The study of removing hydroxyl from silica glass

Zhou Yongheng a,*, Gu Zhenan b

a Laboratory of Photonic Information Technology, South China Normal University, Guangzhou 510631, China
b China Building Materials Academy, Beijing 100024, China

Received 18 November 2005; received in revised form 29 June 2006

Abstract

The removal of hydroxyl from silica glass produced by melting quartz powder under an atmosphere containing hydrogen was investigated. After heat-treatment at the temperature range (700–1200 °C) in nitrogen atmosphere, the effective hydrogen diffusion coefficients were evaluated based on the law of nonsteady-state diffusion. The activation energy obtained is 254 kJ mol⁻¹ for the dehydroxylation process in the heat-treatment temperature range of 700–900 °C, and a different activation energy calculated is 32 kJ mol⁻¹ in the temperature range of 900–1200 °C. The activation energies for the dehydroxylation process at the temperature (700–900 °C) and the higher temperature (900–1200 °C) correspond to the binding energy of SiO–H bond and the activation energy for the diffusion of hydrogen in silica glass respectively, which indicate there is a change of mechanism for dehydroxylation with heat-treatment temperature.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Silica; Water in glass

1. Introduction

Hydroxyl always exists in silica glass. It is important to study the effect of hydroxyl in silica glass on a variety of applications, ranging from traditional (such as lighting products) to the modern (such as optical fibers). A number of papers have discussed the hydroxyl in silica glass produced by hydrolyzation of SiCl₄, the fusion of quartz powder in an oxygen–hydrogen flame or fusion of natural quartz powder under vacuum [1–3].

Conventional silica glass is produced by melting quartz powder under an atmosphere containing hydrogen, and this type of silica glass contains >100 ppm (wt) of hydroxyl. The hydroxyl should be almost entirely removed by heat-treatment before the silica glass is used for envelopes to some types of lamps. The present paper reports the investigation on the temperature dependence of the diffusion coefficient for the removal of Si–OH in silica glass formed under an atmosphere containing hydrogen.

2. Experimental

In this study, the samples of silica glass, which were manufactured by melting quartz powder in a hydrogen atmosphere, were cut into pieces with a dimension of the length of 20 mm, the width of 10 mm, and the thickness of 1 mm. The specimens were heated in a furnace chamber filled with nitrogen atmosphere at the temperature range of 700–1200 °C.

To investigate the changes of concentration of hydroxyl, samples were periodically removed from the furnace to measure the IR transparence spectra with an infrared spectrometer (Perkin–Elmer 1600). Hydrogen and water releasing from the silica glass were tested by quadrupole mass spectrometry (ULVAC-RG202P) in the temperature range of 500–900 °C.

3. Results

Measuring the infrared spectra at the band of 3672 cm⁻¹ can monitor the changes of hydroxyl content in silica glass [4]. Fig. 1 shows the change of spectrum between
the heat-treated sample and the original sample. In this figure, it is seen that the transparency increases at the wave band of 3672 cm\(^{-1}\) after the sample had been heat-treated for 2 h, which shows the reduction of the concentration of hydroxyl in silica glass.

Fig. 2 shows the time dependence of dehydroxylation. The hydroxyl content decreases with the heat-treatment time until the equilibrium is reached. 85% of the total hydroxyl was removed from the specimens after heat-treatment at a temperature of 800 °C for 40 h, and the hydroxyl is almost removed in a short time at a temperature of 1000 °C.

The hydrogen and water released from the silica glass are shown in Fig. 3, which was tested by quadrupole mass spectrometry in the temperature range from 500 to 900 °C. The left axis in Fig. 3 is the ion intensity, which represents the quantity of released gas, at the same time, the values of temperature’s curve can be read in the right axis. The quantity of released gas from the samples changes with time and temperature as shown in Fig. 3. It is clear from Fig. 3 that the quantity of released H\(_2\)O is nearly less 1000 times than that of H\(_2\) at the heat-treated temperature above 700 °C, so the released H\(_2\)O can be ignored in this kind of glass during the process of dehydroxylation.

According to Nonsteady-state diffusion (Fick’s second law) [5], the diffusion function of removing gas from solids is expressed as

\[
\frac{C_1 - C_0}{C_s - C_0} = 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right),
\]

where \(C_1\) represents the concentration at the depth \(x\) after time \(t\), \(C_0\) is the initial concentration, \(C_s\) is the concentration at \(x = 0\), \(D\) is the diffusion coefficient. The expression \(\text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)\) is the Gaussian error function, values of which are given in mathematical tables for various \(\frac{x}{\sqrt{Dt}}\) values; A partial listing is given in Ref. [5].

When Eq. (1) is applied to the dehydroxylation of silica glass, the value of \(C_s\) can be considered as the concentration in the environment (\(C_s = 0\)), so Eq. (1) is reduced to Eq. (2)

\[
C_1 = C_0 \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right).
\]

The behavior of diffusion can normally be expressed by the following Arrhenius equation:

\[
\ln D = \ln D_0 - \frac{Q}{RT},
\]

where \(D_0\) is a temperature independent preexponential (m\(^2\)/s); \(Q\) is the activation energy for diffusion (J/mol); \(R\) is the gas constant, 8.31 J/mol K; \(T\) is absolute temperature (K).

