Hysteresis Curve Variations of MOS Capacitors Passivated by $Ba(PO_3)_2$-$Al(PO_3)_3$-B_2O_3 Glasses

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The purpose of this work is to clarify the relationship between some of the properties of MOS (metal, oxide, silicon) capacitors passivated by $Ba(PO_3)_2$-$Al(PO_3)_3$-B_2O_3 glasses and the hydroxyl contents of the glasses. When substitution of $Al(PO_3)_3$ for $Ba(PO_3)_2$ progressively decreased the OH^- absorption intensity, the C-V (capacitance-voltage) curve shift, ΔV_G in the MOS capacitors decreased.

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 temperature 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 the ultra-high-density integrated circuits.[4]

It has been found that zincborosilicate 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 zincborosilicate 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 shift and the hysteresis of C-V curves are a result of highly polarizable ions and OH^- ions in the glass.[8,9] They are detrimental to the application to MOS devices. In this paper, we discuss the relationship between OH^- ions absorption and shifts in the C-V curve for MOS capacitors passivated with non-crystallizable $Ba(PO_3)_2$-$Al(PO_3)_3$-B_2O_3 glasses with various concentrations of OH^- ions.

$Ba(PO_3)_2$-$Al(PO_3)_3$-B_2O_3 glasses were prepared for the experiments. Batches comprising 1 kg of reagent-grade chemicals were melted at 1200 °C for 5h 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 with a Digi-Labo spectrophotometer with 10 x 20 x 1 mm^3 plates.

Sputter targets were cut from these samples and ground to 75 mm in diameter and 10 mm thick. Glass films 2,000 Å thick were deposited on an SiO_2 layer (500 Å) formed on Si (100) wafers under 1 kW power and 4Pa 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 MHz at room temperature, as described previously.[10] MOS capacitors passivated by these glasses were annealed at 150 °C for 30 mins. in an oxidizing atmosphere.

The glass flow point, T_f was measured with the beam-bending method, as described previously.[10]

The chemical compositions (mol%) prepared for this

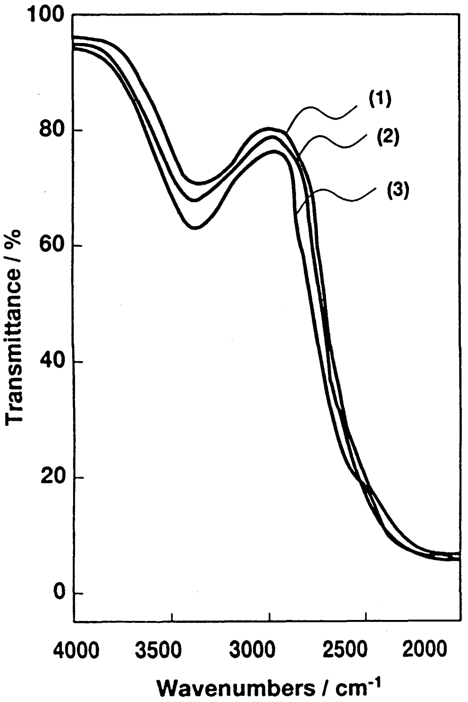


Figure 1.

Intrared transmission spectra for $Ba(PO_3)_2$ - $Al(PO_3)_3$ -B_2O_3 glasses.
(1) glass No. (1)
(2) glass No. (2)
(3) glass No. (3)

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

Glass No.	$Ba(PO_3)_2$ (mol %)	$Al(PO_3)_3$	B_2O_3	T_{OH} (%)	R_{OH}	β_{OH} (cm^{-1})	T_f (°C)	ΔV_G (volt)
(1)	0	50	50	70	0.16	0.26	690	1.0
(2)	15	35	50	68	0.18	0.30	670	2.0
(3)	30	20	50	65	0.19	0.36	660	2.7

experiment are listed in Table 1. Infrared absorption spectra for the glasses are given in Figure 1. The absorption bands around 3,400 cm^{-1} are due to fundamental vibrations arising from OH absorption.[10-12] The relationship between transmittance T_{OH} and reflectivity R_{OH} due to OH absorptions at 3400 cm^{-1} can be represented as follows.[13]

