A method to synthesize SiO$_2$–TiO$_2$ glasses based on the synergy between VAD and ALD techniques: study of TiO$_2$ doping profile along radial direction

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1. Introduction

The high homogeneity of doping profile in silica-based glasses has become a necessity for cutting-edge photonic applications, such as optical micro-lithography for the microchips manufacturing [1] and mirror substrates for Extreme Ultraviolet Lithography (EUVL) [2]. In particular, SiO$_2$–TiO$_2$ glass system has attracted great interest due to its exceptional properties, such as high refractive index and ultra low coefficient of thermal expansion [3]. Currently, these special materials are produced by chemical deposition routes, for example the Vapor-Phase Axial Deposition (VAD) [4] technique. The VAD was originally designed for the fabrication of optical fibers preforms, allowing the synthesis of highly-transparent and bubble-free doped silica glasses, with a precise control of its geometry and refractive index profile [5,6]. However, through the VAD method it is particularly difficult to synthesize glasses with constant dopant distributions along the radius due to the axial direction of nanoparticles deposition. In addition, the boule outer diameter is alternately exposed to the flame because of the rotation movement and is consequently submitted to a cyclic heating and cooling process during the deposition stage, making this method not suitable for the fabrication of optical devices with non-parabolic doping profiles [7,8].

In this context, Rajala et al. [9] proposed the use of the Atomic Layer Deposition (ALD) technique for the doping of porous bodies synthesized by chemical deposition routes, in order to obtain materials with high homogeneity of dopant concentration. Therefore, the reactive groups (hydroxyl groups) contained on the silica surface (nanoparticle) could be used as anchoring elements. According to the ALD, in a first stage the reactive groups would be subjected to self-termination reactions with the dopant precursor, followed by a second reagent responsible for the reformation and reactivation of the hydroxyl groups [10]. In the specific case of the silica–titania glasses manufacturing, the dopant and reformer would be TiCl$_4$ and H$_2$O, respectively. Initially, silica nanoparticles without surface modification are placed in contact with the dopant precursor (TiCl$_4$) generating the anchoring of the titanium atoms with oxygen, resulting in the formation of the first atomic layer over the nanoparticles surface. When the reformer reagent (H$_2$O) is inserted, the chlorine atoms are removed in form of hydrochloric acid (by-product) and, consequently, the reformation of the hydroxyl groups on titanium surface occurs [11]. Thus, the reaction cycles can be repeated until the desired amount of material has been deposited. According to the literature, Norin et al. [12] successfully used the synergy between Modified Chemical Vapor Deposition (MCVD) and ALD as a new method to produce Er-doped...
fibers with commercial quality. However, details about the doping homogeneity along the material are still unclear.

In this work, titania-doped silica glasses have been synthesized through the synergy between VAD and ALD techniques. The effect of ALD parameters, such as chamber temperature, number of cycles and TiCl4 flow time, and VAD parameters, such as H2/O2 ratio were studied on the radial doping profile homogeneity and glass structure by X-ray scanning fluorescence, Raman spectroscopy and X-ray diffraction.

2. Experimental procedure

In the first step, porous boules of pure silica were deposited by the VAD technique\[13,14\]. Amorphous silica nanoparticles (SiO2) were synthesized in a high temperature H2–O2 flame by the hydrolysis and oxidation reactions of the SiCl4 precursor. Silica nanoparticles were axially deposited over a starting target rod, with constant rotation movement at 25 rpm and vertical translation movement with same rate of the soot deposition, to form a cylindrical-shaped porous boule. The standard dimensions adopted for the porous boules were 100 mm (axial) / 40 mm (radial). A five concentric nozzle silica burner with inclination angle of 47° and distance of 55 mm from the target surface was used to provide the gases mixture for the chemical reactions. The SiCl4 flow was set to 150 sccm (carrier gas) at 30 °C, while the H2/O2 ratio was varied as shown in Table 1.

