

Glass-Ceramics for Photonics: Laser Material Processing

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ABSTRACT

Transparent glass-ceramics, activated by luminescent species, present an important class of photonic materials because their specific optical, spectroscopic and structural properties. Several top-down and bottom-up techniques have been developed for transparent glass ceramic fabrication. Among them, laser material processing plays an important role and many significant results have been obtained in the field of waveguide glass ceramics fabrication. Here, after a short description of the state of art regarding laser material processing for glass ceramics, we report on the specific use of CO₂ laser for the fabrication of transparent glass ceramic waveguides.

Keywords: transparent glass-ceramics, laser material processing, CO₂ laser, planar waveguides, crystallization, SiO₂-ZrO₂, SiO₂-HfO₂, attenuation coefficient.

1. LASER MATERIAL PROCESSING FOR GLASS CERAMICS

Laser material processing is a fantastic tool not only to improve optical and structural properties of the materials and to write photonic structures, but also for the development of new materials [1-3]. One of the field where this tool is highly appreciated is the fabrication of transparent glass ceramics. In fact, in order to produce active rare earth nanocrystals in a glass matrix, heat treatment using a furnace has been commonly used, but laser annealing process offers an effective and complementary fabrication method. For laser annealing several types of lasers have been used, differing primarily in wavelength (e.g. XeCl 308 nm, frequency doubled Nd-YAG 532 nm, Nd-YAG 1064 nm, CO₂ 10.6 μm) [4]. It was reported that CO₂ laser annealing can reduce scattering losses in Corning 7059 glasses [2] and ZnO [5] thin-film waveguides fabricated on thermally oxidized silicon substrates. Losses as low as 0.05 dB/cm for Corning 7059 glass waveguides [2] and 0.01 dB/cm for ZnO waveguides [5]

have been achieved by this technique. This study was extended by the same authors to reduce optical scattering losses in the fabrication of other waveguides: Si_3N_4 films fabricated by low pressure chemical vapor deposition, Nb_2O_5 films deposited by RF sputtering, and Ta_2O_5 films produced by both reactive sputtering and thermal oxidation of sputtered tantalum films [6]. The technological appeal of the class of glass-ceramics fostered the research in photonic techniques fabrication and the paper of Livingston and Helvajin devoted to photostructurable glasses paved the way of this research field [7]. They propose a novel approach to material processing that implements laser photoexcitation in a direct-write scheme to establish initial excitation states in a protean material that enables the regulation of a particular phase transformation pathway. Quite recently interesting results has been obtained in the case of GeO_2 sputtered waveguides [3,8,9]. Laser material processing technique was also successfully employed in $\text{SiO}_2\text{-ZrO}_2$ and $\text{SiO}_2\text{-HfO}_2$ planar waveguides, prepared by sol-gel route and activated by Er^{3+} ions [10,4]. Another interesting example concerning specific modification of the luminescence properties induced by laser processing is reported in [11]. The specific interest of this research is related to the manipulation of rare-earth-doped amorphous GeN films. The samples were prepared by the radio-frequency-sputtering method, and light emission from the rare-earth centers was obtained after irradiating the films with a highly focused laser beam. Laser material processing of transparent glass ceramics was also demonstrated employing CW YAG laser [12]. The specific interest of this work is study is to apply laser irradiation to glasses to form a non-linear glass-ceramic system.

Let us look more in detail some results obtained by CO_2 laser action.

2. CO_2 LASER FABRICATION OF TRANSPARENT GLASS CERAMIC WAVEGUIDES

The crystallization phenomenon in different glass-ceramic and glass materials under CO_2 laser action was carefully investigated by Veiko *et al.* [1]. Authors start from the statement that every glass has its own crystallization ability that means that a certain temperature interval exists and glasses can crystallize in this interval. It is also clear that we have to know the crystallization ability and crystallization speed to choose the proper regime for glass melting, manufacturing of different articles and for thermal processing in glass-ceramics manufacture. Crystallization character depends on relation between crystallization centers formation rate, crystal-growing rate from this centers and viscosity. The larger the interval between peak rates of crystal growth and formation of crystallization centers, and lower the rates themselves, the lower the tendency of glass to crystallization. Crystallization of glass materials depends on several factors: chemical composition and viscosity of glass, basic material, mutual solubility of every component, duration of exposure on proper temperatures, existence of crystallization catalysts and conditions of thermal processing of glass.

Table 1. Composition and final thermal annealing parameters for Er^{3+} -activated $\text{SiO}_2\text{-ZrO}_2$ and $\text{SiO}_2\text{-HfO}_2$ planar waveguides.

