Control of optical properties of silica glass synthesized by VAD method for photonic components

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Abstract

High-purity silica glass (SiO2) synthesized by vapor-phase methods has been extensively used as optical material for photolithography due to its high transmittance in the UV range. Furthermore, low birefringence is an essential property in order to attain distortion-free images of fine IC patterns. This research reports the development of low birefringence silica glass for photonic components that excludes the annealing requirement by controlling the processing parameters of the VAD (Vapor-phase Axial Deposition) method. Nanoparticles size radial homogeneity of silica soot boules was characterized by scanning electron microscopy (SEM). It was established a relationship with the birefringence of consolidated boules characterized through polarization spectrophotometry. As the most interesting results, low birefringence silica glass (≤ 2 nm/cm) was synthesized with reduced fabrication time and cost besides simple processing stages by controlling the silica boule bottom shape during deposition processing in correlation with the consolidation time.

1. Introduction

Over the last years, advances in the photolithography technology employed in the high integration microchips print have encouraged many research activities of photonic materials. Exposure light sources (excimer laser) of shorter wavelength to enhance microchips resolution have created a need for improving optical performance of photonic components (e.g. lenses) used in photolithographic tools. Synthetic silica glass (SiO2) has been largely employed as a main material for photonic components. Among commercial photonic glasses currently available, silica glass presents the highest transmissivity in the short wavelength region lower than 400 nm [1,2]. Besides transparency and refractive index radial homogeneity, birefringence of 2 nm/cm or less is of critical importance to achieve distortion-free images of fine projected IC [3].

Synthetic silica boules used for high technology photonic applications are usually synthesized by vapor-phase deposition methods because a large amount of metallic impurities from basic raw materials are eliminated during the process producing silica boules with very low impurities concentrations. In this sense, the VAD (Vapor-phase Axial Deposition) flame aerosol method has been considered a promising technique to outperform the CVD (Chemical Vapor Deposition), currently used as the main method to produce high-purity synthetic silica glass for such purpose. In the VAD method, silica nanoparticles are synthesized in an H2–O2 flame by the hydrolysis and oxidation reactions of SiCl4 axially deposited on a rotating target, forming a cylindrical-shaped soot boule. Afterwards, this boule is consolidated at high-temperature and transformed into a highly transparent glass. Conventional methods require an additional post-consolidation thermal homogenization step (annealing) in order to eliminate the residual stress and therefore, to minimize the birefringence embodied into material during the main stage of its fabrication. However, annealing is expensive and takes a considerable amount of time [4]. In addition, after annealing, a high birefringence usually remains in the outer diameter region of the material and only boule center region can be used. Also, even setting a slow cooling rate, it is difficult to get the same cooling rate in both outer diameter region and the central region. The cooling rate at the outer diameter is faster than at the center, causing a radial fictive temperature fluctuation according to the material thermal history [5]. This can affect the silica density and refractive index, as well as the optical anisotropy which is originated residual stress, resulting in a remaining birefringence [6–8].

This research reports the effect of the boule deposition surface (boule bottom) shape synthesized by VAD method and its correlation with consolidation time on the birefringence magnitude of silica, aiming the development of a high-performance material for photonic components used in photolithography with no require of post-consolidation annealing.
2. Experimental procedure

2.1. Equipment

Silica soot boules were synthesized through the VAD method by using the equipment represented in Fig. 1.

It is basically composed of: (A) deposition chamber, (B) system for controlling gases flux, (C) burner, (D) CCD camera used to monitor the boule deposition region, (E) advanced automation system for controlling the geometrical uniformity of soot silica boules (nanoparticles deposition surface and diameter), and (F) silica boule.

Through an interface developed in National Instruments LabVIEW, one horizontal line (reference line) is placed over the digital image of the boule bottom acquired by the CCD camera in real-time. The reference line position on the boule image is fixed related to the burner exit and it is established at the beginning of each deposition. Based on this horizontal line, the two points of the boule edge (one under the right edge and another under the left edge) are identified by image processing and the distance between them establishes a value for a reference diameter that indicates slightly changes of the boule growth rate. Thus, this reference diameter is used in the automation system as a feedback for a PID controller that adjusts the boule pull up speed, maintaining the uniformity of the soot boule diameter and the deposition surface shape.

