Effect of the preform fabrication process on the properties of all-silica optical fibres

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Abstract. **In this paper, we present a detailed comparison of technical capabilities of processes for the fabrication of all-silica optical fibre preforms with the use of an atmospheric pressure radio frequency plasma (POVD process) and low-pressure microwave plasma (PCVD process) and analyse the origin of the difference in optical properties between fibres produced by these methods. It is shown that the higher temperature of the core material and the higher oxygen partial pressure in preform fabrication by the POVD process lead to an increase in optical losses in the visible and UV spectral regions in the silica fibres with low hydroxyl (OH) content and a decrease in the solarisation resistance of the fibres with high OH content, i.e. to a more rapid increase in background losses in response to UV irradiation. No such drawbacks are detected in the case of the growth of reflective layers by the PCVD process.**

1. Introduction

Because of the rapid progress in medicine and laser processing of materials, there is a growing need for optical fibre with a large numerical aperture, low optical losses and high optical damage threshold (high-power optical fibres). Optical fibres with a pure silica core have proved themselves to be the most viable guides for intense light from industrial and medical lasers [1]. The growing need for high-power optical fibres stimulated the development of processes for the fabrication of preforms with an undoped silica core. The most promising approach for the commercial-scale manufacture of such preforms is to produce a reflective fluorine-doped silica cladding by plasma outside vapour deposition (POVD) [2]. Ceram Optec SIA develops preform fabrication methods that employ an atmospheric pressure radio frequency (rf) plasma (POVD process) and low-pressure microwave plasma [plasma chemical vapour deposition (PCVD)]. The implementation of different preform fabrication processes in one place (Livani, Latvia) and drawing different preforms into fibres using the same equipment offer the possibility of comparing the POVD and PCVD processes within one process area. In this paper, we examine the effect of the

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preform fabrication process on the properties of high-power optical fibres.

2. Description of the POVD and PCVD processes

In the POVD process, gaseous precursors, such as $SiCl_4$ and SF_6, are introduced into an atmospheric pressure inductively coupled air plasma. In each deposition pass, a plasma torch is moved along the length of a silica rod [3]. Commercially available all-silica preforms are typically produced by the POVD process [4, 5]. Figure 1 shows a schematic of the POVD apparatus. The deposition process is run inside a screening box (*1*) fitted with windows for monitoring the process. A synthetic silica glass substrate rod (*2*) is placed on a galss-working lathe (*3*) equipped with a plasma torch (*4*) and is prepared for the deposition process. The same plasma torch (*4*) is used to fuse the rod to service handles (*5*), fire-polish it before deposition and run the deposition process proper. During the deposition, the precusors are introduced into the plasma torch zone through quartz nozzles located in the upper part of the torch. After the deposition process, the resultant preform is separated from the service handles using the same plasma torch.

In the PCVD process, the plasma is generated in an auxiliary tube at a pressure of ~5 mbar in a gas mixture heated to a temperature of ~1100°C [6]. The PCVD process was pro-
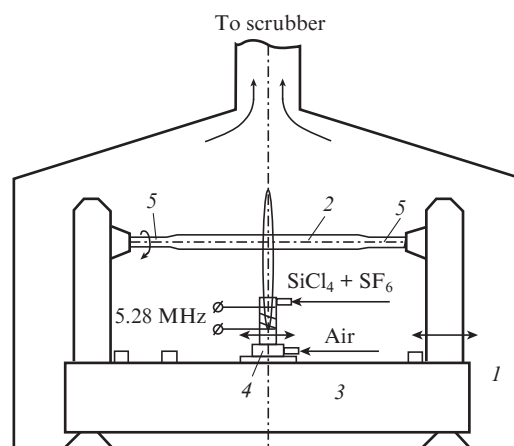

Figure 1. Schematic of the POVD apparatus: (*1*) screening box; (*2*) substrate rod; (*3*) glass-working lathe; (*4*) plasma torch; (*5*) service handles.

