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LETTER TO THE EDITOR

OH-Related Capacitance–Voltage Recovery Effect in MOS Capacitors Passivated by Fluoride-Containing $ZnO–B_2O_3–SiO_2–P_2O_5$ Glasses

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The purpose of this work is to clarify the relationship between some of the properties of MOS capacitors passivated by fluoride-containing zinc borosilicate glasses and the hydroxyl content of the glasses. Substitution of ZnF_2 for ZnO progressively decreases the OH^- absorption coefficient and the $C–V$ curve shift, $\overline{\Delta V_G}$, in the MOS capacitors decreased. A good recovery without hysteresis was observed in the MOS capacitors passivated by glasses with a small concentration of OH^- ions. © 1995 Academic Press, Inc.

Borophosphosilicate glass films formed from inorganic gas sources have been used in high-density integrated circuits as dielectric insulators (1–3). Their advantageous properties are conformal step coverage, effective protection against alkali ions, and a fairly low reflow temperature. Highly doped borophosphosilicate glasses reflow at low temperatures to give step coverage of ultra-high-density integrated circuits, but they have 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 glasses exhibit lower flow temperatures than borophosphosilicate glasses, and they do not suffer from crystallization during the reflow process (5, 6). However, both borophosphosilicate and zinc borosilicate glasses contain a small amount of water (7, 8), and this adversely affects the $C–V$ characteristics of glass-passivated MOS capacitors that are rapidly heated. It has been clarified in past studies that the abnormal $C–V$ curves for these MOS capacitors are a result of highly polarizable ions and OH^- ions in the glass (8, 9).

In this paper, we discuss the relationship between OH^- ion absorption and shifts in the $C–V$ curve for MOS capacitors passivated with zinc borosilicate glasses with various concentrations of ZnF_2.

Zinc borosilicate glasses with various Al_2O_3, and P_2O_5, and ZnF_2 contents were prepared for the experiments. Batches comprising 1 kg of reagent-grade chemicals were melted at 1300°C for 5 hr in an ultra-high-purity platinum crucible with an electric furnace under an oxidizing atmosphere. After homogeneous melting, the glass was poured onto a stainless steel plate and annealed. Infrared transmission spectra were measured with 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 in thickness. Glass films 2000 Å thick were deposited on a SiO_2 layer (500 Å) formed on Si (100) wafers under 1-kW power and 30-mTorr vacuum sputtering conditions in a Perkin–Elmer vacuum system. The glass thickness was measured by the use of a nanometrics SD9-2000T thickness-meter and the Na–D line refractive index (N_D-1.56). Aluminum electrodes were deposited on the glass films. $C–V$ curves for the MOS capacitors were observed at 1 GHz at room temperature, as described previously (10). MOS capacitors passivated by these glasses were annealed at 150°C for 30 min under an oxidizing atmosphere.

The chemical compositions (mole %) prepared for this experiment are listed in Table 1. Infrared absorption spectra for the glasses are given in Fig. 1. The absorption bands around 3500 cm^{-1} are due to fundamental vibrations arising from OH absorption (10–12). The relationship between transmittance T_{OH} and reflectivity R_{OH} can be represented as (13).

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

The absorption coefficient β_{OH} resulting from the fundamental vibration due to OH at around 3500 cm^{-1} is calculated (14, 15) 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.

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TABLE 1
Glass Compositions, T_{OH} R_{OH}, β_{OH}, and $\overline{\Delta V_G}$

Glass No.	ZnO (mole %)	ZnF_2	B_2O_3	SiO_2	Al_2O_3	P_2O_5	T_{OH} (%)	R_{OH}	β_{OH} (cm^{-1})	$\overline{\Delta V_G}$ (V)
(1)	50	0	40	3	2	5	50	0.29	0.77	0.3
(2)	47	3	40	3	2	5	56	0.25	0.58	0.2
(3)	45	5	40	3	2	5	59	0.23	0.50	0.1
(4)	43	7	40	3	2	5	62	0.21	0.42	0
(5)	41	9	40	3	2	5	66	0.18	0.34	0

By substituting Eq. (1), Eq. (2) can be simplified to

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

Water absorption coefficients β_{OH} are computed from Eq. (3). Values of T_{OH}, R_{OH}, and β_{OH} calculated from the infrared absorption spectra in Fig. 1 are listed in Table 1. These experimental data show that the step in the mean C–V curve (see Fig. 2) was shifted $\overline{\Delta V_G}$ toward the right with increasing β_{OH}. As the ZnO content decreased and the ZnF_2 content increased, $\overline{\Delta V_G}$ shifts decreased.

