ABSTRACT

The effects of flame aerosol VAD processing parameters, such as H₂/O₂ ratio, burner-target distance, SiCl₄ gas flux, and the shape of soot preform deposition surface were correlated to the homogeneity of refractive index of post-consolidated silica perform. Interferometry and optical spectrometry techniques were used to determine the refractive index distribution, and the hydroxyl concentration was obtained through Raman spectroscopy. It was concluded that the high radial homogeneity of the refractive index is obtained with flat deposition surface profiles deposited by setting H₂/O₂ ratio >2.0, burner-target distance <45 mm, and SiCl₄ flux ≥ 2.8×10⁻⁶ m³/s.

INTRODUCTION

High purity silica glass (SiO₂) synthesized by flame aerosol method has been extensively employed as optical material for photolithography due to its high transmissivity in the short wavelength region less than 400 nm [1]. Otherwise, when the light source goes through a silica glass element, the photon energy can be absorbed and converted to heat energy, causing changes in the glass density and homogeneity of refractive index [2]. For printing fine geometry of chip patterns, it is required not only the high transmittance in the specified wavelength region, but also refractive index homogeneity less than 5 ppm [3], which can be achieved by controlling the silica structure homogeneity [4] and OH ions incorporated during silica glass synthesis process [5,6]. The CVD (Chemical Vapor Deposition) is a process commonly used for manufacturing synthetic silica glass for stepper lenses. However, the VAD (Vapor-phase Axial Deposition) process is considered one of the best alternatives due to its advantage of controlling the variation of OH concentration and structure of the silica glass.

In the present research, it was studied the effect of VAD processing parameters, such as H₂/O₂ ratio, burner-target distance, and SiCl₄ gas flux on the preform deposition soot surface shape and the homogeneity of the refractive index of silica aiming the development of an ultra-high homogeneity material for optical components.

EXPERIMENTAL PROCEDURE

Silica soot preforms with several deposition surface profiles were deposited by VAD flame aerosol method [7] with H₂/O₂ ratio from 1.0 to 3.0, by maintaining H₂ gas flux in 100×10⁻⁶ m³/s and varying the O₂ gas flux from 33×10⁻⁶ m³/s to 100×10⁻⁶ m³/s. The burner-target distances were set at positions from 34 to 53 mm, and SiCl₄ gas fluxes from 2.2 to 3.2×10⁻⁶ m³/s. It was used a five nozzle burner placed with 42° angle regarding the preform rotation axis, and rotation...
speed of 25 rpm (Fig. 1). During the deposition stage, the preform deposition surface profile is automatically parameterized by two parameters, $\alpha$ and $h$. The $\alpha$ parameter is obtained through the following allometric function:

$$y = c \cdot x^\alpha,$$

where $y$ is the bottom height along the preform axis, $c$ is the magnification coefficient, $x$ is the radial position, and $\alpha$ is the power-law index profile that best fits the preform deposition surface profile. The $h$ parameter is the axial distance from the deposition surface tip to a reference height [8,9].

![Fig. 1. Schematics of the VAD deposition stage.](image)

Afterwards, the soot silica preform was sintered (consolidated) for 2 hours in He gas atmosphere at 1733 K to produce a transparent and bubble free silica preform.

In order to measure the radial and axial distribution of the refractive index with $10^{-6}$ accuracy it was used the interferometry and optical spectrometry techniques. The radial variation of the OH concentration was characterized by Raman spectroscopy. For these measurements, it was prepared 5.0 mm thick disks polished with optical finish obtained by slicing consolidated preforms.

RESULTS AND DISCUSSION

Fig. 2 shows the influence of burner-target distance, $\text{H}_2/\text{O}_2$ ratio, and $\text{SiCl}_4$ gas flux on the shape of soot preform deposition surface, which is represented by the $\alpha$ and $h$ parameters. The increase of the burner-target distance (Fig. 2 (a)) does not significantly affect the values of $h$ parameter, however, it reduces the values of $\alpha$ parameter indicating that larger burner-target distances tend to sharpen the preform deposition surface shape. The $\text{H}_2/\text{O}_2$ ratio (Fig. 2 (b)) and $\text{SiCl}_4$ gas flux (Fig. 2 (c)) fulfill similar effect on preform deposition surface shape. The increase of both parameters reduces the $h$ parameter values and increases the $\alpha$ parameter values. In this case, preform with broad deposition surface shape tends to be deposited.
Fig. 2. Effect of (a) burner-target distance, (b) H₂/O₂ ratio, and (c) SiCl₄ gas flux on the preform deposition surface shape.

Quantitatively, it was noticed that by using H₂/O₂ ratio > 2.0, burner-target distance < 45 mm, and SiCl₄ flux \( \geq 2.8 \times 10^{-6} \text{ m}^3/\text{s} \), soot preforms with flat deposition surface profiles, \( \alpha \geq 3.0 \) and \( h \leq 2.0 \text{ mm} \) were deposited. On the other hand, sharp or parabolic soot deposition surface profiles, that mean, \( \alpha < 3.0 \), \( h > 2.0 \text{mm} \), were obtained by setting H₂/O₂ ratio < 2.0, burner-target distance \( \geq 45 \text{ mm} \), and SiCl₄ flux < \( 2.8 \times 10^{-6} \text{ m}^3/\text{s} \). The variation of H₂/O₂ ratio, burner-target distance, and SiCl₄ gas flux mainly change the flame intensity and its direction from center toward outer diameter of preform, and conversely, yielding different deposition surface shapes.

