CO₂ Laser irradiation of GeO₂ planar waveguide fabricated by rf-sputtering

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Abstract: We present a fabrication protocol combining radio frequency sputtering technique and CO₂ laser annealing for GeO₂ based planar optical waveguides. The effects of pulsed CO₂ laser irradiation on the optical and structural properties of pure GeO₂ planar waveguide are evaluated by different techniques as m-line and micro-Raman spectroscopy and AFM measurements. Amorphous GeO₂ planar waveguide was fabricated by Radio Frequency magnetron sputtering system on v-SiO₂ substrate. An increase of the refractive index of approximately 0.04 at 1.5 µm and a decreasing of the attenuation coefficient from 0.9 to 0.5 dB/cm at 1.5 µm have been observed after pulsed CO₂ laser annealing. Raman spectroscopy and AFM results showed that after an adapted pulsed CO₂ laser annealing, the resulting materials showed a crystalline environment in which the phase of the crystalline GeO₂ varies with varying irradiation time.

Introduction

GeO₂-based glasses have demonstrated to be one of the most promising candidates for a high-functionality material platform for integrated optics. Germania glass exhibits a lower Tg (~ 790 K) and a lower phonon energy (~ 900 cm⁻¹) than SiO₂ based glasses. Moreover, GeO₂ glasses are transparent in the near infrared region and their refractive index allows fabrication of confined structures. Finally, Germania allows fabrication of highly photorefractive planar waveguides [1] and drawing fiber with smaller absorption losses in the middle IR range as compared to silica glass [2]. However the tailoring of the synthesis and optimization of a particular phase of GeO₂ crystals is very important as this material exhibits several polymorphs [3]. For these reasons it is of technological and scientific importance to develop a particular fabrication protocol to allow obtaining optical waveguides based on GeO₂ system that exhibits low attenuation coefficients and simultaneously embed GeO₂ nanocrystals with a particular phase.
In order to produce active rare earth nanocrystals in a glass matrix, heat treatment using a furnace has been commonly used, but a potential candidate for reaching future technology nodes is the laser annealing (LA) process. 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, CO$_2$ 10.6 lm) [4, 5]. It was reported that CO$_2$ laser annealing can reduce scattering losses in Corning 7059 glasses [6, 7] and ZnO [8] thin-film waveguides fabricated on thermally oxidized silicon substrates; losses as low as 0.05 dB/cm for Corning 7059 glass waveguide [6] and 0.01 dB/cm for ZnO waveguides [8] have been achieved by this technique.

This paper is devoted to the fabrication by rf-sputtering of amorphous GeO$_2$ planar waveguide and the investigation of the possibility to derive from this system a glass-ceramic in planar format by sequent CO$_2$ laser irradiation.

**Experimental**

Pure GeO$_2$ planar waveguide was prepared by Radio-frequency Sputtering (RFS) technique. The wave guiding film was deposited on Silica substrate. In order to improve the adhesion of the films, the substrate was cleaned inside the chamber by heating at 120°C for 30' just before the deposition procedure. Sputtering deposition of the film was performed by using 15x3 cm$^2$ Germania target. The residual pressure, before deposition, was about 1.6x10$^{-6}$ mbar. During the deposition process, the substrates were not heated. The sputtering was carried out with an Ar gas at a pressure of 5.4x10$^{-3}$ mbar; the applied rf power was 80 W and the reflected power 0 W. The deposition time, necessary to reach the appropriate thickness for one propagating mode at 1.5 µm, was 1h 58 min.

As prepared GeO$_2$ planar waveguides has been used for the irradiation with pulsed CO$_2$ laser. We use the S50 TEA CO$_2$ laser with a mixture of CO$_2$:N$_2$:He fixed at 33%:33%:33% percentages and is a pulsed laser with 0.8 J per pulse and have 5 Hz repletion rate, 380 ns pulse width and 10.6 µm wavelength with beam diameter of 1.5 cm. The samples were irradiated in air with 1.3 W medium power and irradiation time varies from 1 to 2 hours. The compositional analysis was performed using energy dispersive spectroscopy (EDS), by using a Noran Instruments mod. Voyager apparatus. Standard AFM technique has been used to measure the surface roughness of the samples before and after laser annealing.

