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Eu^{3+}- and Er^{3+}-doped SiO_2–TiO_2 sol-gel films for active planar waveguides*

L.Q. MINH[1], N.T. HUONG[1], C. BARTHOU[2], P. BENALLOUL[2], W. STRĘK[3], T.K. ANH[1,**]

[1]Institute of Materials Science, NCST of Vietnam, Hoang Quoc Viet Road, Hanoi, Vietnam, leminh@ims.ncst.ac.vn

[2]Laboratoire d'Optique des Solides UMR 7601, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

[3]Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 2 Okólna St., 50-950 Wrocław, Poland

Sol-gel films of SiO_2–TiO_2-doped with Eu^{3+} or Er^{3+} ions were prepared by spin coating with a variety of molar concentration ratios of tetraethoxysilane (TEOS) and titanium isopropoxide (TPOT). The ratios of SiO_2–TiO_2 were 90/10, 85/15, 80/20, 75/25 and the concentrations of Eu and Er ions varied from 10^{-3} to $5\cdot10^{-2}$ mol %. Silica–titania films annealed from 150 up to 900 °C decreased their thickness from 300 to 150 nm and increased the refractive index from 1.49 to 1.62. The multilayer (6–8 layers) silica–titania thin films with thickness of about 1.2–1.6 μm have been developed in order to make highly doped with Eu^{3+} or Er^{3+} planar waveguides on silicon substrates. Luminescence spectra, lifetimes as well as FTIR and micro-Raman spectra have been measured. The influence of active ion concentrations and annealing temperature on the luminescence properties and the structure of thin films were investigated.

Key words: *sol-gel method, Eu, Er, thin films*

1. Introduction

In recent years, great interest has been attracted by the development of integrated optics, which is the technology of integrating various optical devices and components for the generation, focusing, splitting, combining, isolation, polarization, coupling, switching, modulating and detection of light, all on a single substrate. The sol–gel process offers a versatile method for depositing amorphous films, based on the hydrolysis and polycondensation of precursors such as metal alkoxides.

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**Corresponding author. Institute of Materials Sciences, NCNST of Vietnam, Hoang Quoc Viet Road, Hanoi, Tel: 7564333/1153 Fax: 84-4-7562039, E-mail: kimanh@ims.ncst.ac.vn.

Trivalent rare earth ions such as Eu^{3+}- or Er^{3+}-doped into SiO_2–TiO_2 matrices are interesting and promising materials for active planar waveguides due to their advantages such as low temperature of processing, high homogeneity and possibility of producing materials with controlled refractive indexes. Optical amplification is also an important application (e.g. at the wavelength of 1.55 μm in channel waveguides doped with Er^{3+} and 980 nm pumps) which involves matrices inside in which concentrations of OH groups should remain extremely low. High refractive index variations between the guide and the cladding are necessary to induce maximum confinement and thus to increase doping efficiency. This field was, until recently, limited to pure inorganic materials or semiconductors. Hybrid materials, because of their versatility, fit both requirements [1].

These new optical materials are SiO_2–TiO_2 thin films containing rare earth ions prepared by the sol-gel technique [2]. The influence of titanium concentration on the refractive index and optical properties of SiO_2–TiO_2 thin films were presented previously [3]. The fabrication of nanoparticles by the sol-gel process opens up interesting possibilities for designing new devices for optical imaging and telecommunication applications. The compactness and performance of integrated lasers and amplifiers are mainly linked to the rare earth doping level. SiO_2–TiO_2 system offers the possibility of producing materials with controlled refractive indexes varying from 1.46 (of pure silica) to 2.2 (pure amorphous TiO_2). SiO_2–TiO_2 thin films doped with rare earth and dyes are intensely investigated as planar waveguides because of their homogeneity and the possibility of tuning the refractive indexes and the wavelength [3]. Sol-gel chemistry, combined with the spin-coating technique, is a good method for production of rare earth-doped planar waveguides [4].

In this paper, we present preparation and optical properties of sol-gel derived SiO_2–TiO_2: Eu as well as SiO_2–TiO_2:Er thin films.

