Comparison of high-purity \( \text{H}_2/\text{O}_2 \) and \( \text{LPG}/\text{O}_2 \) flame-fused silica glasses from sol–gel silica powder

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Abstract

High-quality flame-fused silica glasses were obtained from high-purity starting sol–gel silica powders, under \( \text{H}_2/\text{O}_2 \) and liquid propane gas (LPG)/\( \text{O}_2 \) flames. Neither metallic nor carbon contamination was observed during the fusion process, even by using domestic LPG. The flame-fused sol–gels showed lower impurity levels than silica glasses from natural quartz and of the same order as the commercial synthetic silica glasses (chemical vapor deposition process). By fusion with an LPG/O\(_2\) flame, the aggregation of OH radicals during the fusion process was verified to be about 100 ppm lower with viscosity two times higher than that of silica glasses fused by \( \text{H}_2/\text{O}_2 \). The viscosity of this flame-fused sol–gel silica is lower than the flame-fused silica from rock crystal, but is one order of magnitude higher than that of the synthetic silica glass.

1. Introduction

The recent developments of ultra very large scale integration (UVLSI) have brought about the necessity to achieve ever larger circuit densities [1], that require highly perfect silicon single crystals with much lower impurity levels and well suited silica glasses for photo mask, crucibles, tubes and boats used in the processing of high-purity semiconductors.

Commercial silica glasses with low metallic impurities, i.e., of the order of tenths of ppm in weight, have been obtained only by synthetic processes (chemical vapor deposition (CVD)). Electric-fused and flame-fused silica glasses always show an Al content higher than about 5 ppm remaining from the natural raw quartz. Nowadays, high-purity silica powders made by synthetic processes are available from high-purity sol–gel, whose content of metallic impurities, including Al, can be lower than tenths of ppm. Actually, there are some special types of sol–gel silica powder with impurity levels down to hundredths of ppm for all elements (excluding Fe, with 0.05 ppm).

Flame-fusion experiments were carried out with sol–gel powders using two types of flame: hydrogen/oxygen and liquid propane gas (LPG)/oxygen. Chemical analysis, optical transparency in the IR and UV range and the strength at high
temperature by means of viscosity measurements were carried out on the fused samples.

2. Experimental procedure

2.1. Apparatus and operational conditions

The fusion experiments were conducted with a laboratory-scale Verneuil furnace by using two types of flame. For the hydrogen flame, a new type of quartz glass burner [2] with a venturi to mix the powder with the supporting gas was used. For the LPG flame, two pre-mixed metal burners set on a convergent way to make a focus about 7 cm from the nozzle burner were used. Schematic representations of these two experimental settings of the furnace are shown in Fig. 1.

Various operational fusion conditions were tested; the optimum conditions were established as those listed below:

- rotation speed of ingot 20 rpm;
- head of ingot placed in the focus of the flame 7 cm from the burner;
- gas mixture rate for H₂/O₂ flame, 2.3/1.0;
- gas mixture rate for LPG/O₂ flame, 1.0/2.8;

Table 1

<table>
<thead>
<tr>
<th>Sample a</th>
<th>Impurity concentration (ppm wt)</th>
<th>Particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Al]</td>
<td>[Na]</td>
</tr>
<tr>
<td>SG.AM-1</td>
<td>1.8</td>
<td>0.1</td>
</tr>
<tr>
<td>SG.AM-2</td>
<td>10.8</td>
<td>0.3</td>
</tr>
<tr>
<td>SG.AM-3</td>
<td>0.1</td>
<td>0.08</td>
</tr>
<tr>
<td>SG.AM-4</td>
<td>&lt; 0.1</td>
<td>0.08</td>
</tr>
<tr>
<td>SG.AM-5</td>
<td>&lt; 0.3</td>
<td>0.04</td>
</tr>
<tr>
<td>SG.AM-6</td>
<td>&lt; 0.3</td>
<td>0.04</td>
</tr>
<tr>
<td>SG.AM-7</td>
<td>&lt; 0.3</td>
<td>0.13</td>
</tr>
<tr>
<td>SG.AM-8</td>
<td>0.1</td>
<td>0.11</td>
</tr>
<tr>
<td>SG.AM-9</td>
<td>0.2</td>
<td>0.13</td>
</tr>
<tr>
<td>SG.AM-10</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>SG.CB-1</td>
<td>0.2</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>SG.CB-2</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>SG.CB-3</td>
<td>1.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Kyucera</td>
<td>6</td>
<td>0.9</td>
</tr>
<tr>
<td>Iota-5</td>
<td>8.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 1: Impurities and particle size of the powders used for fusion

