipitates appear responsible of the energy transfer in soda-lime and pure silica, it seems that even undetectable Si precipitates, can act as efficient sensitizers.

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