Waveguide composition	Erbium content [mol%]	Final thermal annealing at 900 °C [min]
$70\text{SiO}_2\text{-}30\text{ZrO}_2$	5	5
$70\text{SiO}_2\text{-}30\text{HfO}_2$	5	5
$80\text{SiO}_2\text{-}20\text{ZrO}_2$	0.5	5
$80\text{SiO}_2\text{-}20\text{ZrO}_2$	0.5	30

Table 2 Composition and CO_2 laser annealing parameters for Er^{3+} -activated $\text{SiO}_2\text{-ZrO}_2$ and $\text{SiO}_2\text{-HfO}_2$ planar waveguides.

Waveguide composition	Erbium content [mol%]	CO_2 laser type	Average power [W]	Irradiation time [min]
$70\text{SiO}_2\text{-}30\text{HfO}_2$	5	CW	13	15
$70\text{SiO}_2\text{-}30\text{ZrO}_2$	5	CW	13	15
$80\text{SiO}_2\text{-}20\text{ZrO}_2$	0.5	CW	10	10
$80\text{SiO}_2\text{-}20\text{ZrO}_2$	0.5	CW	10	20
$80\text{SiO}_2\text{-}20\text{ZrO}_2$	0.5	CW	10	30
$80\text{SiO}_2\text{-}20\text{ZrO}_2$	0.5	Pulsed	30	2.5
$80\text{SiO}_2\text{-}20\text{ZrO}_2$	0.5	Pulsed	30	10
$80\text{SiO}_2\text{-}20\text{ZrO}_2$	0.5	Pulsed	30	15

It was already mentioned that laser material processing can improve spectroscopic properties of the parent glass when rare-earth activated glass ceramics are developed [4,10]. The investigated samples were planar waveguides of silica-zirconia and silica-hafnia activated by Er^{3+} ions and prepared by sol-gel route. The preparation protocol is reported in detail in [4,10]. Briefly, the starting solution, for both systems, was obtained by mixing tetraethylorthosilicate (TEOS), ethanol, de-ionized water, and hydrochloric acid as a catalyst. For silica-hafnia the molar composition $70\text{SiO}_2\text{-}30\text{HfO}_2$ was chosen on the basis of the previous experience [13]. For the $\text{SiO}_2\text{-ZrO}_2$ waveguide, the precursor was ZrOCl_2 and was then added to the solution containing TEOS with

a Si/Zr molar ratio of 70/30 and 80/20. Erbium was added with an Er/(Si + Hf or Zr) molar concentration of 0.5 and 5 mol%. The films were deposited on cleaned pure v-SiO₂ substrates by dip coating and densified by a suitable thermal annealing protocol as presented in Table 1. Other samples were densified with CO₂ laser annealing treatment, as shown in Table 2 employing both CW and pulsed sources.

The schema of the experimental setup used for CO₂ pulsed laser annealing is shown in Fig. 1. In the case of 10.6 μm CW CO₂ laser annealing the beam diameter was 6 mm. The power density of the CO₂ laser beam, with a Gaussian distribution, was around 5.7 W/cm², and the irradiated zone of the waveguide was adjusted to 2 cm diameter; the Gaussian distribution is along the beam cross-section. The waveguides were positioned at around 50 cm from the laser. For the pulsed CO₂ laser irradiation, 80SiO₂-20ZrO₂ planar waveguides has been used. The laser power density, with a Gaussian distribution, was 78 W/cm² for pulsed CO₂ laser irradiation and a pulse period of 400 and 32 μs pulse width. The sample was about 1.5 m from the laser head and Argon C45 was used as a shroud gas for the annealing processes at a flow rate of 2.0 l/min.

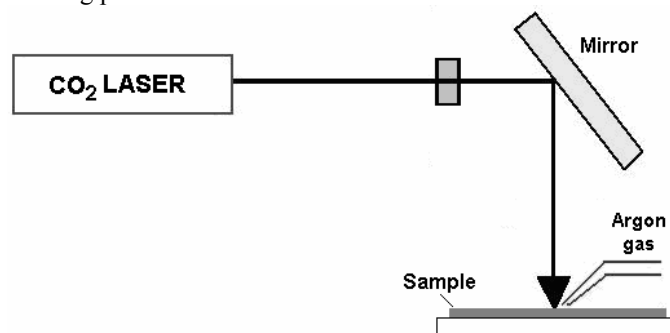


Figure 1. Schema of the experimental setup used for CO₂ pulsed laser annealing.

Optical parameter, i.e. thickness and refractive index of the waveguide, were measured by m-line technique [13]. The losses for the TE₀ mode were evaluated by photometric detection of the light intensity scattered out of the waveguide plane and the photoluminescence spectra were measured in waveguide configuration exciting the TE₀ mode of the investigated waveguides [13].

