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Zirconia and zirconia-organically modified silicate distributed feedback waveguide lasers tunable in the visible

Dennis Lo,[a] Lei Shi, Jun Wang, and Guo-Xuan Zhang
Physics Department, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Xiao-lei Zhu
Shanghai Institute of Optics and Fine Mechanics, The Chinese Academy of Sciences, Shanghai, China

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Zirconia and zirconia-organically modified silicate waveguides of refractive index from 1.56 to 1.64 and thickness from 0.6 to 1.4 μm were prepared by the sol-gel method. Narrow linewidth (<0.5 nm) lasing was observed in dye-doped zirconia and zirconia-organically modified silicates waveguides. Tuning of the output wavelength was achieved by varying the period of the gain modulation generated by a nanosecond Nd:yttritium–aluminum–garnet laser at 532 nm. Tuning ranges were 586–618 nm and 629–657 nm for rhodamine 6G and rhodamine B, respectively. The threshold pump energy was about 50 μJ for rhodamine 6G-doped zirconia film on glass substrates. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1512949]

Zirconia (ZrO_2) is a very useful optical material because of the wide optical transparency and the high mechanical strength and resistance to chemical reaction. Combined with its high refractive index, zirconia films on glass or quartz substrates hold good promise for a wide range of applications in integrated optics. Recently the sol-gel method has been successfully developed for the preparation of zirconia, titania and silica thin films.[1] In particular Sorek *et al.* prepared and characterized zirconia and zirconia-organically modified silicates (ORMOSIL) waveguides.[2] Zevin *et al.* demonstrated zirconia waveguide amplifiers doped with a number of laser dyes.[3] The optical properties of infrared dye in zirconia films were reported by Casalboni *et al.*[4] Thick zirconia films up to 30 μm were developed by Del Monte *et al.*[5]

The active device such as laser is a critical enabling technology to integrated optics. Thin film waveguide lasers are desired for their efficient coupling with planar lightwave circuit. The sol-gel method is particularly relevant for the fabrication of active device since large number of functional components (e.g., rare-earth elements, semiconductors, organic dyes) can be introduced into the glass matrix.[1,6] Laser action from thin film structure can be induced using the distributed feedback (DFB) configuration.[7] We recently demonstrated a distributed feedback waveguide laser based on titania–silica thin film prepared by the sol-gel method.[8] Multiple-mode lasing and optical confinement were observed. Zirconia thin films appear to be superior to titania films in view of the optical transmission of zirconia deep into the UV and the absence of catalytic photodegradation of organic dopants.[2] Hence, zirconia seems ideal as a host matrix for functional organic dopants.

We report in this letter the observation of tunable DFB laser action from dye-doped zirconia and zirconia–ORMOSIL thin films. Rhodamine 6G (R6G) and rhodamine B (RB) doped zirconia and zirconia–ORMOSIL thin films were prepared in low temperature on glass or fused quartz substrates. A periodic gain modulation was generated by a frequency-doubled Nd:yttritium–aluminum–garnet (YAG) laser in the film. Lasing commenced (evidenced by spectral collapse) when the pump energy was 50 μJ for R6G-doped zirconia films. Single mode laser action was observed in both zirconia and zirconia–ORMOSIL films. The preparation of good optical quality zirconia and zirconia–ORMOSIL waveguide was key to the demonstration of tunable DFB laser action. The main difficulty in preparing zirconia films from zirconia alkoxides laid in the rapid hydrolysis and subsequent precipitation of colloidal zirconia upon water addition to the zirconia precursors.[2] Ganguli and Kundu were the first ones to prepare transparent zirconia films by dissolving zirconia propoxide in dried solvents.[9] Alternatively the zirconia precursor can be stabilized by complexing agents such as acetic acid or acetylacetonate.[10] Hybrid organic/inorganic zirconia–ORMOSIL films can also be prepared by the incorporation of an organic modifier γ-glycidyloxypropyltimethoxysilane (GLYMO). The presence of GLYMO in the films served to reduce the porosity and to improve the mechanical strength. The addition of R6G and RB dyes made zirconia and zirconia–ORMOSIL film laser active.

