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Photoluminescence optimization of Er-doped SiO_2 films synthesized by radiofrequency magnetron sputtering with energetic treatments during and after deposition

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ABSTRACT

By radiofrequency magnetron sputtering co-deposition we synthesized Er:SiO_2 film 0.5 μm thick on silica substrates, with Er content <0.3 atomic %. By changing the preparation condition (during deposition we have used an additional negative bias voltage applied to the substrates for inducing a low-energy ion bombardment, with or without a contemporary heating) and by varying the thermal treatment after the synthesis (the best conditions were 1 h in the range 700–800 °C, in air) we have obtained an Er:SiO_2 system with an intense photoluminescence emission at λ = 1.54 μm. The best-performing Er:SiO_2 samples obtained by sputtering have shown a photoluminescence response comparable to that of the typical Er:SiO_2 thin film systems obtained by conventional techniques used in applicative framework.

1. Introduction

As a consequence of the increasing demand for telecommunications, a strong impulse towards the synthesis and the development of photonic materials is constantly addressed. The optical communication technology has been largely attracted by materials doped with rare-earth (RE) elements such as erbium, to be used as active elements in photonic devices: actually, the Er^{3+} ions transition at 1.54 μm of wavelength falls in the range of minimum transmission loss for silica optical fibers [1]. As far as the optical data processing is concerned, the frontier is represented by planar integrated optical devices in which all the optical components are fabricated and directly integrated on a single chip, with the goal of obtaining an all optical communication network [2].

Different techniques are used for preparing Er-doped silica films [3], for instance Er-doping during the silica film synthesis by chemical vapor deposition (CVD) methods or Er implantation in silica substrates. The main drawbacks of ion implantation are the need of two or more implantation steps at different energies for obtaining the required Er-implanted concentration profile (for matching the distribution of the field profile of the optical mode in the waveguide), and of a post-implantation high-temperature annealing step to remove the damage caused by implantation. In the CVD synthesis, the presence of a considerable amount of hydroxyl groups in the films, that can act as quenching centers for the excited state energy, is an important drawback: high-temperature thermal treatments are consequently necessary to remove the undesired hydroxyl groups. In general, the need of high-temperature treatments can however prevent the integration with Si-based electronics.

The sputtering technique is a synthesis approach that allows a production of glass films at relatively low temperature, with a small amount of hydroxyl contaminants; post-synthesis thermal treatments at lower temperature are possible for activating the Er photoemission; the erbium is expected to be homogeneously dispersed within the host material, and its local concentration can be easily changed by acting (in the case of a multisources configuration) on the Er source power to obtain the desired depth profile. With a multisources configuration for co-sputtering and by changing the substrate temperature and/or pressure and composition of the working gas and/or by applying a bias potential to the substrate during deposition, mixed compounds can be produced and different microstructures of the growing host matrix can be obtained.

In literature several investigations of Er:SiO_2 systems obtained by sputtering deposition are present (see for instance Refs. [4,5]). Usually the syntheses adopted are characterized by the following two peculiarities: i) the use of only one rf source for the deposition, with a SiO_2 target covered by small pieces of Er or Er_2O_3, and ii) the choice of suitable working conditions in order to have substoichiometric silica film as host matrix for erbium (this is done for having, after the post-synthesis thermal annealing, a stoichiometric host silica matrix

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containing also Si aggregates able to sensitize the erbium ions). The latter characteristic interferes with the complete optimization of the erbium ion sites needed to maximize the Er^{3+} photoluminescence intensity, being the photoluminescence strongly influenced by the presence of sensitizing species inside the host matrix.

In the present study we report on the synthesis of Er:SiO_2 films by rf magnetron sputtering co-deposition, investigating the effects of several preparation parameters in order to optimize the photoluminescence performances of the Er^{3+} ions embedded in a stoichiometric silica matrix. The effects of a simple thermal treatment during the film deposition were recently investigated for this kind of systems [6]. Here, we examine in particular the possibility to improve both the intensity of the emitted 1.54 μm signal and the figure of merit of the material by means of different energetic treatments performed on the growing Er-doped films, namely thermal heating and/or low-energy ion bombardment. These energetic treatments allow exploring different microstructural growing condition for the deposited material, thus possibly permitting an improvement of the final properties in general, and of the photoluminescence optical performances in our special case.

