Influence of phosphorous precursors on spectroscopic properties of Er$^{3+}$-activated SiO$_2$-HfO$_2$-P$_2$O$_5$ planar waveguides

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Abstract. (70-x)SiO$_2$-30HfO$_2$-xP$_2$O$_5$ (x= 5, 10 mol %) glass planar waveguides activated by 0.5 mol% Er$^{3+}$ ions were prepared by sol-gel route. Several phosphorous precursors have been investigated for the synthesis of a dielectric stable sol useful for the realization of planar waveguides. The waveguides were investigated by different diagnostic techniques. The optical properties such as refractive index, thickness, number of propagating modes and attenuation coefficient were measured at 632.8 and 543.5 nm by prism coupling technique. Transmission measurements were carried out in order to assess the transparency of the deposited films. Photoluminescence measurements and lifetime decay curves of the Er$^{3+}$ transition ($^4$I$_{13/2}$ $\rightarrow$ $^4$I$_{15/2}$) were performed in order to investigate the role of P$_2$O$_5$.

1. Introduction

Silica glass (SiO$_2$ glass) is one of the most important materials in photonics [1]. Considering that it has many attractive properties, such as high UV transparency, high mechanical strength, high glass transition temperature, extremely low thermal expansion, and low reflective index, it has various potential uses in many optical devices, such as in waveguides and lasers. However the needs for compact and efficient photonic devices obtained by rare-earth-activated-glasses still drive the research of novel glass composition and optimized fabrication protocols [2, 3]. Considering the case of silica glass-based Erbium Doped Waveguide Amplifiers (EDWAs) their short length (around few centimetres) generally imposes a high Er$^{3+}$ doping level which may produce clustering effects [4]. These phenomena, due to the ion-ion interactions, lead to undesirable luminescence quenching, thus reducing the performance of the amplifier. At the same time the difficulty of low solubility of rare-
earth in silica is due to the mismatch in size and valence between the rare-earth ions and the constituents of the silica network. A possible way to increase the amounts of rare-earth ions in the matrix avoiding or reducing clustering effects is the addition of co-doping agents, such as $P_2O_5$ or $Al_2O_3$ [5, 6]; their role resides in non-bridging oxygen’s formation that benefits better rare-earth ions incorporation. Moreover from a technological point of view physical and chemical deposition techniques such Flame Hydrolysis Deposition (FHD) and Plasma Enhanced Chemical Vapor Deposition (PECVD) have important drawbacks associated to the incorporation of rare earth ions in silicate glasses due to the high process temperatures in the first case [7], and the low vapour pressure of most erbium compounds in the second [8]. Therefore there is a need to investigate complementary approaches for depositing Er-doped silicate glass, which can incorporate the full range of codopants needed to tailor the Er environment. One possibility is the sol-gel route, which allows very flexible chemistry and low process temperatures. In this paper we have investigated planar waveguides with compositions (70-x) SiO$_2$-30HfO$_2$ -xP$_2$O$_5$ (x= 5, 10 mol %), activated by 0.5 mol% Er$^{3+}$ ions. We used different phosphorus precursors focusing the attention of their influence on the optical and spectroscopic properties.

