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LETTER TO THE EDITOR

Removal of OH Absorption Bands Due to Pyrohydrolysis Reactions in Fluoride-Containing Borosilicate Glasses

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The purpose of this study is to decrease and to remove OH ions and H_2O in borosilicate glasses. Fluoride-containing borosilicate glasses followed by dry-air-bubbling showed the significant decrease of OH absorption bands around 3500 cm^{-1}. The decrease of OH absorption bands was elucidated by the use of pyrohydrolysis reactions in these glasses where fluoride ions react with OH ions or H_2O during melting. The rates of the decrease of OH absorption bands substantially depend on high valence cations of fluorides. Particularly, the decrease rates of OH absorption coefficients were in the order of ZrF_4-containing glass > AlF_3-containing glass > ZnF_2-containing glass. ZrF_4-containing glass treated by dry-air-bubbling showed a good capability to remove OH absorption band. Fluoride-containing glasses showed the low flow point in comparison with fluoride-free glasses. © 1997 Academic Press

Borophosphosilicate glass films formed from inorganic gas sources have been widely used in high-density integrated circuits as dielectric insulators (1–3). The advantageous properties of such films are conformal step coverage, effective protection against alkali ions, and fairly low reflow temperature. Highly doped borophosphosilicate glasses reflow at low temperatures to give step coverage of ultra-high-density integrated circuits, but they also suffer from a tendency to crystallize during the reflow process (4). Such crystallization is a fatal drawback in the planarization of ultra-high-density integrated circuits (4).

It has been found that zinc borosilicate and lead borosilicate glasses have even lower flow temperatures than borophosphosilicate glasses, and they do not suffer from this problem of crystallite formation during reflow (5, 6). Past studies have shown that the hysteresis *C–V* curves of MOS capacitors are a result of highly polarizable ions and OH radicals in the glass (8, 9).

In this paper, we discuss the improvement of OH absorption coefficients around 3500 cm^{-1} in fluoride-containing B_2O_3–SiO_2 glasses and the effects of dry air treatment of these glasses (7).

ZrO_2, Al_2O_3, ZnO, ZrF_4, AlF_3, and ZnF_2-containing B_2O_3–SiO_2 glasses were prepared for use in our experiments. Batches comprising 1 kg of reagent-grade chemicals were melted at 1300°C for 5 h in an ultra-high-purity platinum crucible with an electric furnace under an oxidizing atmosphere. After homogeneous melting, the glass was poured into a stainless steel plate and annealed. Infrared transmission spectra were measured using a Digi-Laboratory spectrophotometer with $10 \times 20 \times 1$ mm plates. Glass flow points were obtained from thermal expansion curves using a method previously described (10, 11). Dry air was blown by bubbling through molten glass for 0.5 h during melting, using a platinum tube. After bubbling, the molten glass was poured into a stainless steel plate and annealed.

The relationship between transmittance T_{OH} and reflectivity R_{OH} can be represented as (12)

$$T_{OH} = 1 - [R_{OH}(1 - R_{OH}) + R_{OH}] = (1 - R_{OH})^2. \quad (1)$$

The absorption coefficient β_{OH} (13) resulting from the fundamental vibration due to OH ions at around 3500 cm^{-1} is calculated from

$$T_{OH} = [(1 - R_{OH})^2 e^{-\beta_{OH} t}]/[1 - R_{OH}^2 e^{-2\beta_{OH} t}], \quad (2)$$

where t is the glass thickness.

By substituting (1), (2) can be simplified as

$$e^{-\beta_{OH} t} + R_{OH}^2 e^{-2\beta_{OH} t} = 1. \quad (3)$$

Absorption coefficients β_{OH} are computed from Eq. (3).

