



Nanostructured Er³⁺-doped SiO₂-TiO₂ and SiO₂-TiO₂-Al₂O₃ sol-gel thin films for integrated optics



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ARTICLE INFO

Article history:

Received 9 April 2015

Received in revised form 12 May 2015

Accepted 12 May 2015

Available online 28 May 2015

Keywords:

Oxide films

Sol-gel method

Er³⁺ doped SiO₂-TiO₂ or SiO₂-TiO₂-Al₂O₃

systems

Waveguides

ABSTRACT

The nanostructured multilayer silica-titania or silica-titania-alumina films doped with Er³⁺ were prepared by sol-gel method. The sol-gel method is a flexible and convenient way to prepare oxide films on several types of substrates, and for this reason it was extensively investigated for optical waveguides fabrication. The selected molar composition was 90%SiO₂-10%TiO₂ or 85%SiO₂-10%TiO₂-5% Al₂O₃ and 0.5% Er₂O₃.

The films were characterized by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Spectroellipsometry (SE), as well as by Atomic Force Microscopy (AFM) and photoluminescence (PL). The films deposited on Si/SiO₂ substrate by dip-coating or spin-coating, followed by annealing at 900 °C, presented homogenous and continuous surface and good adherence to the substrate. Differences were noticed in the structure and properties of the prepared films, depending on the composition and the number of deposited layers.

Channel optical waveguides were obtained by patterning Er³⁺-doped SiO₂-TiO₂ and SiO₂-TiO₂-Al₂O₃ sol-gel layers deposited on oxidized silicon wafers.

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1. Introduction

The wet chemical methods for the synthesis of the films with optical properties are attractive for many optical technologies, a great attention being conferred to optical waveguides with 2D confinement that are the main component the photonic integrated circuits.

Among the different technologies which are employed to develop materials suitable for photonics, sol-gel processing exhibits several advantages in terms of composition, rare-earth solubility, design, tailoring of optical properties as well as fabrication of films, waveguides, photonic crystals, and bulk glasses. The binary silica-based systems, such as silica-titania [1–3], silica-hafnia [3], silica-alumina [4], silica-alumina [5], silica-zirconia [6] and phosphosilicate [7] are of particular interest allowing the tailoring of the optical and spectroscopic properties. Nonlinear effects have been also observed in silica-titania waveguides, i.e. photo induced optical second harmonic generation [8].

Silica-titania films may be used also as waveguide layers for application in planar evanescent wave sensors. They possess low

optical losses and they demonstrate a possibility of formation of the photo induced optical second harmonic generation [3].

Although rare earth doped materials have been studied and used for the last 40 years in a variety of photonic applications, such as frequency up converters, optical amplifiers and lasers [8], they are still of high interest.

The optical communication technology has been largely attracted by erbium-doped materials as active element in photonic devices [8,9], due to the fact that trivalent Er ions' transition at 1.5 μm [10] matches the range of minimum transmission loss for silica-based optical fibers.

Er³⁺-doped Al₂O₃ has attracted much attention as a promising candidate for developing 1.5 μm optical waveguide amplifiers [11,12].

In particular, erbium-doped phosphate glasses are interesting materials for active waveguide fabrication and potential application in photonic integrated circuits since they have comparably large emission cross-section and weak interaction among active ions [9]. These characteristics are important for efficient amplification at 1.5 μm in planar waveguides, as the short optical path requires large Er³⁺ concentrations. However, with increasing Er³⁺ concentration, energy transfer processes, such as up conversion

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or energy migration, become relevant, decreasing the emission quantum yield of the $^4I_{15/2}$ excited state [9–14].

On the one hand, these processes are detrimental to the efficiency of optical amplification and lasing at 1.5 μm , but on the other hand, they open applications as energy up converters [15], as well as diode pumped visible and ultraviolet laser devices [1,16]. Zampedri and coworkers [17] prepared in the SiO_2 – TiO_2 binary system planar wave guides activated with 1% molar Er^{3+} , considering that for obtaining good optical and spectroscopic properties, the TiO_2 content should be in the molar ratio of 7–12%. A spectral width of 46 nm and a life time $\tau_{1/e}$ of 4.5 ms were noticed for these TiO_2 concentrations.

The multilayer silica–titania waveguides undoped and doped with Er^{3+} were prepared also using the sol–gel method by Zaharescu et al. [18]. The selected molar composition was 90% SiO_2 –10% TiO_2 and the films were deposited on SiO_2/Si substrate by dip coating and by spin coating methods, followed by annealing at 900 °C. Fang et al. [19] prepared Er-doped SiO_2 – TiO_2 by UV-photo-CVD and studied their properties by FT-IR and XPS methods. High quality as-deposited films with various Ti/Si ratios and low carbon contents have been obtained.

Recently Bouajaj et al. [20] studied the properties of the Erbium-activated silica–titania and silica–hafnia planar waveguides prepared by the sol–gel route. The films were deposited on vitreous silica substrates using a dip-coating technique and their structural and optical properties were compared.

Almeida et al. [21,22] obtained multilayer planar waveguides in the SiO_2 – TiO_2 binary doped with Er^{3+} , deposited by spinning on glass or silicon monocrystal and co-doped with silver or alumina and ytterbium.

The influence of the co-doping with Al or P of Er^{3+} -doped SiO_2 – TiO_2 binary system was also studied [23].

Rocca et al. [24] studied SiO_2 xerogel, doped with rare earth (Pr^{3+} , Tb^{3+} , Er^{3+}) by X-ray absorption spectroscopy and X-ray diffraction, while d'Acapito [25] studied the Er^{3+} ion coordination in SiO_2 – TiO_2 – HfO_2 sol–gel films, by EXAFS.