2. Experimental setup
Multilayer wave guiding films activated with rare-earths were produced by sol-gel approach employing the motor driven dip-coating set-up. For film-forming solution (70-x)SiO$_2$-30HfO$_2$ -xP$_2$O$_5$ (x= 5, 10 mol %), activated by 0.5 mol% Er$^{3+}$ ions was prepared by mixing tetraethylorthosilicate (TEOS), ethanol, deionised water and hydrochloric acid as a catalyst, then pre-hydrolysed for 1 hour at 65 °C. A second solution was obtained by dissolving HfOCl$_2$•8H$_2$O as hafnia precursor in ethanol and then added to the TEOS solutions. Phosphorous and erbium Er(NO$_3$)$_3$⋅5H$_2$O precursors were mixed with final solution. Synthesis occurred under continuous stirring for 16 h at room temperature. The films were deposited on clean silica substrates with roughness of about 2 nm. Films were formed by dip-coating, with a dipping rate of 40 mm/min. After each dip, layer was subjected to annealing in air for 50 s at 900 °C. After a 10-dip cycle, the film was heated for 2 min at 900 °C after each tenth layer. In order to obtain a fully densified structure a further annealing at 900 °C for 5 min was performed [2]. The thickness and the refractive index at 632.8 and 543.5 nm were measured in TE polarization by an m-line apparatus based on the prism coupling technique [9, 10]. The losses at 632.8 nm were evaluated by photometric detection of the light intensity scattered out of the waveguide plane exciting the transverse electric TE$_0$ mode. Photoluminescence spectroscopy was performed using the 514.5 nm line of an Ar+ ion laser as excitation source. The luminescence was dispersed by a 320 mm single-grating monochromator with a resolution of 2 nm. The light was detected using a Photo Multiplier Tube (PMT) and standard lock-in technique [11]. Decay curves were obtained recording the signal by a digital oscilloscope.

3. Results and discussion
The choice of a suitable phosphorous precursor (PP) is a key point towards the realization of low losses waveguides operating at 1.5 µm with high Er$^{3+}$ ions content. Several PPs (reported in table 1) have been investigated for the synthesis of a dielectric stable sol useful for the realization of planar waveguides. The composition and the optical parameters of the Er$^{3+}$-activated silica-hafnia-phosphorous oxide planar waveguides (called Wx) are reported in table 1.
Table 1. Phosphorous precursors and optical properties of SiO₂–HfO₂–P₂O₅ planar waveguides activated with 0.5% mol of Er³⁺ ions.

| Label | Phosphorous precursors | P₂O₅ mol % | Layers number | Thickness ±0.3 µm | Refractive index ±0.0005 | TE Modes number |
|-------|------------------------|-------------|---------------|-------------------|--------------------------|----------------|
| W1    | C₆H₁₅O₃P              | 5           | 5             | -                 | 1.5762                   | 1              |
| W2    | (CH₂CH₃O)₃PO          | 10          | 18            | 0.8               | 1.5868                   | 2              |
| W3    | (CH₃CH₂O)₃PO          | 5           | 18            | 0.9               | 1.5716                   | 2              |
| W4    | H₃PO₄                 | 5           | 30            | 1.4               | 1.5585                   | 3              |

The systems W1, W2 and W3 present an opaque and whitish appearance attributable to the low solubility in the matrix of the PPs, indicating that these reagents are not suitable for the realization of optical devices.

The use of H₃PO₄ as phosphorous precursor permits to realize a waveguide (W4) that present a good transparency: over 92% in a wide range from 400 to 2000 nm, as evidenced in figure 1 by means of transmission measurement and allows to realize thick guiding film that support single mode at 1.5µm.

Figure 1. Transmission spectrum of the planar waveguide W4 doped by 0.5 mol % Er³⁺ ions.

Figure 2 and figure 3 report the profile of the refractive index and of the TE₀ mode squared electric field of the waveguide W4, respectively. The TE₀ mode is computed for 632.8 nm and 1542 nm for the choice of the parameters determined by the m-line measurement.

The refractive index profile of the W4 waveguide can be reconstructed from the effective refractive indices at 632.8 nm by an inverse Wentzel–Kramers–Brillouin method [12], in particular from figure 2 we can observe that the W4 exhibits a single step profile with a uniform refractive index throughout the whole thickness.

The modelling of the square electric field, reported in figure 3, indicates that the optical parameters of the waveguide, i.e. refractive index and thickness, appear appropriate for application in the third telecommunication window (λ=1.5 µm). In fact, the confinement coefficient of the TE₀ mode, defined as the ratio of the intensity in the waveguiding film to the total intensity, which includes also the squared evanescent field, is 0.98 and 0.87 at 632.8 nm and 1542 nm, respectively.
Photoluminescence measurements were performed in order to investigate the effect of P$_2$O$_5$, comparing the spectroscopic features of the W4 with those of a waveguide with the following molar composition 70SiO$_2$-30HfO$_2$ activated with 0.5% mol (WU), doped with the same Er$^{3+}$ ions concentration.

