

## Dry Oxidation Study on CVD-SiO<sub>2</sub>/Thermal-SiO<sub>2</sub>/Si Structure

Shigeki KURODA, Kenji NISHI, and Jun UEDA

Oki Electric Industry Co.,Ltd.

550-1 Higashiasakawa, Hachioji-shi, Tokyo 193, Japan

Silicon dioxide growth in dry oxygen has been investigated on CVD-SiO<sub>2</sub>/Thermal-SiO<sub>2</sub>/Si multilayer structure at 900°C and 1000°C. Borophosphosilicate glass (BPSG), phosphosilicate glass (PSG) and non-doped silica glass (NSG) have been used as the CVD-SiO<sub>2</sub> layers. A growth enhancement is found for thermal-SiO<sub>2</sub> under BPSG and PSG layer which results in thicker thermal-SiO<sub>2</sub> than thermal-SiO<sub>2</sub>/Si without CVD-layer. A new enhanced oxidation model, which takes into account the liquid-like nature of BPSG and PSG during oxidation, is proposed to explain the experimental results.

### 1. INTRODUCTION

Thermal oxidation of silicon is one of the key process in VLSI fabrication technology, and the growth kinetics has long been studied by many authors<sup>1-5)</sup>, under various conditions. In these studies, thermal-SiO<sub>2</sub>(T-SiO<sub>2</sub>) is directly exposed to ambients.

With shrinking device size, recent fabrication process becomes more complex and sometimes needs thermal processing in oxidizing ambients on multilayer structures in which silicon or T-SiO<sub>2</sub>/Si is capped by a material which allows diffusion or penetration of oxidizing species. In this case, the conventional oxidation model cannot be directly applied to the growth of SiO<sub>2</sub>.

In this study, investigation has been focused on the thermal growth of SiO<sub>2</sub> in dry oxygen where T-SiO<sub>2</sub> is capped by CVD-SiO<sub>2</sub>. The structure appears in MOSFET with a spacer for LDD (lightly doped drain) structure. Borophosphosilicate glass (BPSG), phosphosilicate glass(PSG), and non-doped

silica glass(NSG) were used for CVD-SiO<sub>2</sub>. The abnormal oxidation rate enhancement has been observed in case of BPSG and PSG. A new model is proposed to explain the experimental results.

### 2. EXPERIMENTAL

All substrates were (100)-oriented 3.26-4.24 ohm-cm p-type silicon wafers. Figure 1 illustrates three sample groups prepared in this study. The group (A) forms the main structure to be examined. The group (B) was prepared to correct the densification effects on the thickness measurements of the group (A). The group (C) was also prepared for comparison with the group (A). The group (A) and (C) wafers were first oxidized in dry O<sub>2</sub> at 950°C to grow approximately 10nm of T-SiO<sub>2</sub>. Three types of 100nm films, namely BPSG containing 3.5 wt% boron and 7.0 wt% phosphorus, PSG containing 7.0 wt% phosphorus, or NSG, were deposited on the top of T-SiO<sub>2</sub> of the group (A) wafers by atmospheric pressure CVD. For the group (B), the same type of CVD films as those of

group (A) were deposited over the low pressure CVD  $\text{Si}_3\text{N}_4$  layer of about 150nm. The dry oxidation was carried out at  $900^\circ\text{C}$  and  $1000^\circ\text{C}$  for all samples. The film thickness  $X_a$ ,  $X_b$  and  $X_c$  shown in Fig.1, were measured by an interference technique and a mechanical stylus technique. The increase ( $\Delta X$ ) in the  $\text{T-SiO}_2$  thickness for corresponding oxidation time and temperature is determined by the following relationship;  $\Delta X = (X_a - X_b) - X_i$ , where  $(X_a - X_b)$  represents the total thickness of  $\text{T-SiO}_2$  after oxidation and  $X_i$  is the initial  $\text{T-SiO}_2$  thickness (10nm before oxidation). The chemical impurity concentration in the silicon substrate was measured by SIMS. The sheet resistance was measured by the four-point probe method.

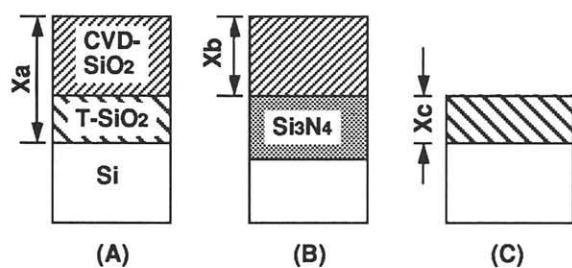


Fig.1 Schematic cross-section views of the three different groups of samples used in this work.