Aiming the doping of porous boules, a custom-made system based on ALD principles was developed. Fig. 1 illustrates a schematic diagram of the doping system, which is composed by an inner tube (i) with a set of attached electrical resistances (ii) responsible for the heating and maintaining of the temperature within the chamber. The internal temperature was measured by a thermocouple (iii) and controlled in closed loop. The insertion of the precursor vapors was done by bubbling the liquid reagents (iv) using high purity helium (v) as a carrier gas, which has its flow ensured through mass flow controllers (MFC) (vi). All the vapor lines were kept under heating by using thermal tapes (vii) in order to prevent the condensation of precursors. The sequence of admission of vapors was adjusted by a set of valves coupled to the chamber entrance (Admission Control) (viii). After the passage of precursors through the reactor, a set of valves (Exhaust control) (ix) controls the flow of the by-products, directing them to the effluent treatment (x) or allowing the chamber evacuation (xi).

In the second step, porous boules of pure silica were doped by the ALD technique. Initially, the boules were dried for 1 h at 90 °C under vacuum atmosphere. The vacuum inside the chamber was broken using dry N2 followed by the adjustment of working temperature. The first ALD cycle starts from this point with the admission of TiCl4\(_{(v)}\) reagent with a flow rate of 0.2 g/min. Then, the chamber was purged to remove the non-reacted precursor and the by-products, by using dry N2\(_{(g)}\) in order to perform a rough cleaning, and vacuum to promote a fine cleaning. Afterwards, H2O was admitted with a flow rate of 0.4 g/min for 30 min, followed by purge as described for the TiCl4. Thus, the ALD cycle was repeated until the desired amount of material was deposited. The values for parameters of the ALD process varied in this work are also summarized in Table 1.

In the third and final step, the porous doped boules were consolidated for 2 h in helium gas atmosphere at 1400 °C using a tubular electric furnace. Silica–titania samples were prepared by slicing the consolidated boules perpendicularly to longitudinal axes. The 3.0 mm thick disks were polished (optical finish) for all characterizations.

The radial distribution of titania was determined by X-ray scanning fluorescence (XRF) using a Rigaku RIX3100 spectrometer equipped with a rhodium X-ray tube, operating at 50 kV and 80 mA. A LiF (200) analyzer crystal. The measurements were performed along the diameter in a 1.0 mm step and TiO2 concentrations were obtained by a calibration curve. The standard deviation value was adopted for comparative purposes in order to

<table>
<thead>
<tr>
<th>Sample</th>
<th>VAD condition</th>
<th>ALD conditions</th>
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<tbody>
<tr>
<td></td>
<td>H2/O2 ratio</td>
<td>Number of cycles</td>
</tr>
<tr>
<td>1</td>
<td>1.10</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1.10</td>
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<tr>
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<td>1.00</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>1.17</td>
<td>4</td>
</tr>
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estimate the homogeneity of the doping profile. The more constant is the profile, the closer to zero is the deviation. The standard deviation estimated for a same measure was approximately ±0.07 wt% TiO₂.

The glass structure was studied by micro-Raman spectroscopy and X-ray diffraction technique (XRD). Raman measurements were performed using a spectral excitation provided by an argon ion laser, using the 514.5 nm laser line and collected in the backscattering geometry. The scattered light was analyzed in a T64000 Jobin Yvon spectrometer, equipped with a N₂-cooled charge-coupled device (CCD) system. The wavenumbers of the Raman bands are expected to be accurate to within ±2 cm⁻¹. The X-ray measurements were provided by a DMax2200 Rigaku X-ray diffractometer equipped with CuKα fine focus tube and Ni filter. The X-ray source parameters were set to 40 kV and 20 mA, angular 2θ range of 21–31° with step of 0.01° and detection time of 8 s/step.

The average density was estimated by an image treatment software. The porous boule volume was determined by approximating its geometry to a solid of revolution, since the boule rotation has a constant angular speed during the nanoparticles deposition. Average density was reported as ±0.01 g/cm³.

