NANOSTRUCTURED SILICA-BASED GLASS FOR ENGINEERED PHOTONIC PRODUCTS

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SYNOPSIS

Among the various types of engineered photonic products, the nanostructured silica made by the flame aerosol method presents an increasing interest as optical fiber sensors and lasers for use in mechano-informatics and automation and control systems. That is the case of fiber sensor for optical strain gauges in bridges, buildings, traffic control of vehicles, and smart structures. The present research reports an advanced processing technique, the synthesis of nanostructured preform, which allows to control the nanoporosity and nanoparticle size distribution during the early stages of processing and thermal consolidation in order to make improvements of key properties of such devices.

INTRODUCTION

Besides the strategic application for optical communications, the silica-based optical fibers have presently a wide range of use as optical sensors and lasers. That is the case for example of fiber Bragg grating, FBG (Kersey, 1997), polarization maintaining fiber, PMF (Wang, 2005), and erbium-doped fiber, EDF (Bayart, 2003).

The most usual fiber Bragg grating is a silica-germania single-mode optical fiber with a periodic or aperiodic perturbation of the order of hundreds of nanometers of the effective refractive index in the core. This leads to the reflection of light propagating through the fiber in a narrow range of wavelengths in order to fulfill the Bragg condition. In other words, the wavenumber of the grating matches the difference of the wavenumbers of the incident and reflected waves. However, as the wavelengths of maximum reflectivity depend also on temperature and strain, fiber Bragg grating is quite useful for temperature and strain sensors. The fabrication of fiber Bragg grating uses illumination of the core material with ultraviolet laser light, which induces a permanent modification in the refractive index (Bennion, 1996). Therefore, one of the key points of this technology is to make improvements in the photosensitivity property of silica-germania optical fiber.

On the other hand, silica-germania polarization maintaining fiber has also a wide range of application to detect temperature, pressure, acoustic signals, current, rotation, and magnetic field. This technology will be a subject of another contribution article in this conference (Fujiwara, 2006).

In the case of erbium-doped single mode fiber, which is also silica-based optical fiber, it is widely used in optical communications systems for compensating the loss of long fiber spans. It is the most deployed fiber amplifier as its amplification window spectra coincides with the silica-based communication bandwidth (around 1525-1610 nm). In addition, erbium-doped
fiber can also be used as tunable laser (erbium-doped fiber ring laser, EDFRL) for a number of advanced applications.

However, functional properties of such kind of fibers depend on special procedures in order to introduce other types of atoms in the silica structure using dopants, such as germanium, erbium, or titanium. The main requirements for property improvements are high concentration of dopants, vitreous structure of the binary system (e.g., SiO₂:GeO₂) as perfect as possible without any kind of clustering, and good homogeneity in terms of density fluctuations and birefringence. In the present research, an advanced process of nanoporous preform deposition by the synthesis of SiO₂ and GeO₂ (TiO₂) nanoparticles is presented. By thermo-chemical treatment, the nanostructured preform is dehydrated and consolidated into a transparent preform that will constitute the main part of the fiber nucleous. Pure silica cladding is added in an additional process denoted as “soot-overcladding”. Finally, the manufactured preform is drawn into optical fiber.

NANOTECHNOLOGICAL PROCESSING – STATE OF THE ART

Nanostructured pure or doped silica preforms are synthesized by flame aerosol method by hydrolysis and oxidation of metallic halides (SiCl₄ and GeCl₄, or SiCl₄ and TiCl₄) through the vapor-phase axial deposition technology (VAD) (Suzuki, 1998; Izawa, 2000). The basic chemical reaction for the formation of glass oxide is:

\[
\text{SiCl}_4 + 2\text{H}_2 + \text{O}_2 \rightarrow \text{SiO}_2 + 4\text{HCl}. \quad (1)
\]

GeCl₄ (TiCl₄) halide was also simultaneously used in conjunction with SiCl₄, resulting in SiO₂:GeO₂ (SiO₂:TiO₂) porous glass. A torch composed of 5 concentric silica tubes corresponding to 5 gas-flow channels was used (Fig. 1). SiCl₄ and GeCl₄ (TiCl₄) halides were injected in the central channel by a carrier \text{O}_2 gas. Hydrogen and oxygen gases were alternately blown through the concentric torch channels. Inert gas, such as nitrogen was intercalated to halide vapors and the hydrogen/oxygen gases. Due to the large number of process parameters simultaneously involved in this technology, automation system for on-line control of geometrical homogeneity of the preform (Ono, 2002), and the doping profile of GeO₂ (Santos, 2006a) was developed. Fig. 2 shows a schematic view of the deposition equipment. Nanoparticles of silica and doping oxides (soot) are deposited onto a rotating substrate, which has also a vertical translation movement of the same speed of soot deposition. The uniformity control of the diameter of preform is conducted by a feedback system using LabVIEW, which allows an accuracy of +/- 100 µm in the diameter of preform along its axial direction.

Fig. 1. Five-channel torch for the synthesis of silica-based nanoparticles.
On the other hand, it has been observed that the doping profile of the preform depends on the deposition surface profile, which depends directly on the temperature profile (Santos, 2006b). Therefore, a real time monitoring of such deposition surface profile has been conducted through its parameterization using an allometric function. Doping of erbium was performed by immersion of nanoporous preform in liquid solution of ErCl₃ and ethanol.