The boule deposition surface shape is monitored and parameterized through the \( h \) parameter defined as the distance between the lowest point of boule end tip and the reference diameter mean point [9] (Fig. 2).

This automation system is essential to control boules physical properties, besides the optical performance since boule bottom shape is simultaneously affected by several processing parameters involved in the VAD deposition, such as deposition angle, burner-target distance, \( \text{H}_2/\text{O}_2 \) ratio, and \( \text{SiCl}_4 \) gas flux. In fact, boules with refractive index homogeneity about 1 ppm could be synthesized through the control and monitoring on-line of boules bottom shape [10].

2.2. Samples fabrication

Several boules were produced by VAD method by changing the burner-target distance \( D \) (34–57 mm), \( \text{H}_2 \) (3000–6000 sccm) and \( \text{O}_2 \) (2000–4000 sccm) gases fluxes. It was used a \( \text{H}_2/\text{O}_2 \) ratio of 1.5, \( \text{SiCl}_4 \) gas flux of 150 sccm, boule rotation speed of 25 rpm, and an inclination angle of 42° between burner and target (Fig. 3). The combination of these different deposition conditions made possible to obtain boules of different deposition surface shape automatically parameterized in real-time by \( h \) parameter [9].

Subsequent to the deposition stage, the silica boules were consolidated for 2 h in an electric furnace with He gas atmosphere at 1400 °C. A group of boules were also consolidated at 4, 6, and 8 h in order to study the effect of consolidation time on birefringence. The processing conditions used are listed in Table 1. The consolidation time of 2 h was considered as a standard time condition.

2.3. Scanning electron microscopy

Silica soot samples collected from the center and outer diameter regions from soot boules were characterized through the SEM (scanning electron microscopy) by using the Jeol Electron microscopy JXA-840A model. The nanoparticles size (mean...
diameter – \( \varphi \) and its radial variation were determined through SCION Image software (Scion Corp.).

### 2.4. Birefringence measurement

An Uniopt polarization spectrometry was employed to measure the birefringence of silica samples of 5.0 mm thickness obtained by slicing consolidated boules. These disk-shaped samples were polished (optical finish) and measurements were performed along radial direction from center in a 2.0 mm step and 30° rotating angle. For this study, the highest birefringence value measured in the whole sample was considered as being the sample birefringence.

### 3. Results and discussions

In the VAD method, the boule deposition surface is shaped as a consequence of used settings of various deposition parameters. In this way, the understanding of its formation mechanism under several conditions is essential for the on-line monitoring and control of silica manufacturing process. By varying the fuel gases flux (\( H_2 \) and \( O_2 \)) and the burner-target distance, it was possible to obtain boules with different deposition surface shapes, represented by the \( h \) parameter (Fig. 4). It was noticed a flattening of the boule bottom shape and a decrease of \( h \) value (\( h \leq 2.0 \text{ mm} \)) for \( D > 45 \text{ mm} \) and \( H_2 \) and \( O_2 \) gases flux higher than 4500–3000 sccm, respectively. On the other hand, \( h > 2.0 \text{ mm} \) was obtained by decreasing fuel gas fluxes and burner-target distance indicating that lower values of distances \( D \) and gas fluxes sharpen the preform bottom shape.

By comparing the \( h \) value and birefringence (Fig. 5 (a)) measured on samples consolidated for 2 h, it was observed a linear correlation tendency between them, where a birefringence \( \leq 2 \text{ nm/cm} \) was achieved with \( h \leq 2.0 \text{ mm} \). This result can be corroborated through the illustration of Fig. 5 (b), which presents examples of a continuous increasing birefringence, mainly in the outer diameter region, when \( h \) values were increased (sharpened deposition surface profile).

In high-purity silica glass, the birefringence is caused by optical anisotropy originated from residual stress due to the material thermal history and deformation in glass forming process [6,7,11].