Two types of H_2O molecules and OH ions are situated in the network structure of glasses; the behavior of their reactions is somewhat different. Pyrohydrolysis reactions of H_2O molecules with fluoride compounds in glasses are

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TABLE 1
Glass Compositions and Treatments and Values of T_{OH}, R_{OH}, β_{OH}, and T_f

Glass no.	Treatment	ZrO_2 (mol%)	Al_2O_3	ZnO	ZrF_4	AlF_3	ZnF_2	B_2O_3	SiO_2	T_{OH} (%)	R_{OH}	β_{OH} (cm^{-1})	T_f (°C)
(1)		10						60	30	62	0.21	0.42	880
(2)			10					60	30	56	0.25	0.59	890
(3)				10				60	30	47	0.31	0.87	850
(4)					10			60	30	65	0.19	0.36	850
(5)						10		60	30	59	0.23	0.50	865
(6)							10	60	30	50	0.29	0.77	840
(7)	Bubbled				10			60	30	74	0.14	0.18	860
(8)	Bubbled					10		60	30	68	0.17	0.35	870
(9)	Bubbled						10	60	30	62	0.21	0.42	850

represented as follows:

$$ZrF_4 + 2H_2O \rightarrow ZrO_2 + 4HF\uparrow \quad (4)$$

$$AlF_3 + \tfrac{3}{2}H_2O \rightarrow \tfrac{1}{2}Al_2O_3 + 3HF\uparrow \quad (5)$$

$$ZrF_2 + H_2O \rightarrow ZnO + 2HF\uparrow . \quad (6)$$

In the same way, in cases where OH ions react with fluoride compounds, pyrohydrolysis reactions are as follows:

$$ZrF_4 + 4OH \rightarrow ZrO_2 + 4HF\uparrow + O_2\uparrow \quad (7)$$

$$AlF_3 + 3OH \rightarrow \tfrac{1}{2}Al_2O_3 + 3HF\uparrow + \tfrac{3}{4}O_2\uparrow \quad (8)$$

$$ZnF_2 + 2OH \rightarrow ZnO + 2HF\uparrow + \tfrac{1}{2}O_2\uparrow . \quad (9)$$

As shown in Eqs. (4)–(6) and (7)–(9), high valence fluoride cations have a tendency to react with more H_2O molecules and OH ions in glasses and their reaction rates are in the order $Zr^{4+} > Al^{3+} > Zn^{2+}$.

Glass compositions, OH absorption coefficients β_{OH} calculated from Eq. (3), and flow point T_f are given in Table 1. The experimental data also show that their reaction rates of fluoride compounds with OH ions are in the order $ZrF_4 > AlF_3 > ZnF_2$, as shown in Table 1 (4)–(6). It was confirmed by atomic absorption spectroscopy that the F^- contents of glasses (4)–(6) before bubbling were 5–6%, respectively, and those of glasses (7)–(9) after bubbling were 2–3%, respectively.

Infrared transmission spectra for these glasses are given in Figs. 1–3. The absorption bands around 3500 cm^{-1} are due to fundamental vibrations arising from OH absorption (14). As represented in Figs. 1–3, the absorption intensities of OH bands decreased when fluoride compounds were introduced into glasses and dry air was bubbled through the molten glasses.

Particularly, dry-air-bubbled glasses showed the weakest absorption bands. Figure 3 showed that the amounts of OH concentration removed were in the order ZrF_4-containing glass > AlF_3-containing glass > ZnF_2-containing glass. The experimental data showed that high valence cations of fluoride compounds are favorable for the removal of OH ions.

Typical measured thermal expansion curves of these glasses are represented in Fig. 4, which shows glass transition points and flow points. Flow points of fluoride-containing glasses are lower than those of fluoride-free glasses (15). As fluoride concentration decreased following the bubbling,

