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journal homepage: www.elsevier.com/locate/optmat Structural and optical characterization of $\text{ZrO}_2\text{:CeO}_2$ slab waveguides obtained via sol–gelF. Rey-García^{a,*}, M.T. Flores-Arias^{a,*}, C. Gómez-Reino^a, G.F. De La Fuente^{b,*}, W. Assenmacher^c,
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ABSTRACT

Planar multilayer $\text{ZrO}_2\text{:CeO}_2$ slab waveguides were prepared by a sol–gel route and dip-coating technique onto commercial glass substrates. The coatings were microstructurally characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and by optical confocal microscopy. Coating thicknesses of ca. 500 nm and refractive index values of 2.069 ± 0.001 and 2.087 ± 0.001 , respectively for TE and TM light polarization modes, were calculated by Dark m-line spectroscopy. This is consistent with the birefringent character of the coating, associated to the presence of anisotropic crystalline phases within the coating's vitreous matrix. Finally, propagation losses of 0.9 ± 0.2 and 1.5 ± 0.2 dB/cm were determined by the scattered light measurement for TE and TM polarization modes, respectively.

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1. Introduction

One of the most dynamic fields of investigation in optics is related to the preparation of planar waveguides. A number of methods and materials have been used during years by researchers to obtain planar waveguides [1–8]. These techniques include, in many instances, the use of vacuum systems [2], different types of lasers [1–6], or even ion accelerators [7], which usually increase process costs significantly. Varying coating and substrate compositions have been explored, in many cases based on the use of expensive raw materials or on complex and economically expensive production processes, implying a disadvantage towards their application at an industrial scale.

Several authors have recently focused their attention on glasses based on oxides of heavy elements (TeO_2 , GeO_2 , Bi_2O_3 , PbO , etc.) as promising materials for photonic devices [9–11]. The preparation of these materials is based on the use of toxic constituents, specialty reactants or, in some cases, special atmospheres or high

melting temperatures. All of these also increase the cost of the final, desired waveguide.

An alternative method to obtain planar waveguides is based on sol–gel methodology [12], which is widely used in different fields of science and technology. For example, biosensors [13], bulk materials [14], superconductors [15], fuel cells [16], ceramic composites [17], which include a wide range of compositions, have been obtained by sol–gel processing. For the present purpose, the latter is a convenient method to obtain coatings with controlled thickness and refractive index. The sol–gel process is suitable to produce both thin and thick films by single and multi-deposition techniques. Channel waveguides with different geometries can be obtained afterwards by techniques like selective etching. Film coatings can be also deposited with the sol–gel technique. Several papers dealing with planar waveguides prepared with this method have been reported in the literature and are worthy of mention [18–23].

The microstructure of sol–gel derived coatings, thus their optical properties, is affected by different parameters involved in their synthesis. These include starting materials and thermal processing conditions, among others [24–26]. The optimization and control of all these parameters enable the use of the sol–gel technique for the fabrication of waveguides [12]. These help to attain coatings with

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low surface roughness, an important advantage provided by sol-gel to significantly decrease propagation losses.

Different studies have been published on the zirconia-ceria system and, in most cases, the synthesis method employed chloride precursors [27–30]. Generally, published literature reports have appeared centered on the study of zirconia films stabilized with ceria. Although some authors report their use as anticorrosive protection films [29], one of their main applications is related to their use in automotive exhaust, three-way catalysts, and as an electrolyte for solid oxide fuel cells (SOFCs) [30,31].

Concerning microstructural studies, only a few authors have employed transmission electron microscopy (TEM) to study the structural characteristics found between sol-gel derived films and substrates near their interface. Several papers report, however, on the study of thin films not obtained by sol-gel, specifically their interfaces and their crystalline structures using TEM [32–34].

The sol-gel system studied in this work is based on the combination of zirconia-ceria oxides from solutions of alkoxide precursors, following the acid catalyzed route. The $\text{ZrO}_2\text{:CeO}_2$ (70:30) composition provides a high refractive index of ca. 2.0. As it is well-known, the guidance capability of a waveguide is based on the difference between the index of the waveguide and that of the substrate. As this difference increases, the guidance becomes stronger, allowing tighter bends and enhanced 'optical' integrability [35]. In order to realize the optical characterization in a system with sufficient thickness to be used in potential industrial applications, multilayer architectures were developed based on the zirconia-ceria sol, in order to obtain a multilayer structure by dip-coating onto commercial glass substrates [12,36]. The aim of this work is thus the microstructural and optical study of a slab waveguide, fabricated as a multilayer of $\text{ZrO}_2\text{:CeO}_2$ using the sol-gel method. The structural features and surface roughness of the sol-gel derived film were studied by electron microscopy and optical confocal microscopy, respectively. The presence of crystalline phases was studied by X-ray diffraction. Optical characterization of the multilayer film was performed using Dark m-line spectroscopy and waveguide losses were measured using the scattered light method. Dark m-line spectroscopy is a widely used technique for the characterization of planar optical waveguides, which allows access to important waveguide parameters, i.e. waveguide thickness and refractive index [35,37–39].