The C–V characteristics of MOS capacitors passivated with these glasses are shown in Fig. 2. Figure 2, parts (1)–(5), shows the C–V characteristics of rapidly thermally annealed MOS capacitors. The C–V curves for MOS capacitors passivated by glasses with greater OH^- content were shifted toward the right and showed hysteresis loops. Thus, these peculiar C–V characteristics result from the OH^- content in the glasses (9). The mean C–V curve shifts $\overline{\Delta V_G}$ listed in Table 1, are the mean values at the midpoints of forward and backward hysteresis C–V curves.

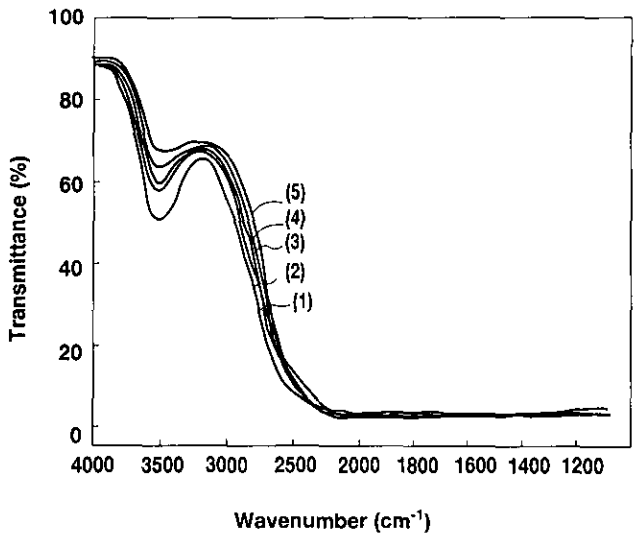

FIG. 1. Infrared absorption spectra for zinc borosilicate glasses with a varied content of ZnF_2 for glass Nos. (1), (2), (3), (4), and (5).

It is presumed that protons and OH^- ions react with fluorine ions in glasses as represented in

$$2H^+ + 2OH^- + 2F_2^- \rightarrow 4HF \uparrow + O_2 \uparrow. \quad (4)$$

Consequently, the reaction of protons and OH^- ions with fluoride groups in glasses would be advantageous as a means of improving their infrared absorption transmission in the region of the water peaks. The loss of hydrogenous and hydroxyl species is related to the disappearance of C–V hysteresis. The hydrogenous and

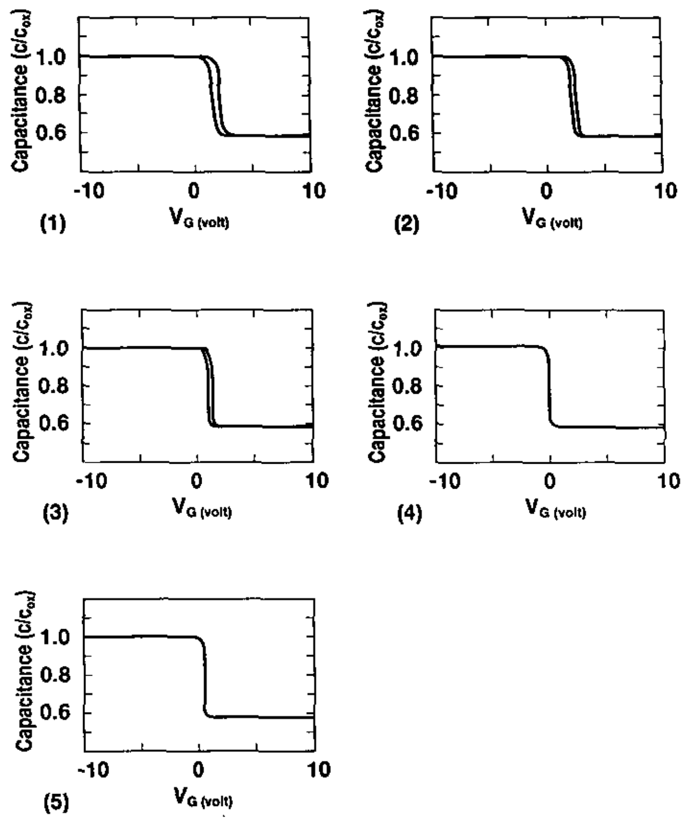

FIG. 2. C–V characteristics for rapidly thermally annealed MOS capacitors passivated by zinc borosilicate glasses (1), (2), (3), (4), and (5) with varying content of ZnF_2.

hydroxyl defects are responsible for the polarizing mechanism. This shift is related to hydrogen- and hydroxyl-related vacancies in water-containing glasses.

After the annealing was performed, the MOS capacitors passivated by zinc borosilicate glasses with low water content showed the recovery of C–V characteristics. When the OH^- absorption coefficient was increased, there was an adverse effect on the recovery of hysteresis C–V curve shifts. By the substitution of 9 mol% ZnF_2 for ZnO, it is possible to eliminate the undesired $\overline{\Delta V_G}$ shift and hysteresis in MOS capacitors passivated with zinc borosilicate glasses.

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