Journal of the European Ceramic Society 16 (1996) 915-917

S0955-2219(96)00006-4
0955-2219/96/$15.00 +.00

Exposure to Water Vapor of MOS Capacitors Passivated with PbO-based Glasses

Keiji Kobayashi

Toshiba ULSI Research Center, 1-Komukai Toshiba-cho Kawasaki, Japan

(Received 29 September 1995; revised version received 5 December 1995; accepted 12 December 1995)

Abstract

The capacitance and voltage (C–V) characteristics of metal, oxide, and silicon (MOS) capacitors passivated by PbO-based glasses with various water concentrations and with exposure to water vapor and to heating were investigated. As the OH^- absorption coefficients of the glass increased, adverse effects on the recovery of hysteresis loops of C–V curve shifts were observed. Water vapor had an adverse effect on the hysteresis loops and ΔV_G shifts of MOS capacitors, but they were somewhat improved, following heating at 400°C for 1 h.

1 Introduction

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 the ultra-high-density integrated circuits.[4] It has been found that zincborosilicate and leadborosilicate 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] When leadborosilicate glasses contain small amounts of water and they are exposed to water vapor,[7,8] it is interesting to investigate the C–V characteristics of MOS devices passivated with them. 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 improvement of C–V curves of MOS capacitors passivated with PbO-based glasses exposed to water vapor and investigate the potential for the application of these glasses to MOS devices.

2 Experimental

PbO-based 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.

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 4 Pa 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 MHz at room temperature, as described previously.[10] The MOS capacitors were exposed to water vapor at 80°C for 1 h and heated at 400°C for 1 h in an oxidizing atmosphere.

3 Results and Discussion

The chemical compositions (mol%) of various glasses, their absorption coefficients, β_{OH}, and C–V curve shift, ΔV_G, are listed in Tables 1 and 2. Infrared absorption spectra for these glasses are

Table 1. Lists of glass compositions (mol%)

Glass No	PbO (mol%)	PbF_2 (mol%)	B_2O_3 (mol%)	SiO_2 (mol%)
1	37	5	15	43
2	42	0	15	43

Table 2. Lists of T_{OH}, R_{OH}, β_{OH} and ΔV_G: (1) glass no. (1); (2) glass no. (2); (3) glass no. (1) exposed to water vapor at 80°C for 1 h. (4) glass no. (2) exposed to water vapor at 80°C for 1 h; (5) glass no. (1) exposed to water vapor at 80°C for 1 h and heated at 400°C for 1 h; (6) glass no. (2) exposed to water vapor at 80°C for 1 h and heated at 400°C for 1 h

	T_{OH} (%)	R_{OH}	β_{OH} (cm^{-1})	ΔV_G (V)
1	62	0·23	0·03	1·0
2	56	0·28	0·06	1·5
3	38	0·43	0·23	2·5
4	32	0·49	0·38	3·0
5	59	0·26	0·05	1·2
6	50	0·33	0·10	1·6

given in Fig. 1. The absorption bands around 3 500 cm^{-1} are due to fundamental vibrations arising from OH ions absorption.[11-13]

The relationship between transmittance, T_{OH}, and reflectivity, R_{OH}, can be represented as follows:[14]

$$T_{OH} \doteq (1 - R_{OH})^2 (1 + R_{OH}^2 + R_{OH}^4 + \cdots\cdots) \quad (1)$$

when R_{OH} is small,

$$T_{OH} \doteq (1 - R_{OH})^2 (1 + R_{OH}^2) \quad (2)$$

The absorption coefficient β_{OH}[15] resulting from the fundamental vibration due to OH at around 3 500 cm^{-1} is calculated from eqn (3)

$$T_{OH} = [(1 - R_{OH})^2 e^{-\beta_{OH}t}]/[1 - R_{OH}^2 e^{-2\beta_{OH}t}] \quad (3)$$

where t is the glass thickness.

By substituting eqn (2), eqn (3) can be represented as follows:

$$R_{OH}^2(R_{OH}^2 + 1) e^{-2\beta_{OH}t} + e^{-\beta_{OH}t} - R_{OH}^2 = 1 \quad (4)$$

Values of OH absorption coefficients β_{OH} are computed from eqn (4). Values of T_{OH}, R_{OH}, and β_{OH} calculated from the infrared absorption spectra in Fig. 1 are also listed in Table 2. With regard to the C–V curve shifts in MOS capacitors, when OH absorption coefficients increased, ΔV_G shifts also increased. It has been observed by Li *et al.*[9] that water vapor exercises much adverse influence on the C–V characteristics of MOS capacitors. However, we are able to expect the recovery of hysteresis loops and the ΔV_G shift of C–V curves, following the heating of the MOS capacitors exposed to water vapor.

The C–V characteristics of MOS capacitors passivated with these glasses and the effects of water vapor and heating to MOS capacitors are shown in Fig. 2. The errors of R_{OH}, β_{OH} and ΔV_G values were within ±1% and the hysteresis curves for these MOS capacitors also showed good reproducible capability as required for the MOS device passivations.

In the molten glass, fluoride compound reacts with water in the batch, as represented in eqn (5) and, therefore, the fluoride compound is useful for the removal of OH^- ions in glasses.

$$ZnF_2 + H_2O \rightarrow ZnO + 2HF\uparrow \quad (5)$$

Thus, these peculiar C–V characteristics represent the recovery of C–V curve shifts and the hysteresis loops as the coefficients of OH absorption decrease. Water vapor showed an adverse effect on the C–V hysteresis curves, but the improvement of them was observed, following the heating.

