Journal of the European Ceramic Society **16** (1996) 911 914

0955-2219(95)00210-3
0955-2219/96/$15.00 +.00

Viscous Flow of ZnF_2–PbF_2–SiO_2–B_2O_3–GeO_2 glasses and their application to MOS capacitors

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(Received 29 September 1995; revised version received 17 November 1995; accepted 29 November 1995)

Abstract

The capacitance and voltage (C–V) characteristics of metal, oxide, and silicon (MOS) capacitors passivated by ZnF_2–PbF_2–SiO_2–B_2O_3–GeO_2 glasses with various water and fluoride contents were investigated. As the OH absorption coefficients of the glass increased, adverse effects on the recovery of hysteresis loops of the C–V curve shifts were observed. The water content was closely related to the fluoride content in these glasses. The viscous flow point of the glass was lowered with an increasing degree of ionic character obtained from Hannay's equation.

1 Introduction

Borophosphosilicate glass films formed from inorganic gas sources have been widely used in high-density integrated circuits such 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 the ultra-high-density integrated circuits.[4] It has been found that zincborosilicate glasses have even lower flow temperatures than borophosphosilicate glasses, and they do not suffer from the problem of crystallite formation during the reflow process.[5,6] However, both borophosphosilicate and zincborosilicate glasses contain small amounts of water,[7,8] and this adversely affects the C–V characteristics of MOS devices if they are rapidly heated. Past studies have shown that the abnormal C–V curves of MOS capacitors are a result of highly polarizable ions and OH^- radical in the glass.[8,9]

In this paper, we discuss the relationship between OH^- radical absorption and shifts in the C–V curve for MOS capacitors passivated using non-crystallizable ZnF_2–PbF_2–SiO_2–B_2O_3–GeO_2 glasses with ionic bonds, and investigate the application of these glasses to MOS capacitors.

2 Experimental

ZnF_2–PbF_2–SiO_2–B_2O_3–GeO_2 glasses were prepared for use in the 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 in an oxidizing atmosphere. After homogeneous melting, the glass was poured onto a stainless steel plate and annealed. Infrared transmission spectra were measured using a Digi-Labo spectrophotometer with 10 × 20 × 1 mm plates. Glass flow points were obtained from thermal expansion curves, using a method previously described.[10]

Sputter targets were cut from these samples and ground to 75 mm in diameter and 10 mm thick. Glass films 0·5 μm thick were deposited on a SiO_2 layer (0·3 μm) on Si (100) wafers under 1 kW power and 30 millitorr vacuum sputtering conditions using a Perkin-Elmer vacuum system. The glass thickness was measured by the use of a nanometrics SD9-2000T thickness meter using the Na–D line refractive index (N_D—1·56). Aluminium electrodes were deposited on the glass films. C–V curves for these MOS capacitors were observed at 1 GHz at room temperature, as described previously.[11]

3 Results and Discussion

Low-temperature glass reflow has been studied and used in the planarization of MOS devices and the fabrication of multi-level interconnections.[5,6] It is thought that glass reflow is controlled by viscosity, which is in turn controlled by composition, chemical bond[12] and structure.[13,14] Namely, glass with 'low connectivity'[12] and 'a released structure'[13] is less viscous than that without such properties. It is to be expected that ionic bonds would give rise to a greater degree of viscous flow than covalent bonds. It seems useful to use Hannay's equation[15] to determine the ionic character of the halide compounds and, moreover, to apply the equation to halide glasses seems a useful way to estimate the bonding states of glass molecules. Hannay and Smyth[15] proposed an experimental equation for ionic bonding as follows;

Degree of ionic character, (%)

$$I_i = 16\,(x_A - x_B) + 3{\cdot}5\,(x_A - x_B)^2 = (x_A - x_B)\,[16 + 3{\cdot}5\,(x_A - x_B)] \qquad (1)$$

where $(x_A - x_B)$ is the electronegativity difference for a bond $A - B$ $(x_A > x_B)$.

The ionic character of a glass, I (%), can be described approximately as follows:

$$I = \Sigma I_i M_i \qquad (2)$$

where I_i is the ionic character of a single bond $A - B$ making up the glass.

M_i is the mole percentage of the ions making up the glass. The author estimated the ionic character of glasses, using eqns (1) and (2).