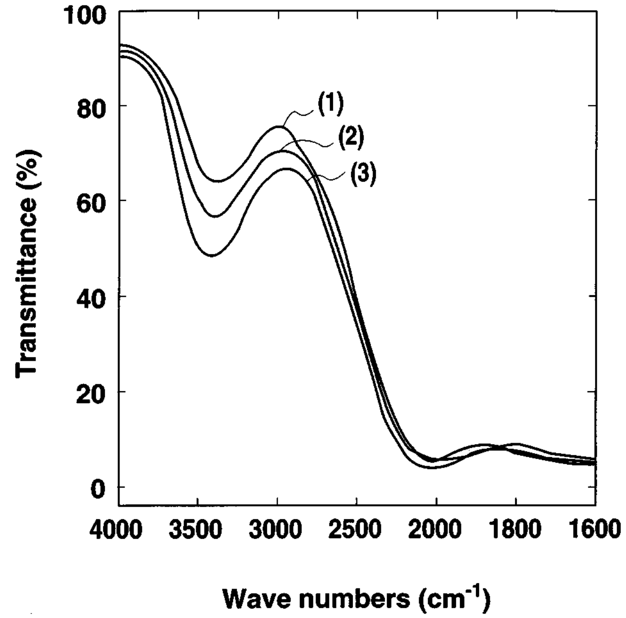

FIG. 1. Infrared transmission spectra of glasses: (1) glass No. (1), (2) glass No. (2), (3) glass No. (3).

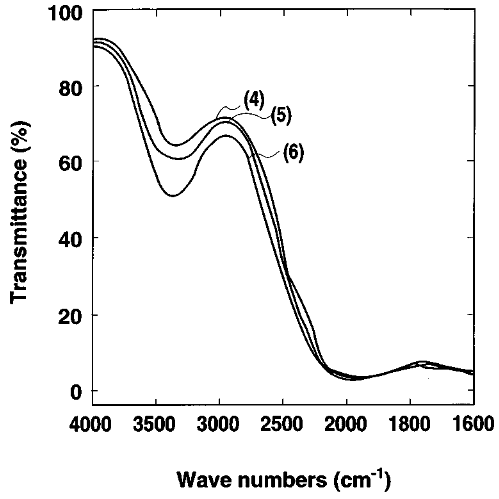

FIG. 2. Infrared transmission spectra of glasses: (4) glass No. (4), (5) glass No. (5), (6) glass No. (6).

flow points of bubbled glasses were somewhat lowered. It is thought that glass reflow is caused by viscosity, which is determined by composition, chemical bonding (15), and structure (16). Namely, glass with low connectivity (15) and a released structure (16) is more viscous than that without such properties. It is to be expected that ionic bonds would give rise to more viscous flow than covalent bonds. The fluoride ion is ionic and has weak bonds. Therefore, fluoride-containing glass showed a low flow point. Absorption coefficients β_{OH} and flow points T_{f} are given in Fig. 4.

The decrease rates of OH absorption coefficients calculated from infrared transmission spectra around 3500 cm^{-1} coincided approximately with those for the stoichiometrical calculation based on the pyrohydrolysis reactions. The rates of reduction of the OH absorption bands were in the order Zr^{4+} ions > Al^{3+} ions > Zn^{2+} ions. High valence cations of fluorides favored rapid decrease of OH absorption bands. The increase in the strength of the hydrogen bonds in the glasses containing fluorine is probably due to the formation of hydrogen bonds of the type O–H ··· F. Hydrogen bonds of this type will be stronger than those of the type O–H ··· O because of the greater electrostatic attraction of hydrogen for fluorine. There is a greater electronegativity difference. The general diffusiveness of the OH bonds can be explained by postulating a distribution of associated OH groups of the type O–H ··· O and O–H ··· F. A better way of envisaging OH frequency distribution is to consider the tetrahedra types, which include SiO_4, Si_3OF, Si_2F_2, and so on. The overall electronegativities of these tetrahedra will vary and so also will the frequencies of the