2. Experimental

Inorganic zirconia-ceria (ZrCe) sol was prepared by acid catalysis of tetraisopropoxyzirconate (TPZ: $\text{Zr}(\text{OCH}(\text{CH}_3)_2)_4$, 23–28% free alcohol, ABCR) in an ethanol solution during 1 h under stirring. Acetic acid was employed as a chelating agent to control hydrolysis and condensation reactions; cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) was used as cerium precursor, and was added in a dropwise manner to the ethanol solution. The sol, with molar ratio 70:30 of $\text{ZrO}_2\text{:CeO}_2$, must be kept at 4 °C during 1 day before use.

Firstly, the substrates were cleaned in an ultrasonic bath with absolute ethanol for 15 min [12]. The single layer coating was prepared by dip-coating the sol onto a commercial glass substrate at a withdrawal rate of 36.7 cm/min. Thermal treatment (calcination) was performed at 450 °C during 1 h. Multilayer coatings were obtained by dip-coating, applying successively the corresponding sol onto previously coated commercial glass substrates, at withdrawal rates of 24.5 cm/min. Two four-layer structures were prepared using intermediate heat treatments at 400 °C and 450 °C during 15 min, after each dip-coating step. The final heat treatments were carried out at 400 °C and 450 °C during 1 h, respectively.

Microstructural studies were carried on single layer step-index waveguides with TEM. The coated substrates were prepared in cross-section by gluing two samples face-to-face, followed by mechanical grinding and dimpling to a thickness of 20 µm; final

thinning was performed by ion beam milling. Imaging and microanalysis by energy-dispersive X-ray spectroscopy (EDXS) were conducted in a high-resolution transmission electron microscope operated at 300 kV (Philips CM 300 FEG/UT), equipped with an EDXS detector (HPGe detector, Noran Inc.) and analytical system (Noran Inc.). A Siemens D5005 X-ray diffractometer was used for the analysis of possible crystalline structures that may have formed within the coating during the heat treatment step.

The surface morphology was studied using a Sensofar Plu 2300 reflecting confocal microscope provided with reconstruction and analysis software. This technique was employed to measure the surface roughness in a statistical manner in the Confocal mode. According to the manufacturer, the use a 100× objective lens provides a vertical resolution below 3 nm within a scanning area of $123 \times 92 \mu\text{m}^2$.

The mono and multilayer coatings were optically characterized by Dark m-line spectroscopy [37]. The waveguide propagation loss measurements were performed by the scattered light method on 500 nm-thick, multilayer samples.

The Dark m-line spectroscopy, determined with the COMPASSO instrument, was used for the investigation of the TE and TM modes on sol-gel specimens. The equipment consists of a laser that strikes on an isosceles prism placed in contact with the sample (optical contact is achieved applying pressure). The prism/waveguide set is placed onto a rotational stage to allow variation of the incidence angle. The light reflected at the prism/waveguide interface (by total internal reflection) is recorded by a photodiode. At certain angles, when the modes of the waveguide are coupled, a minimum of the intensity of the reflected light signal, which is monitored by a photodiode, is detected. The basic scheme of the equipment is shown in Fig. 1. This apparatus is controlled by a computer with dedicated software. Two lasers are available with wavelengths of 635 nm and 1550 nm, as well as two prisms, made of GGG and Rutile, which allow measuring the refractive index between 1.5 and 1.9 and between 1.9 and 2.4, respectively. The thickness and the effective refractive index of each waveguide are calculated after a mathematical analysis of the data based on the WKB method [37]. The measure of the waveguide propagation losses is instead obtained by an image capture device, specifically a vidicon camera (Hamamatsu) which collects the light scattered out of the plane of the film (Fig. 2). Scattered light is assumed to be proportional to the guided light and the decay curve of scattered light along the propagation length can be fitted by an exponential curve to calculate the attenuation coefficient.