Fig. 3 (a) presents the correlation between \( \alpha \) and \( h \) parameters for various samples. When \( \alpha \geq 3.0 \) and \( h \leq 2.0 \text{mm} \) silica preforms with homogeneous refractive index of \( \Delta n \leq 3 \text{ppm} \) (difference between maximum and minimum values of refractive index) are produced. For any other \( \alpha \) and \( h \) values, higher refractive index radial variation \( (\Delta n > 3 \text{ppm}) \) is obtained. The correlation of \( \alpha \) and \( h \) with \( \Delta n \) is presented in Fig. 3 (b). Although the data are slightly scattered, there is a clear correlation between \( \Delta n \) and the shape of soot preform deposition surface.

This result can be corroborated through the illustration of Fig. 4, which presents in Fig. 4 (a) three different soot deposition surface shapes of preform S1 (\( \alpha = 3.1 \pm 0.1 \) and \( h = 3.8 \pm 0.1 \text{mm} \)), preform S2 (\( \alpha = 1.8 \pm 0.1 \) and \( h = 4.9 \pm 0.1 \text{mm} \)), and preform S3 (\( \alpha = 3.1 \pm 0.1 \) and \( h = 1.6 \pm 0.1 \text{mm} \)).
The corresponding values of the refractive index along the radial direction of consolidated preforms are shown in Fig. 4 (b).

\[ (a) \quad (b) \]

Fig. 4. Example of correlation between the preform deposition surface profile and refractive index homogeneity (a) deposition surface shapes of preform S1 ($\alpha = 3.1 \pm 0.1$ and $h = 3.8 \pm 0.1$ mm), preform S2 ($\alpha = 1.8 \pm 0.1$ and $h = 4.9 \pm 0.1$ mm), preform S3 ($\alpha = 3.1 \pm 0.1$ and $h = 1.6 \pm 0.1$ mm). (b) Corresponding refractive index along the radial direction.

The refractive index in synthetic silica glass is greatly influenced by the hydroxyl concentration [5], whose radial variation can also be correlated to the soot preform deposition surface profile, where lower variations were obtained in preforms with flat deposition surface profile [10]. According to this result, the radial variation of hydroxyl concentration of two preforms deposited with different $\alpha$ values and the same $h$ value is illustrated in Fig. 5 (a).

\[ (a) \quad (b) \]

Fig. 5. (a) Effect of $\alpha$ parameter, and (b) $h$ parameter on the radial variation of hydroxyl concentration.
It can be observed that the $\Delta[OH]$ is lower in the preform synthesized with higher $\alpha$ value. In fact, for $\alpha=3.1$, $\Delta[OH]$ of 26ppm was achieved, while for $\alpha=1.7$, higher $\Delta[OH]$ of 59ppm was obtained. In the same way, according to Fig. 5 (b), it was verified that for preforms presenting the same $\alpha$ value, the $\Delta[OH]$ is directly proportional to the $h$ parameter. In this case, $\Delta[OH]$ of 15ppm and 26ppm were obtained for $h=1.6\text{mm}$ and $h=3.8\text{mm}$, respectively.

Likewise the radial homogeneity of refractive index, its axial homogeneity is also a very important property in silica for optical components since one silica preform can be used to manufacture a number of lenses. Furthermore, the optical system incorporated in the stepper is composed of a combination of a large number of lenses, even a small variation of refractive index per a single lens can lead to a significant decrease in the printed circuit quality.

In order to verify the influence of deposition surface profile on the axial homogeneity in refractive index, the preforms S6 and S7 were analyzed. In the S6 preform, the $\alpha$ and $h$ parameters have presented a small variation during the deposition process (Fig. 6 (a)). It was verified that the axial uniformity of the preform deposition surface profile during the deposition ensures the axial uniformity of the refractive index distribution. In this case, the maximum variation of 3.0% in the $\alpha$ value and 3.6% in the $h$ value did not significantly affect the axial distribution of refractive index. On the other hand, for the S7 preform in (Fig. 6 (b)), it was observed that significant variations in the $\alpha$ value of 13.3% and in the $h$ distance of 2.6% resulted in a remarkable axial distribution of refractive index.

The Fig. 7 shows the refractive index radial distribution from the upper and lower extremities of the preforms S6 and S7. The preform deposition surface variation is probably a consequence of the process non-stability, such as deposition chamber inner pressure variation and flame turbulence.

![Fig. 6. (a) Variation of preform deposition surface profile during deposition stage of preform S6, and (b) Variation of preform deposition surface profile during deposition stage of preform S7.](image)
CONCLUSIONS

In conclusion, synthetic silica glass preforms with high homogeneity of refractive index along radial and axial directions can be obtained by controlling the shape of preform deposition surface. The high radial homogeneity of refractive indexes is obtained with flat deposition surface profiles by using $\text{H}_2/\text{O}_2$ ratio $> 2.0$, burner-target distance $< 45$ mm, and $\text{SiCl}_4$ flux $\geq 2.8\times10^{-6}$ m$^3$/s. Particularly, when $\alpha \geq 3.0$ and $h \leq 2.0$ mm silica preforms with homogeneous refractive index of $\Delta n \leq 3$ ppm can be produced. The axial homogeneity of refractive index is obtained by controlling the variation of $\alpha$ and $h$ parameters during the deposition stage.

ACKNOWLEDGEMENTS

The authors would like to acknowledge FINEP/PADCT-III, Fapesp/PIPE, CNPq/Universal, CNPq/RHAE and CAPES for the financial support. JSS would like to acknowledge the scholarships from Fapesp, EO and AASL from CNPq.

REFERENCES


