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Synthesis and characterization of erbium-doped SiO_2-TiO_2 thin films prepared by sol-gel and dip-coating techniques onto commercial glass substrates as a route for obtaining active GRadient-INdex materials

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ABSTRACT

In this work, SiO_2-TiO_2 films doped with erbium were prepared by dip-coating sol-gel process onto commercial glass substrates. The surface morphology of the films was characterized using atomic force microscopy, while thickness, refractive index, extinction coefficient and porosity of the films were determined by ellipsometric measurements in a wavelength region of 400–1000 nm. Optical constants and porosity were found to vary with erbium concentration. The proof of principle presented in this paper is applicable to systems of different nature by tailoring the sol-gel precursors in such a way that active GRadient-INdex media described by a complex, parabolic-like refractive index distribution for beam shaping purposes is obtained.

1. Introduction

In this paper, we explore the possibility of using the chemical route known as sol-gel process for active GRadient-INdex (GRIN) media preparation. GRIN media are inhomogeneous materials where the refractive index varies point to point. The term active refers to the capability of the medium to amplify (gain medium) or attenuate (loss medium) the irradiance of light, typically a laser beam. This capability is related to the imaginary part of the refractive index. The sol-gel route has been demonstrated as an alternative for the preparation of glasses and ceramic materials at considerably lower temperatures compared to conventional techniques, being a cost effective method that can be deposited on substrates with different shapes [1]. Some of the advantages of this method include the possibility to precisely control the stoichiometry, producing multicomponent homogeneous systems not previously available and obtaining of high-purity materials for electronics and optics [2]. In particular, sol-gel is a versatile way for thin film manufacturing which permits to control the refractive index and thickness of the coatings [3]. Optical properties of rare-earth-doped materials prepared via sol-gel have been widely investigated for photonic applications where optical activity through the use of rare-earth dopants is a key requirement due to the ease of introducing a wide variety of dopants [4–7].

Lasers have become ubiquitous and are key tools in multiple technologies comprising industry, medicine, scientific research, communications or entertainment, among others. In most cases, the output beams emitted by the lasers sources must be reshaped in order to get optimized results for a given application [8,9]. The optical devices that can perform this operation are called beam shapers. The most typical example of beam shaping is the Gaussian-to-flat-top conversion where a beam, described by a Gaussian distribution profile, is turned into a beam with a uniform irradiance distribution. Practically since laser invention, beam shapers devices have been gaining importance and several approaches for Gaussian-to-uniform beam conversion have been proposed. Shaping of laser beams can be accomplished within the laser cavity (intra-cavity beam shaping), based on generating a flat-top beam directly as the cavity output mode or external to the cavity (extra-cavity beam shaping). In this case, beam shaping is achieved by manipulating the output beam from a laser with suitably chosen

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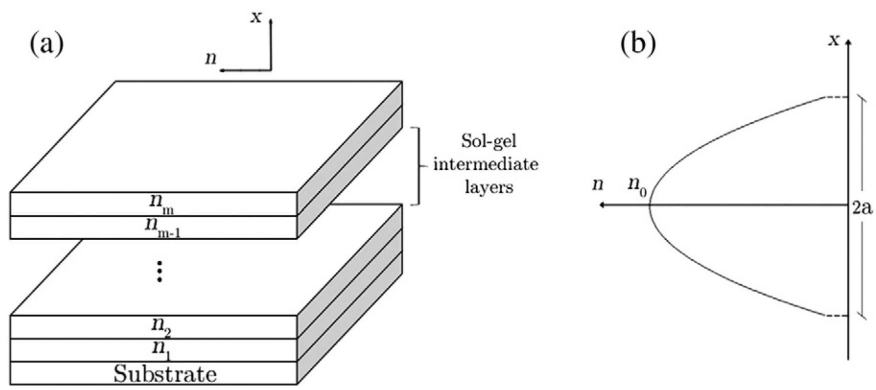

Fig. 1. Geometry of the planar active GRIN material: (a) sol-gel coatings with different complex refractive indices are progressively grown onto the glass substrate to generate a final structure characterized by (b) a parabolic-like profile distribution for both the real and imaginary part of the complex refractive index.

amplitude and/or phase elements. Active GRIN rod lenses, described by both complex gradient parameter and parabolic refractive index profile, have been demonstrated by some of the authors to be a suitable solution for laser beam shaping purposes [10].

To investigate sol-gel thin films for optically active GRIN materials preparation, crack-free non-doped and Erbium-doped SiO_2–TiO_2 samples have been produced by a sol-gel method combined with dip-coating deposition technique and characterized by optical constants and morphological analysis. The optical and mechanical properties of the films could be designed and controlled by varying the silicon, titanium and erbium molar ratios. Refraction index, extinction coefficient and porosity of the thin films have been obtained by spectral ellipsometry (SE) measurements, while morphological properties of the films have been studied by atomic force microscopy (AFM).