Table 3. Optical and spectroscopic parameters of the 0.5 mol% Er³⁺-activated 70SiO₂-30ZrO₂ and 70SiO₂-30HfO₂ planar waveguides: BTA before thermal annealing; ATA after thermal annealing; IT irradiation time; LA laser annealing.

Waveguide composition	Annealing procedure	Refractive index @ 1.5μm TE polarization	⁴ I _{13/2} Bandwidth	⁴ I _{13/2} Lifetime (±0.5 ms)	Attenuation coefficient @ 633 nm
70SiO ₂ -30HfO ₂	BTA	1.583	50	≤ 0.5	≥ 2
70SiO ₂ -30HfO ₂	ATA T = 900 °C; t = 5 min	1.589	47	0.8	≥ 2
70SiO ₂ -30HfO ₂	After CW LA IT = 15 min	1.621	49	0.7	0.8
80SiO ₂ -20ZrO ₂	Before LA	1.548	46	4.6	≥ 2
80SiO ₂ -20ZrO ₂	After CW LA IT = 10 min	1.561	48	4.5	1.5
80SiO ₂ -20ZrO ₂	After CW LA IT = 20 min	1.563	48	5.4	1.4
80SiO ₂ -20ZrO ₂	After CW LA IT = 30 min	1.566	48	5.9	1.1

The optical and spectroscopic parameters for the continuous CO₂ laser irradiated planar waveguides are reported in Table 3. The thermal annealed samples are also reported for comparison. The parameters measured before and in the case of the standard thermal annealing are given, to better evidence the effect of the CW laser processing.

The waveguides present a thickness ranging from 0.63 to 0.99 μm. All waveguides support one TE and TM modes at 1319 nm and 1542 nm. For the 70SiO₂-30HfO₂ and 70SiO₂-30ZrO₂ planar waveguides doped with 5 mol% Er³⁺ after thermal annealing the refractive indexes measured in TE polarization are quite similar to those obtained in TM polarization, indicating that the birefringence is negligible in the systems and similar differences are obtained for the refractive indexes for the samples treated with CO₂ laser annealing, indicating that the laser annealing do not induce birefringence in these systems.

Comparing the refractive indexes in the SiO₂-HfO₂ samples before and after the CO₂ laser irradiation we observe a variation Δ*n* of about 0.04, for example at 1542 nm the refractive index in TE polarization is 1.583 nm before any final treatment, 1.589 after thermal conventional annealing and 1.621 after CO₂ laser annealing. The increasing of the refractive index observed with laser annealing can suggest that with this laser treatment a better densification of the system is achieved in respect to the use of only thermal annealing. As a matter of fact, as

appear in the Table 3, the SiO₂-ZrO₂ samples, shown after thermal annealing similar values of refractive index than before the annealing, but with CO₂ laser annealing we observe a variation Δn of about 0.01.

Finally, we have observed that laser annealing can lead to waveguides with a lower attenuation coefficient, than the attenuation coefficient obtained after the thermal annealing. In fact we observe an attenuation coefficient at 632 nm of 0.80 and 1.1 dB/cm for silica-hafnia and silica-zirconia waveguides respectively for the irradiated systems while we obtain attenuation coefficient higher than 2 dB/cm for the systems processed with thermal annealing. The decreasing of the attenuation coefficient on the CO₂ laser irradiated systems, has been attributed to the elimination of surface irregularities. Propagation losses are enough low at all the investigated wavelength, including at 1550 nm, which thus make these waveguide glass ceramics a suitable candidate to develop amplifier in the C telecommunication band.

An increase of the lifetime from 4.6 ms before and 7.0 ms after pulsed CO₂ laser annealing was measured for 80SiO₂-20ZrO₂ with 0.5 mol% Er³⁺-activated.

This behavior can be related to a better structural order of the erbium environment. It is well known that a crystalline environment around the rare earth induce a shortening in the phonon energies. Indeed the phonon energy of the surrounding environment of the rare earth ions is proportional to the non-radiation contribution of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition. [4].

CONCLUSIONS

Laser material top-down processing can be successfully employed to tailor the optical, spectroscopic and structural properties of rare-earth-activated glass-based planar waveguides. The important role of CO₂ laser is evidenced in the case of 70SiO₂-30HfO₂ and 70SiO₂-30ZrO₂ activated by Er³⁺ ions. Depending on the CW or pulsed irradiation as well as on the irradiation time and fluency local crystallization or smoothing of the surface can be achieved. Laser material processing is nowadays a consolidated tool for fabrication of transparent glass ceramics although the crystallization mechanism remain an open investigation subject.

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