Change of Electrical Properties by Heat Treatment in Various Kinds of Silica Glasses

Kazunao Yamamoto and Hiroshi Namikawa*

Department of Physics, Shokugyokunren University, 4-1-1 Hashimotodai, Sagamihara, 229 Japan
* Research & Development Division, Nippon Sanso K.K., 4-320 Koshizuka, Saiwaiku, Kawasaki, Japan 210

Abstract

Heat treatment effect on the electrical properties of various kinds of silica glasses was investigated. The electrical conductivity was greatly changed by the heating at 1000 °C depending on the kinds of glasses and the heating time. Ununiform distributions of the local conductivity were observed, suggesting that an electrically neutral material was release by the heating at 1000 °C and resulted in the decrease of the local conductivity. After a sufficient heating, an reversible phenomenon took place, in which the electrical conductivity increased slowly at about 200°C and decreased rapidly at 1000 °C. An explanation was discussed on the basis of an assumption that the heat treatment effect is due to residual water.

1. Introduction

In general,electrical properties of insulators is strongly sensitive to the structure and composition. Therefore, the electrical measurement is expected to be one of the effective means for the detection of nice distinctions of structure. We investigated the electrical properties of various kinds of silica glasses and it was found that the electrical conductivity was greatly changed by heat treatment.

In the present report, we show experimental results of type II and type III silica glasses and discuss an explanation on the basis of an assumption that the heat treatment effect is due to residual water in the silica glasses.

2. Experimental Procedure

Table 1 shows manufacturing methods of the silica glasses measured. The silica glasses contained from 1 ppm to 1000 ppm water in the order of magnitude. In this report we will mainly deal with the No.1 and No.2 glasses and name them for short the SICL4-FLAME glass and the QUARTZ-FLAME glass, respectively.

A sample for the electrical measurement was a plate of about 2 mm thick. The experimental procedures were as follows:

(1) A sample was quenched after heated at 1000 °C in air and the change of the electrical conductivity was measured.

(2) In order to examine the distribution of the local conductivity, both surfaces of the quenched sample was ground gradually and the relation between the electrical conductivity

and the thickness of the sample was measured.

(3) The quenched sample was kept at about 200 °C and the change of the electrical conductivity with time was examined.

3. Experimental results

3.1 Change of electrical conductivity by the heating at 1000 °C

In Fig.1 two solid lines show the relations between the electrical conductivity and the heating time at 1000 °C in the SICL4-FLAME glass and the QUARTZ-FLAME glass, respectively. The electrical conductivity is expressed by a value relative to that of an original sample never heated (the relative conductivity).

When an original sample of the SICL4-FLAME glass was heated at 1000 °C for only 0.3 hours and quenched, the electrical conductivity decreased to one order of magnitude smaller that its original value. As the heating time increased further, the electrical conductivity decreased monotonously. After more than 100 hours it decreased to almost 3 order in magnitude much smaller than its original value.

In the QUARTZ-FLAME glass the electrical conductivity increased slowly up to about 100 hours, then decreased.

3.2 Distribution of local conductivity.

In order to examine whether the change of the electrical conductivity mentioned in the previous section was uniform or not, both surfaces of the quenched sample were ground gradually and the relation between the electrical conductivity and the thickness of the sample was measured. In Fig.2 the results of the SICL4-FLAME glass and the QUARTZ-FLAME glass are shown.

In the SICL4-FLAME glass (solid lines in the figure) the electrical conductivity of a sample which heated at 1000 °C for only 0.3 hours was one order in magnitude smaller than its original value. When both surfaces of the sample were ground slightly, the electrical conductivity recovered approximately to its original value. This indicates that the local conductivity near the surface was greatly decreased by the heating at 1000 °C. As the sample was heated further, the local conductivity decreased and became uniform as indicated by the other solid lines in the figure. Such a ununiform decrease of the local conductivity suggests that the surface took part in the decrease of the local conductivity. The most plausible explanation is that an material, which is electrically neutral, was released through the surface by the heating at 1000 °C and resulted in the decrease of the local conductivity.