The remainder of the paper is organized as follows: Section 2 introduces the use of sol-gel processes in glass technology and reports on the theory of Gaussian-to-uniform beam shaping conversion by active GRIN materials. In Section 3, experimental procedure for preparation of non-doped and erbium-doped SiO_2–TiO_2 thin films is presented. The characterization of the samples is presented in Section 4. Finally, Section 5 summarizes the results of this work and draws conclusions.

2. Sol-gel route for GRadient-INdex media fabrication

2.1. Sol-gel for optics elements preparation

The sol-gel process is a powerful and versatile method for producing numerous kinds of materials with interesting optical and photonic properties, i.e., GRadient-INdex elements. It presents some advantages over existing production methods, including control of composition and low processing temperature, as well as the capability to form different refractive index profiles. Sol-gel route was first proposed for production of optical materials by M. Ebelmen in 1845 [11]. This process involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and its gelation to form a network in a continuous liquid phase (gel). The reactions implicated in the sol-gel chemistry are based on the hydrolysis and condensation of the starting materials or precursors, which normally consist of alkoxides and inorganic solutions to produce silicates, alumina and zirconia, among others. A large number of optical elements encompassing bulk optics, active waveguides, solid lasers, materials for nonlinear optics, gradient refractive index materials and chemical and biological sensors have been prepared by sol-gel methods [12–14].

Sol-gel process is especially suitable for preparation of GRIN materials due to the possibility of tuning the refractive index profile in accordance to the requirements of the application. In particular, the fabrication of radial GRIN media, where the index profile varies continuously from the optical axis to the periphery along the transverse direction in such a way that the surfaces of constant index are concentric cylinders about the optical axis, by sol-gel has been reported by two different methods. These methods are based in partial leaching of index-modifying cations from an alcoxy-derived wet gel and interdiffusion of index-modifying cations in the liquid phase of a wet gel [15,16]. In this work, we have prepared and characterized thin films as a preliminary step for growing layer stacks with progressively different refractive indices where the final complex refractive index of the structure is characterized by a parabolic-like distribution. The refractive index of each film is tailored by mainly selecting the type of the precursor and its concentration.

Table 1
Erbium nominal concentration (at.%) in the sol.

	Er (at.%)
Sample A	0
Sample B	0.3
Sample C	1
Sample D	2

2.2. Modelling of Gaussian-to-uniform beam shaping by active GRIN materials

In this section, the condition that must be fulfilled for performing beam shaping through GRIN media characterized by a parabolic and complex refractive index profile is presented [10]. This general beam shaping condition has been determined by some of the authors by studying light propagation in active media and by obtaining the expressions that describe the radius of curvature and the beam half-width at a given plane $z = z_1$ inside the GRIN material.

A planar active GRIN medium of length d and semiaperture a is considered. This medium can be described by a gain or loss parabolic transverse refractive index profile [17] given by Eq. (1)

$$n(x, z) = n_0\left[1 - g^2(z)x^2/2\right] \tag{1}$$

with condition

$$0 \le z \le d \tag{2}$$

where n_0 represents the complex refractive index along the z axis and $g(z)$ symbolizes the complex gradient parameter.

Eq. (1) can be expressed in the form $n(x, z) = n_R + ik$, where n_R and k represent the real and the imaginary part of the refractive index,