The thickness and the refractive index of the waveguide at 632.8, 1319 and 1542 nm were measured in TE and TM polarizations, by an m-line apparatus (Metricon model 2010) based on prism coupling technique. The losses at 632.8, 1319 and 1542 nm were evaluated by collecting the light
intensity scattered out of the waveguide plane for the TE\(_{0}\) mode using a fiber scanner. More detail about the experimental setup can be found here [9]. Raman scattering measurements were performed at room temperature in a wave number range between 100 and 1000 cm\(^{-1}\) by Horiba-Jobin-Yvon, LabRam Aramis Micro Raman set up with exciting radiation at 633 nm by using He-Ne laser with power 20 mW. To avoid unwanted laser-induced transformations, neutral filters of different optical densities were used, whenever necessary. The resolution was about 0.35 cm\(^{-1}\)/pixel.

**Results and Discussions**

Table 1 reports the optical parameters for as prepared sample and after CO\(_2\) laser irradiation for 2 h. The waveguide present thickness around 1 µm and support one TE and TM mode at 1319 and 1542 nm. No change in the thickness was evidenced after the laser irradiation. The refractive indices measured in TE and TM polarizations are equal within the experimental uncertainty, so that film birefringence can be considered negligible. Moreover the laser irradiation do not induce changes between the refractive indices measured in TE and TM polarizations so we can affirm that in these conditions that the CO\(_2\) laser annealing do not induce birefringence in these systems.

**Table 1:** Optical parameters for as prepared sample and after CO\(_2\) laser irradiation for 2h.

| Laser wavelength (nm) | Refractive Index | Thickness (µm) | Attenuation coefficient (dB/cm) |
|-----------------------|------------------|----------------|-------------------------------|
|                       | TE   | TM     |                  |                               |
| 632                   | Before LA | 1.614±0.001 | 1.616±0.001 | 1.1±0.1 | 1.9±0.2 |
|                       | After LA  | 1.652±0.001 | 1.653±0.001 | 1.1±0.1 | 1.1±0.2 |
| 1319                  | Before LA | 1.590±0.01  | 1.590±0.01  | 1.0±0.1 | 1.4±0.2 |
|                       | After LA  | 1.631±0.01  | 1.634±0.01  | 1.0±0.1 | 0.7±0.2 |
| 1542                  | Before LA | 1.585±0.01  | 1.585±0.01  | 1.0±0.1 | 0.9±0.2 |
|                       | After LA  | 1.623±0.01  | 1.624±0.01  | 1.0±0.1 | 0.5±0.2 |

Comparing the refractive indices in GeO\(_2\) waveguide before and after the CO\(_2\) laser irradiation, we observe an increasing of refractive index about 0.04 with the irradiation for all the considered wavelengths. Similar results were obtained in other systems treated with CO\(_2\) laser irradiation [10]. We have observed that laser annealing can lead to waveguides with a lower attenuation coefficient, than the attenuation co-efficient obtained with as prepared sample. In fact, we observe an attenuation coefficient of 0.5 dB/cm at 1542 nm, respectively for the irradiated system while we obtain attenuation coefficient of 0.9 dB/cm for the system before laser annealing. The decrease in the attenuation coefficient on the CO\(_2\) laser irradiated systems, has been attributed by Dutta et al [7] to the reduction of surface irregularities and this effect carry out the reduction of the attenuation coefficient with the CO\(_2\) laser irradiation at all the considered wavelengths as shown in Table 1. EDS analysis was used to
monitor the composition of the samples as deposited and after the laser annealing processes. The measurements confirm that the composition of the sample is not affected by the laser treatment and the correct ratio between Germanium and Oxygen is always present.