The chemical composition (mol%) of various glasses, their absorption coefficients, β_{OH}, ionic character, flow points, T_f, and C–V curve shift, ΔV_G, are listed in Table 1. Infrared absorption spectra for these glasses are given in Fig. 1. The absorption bands around 3·500 cm^{-1} are due to fundamental vibrations arising from OH ions absorption.[16,17]

The relationship between transmittance T_{OH} and reflectivity R_{OH} can be represented as follows:[18]

$$T_{OH} = (1 - R_{OH})^2\,(1 + R_{OH}^2 + R_{OH}^4 + \cdots\cdots) \qquad (3)$$

when R_{OH} is small,

$$T_{OH} \fallingdotseq (1 - R_{OH})^2\,(1 + R_{OH}^2) \qquad (4)$$

The absorption coefficient β_{OH}[19] resulting from the fundamental vibration due to OH at around 3·500 cm^{-1} is calculated from eqn (5)

$$T_{OH} = [(1 - R_{OH})^2\, e^{-\beta_{OH}t}]/[1 - R_{OH}^2 e^{-2\beta_{OH}t}] \qquad (5)$$

where t is the glass thickness.

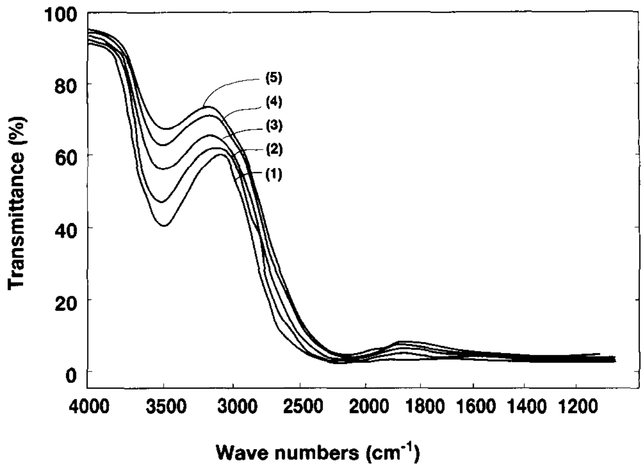

Fig. 1. Infrared absorption spectra for ZnF_2–PbF_2–SiO_2–B_2O_3–GeO_2 glasses: (1) glass no. 1; (2) glass no. 2; (3) glass no. 3; (4) glass no. 4; (5) glass no. 5.

By substituting eqn (4), eqn (5) can be represented as follows:

$$R_{OH}^2(R_{OH}^2 + 1)e^{-2\beta_{OH}t} + e^{-\beta_{OH}t} - R_{OH}^2 = 1 \qquad (6)$$

Values of OH^- absorption coefficients β_{OH} are computed from eqn (6). Values of T_{OH}, R_{OH}, and β_{OH} calculated from the infrared absorption spectra in Fig. 1 are also listed in Table 1. Infrared absorption spectra of these glasses are given in Fig. 1, which shows the decrease of OH absorption bands with the increase of fluoride contents in glasses. Fluoride compounds react with water in the batch during melting, as represented in eqn (7)

$$RF_2 + H_2O \rightarrow RO + 2HF\uparrow, \qquad (7)$$

where R=Zn, Pb.

Consequently, the reaction of water by fluoride groups in glasses would be advantageous as a means of improving their infrared absorption transmissions in the region of the water peaks.

Thermal expansion curves of ZnF_2–PbF_2–SiO_2–B_2O_3–GeO_2 glasses are given in Figs 2 and 3, which also show the glass flow points. Flow points fell with increasing of ionic character in the chemical bonds. This tendency is clear in Table 1. With regard to the C–V curve shifts in MOS capacitors, when OH absorption coefficients increased, ΔV_G shifts also increased. The C–V characteristics of MOS capacitors passivated with these glasses are

Table 1. Lists of glass compositions, T_{OH}, R_{OH}, β_{OH}, T_f, ionic character I, and ΔV_G

Glass no.	ZnF_2 *(mol%)*	PbF_2	SiO_2	B_2O_3	GeO_2	T_{OH} *(%)*	R_{OH}	β_{OH} *(cm^{-1})*	I *(%)*	T_f *(°C)*	ΔV_G *(volt)*
1	2	1	37	40	20	40	0·42	0·22	35·7	780	2·1
2	4	2	34	40	20	47	0·35	0·12	36·3	774	1·8
3	6	3	31	40	20	56	0·28	0·06	36·9	768	1·2
4	8	4	28	40	20	62	0·23	0·03	37·4	760	0·8
5	10	5	25	40	20	65	0·21	0·02	38·0	755	0·6