posed for silica deposition on the inner surface of a silica tube [7], and a distinctive feature of Ceram Optec apparatuses is that the substrate rod is located inside the tube. The silica tube with the deposit is here used only as a reactor for silica deposition on the rod, rather than being the end product. Figure 2 shows a schematic of the PCVD system. Before beginning the process, an assembly should be prepared using auxiliary equipment. To this end, it is necessary to fuse service handles (*1*) to the substrate rod (*2*), fire-polish the rod and then place it, together with the service handles, in the silica tube reactor (*3*). The assembly is then mounted in a microwave resonator (*4*), the top end of the tube reactor is hermetically connected to a precursor delivery system and its bottom end is connected to a vacuum system. A part of the assembly, along the path of the microwave resonator, is placed in a furnace (*5*) and heated to a temperature of $\sim$1100 °C. After a plasma (*7*) is initiated, the precursors are fed to the top part of the tube through a vacuum-tight rotary joint (*6*). The vertical reciprocation of the resonator and the rotation of the substrate rod in the tube reactor ensure uni-
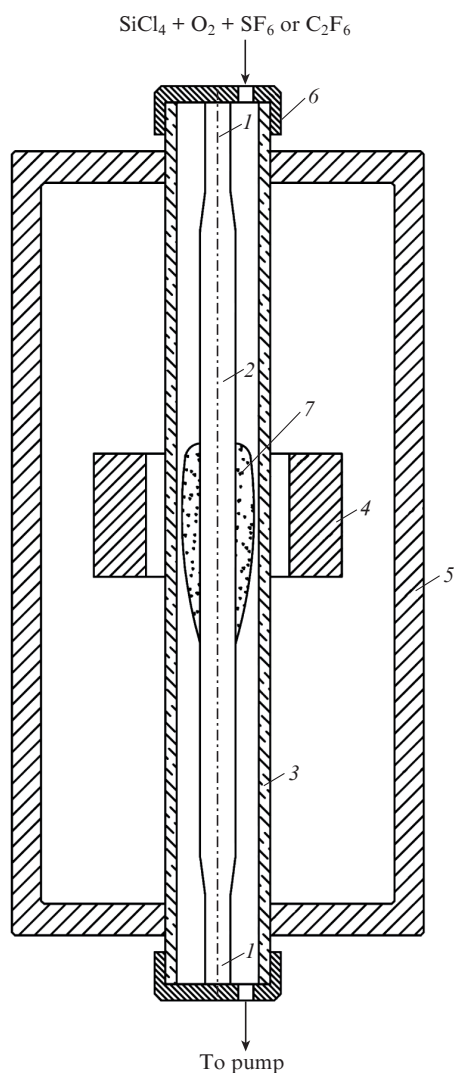
form growth of fluorine-doped silica glass layers. After the deposition process, the service handles are separated using auxiliary equipment and are reused if possible, whereas the tube reactor is recycled.

In both deposition processes, fluorine-doped silica layers are produced on the outer surface of a glass substrate. The maximum length of the preforms produced at Ceram Optec by the POVD and PCVD processes is 1100 mm, and their maximum diameters are 50 and 30 mm, respectively. The complete POVD preform fabrication cycle, including POVD and subsequent processing of the preform, can be performed using only the main apparatus and requires no additional equipment. The POVD apparatus can readily be modified to increase the substrate rod diameter. At the same time, the POVD rate decreases with increasing fluorine precursor concentration in the starting mixture. Accordingly, deposition efficiency decreases with increasing desired fluorine concentration in the deposit. For example, the deposition rate for layers with $\Delta n = -0.022$ is a factor of 6 lower than that for undoped silica.

The PCVD process requires not only the main apparatus but also a tube rinsing system, a galss-working lathe and reactor tubes as consumables. The preprocessing steps take a long time and require air cleanliness. On the other hand, the PCVD process enables the growth of heavily doped layers with $\Delta n = -0.028$, which allows the numerical aperture of preforms to reach 0.3 in the case of an undoped silica core. The deposition rate is essentially independent of fluorine concentration and approaches that of undoped silica in the POVD process.

In the PCVD process, the shape of noncircular silica preforms cannot be changed in the course of deposition. Figure 3 shows a photograph of a preform with an octagonal cross section of its core, and Fig. 4 shows a cleaved end of a square-core fibre (the preform was produced in the PCVD system). The rounding of the corners of the core is determined by the deposition process. In the case of a square core cross section, it can be quantified by the ratio of the rounding diameter to the side length of the core. For the fibre represented in Fig. 4, this ratio is 0.058 (or 5.8%). Attempts to use the POVD process in the case of a square core cross section led to considerable rounding of the corners of the square. The ratio of the rounding diameter to the side length of the core in the case of the POVD process was at least 40%.
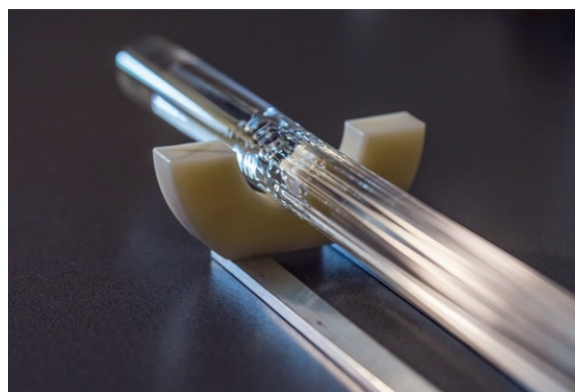