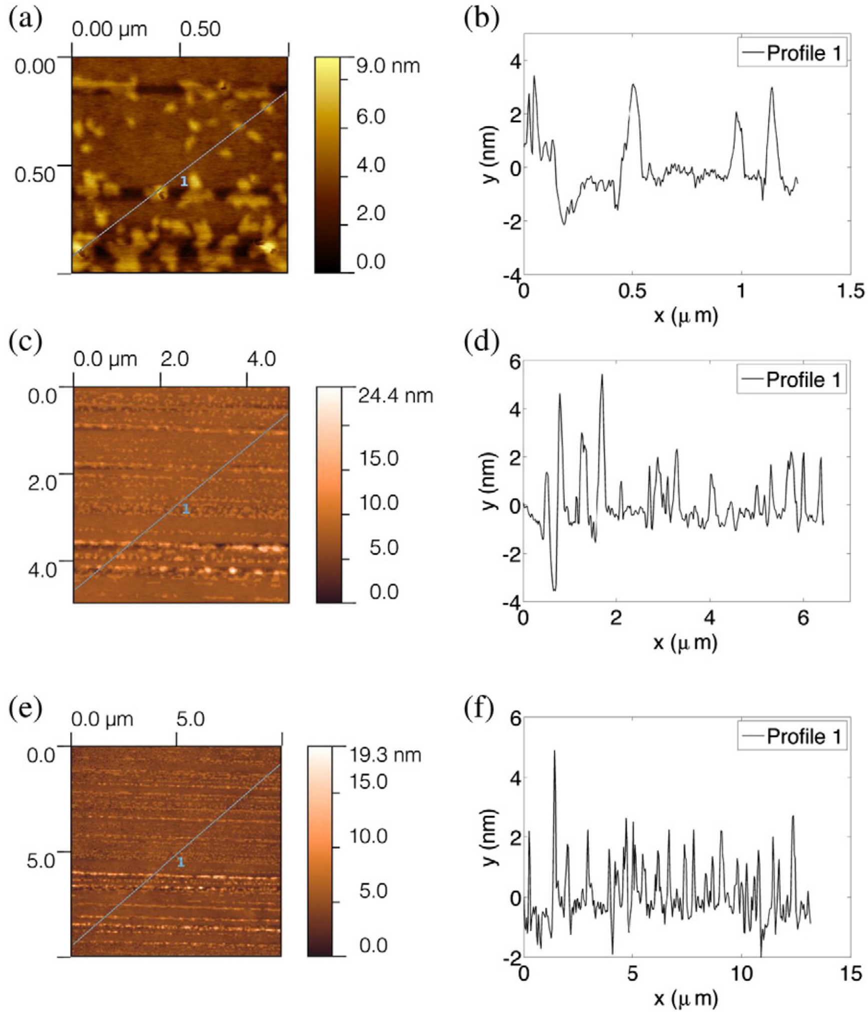

Fig. 2. Two-dimensional tapping mode in air AFM images of SiO_2-TiO_2 thin film prepared onto a commercial glass substrate by sol-gel dip-coating for scan areas of 1 µm (a), 5 µm (c) and 10 µm (e), and section profiles recorded along the grey line indicated (b), (d) and (f).

respectively. The sign of the imaginary part of the refractive index indicates if we have a media with gain ($k < 0$) or loss ($k > 0$). The real part of $g(z)$ determines the transverse parabolic profile while the imaginary part is related to the effect of gain or loss on both profiles, respectively. The active material is regarded as a beam shaper system when a specific condition on the beam waist is verified [10].

The planar active GRIN material can be obtained by consecutive deposition on the glass substrate of sol-gel coatings with different complex refractive indices n_1, n_2,..., n_m (m is an integer) as shown in Fig. 1a). In this manner, a final multilayer GRIN structure, characterized by a complex refractive index with a parabolic-like profile distribution for both its real and imaginary part (Fig. 1b), can be generated.

3. Experimental and characterization

3.1. Sol preparation

A series of Er^{3+}-doped $70SiO_2$-$30TiO_2$ sols in the range 0–2.0 at.% of Er were prepared using methyltriethoxysilane (MTES, $CH_3Si(OCH_2CH_3)_3$, 98%, ABCR) and titanium isopropoxide (TISP, $Ti[OCH(CH_3)_2]_4$, 97%, ABCR) (precursors for silica and titanium, respectively) in acid environment. The preparation process was identical for all sols and conducted in two steps. Initially, MTES is pre-hydrolyzed in the presence of HCl (0.1N) with ethanol as solvent. Then, this mixture is stirred for 1 h at room temperature. Titanium isopropoxide is dissolved in ethanol and complexed by adding glacial acetic acid (AcH). After stirring for 1 h, this second sol is mixed to the MTES sol and then distilled water is added drop by drop until hydrolysis is completed. Finally, erbium nitrate pentahydrate ($Er(NO_3)_3 \cdot 5H_2O$, 99.9%, ABCR) is also added to the mixture, and maintained under stirring for one more hour. The ratios used for the preparation of the sol were silica/titania = 70/30, H_2O/Alcoxides = 1.5 and Alcoxides/AcH = 1 with final concentration of 100g/l. Table 1 lists the different atomic percentage of erbium precursor used.

3.2. Film deposition by dip-coating

Films were deposited on well-cleaned commercial glass substrates by dip-coating technique using a withdrawal rate of 20 cm/min for SiO_2-TiO_2 coatings and 10 cm/min for Er-SiO_2-TiO_2 coatings. Substrates were first washed in distilled water, dried and finally washed in ethanol. Further, the coatings were heat treated at 450 °C for 30 min using a ramp rate of 10 °C/min in air atmosphere. One advantage of the sol-gel process is that coatings with high optical quality using low sintering temperature can be obtained. The decrease of the sintering temperature is crucial with a view to future industrial application.

The SiO_2-TiO_2 system was selected because the variation of SiO_2/TiO_2 molar ratios allows to obtain optical layers with intermediate refractive index between the SiO_2 and TiO_2 (n = 1.46 and n = 2.7, respectively, at wavelength of 632.8 nm). In particular, $70SiO_2$:$30TiO_2$ composition was selected taking into account that we are interested on coatings with thick thickness around 200 nm and refractive indices

