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Erbium activated HfO_2 based glass–ceramics waveguides for photonics

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Abstract

$(100 - x)SiO_2 - xHfO_2$ ($x = 10$, 20, 30 mol) glass–ceramics planar waveguides activated by 0.3 mol% Er^{3+} ions were prepared by sol–gel route, using dip-coating deposition on v-SiO_2 substrates. High resolution transmission electron microscopy has shown that after an adapted heat treatment, the resulting materials show nanocrystalline structures. The glass–ceramics waveguides were characterized by m-line, Raman, losses measurements, and photoluminescence spectroscopy. Photoluminescence spectroscopy has demonstrated the embedding of erbium ions in the nanocrystals. The results are discussed with the aim of assessing the role of hafnia on the structural, optical and spectroscopic properties of erbium doped silica hafnia glass–ceramics planar waveguides.

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1. Introduction

Erbium doped materials have been widely investigated for several years as Er^{3+} ions exhibit emission at 1500 nm, which coincides with the minimum-loss transmission window of silica based optical fibers telecommunication systems [1]. For this reason, huge efforts have been made in developing Er^{3+}-activated materials suitable for efficient optical waveguide amplifiers fabrication.

In the case of integrated systems like OPWAs (Optical Planar Waveguide Amplifiers), used for local networks (LAN), this one must be as short as possible, which necessary leads to have high rare earth concentration. Unfortunately high rare earth concentration in glasses leads to the formation of chemical clusters and interaction clusters which reduce the efficiency of the amplifier due to energy transfer coming from non-radiative processes [2–5].

It was demonstrated that transparent glass ceramics may be a valid alternative system to control the chemical parameters of the rare earth, and thus may avoid undesirable effect like clustering [3]. This class of materials is of great importance in photonics, because they combine the glass mechanical and optical properties with a crystal-like rare-earth ion environment. Erbium containing nanocrystals in a glassy matrix exhibit higher optical cross-sections of the erbium transitions [6,7]. Since the pioneer work of

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1993, when Wang and Ohwaki discovered novel glass-ceramic system characterized by a transparency comparable to a glass [8], considerable efforts have been made in order to fabricate rare earth activated glass–ceramic materials with active ions embedded in the crystalline phase.

In this work we extend our recent results on transparent glass ceramics [9,10], presenting the fabrication protocol and the optical, structural and spectroscopic assessment of sol–gel derived erbium activated HfO_2 based glass–ceramics waveguides.

2. Experimental

$(100 - x)SiO_2 - xHfO_2$ ($x = 10$, 20, 30 mol) planar waveguides, activated by 0.3 mol% Er^{3+} ions were prepared by sol–gel route, using dip-coating deposition on v-SiO_2 substrates cleaned by ultra-sound and alcohol. The starting solution, obtained by mixing tetraethylorthosilicate (TEOS), ethanol, deionized water and hydrochloric acid as a catalyst, was prehydrolyzed for 1 h at 65 °C. The molar ratio of TEOS:HCl:EtOH:H_2O was 1:0.01: 37.9:2. An ethanolic colloidal suspension was prepared using as a precursor $HfOCl_2$ [11,12], and then added to the TEOS solution with a Si/Hf molar ratio of 90/10, 80/20, and 70/30. Erbium was added as $Er(NO_3)_3 \cdot 5\,H_2O$ with an Er/(Si + Hf) molar concentration of 0.3 mol%. Erbium-activated silica–hafnia films were deposited on v-SiO_2 substrates by dip coating, with a dipping rate of 40 mm/min. Before further coating, each layer was annealed in air for 50 s at 900 °C. Final films, resulting of 30 coatings, were stabilized by a last treatment in air introducing them directly in the furnace at 900 °C (optimized temperature to fully densify the waveguides) for 5, 210 min and 30 h for the waveguides W30, W20, W10, respectively (Table 1) [13]. As a result of this procedure, transparent and crack free waveguides were obtained. In order to nucleate nanocrystals inside the planar waveguide, an additional heat treatment was performed in air at a temperature of 1000 °C for 30 min [9,10]. The waveguides were characterized by several techniques including photoluminescence (PL) spectroscopy, lifetime measurements, losses measurements, modal measurements, Raman spectroscopy and high resolution transmission electron microscopy (HRTEM).

Specimens for HRTEM observations were prepared by scraping off the thin films in ethanol using a diamond knife. A drop of the suspension is deposited and dried onto a carbon coated copper grid. HRTEM study of the scraped samples was performed in a 200 kV side entry JEOL 2010 FEG Transmission Electron Microscope fitted with a double tilt sample holder (tilt ± 30°). The chemical composition of the deposited material was determined by Energy Dispersive X-ray analysis (EDX) using an EDAX EDX Spectrometer coupled with the 200 KV microscope.

The TE_0 mode waveguiding excitation was used for both Raman and PL measurements, by detecting the light coming out from the waveguide surface. PL spectroscopy, in the region of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions, 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

Table 1
Physical and optical parameters of the 0.3 mol% Er^{3+}-activated SiO_2–HfO_2 planar waveguides annealed at 1000 °C for 30 min

Sample label	SiO_2–HfO_2 (mol%)	n@1532 nm in TE polarization (±0.001)	Band-width (±1 nm)	Heat treatment of the precursor waveguide at 900 °C
W10	90–10	1.485	28	30 h
W20	80–20	1.538	19	210 min
W30	70–30	1.597	17	5 min

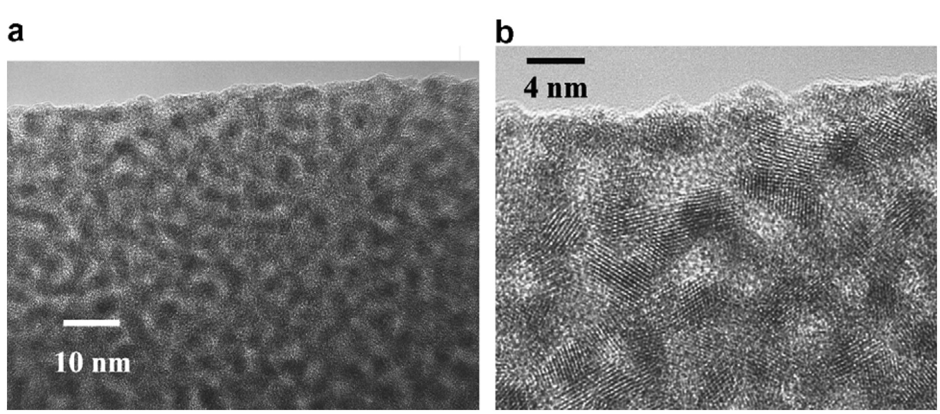

Fig. 1. HRTEM image of the silica hafnia W30 sample, annealed at 1000 °C for 30 min, showing HfO_2 nanocrystals homogeneously dispersed in the amorphous matrix (a). Single domain nanocrystals are clearly evidenced in (b).