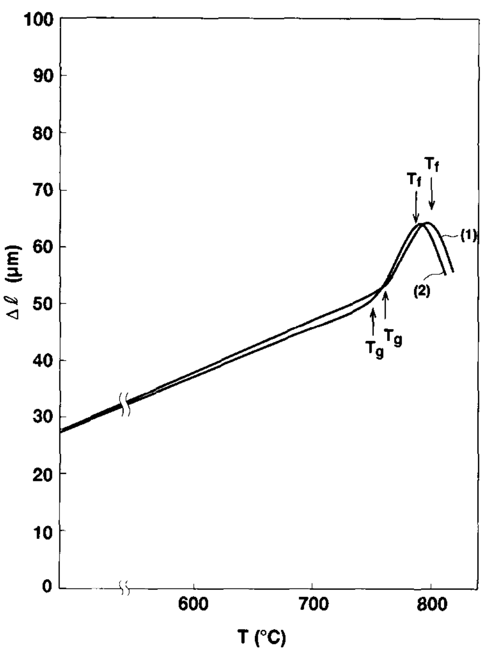

Fig. 2. Thermal expansion curves for ZnF_2–PbF_2–SiO_2–B_2O_3–GeO_2 glasses: (1) glass: no. 1; (2) glass No. 2.

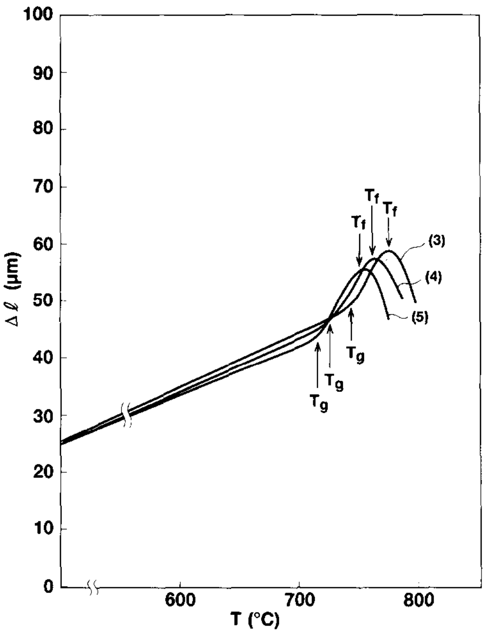

Fig. 3. Thermal expansion curves for ZnF_2–PbF_2–SiO_2–B_2O_3–GeO_2 glasses: (3) glass no. 3; (4) glass no. 4; (5) glass no. 5.

shown in Fig. 4. Figure 4 (1–5), shows the C–V characteristics of MOS capacitors. All the C–V curves for capacitors passivated with these glasses were shifted towards the right. Thus, these peculiar C–V characteristics represent the recovery of C–V curve shifts as the coefficients of OH absorption decrease.

With increasing β_{OH}, the C–V curves shift towards the right. The mean C–V curve shifts, ΔV_G, at the mid-point of forward and backward hysteresis curves are summarized in Table 1.

These shifts in the C–V curves indicate that the total number of positive oxide charges increases.