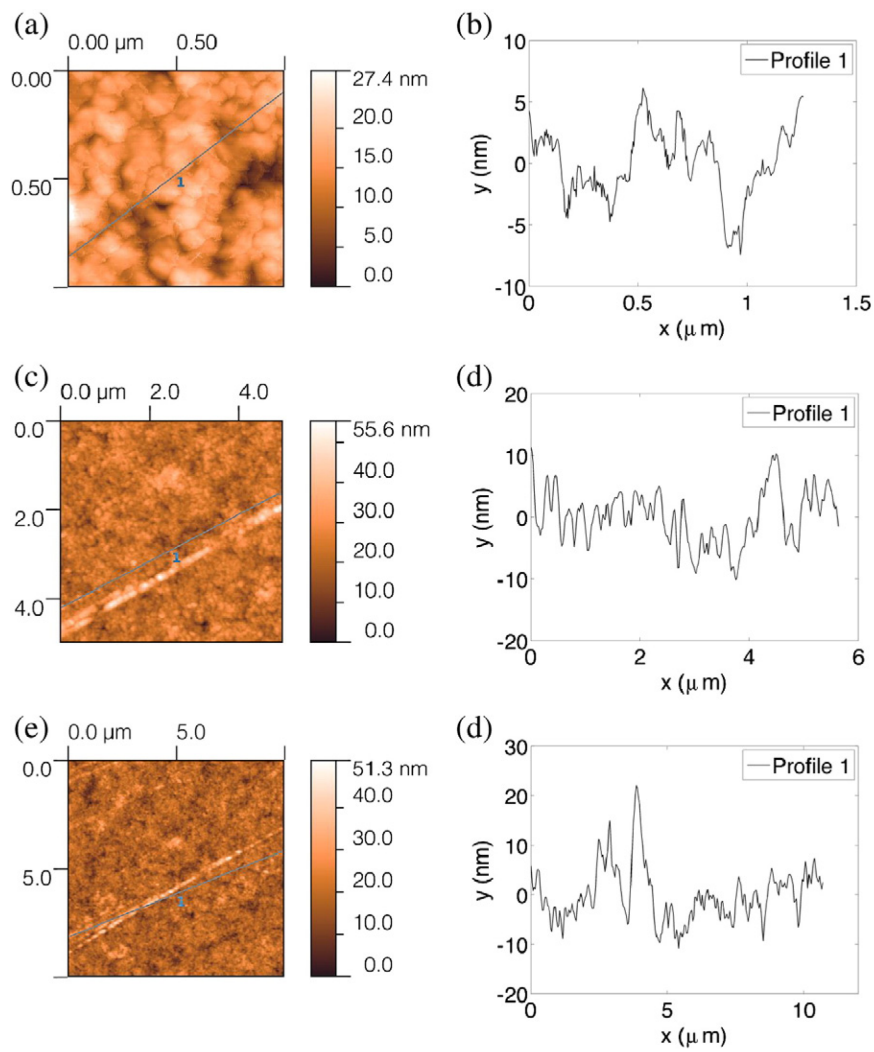

Fig. 3. Two-dimensional tapping mode in air AFM images of 0.3%-Er SiO_2-TiO_2 thin film prepared onto glass substrate by sol-gel dip-coating for scan areas of 1 µm (a), 5 µm (c) and 10 µm (e), and section profiles recorded along the grey line indicated (b), (d) and (f).

in the interval (1.5–1.65). In addition to this, the incorporation of dopants such as rare-earths is possible. On the other hand, the use of glass substrates allows cost minimization due to their reduced prices and that the fabrication process can be carried out at low temperatures.

3.3. Characterization of erbium-doped SiO_2-TiO_2 thin films

3.3.1. Atomic force microscopy

The thin films obtained by dip-coating immersion technique were examined by atomic force microscopy (AFM). The experiments were performed using a Bruker Dimension Icon® Atomic Force Microscope, at the International Iberian Nanotechology Laboratory (INL). The microscope was operated under intermittent contact mode, also referred to as tapping mode, in air at a line scan rate of 1–2 Hz. The cantilever tip had a height of 10–15 µm and a tip radius of 10 nm. Typical cantilever resonance frequency varied between 350 and 367 kHz at a force constants between 20 and 80 Nm^{-1}. The scan sizes were 1, 5 and 10 µm. Images were analysed using Gwyddion software.

3.3.2. Spectral ellipsometry

Ellipsometry is an optical and non-destructive technique that can provide significant insight into film structures. It is commonly used to determine thin films properties as thickness (h), optical constants (n, k) and percentage of porosity (Π) of thin films through an analysis of the state of polarization of the light that is reflected from the sample [18]. Ellipsometry measurements were performed using a Spectral Ellipsometer (M-2000UTM, J.A. Co., Woollam), at the *Instituto de Cerámica y Vidrio* (ICV). The spectra were taken in the wavelength range of 400 and 1000 nm at incident angles of 65°, 70° and 75°. To analyse the collected data, all angular spectra is combined and the fitting is performed considering all the data simultaneously. The data were fitted with WVASE32 software using Cauchy model.

Based on measured refractive index n, and assuming that the pores of the layer are filled up solely with air, their porosity percentage Π can be determined using the following equation [19,20],

$$\Pi = 1 - \left[\frac{n_p^2 - 1}{n_p^2 + 2}\right] \Big/ \left[\frac{n_b^2 - 1}{n_b^2 + 2}\right] \quad (3)$$

where n_p and n_b correspond to the refractive index of the reference film (the undoped film in this study) and the refractive index of the erbium-doped film, respectively.