### 3. RESULTS AND DISCUSSION

Figure 2 shows the  $\text{T-SiO}_2$  growth characteristics of group (A) at  $900^\circ\text{C}$  and  $1000^\circ\text{C}$ . The vertical axis represents the increase in the oxide thickness from its initial thickness (10nm). The results of the group (C) with no CVD-layer are also shown as a dashed line for comparison. At  $900^\circ\text{C}$  and  $1000^\circ\text{C}$ , the thermal oxide growth rate increases with NSG, PSG and BPSG as the CVD- $\text{SiO}_2$ . Moreover, although group (A) wafers formed thicker oxide layers when CVD-layers are regarded as oxide, the oxide growth with BPSG is more enhanced than group (C) with no CVD-layer. The oxide growth with PSG is almost the same as that without a cap. Generally, the greater the initial oxide

thickness is, the smaller the oxidation rate becomes. Therefore, these results demonstrate that with BPSG and PSG layers, the oxidation of silicon substrate is rather enhanced.

Doping of impurities, especially n-type dopants, into the silicon substrate, is known to enhance the oxide growth<sup>2-5</sup>. In order to investigate this possibility, impurity concentration and the type of conductivity at the surface were measured. Phosphorus with the concentration of about  $1 \times 10^{19} \text{ cm}^{-3}$  was found at the silicon surface for the BPSG-capped samples oxidized at  $1000^\circ\text{C}$ . This concentration is not high enough to explain the large oxidation enhancement. Moreover, no phosphorus or boron was detected and also the type of conductivity show p-type for other samples. Considering that oxidation enhancement is observed also at  $900^\circ\text{C}$ , doping of impurities cannot be the main cause for the oxidation enhancement.

Irene and Dong<sup>5</sup> pointed out that incorporation of phosphorus into  $\text{SiO}_2$  causes a loosening of  $\text{SiO}_2$  network and enhances oxygen diffusion. Gualandris et al.<sup>6</sup>

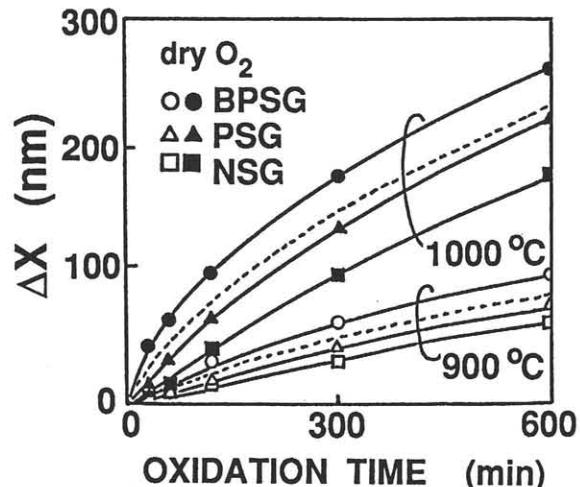


Fig.2 Increase in oxide thickness ( $\Delta X$ ) from its initial thickness (10nm) vs. oxidation time. BPSG, PSG and NSG are the caps on thermal  $\text{SiO}_2$ . The dashed lines represent the results for no CVD- $\text{SiO}_2$  as a cap.

ascribed the increase in apparent thickness of PSG (about 1000 nm) on silicon densified in steam atmosphere to the growth of a thin thermal  $\text{SiO}_2$  layer between PSG and silicon substrate. They pointed out that the diffusion coefficient of oxidant species in CVD oxide can be very high, which reflects the porous nature of the PSG film.

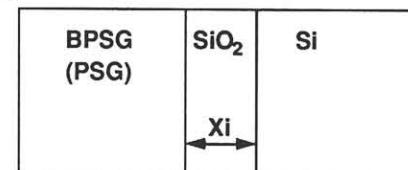
The porous nature or the loosening of  $\text{SiO}_2$  network is also expected for BPSG and PSG in this work. Therefore, it is possible that the high oxygen diffusivity in BPSG and PSG causes the oxide growth enhancement. However, even if the oxygen diffusion in CVD- $\text{SiO}_2$  is infinitely high, it is not still enough to explain that the oxide growth with thick BPSG is more enhanced than that with no CVD- $\text{SiO}_2$ .

Yamaji et al.<sup>7)</sup> showed that the liquid phase exists in heavily phosphorus doped  $\text{SiO}_2$  at diffusion temperatures, and results in the phosphorus diffusivity increase. Ghoshtagore<sup>8)</sup> introduced the three-zone multiphase model of PSG on T- $\text{SiO}_2$  from their radiotracer experiment. According to his model, PSG in which the  $\text{P}_2\text{O}_5$  concentration is above its solid solubility, forms the layer that is composed of solid  $\text{SiO}_2$  and a fixed composition PSG liquid. In our experiment, PSG also forms the liquid-like layer because the  $\text{P}_2\text{O}_5$  concentration is above its solubility at the oxidation temperature. Therefore, an interface between the liquid-like PSG and the solid-like T- $\text{SiO}_2$  can be defined where the  $\text{P}_2\text{O}_5$  concentration crosses the solid solubility. Similarly, this Liquid-like/Solid-like (L/S) interface can be defined for BPSG samples. Assuming that the L/S interface moves toward the Si surface due to the diffusion of phosphorus and boron which results in the "melting" of the upper part of thermal  $\text{SiO}_2$  under BPSG or PSG, the solid-like T- $\text{SiO}_2$  decrease during oxidation. As boron in BPSG

lower the viscosity<sup>9)</sup>, the diffusion of phosphorus and boron in BPSG is more enhanced than in PSG. Thus, the moving rate of the L/S interface is higher for BPSG than for PSG, corresponding to the tendency of enhanced oxide growth shown in Fig.2.