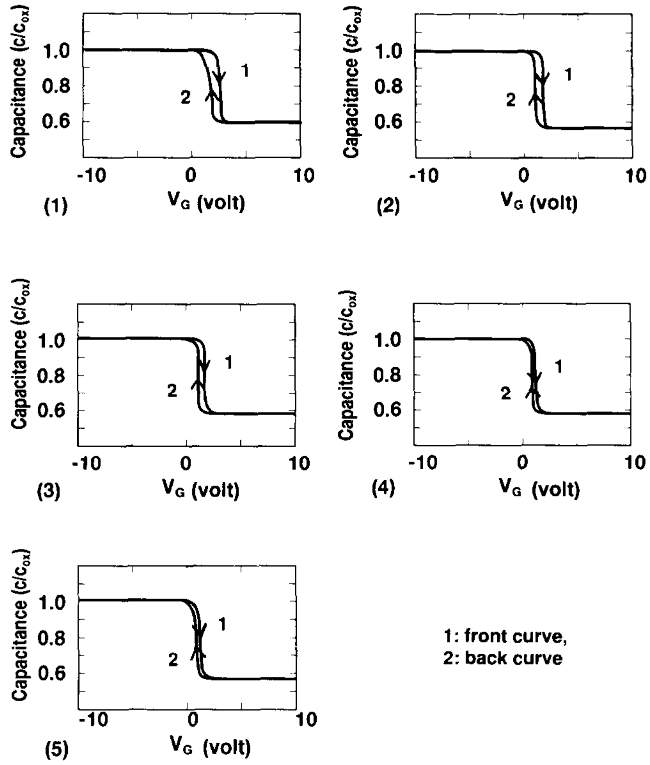

Fig. 4. C–V characteristics of rapidly thermally annealed MOS capacitors passivated with various ZnF_2–PbF_2–SiO_2–B_2O_3–GeO_2 glasses: (1) passivated with glass no. 1; (2) passivated with glass no. 2; (3) passivated with glass no. 3; (4) passivated with glass no. 4; (5) passivated with glass no. 5.

It is reasonable to expect that these positive charges are hydrogen-related vacancies.[9] The loss of hydrogeneous species is related to the disappearance of C–V hysteresis. A hydrogeneous complex is responsible for the carrier trapping mechanism.[9] These shifts are related to hydrogen-related vacancies in water-containing glasses.[9]

4 Conclusion

When the viscous flow point of these glasses became higher, degree of ionic bonding character was reduced and OH absorption coefficient was raised. This tendency may be due to the result of fluoride contents in molten glasses. The viscous flow is reasonably confirmed from the ionic character of bonding state as calculated from Hannay's experimental equation.

The MOS capacitors passivated with ZnF_2–PbF_2–SiO_2–B_2O_3–GeO_2 glasses containing low concentrations of water exhibited the best recovery in their C–V characteristics. With increasing OH absorption coefficient, an adverse effect was seen on the recovery of hysteresis C–V curve shifts. The relationship between recovery from peculiar hysteresis C–V curve shifts and OH absorption coefficient was briefly discussed.

Acknowledgement

The author would like to thank Dr H. Sasaki in Toshiba Research and Development Center for the measurement of infrared absorption spectra.

References

1. Hurley, K. H., *Solid St. Technol.*, **30** (1987) 103.
2. Dickinson, Jr J. E. & deJong, B. H. W. S., *J. Non-cryst. Solids*, **102** (1988) 196.
3. Raley, N. F. & Losee, D. L., *J. Electrochem. Soc.*, **135** (1988) 2640.
4. Schnable, G. L., Fisher, A. W. & Shaw, J. M. *J. Electrochem. Soc.*, **137** (1990) 3973.
5. Kobayashi, K., *J. Non-cryst. Solids,* **88** (1986) 229.
6. Kobayashi, K., *J. Non-cryst. Solids*, (to be published).
7. Kobayashi, K., *J. Electrochem. Soc.*, **131** (1984) 2190.
8. Rojas, S., Gomarasca, R., Zanotti, L., Borghesi, P., Sassela, A., Ottaviani, G., Moro, L. & Lazzeri, P., *J. Vac. Sci. Technol. B*, **10** (1992) 633.
9. Li, S. C., Murarka, S. P., Guo, X. S. & Landford, W. A., *J. Appl. Phys.*, **72** (1992) 2947.
10. Baret, G., Madar, R. & Bernar, C., *J. Electrochem. Soc.*, **138** (1991) 2835.
11. Kobayashi, K., *J. Non-cryst. Solids*, **124** (1990) 229.
12. Kobayashi, K., *J. Non-cryst. Solids,* **159** (1993) 274.
13. Kobayashi, K., *Glass Technol.*, **29** (1988) 253.
14. Kobayashi, K., *Glass Technol.*, **30** (1989) 110.
15. Hannay, N. B. & Smyth, C. P., *J. Amer. Chem. Soc.*, **68** (1946) 171.
16. Shaw, C. M. & Shelby, J. E., *Phys. Chem. Glasses*, **34** (1993) 35.
17. Kobayashi, K., *Glass Technol.,* **34** (1993) 120.
18. Rulller, J. A. & Shelby, J. E., *Phys. Chem. Glasses*, **33** (1992) 177.
19. Naruse, A., *Garasukogaku*, Kyoritsu shuppan, Tokyo, 1959, p. 304 .