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Citation: Applied Physics Letters **81**, 28 (2002); doi: 10.1063/1.1489477
View online: http://dx.doi.org/10.1063/1.1489477
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/81/1?ver=pdfcov
Published by the AIP Publishing

Sol-gel Er-doped SiO_2-HfO_2 planar waveguides: A viable system for 1.5 μm application

R. R. Gonçalves[a] and G. Carturan
Dipartimento di Ingegneria dei Materiali, Università di Trento, Via Mesiano 77, I-38050 Trento, Italy

L. Zampedri and M. Ferrari
CNR-IFN, Istituto di Fotonica e Nanotecnologie, Via Sommarive 14, I-38050 Povo, Trento, Italy

M. Montagna and A. Chiasera
Dipartimento di Fisica and INFM, Università di Trento, Via Sommarive 14, I-38050 Povo, Trento, Italy

G. C. Righini and S. Pelli
CNR-IFAC, Istituto di Fisica Applicata "Nello Carrara," Via Panciatichi 64, I-50127 Firenze, Italy

S. J. L. Ribeiro and Y. Messaddeq
Institute of Chemistry-UNESP, P.O. Box 355, 14801-970, Araraquara, SP, Brazil

(Received 14 February 2002; accepted for publication 30 April 2002)

$70SiO_2-30HfO_2$ planar waveguides, doped with Er^{3+} concentrations ranging from 0.3 to 1 mol %, were prepared by sol-gel route, using dip-coating deposition on silica glass substrates. The waveguides show high densification degree, effective intermingling of the two components of the film, and uniform surface morphology. Propagation losses of about 1 dB/cm were measured at 632.8 nm. When pumped with 987 or 514.5 nm continuous-wave laser light, the waveguides show the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission band with a bandwidth of 48 nm. The spectral features are found independent both on erbium content and excitation wavelength. The $^4I_{13/2}$ level decay curves presented a single-exponential profile, with a lifetime between 2.9 and 5.0 ms, depending on the erbium concentration. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1489477]

The sol-gel technique is playing an increasing role in the development of optical materials for application in integrated optics.[1–3] In particular, SiO_2 based planar waveguides produced by sol-gel route, could be promising materials for Er-doped waveguide amplifiers (EDWA) to be used in metropolitan area networks.[1–5] The key requirements for developing EDWAs by the sol-gel route are: (i) refractive index and thickness of the film have to be tailored, in order to satisfy both single-mode condition at 1.5 μm and efficient coupling to fibers; (ii) the structural and optical homogeneity have to be optimized, in order to reduce losses and rare-earth clustering;[1,5] and (iii) the OH groups must be effectively removed, because the $^4I_{13/2}$ luminescence of OH^--coordinated Er^{3+} ions is completely quenched by two phonon-OH mechanism.[6,7] Among the silica-based systems, binary SiO_2-TiO_2 has been widely used to produce Er-activated planar waveguides by sol-gel route.[1,2,8,9] However, in the silica-titania system, there is a tendency for separation between SiO_2-rich and TiO_2-rich phases. Undesirable phase precipitation can take place as a consequence of the thermal treatment, necessary to achieve full densification of the film, or during the reflow process.[10,11] The reduction of nanoscale homogeneity induces an increase in the optical attenuation.[12] Moreover, the precipitation of passive titania crystalline phases drastically shortens the lifetime of the $^4I_{13/2}$ level.[4]

Hafnium, like Ti, belongs to group 4 in the periodic table. Its oxide is transparent over a wide range of wavelengths and exhibits high refractive index.[13] For these reasons, the SiO_2-HfO_2 binary system could be a useful candidate for waveguide preparation. However, only a few papers report on HfO_2-based films obtained by the sol-gel route.[14–16]

This letter presents preliminary results on the fabrication of erbium activated SiO_2-HfO_2 planar waveguides prepared by the sol-gel method.

The starting solution, obtained by mixing tetraethylorthosilicate (TEOS), ethanol, de-ionized water, and hydrochloric acid as a catalyst, was prehydrolysed 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 $HfOCl_2$[16] and then added to the TEOS solutions, with a Si/Hf molar ratio of 70/30. Erbium was added as $Er(NO_3)_3 \cdot 5H_2O$ with a $Er/(Si+Hf)$ molar concentration ranging from 0.3 to 1 mol %. The final mixture was left at room temperature under stirring for 16 h. The obtained sol was filtered with a 0.2 μm Millipore filter. Erbium-activated silica-hafnia films were deposited on silica 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. After ten dipping cycles, the film was heated for 2 min at 900 °C. Final films, resulting from 20 coatings, were stabilized by the last treatment for 5 min in air at 900 °C. As a result of the procedure, transparent and crack-free waveguides were obtained. The deposition conditions were the same for all samples.