Figure 2. Schematic of the PCVD system: (*1*) service handles; (*2*) substrate rod; (*3*) silica tube reactor; (*4*) microwave resonator; (*5*) electric furnace; (*6*) vacuum-tight rotary joint; (*7*) plasma.

SiCl$_4$ + O$_2$ + SF$_6$ or C$_2$F$_6$

To pump

Figure 3. (Colour online) Assembly after PCVD: octagonal preform with a reflective cladding (at the right) and a service handle (at the left).
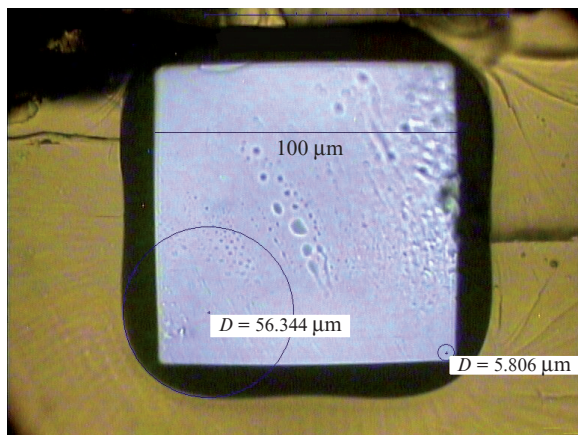
Figure 4. Cleaved end of a WFRCT100x100/123x123/250A square-core fibre drawn out from an PCVD preform. Drawing conditions: furnace temperature, 1770 °C; draw rate, 7 m min^{-1}.

3. Experimental

The numerical aperture of preforms was evaluated from refractive index profiles measured with a P102 preform analyser (York Technology, USA). The preforms produced by the POVD and PCVD processes had essentially identical index profiles (Fig. 5). The spectral characteristics of the fibres in the range 200–1700 nm were measured by the cutback technique using a Spectro 320D optical scanning spectrometer (Instrument Systems, Germany). The UV source used in assessing the solarisation resistance of our samples was a D2plus deuterium lamp (Heraeus Noblelight, UK). The UV radiation was focused by CaF_2 lenses in a box under flowing nitrogen. A higher power source of radiation at a wavelength of 193 nm was a PSX-100 ArF excimer laser (Neweks, Estonia), which was pulsed at a repetition rate of 10 Hz ($\tau \approx$ 5 ns).
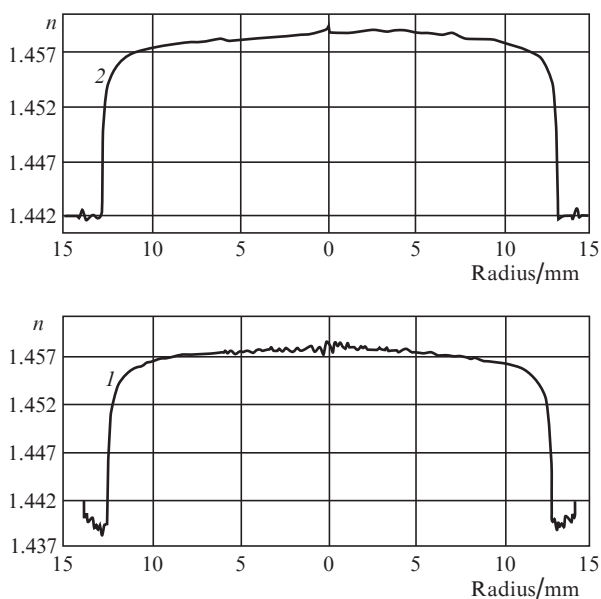

Figure 5. Refractive index (n) profiles of the preforms produced by the (1) POVD and (2) PCVD processes.