In this paper a comparative study of the sol–gel preparation of the nanostructured multilayer Er^{3+} -silica–titania and Er^{3+} -silica–titania–alumina films was approached in order to better establish the influence of the Al_2O_3 presence in the films composition on their optical properties. A second aim is the development of a cheap and reproducible technology process for deposition and patterning of Er^{3+} -doped sol–gel layers for fabrication of optical waveguides with rectangular cross section (channel waveguides). The previous papers on Er^{3+} -doped sol–gel layers [4,7,17,20,21,23] present the fabrication of planar waveguides. Our attention was focused on optimization of the patterning process to allow the fabrication of waveguides with 2D confinement that are required in optical communications, interconnects and sensors.

2. Experimental

2.1. Films preparation

The obtaining of the nanostructured oxide films by sol–gel method was studied and the experimental conditions used are

Table 1
Composition of the starting solutions and the experimental conditions for preparation of Er^{3+} -doped SiO_2 – TiO_2 and SiO_2 – TiO_2 – Al_2O_3 films.

Sample	Reagents	Molar ratio				pH	Experimental conditions	
		$\frac{\text{ROH}}{\sum \text{precursor}}$	$\frac{\text{H}_2\text{O}}{\sum \text{precursor}}$	$\frac{\text{catalyst}}{\sum \text{precursor}}$	$\frac{\text{Er}_2\text{O}_3}{\sum \text{precursor}}$		T (°C)	t (h)
ST-Er	$\text{Si}(\text{OC}_2\text{H}_5)_4 + \text{Ti}(\text{OC}_2\text{H}_5)_4 + \text{ErCl}_3$	9.1	1.85	0.0174	0.5	3	50	3
STA-Er	$\text{Si}(\text{OC}_2\text{H}_5)_4 + \text{Ti}(\text{OC}_2\text{H}_5)_4 + \text{Al}(\text{NO}_3)_3 + \text{ErCl}_3$	19.3	1.85	0.0174	0.5	3.5	50	3

R = $-\text{C}_2\text{H}_5$; 0.5 mol% Er_2O_3 .

presented in Table 1. The selected compositions in the SiO_2 – TiO_2 binary and SiO_2 – TiO_2 – Al_2O_3 ternary system, doped with Er_2O_3 were the following: 90% SiO_2 –10% TiO_2 or 85% SiO_2 –10% TiO_2 –5% Al_2O_3 and 0.5% Er_2O_3 . The compositions were selected based on the literature data and our previous works [17,18].

As precursors the corresponding alkoxides: tetraethyl-orthosilicate (TEOS) (Merck) as SiO_2 and tetraethyl-ortotitanate (Merck) as TiO_2 sources and salts: $\text{Al}(\text{NO}_3)_3$ (Aldrich) as Al_2O_3 source and ErCl_3 (Aldrich) as erbium source were used. The ethanol was used as solvent, the nitric acid as catalyst and the water for hydrolysis. The reaction was kept under stirring on water bath at 50 °C for 3 h.

From the prepared solutions, films were deposited on Si/SiO_2 substrate by dip-coating method with a withdrawal rate of 5 cm/min and by spin-coating method (2300 rpm). Before deposition, the solutions were aged for 24 h. The films were thermally treated at 900 °C for 30 min, using a heating rate of 5 °C/min. For multilayer films after each deposition a thermal treatment at 900 °C for 1 min, using a heating rate of 5 °C/min was applied.

The multilayer films with 1, 2, 5 or 10 layers (further denoted WTT – film without thermal treatment; 1–10TT with thermal treatment) were obtained.

2.2. Films characterization

The morphology of the samples was investigated by scanning electron microscopy (SEM) using a high-resolution microscope, FEI Quanta 3D FEG model, operating at 20 kV, equipped with an energy dispersive X-ray (EDX) spectrometer Apollo X. The analyses were done in high vacuum mode, with Everhart–Thornley secondary electron detector.

The structure of the thin films was determined by X-ray diffraction (XRD) method. The asymmetrical reflection measurements were performed with an Ultima IV diffractometer (Rigaku Corp., Japan), equipped with parallel beam optics and a thin film attachment, using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$), operated at 30 mA and 40 kV, over the range $5 < 2\theta < 90^\circ$, at a scanning rate of 5°/min and at a fixed incident angle ($\omega = 0.5^\circ$) to determine both surface and near-surface structures.

To evaluate the optical constants and the thickness of the films, optical measurements were performed using a J.A. Woollam Co., Inc. spectroscopic ellipsometer setup. The spectra cover the wavelength range from 300 to 1000 nm with wavelength steps of 5 nm, at an angle of incidence of 70°. All measurements were performed in air at room temperature.

The AFM experiments were carried out on two equipments: Park Systems (Figs. 7 and 8) and EasyScan2 (Fig. 9). AFM measurements carried in the non-contact were made with XE-100 apparatus from Park Systems equipped with flexure-guided, cross-talked eliminated scanners and it was used the XEI program (v.1.8.0) for planarization method (tilt removal) and subsequent statistical data analysis, including the calculation of the root mean square (RMS) roughness. EasyScan2 AFM (Nanosurf® – AG Switzerland) was used in intermittent contact working mode using a high resolution scanner of 10 $\mu\text{m} \times 10 \mu\text{m}$ (X–Y) with vertical Z-range of 2 μm , Z-axis resolution 0.027 nm and a X–Y linearity mean error of less than

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