2. Experimental

Preparation of the sol-gel thin films involves two main starting precursors: tetraethylorthosilicate ($Si(OC_2H_5)_4$, TEOS, 98%, Merck) and tetraisopropylorthotitanate ($Ti(OC_3H_7)_4$, TPOT, 97%, Fluka). Spin-on-glass method on Si substrates was employed to produce films. The film preparation was performed in a clean room of the class 100. Because TEOS and TPOT have very different hydrolysis rates, TEOS was first pre-hydrolyzed before adding TPOT in order to obtain clear solutions (hydrolyzates). The velocities of spin coating were 1000, 2000 or 3000 c/min. Molar ratios of TEOS–TPOT were 90/10, 85/15, 80/20 and 75/25. Eu and Er were doped by addition of $Eu(CH_3COOH)_3$/(TEOS+TPOT) and $Er(CH_3COOH)_3$/(TEOS+TPOT) with different concentrations varying from $5\cdot10^{-2}$ to $4\cdot10^{-3}$ mol/dm^3. The films were fabricated on single-crystal silicon wafers (111) using a photoresist spinner. These films were spun at 1500–2500 rpm for 30 sec after deposition, then annealed at 50 °C for 48 hrs and then sintered at temperatures between 150 °C and 900 °C for different times in a clean room of class 100.

The thickness and refractive indexes were measured using a spectroellipsometer. The thermogravimetric analysis (DTG or TGA) and vibrational spectroscopic (FTIR and micro-Raman) methods were performed in order to investigate the chemical reactions and structural transition during the thermal treatment process. The DSC nad TG spectra were measured using Shimadzu DSC-50 (Japan). IR spectra were recorded using Shimadzu 5000 with a FTIR adapter. The samples were checked by means of X-ray diffractometer D 5000 (Siemens).

The photoluminescence spectra were studied on a monochromator Jobin Yvon HR 460, and a multichannel CCD detector from Instruments SA (model Spectraview 2D). This set-up has resolution of 0.2 nm/point with a slit 0.02 mm in the visible range. Triax 320 was used for infrared measurements. The luminescent spectra were also measured using a Spex 1250M monochromator with a high-resolution grating. Hg-Xe lamp (500 W, Oriel), nitrogen, argon, and Ti-sapphire lasers were used as excitation sources for the different wavelengths. The decay profiles were analyzed by a PM Hamamatsu R928 and Nicolet 490 scope with a time constant of the order of 7 ns.

3. Results and discussion

The refractive index of the sol-gel silica–titania thin films changes from 1.49 to 1.60 depending on the Ti concentration. Refractive indexes and thickness of $90SiO_2$–$10TiO_2$, $85SiO_2$–$15TiO_2$ and $80SiO_2$–$20TiO_2$ thin films obtained at different annealing temperatures are presented in the table. The results of heating of the $(100 - x)SiO_2$–$xTiO_2$ films in the temperature range from 150 °C to 1000 °C indicate that while film thickness decreases (up to 800 °C), their index increases reaching constant values after heating at 800 °C for 10–25 min.

Table. Thickness (d) and refractive index (n) of $(100 - x)SiO_2$–$xTiO_2$ thin films at different annealing temperatures (T)

$90SiO_2$–$10TiO_2$			$85SiO_2$–$15TiO_2$			$80SiO_2$–$20TiO_2$		
T/°C	D/nm	n	T/°C	D/nm	n	T/°C	D/nm	n
150	209.90	1.49	150	184.12	1.50	150	192.14	1.53
300	201.70	1.50	300	167.36	1.53	300	155.96	1.57
500	184.50	1.50	500	152.47	1.54	500	152.01	1.57
700	157.26	1.51	700	131.65	1.56	700	142.16	1.58
800	159.95	1,52	800	124.68	1.56	800	129.12	1.60
900	135.05	1,53	900	123.07	1.56	900	126.96	1.60

Some reaction parameters such as molar ratios of (TEOS + TPOT) to H_2O, pH, refluxing temperature and reaction times were investigated during preparation of the solutions in order to minimize the final content of residual hydroxyl groups and the phase separation between silica and titania. Furthermore, the use of acetylaceton (ACT) as an inhibitor for hydrolysis reaction of TPOT has already been shown to be of great value in improving the sol-gel processing. The stability of the initial sol-gel solution of the two metal alkoxides of silicon and titania enables preparation of homogeneous mixtures.