4. Discussion

4.1. Fibres with low hydroxyl content (WF fibres)

Water-free (WF) silica fibres are traditionally used in the visible and near-IR spectral regions (700–2000 nm), but there is a permanent need for fibres transparent in a broader wavelength range (300–2000 nm). The measured spectral characteristics of the WF fibres drawn out from the POVD and PCVD preforms differ significantly (Fig. 6). The POVD fibres have increased optical losses at wavelengths λ_{max} = 330 and 640 nm. The absorption peak at λ_{max} = 640 nm often originates from the drawing of thin fibres under nonoptimal conditions [8], but according to our observations the increased absorption at λ_{max} = 640 nm is related as well to the preform fabrication process. Increased spectral losses in the WF fibres near λ_{max} = 330 and 640 nm are indicated as well in catalogues of manufacturers that employ the POVD process to fabricate all-silica preforms [3, 4], which lends support to the assumption that the deposition method influences the spectral loss in WF fibres. The fibres drawn out from the PCVD preforms have no increased loss at λ_{max} = 330 nm, and the peak at λ = 640 nm is considerably weaker, if any, than that for the POVD fibre. We assume this phenomenon to be due to oxygen diffusion into the core material in the course of deposition. Excess oxygen leads to the formation of nonbridging oxygen hole centres, which absorb at λ_{max} = 266 and 640 nm, and reacts with SiCl groups in the silica to form molecular chlorine, which has an absorption band centred at λ = 330 nm [9]:

$$2(\equiv SiCl) + \frac{1}{2}O_2 \rightarrow (\equiv Si-O-Si \equiv) + Cl_2. \qquad (1)$$
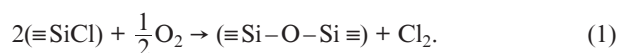
In (1) and the other schemes below, the bonds of the Si atoms that do not participate in any interaction are represented by three dashes.
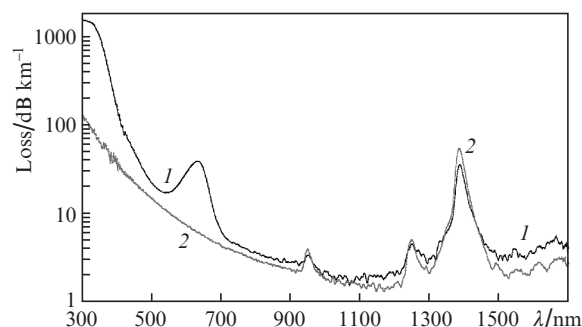

Figure 6. Loss spectra of the WF125/160/250A fibres drawn out from the (1) POVD and (2) PCVD preforms.

Enhanced oxygen diffusion in the POVD process can be accounted for by the necessity of superheating the surface of the silica seed, which is the preform core. The superheating temperature may reach 2100 °C [10], and the oxygen partial pressure is close to that in atmospheric air (200 mbar). At the same time, a low-pressure microwave plasma burns at an oxygen partial pressure near 4 mbar, and the fluorine-doped silica layers can be sintered without superheating of the core

material. The lower temperature of the silica seed in the PCVD process allows one to slow down diffusion processes and reaction (1).

4.2. Fibres with high hydroxyl content (UV fibres)

Silica with high hydroxyl content (near 1000 ppm) is used in the fabrication of fibres for the UV spectral region. Rods for OH-rich preforms are typically produced by direct, one-step silica deposition. Raw materials are introduced into the flame of an oxygen–hydrogen burner whose power is sufficient for both silica deposition in the form of fumed silica and sintering of the deposit. The content of SiCl groups in UV silica is negligible compared to that in WF silica, which is dehydrated via treatment with chlorine before sintering. The use of a hydrogen-enriched flame for sintering may, in turn, lead to the presence of excess hydrogen in the sintered structure. No significant distinctions between the spectral characteristics of the UV fibres produced by the POVD and PCVD methods were detected, but the deposition method was found to influence the solarisation resistance of the UV fibres (Fig. 7).
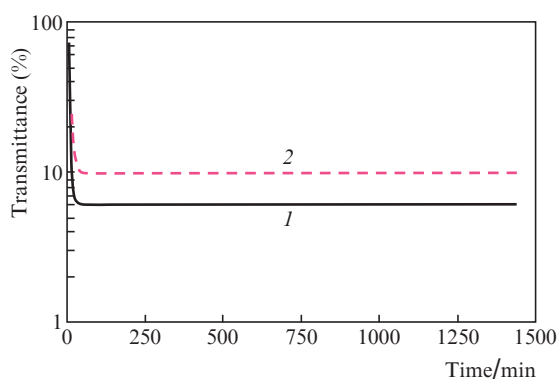
Figure 7. Transmittance at $\lambda = 214$ nm as a function of irradiation time for 2-m lengths of the UV200/220/245P fibres produced by the (*1*) POVD and (*2*) PCVD processes. Light source: D2plus lamp.