Through the \( h \) value monitoring during the boule deposition, it is possible to predict indirectly the radial homogeneity of the soot nanostructure. Once the \( h \) parameter defines the burner-target distance, its variation affects the temperature radial distribution of the boule deposition surface. In the flame aerosol method the surface deposition temperature is the main parameter that determines the silica nanoparticles size [12], therefore, there is a tight correlation between the \( h \) parameter and the nanoparticles size in radial distribution. Decreasing the \( h \) value implies on a flatter boule bottom shape, as well as a lower radial variation of temperature, Fig. 6, which shows the radial variation of temperature in the plane from burner axes to silica boule axes. This radial temperature homogeneity results in a higher homogeneity of soot nanostructure along the radial direction. In these cases, the nanoparticles size of center and outer diameter regions are very similar, the best condition that minimized the birefringence.

Fig. 7 presents the correlation among \( h \), \( \Delta \varphi \) (nanoparticles size difference between center and outer diameter), and birefringence for standard consolidation time of 2 h. In particular, for \( h \leq 2.0 \text{ mm} \) and \( \Delta \varphi = 3 \text{ nm} \), the smallest birefringence (\( \leq 2 \text{ nm/cm} \)) was attained. On the other hand, for \( h = 4.0 \text{ mm} \) and a difference in nanoparticle size between center and outer regions of \( \Delta \varphi = 16 \text{ nm} \), it was produced a birefringence of 12 nm/cm.

Knowing that annealing is very efficient in decreasing high birefringent samples, a long consolidation time was also considered to be effective to improve the birefringence present in high heterogeneous soot boules (Fig. 8).

It was verified that the effect of consolidation time on birefringence has a direct relationship with the radial homogeneity of material nanostructure and its structural relaxation which is faster in boules produced with \( h \leq 2.0 \text{ mm} \). In this case, the standard consolidation time (2 h) is sufficient to obtain a satisfactory structural relaxation and, therefore, minimize the stress embodied in the material during its synthesis. On the other hand, for these boules with \( h \leq 2.0 \text{ mm} \) (high soot nanostructural homogeneity), consolidation times above 2 h have instigated an increase of the birefringence, particularly due to a thermal gradient during the boule consolidation. In this stage, there is a difference in the cooling rate along the boules radius, where the cooling rate of the outer diameter is inevitably faster than at the center, generating stress in silica.

For general case, the structural relaxation is complete when this material is kept at a certain temperature for enough time, where

<table>
<thead>
<tr>
<th>Boule</th>
<th>( H_2 ) (sccm)</th>
<th>( O_2 ) (sccm)</th>
<th>Distance (mm)</th>
<th>( h ) (mm)</th>
<th>Consolidation time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>6000</td>
<td>4000</td>
<td>57</td>
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<td>6000</td>
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<td>2</td>
</tr>
<tr>
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<td>3000</td>
<td>4000</td>
<td>6</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>A4</td>
<td>2000</td>
<td>6000</td>
<td>8</td>
<td>4</td>
<td>2</td>
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<td>45</td>
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<td>4500</td>
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Fig. 4. Evolution of silica boules deposition surface shape by increasing \( h \) parameter.
the more heterogeneity demands higher time. In fact, the smallest birefringence of 2 nm/cm was obtained with $h = 2.0$ mm and consolidation time of 2 h; and $h = 3.5$ mm and time $\geq 6$ h (Fig. 8).

Moreover, by analyzing the Fig. 8, it is interesting to note that although the long consolidation time was favorable in decreasing the birefringence of boules deposited with $h$ value of 4.0 mm, the time used was not enough to achieve the same birefringence level ($\leq 2$ nm/cm) of the other samples due to its high soot nanostructural heterogeneity.

According to the best results found on the relationship between $h$ values and consolidation time suitable to produce boules with low birefringence without additional annealing, it was observed that it is desirable to produce boules with $h$ values lower than 3.5 mm.

**3. Conclusions**

In this study, we have found that a radial variation of the silica nanoparticles size can lead to a significant birefringence arising in the material. Thus, it is of major importance to synthesize soot boules with high nanostructure radial homogeneity to minimize the occurrence of birefringence.

Through the VAD flame aerosol method it was possible to synthesize low birefringence silica glass without additional annealing by correlating the silica boule bottom shape and consolidation time. Birefringence $\leq 2$ nm/cm can be achieved with $h \leq 2$ mm and consolidation time $2$ h as well as it was produced with $h \geq 3.5$ mm and consolidation time $\geq 6$ h.

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