The FTIR spectra of $80SiO_2/20TiO_2$ thin films obtained at different temperatures have been already presented [4]. In the spectra of films sintered at <750 °C the O–H stretching feature is observed near 3450 cm^{-1}, where both H_2O (~3350 cm^{-1}), SiOH (~3680 cm^{-1}) components are present. The Si–O–Si vibrational modes ascribed to the transverse optical rocking, symmetric stretching and asymmetric stretching are observed at ~460 cm^{-1}, 800 cm^{-1} and 1085 cm^{-1}. An intense shoulder is also observed at about 1250 cm^{-1}. It is related to the longitudinal optical component of the high-frequency vibration of SiO_2. All spectra exhibit a band centred near 920–940 cm^{-1}. On the other hand, in the micro-Raman spectra of the TiO_2 films (heated at 800 °C) several stretching vibrations of Si–OH and Si–O–Ti^{4+} linkages with characteristic bands at 633, 510, 388, 130 cm^{-1} are present. The vibrations are similar to those observed for the anatase modification. When the molar ratio (x) of the ($100 - x$) SiO_2–$x TiO_2$ film was raised, the bands (at 1600 and 1340 cm^{-1}) characteristic of the Si–O–Si bonds could be observed.

In short, three kinds of physicochemical processes may occur when temperature is increased during thermal densification of gel films. First, residual water and residual organic groups are released, emptying the pores in the films. Second, the porous skeleton collapses, causing film shrinkage accompanied by structural relaxation, which can be described by the viscous sintering kinetic theory. Finally, crystallisation or phase separation may occur at high enough temperatures, depending on the chemical composition and dynamic conditions. According to the FTIR spectra, the C–H vibration were not found near 3000 cm^{-1} even before sintering, showing that most organics were immediately removed during spinning, before thermal densification occured.

The film shrinkage continues up to 900 °C. Densification at 1000 °C does not lead to continuous shrinkage due to oxidation of the silicon substrate. The refractive index also reaches a constant value, corresponding to each temperature. In addition, the results of TGA and DTG analyses of the gel films show that in the temperature range from 600 °C to 1000 °C the weight loss is negligible. This can be used to optimize annealing conditions in order to relax residual stresses of the SiO_2–TiO_2 gel films.

The sol-gel thin films SiO_2–TiO_2:Eu at different annealing temperatures demonstrate characteristic $^5D_0$–^7F_J transitions of Eu^{3+} in luminescent spectra. The spectra recorded at two different annealing temperatures (500 °C and 700 °C) are shown in Fig. 1. The luminescence decay profiles of the thin film SiO_2–TiO_2[75/25] :Eu ($1\cdot10^{-2}$ mol/dm^3) annealed at 400 °C during 15 min are shown in Fig. 2.

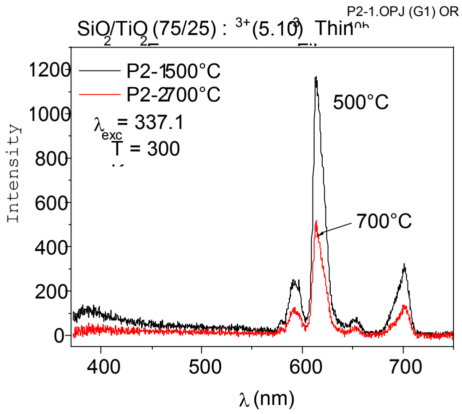

Fig. 1. The luminescence spectra
of SiO_2–TiO_2: Eu ($5 \cdot 10^{-2}$ mol/dm^3)