4. Results and discussion

4.1. AFM morphological analysis of erbium-doped SiO_2-TiO_2 thin films prepared by sol-gel dip-coating process

Figs. 2, 3, 4 and 5 show atomic force microscopy (AFM) images of non-doped and erbium-doped monolayers in atomic percentages 0.3

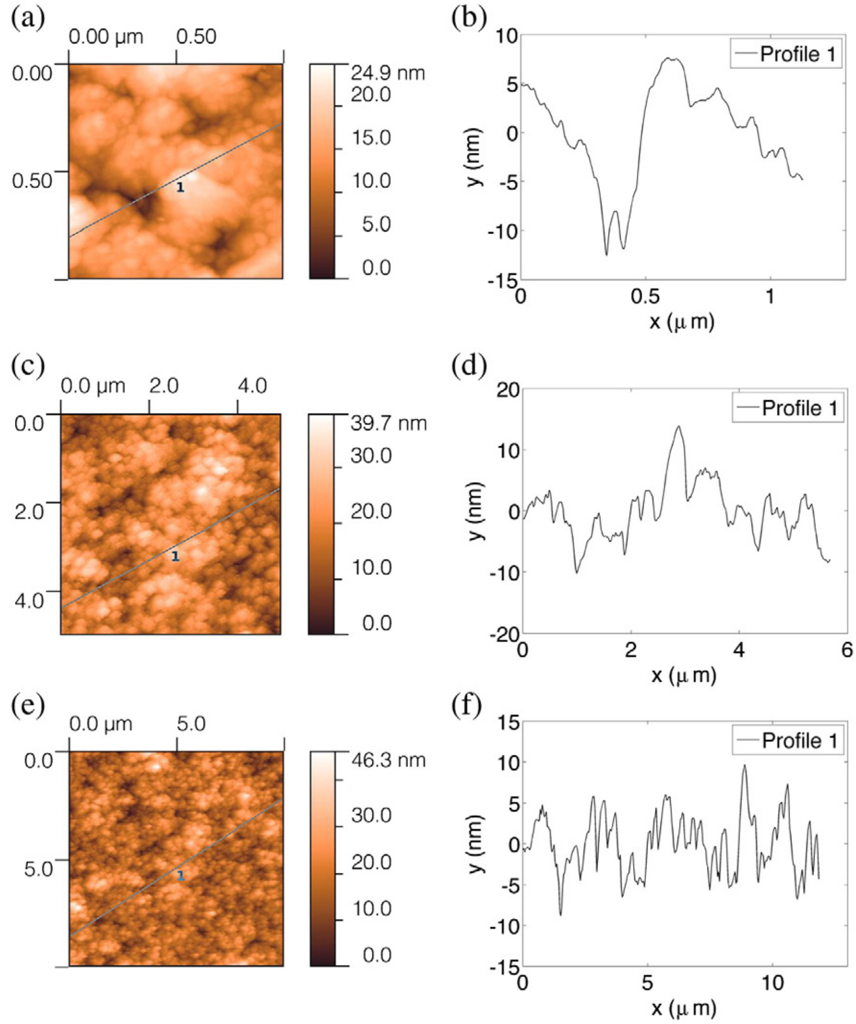

Fig. 4. Two-dimensional tapping mode in air AFM images of 1%-Er-SiO_2-TiO_2 thin film prepared onto glass substrate by sol-gel dip-coating for scan areas of 1 µm (a), 5 µm (c) and 10 µm (e), and section profiles recorded along the grey line indicated (b), (d) and (f).

to 2 at.% deposited onto commercial glass substrates by sol-gel dip-coating and after annealing at 450 °C. From the topographical data, the most commonly roughness parameters, the arithmetic roughness (R_a) and the root-mean-square roughness (R_q or R_{rms}), were evaluated [21]. Both parameters have a positive correlation, i.e., higher values mean greater topographical variation. While R_a and R_q describe the magnitude of the roughness-larger values correspond to rougher, surfaces skewness (R_{sk}) and kurtosis (R_{ku}) describe the distribution of the sample height. Skewness (R_{sk}) is a measure of the average of the first derivative of the surface, i.e., the departure of the surface from symmetry. A negative value of R_{sk} indicates that the surface is made up of valleys, whereas a surface with a positive skewness is said to contain mainly peaks and asperities. Therefore, a negatively skewed surface is good for lubrication purposes. On the other hand, kurtosis describes of sharpness of profile peaks. A distribution with high kurtosis would have a small number of extreme heights (i.e., a few very high peaks or very low valleys), as opposed to many moderate height features (which will give lower, or negative kurtosis values). The results have been listed in Table 2, showing that smooth surfaces are obtained. The smallest surface roughness values were obtained for sample A (Table 1).

No significant change in the topography of the films from no-doped, 0.3% and 1%Er-SiO_2-TiO_2 films was observed during the visual inspection of AFM images. In general, the topography shows irregular granules of different shapes, sizes and separations. However, the doped film with 2 at.% erbium (sample D) shows significantly structural changes with respect to the other films. The AFM image shows a surface topography such as honeycomb structured porous. The pore size diameter was estimated to 250 nm. As a general feature exposed by AFM analysis, it can be appreciated that valleys, mountains and island clusters become higher as erbium concentration increases.