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

The absorption intensity β_{OH} resulting from the fundamental vibration due to OH at around 3,400 cm^{-1} is calculated[14,15] from Eq.(2)

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

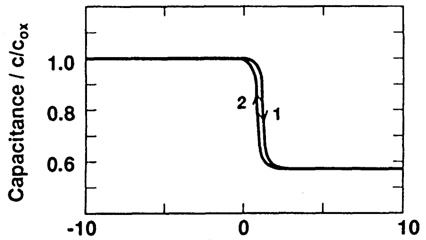
where t is the glass thickness.

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

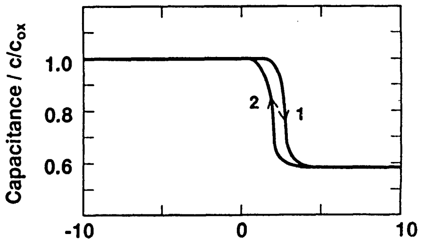
$$1 = e^{-\beta_{OH} t} + R_{OH}^2 \ e^{-2\beta_{OH} t} \qquad (3)$$

Water absorption intensities β_{OH} are calculated from Eq.(3). Values of T_{OH}, R_{OH}, and β_{OH} calculated from the infrared absorption spectra in Figure 1 are listed in Table 1.

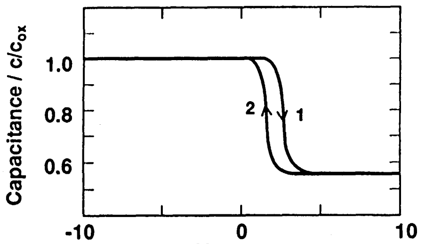
The C-V characteristics of MOS capacitors passivated with these glasses are shown in Figure 2, where C is the capacitance of glass and C_{OX} is the capacitance of SiO_2. Figure 2 (1)~(3), respectively, show the C-V characteristics of rapid thermally annealed MOS capacitors. The C-V curves for MOS capacitors passivated by these glasses with greater OH^- content were shifted towards the higher voltage 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, ΔV_G listed in Table 1 are the mean values at the mid points of forward and backward hysteresis C-V curves. As the $Ba(PO_3)_2$ content increased and the $Al(PO_3)_3$ content decreased, ΔV_G shifts increased.



(1) passivated by glass No. (1)



(2) passivated by glass No. (2)



(3) passivated by glass No. (3)

Figure 2.

C-V characteristics for rapid thermal annealed MOS capacitors passivated by Ba $(PO_3)_2$ - Al $(PO_3)_3$ -B_2O_3 glasses.
1 is a forward curve, 2 is a backward curve.

The increase of $Al(PO_3)_3$ content 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 hydrogeneous and hydroxyl defects are responsible for the polarizing mechanism. This shift is related to hydrogen and hydroxyl-related vacancies in water-containing glasses.

After annealing, the MOS capacitors passivated by these glasses with a low content of water showed the recovery of the shift of C-V curves. On increasing the OH^- absorption coefficient, there was an adverse effect on the recovery of hysteresis C-V curve shifts. Abe and coworkers observed protonic conduction in alkali earth metaphosphate glasses containing water.[6] They studied the mobility of protons increased with the increase of OH····O hydrogen bonding in these glasses. It was presumed that the hysteresis in the C-V curve was related to the mobility of protons. The hysteresis of C-V curve is unfavorable for the application of glass to MOS device, because it shows the undesirable I-V (current-voltage) curve of the device passivated by OH^- containing glass. By the substitution of $Ba(PO_3)_2$ for $Al(PO_3)_3$, the flow point, T_f was lowered.

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