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Compositional Profiles in Silica-Based Sol-Gel Films Doped with Erbium and Silver, by RBS and ERDA

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Abstract. The photoluminescence efficiency of Er-doped silica-titania planar waveguides, prepared by sol-gel processing, may in principle be enhanced through the incorporation of silver metal particles. On the other hand, the presence of residual OH groups limits the optical activity of the Er^{3+} ions. In this work, we have used Rutherford Backscattering Spectrometry (RBS), combined with Elastic Recoil Detection Analysis (ERDA), in order to study the incorporation of Ag and H species as a function of the heat treatments used to densify the sol-gel films. Ultraviolet–visible spectroscopy and Fourier transform infrared (FTIR) spectroscopy were used to support and expand the interpretation of the RBS and ERDA data. The RBS results indicate a homogeneous distribution of Er in the as-deposited films. On the contrary, Ag displays a bimodal in-depth profile, centred at the air/film and film/Si substrate interfaces. Heat treatments at up to 700°C eventually lead to in-diffusion and segregation of most of the Ag species at the latter interface. The hydrogen concentration reaches minimum values after heat treatments at 500 and 900°C, with apparently larger values for temperatures in between. During these heat treatments, the Er profile remains stable.

Keywords: erbium-doped waveguides, silver-doped waveguides, silica-titania films, RBS/ERDA studies

1. Introduction

The basis of integrated optics (IO) components and circuits is a planar waveguide structure, for which sol-gel processing is one of the cheapest and most versatile methods, allowing the fabrication of passive and active IO components, including Er^{3+}-doped silica-titania based planar waveguides [1–6].

The sol-gel method enables the incorporation of a larger Er concentration than is possible by conventional glass melting and it is also an easy way of incorporating Ag° metal particles, which may be able to intensify the rare-earth photoluminescence (PL), as previously suggested [7, 8]. Nevertheless, some problems still limit the fluorescence performance of the rare-earth ions in such active materials, namely residual OH species, which reduce the lifetime of the $^4I_{13/2}$metastable level for emission at 1.5 μm and thus limit the corresponding quantum efficiency. In addition, a previously reported Er^{3+} PL quenching phenomenon [9], despite reversible, can also occur in this type of films when they are not completely densified, due to the interaction of OH groups, present near the inner surface of the residual pores, with Er^{3+} ions. Therefore, several heat treatments and compositions have been tried in order to avoid this quenching phenomenon. Alumina has been added to the Er^{3+}-doped silica-titania films and hafnia has been used to replace

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titania, with the aim of obtaining fully densified films [Almeida et al., these proceedings].

A detailed analysis of the prepared samples has been made, using RBS and ERDA, in order to obtain compositional, structural and density information on the present silicate films.

2. Experimental Procedure

A series of Er^{3+}-doped (0.25–2.0 mol% $ErO_{1.5}$) silica-titania films with 80 mol% SiO_2 and 20 mol% TiO_2, co-doped with 0–1 mol% Ag, were prepared, by spin-coating, on silica glass plates, polished single crystal Si substrates, or silicon substrates covered with a ~5 μm thick SiO_2 buffer layer deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD), according to the basic procedures described in [4]. In some cases, Al_2O_3 was also added to the Er^{3+}-doped silica-titania solutions, or $HfOCl_2$ was added as a hafnia precursor, instead of the titania precursor, TPOT (titanium isopropoxide), in order to prepare silica-hafnia based films.

The atomic composition of the sol-gel films was measured by RBS, using a 1 mm diameter collimated beam of $^4He^+$ions with an energy of 2.0 MeV. The backscattered particles were detected at a scattering angle of 160° (Cornell geometry), or close to 180°, using silicon surface barrier (SSB) detectors with resolutions of 13 and 16 keV, respectively. The ERDA experiments were done simultaneously, using a SSB detector positioned at a scattering angle of 24°, in order to detect the hydrogen recoils. A 8.2×10^{19} cm^{-2} Kapton stopping foil, placed before the detector, stopped all the $^4He^+$ backscattered particles, but not H. All spectra pertaining to each sample were simultaneously analysed and a unique solution was extracted using the NDF code [10]. Details of the optical measurements (UV-visible and FTIR spectroscopies) can be found in [1, 9].

3. Results and Discussion

Figure 1 shows the RBS experimental spectra and corresponding fits for a sample deposited on silicon, heat treated at different temperatures, up to 900°C. After deposition, all the elements, except silver, are homogeneously distributed throughout the entire thickness of the films. Silver is concentrated especially at the film surface (channel # ~417) and/or at the interface between the film and the silicon substrate (channel # ~375), depending on the temperature of heat treatment.