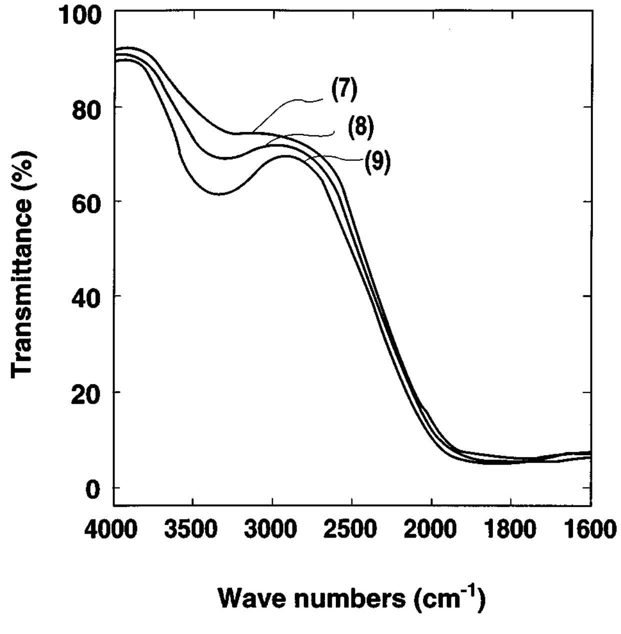

FIG. 3. Infrared transmission spectra of glasses: (7) glass No. (7), (8) glass No. (8), (9) glass No. (9).

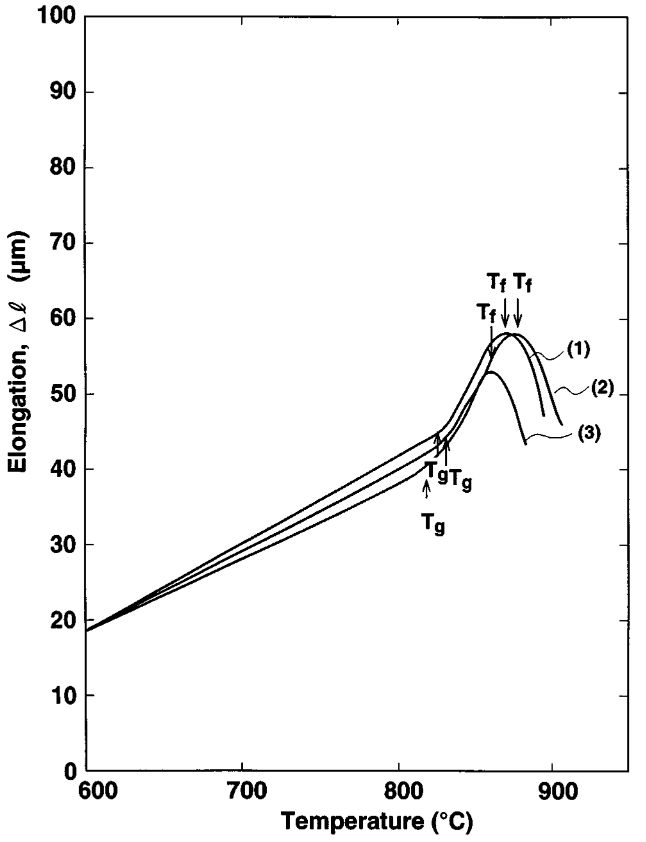

FIG. 4. Typical thermal expansion curves of glasses treated by dry-air bubbling: (1) glass No. (7), (2) glass No. (8), (3) glass No. (9).

OH groups hydrogen bonded to the oxygen or fluorine atoms. The frequencies decrease when fluorine is added to the batch. OH groups associate with tetrahedra-containing fluorine. These hydrogens are brought into contact with fluorine atoms, facilitating the formation of HF, represented as follows (17).

$$\text{Si–OH} \cdots \text{F–Si} \rightarrow \text{Si–O–Si} + \text{HF}\uparrow . \qquad (10)$$

It was presumed that F^- ions participate in the network, forming positions of tetrahedra of SiO_4. OH groups associated with tetrahedra-containing fluorine decrease, as shown in Eq. (10).

From the point of view, the addition of fluorides to the glasses was the efficient method for removing the water bands. The complete removal of the bands could be achieved with 10 mol% additions of ZrF_4, following the bubbling treatment. The combination of addition of ZrF_4 and the dry-air bubbling could be adopted for obtaining water-free glass on a large scale.

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