Effects of OH-Group on Distribution of Refractive Index in Silica Glass

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To study the effects of the fictive temperature, $T_f$, and the OH-group on the refractive index, $n$, of silica glass, several samples were prepared containing from 680 to 850 wt ppm of OH-group in different distribution patterns. Trimethoxymethylsilane was used as a raw material and hence the samples contained no detectable chlorine, whose inhomogeneous distribution was an important factor affecting local change of $n$ for commercial silica glasses. For a sample with homogeneous OH-group distribution, the distribution pattern in $n$ after stress-free annealing was determined by measuring the local deviations in $n$, $\Delta n$, with a laser interferometer. The distribution pattern was considered to be due to the distribution in $T_f$. The $\Delta n$ distributions observed for the annealed samples with various OH-group distribution patterns agreed well with those calculated as a simple summation of the $\Delta n$ due to the local deviation in $T_f$, i.e. $\Delta n = -1 \times 10^{-7} / \text{OH (wt ppm)}$, and the $\Delta n$ due to the local deviation in $T_f$. A way to manufacture silica glass with sufficiently homogeneous refractive index distribution was discussed.

Key-words: Silica glass, Oxy-hydrogen flame hydrolysis method, Refractive index, Fictive temperature, OH-group, Excimer laser

1. Introduction

In developing UV excimer lasers as a light source for advanced processing, such as lithography and photo-etching in LSI-making, photochemical processes, and optical machining, silica glass is often used as a material for optical parts. For such a service, however, the silica glass must be highly homogeneous in the refractive index, $n$, where the primary importance is that the deviation from the level of $n = 1.4585$ (at 589 nm), $\Delta n$, should be less than ca. $3 \times 10^{-6}$ throughout the silica glass blank.

Now, it has been shown by many researchers that $n$ is affected by fictive temperature, $T_f$, OH-group, $\text{Cl}$, $\text{F}$, and metallic impurities. In this study, the effects of $T_f$ and the local deviations in the concentration of OH-group, $\Delta \text{OH}$, were studied. The silica glasses were chosen as the samples, which were prepared by the oxy-hydrogen flame hydrolysis method so as to contain appreciable amounts of OH-group in different distribution patterns. The distribution pattern of $\Delta n$ in a stress-free sample with homogeneous OH-group distribution was determined by interferometry. This distribution pattern was considered as indicating the distribution pattern of $T_f$ which had been established on annealing process. In order to obtain the effects of OH-group on $n$, $\Delta n$ distributions were determined for four glasses with various distribution patterns of OH-group. The determined $\Delta n$ distributions were compared with the $\Delta n$ distributions calculated on the bases of $\Delta T_f$ and $\Delta \text{OH}$ for these four glasses. Moreover, the conditions to manufacture a silica glass with homogeneous $\Delta n$ distribution were discussed.

2. Experimental

2.1 Sample preparation

Several silica glass ingots were manufactured from a high purity trimethoxymethylsilane (CH$_3$ Si(OCH$_3$)$_3$) by the oxy-hydrogen flame hydrolysis method (Fig. 1). The presence of impurity species except OH-group was insignificant: Cl was not detected in nephelometry; nor F in electron probe microanalysis; atomic absorption spectrometry showed Li, Na, and K to be less than 50 wt ppb each, and Mg, Ca, Ti, Cr, Fe, Ni, and Cu, less than 10

![Fig. 1. Apparatus for oxy-hydrogen flame hydrolysis method (the direct method) of synthesizing high purity silica glasses.](image-url)
Effects of OH-Group on Distribution of Refractive Index in Silica Glass

wt ppb; the oxygen-associated defects were not detected by UV or VUV transmission method.\(^{6)-10}\)

In manufacturing the ingots, the distribution pattern of the OH-group was changed by varying the manner of application of the oxy-hydrogen flame to the rotating ingot.

1) Sample No. 1: the oxy-hydrogen flame was uniformly applied to the ingot head so as to distribute the OH-group homogeneously (Fig. 2-a);
2) Sample No. 2: the oxy-hydrogen flame was divided with two parts. One was directed to the ingot head, while the other directed obliquely to the periphery. Then, concentration of OH-group will show a wavy distribution pattern (Fig. 2-b);
3) Sample No. 3: the flame was directed only to the periphery so as to make the distribution pattern concave (Fig. 2-c); and
4) Sample Nos. 4 and 5: the flame was concentrated only to the center so as to make the distribution pattern convex (Fig. 2-d).