In Table 2, we can see that both the arithmetic roughness and root-mean-square have larger values as erbium concentration increases. R_a and R_q values also increase as function of the inspected scan area of the sample. For samples A, B and C, skewness has mostly positive values close to zero, which indicates a surface with no accentuated protruding features. On the contrary, sample D has a negative skewness for all scan areas, meaning that there are pits or depressions in the surface. Kurtosis values are higher for samples A and D, showing that the surfaces have a small number of extreme heights, while samples B and C have lower kurtosis values, meaning that there are moderate height features.

4.2. Optical constants and porosity by spectral ellipsometry

From the fitting of ellipsometric spectra, using Cauchy dispersion model, the optical constants, refractive index and extinction coefficient in the wavelength range from 400 nm to 1000 nm, and thickness of doped and undoped SiO_2-TiO_2 coatings were obtained. The refractive index remains below to undoped SiO_2-TiO_2 film (see Fig. 6a). At $\lambda =$ 633 nm refractive indexes of 1.612, 1.597, 1.571 and 1.529 were obtained for samples A, B, C and D, respectively. The evolution of the refractive index for Er-doped coatings indicates that there is a significant

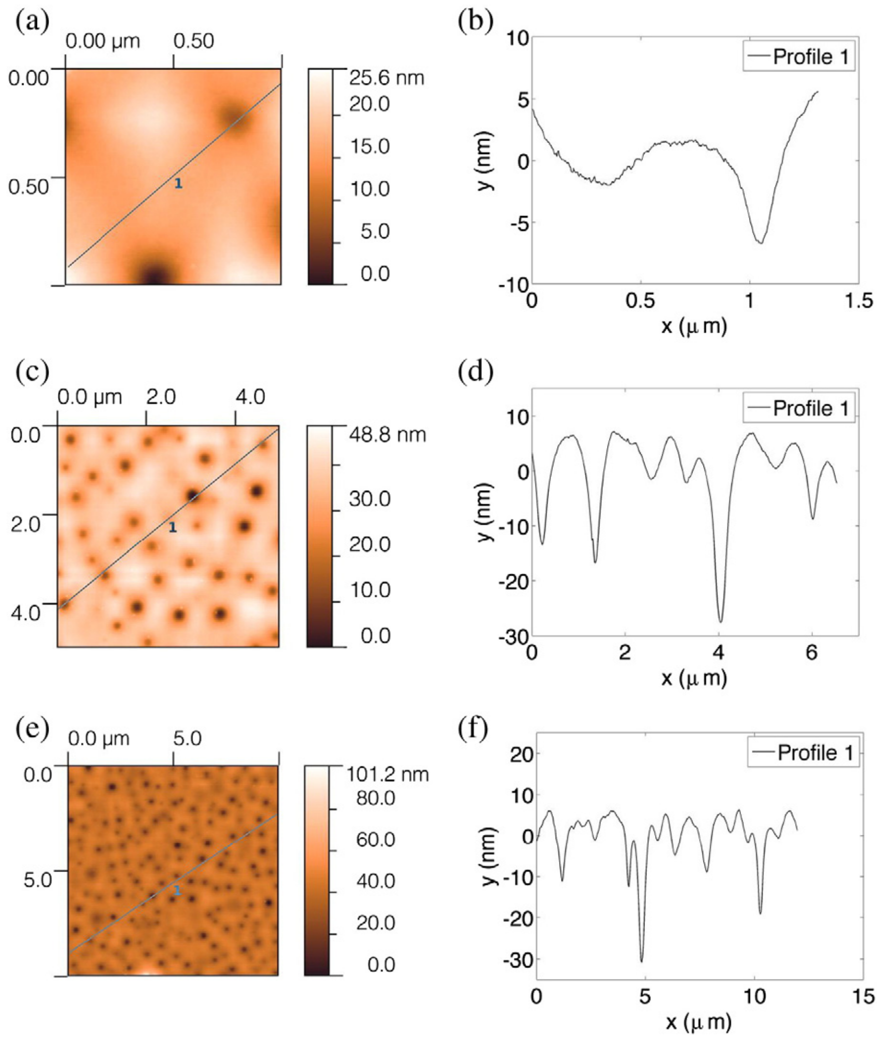

Fig. 5. Two-dimensional tapping mode in air AFM images of 2%- Er-SiO_2-TiO_2 thin film prepared onto glass substrate by sol-gel dip-coating for scan areas of 1 µm (a), 5 µm (c) and 10 µm (e), and section profiles recorded along the grey line indicated (b), (d) and (f).

decrease of n with the dopant, while the porosity of the coating enhances with the dopant concentration. It can be seen in Fig. 5 that the size and number of porous in sample D has notably increased in relation to samples A, B and C. In order to determine the relative porosity of the erbium-doped films, Eq. (3) was used. Porosity values of 2%, 5.4% and 11.25% were determined as a function of dopant concentration.