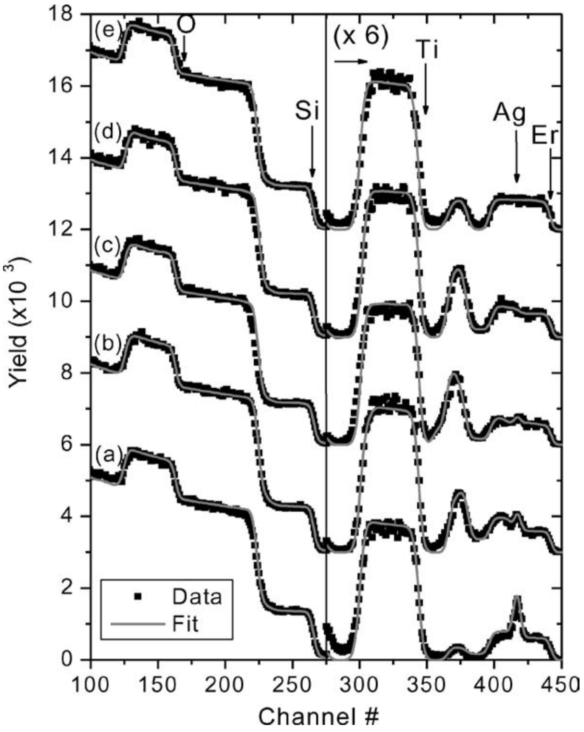

Figure 1. RBS spectra of a 78.8% SiO_2-19.7% TiO_2-0.5% $ErO_{1.5}$-1% Ag sample: (a) as-deposited; (b) treated at 500°C, for 6 min; (c) treated at 700°C, for 6 min; (d) treated at 900°C, for 6 min; (e) treated at 900°C, for 30 min. (Spectra obtained with a 2.0 MeV $^4He^+$ beam, tilt angle of 45° and scattering angle of 180°).

The best fitting to the experimental results gives the following concentration values, in atomic percentage: Er (0.09%), Ti (5%), Si (27%) and O (64%). All these values, except for Er, agree, within the experimental error (~5%), with the nominal composition of the initial solution, 26.5% Si, 6.6% Ti, 66.4% O, 0.17% Er and 0.34% Ag. The density of the doped silica-titania films was also calculated at approximately 2.5 ± 0.2 $g{\cdot}cm^{-3}$.

We have noted a lower integrated signal for the as-deposited sample, which could be due to slight differences in film thickness, or, most likely in the accumulated charge during Rutherford Backscattering analysis. All spectra are plotted with the same normalized charge, but its measurement has an associated error of up 5%. Such difference does not, however, affect the results presented.

Figure 2 shows the evolution, followed by UV-visible spectroscopy, of the optical absorption of

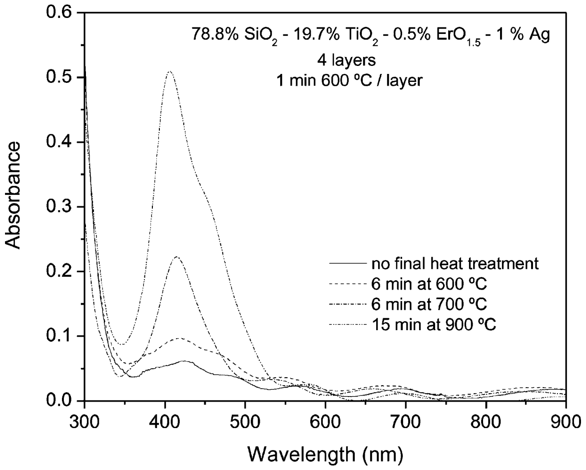

Figure 2. Optical absorption spectra of 78.8% SiO_2-19.7% TiO_2-0.5% $ErO_{1.5}$-1% Ag films, after different final heat treatments.

Ag-doped films, following thermal densification in air at temperatures up to 900°C. The peak observed at about 415 nm is characteristic of surface plasmon absorption by metallic silver (Ag°) nanoparticles, formed by the thermal conversion of ionic silver, Ag^+, with sizes between ~2–4 nm [6]. When the silver content is about 1 mol%, films heat treated at 600°C already show a very weak surface plasmon resonance, which indicates the presence of Ag° nanoparticles. This fact underlines the tendency for metallic silver segregation. In fact, the RBS data corresponding to treatments at temperatures above 500°C show the migration of silver towards the film/Si substrate interface; this phenomenon tends to increase, during the thermal densification of the films, as the heat treatment temperature (Fig. 1(b–d), or time (Fig. 1(e)), increase.