3. Results and discussion

3.1. Effects of the ALD parameters

Fig. 2 shows the radial doping profile of samples prepared using different TiCl₄ flow times and chamber temperatures for one ALD cycle. Comparing the samples prepared at room temperature (sample 1) and 90 °C (sample 2) with a constant TiCl₄ flow time of 30 min, we have observed that the increase in the chamber temperature induces the homogenization of doping profile. In fact, the sample 1 presented a standard deviation of ±0.26 wt% TiO₂, whereas a smaller standard deviation of ±0.05 wt% TiO₂ was obtained in the sample 2 doped at 90 °C. The lower doping profile homogeneity of sample 1 can be attributed to a higher dopant concentration on the edges caused by an undesirable condensation effect of titanium tetrachloride on the porous boule surface during the doping process. This effect probably occurred because the TiCl₄ vapor was found at higher temperature than the measured inside the chamber.

By comparing the samples prepared during 30 (sample 2) and 120 min (sample 3) of TiCl₄ flow at 90 °C, we observed that the ra-
Dial doping profiles of both samples were almost similar, as shown in Fig. 2. This result is consistent with the ALD theory, which states that, after saturation of the active groups present on the substrate surface, there would be no increase in the dopant amount [10]. Hence, the time required for the saturation of first cycle is less than 30 min at 90 °C. Also, it was noticed that this temperature was sufficient to avoid the condensation effect even for a long time of TiCl₄ flow. Both samples presented high radial doping profile homogeneity with standard deviations of ±0.05 and ±0.08 wt% TiO₂, for samples 2 and 3, respectively.

Concerning the effect of the chamber temperature for four ALD cycles, Fig. 3a shows the image and the doping profile for sample 5 prepared at room temperature. We have observed that the material exhibited a low radial doping homogeneity with standard deviation of ±1.99 wt%. Furthermore, the doping profile presented a pronounced parabolic shape, suggesting that during the doping stage, the condensation of the titanium tetrachloride occurred on the porous boule surface, as described for sample 1, and that the doping process performed at room temperature was not adequate for the formation of a radial TiO₂ profile with satisfactory homogeneity. In order to avoid this effect, the chamber temperature was raised and maintained at 90 °C during the four ALD cycles. Fig. 3b shows an image and the doping profile for sample 6 prepared at 90 °C. In this case, we observed that the chamber temperature affects significantly the radial doping profile homogeneity and the average doping concentration since the standard deviation decreases of ±2.11 (sample 5) to ±0.35 wt% TiO₂, which means a great improvement of the doping profile homogeneity. Also, the average concentration of TiO₂ was decreased which was expected due the reduction of the condensation effect.

In the image of Fig. 3a, we visualized the presence of three distinct regions, with a transparent portion (Vis) in the central region of the sample (i), and opaque areas in the intermediate (ii) and peripheral (iii) regions, with a blue and white tint, respectively. Thus, in order to investigate the glass structure formed in these three regions, Raman scattering measurements were performed, as shown in Fig. 4. The Raman spectrum for region i revealed that the material was completely amorphous, and comparing to the pure silica spectrum [15], we observed a reasonable similarity, except by the presence of the polarized and depolarized band at 933 and 1106 cm⁻¹, respectively, associated with vibrations of mixed Si–O–Ti bonds [16], suggesting the formation of silica–titania on glassy state. According to the model proposed in Fig. 5 for region (i), the oxides mixture occurs during the consolidation process and a complete solubilization of TiO₂ on SiO₂ could be achieved.

On the other hand, the Raman spectra for opaque regions (ii and iii) showed the same bands associated with silica–titania on glassy state as described for region (i), however, it also revealed the presence of additional bands related with the anatase crystalline phase (e.g. 144 (inset) and 635 cm⁻¹ [17]). In the model proposed in Fig. 5 for regions (ii) and (iii), the formation of segregated anatase phase

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**Fig. 4.** Raman spectra of silica glass and regions i, ii, and iii of sample prepared with four ALD at room temperature (sample 5); Inset, detail of the frequency 144 cm⁻¹ for the three regions and silica glass.