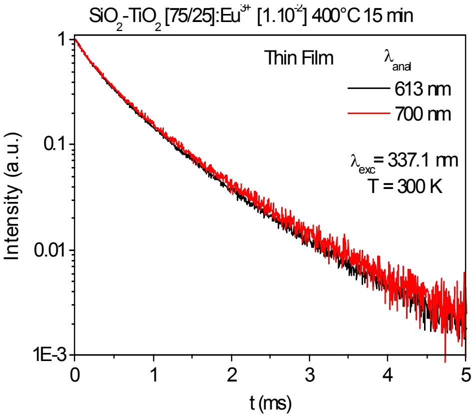

Fig. 2. The emission decay profiles of the
thin film SiO_2–TiO_2: Eu ($1 \cdot 10^{-2}$ mol/dm^3), 400 °C

The luminescence spectra of SiO_2–TiO_2 :Er samples were measured with an argon laser as an excitation source. For the emission spectra in the visible range, an interference filter (490 nm) was used to select the wavelength of excitation λ_{exc} = 488 nm or 514.5 nm. For the emission spectra in the near IR range, all the lines of the argon laser were used (no filter).

We have measured the $^4I_{13/2}$–$^4I_{15/2}$ transition of Er^{3+} in the infrared region. The thermal processing decreased the presence of OH and transformed the structure of TiO_2 from anatase into rutile. The luminescence spectrum of the SiO_2–TiO_2:Er 10^{-2} mol/dm^3 annealed at 1000 °C using an argon laser as an excitation source is shown in Fig. 3a. A similar spectrum was observed using a sapphire laser (Fig. 3b).

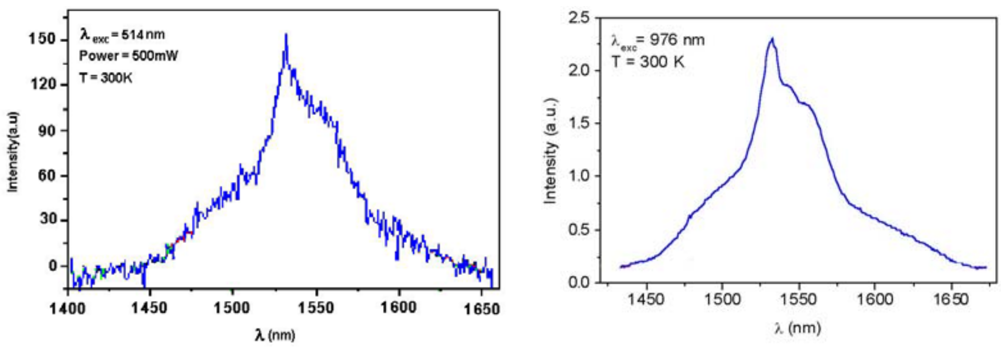

Fig. 3. Luminescence spectrum of: a) SiO_2–TiO_2:1% Er with 514 nm excitation,
b) SiO_2–TiO_2: 1% Er with 830 nm excitation

4. Conclusions

The sol-gel derived SiO_2–TiO_2 thin films doped with Eu^{3+} and Er^{3+} were prepared. Their optical properties were studied as a function of active ion concentration and different anealing temperatures. The characteristic emission transitions of Eu^{3+} and Er^{3+} ions were observed. The refractive index of SiO_2–TiO_2 thin films can be tailored in a wide range by controlling the relative quantity of the starting precursors. Thin films of $(100 - x)SiO_2$–$xTiO_2$ doped with Eu^{3+} and Er^{3+} ions were spin coated on Si substrates. The effect of thermal treatment was investigated by means of vibrational spectroscopic measurements. We have found that the film thickness decreases whereas the refractive index increases continuously with increasing temperature of annealing. The experimental results demonstrate that for consecutive spin coating depositions each spun layer should be annealed at 750 °C to release residual stresses. The luminescence measurements indicate that the SiO_2–TiO_2 films doped with Eu^{3+} and Er^{3+} are promising materials for planar waveguides [5, 6].

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