In the QUARTZ-FLAME glass (dotted lines) the change of the local conductivity was more complicated than that in the SICL4-FLAME glass. As is clear from the figure the local conductivity generally increased up to about 100 hours, then decreased. In addition, ununiform distributions of the local conductivity were observed in the same manner as the SICL4-FLAME glass.

The ununiform distributions of the local conductivity were observed in all the silica glasses measured.

3.3 A reversible phenomenon

An example of the results of the third experiment mentioned in chapter 2 is shown in Fig.3. When a sample of the SICL4-FLAME glass, which had been heated at 1000 °C for 100 hours and quenched, was kept at about 200 °C, the electrical conductivity increased slowly with time as shown by the solid line in the figure. The final value was more than 20 times as large as the initial value. When the sample, whose electrical conductivity had increased at about 200 °C, was heated again at 1000 °C for only few minutes and quenched, the electrical conductivity recovered to the initial value. When the sample was kept at about 200°C once more, the electrical conductivity increased again. This reversible phenomenon was observed in all the silica glasses measured. In Fig.1 black points show the final values of the samples kept at about 200 °C.

The change of the local conductivity with the reversible phenomenon was examined in the same way as that mentioned in section 3.2. The results are shown schematically in Fig.4. Solid lines shows the distributions of the local conductivity of the samples which were quenched after the heating at 1000 °C. When the samples were kept at about 200 °C, the local conductivity increased to values as indicated by dotted lines in the figure. As is clear from the figure, the reversible phenomenon took place where the local conductivity had been decreased by the heating at 1000 °C.

3.4 Infrared spectra

In section 2.2 it was suggested that an electrically neutral material was released by the heating at 1000 °C and resulted in the decrease of the local conductivity. The SICL4-FLAME glass and the QUARTZ-FLAME glass contained water about 1000 ppm and 100 ppm, respectively. Fig.5 shows the infrared spectra, in which peaks at about 2.7 microns are due to water1). As is clear from the figure, water decreased by the heating at 1000 °C in air.

4. Discussions

The experimental results shown in the previous chapter suggest that the change of electrical properties is due to residual water in the sample. On the basis of the suggestion we will discuss a model to explain the experimental results.

The basic assumptions are as follows:

(1) Electrical charge carriers are protons supplied by residual water2),3)

(2) Water is released by the heating at 1000 °C. This has been confirmed from the infrared spectra as shown in Fig.5.

(3) Water in silica glasses exists not only as OH group but also H_2O molecule.

(4) The source of carrier supply is OH group. Therefore, if the amount of OH group increases and decreases, the electrical conductivity does the same.

(5) A reversible reaction as shown in Fig.6 takes place where water has been decreased by the heating at 1000 °C. In the figure

a H_2O molecule changes to a pair of OH groups at 200 °C and the inverse reaction takes place at 1000 °C. This reaction causes the reversible phenomenon mentioned in section 3.3 through the change of the amount of OH group.

The experimental results of the SICL4-FLAME glass can be explained generally by the above assumptions as shown in Fig.7. On the other hand, the changes of the electrical conductivity of the other silica glasses were more complicated than that of the SICL4-FLAME glass. For example, the electrical conductivity of the QUARTZ-FLAME glass increased at first, then decreased. Furthermore, in the case of the No.4 glass in table 1, the electrical conductivity changed in 3 steps; rapid increase, slow increase and ununiform decrease. These facts suggest that the state of water in silica glasses is very complicated. More detailed investigations are required to elucidate the problem.

5. Conclusions

The heat treatment effects on the electrical properties in various kinds of silica glasses were investigated and the following results were obtained.

(1) When a type III silica glass, which was synthesized from $SiCl_4$ in a flame, was heated at 1000 °C and quenched, the electrical conductivity decreased with the heating time to almost 3 order in magnitude much smaller than its original value.

(2) The changes of the electrical conductivity in the other silica glasses were more complicated. In a type II silica glass, which was prepared by fusion of quartz crystal in a flame, the

electrical conductivity increased at first, then decreased.

(3) Ununiform distributions of the local conductivity were observed, suggesting that an electrically neutral material was released from inside to outside by the heating at 1000 °C and resulted in the decrease of the electrical conductivity.