Moreover, the higher temperature heat treatments, at 700°C for 6 min or 900°C for 6 min, lead to a significant decrease in the overall concentration of silver in the films, from 0.1 at% to approximately 0.06 at%. The high mobility of silver in the films and its tendency to segregate, preferentially at the film/substrate interface, might be related to its low solubility in the glassy matrix.

However, results not shown in this paper, for films deposited on vitreous SiO_2, reveal a different behaviour. In this case, even for temperatures as high as 900°C, silver tends to remain homogeneously distributed inside the film and no silver was detected inside the SiO_2 substrate, as opposed to what is found with Si substrates. It should be noted that the thermal expansion coefficients (α) scale as $\alpha(\text{Si}) > \alpha$ (silicate film) $> \alpha$ (SiO_2) [11]. This suggests the possibility that the difference between the thermal expansion coefficients plays a role in the segregation behaviour of silver. In fact, when using silicon substrates covered with a thick (~5 μm) SiO_2 buffer layer, some silver migration is observed towards the substrate and part of the silver is also detected inside the substrate (for the highest heat treatment temperatures), but less than when the substrate is only Si (without a SiO_2 buffer layer).

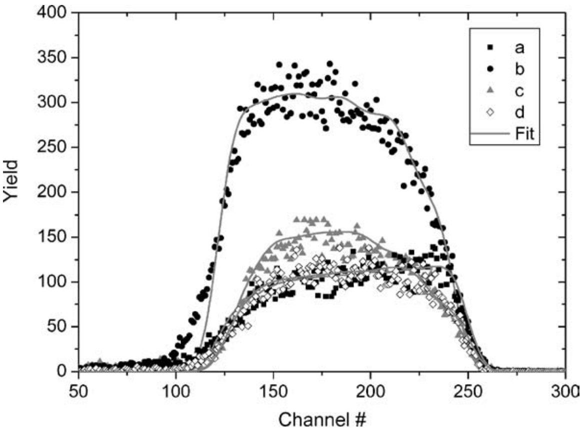

Figure 3. ERDA spectra of 78.8% SiO_2-19.7% TiO_2-0.5% $ErO_{1.5}$-1% Ag films: (a) as-deposited; (b) treated at 700°C, for 6 min; (c) treated at 900°C, for 6 min; (d) treated at 900°C, for 30 min. (Spectra obtained with a 2.0 MeV $^4He^+$ beam, tilt angle of 78° and scattering angle of 24°).

Figure 3 shows the experimental H profiles and corresponding fits, for the same films of Fig. 1. It can be observed that the hydrogen content remains constant up to 500°C, it presents a significant increase for 700°C and drops to the initial values at 900°C. It is also found that longer heat treatments at 900°C lead to a continuous elimination of H. These results, including the unexpected increase of the H concentration following the 700°C treatment, were confirmed by the ERDA measurements for other similar films.

The FTIR absorption spectra of some of the films previously discussed were recorded (Fig. 4), with the aim of investigating if the presence of H in the films could be associated with OH groups, most likely in silanol (Si—OH) species. The results indicate a continuous tendency for the reduction of OH groups (decrease/elimination of the band at ~3400 cm^{-1}, assigned to O—H stretching in SiO—H) with the heat treatment temperature, suggesting the possibility that some H atoms may be bonded to other species, especially following the 700°C treatment, e.g. in $Si—H_n$ bonds.

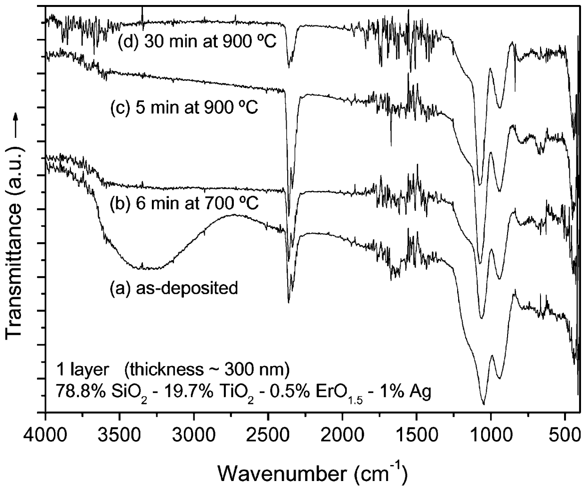

Figure 4. FTIR absorption spectra of 78.8% SiO_2-19.7% TiO_2-0.5% $ErO_{1.5}$-1% Ag films: (a) asdeposited; (b) after heat treatment at 700°C, for 6 min; (c) after heat treatment at 900°C, for 5 min; (d) after heat treatment at 900°C, for 30 min.