We largely followed the preparation procedures of Sorek *et al.* to fabricate dye-doped zirconia and zirconia–ORMOSIL films on glass or fused quartz substrates.[2] The refractive indices of the glass and fused quartz substrates were 1.51 and 1.46, respectively. The starting solutions consisted of zirconium *n*-propoxide and acetic acid. After the solutions were magnetically stirred for an hour, a few drops of 2-propanol were added to adjust the viscosity that in combination of the speed of spin coating determined the thickness of the films. The water needed for hydrolysis was mixed with acetic acid (1:3 by volume) and introduced drop by drop to the solutions. The molar ratio of zirconium *n*-propoxide to acetic acid was about 1:4 in the final solutions. Finally, laser dyes were added until the desired concentration was reached. For zirconia–ORMOSIL films, the organic modifier GLYMO was introduced in the initial solu-

[a]Electronic mail: dlo@phy.cuhk.edu.hk

tions. Dye-doped zirconia and zirconia–ORMOSIL films were obtained by spin-coating glass or fused quartz substrates with the final solutions. Cladded on one side by the low index substrate and the other by air, the film on substrate structure behaved as an asymmetric waveguide. Depending on the viscosity of the solution and the spinning speed, films of thickness varying from 0.6 to 1.4 μm were obtained. Prepared at room temperature, the refractive index for both zirconia and zirconia–ORMOSIL films was 1.56 to 1.57. Refractive index up to 1.64 was obtained when the films were kept at 60 °C for 2 days. Atomic force microscopy revealed that the surface of the films appeared to be amorphous with a random distribution of zirconia gel particles.

The waveguiding properties of doped and undoped zirconia and zirconia–ORMOSIL films were characterized using a commercial prism coupler (Metricon model 2010) at 633 nm. Multiple waveguide modes (for both TE and TM) were observed for films of thickness greater than 1 μm. Only one mode was allowed for films of thickness of about 0.6 μm. Refractive index and the thickness of the film were simultaneously determined from the propagation angles of the waveguide modes. Comparing the scanning prism coupler results for zirconia and for zirconia–ORMOSIL films, it was revealed that zirconia–ORMOSIL films had better waveguiding properties as evidenced by the sharp and better resolved guiding modes. Indeed we were to make waveguiding zirconia–ORMOSIL films of thickness up to 2.8 μm, whilst zirconia films of similar thickness often had poor waveguiding properties (absence of waveguide modes) probably resulting from poor surface smoothness. For comparison purpose, the well-studied titania–silica films had a tendency to phase separate and the surface integrity of films of thickness >2 μm was difficult to maintain. There were no measurable differences in refractive index for dye-doped and undoped waveguides for dye concentrations up to 2×10^{-3} M/l. A Hitachi spectrophotometer was used to study the absorption/transmission properties of the waveguides. The transmission trace of a typical undoped zirconia waveguide of 0.6 μm thickness on fused quartz showed excellent transmission from 210 nm to the near infrared. For zirconia–ORMOSIL films, increased absorption in the deep UV (210–280 nm) was observed. Figure 1 showed the absorption spectra of RB-doped (a) and R6G-doped (b) zirconia waveguides. The R6G-doped waveguide had an absorption peak near 530 nm, thus allowing efficient pumping at 532 nm by frequency-doubled Nd:YAG laser. On the contrary the absorption peak of RB was at 580 nm. High RB concentration of 5×10^{-2}M/l was achieved in the zirconia films which partly made up for the weaker absorption of the pump laser, whilst the highest concentration for R6G was 7×10^{-3} M/l.

Narrow linewidth laser action was achieved in both dye-doped zirconia and zirconia-ORMOSIL waveguides. The optical arrangement was identical to that used in our previous experiments in obtaining DFB laser action in dye-doped sol-gel silica slabs and in titania–silica waveguides.[6,11] Briefly a holographic grating of 1800 lines/mm served as a beamsplitter for the frequency-doubled output from a 6 ns Nd:YAG laser of relatively low spatial coherence. Incidenton the grating, the pump beam from the Nd:YAG laser was diffracted