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 2.

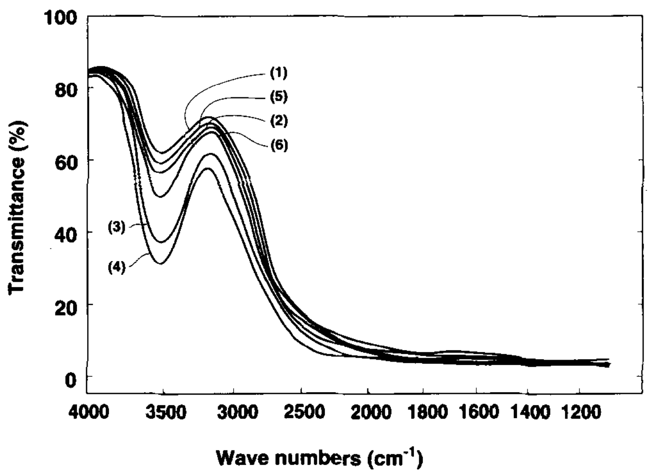

Fig. 1. Infrared absorption spectra for PbO-based glasses: (1) glass no. (1); (2) glass no. (2); (3) glass no. (1) exposed to water vapor at 80°C for 1 h; (4) glass no. (2) exposed to water vapor at 80°C for 1 h; (5) glass no. (1) exposed to water vapor at 80°C for 1 hour and heated at 400°C for 1 h; (6) glass no. (2) exposed to water vapor at 80°C for 1 h and heated at 400°CC for 1 h.

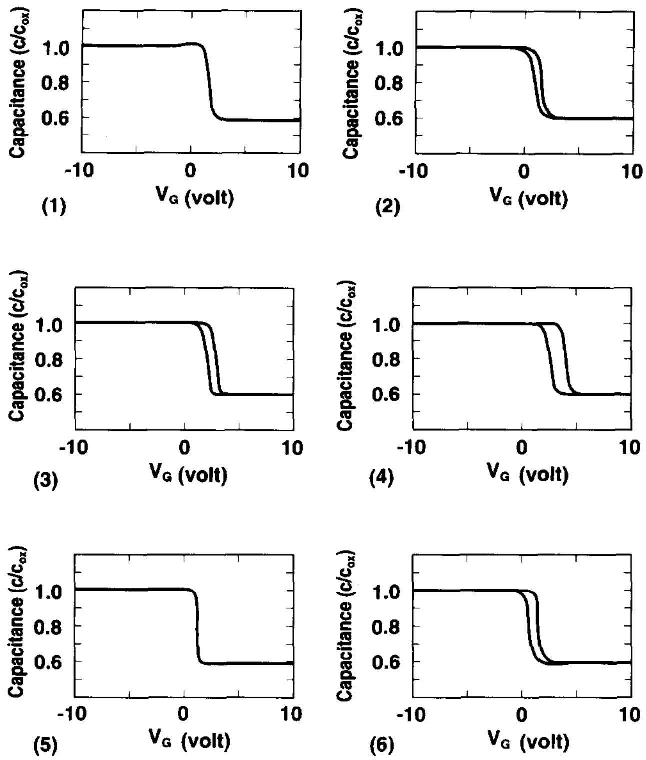

Fig. 2. C–V hysteresis curves of MOS capacitors passivated with PbO-based glasses: (1) passivated with glass no. (1); (2) passivated with glass no. (2); (3) passivated with glass no. (1) and exposed to water vapor at 80°C for 1 h; (4) passivated with glass no. (2) and exposed to water vapor at 80°C for 1 h; (5) passivated with glass no. (1), exposed to water vapor at 80°C for 1 h and heated at 400°C for 1 h; (6) passivated with glass no. (2), exposed to water vapor at 80°C for 1 h and heated at 400°C for 1 h.

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

The MOS capacitors passivated with PbO-based glasses containing low concentrations of water exhibited the best C–V characteristics. With increasing OH absorption coefficient, an adverse effect was seen on the recovery of hysteresis C–V curve shifts. Water vapor exercised much adverse influence on the C–V curves of MOS capacitors, but some improvement of the hysteresis loops and ΔV_G shifts was observed, following the heating of MOS capacitors. After the heating, the recovery of hysteresis and ΔV_G shifts for these MOS capacitors showed good reproducible capability as required for the MOS device passivations. The relationship between the recovery from peculiar hysteresis C–V curve shifts and OH absorption coefficient was briefly discussed.

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.*, **135** (1990) 3973.
5. Kobayashi, K., *J. Non-cryst. Solids*, **88** (1986) 229.
6. Kobayashi, K., *J. Non-cryst. Solids*, **109** (1989) 277.
7. Kobayashi, K., *J. Electrochem. Soc.*, **131** (1984) 2190.
8. Rojas, S., Gomarasca, R., Zanotti, L., Borghesi, A., 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. & Lanford W. A., *J. Appl. Phys.*, **72** (1992) 2947.
10. Kobayashi, K., *J. Non-cryst. Solids*, **124** (1990) 229.
11. Shaw, C. M. & Shelby, J. E., *Phys. Chem. Glasses*, **34** (1993).
12. Kobayashi, K., *Glass Technol.*, **34** (1993) 120.
13. Ruller, J. A. & Shelby J. E., *Phys. Chem. Glasses*, **33** (1992) 177.
14. Naruse, A., *Garasukogaku*, Kyoritsu Shuppan, Tokyo, 1959, p. 304.
15. Zhenhua, L. & Frischat, G. H., *J. Non-cryst. Solids*, **163** (1993) 169.