Sample a: Impurity concentration (ppm wt) and Particle size (μm)

a Nomenclature of the samples: SG, sol-gel quartz powder; CB, cristobalite; AM, amorphous; alpha quartz, Kyucera and Iota-5 powders.

b Not measured.
least 55 mm in length. All types of powder listed in Table 1 were fused by the hydrogen flame and four of them were also fused by the LPG flame.

2.2. Starting Raw Materials

In the present experiment, 15 different types of quartz powder were selected: three sol–gel powders heat-treated to crystallize them into cristobalite (SG. CB-1, 2 and 3); 10 sol–gel amorphous powders (SG. AM-1 to 10), the powder SG. AM-10 with a very low level of metallic impurities; and two high-purity commercial powders from natural rock crystal (Kyocera and Iota) used as standard powders for fusion. The sol–gel powders were obtained by two processes: (i) from sodium silicate solution (‘water glass’), purified and densified to pure SiO$_2$, prepared by Nitto Chemical, and (ii) from pure tetramethoxy silane Si(OCH$_3$)$_4$ (powder SG. AM-10), made by Mitsubishi Kasei.

The nominal specifications of impurity content and the particle size of the powders are listed in Table 1.

3. Experimental results

The silica glass ingots obtained in this experiment were transparent with low bubble contents when observed by optical inspectoscopy. The data collected from the fusion experiments are shown in Table 2, for hydrogen and LPG flames.

The growing rate and fusion yield were typical for each powder, and were verified to be dependent on the particle size distribution (within the range selected, according to Table 1) and also by the heat treatment of the powder [3].

3.1. Chemical analysis of the fused silicas

Four samples were selected to verify the contamination during the fusion process by the different flames. Metallic impurities were measured by atomic absorption spectroscopy (AAS) and induction couple plasma – atomic emission spectroscopy (ICP–AES), both with detection limit lower than 0.1 ppm for all elements analyzed. Determinations of carbon were realized in six samples from three different powders: three sam-

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Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fusion time (min)</th>
<th>Fusion temperature (°C)</th>
<th>Powder flux (g/min)</th>
<th>Growing rate (g/min)</th>
<th>Ingot weight (g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG.AM-1</td>
<td>119</td>
<td>1700</td>
<td>0.8</td>
<td>0.37</td>
<td>44.0</td>
<td>48.9</td>
</tr>
<tr>
<td>SG.AM-1 *</td>
<td>130</td>
<td>1800</td>
<td>0.8</td>
<td>0.31</td>
<td>40.9</td>
<td>40.1</td>
</tr>
<tr>
<td>SG.AM-2</td>
<td>116</td>
<td>1680</td>
<td>0.6</td>
<td>0.29</td>
<td>33.3</td>
<td>46.2</td>
</tr>
<tr>
<td>SG.AM-2 *</td>
<td>105</td>
<td>1800</td>
<td>0.7</td>
<td>0.32</td>
<td>34.1</td>
<td>44.9</td>
</tr>
<tr>
<td>SG.AM-3</td>
<td>94</td>
<td>~1700</td>
<td>0.84</td>
<td>0.27</td>
<td>25.6</td>
<td>27.4</td>
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<tr>
<td>SG.AM-4</td>
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<td>~1700</td>
<td>0.95</td>
<td>0.22</td>
<td>24.3</td>
<td>23.1</td>
</tr>
<tr>
<td>SG.AM-5</td>
<td>90</td>
<td>~1700</td>
<td>1.00</td>
<td>0.25</td>
<td>22.5</td>
<td>25.0</td>
</tr>
<tr>
<td>SG.AM-6</td>
<td>85</td>
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<td>0.25</td>
<td>21.5</td>
<td>25.9</td>
</tr>
<tr>
<td>SG.AM-7</td>
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<td>~1720</td>
<td>0.93</td>
<td>0.33</td>
<td>29.8</td>
<td>35.5</td>
</tr>
<tr>
<td>SG.AM-8</td>
<td>60</td>
<td>~1700</td>
<td>1.48</td>
<td>0.36</td>
<td>21.7</td>
<td>24.4</td>
</tr>
<tr>
<td>SG.AM-9</td>
<td>92</td>
<td>~1700</td>
<td>1.21</td>
<td>0.25</td>
<td>23.3</td>
<td>21.0</td>
</tr>
<tr>
<td>SG.AM-10</td>
<td>130</td>
<td>~1730</td>
<td>1.09</td>
<td>0.21</td>
<td>27.0</td>
<td>19.0</td>
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<tr>
<td>SG.CB-1</td>
<td>110</td>
<td>1700</td>
<td>1.1</td>
<td>0.23</td>
<td>25.2</td>
<td>20.8</td>
</tr>
<tr>
<td>SG.CB-2</td>
<td>90</td>
<td>1700</td>
<td>1.2</td>
<td>0.28</td>
<td>25.6</td>
<td>24.6</td>
</tr>
<tr>
<td>SG.CB-3</td>
<td>101</td>
<td>1700</td>
<td>0.9</td>
<td>0.26</td>
<td>26.4</td>
<td>29.3</td>
</tr>
<tr>
<td>SG.CB-3 *</td>
<td>90</td>
<td>1800</td>
<td>1.1</td>
<td>0.38</td>
<td>33.8</td>
<td>34.5</td>
</tr>
<tr>
<td>Kyocera</td>
<td>100</td>
<td>–</td>
<td>1.1</td>
<td>0.45</td>
<td>45.0</td>
<td>42.4</td>
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<td>Kyocera *</td>
<td>130</td>
<td>1800</td>
<td>0.9</td>
<td>0.29</td>
<td>36.3</td>
<td>30.2</td>
</tr>
<tr>
<td>Iota-5</td>
<td>127</td>
<td>1700</td>
<td>1.2</td>
<td>0.30</td>
<td>37.8</td>
<td>24.5</td>
</tr>
</tbody>
</table>