(4) An reversible phenomenon took place where the local conductivity had been decreased by the heating at 1000 °C, in which the local conductivity increased slowly at a temperature about 200 °C and decreased rapidly at 1000 °C.

(5) According to the infrared spectra water was decreased by the heating at 1000 °C.

(6) To explain the experimental results a model was discussed on an assumption that the electrical conductivity is protonic conduction due to residual water.

Acknowledgment

The authors thanks Dr. A. Hayashi and Dr. H. Imai very much for providing samples.

Reference

1) R. F. Bartholomew, B. L. Butler, H. L. Hoover and C. K. Wu, "Infrared Spectra of a Water-Containing Glass," J. Am. Ceram. Soc., 63 [9-10] 481-5 (1980).

2) Y. Abe, H. Hosono, Y. Ohta and L. L. Hench, "Protonic conduction in oxide glasses: Simple relation between electrical conductivity, activation energy, and the O-H bonding state," Phys. Rev. B, 38 [14] 10166-9 (1988).

3) H. Hosono, T. Kamae and Y. Abe, Electrical Conduction in Magnesium Phosphate Glasses Containing Heavy Water," J. Am. Ceram. Soc., 72 [2] 294-7 (1989).

Table 1.

Manufacturing methods of silica glasses measured. No. 1 and No. 2 glasses are named for short the SICL4-FLAME glass and the QUARTZ-FLAME glass, respectively.

No.	MATERIAL	TREATMENT
1.	$SiCl_4$	SYNTHESIS IN A FLAME
2.	QUARTZ	FUSION IN A FLAME
3.	QUARTZ	ELECTRIC MELTING
4.	CRISTOBALITE	HEATING IN VACUUM
5.	CRISTOBALITE	FUSION IN A FLAME