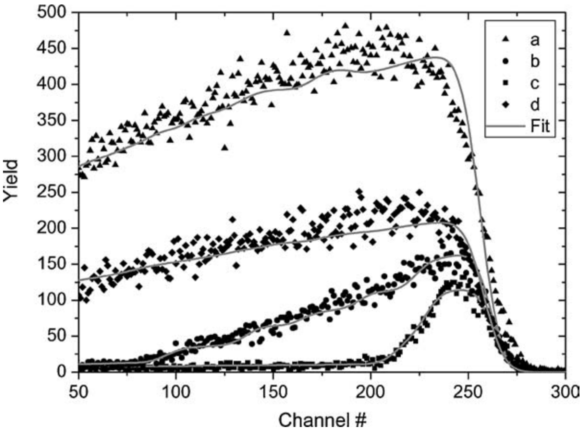

Figure 5. ERDA spectra of the following films (thickness ~1 μm): (a) 69.6% SiO_2-29.9% HfO_2-0.5% $ErO_{1.5}$, 1 min 750°C/layer, no final heat treatment; (b) 72.2% SiO_2-18.3% TiO_2-9.0% $AlO_{1.5}$-0.5% $ErO_{1.5}$, 2 min at 900°C/layer +20 min at 900°C in the end; (c) 69.6% SiO_2-29.9% HfO_2-0.5% $ErO_{1.5}$, 2 min at 900°C/layer +20 min at 900°C; (d) 79.6% SiO_2-19.9% TiO_2-0.5% $ErO_{1.5}$, 2 min at 900°C/layer +20 min at 900°C. (Spectra obtained with a 2.0 MeV $^4He^+$ beam, tilt angle of 78° and scattering angle of 24°).

However, this possibility could not be confirmed by IR spectroscopy, since no bands could be found in the region of ~2000–2200 cm^{-1} (Si—H, Si—H_2 or Si—H_3) [12]. On the other hand, it is reasonable in principle that the ERDA technique determines a higher H content than the IR measurements, since ERDA is a direct method to determine the total amount of bonded and non-bonded hydrogen in the films, including any possible molecular H_2 trapped in microvoids (pores), whereas IR spectroscopy detects only bonded hydrogen.

The behaviour of the H species changes significantly when Al_2O_3 is incorporated into the films, or when hafnia replaces titania, leading to better densified films. Figure 5 shows the ERDA spectra of four different planar waveguides, including one doped with Al (SiO_2-TiO_2-$AlO_{1.5}$-$ErO_{1.5}$) and another containing HfO_2 instead of TiO_2(SiO_2-HfO_2-$ErO_{1.5}$), after final heat treatments at 900°C, for 20 min. The two other spectra correspond to an Er^{3+}-doped silica-titania waveguide, with the same heat treatment and a silica-hafnia waveguide, heat-treated at only 750°C between each layer. It is found, for the samples of Fig. 5(b) and (c), that most H species are segregated in a thin layer near the film surface.

Regarding the PL efficiency, the waveguide of Fig. 5(a) had the poorest performance, since it still had a significant amount of OH species left, resulting in strong Er^{3+} PL quenching. Among the other three waveguides shown in Fig. 5, subjected to the same heat treatment at 900 °C, silica-titania was the one with worst fluorescence performance, presumably because of incomplete densification [9], while the waveguides containing alumina and especially those containing hafnia appear to offer the best performance, in terms of stability and strength of the PL signal. This can also be correlated with the higher H content, measured by ERDA, for the silica-titania waveguide (Fig. 5(d)), compared to the other two waveguides (Fig. 5(b) and (c)), despite the same heat treatment. For the films containing Al_2O_3 or HfO_2, all the H present is concentrated on a small layer at the film surface, suggesting that the presence of Al or Hf may reduce the solubility of H in the films, possibly as a result of a better densification. The waveguide containing HfO_2 had the lowest H content (Fig. 5(c)) and, according to recent PL measurements, it showed the strongest PL signal.

4. Conclusions

In homogeneous Er^{3+}-doped silica-titania films, deposited on Si, silica-on-silicon or v-SiO_2 substrates, silver was the only element whose distribution varied across the film thickness, following selected heat treatments. Here, the homogeneous incorporation of silver into the films was prevented by its segregation, mostly at the film/substrate interface. The segregation behaviour of silver, in metallic nanoparticle form, was found to vary with the substrate used. Heat treatments at high temperature (900°C), for long enough times, caused most silver to diffuse into the silicon substrate, but considerably less into a silica substrate. The hydrogen concentration was found to have a maximum value after heat treatment at 700°C, which was not explained by FTIR results, suggesting that the H complexes detected by ERDA are not exclusively silanol (Si—OH) groups. The waveguides with less hydrogen offered the best PL performance.

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