Then one disk specimen of 110 (dia.) × 50 (t) mm was taken from each ingot. To relieve the internal stress and to establish the fictive temperature distribution precisely, each specimen was annealed at 1200°C for 50 h in an electric furnace with MoSi\(_2\) heaters, and then was cooled slowly to room temperature in 100 h. Here, the temperature of 1200°C was selected so as to be clearly higher than the annealing point for industrial silica glass products, i.e., ca. 1120°C (viscosity, log \(\eta\) = 13.0).

2.2 Determination of OH-group distribution

The concentration of the OH-group was determined by the IR absorption method\(^{11}\) (using Japan Spectroscopic’s UVIDEC-590) for the central 90 mm diameter area of each disk specimen before and after annealing. Since the OH-group distribution should be axially symmetrical owing to the rotation given to the ingot during manufacture, measurements were taken at 5 mm intervals along diameter through the 50 mm thickness, as shown in Fig. 3.

The precision of OH-group analysis was found to be ±1 ppm in the ten measurements taken for the same spot of a sample.

2.3 Determination of distribution of refractive index

The \(\Delta n\) distribution pattern was determined by the interferometry technique (Canon, Model ZYGO Mark III), using He-Ne laser (\(\lambda = 633\) nm). The two planes of each specimen were ground to be parallel (i.e., without polishing the specimen surface to optical flat), and the measurements were performed with the oil-on-plate method for the central 90 mm diameter area.

The detection limit for \(\Delta n\) was \(5 \times 10^{-7}\), and the precision was \(\pm 3 \times 10^{-7}\) which was determined by repeating trials ten times over.

3. Results

The distribution pattern of the OH-group of the Sample 1 was flat with OH-group content of 750±3 wt ppm. The results of OH-group analyses for other samples are shown in Fig. 4, a to d, proving that the distribution pattern was varied as designed.

There was no substantial loss of OH-group during annealing except the shallow surface layer of 1 to 3 mm, where the decrease of 3 to 5 ppm was noted.

The results of \(\Delta n\) measurements are shown in Figs. 5 and 6. The distribution pattern of Sample 1 was smooth concave surface: the \(\Delta n\) increased by \(3 \times 10^{-6}\) with going from center toward periphery.
along a radius, describing an approximately quadratic curve as shown in Fig. 5. On the other hand, the distribution patterns of Samples 2, 3, 4 and 5 are complex as shown in Figs. 6-a, b, c, and d, where the $\Delta n$ over the central 90 mm diameter portion was $5 \times 10^{-6}$, $3 \times 10^{-6}$, $6 \times 10^{-6}$ and $8 \times 10^{-6}$, respectively.

4. Discussion

4.1 Estimation of the refractive index distribution

The refractive indices of the present silica glass samples should be viewed as a product solely of the fictive temperature, $T_f$, and the OH-group, because the impurity species except OH-group were insignificant.

As for the local $T_f$, Brückner$^{11}$ has shown that the time needed to establish one depends greatly on the annealing temperature (e.g., where only several seconds are sufficient at 1500°C, several tens of hours are necessary at 1200°C). So, a fast cooling (e.g., at a rate of several hundreds of degrees per second), after homogenization at a high enough temperature will preserve the fictive temperature set at that temperature. Whereas slow cooling (e.g., several degrees per hour) will shift $T_f$ downwards. Here, the difference in $T_f$ will manifest itself as a slight difference in the Si–O–Si bond angle,$^{10}$ resulting in a structural difference and variation in the density,$^{11}$ and the variation in $n$.

This notion is interpreted in the present study as follows: A constant $T_f$ was thought to be established throughout a specimen by annealing at 1200°C for 50 h. During subsequent slow cooling to room temperature, however, the difference of cooling rate at the various parts of the specimen caused an inhomogeneity of fictive temperature in it. The cooling
rate of the periphery of the specimen is faster than that of the center. Thus, the local $T_f$ at the periphery became higher than that at the center. This is reflected in the $\Delta n$ distribution pattern of Sample 1 (Fig. 5), where the overall deviation in $T_f$, $\Delta T_f$, for the overall $\Delta n = 3 \times 10^{-6}$ is ca. 2°C.\(^1\)

Now, according to Hetherington and Jack,\(^3\) $n$ will decrease at a rate of $1 \times 10^{-6}$ for every 0.001 wt% (i.e., 10 wt ppm) increase in the OH-group: namely, $\Delta n = -1 \times 10^{-7}/\Delta$OH (wt ppm). The results of $\Delta n$ for Samples 2, 3, 4 and 5 calculated on the bases of their $\Delta$OH profiles (Fig. 4) and the contributions from $T_f$ (Fig. 5) are shown in Figs. 7-a, b, c and d, respectively. Table 1 presents a comparison between the results from the calculations and the interferometry measurements for the central 90 mm diameter part of each specimen. The agreement between the two is quite satisfactory.

