Evaluating the Homogeneity of a Synthetic Silica Glass Ingot Using Ultrasonic Microspectroscopy Technology

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1. Introduction

Synthetic silica (SiO₂) glass is widely used for optical components because of its high purity and high optical transmission. As semiconductor large-scale integrated circuits using such glass become miniaturized, the homogeneity of the refractive index must be further improved for lenses in optical lithography systems. The refractive index of SiO₂ glass depends both on concentrations of dopants and impurities such as hydroxyl (OH) and chlorine and on the fictive temperature (T_F), a parameter related to the thermal history ¹. We proposed a method of evaluating T_F of SiO₂ glass using ultrasonic microspectroscopy (UMS) technology by measuring longitudinal-wave velocity ² and demonstrated that the resolution of T_F is one to two orders of magnitude greater than that measured by conventional methods ³,⁴. We applied our method to evaluating the homogeneity of a SiO₂ glass ingot.

2. Specimens

Specimens were prepared from a 600 mm (φ) × 600 mm (l) commercial SiO₂ glass ingot (ES; Tosoh SGM) produced by the direct method. Fabricated SiO₂ glass ingots are usually annealed at high temperatures in order to reduce residual stress. To compare acoustic properties before and after annealing, a specimen was first prepared in the radial direction at about 200 mm from the top of the ingot without annealing. The rest of the ingot was annealed. An annealed specimen with the same height as the ingot was also prepared. Several specimens were also prepared from the central parts for heat-treatment at desired annealing temperatures from 850°C to 1150°C to obtain calibration lines between acoustic properties and T_F.

3. Experiments and discussion

Leaky-surface-acoustic-wave velocities (V_LSAW) were measured by a line-focus-beam ultrasonic material characterization (LFB-UMC) system at 225 MHz ⁵. Longitudinal velocities (V_l) were measured around 200 MHz by replacing the LFB ultrasonic device with a plane-wave ultrasonic device. Densities (ρ) were measured based on the Archimedes principle. OH concentrations {C(OH)} were measured by infrared spectroscopy ⁶. Optical retardation was measured by optical heterodyne interferometry.

Acoustic properties were measured for specimens heat-treated at different annealing temperatures. We obtained linear relationships between acoustic properties and annealing temperatures for specimens annealed at temperatures below 900°C and could thus obtain the following relationships among V_l [m/s], V_LSAW [m/s], ρ [kg/m³], and T_F [°C].

\[
V_l = 156.5 \times 10^{-3} \times T_F + 5782.8 \quad (1)
\]
\[
V_LSAW = 0.9 \times 10^{-3} \times T_F + 3419.7 \quad (2)
\]
\[
\rho = 6.0 \times 10^{-3} \times T_F + 2194.5 \quad (3)
\]

Table 1 presents sensitivities and resolutions of fictive temperatures determined by measuring acoustic properties. Measured V_LSAW and V_l distributions are presented in Figs. 1(A) and (B) as a function of distance from the center. Error bars in Fig. 1(B) represent maximum errors caused by thickness distributions of specimens except for the center positions. Maximum differences of V_LSAW...
Table 1. Sensitivities and resolutions for fictive temperature of SiO$_2$ glass (ES) determined by acoustic property measurements.

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<th>Sensitivity</th>
<th>Resolution</th>
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<tr>
<td>Longitudinal</td>
<td>$6.4^\circ$C/(m/s)</td>
<td>$0.3^\circ$C</td>
</tr>
<tr>
<td>LSAW velocity</td>
<td>$1075^\circ$C/(m/s)</td>
<td>$183^\circ$C</td>
</tr>
<tr>
<td>Density</td>
<td>$168^\circ$C/(kg/m$^3$)</td>
<td>$8.4^\circ$C</td>
</tr>
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($(V_L)$ is $2.31$ m/s ($3.10$ m/s). We observed that $V_{LSAW}$ increased from the center to the edge, took a local maximum at $218$ mm, and decreased around the ingot edge. $V_{LSAW}$ distributions before and after annealing exhibited similar tendencies, although $V_{LSAW}$ slightly increased after annealing. We observed that $V_L$ took a local minimum at $190$ mm and increased around the ingot edge. $V_L$ decreased by $8$ to $9$ m/s after annealing. Figure 1(C) presents the results of OH concentration distribution for the annealed specimens. OH concentrations were constant for specimens taken from around the center of the ingot and decreased by $140$ wtppm around the ingot edge. Acoustic properties also depend on $C$(OH). The maximum difference of $T_F$ for the annealed specimen was estimated from $V_L$ variation using eq. (1) to be $19^\circ$C. Here, velocity changes caused by $C$(OH) distributions were corrected using the results of ref. 2. $T_F$ around the central axis was estimated to be $982^\circ$C before annealing and $933^\circ$C after annealing. Annealing thus decreased $T_F$ about $50^\circ$C. We also measured $T_F$ distributions for the annealed specimen by IR spectroscopy$^3$, and the results indicated a tendency similar to those estimated from $V_L$. Optical retardation for the annealed specimen indicated residual stresses around the ingot edge (Fig. 1(D)). $V_{LSAW}$ decreased in the same region, so $V_{LSAW}$ could be influenced by the residual stresses. These effects could not be reduced by annealing, considering the result of $V_{LSAW}$ distributions.

4. Summary

We demonstrated that $T_F$ distributions of SiO$_2$ glass ingots can be obtained by $V_L$ measurements and that variations caused by the residual stresses could be evaluated by $V_{LSAW}$ measurements. This ultrasonic method is extremely useful for improving the homogeneity of SiO$_2$ glass ingots.

Fig. 1. Distributions of LSAW velocities (A), longitudinal velocities (B), OH concentrations (C), and optical retardation (D) measured for synthetic silica glass specimens.

Acknowledgments

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References