In figure 4 is reported the photoluminescence (PL) spectra of transition $^4$I$_{13/2}$ $\rightarrow$ $^4$I$_{15/2}$ of Er$^{3+}$ ions acquired from the sample WU and W4. Analyzing figure 4 is possible to observe that luminescence shape is similar for both the samples with a main emission peak at 1533 nm and a spectral bandwidth of 48 nm, measured at 3 dB from the maximum of the intensity. The shape of the emission spectrum is characteristic of the $^4$I$_{13/2}$ $\rightarrow$ $^4$I$_{15/2}$ transition of Er$^{3+}$ ions in silicate glasses.

Figure 5 reports the luminescence decay curve from the metastable level $^4$I$_{13/2}$ $\rightarrow$ $^4$I$_{15/2}$ for the W4 waveguide obtained upon excitation at 514 nm; we can notice that the decay curve exhibits a single

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**Figure 2.** Refractive index profile of the W4 waveguide reconstructed from modal measurements at 632.8 nm for the TE. The effective indices of the TE (•) modes are reported.

**Figure 3.** Calculated squared electric field profiles of the TE$_0$ mode at 632.8 and 1542 nm (a) and (b), respectively, across the layered structure, cladding of air, waveguide and the SiO$_2$ substrate of the W4 planar waveguide.

**Figure 4.** Room temperature PL spectra relative to the $^4$I$_{13/2}$ $\rightarrow$ $^4$I$_{15/2}$ transition of Er$^{3+}$ ions for W4 (a) and WU (b) waveguides upon excitation at 514 nm.

**Figure 5.** Decay curve of the luminescence from the $^4$I$_{13/2}$ $\rightarrow$ $^4$I$_{15/2}$ metastable state of Er$^{3+}$ ions for the W4 waveguide. The red solid line represents single exponential fits to the decay data.
exponential behavior, indicating that $\text{Er}^{3+}$ ions all occupy sites characterized by similar local environment and the value of the measured lifetime $\tau_{W4} = 5.7 \pm 0.1$ ms. This value can be compared with that obtained on the sample WU ($\tau_{Wu} = 5.1 \pm 0.1$ ms) and discussed in ref [13]. The increase of the lifetime measured for the sample W4 with respect to WU can be attributed to the presence of $\text{P}_2\text{O}_5$ in the matrix indicating that the phosphorous oxide can increase the $\text{Er}^{3+}$ ions solubility.

4. Conclusions
In conclusion $\text{Er}^{3+}$ activated $\text{SiO}_2$-$30\text{HfO}_2$-$5\text{P}_2\text{O}_5$ waveguides (WGs) were prepared via the sol–gel method and dip coating processing. We have studied the influence of the phosphorus precursors on the optical properties of planar waveguides demonstrating that $\text{H}_3\text{PO}_4$ precursor allows to obtain a guiding transparent film. The waveguide realized (W4) supports a single and well confined (87%) mode at 1.5$\mu$m, presents a single step refractive index profile and an attenuation coefficient of about 3.5dB/cm at 632.8 nm. Luminescence in the third telecom region, with a spectral width of 48 nm and a single exponential lifetime of 5.7 ms, was observed upon excitation at 514.5 nm. Finally the increase of the lifetime of the W4 with respect to that obtained on a complementary WG not codoped with $\text{P}_2\text{O}_5$ indicates that the phosphorous oxide can increase the $\text{Er}^{3+}$ ions solubility reducing the concentration quenching.

5. Acknowledgments
This research is performed in the framework of MAE “Smart optical nanostructures for green photonics” (2013–2015) and CNR-PAS (2014-2016) projects.

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