The thickness of the waveguides and the refractive index at 632.8 and 543.5 nm, were measured by an *m*-line apparatus based on the prism coupling technique.[16] The losses at 632.8 nm, for the TE_0 mode, were evaluated by photometric

[a]Author to whom correspondence should be addressed; electronic mail: rocha@science.unitn.it

TABLE I. Optical and spectroscopic parameters of the Er^{3+}-activated $70SiO_2-30HfO_2$ planar waveguides.

Waveguide label	W3	W5	W10
Er^{3+} mol %	0.3	0.5	1.0
Thickness (± 0.05 μm)	0.60	0.62	0.68
Number of modes @ 632.8 nm	2	2	2
Number of modes @ 543.5 nm	2	2	2
Refractive index			
@ 632.8 nm (± 0.005) (TE)	1.627	1.627	1.627
(TM)	1.614	1.614	1.614
@ 543.5 nm (± 0.005) (TE)	1.633	1.633	1.633
(TE)	1.620	1.620	1.620
Attenuation coefficient			
@ 632.8 nm (± 0.3 dB/cm)	1.0	1.2	1.4
Bandwidth (± 2 nm)			
Excitation @ 514.5 nm	49	48	48
Excitation @ 987 nm	48	48	47
Lifetime (± 0.5 ms)			
Excitation @ 514.5 nm	5.0	4.2	2.7
Excitation @ 987 nm	5.0	4.1	2.9

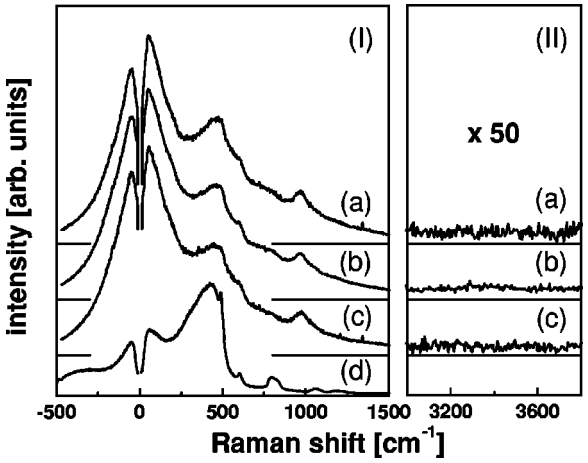

FIG. 1. Raman spectra of (a) W3, (b) W5, and (c) W10 planar waveguides, collected in VV polarization with excitation of the TE_0 mode at 457.9 nm (I) and 514.5 nm (II). The Raman spectrum of the v-SiO_2 (d) is also reported for comparison.

detection of the light intensity scattered out of the waveguide plane.[12,16] The TE_0 mode waveguiding excitation was used for both Raman and photoluminescence measurements, with the scattered light being detected from the front of the waveguide. The Raman spectra were collected in VV polarization. Standard lock-in techniques were employed for photoluminescence (PL) measurements, in the region of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions. The details about the experimental setup were previously reported.[7,9,11]

The optical and spectroscopic parameters are reported in Table I.

All samples support two TE and TM modes at 632.8 and 543.5 nm and the refractive index of the waveguides does not change with the Er^{3+} content. The refractive index of the waveguides is in rough agreement with the value calculated at 633 nm by the Lorentz–Lorenz equation using $n=1.457$ and $n=1.97$ for the refractive index of SiO_2 and HfO_2, respectively. This is an indication that a high densification degree has been achieved. For all samples and both at 632.8 and 543.5 nm the refractive index measured in TE polarization is higher ($\Delta n=0.013$) than in TM polarization, indicating that birefringence is not negligible in our system. Propagation loss ranging from 1 to 1.4 dB/cm is measured. Scanning electron microscopy micrographs, obtained by an JEOL-JSM 6300 apparatus at 15 kV, show a uniform surface morphology for all samples with absence of structures up to a magnification 40 000×.

Further indications about the structural properties of the waveguides are obtained by Raman measurements. Figure 1 shows the Raman spectra of the $70SiO_2-30HfO_2$ planar waveguides: (a) W3, (b) W5, and (c) W10. The Raman spectrum of the v-SiO_2 is also reported for comparison [Fig. 1(I)(d)].