In figure 1, we have reported the Micro Raman spectra carried out at room temperature for GeO$_2$ planar waveguide before and after laser irradiation of different time. The Raman spectra observed from the as prepared GeO$_2$ waveguide before irradiation is typical of GeO$_2$ amorphous system. In fact, the broad peak at 440 cm$^{-1}$ clearly indicates the amorphous nature of GeO$_2$ film [11]. After 1 hour CO$_2$ laser irradiation, the Raman spectra indicate that the presence of rutile like GeO$_2$ crystalline phase. The peaks observing in the Raman spectra after 1h CO$_2$ laser irradiation are in good agreement with those reported in the literature [11]. The peak at 302 cm$^{-1}$ corresponds to Ge optical phonons, being related to Ge–Ge bonds [12].

After 2 hours CO$_2$ laser irradiation, the Raman spectrum on the GeO$_2$ planar waveguide shows that the presence of trigonal GeO$_2$ crystal phase. The peaks at 123, 166 and 263 cm$^{-1}$ correspond, in fact, to the complex translation and rotation of GeO$_4$ tetrahedra [13]. The peak at 882 cm$^{-1}$ is assigned to Ge-O stretching motion with tetrahedral GeO$_4$ units [14]. A shift in the band at 447 cm$^{-1}$ is due to symmetric Ge-O-Ge stretching [14]. The peaks observing at 490 and 603 cm$^{-1}$ are D$_1$ and D$_2$ defect bands from the Silica substrate. All the bands in the spectrum obtained for the GeO$_2$ waveguide after 2 hours CO$_2$ laser irradiation are in good agreement with those of GeO$_2$ calcinated under $T = 1050$ °C [15].

![Figure 1: Micro Raman measurements carried out at room temperature for GeO$_2$ planar waveguide before and after CO$_2$ laser irradiation for 1 h and 2h.](image-url)
Figure 2. AFM image of a 1.98 x 1.91 $\mu m^2$ area on the as prepared sample (A) and after 2h of CO$_2$ laser irradiation (B).

The AFM image of a 1.98 x 1.91 $\mu m^2$ area on the as prepared sample (A) and after 2h of CO$_2$ laser irradiation (B) are reported in figure 2. AFM analysis put in evidence a roughness of 1.1 nm in the as prepared sample and a roughness of 0.7 nm for the waveguide after 2 h of CO$_2$ irradiation. This result is in agreement with the reduction of the attenuation coefficient with the laser annealing. Moreover the AFM image of figure 2 (B) show the presence of structures of nanometric scale on the surface of the sample with the dimension ranging from 10 to 50 nm attributed to the presence of GeO$_2$ nanocrystals. It is interesting to note as although the presence of these scattering points that can increase the attenuation coefficient [16] the protocol develop for the CO$_2$ irradiation allow to reduce the total value of the attenuation coefficient.

Conclusions

We have developed a fabrication protocol to prepare GeO$_2$ planar waveguide by Radio Frequency Magnetron sputtering technique. Moreover we note that using an adapted irradiation procedure, the pulsed CO$_2$ laser irradiation induced optical and structural changes in GeO$_2$ planar waveguide. The refractive index changes in the GeO$_2$ planar waveguide after 2 h of CO$_2$ laser irradiation were 0.04. The technique of laser annealing has been shown to significantly reduce propagation loss on GeO$_2$ planar waveguide. Low attenuation coefficients of 0.7 and 0.5 dB/cm at 1319 and 1542 nm, respectively, were measured after irradiation. Raman results have shown that after laser treatment GeO$_2$ planar waveguide shown rutile like and trigonal crystal phase after 1 h and 2 h irradiation respectively. AFM measurements shows that the surface roughness decreased from 1.1 to 0.7 nm after CO$_2$ laser irradiation and put in evidence the presence of structures of nanometric scale on the surface of the sample with the dimension ranging from 10 to 50 nm attributed to the presence of GeO$_2$ nanocrystals.
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