**Fig. 5.** Model proposed for the formation for SiO₂–TiO₂ glass and TiO₂ clusters during the consolidation process at 1400 °C.

**Fig. 6.** Raman spectra of silica glass and regions (i), (ii), and (iii) of sample prepared with four ALD at 90 °C (sample 6).

**Fig. 7.** Radial doping profile of samples with average densities of the porous boule of (●) 0.06 (sample 4), (▲) 0.11 (sample 6), (■) 0.16 g/cm³ (sample 7). Radial doping profile of the sample 4 (○) after surface melting treatment.
can be attributed to the local saturation in the oxides solubility, suggesting that the temperature (1400 °C) used in the consolidation process does not provide enough mobility in these regions, which contains a higher amount of titania than the region (i), causing a partial solubilization of the TiO2. Thus, opacity in these regions could be attributed to the nucleation and crystal growth of this segregated phase.

Raman measurements for the three regions of the sample 6, revealed that the material was completely amorphous (Fig. 6) as well as the presence of the polarized and depolarized band at 933 and 106 cm⁻¹, respectively, indicating the formation of silica–titania glassy state for these regions.

3.2. Effects of the VAD parameters

Regarding the effect of the VAD parameters on the doping homogeneity and glass structure, we synthesized three porous boules with different average densities by setting different H2/O2 ratios, which were doped at the same ALD conditions. The H2/O2 ratios used were 0.83 (sample 4), 1.00 (sample 6) and 1.17 (sample 7) which produced porous boules with average densities of 0.06, 0.11 and 0.16 g/cm³, respectively. Fig. 7 shows the radial doping profile for these samples. Qualitatively, it was verified that the standard deviation and average concentration of TiO2 were similar for porous boules with average densities between 0.11 and 0.16 g/cm³. However, for sample 4 with a very small average density, we have observed a higher TiO2 average concentration than sample 6 and sample 7. This result can be attributed to the fact that flames with minor H2/O2 ratios, i.e. lower temperatures, tend to form smaller nanoparticles due to lower interparticles coalescence. Thus, increasing the specific surface area, a higher amount of hydroxyl groups per volume unit can be found. However, with respect to the doping profile of sample 4, more studies are being conducted to explain the difference in profile homogeneity.

After conventional consolidation process at 1400 °C, the sample 4 was found to be completely opaque, as shown in Fig. 8(a1). XRD measurements (Fig. 8a) revealed the presence of anatase phase (2θ = 25.4°) and a small amount of rutile phase (2θ = 27.5°) in the structure. Thus, this sample was submitted to an additional surface melting treatment at 1900 °C using a pre-mix hydrogen flame. After the heat treatment, the material was changed to a completely transparent and with amorphous structure, as shown in Fig. 8(b1) and (b), respectively. Moreover, the doping profile was practically maintained the same even after the treatment (Fig. 7). This result suggests that the segregated phases were solubilized in the silica structure during the melting process.

4. Conclusion

The synergy between the VAD and ALD techniques proved to be a very promising method for the synthesis of glasses with high doping homogeneity. In case of TiO2–SiO2 glasses, we observed that the increase of the ALD chamber temperature (90 °C) has a significant effect on the radial doping profile homogeneity, causing the suppression of the condensation effect, achieving a higher homogeneity (constant profile) for one and four cycles. We also observed that porous boules with higher average densities tended to produce more homogeneous doping profiles. Regarding the glass formation and crystallization we concluded that the TiO2–SiO2 glass was formed by diffusion of TiO2 on silica matrix during the consolidation process at a high temperature (1400 °C), since the emergence of anatase clusters was attributed to local saturation in the oxides solubility. The opacity of some samples can be explained by to the TiO2 nucleation and crystal growth of segregated phase, which could be completely eliminated by heat treatment in flame. This treatment not only transformed the sample in a completely transparent and amorphous material, but also preserved the doping profile.

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