The spectral dependence of extinction coefficient is represented in Fig. 6b. Positive values of k in the wavelength range from 400 nm to 1000 nm are obtained, which are suitable for fabrication of an active GRIN media with loss by multilayering deposition. The behaviour of k is similar for samples A, B and C; however, a significant difference is evidenced for sample D, with the highest value of the extinction coefficient along the whole spectral range, which is most likely due to the disparity of the surface morphology (Fig. 6b) compared to the other deposited samples.

Finally, the thickness of the films is measured and values between 230 and 300 nm were obtained (see Fig. 7).

Table 2
Arithmetic roughness (R_a), root-mean-square roughness (R_q), skew (R_{sk}) and kurtosis (R_{ku}) of the A, B, C and D samples.

Er concentration (at.%)	Scan size (µm)	T (°C)	R_a (nm)	R_q (nm)	R_{sk}	R_{ku}
0	1	450	0.702	1.008	0.432	1.99
	5	450	0.82	1.28	2.41	11.7
	10	450	1.11	1.55	1.57	6.91
0.3	1	450	3.16	3.90	−0.103	−0.261
	5	450	3.88	5.25	0.818	2.96
	10	450	3.53	4.67	0.548	2.28
1	1	450	2.6	3.46	−0.168	0.61
	5	450	4.19	5.31	0.121	0.027
	10	450	4.06	5.25	0.42	0.908
2	1	450	2.15	3.08	−0.991	3.59
	5	450	4.10	5.74	−1.55	3.93
	10	450	4.14	5.81	−1.36	5.57

5. Conclusions

This study is focused on the preparation of active GRIN materials described by a complex, parabolic-like refractive index distribution for beam shaping purposes. The fabrication of active GRIN materials by optically active multilayer stacks growing by sol-gel chemical procedure has been proposed. By tailoring the precursors concentration in a suitable way, thin film optical properties can be selected for the desired application. In this way, non-doped and erbium-in atomic percentages in the range 0.3 to 2 at.%-doped monolayers were deposited onto commercial glass substrates and characterized by means of atomic force microscopy and spectral ellipsometry. On the one hand, AFM images of the as-deposited and annealed films reveal smooth surfaces and the formation of a porous granular structure where valleys, mountains and island clusters become bigger as films erbium

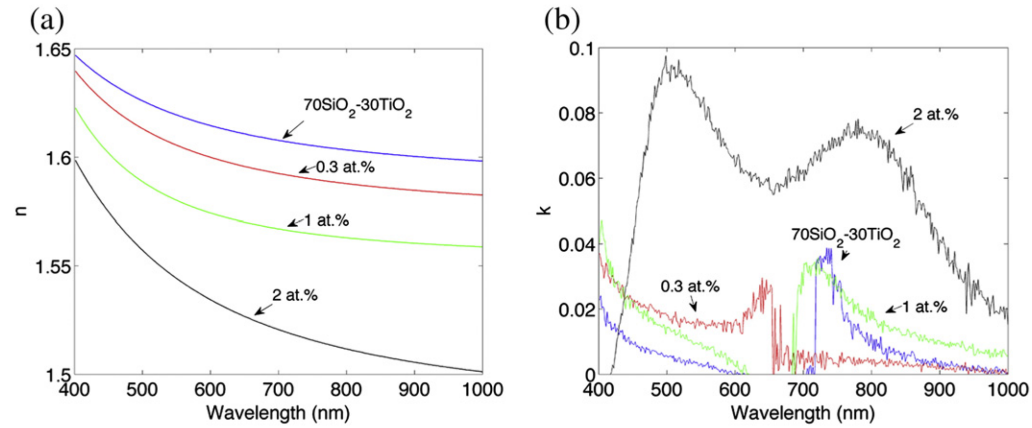

Fig. 6. Ellipsometric measurements of the erbium-doped SiO_2-TiO_2 sol-gel thin films compared to undoped SiO_2-TiO_2 coating: (a) Refractive index, *n*, and (b) extinction coefficient, *k*, versus wavelength, λ, of the studied samples.

concentration increases. The surface roughness values are in the range between 1.11 nm and 4.14 nm for a 10 μm scan size. On the other hand, spectral ellipsometry measurements show that the refractive index decreases with increasing dopant concentration and remains below to undoped SiO_2-TiO_2 film, while thicknesses in the range 230–300 nm were obtained. Besides, changes of the extinction coefficient with wavelength are also presented showing as the most relevant feature that nonzero extinction coefficient, together with a larger value compared to the rest of deposited samples, is obtained for the 2 at.% Erbium-doped film. Finally, porosity of the films was determined by using the refractive indices of the films determined by spectral ellipsometry, demonstrating that the most porous film is obtained to higher erbium concentration. Further studies on preparation of active GRIN materials using the sol-gel technology are currently in progress.