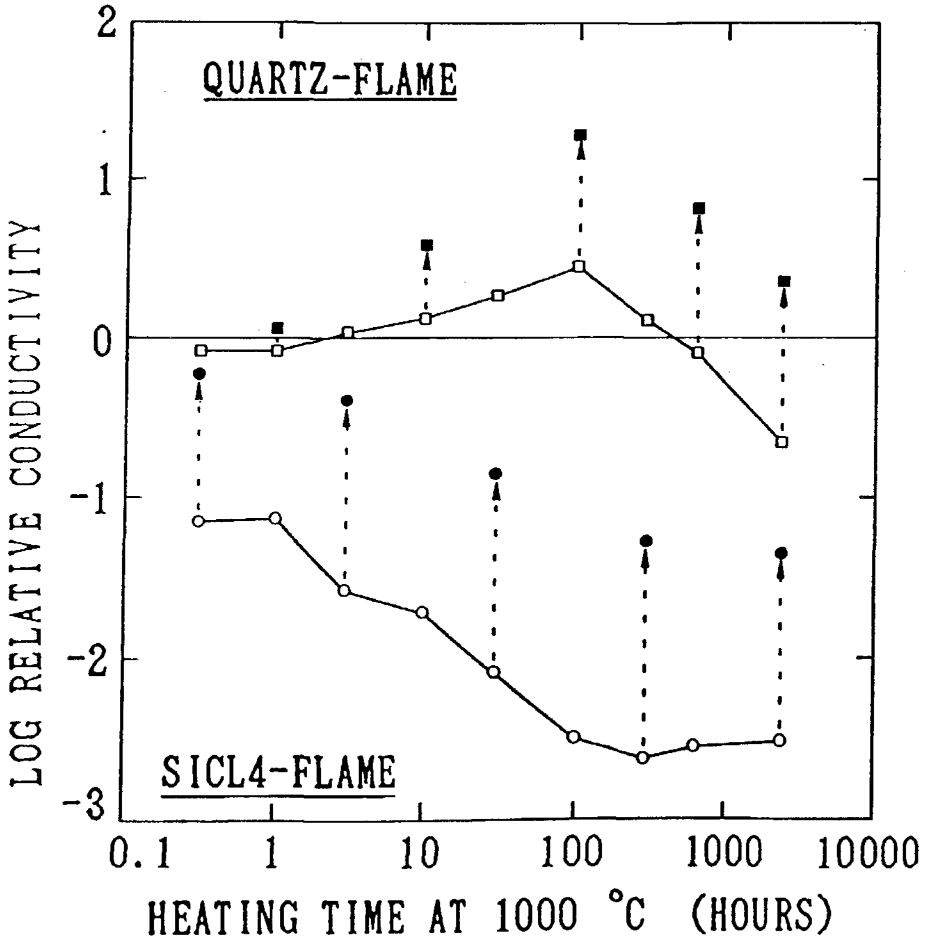

Fig. 1

Relation between electrical conductivity and the heating time at 1000 °C in the SICL4-FLAME glass (electrical conductivity was measured at 180 °C) and the QUARTZ-FLAME glass (130 °C). Electrical conductivity is expressed by value relative to that of an original sample never heated (relative conductivity). Solid lines show electrical conductivities of the quenched samples. When the quenched samples were kept at about 200 °C, electrical conductivity decreased as indicated by arrows.

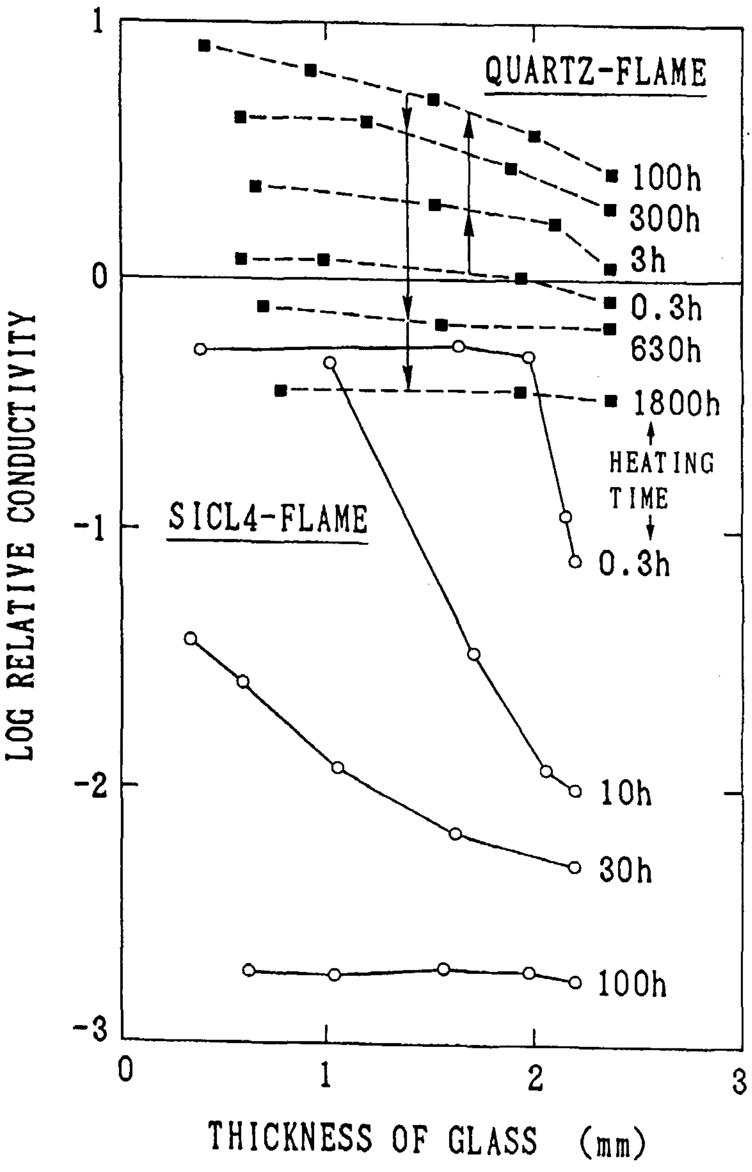

Fig. 2

Relation between relative conductivity and thickness of samples which were heated at 1000 °C and quenched. Solid and dotted lines are those of the SICL4-FLAME glass and the QUARTZ-FLAME glass, respectively.