The results of calculated diffusion coefficient of hydroxyl in the thermal process are shown in Fig. 4.

It can be seen in Fig. 4 that the slope of the line in the range of 700–900 °C is obviously different from that in the temperature range of 900–1200 °C. A change in slope occurs in the dehydroxylation process at the temperature of 900 °C. If the diffusion data in Fig. 4 are divided into two parts at the point of temperature 900 °C, both of the two parts are well fit to the Arrhenius equation.
respectively. The activation energy obtained from Eq. (3) is 254 kJ mol$^{-1}$ for the dehydroxylation process in the range heat-treatment temperature of 700–900 °C, which corresponds with the activation energy of 260–266 kJ mol$^{-1}$ for the dehydroxylation reaction in silica glass reported by Shelby [6]. The activation energy calculated by the Fig. 4 was 32 kJ mol$^{-1}$ in the temperature range of 900–1200 °C, and the value was in good agreement with the activation energy of 37–43.7 kJ mol$^{-1}$ for the diffusion of hydrogen in silica glass reported in the literatures [6–8]. Similar changes in the activation energy have been reported by McGinnis who studied the dehydroxylation of silica glass produced by the hydrolyzation of SiCl$_4$ and the fusion of quartz powder in an oxygen–hydrogen flame [9].

4. Discussion

Molecular hydrogen and water were analyzed by quadrupole mass spectrometry in this study. But the results of Fig. 3 cannot prove the hydroxyl being converted into H$_2$O because only a small quantity of H$_2$O was released. We think that hydroxyl is removed by releasing hydrogen from the glass, which is similar to the results proved by Morimoto et al. [10].

Shelby and Tomozawa described the reaction of dehydroxylation of the silica glass as Eq. (4) [6,11], both of them indicate that hydroxyl and hydride can be removed from the silica glass by heat-treatment at a temperature >700 °C, through the process below.

$$\text{Si-OH} + \text{SiH} \rightarrow \text{Si-O-Si} + \text{SiH}_2$$ (4)

Molecular hydrogen can migrate through the network of polyhedral interstices in the glass [12]. So the process the dehydroxylation of silica glass includes the breaking of the SiO–H bond, the condensing of H$^+$ ions to form molecular hydrogen, and the diffusion of the molecular hydrogen in the glass.

In this study, the activation energy for dehydroxylation at the temperature range of 700–900 °C is 254 kJ mol$^{-1}$ which is close to the binding energy of the SiO–H and greater than the activation energy for the diffusion of hydrogen molecules in silica glass. The activation energy 254 kJ mol$^{-1}$ is used to break the SiO–H bond. Because the SiO–H bond is more stable than the Si–H bond [13]. It is obvious that the breaking of SiO–H is the controlling process of dehydroxylation in the temperature range of 700–900 °C. So the dehydroxylation process is a reaction controlled process in the temperature range of 700–900 °C.

On the other hand, when the heat-treatment above 900 °C, the activation energy for dehydroxylation process is 32 kJ/mol, which approximates to the activation energy for the diffusion of molecular hydrogen in silica glass. So we supposing that the diffusion of hydrogen molecules dominate the process in the temperature range of 900–1200 °C.

It is well known that many properties of silica glass depend on the fictive temperature ($T_f$). The fictive temperature of a glass is defined as ‘the temperature at which the glass would find itself in equilibrium if suddenly brought to that temperature from its given state’. When a glass is heat-treated at a constant temperature, its fictive temperature approaches the heat-treatment temperature. The fictive temperature is not accessible by direct measurement. However the fundamental structural band at 1122 cm$^{-1}$ in IR reflection as well as an overtone of this band at 2260 cm$^{-1}$ in IR transmission are related to $T_f$ [14,15]. Agarwal reported that the glass structure can be modified by various thermal processes, and there exists an ‘anomalous regions’ in the range of fictive temperature from 1000 to 1500 °C, and the average Si–O–Si bond angle in the glass structure decreases by about 1.3° when the fictive temperature increased from 950 to 1400 °C, which is close to the turning point of the lines in Fig. 4 [15,16]. It is possible to explain the change in activation energy by the modification of structure. We estimate that the changes of the bond angle of Si–O–Si in the network lead to the SiO–H bond breaking easily, so that the more active H$^+$ ions will appear in silica glass at high temperature. Thus the dehydroxylation of silica glass consequently changes into a diffusion controlled of hydrogen molecular from a reaction controlled process.

5. Conclusions

There are two steps in the process of dehydroxylation of silica glass produced by melting quartz powder under an atmosphere containing hydrogen. One is the chemical reaction of Eq. (4), the other is the diffusion of molecular hydrogen. In heat-treatment temperature range of 700–900 °C, the dehydroxylation of silica glass is a reaction controlled process, when the heat-treatment temperature increase to the range of 900–1200 °C, it changes into a diffusion of molecular hydrogen controlled process.

References