Acknowledgments

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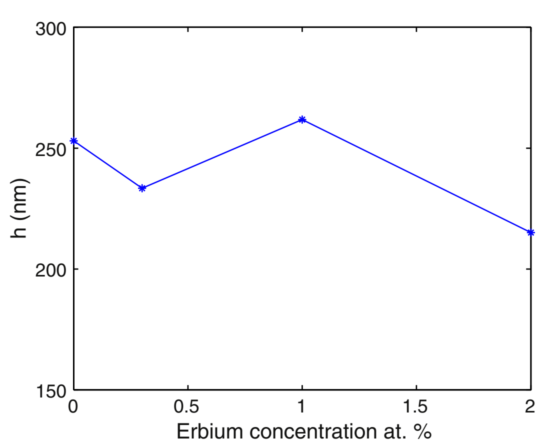

Fig. 7. Thickness of the deposited undoped and Er-doped SiO_2-TiO_2 thin films as a function of dopant concentration.

References

[1] L.C. Klein, Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Specialty Shapes, 1st edition William Andrew, Park Ridge, N.J., U.S.A., 1989
[2] F. Rey-García, C. Gómez-Reino, M.T. Flores-Arias, G.F. De La Fuente, A. Durán, Y. Castro, Sol–gel coatings: an alternative route for producing planar optical waveguides, Thin Solid Films 519 (22) (2011) 7982.
[3] S.M. Attia, Jue Wang, Guangming Wu Jun Shen, Jianhua Ma, Review on sol-gel derived coatings: process, techniques and optical applications, J. Mater. Sci. Technol. 18 (03) (2002) 211.
[4] E.M. Yeatman, M.M. Ahmad, O. McCarthy, A. Martucci, M. Guglielmi, Sol-gel fabrication of rare-earth doped photonic components, J. Sol-Gel Sci. Technol. 11 (19) (2000) 231.
[5] R.R. Gonçalves, Y. Messaddeq, A. Chiasera, Y. Jestin, M. Ferrari, S.J.L. Ribeiro, Erbium-activated silica-zirconia planar waveguides prepared by sol-gel route, Thin Solid Films 516 (2008) 3094.
[6] Y. Qiao, N. Da, D. Chen, W. Ma, Q. Zhou, J. Qiu, Spectroscopic properties of Nd3+, Yb3 + -doped and Nd3 + –Yb3 + -codoped high silica glass, J. Mater. Sci. 44 (2009) 4026.
[7] Rui M. Almeida, Ana C. Marques, Rare earth-doped photonic crystals via sol–gel, J. Mater. Sci. Mater. Electron. 20 (2009) S307.
[8] Fred M. Dickey, Scott C. Holswade, Laser Beam Shaping: Theory and Techniques, CRC Press, New York, 2000.
[9] F.M. Dickey, S.C. Holswade, D.L. Shealy, Laser Beam Shaping Applications, CRC Press, 2005.
[10] A.I. Gómez-Varela, M.T. Flores-Arias, C. Bao-Varela, C. Gómez-Reino, Focusing, collimation and beam shaping by active GRIN rod lenses: theory and simulation, Opt. Lasers Eng. 50 (2012) 1706.
[11] M. Ebelmen, C. R. Acad. Sci. Fr. 21 (1845) 502.
[12] L.C. Klein, Sol-Gel Optics: Processing and Applications, Springer Science & Business Media, 1994.
[13] R. Reisfeld, T.s. Saraidarov, Innovative materials based on sol-gel technology, Opt. Mater. 28 (2006) 64.
[14] R. Reisfeld, New materials for nonlinear optics, in: R. Reisfeld, C.K. Jorgensen (Eds.), Optical and electronic phenomena in sol-gel glasses and modern applications, Structure and Bonding, 85, Springer 1996, p. 99.
[15] M. Yamane, J. Brian Caldwell, Duncan T. Moore, Preparation of gradient-index glass rods by the sol-gel process, MRS Proc. 73 (1986) 765.
[16] M. Yamane, A. Yasumori, M. Iwasaki, K. Hayashi, Graded index materials by the sol-gel process, Proc. SPIE, 1328, Sol-Gel Optics, 1990. 133.
[17] C. Gómez-Reino, M.V. Pérez, C. Bao, GRIN Optics: Fundamentals and Applications, Springer Verlag, Berlin, 2002.
[18] H. Fujiwara, Spectroscopic Ellipsometry: Principles and Applications, 1st edition Wiley, Chichester, England; Hoboken, NJ, 2007.
[19] E. Skoczek, J. Jaglarz, P. Karasiński, Ellipsometric and spectrophotometric investigations of porous silica thin films produced by sol-gel method, Acta Phys. Pol. A 120 (4) (2011) 732.
[20] M.R. Baklanov, K.P. Mogilnikov, V.G. Polovinkin, F.N. Dultsev, Determination of pore size distribution in thin films by ellipsometric porosimetry, J. Vac. Sci. Technol. B 18 (3) (2000) 1385.
[21] P. Eaton, P. West, Atomic Force Microscopy, Oxford University Press, Oxford; New York, 2010.