From this observation, following conclusions are drawn:

1. The local refractive index of a silica glass is determined by the local fictive temperature and the local OH-group concentration.
2. For the effect of the OH-group on the refractive index, $\Delta n = -1 \times 10^{-7}/\Delta$OH (wt ppm) is a reasonable description.

4.2 Criteria for manufacturing silica glass blanks with homogeneous refractive index distribution

To manufacture a silica glass with homogeneous refractive index distribution, three cases are conceivable as shown in Table 2.

Case A (represented by Sample 3): The distribution pattern of the OH-group is of a concave surface. In this case, the OH-group deviation of $\Delta$OH = 30 ppm, which gives rise to $\Delta n = 3 \times 10^{-6}$ at the center (Fig. 4-b), effectively cancels out the effect of the local $T_f$. The net $\Delta n$ obtained was $-3 \times 10^{-6}$ at the center (Fig. 5). Thus, the sample satisfies the desired homogeneity criterion of $\Delta n < \text{ca. } 3 \times 10^{-6}$.

Case B (represented by Samples 4 and 5): The distribution profile of the OH-group is of a convex surface. In this case, the $\Delta n$ due to local OH-group is augmented by the local $T_f$, rather than offset, so that only low quality glasses can be produced even if $\Delta$OH is held to 30 ppm level as in Case A.

Case C: This is a case where the distribution profile of the OH-group is of the concave surface as in the Case A, but $\Delta$OH is much higher, say 150 ppm. Then the contribution of the OH-group overshadows that of the local $T_f$ so that manufacture of high quality blanks is no longer possible.

Table 1. Comparison of calculations and measurements for deviation in refractive index, $\Delta n$.

<table>
<thead>
<tr>
<th></th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
</tr>
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<tr>
<td>Calculations</td>
<td>$4.2 \times 10^{-8}$</td>
<td>$3.0 \times 10^{-8}$</td>
<td>$8.0 \times 10^{-8}$</td>
<td>$9.9 \times 10^{-8}$</td>
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<tr>
<td>Measurements, for Refractive Index Deviations, $\Delta n$</td>
<td>$5 \times 10^{-8}$</td>
<td>$3 \times 10^{-8}$</td>
<td>$6 \times 10^{-8}$</td>
<td>$8 \times 10^{-8}$</td>
</tr>
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</table>

Table 2. The three cases of controlling the refractive index distribution.

<table>
<thead>
<tr>
<th>CASE</th>
<th>OH GROUP DISTRIBUTION</th>
<th>FICTIVE TEMPERATURE DISTRIBUTION</th>
<th>OH+FICTIVE TEMPERATURE DISTRIBUTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>$\Delta$OH = 30 ppm</td>
<td>$\Delta T_f = 2^\circ C$</td>
<td>$\Delta n = 3 \times 10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>$\Delta$OH = 150 ppm</td>
<td>$\Delta T_f = 2^\circ C$</td>
<td>$\Delta n = 3 \times 10^{-6}$</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>$\Delta$OH = 150 ppm</td>
<td>$\Delta T_f = 2^\circ C$</td>
<td>$\Delta n = 3 \times 10^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>$\Delta$OH = 6 \times 10^{-5}</td>
<td></td>
<td></td>
</tr>
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</table>
5. Conclusions

In studying the distribution patterns of the refractive index, $n$, of silica glass samples, following conclusions have been drawn:

1. The local $n$ in a silica glass without Cl, F, oxygen-associated defects and metallic impurities is determined solely by the fictive temperature, $T_f$, and the OH-group concentration of that location.

2. The effect of OH-group is to decrease $n$ at a rate of $\Delta n_{OH} = -1 \times 10^{-7}/\Delta OH$ (wt ppm).

3. Even if a silica glass with homogeneous OH-group distribution is manufactured, its $n$ distribution is not necessarily homogeneous. Because the local $T_f$ at the periphery of the glass is higher than that at the center during slow cooling process after annealing.

4. Nonetheless, manufacture of silica glass with a sufficiently homogeneous $n$ distribution is possible by the following steps: first, $n$ distribution pattern is determined using the sample with homogeneous OH-group distribution; secondly, the contribution of the difference in $T_f$ between the periphery and the center for a given cooling rate is considered; last, the OH-group distribution in the silica glass is modified so as to compensate the effect of the $T_f$ distribution.

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References