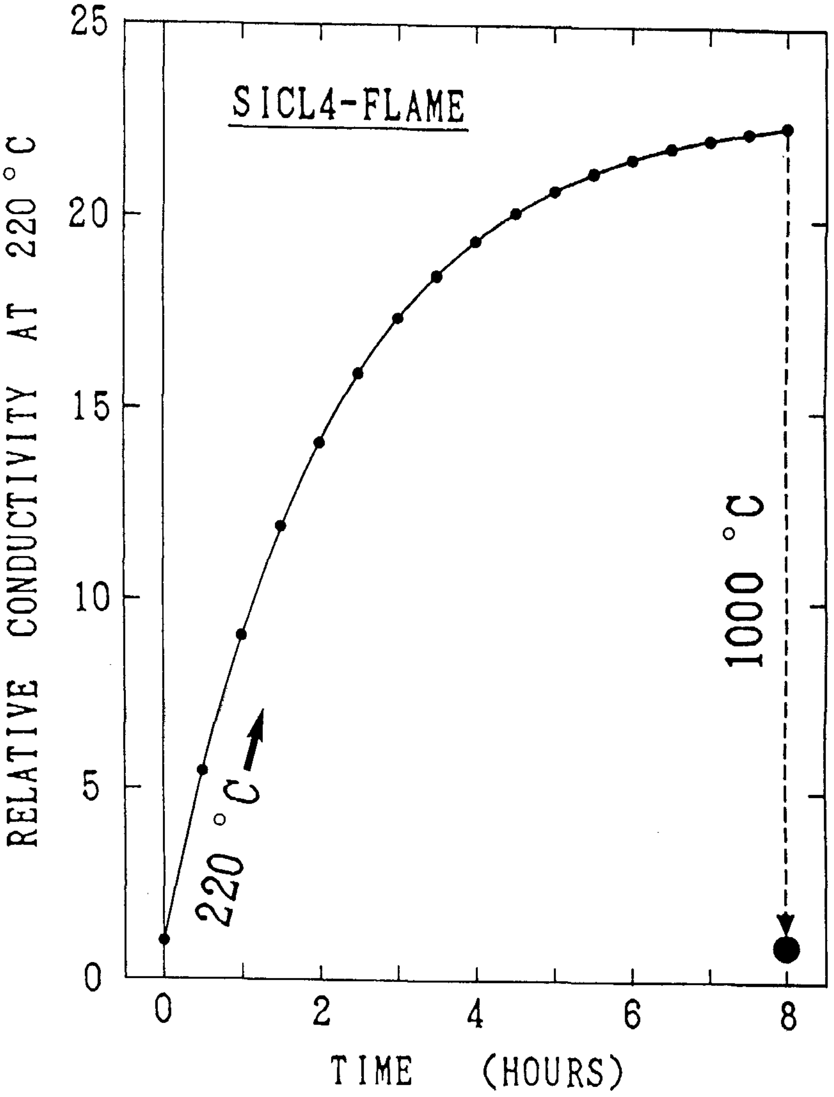

Fig. 3

Reversible phenomenon in the SICL4-FLAME glass. Electrical conductivity of the quenched sample increased with time at about 200 °C as the solid line. When the sample was heated again at 1000 °C for only few minutes and quenched, electrical conductivity decreased as indicated by arrow.