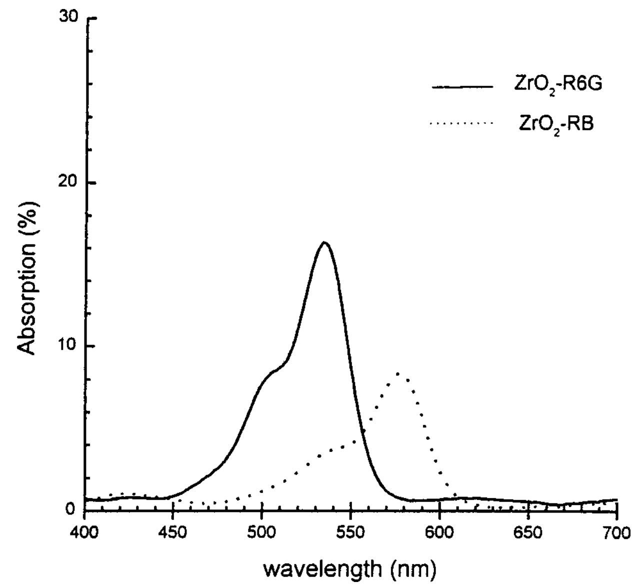

FIG. 1. Absorption spectra for RB-doped zirconia film and R6G-doped zirconia film.

into ± 1 orders of approximately equal intensities. The diffracted beams were redirected to combine on the zirconia or zirconia–ORMOSIL films at an intersection angle of 2θ, forming a fringe pattern. A periodical modulation of gain was thus created in the dye-doped glass film that served as the gain medium. The output wavelength of the dye-doped

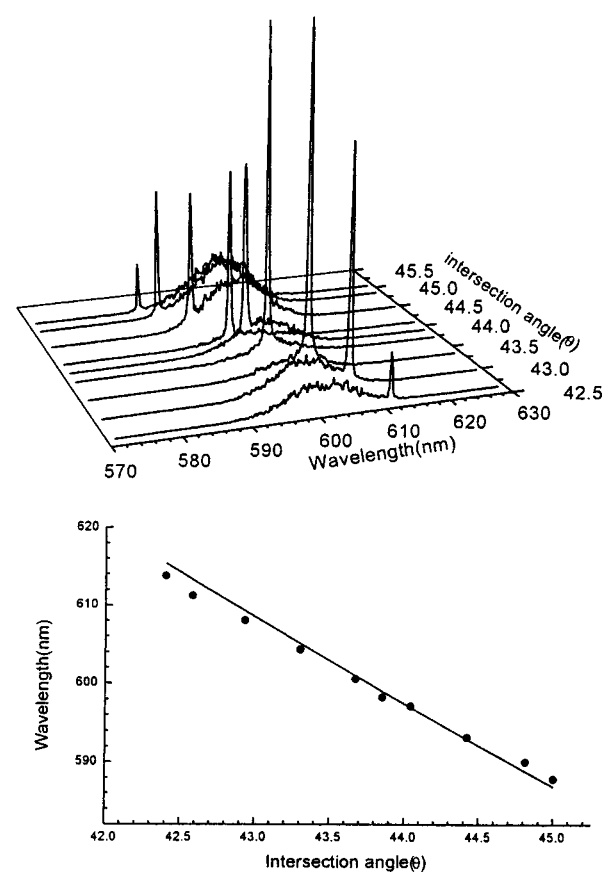

FIG. 2. Laser emission spectra for the DFB R6G-doped zirconia waveguide laser on glass substrate (top). Data of angle tuning vs theoretical fit (bottom).

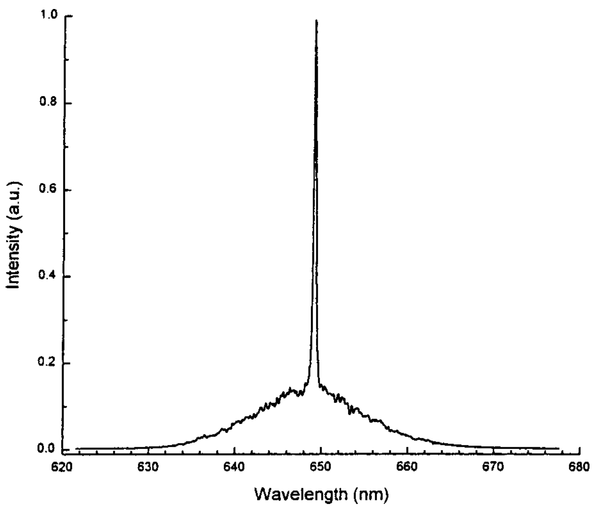

FIG. 3. Laser emission spectrum as the DFB RB-doped waveguide laser on glass substrate.