2. Experimental details

Erbium-doped silica films were synthesized by simultaneous deposition of silica and erbia on fused silica slides of 25×75 mm^2, 1 mm thick, in a radiofrequency magnetron sputtering deposition apparatus. Co-depositions were performed by means of two 13.56 MHz radiofrequency sources acting in a neutral atmosphere (pure Ar), at a working pressure of 0.40 Pa. The magnetron sources were tilted offline to adjust the deposition focal point on the silica substrates. During depositions, the sample holder was rotated at 5 rpm to have a good homogeneity of the film composition and thickness; it also could be intentionally heated up to 500 °C by means of two quartz lamps illuminating the back of the sample holder. Without intentional heating, the temperature of the sample during deposition did not exceed few tens of Celsius degrees, i.e. near to the room temperature, RT. In order to have an Er concentration close to 10^{20} atoms/cm^3, the rf power to the 2 inch diameter targets was fixed at 150 and 12 W for silica and erbia, respectively. After a four-step cleaning in ultrasonic bath (deionized H_2O, trichloroethylene, acetone, isopropyl alcohol), immediately before the deposition the silica slide substrates were rf-biased at 20 W for 20 min to remove possible surface contaminations. The thickness of the removed layer was estimated to be about 10 nm. The 75 min co-deposition of silica and erbia (to obtain the Er-doped silica film) was followed by a single silica deposition for 15 min (to have a capping protective layer on the Er-doped film). Three different deposition routes were explored: in the first, no additional energetic treatments were performed during deposition; in the second, a radiofrequency bias with power ranging from 5 to 42 W was applied to the substrates during the co-deposition, resulting in a negative mean voltage able to induce a low-energy Ar^+ bombardment of the film during its formation. In the third, a contemporary heating of the substrate was made during its radiofrequency biasing. Immediately after the synthesis the samples were put in a dry box and kept at a pressure around 1 Pa for avoiding moisture contamination until the final thermal annealing. The thermal annealing of the as-deposited samples was performed in air or in pure nitrogen at different temperatures in the range 500–1100 °C.

Composition of the samples and concentration profiles of the different elements were obtained by Rutherford backscattering spectroscopy (RBS) measurements, performed at Laboratori Nazionali INFN-Legnaro, Italy by using a $^4He^+$ beam at the energy of 2.0 MeV, with the detector placed at 160° with respect to the incident beam direction.

The analysis of the optical emission properties was performed at room temperature by photoluminescence (PL) spectroscopy, under pumping by the 488 nm line of a mechanically chopped Ar multi-line laser operating at 25 mW, with a beam spot of 1 mm diameter. In some measurements the pumping was performed by using the 476.5 nm laser line, that is non-resonant with the characteristic Er absorption lines and, for this reason, that can highlight the possible presence of indirect RE excitation processes mediated by photosensitizing agents. The PL signal was analyzed by a single grating monochromator and detected by a near-infrared photomultiplier tube cooled by liquid nitrogen. Being the total number of erbium atoms slightly different from sample to sample, any reported PL intensity is the detected value divided by the erbium amount in that sample (as measured by RBS). For the analysis of the dynamics involved in the luminescence emission, the signal was acquired through the same near-IR photomultiplier detector and recorded with the use of a digital oscilloscope.

3. Results and analysis

Er:SiO_2 films were first deposited at room temperature, RT (i.e. without intentional heating of the substrate during the film deposition), with no rf substrate biasing (0 V sample) and with different negative mean voltages due to rf bias (−50 V, −75 V, −150 V, and −300 V samples), obtained with 5 W, 6 W, 13 W, and 42 W of power, respectively. A random variation of about ±5 V was observed for the self-bias values. RBS measurements allow determining in any sample the concentration of erbium atoms in a very precise and accurate way. This is a crucial point, because the intrinsic variability of the target erosion and deposition rates (related to the different plasma conditions tested during the syntheses) can induce the growth of films with different composition. About all the RBS results, the relative uncertainties are about 5% for the doses, about 10% for the concentrations. The Er-doped film thicknesses have been estimated starting from the density of the bulk silica: the reported values can underestimate the true ones by about 10%. In Table 1 we report the RBS experimental data for the series of samples deposited at RT. The final film thickness was roughly the same for all the samples (about 0.5 μm); only the film deposited with rf bias yielding the strongest negative voltage (−300 V) showed a thickness of about 0.2 μm. In all samples a certain amount of the working gas (Ar) is trapped inside the film: this is a typical behavior shown by the sputter-deposited films. RBS spectra showed a uniform in-depth distribution of erbium inside the doped layer of the different samples; the distribution profiles did not change after the subsequent thermal treatments needed for the optimization of the Er

Table 1
RBS results of the samples synthesized by varying the bias of the substrate during deposition performed at RT.

Negative voltage (V)	Erbium		Argon		O/Si (±0.05)	Er-doped film thickness (nm)
	Total amount (Er cm^{-2})	Conc. (Er cm^{-3})	Total amount (Ar cm^{-2})	Conc. (Ar cm^{-3})		
0	3.7×10^{15}	8.8×10^{19}	1.4×10^{16}	0.3×10^{21}	2.05	420
−50	3.9×10^{15}	6.6×10^{19}	6.5×10^{16}	1.1×10^{21}	2.05	590
−75	3.4×10^{15}	7.7×10^{19}	6.8×10^{16}	1.5×10^{21}	2.05	440
−150	3.3×10^{15}	8.9×10^{19}	5.3×10^{16}	1.4×10^{21}	2.10	370
−300	3.8×10^{15}	17×10^{19}	2.8×10^{16}	1.3×10^{21}	2.15	220