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SHORT COMMUNICATION

Viscous flow and MOS properties of MgF_2–B_2O_3–GeO_2–SiO_2 glasses with ionic bonds

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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 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 ultrahigh-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 ultrahigh-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 this 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 radicals 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 noncrystallizable MgF_2–B_2O_3–GeO_2–SiO_2 glasses with ionic bonds, and investigate the application of these glasses to MOS capacitors.

2. Experimental details

MgF_2–B_2O_3–GeO_2–SiO_2 glasses were prepared for use in the experiments. Batches comprising 1 kg of reagent-grade chemicals were melted at 1300 °C for five hours in an ultrahigh-purity platinum crucible using 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 mm × 20 mm × 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 (1 0 0) 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 sodium 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 multilevel interconnections [5, 6]. It is thought that glass reflow is caused by viscosity, which is responsible for composition, chemical bond [12] and structure [13, 14]. Namely, glass with 'low connectivity [12]' and 'a released structure [13]' 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. It is 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 is a useful way of estimating the bonding states of glass molecules. Hannay and Smyth [15] proposed an experimental equation for ionic bonding in which the degree of ionic character, I_i (%), is given by

$$\begin{aligned} I_i &= 16(x_A - x_B) + 3.5(x_A - x_B)^2 \\ &= (x_A - x_B)[16 + 3.5(x_A - x_B)] \qquad (1) \end{aligned}$$

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:

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

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 ionic character of glasses have been estimated using Equations 1 and 2.

The chemical composition (mol %) of various glasses, their OH absorption coefficients, ionic character, flow points and V_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 absorption [16, 17].

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

Glass	MgF_2/mol %	B_2O_3	GeO_2	SiO_2	T_{OH}/%	R_{OH}	β_{OH}/cm^{-1}	I/%	T_f/°C	ΔV_G/V
1	30	35	20	15	32	0.43	1.51	45.89	786	0.1
2	25	35	20	20	27	0.48	1.76	44.24	790	0.5
3	20	35	20	25	24	0.51	1.89	42.40	793	0.7
4	15	35	20	30	21	0.54	2.10	40.66	800	1.0
5	10	35	20	35	20	0.55	2.20	38.90	805	1.2

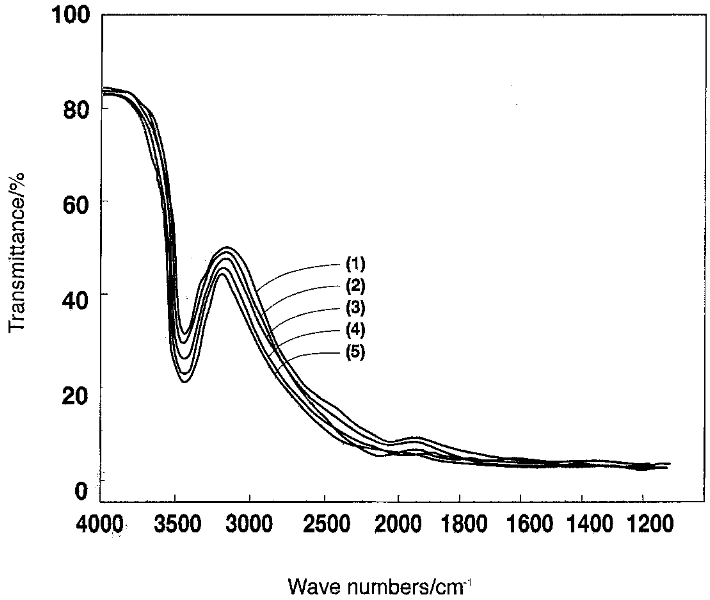

Fig. 1. Infrared absorption spectra for MgF_2–B_2O_3–GeO_2–SiO_2 glasses. Curve labels refer to glass number.

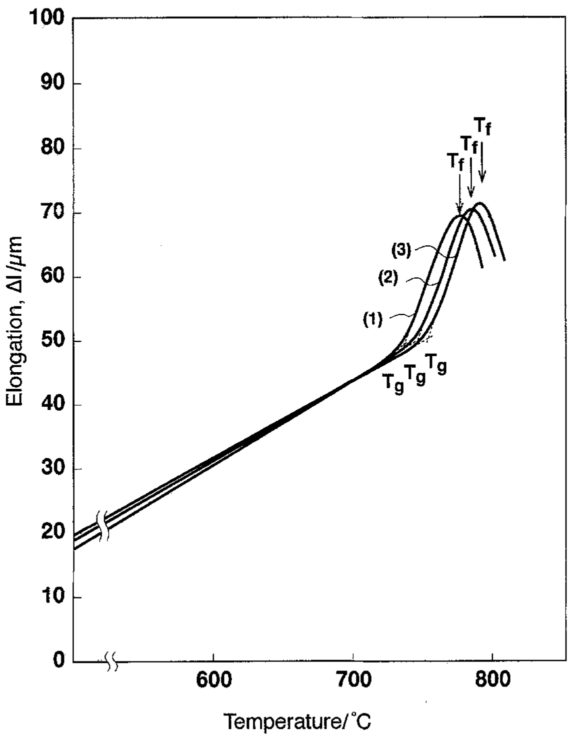

Fig. 2. Thermal expansion curves for MgF_2–B_2O_3–GeO_2–SiO_2 glasses. Curve labels refer to glass number.