The solarisation resistance of fibres is traditionally assessed from changes in the optical loss in the range 210–220 nm, where the increase in optical loss is contributed largely by the E′ centre, which has an absorption band peaking at $\lambda = 214$ nm. A similar effect of the fabrication method on radiation resistance was reported by Tomashuk and Zabezhailov [10]. We assume that the reduction in solarisation resistance is due to the interaction of residual hydrogen with amorphous silica at elevated temperatures [11]:

$$(\equiv Si-O-Si\equiv) + H_2 \xrightarrow{T} (\equiv Si-OH) + (\equiv Si-H). \qquad (2)$$
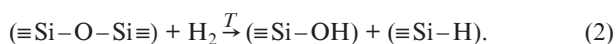
Favourable conditions for reaction (2) are created during both the growth of a reflective cladding on a substrate rod and the fibre drawing process.

The UV-induced increase in optical loss can, in turn, be accounted for by an increase in the concentration of E′ centres, which are formed from $\equiv Si-H$ groups according to the reaction scheme

$$(\equiv Si-H) \xrightarrow{UV} (\equiv Si*) + H. \qquad (3)$$

On the right-hand side of (3), the E′ centre is represented as $\equiv Si*$, where $*$ denotes an unpaired electron in the silicon atom.

The high temperature of the substrate rod during the POVD process leads to an increase in the concentration of $\equiv Si-H$ groups and an increase in the optical loss at a wavelength of 214 nm if the fibre is used in the UV spectral region, due to E′ centres. Analysis of induced loss spectra of a fibre irradiated with an excimer laser ($\lambda = 193$ nm) confirms that the concentration of E′ centres in the POVD fibre rises more rapidly. Note that the band at $\lambda = 266$ nm, due to nonbridging oxygen, emerged more rapidly in the absorption spectrum of the PCVD fibre (Fig. 8). Most likely, the hydrogen resulting from reaction (3) first reacted with nonbridging oxygen, a more reactive defect species. In the POVD glass, the active-hydrogen concentration is higher and the defect observed at $\lambda = 266$ nm is more rapidly suppressed.
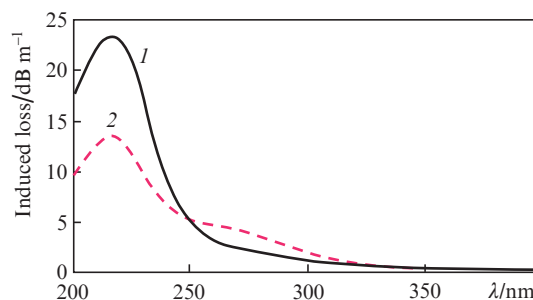
Figure 8. Induced loss spectra of 1-m-long UV200/220/245P fibres produced by the (*1*) POVD and (*2*) PCVD processes. The spectra were measured immediately after ArF laser irradiation to a fluence of 10^3 J cm^{-2}.

5. Conclusions

In this study, we have carried out a detailed comparison of the POVD and PCVD processes for the growth of the reflective claddings of all-silica preforms and analysed the origin of the difference in optical properties between fibres produced by these methods.

It has been shown that the lower temperature of the silica seed in the PCVD process allows one to slow down chemical reactions and diffusion processes in the silica substrate rod. In the case of silica with a low concentration of OH groups, this leads to a reduction in losses at wavelengths of 266, 330 and 640 nm. Preforms having a UV silica core after PCVD have a higher solarisation resistance. Independent of the nature of undoped silica, the PCVD process causes no changes in the shape of noncircular preforms.

Using POVD and PCVD, as well as alternating these processes, one can accurately control the shape of the preform core and the thickness of its reflective layers and influence the solarisation resistance and spectral characteristics of the fibres drawn out from them.

The POVD and PCVD processes have been compared for the first time using industrial equipment. The products described in this paper are commercially available, rather than being single test samples.

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