* Not measured.
3.2. Optical transmittance in the IR and UV range

For optical measurements, a plate of 2 mm thickness was cut from each fused ingot, and polished to optical transparency.

The IR spectra were taken by a Fourier transform spectrophotometer (JASCO 5-M/FT), from 4300 to 2000 cm\(^{-1}\). The absorption at 2.73 \(\mu\text{m}\) is attributed to the presence of free OH [4] and is observed in every sample. Silica glasses fused by LPG show lower absorption than those fused by hydrogen flame. The OH content estimated from the IR spectra by the relation proposed by Hetherington and Jack [5] are listed in Table 4.

The UV transmittance spectra of silica glasses were taken by a Hitachi spectrophotometer model 340. The spectra show no difference within samples fused from the same powder and different flames, but large discrepancies at short wavelength are observed between silica glasses from rock crystal and from sol-gel, independent of the flame used. Fig. 2 shows a comparison between the UV spectra of samples Kyucera flame-fused and SG. AM-2 flame-fused.

3.3. Evaluation of the silica glass strength by viscosity measurements

The strength of the silica glasses at high temperatures was determined by means of viscosity measurements, using the beam-bending method.

Table 3
Impurities of hydrogen and LPG (*) flame-fused silica glasses

<table>
<thead>
<tr>
<th>Samples</th>
<th>Impurity concentration (ppm wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Al]</td>
</tr>
<tr>
<td>SG.AM-1</td>
<td>1.5</td>
</tr>
<tr>
<td>SG.AM-1 *</td>
<td>1.7</td>
</tr>
<tr>
<td>SG.AM-2</td>
<td>11.5</td>
</tr>
<tr>
<td>SG.AM-2 *</td>
<td>11.4</td>
</tr>
<tr>
<td>SG.CB-3</td>
<td>1.7</td>
</tr>
<tr>
<td>SG.CB-3 *</td>
<td>2.0</td>
</tr>
<tr>
<td>Kyucera</td>
<td>6.7</td>
</tr>
<tr>
<td>Kyucera *</td>
<td>7.0</td>
</tr>
</tbody>
</table>

a Na and K were analyzed by AAS and the other metallic elements by ICP-AES; K and Li were not detected in any samples.
b The C content is an average of three measurements for each sample, with standard deviation of about 4 ppm;
c Not analyzed.
From each fused silica glass ingot, three glass beams were cut by a diamond saw and polished with white abrasive alumina to have a rectangular cross-section, with final dimensions of about $3 \times 5 \times 50$ mm$^3$. Special care was taken to have the uniformity and parallelism of the faces with dimension differences within $\pm 0.01$ mm along each beam. For every beam, the viscosity was measured at three different steps of temperature: 1100, 1200 and 1300°C, by an improved beam-bending viscosimeter [9] (model Rheotronic (Tokyo Inc.).