Subsequently, the dehydration process consisted of a thermo-chemical treatment at T~1200°C in chlorine gas atmosphere with the purpose to remove hydroxyls and metallic impurities. The basic reactions that occur during the dehydration process (Chida, 1982) are:

\[
2\text{H}_2\text{O} + 2\text{Cl}_2 \leftrightarrow 4\text{HCl} + \text{O}_2 \tag{2}
\]

\[
2\text{Si-OH} + 2\text{Cl}_2 \leftrightarrow 2\text{Si-Cl} + 2\text{HCl} + \text{O}_2.
\]

Hydroxyl content can be controlled in this stage depending on the time, temperature and chlorine flux, but concentration values down to 50 ppb can be earned without difficulty.

In the next step, consolidation process of heat-treatment at temperatures above 1400°C under controlled atmosphere takes place to transform the porous body into a highly transparent bubble-free preform. Metallic impurities are less than 1 ppb order.

Related to the manufacture improvement of fiber Bragg grating, a methodology to control and to enhance defect centers associated with the second-order harmonic generation and photosensitivity in SiO₂:GeO₂ glass has been developed in our laboratory (Cuevas, 2004, 2006). The effect is directly related to the exponential increase of germanium oxygen deficient centers by simultaneous decrease of \( \text{H}_2/\text{O}_2 \) ratio and temperature increase during nanostructured preform deposition (Suzuki, 2004).

**RESULTS**

Nanostructured silica-germania preforms under optimized conditions are obtained using the procedure described above. Fig. 3 shows a representative image by scanning electron
microscopy of “as-deposited” silica nanoparticles with dimensions ranging ~100 nm. The relevant point in this research is the particle size distribution that can be controlled by the H$_2$/O$_2$ ratio and the distance of the torch mouthpiece to the substrate. On the other hand, the nanoporosity, that means the nanoparticle size distribution which depends on the process parameters, can also be controlled by heat-treatment. That procedure results in a much smaller nanoporous size distribution. Fig. 4 presents the nanoparticle radius distribution of small angle X-ray scattering data observed by GNOM software. It can be observed that for higher temperature of heat-treatment, the average porous size decreases. Consequently, nanoporosity of the whole body can be decreased.

Fig. 3. Silica nanoparticles synthesized by aerosol flame VAD technology.

Fig. 4. Control of particle size distribution and nanoporosity by thermal treatment.

Fig. 5.a shows a representative result of nanoporosity measurement by BET – Brunauer, Emmet and Teller technique and their dependence with density. Control of nanoporosity is essential to earn high concentrations of doped erbium (Fig. 5.b).
Erbium-doped nanostructured core-preform containing GeO$_2$ doping profile is then dehydrated and consolidated giving origin to the nucleous-preform. The ratio of cladding/nucleous diameters are adjusted by stretching and soot-overcladding processes. Fig. 6 shows a sequence of soot-overcladding deposition for the manufacture of erbium doped fiber preform. Figures 7 and 8 show the erbium-doped fiber preform and the erbium-doped fiber itself, respectively.
The main characteristics of erbium doped fibers made in the present research project are listed in Table 1. The measured erbium life-time was 12.5 ms for the three fibers. These results fulfill the requirements for a number of technological applications, but the most important point is the potentiality of the present methodology to make improvements for new properties of silica-based optical fiber sensors.

Table 1. Main characteristics of erbium doped fiber made in this research project.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fiber #1</th>
<th>Fiber #2</th>
<th>Fiber #3</th>
<th>Estimated error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modal field (@1.3µm)</td>
<td>7.6</td>
<td>6.9</td>
<td>6.9</td>
<td>0.2 µm</td>
</tr>
<tr>
<td>Modal field @1.55µm</td>
<td>9.6(b)</td>
<td>8.4(b)</td>
<td>8.7(b)</td>
<td>0.5 µm</td>
</tr>
<tr>
<td>Wavelength of cutting (nm)</td>
<td>885</td>
<td>954</td>
<td>875</td>
<td>20 nm</td>
</tr>
<tr>
<td>$\phi_{nucleous}$ (µm)</td>
<td>5.3</td>
<td>6.3</td>
<td>5.4</td>
<td>0.2 µm</td>
</tr>
<tr>
<td>$\phi_{cladding}$ (µm)</td>
<td>124.5</td>
<td>122.4</td>
<td>124.6</td>
<td>0.5 µm</td>
</tr>
<tr>
<td>$\phi_{coating}$ (µm)</td>
<td>222</td>
<td>226</td>
<td></td>
<td>2 µm</td>
</tr>
<tr>
<td>Coating concent.</td>
<td></td>
<td>0.94</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>Splicing by fusion</td>
<td>OK</td>
<td>OK</td>
<td>OK</td>
<td></td>
</tr>
<tr>
<td>Absorption in 980nm</td>
<td>3.9</td>
<td>5.0</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>Abs width (half width)</td>
<td>40 nm</td>
<td>25 nm</td>
<td>10 nm</td>
<td></td>
</tr>
<tr>
<td>Absorption in 1535 nm</td>
<td>2.8</td>
<td>1.5</td>
<td>0.4</td>
<td></td>
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<tr>
<td>Gain</td>
<td>20 dB</td>
<td></td>
<td>17 dB</td>
<td></td>
</tr>
</tbody>
</table>
CONCLUSIONS

The possibility to control de particle size distribution, as well as the nanoporosity of pure- and doped-silica in the early stages of soot preform deposition allow to make improvements of optical fiber key properties, such as photosensitivity of silica-germania for fiber Bragg grating manufacture, and rare-earth doping for special fibers. The application of the present procedure is of great interest to develop new properties related to optical fiber sensors.

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REFERENCES

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