As observed comparing the Raman spectra of the silica-hafnia waveguides (W3, W5, W10) with that of the fused silica [Fig. 1(I)], the presence of hafnium oxide promotes a strong modification of the silica structure. The disruption of silica network is indicated by: (i) the broadening of the Raman bands; (ii) the decrease of the intensity of the band at about 800 cm^{-1}, attributed to skeletral network Si–O–Si symmetric stretching; (iii) the absence of the 490 cm^{-1} D1 sharp defect band, assigned to the $(SiO)_4$-ring vibration; (iv) the absence of the bands at 1060 and 1190 cm^{-1} proper of the silica network; (v) the strong intensity of the boson peak, at about 55 cm^{-1}, which dominates the Raman spectrum; and (vi) the presence of the band centered at 970 cm^{-1}, attributed to the Si–O–Hf stretching.[15] The appearance of the 970 cm^{-1} Raman band suggests the effective molecular mingling of SiO_2 and HfO_2 components of the films. A complete densification is achieved for all samples. In fact, the bands characteristic of the OH groups in silicate glasses, generally observable at 3670 and 3750 cm^{-1}, are absent in the portion of the Raman spectra shown in Fig. 1(II).[7,9] The Raman spectra do not show any evidence of hafnia crystallization, that would display several sharp peaks in the region between 100 and 800 cm^{-1}.[17,18]

The PL spectra relative to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of the Er^{3+} ions for the W3 waveguide were obtained upon excitation at 987 nm (inset of Fig. 2) and 514.5 nm, with a pump power of 110 and 180 mW, respectively. The PL spectrum in the inset of Fig. 2 exhibits a main emission peak at 1.53 μm with a shoulder at about 1.55 μm and a spectral

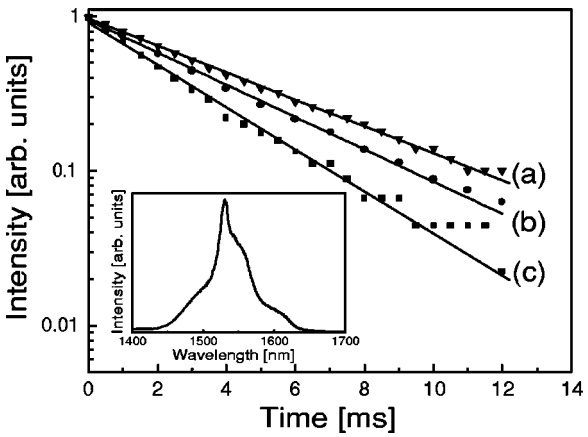

FIG. 2. Decay curves of the luminescence from the $^4I_{13/2}$ metastable state of Er^{3+} ions in the (a) W3, (b) W5, and (c) W10 planar waveguides, upon 987 nm excitation. The solid lines represent single exponential fits to the decay data. PL spectrum of Er^{3+} ions for W3 waveguide, upon 987 nm excitation, is reported in the inset.

bandwidth of about 48 nm, measured at 3 dB from the maximum of the intensity. The shape and the bandwidth of the emission spectra do not change with the excitation wavelength, indicating negligible site selection. The PL spectra of the W3, W5, and W10 waveguides are quite similar, according to a constant site-to-site inhomogeneity, at least for Er^{3+} content up to 1 mol % (see Table I). This fact may not be trivial and deserves some comments. In our SiO_2-HfO_2 matrices characterized by full densification and molecular homogeneity, Hf^{4+} calls for coordination numbers higher than four with maintenance of Hf–O–Si bonds, which lead to the prouved disruption of SiO_2 network. As a consequence, Hf^{4+} increases the number of Si–O nonbridging groups[15] accounting for a general network flexibility,[19] which may conceivably accommodate Er^{3+} contents without appreciable matrix strains.

Figure 2 shows the decay curve of the $^4I_{13/2}$ metastable state obtained upon 987 nm excitation, for the W3, W5, and W10 waveguides. The curves can be fitted by a single exponential function and a lifetime of 5.0 ms (W3), 4.1 ms (W5), and 2.9 ms (W10), is obtained (see Table I). The same lifetimes were measured upon 514.5 nm excitation. The decrease of the lifetime with the increase of the erbium concentration suggests that energy transfer processes, including crossrelaxation and upconversion, are effective. In fact, infrared-to-green upconversion upon 987 nm excitation is observed in all the waveguides, green emission being visible with the naked eye.

In conclusion, Er^{3+}-activated $70SiO_2-30HfO_2$ planar waveguides with valuable optical and structural properties can be prepared by the sol-gel technique with dip-coating processing. Measurements are in progress to detail the microstructure of this composite with the aim of improving its spectroscopic features for successful EDWA fabrication.

The authors are indebted to C. Armellini, R. Belli, and E. Moser for their invaluable technical support. This research was performed in the context of the CNR-ICCTI and CNR-CNCPRST projects.

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