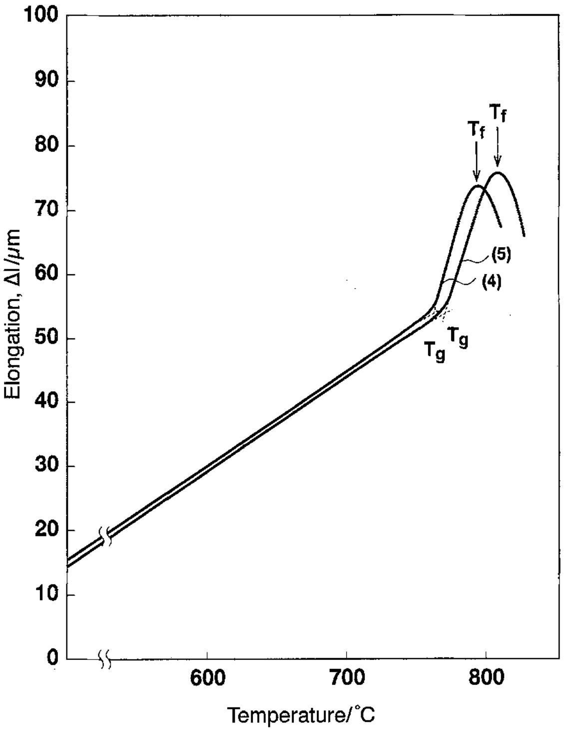

Fig. 3. Thermal expansion curves for MgF_2–B_2O_3–GeO_2–SiO_2 glasses. Curve labels refer to glass number.

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

$$T_{OH} = 1 - [R_{OH}(1 - R_{OH}) + R_{OH}] = (1 - R_{OH})^2 \tag{3}$$

The absorption coefficient β_{OH} [19] resulting from the fundamental vibration due to OH at around 3 500 cm^{-1} is calculated from Equation 4:

$$T_{OH} = [(1 - R_{OH})^2 \, e^{-\beta_{OH} t}]/[1 - R_{OH}^2 e^{-2\beta_{OH} t}] \tag{4}$$

where t is the glass thickness.

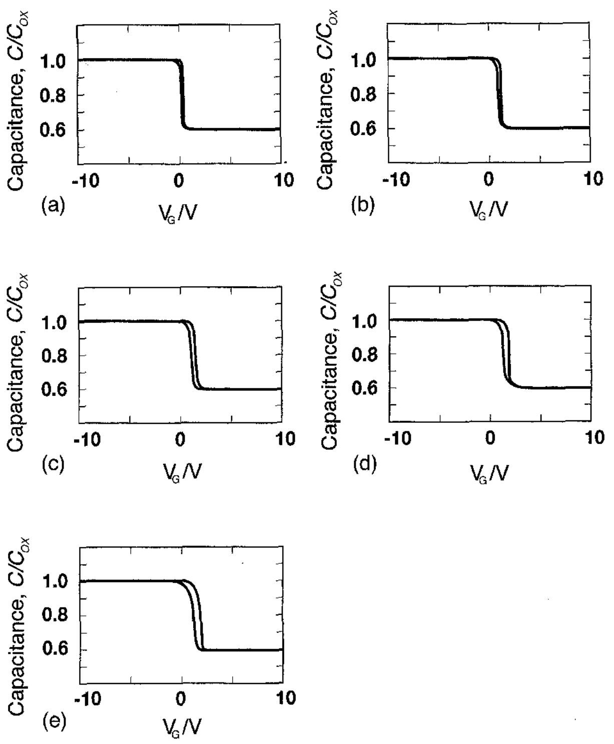

Fig. 4. $C-V$ characteristics of rapid thermally annealed MOS capacitors passivated with various MgF_2–B_2O_3–GeO_2–SiO_2 glasses. Characteristics (a)–(e) refer to glasses 1–5, respectively.

By substituting Equation 3, Equation 4 can be simplified as follows:

$$1 = e^{-\beta_{OH}t} + R_{OH}^2 e^{-2\beta_{OH}t} \qquad (5)$$

Water absorption coefficients β_{OH} are computed from Equation 5. Values of T_{OH}, R_{OH}, and β_{OH} calculated from the infrared absorption spectra in Fig. 1 are also listed in Table 1. Thermal expansion curves of MgF_2–B_2O_3–GeO_2–SiO_2 glasses are given in Fig. 2 and Fig. 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, V_G shifts also increased.

The $C-V$ characteristics of MOS capacitors passivated with these glasses are shown in Fig. 4. Figure 4 shows the $C-V$ characteristics of MOS capacitors. All the $C-V$ curves for capacitors passivated by these glasses were shifted to 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 to the right. The mean $C-V$ curve shifts, ΔV_G, are summarized in Table 1.

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].

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