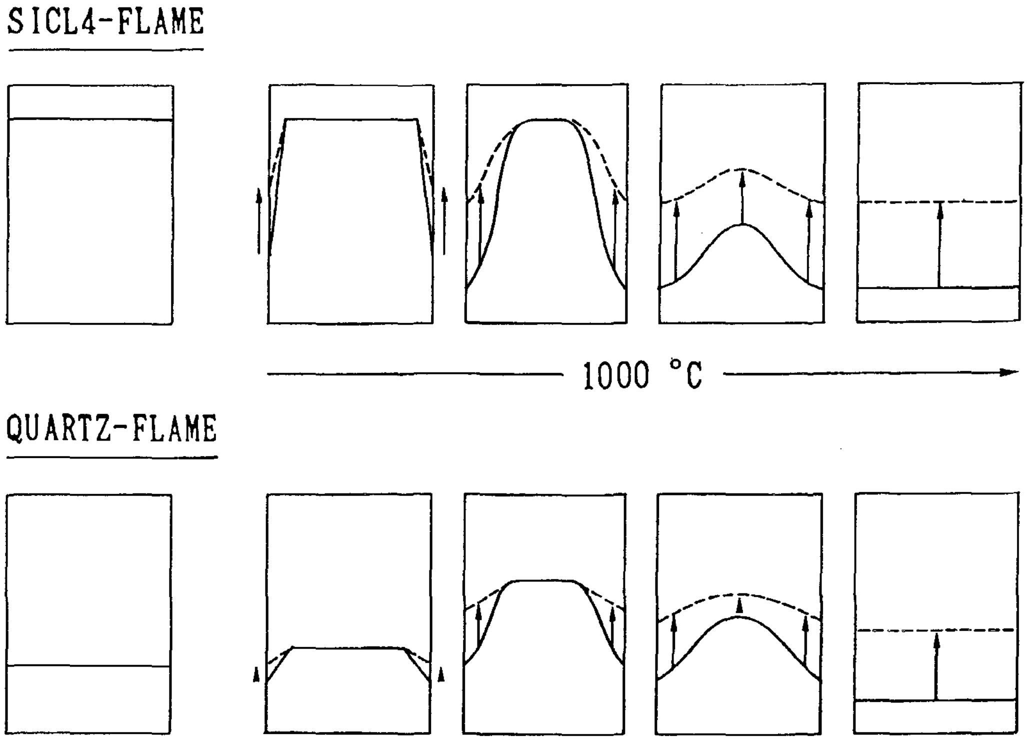

Fig. 4

Schematic diagram of distribution of local conductivity in the SICL4-FLAME glass and the QUARTZ-FLAME glass. When samples were heated at 1000 °C and quenched, local conductivities changed with heating time as shown by solid lines. When the quenched samples were kept at about 200 °C, local conductivities increased to values as shown by dotted lines.

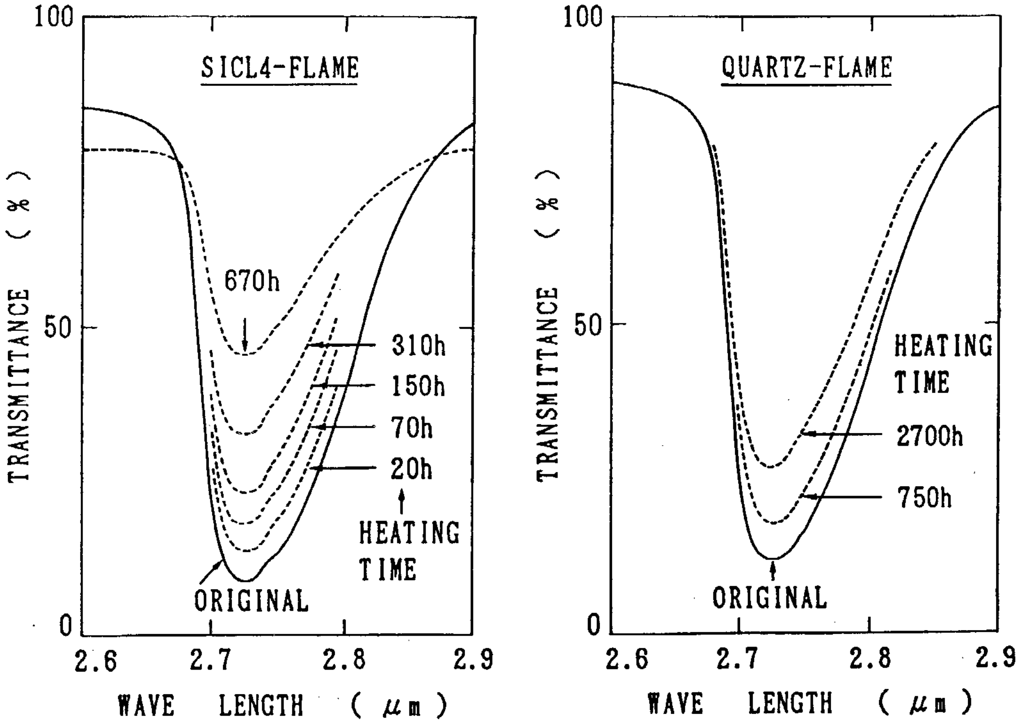

Fig. 5

Infrared spectra of the SICL4-FLAME glass and the QUARTZ-FLAME glass. Peaks at about 2.7 microns are due to water. Solid lines are spectra of original samples. When samples were heated at 1000 °C, water decreased as indicated by dotted lines.