3. Results and discussion

Two kinds of structures were prepared to evaluate the quality of $\text{ZrO}_2\text{:CeO}_2$ (70:30) slab waveguides. The first sample studied was a 70:30 $\text{ZrO}_2\text{:CeO}_2$ single layer, denoted by ZrCe; this sample was microstructurally characterized by TEM to study the process involved in the coupling and bonding of the waveguide to the glass substrate. Previous sol-gel work has allowed development of multilayer structures in order to obtain waveguides with sufficient thickness to easily achieve laser light guidance and to characterize their propagation losses [36]. For this reason, a 70:30 $\text{ZrO}_2\text{:CeO}_2$ multilayer coating, named ZrCe-M, was also prepared onto commercial glass substrates. This was done by stacking up to 4 single layers in subsequent deposition and drying steps.

The study of the ZrCe sample allows us to observe a good level of adherence between the sol-gel coating and the glass substrate, as shown in the TEM image of a single layer (thickness ca. 140 nm) in Fig. 3. No discontinuities arising from cracks or mismatches are observed between both phases, identified clearly in the micrograph. The process responsible for the optimum chemical matching between the coating and the substrate materials was

Fig. 1. Scheme of the Dark m-line spectrometer. The light of the laser beam strikes on an isosceles prism placed in contact with the sample. The prism/waveguide set is placed onto a rotational stage, which allows varying the incidence angle. The light reflected at the prism/waveguide interface is monitored by a photodiode [37].

Fig. 2. Waveguide loss measurement setup. The light of the laser is coupled into the coating by a rectangular prism. A vidicon camera (Hamamatsu) collects the light scattered out of the plane along the film.

Fig. 3. TEM image of a ZrCe single layer sample prepared by dip-coating of the corresponding sol onto a glass substrate and heat treated at 450 °C. The TEM specimen is prepared and viewed in cross-section. A well-defined interface is observed between the apparently continuous and homogeneous coating and the substrate.

Fig. 4. XRD patterns (Cu K α radiation) of the commercial glass substrate (black), substrate with a ZrCe single layer (blue) and substrate with the ZrCe multilayer (red). The broad Bragg peaks at 30° and 50° 2-theta ($d = 2.99$ Å and 1.83 Å, respectively) correspond to tetragonal (Zr,Ce)O₂ which appear after heat treatment at 450 °C. Inset on top: calculated XRD-pattern of (Zr_{0.75}Ce_{0.25})O₂, $P4_2/nmc$, $a = 366.8$ pm, $c = 523.2$ pm [43]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

substrate region adjacent to the coating is depleted of alkali cations, compared to the original glass substrate.

After heat treatment, X-ray diffraction analyses show some degree of crystallinity in the multilayer samples (Fig. 4). The position of Bragg peaks can be assigned to tetragonal ZrO₂ and the broad peak width indicates nanometer-sized crystals. In fact, Crepaldi et al. [30] studied the preparation of thin films of Y₂O₃-ZrO₂ and Ce₂O₃-ZrO₂ by evaporation-induced self-assembly (EISA) and reported the presence of different ZrO₂ nanocrystalline particles. Their morphology was observed to depend on the annealing temperature; at 300 °C 3D cubic nanostructures were present, while 2D hexagonal structures were predominant at 500 °C. Moreover, Crepaldi et al. [30] observed that it is possible to obtain multilayers free of organic compounds at an annealing temperature of 400 °C. Ruiz et al. [40] and Sotelo et al. [41] have demonstrated that a combustion process takes place during formation of oxide films from sol-gel coatings. Combustion processes are supposed to raise the internal temperature of the substance via exothermic reactions far above the chosen annealing temperature. This is in agreement with the study of Liu et al. [28], who reported on the presence of tetragonal ZrO₂ within thin films with a composition of ZrO₂:CeO₂ = 87:13. These were prepared by the sol-gel technique and annealed at 600 °C, even though, according to the phase diagram

Fig. 5. Confocal micrograph of the surface of the ZrCe-M sample annealed at 450 °C. A relatively uniform surface is observed with an R_a value of 7 nm, just above the resolution limit of this microscope using a 100 $\times$ objective.

Table 1

TE and TM mode indices (± 0.001) obtained for ZrCe-M slab waveguides using the WKB method [37]. The refractive index of the commercial microscope slide employed as substrate is 1.512 ± 0.001 .