The viscosity values of all fused silica glasses are listed in Table 4, whose data are an average of three measurements. The standard deviations were calculated to be about $\pm 0.04$ (for $\eta_{\text{poise}}$) at 1300°C, $\pm 0.03$ at 1200°C, and $\pm 0.05$ at 1100°C.

### 4. Discussion

Comparison of the metallic impurities in powders (Table 1) and impurities in bulk of the fused silicas by hydrogen and LPG flames do not show contamination due to the fusion process, and in the case of alkali metals a purification was observed. For Na, the fused silicas presented an impurity level approximately five times lower than that of the starting silica powder.

It was expected that fusion by the LPG flame could contaminate the silica glasses with carbon during the fusion process, due to its presence (and its radicals) in the flame; however the results listed in Table 3 do not show significant differences within samples fused from the same powder and by different flames.

The data in Table 4 show that the aggregation of OH radicals during the fusion process is approximately 100 ppm lower for silica glasses fused by the LPG flame than that by the hydrogen flame. The lower aggregation of OH by the LPG flame can be explained by its more strongly reducing atmosphere than the hydrogen flame, with low partial pressure of OH, and probably by the dehydroxylating effect of carbon in silica glass observed by Elmer and Meissner on the study to increase the annealing point of vycor glass [6].

In Fig. 2, we can observe a superposition of two spectra in the range longer than 260 nm. Down to 255 nm, the transmittance of sol-gel fused silica becomes higher up to a value of 75% compared with 35% (natural quartz fused material) at a wavelength of 190 nm. This higher absorption at short UV wavelengths of silica glasses from natural quartz is due to color centers caused by metallic impurities and intrinsic defects like $E'$ centers [4, 7, 8].

The viscosity data show that the flame-fused silica glasses from sol-gel have lower viscosity than those from rock crystal, but higher than synthetic silica glasses. Fig. 3 shows a comparison of the viscosity values of the flame-fused silica glasses from this experiment and commercial silica glasses obtained through various processes.

The flame-fused sol-gel silica glasses have about the same concentration of metallic impurities in comparison with synthetic silica glasses by the CVD process, but their viscosity values are about one order of magnitude higher. The effect of lowering the viscosity of silica glass by OH and also by Cl$^-$ has been studied by many researchers [4–6, 10, 11]. This effect may be responsible for the large differences of viscosities observed, since the flame-fused sol-gel presents about 200 ppm
of OH in comparison with about 1200 ppm of OH for the synthetic one.

The silica glasses fused under the LPG flame show viscosity values about two times higher than those fused under hydrogen flame. This higher viscosity may also be due to the lower OH contents of silica glasses by LPG flame as represented in Fig. 4, but the partial evaporation of the silica in conjunction with the alkali metals impurity [11] by the strongly reducing atmosphere of the LPG flame may also contribute to increase the viscosity.

5. Conclusions

High-quality flame-fused silica glasses by the Verneuil method can be obtained from high-purity sol–gel silica powders without metallic contamination during the fusion process, even for the LPG flame. Moreover this flame-fused sol–gel can have impurity levels of the same order or lower than commercial synthetic silica glasses by the CVD process (it will depend on the purity of the starting powder for fusion).
Because of the low OH content, this flame-fused silica has a viscosity one order of magnitude higher than that of the synthetic silica glass for the same metallic impurity level. Also the use of the LPG flame can increase the viscosity even more, by a factor of two (at 1200°C) compared with that of silica fused by the hydrogen flame.

The silicas fused by hydrogen and LPG flames from the same starting powder show the same optical transmittance in the UV range, and the one fused by LPG shows a higher transmittance in the IR range, at 2.73 μm, because of its lower OH content.

From the present evaluation, only positive aspects were observed on the use of the LPG flame for the fusion of quartz by the Verneuil method, making possible the production of high-quality silica glasses with high viscosity values.

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References