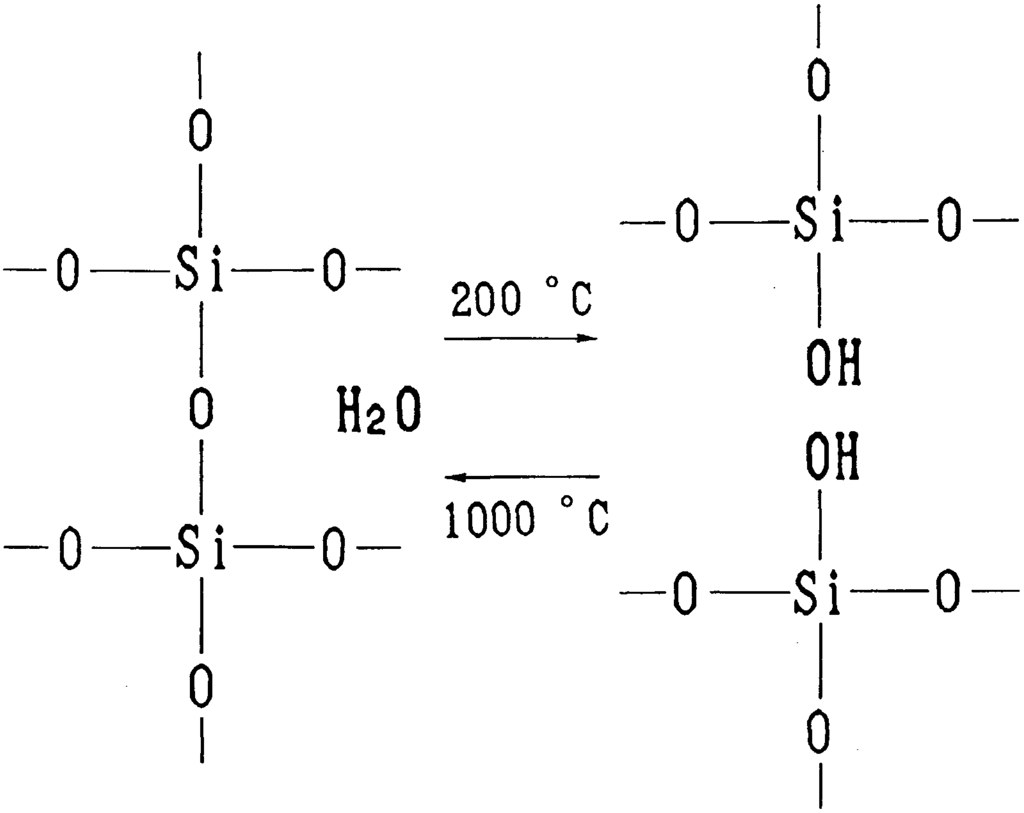

Fig. 6

A reversible reaction which takes place where water has been decreased by the heating at 1000 °C. As amount of OH group increases and decreases, the electrical conductivity does the same.

Fig. 7

An explanation of heat-treatment effect in the SICL4-FLAME glass. (A); In initial stage of the heating at 1000 °C, OH groups near surfaces change to H_2O molecules, which migrate inside the sample and escape from surfaces. (B); After a sufficient heating the total amount of water has decreased and H_2O molecules have been formed. When the sample was quenched, this state is frozen. Electrical conductivity is smaller than its original value, since amount of OH group has decreased. (C); When the quenched samples are kept at about 200 °C, H_2O molecules change slowly to OH groups. As amount of OH group increases, electrical conductivity does the same. When the sample is heated again at 1000 °C, change from (C) to (B) takes place rapidly. This change is reversible.