Wavelength	Prism	TE		Prism	TM
635 nm	rutile	N_0	2.011	rutile	N_0
	GGG	N_1	1.808	GGG	N_1
	GGG	N_2	1.532	–	–
1550 nm	rutile	N_0	1.883	rutile	N_0

Fig. 7. Experimental data representing the value of the intensity of the scattered light (proportional to the propagated power, y axis) versus the propagation length (x axis) for the TE polarization. Inset: CCD image of the slab waveguide guiding at 633 nm in TE polarization. The vertical light line indicates one position of the sequentially sampled intensity profile of the guided light along the propagation path.

mental section. The COMPASSO instrument was thus employed to characterize the waveguide modes of this multilayer ZrCe-M coating heat treated at 450 °C. This was carried out for both, TM and TE light polarization. In addition, it was used to determine the thickness and refractive index of the waveguides using the WKB method [37]. For the TE polarization of light, three modes were found at a wavelength of 635 nm, as observed in Fig. 6. In this figure the three dips marked with upward arrows correspond to the N_0 (left), N_1 (center) and N_2 (right) TE polarization modes. The arrow pointing downwards on the left side figure originates on the signal arising from the coating–substrate interface, and

Fig. 6. TE polarization modes observed with the COMPASSO apparatus at 635 nm for the ZrCe-M slab waveguide heat treated at 450 °C. The dips correspond to the TE polarization modes (N_0 , left upward direction; N_1 , center; N_2 , right). The knee signal marked with a downward arrow, on the left figure, arises from the coating–substrate interface.

corresponds to the substrate's index of refraction. For TM polarization, however, only two modes were measured. The waveguide modes were also investigated in the near-IR part of the spectrum ($\lambda = 1550$ nm), yielding only one mode for each, TE and TM polarization (Table 1). The multilayer ZrCe-M sample heat treated at 400°C was also characterized using the COMPASSO apparatus, yielding similar values and number of modes as the sample described here, heat-treated at 450°C .

The mathematical treatment of the data confirms the birefringence of the zirconia-ceria slab waveguide. The film indices for TE and TM polarization of the light are quite different, with calculated values of 2.069 ± 0.001 and 2.087 ± 0.001 for TE and TM polarization, respectively, at $\lambda = 635$ nm. In both cases the calculations of the coating thicknesses report values of ca. 500 nm. This property means that the coating will behave optically different depending on the polarization state of the beam coupled to the waveguide. The material birefringence is associated with the presence of tetragonal structures within the coating; these structures are anisotropic and thus, when the light strikes them, their behavior differs depending on the polarization of light.

The measure of propagation losses is obtained by an image capture device, specifically a vidicon camera which collects the light scattered out of the plane of the film (inset of Fig. 7). The mathematical treatment of the collected signal allows obtaining the propagation coefficient α (Fig. 7). The ZrCe-M sample presents two values for the attenuation coefficient at a wavelength of 633 nm: 0.9 ± 0.2 dB/cm and 1.5 ± 0.2 dB/cm, for TE and TM polarization, respectively. Thus, the losses are found to be significantly dependent on the polarization of the beam coupled to the waveguide. Bihn et al. [47] previously reported this property for a ZrO_2 waveguide obtained by ion-assisted deposition, observing how the attenuation coefficient depends on the polarization of the light.

4. Conclusions

$\text{ZrO}_2\text{:CeO}_2$ (70:30) slab multilayer waveguides were fabricated on commercial glass substrates by a sol-gel dip-coating technique. Low mean coating surface roughness values, approaching 7 nm, were observed by optical confocal microscopy. Microstructural characterization by TEM revealed a continuous and uniform matching interface between waveguide and substrate, as well as between layers conforming the waveguide. Waveguide optical characterization by Dark m-line spectroscopy for a wavelength of 635 nm was performed on selected representative samples, resulting in refractive index values of 2.069 ± 0.001 and 2.087 ± 0.001 for TE and TM polarization modes, respectively. In addition, thickness values approaching 500 nm were determined for the waveguide layer. An image capture device was used to characterize propagation losses at $\lambda = 633$ nm, yielding values of 0.9 ± 0.2 dB/cm and 1.5 ± 0.2 dB/cm for TE and TM, respectively. These results were explained in terms of birefringence phenomena, arising from the presence of nanometer-sized, tetragonal zirconia crystals. The obtained results on $\text{Ce}_2\text{O}_3\text{-ZrO}_2$ waveguides at 633 nm can be used to explore different oxide compositions for the fabrication of birefringent waveguides useful at wavelengths suitable for optical communication windows.

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