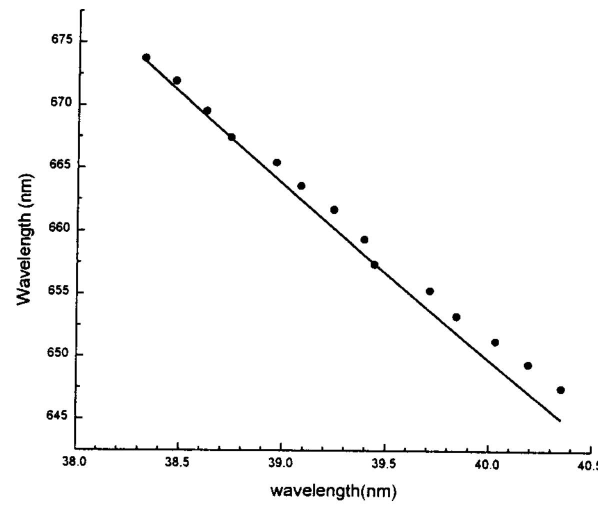

FIG. 4. Data of angle tuning vs theoretical fit for RB-doped zirconia–ORMOSIL waveguide laser.

zirconia waveguide laser followed the Bragg condition at $\lambda_L = 2\eta\Lambda/M$, where η was the refractive index of the gain medium at λ_L, Λ was the period of the gain modulation (the fringe pattern), and M was the Bragg reflection order. In the present experiments, second order Bragg condition was satisfied ($M=2$). When pumped by another laser at wavelength λ_P, the modulation period Λ is given as $\Lambda = \lambda_p/2\sin\theta$. Tuning of λ_L can be achieved by varying the intersection angle and thus the gain period. A 0.3 m spectrograph/array detector system was employed for spectral measurement of the laser output. The time wave forms were measured using a PIN photodiode and a fast digital oscilloscope.

DFB laser action was observed in R6G-doped zirconia film on glass substrate. The film had a thickness of 0.62 μm and a refractive index of 1.56. The dye concentration was 4×10^{-3} M/l. The threshold pump laser energy was about 50 μJ. Accounting for reflection and transmission losses of the pump laser, the actual energy delivered to the film was about 8 μJ. Tuning of the output wavelength was achieved by varying the intersection angle (θ) of the crossing beams. Single mode lasing was observed throughout the tuning range from 586 to 618 nm (top of Fig. 2). The laser output spectra had a structure of a single prominent peak near the center of the gain profile (600 nm). As the laser was tuned way from the gain center, significant amplified spontaneous emission appeared in the background. The linewidth of the laser output was narrow at about 0.5 nm which was in fact the resolution limit of our detection system. The bottom of Fig. 2 showed the experimental data of the angle tuning versus the theoretical fit of Bragg condition (solid line), in which the refractive index 1.56 determined independently by the prism coupler was used. Good agreement was seen. As the pump energy increased from 50 to 350 μJ, the DFB laser output energy increased linearly. We also observed DFB laser action in RB-doped zirconia wavguides. The initial dye concentration was 2×10^{-3} M/l. Narrow linewdith lasing was demonstrated (Fig. 3). Angle tuning of the output wavelength was obtained from 629 to 657 nm. The threshold pump energy for RB was higher by a factor of 2 probably a result of the weaker absorption of the pump.

Sol-gel glass films of thickness >10 μm were required for volume holography, optical storage, and information processing.[12] Films of such thickness can be fabricated by the introduction of an organic modifier into the inorganic network to reduce stress during evaporation. As mentioned earlier, GLYMO was used as the organic modifier in the fabrication of the zirconia–ORMOSIL waveguides. We prepared doped and undoped hybrid zirconia–ORMOSIL films on glass substrates by spin coating. The thickness of the hybrid films was up to 2 μm and the refractive index up to 1.64. We demonstrated DFB laser action in RB-doped zirconia–ORMOSIL waveguide of thickness of 1.34 μm and a refractive index of 1.57. Wavelength tuning around 650 nm was achieved with a range of 27 nm. Figure 4 showed the angle tuning data versus the theoretical fit. Good agreement was observed. The zirconia–ORMOSIL film thickness can be increased if dip-coating technique is applied.

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