Figure 3 shows a model which explains the observed enhanced oxide growth on CVD- $\text{SiO}_2$ /T- $\text{SiO}_2$ /Si structure. Fig.3, (a) and (b) represents the schematic sample structure before and during oxidation, respectively. In this model, the BPSG or PSG layer forms the liquid-like layer with thickness of  $X_L$  during oxidation. The second layer is the solid-like thermal  $\text{SiO}_2$  with thickness of  $(X_S - L)$  grown by silicon oxidation at the  $\text{SiO}_2$ /Si interface, where  $L$  is a characteristic length which describes the movement of L/S interface. In the liquid-like layer, the oxidant diffusivity,  $D_L$ , is much faster than oxidant diffusivity,  $D_S$ , in the solid-like layer. In this case, the solid-like layer growth mainly controls the oxidation of whole system.

(a) as-depo



(b) dry  $\text{O}_2$

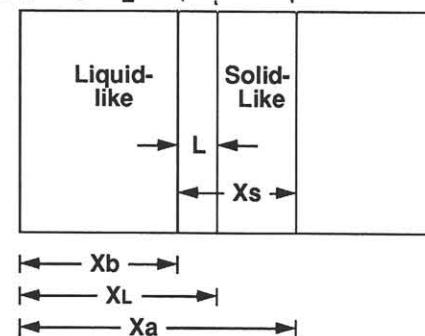


Fig.3 Oxidation model for CVD- $\text{SiO}_2$ /T- $\text{SiO}_2$ /Si structure.  $X_a$  and  $X_b$  represent the thickness shown in Fig.1.

The oxidation rate, therefore, can be expressed as follows:

$$\frac{dX_S}{dt} = B/(2(X_S - L) + A + 2X_L D_S / D_L), \quad (1)$$

where  $B$  and  $B/A$  are parabolic and linear rate constants, respectively. The characteristic length  $L$  is related to the impurity diffusion from CVD- $\text{SiO}_2$  to T- $\text{SiO}_2$  as  $L = p(Dt)^{1/2}$ , where  $p$  is the proportional constant and  $D$  is the diffusion coefficient of impurity in  $\text{SiO}_2$ . Equation (1) shows that if  $L$  and  $D_L$  increase, the oxide growth rate increase. In other words, the effective thickness of T- $\text{SiO}_2$  decreases during oxidation. When  $L=0$  and  $X_L=0$ , that is, no liquid-like layer is formed, equation (1) reduces to linear parabolic law<sup>1)</sup>.

Figure 4 shows the experimental and calculated values of the increase in the oxide thickness vs. oxidation time same as Fig.2. The value from reference 7) is used as the phosphorus diffusivity which depends on the phosphorus concentration in  $\text{SiO}_2$ .

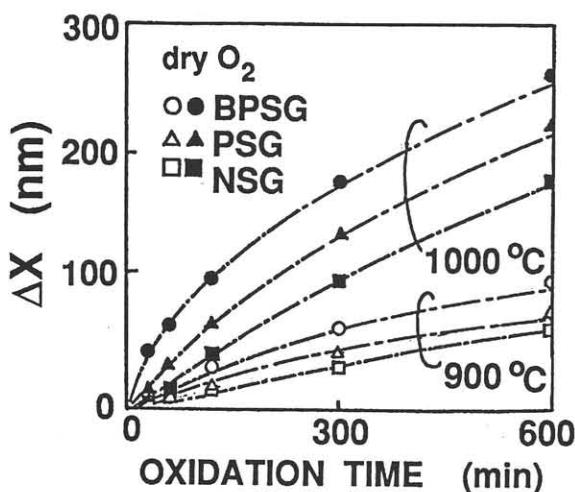


Fig.4 Comparison of the calculated increase in oxide thickness ( $\Delta X$ ) with the experimental results. Broken lines represent the calculated results.

Values for  $B$ ,  $A$ , and  $D_S$  were taken from the literatures<sup>2,3)</sup>. NSG has been treated as the solid-like layer or T- $\text{SiO}_2$ . The value of  $p$  for BPSG and PSG has been varied over the range of 0.1-10 depending on oxidation conditions. The calculated results show a good agreement to the experimental results.

#### 4. CONCLUSION

Thermal oxide growth on CVD- $\text{SiO}_2$ /T- $\text{SiO}_2$ /Si multilayer structure in dry oxygen has been investigated. The abnormal oxidation enhancement has been observed for the samples with BPSG or PSG. This enhancement has the order BPSG > PSG, and results in thicker oxide with CVD layer than with no CVD layer. An oxidation model for the multilayer structure has been proposed. The model, which incorporates the movement of interface between liquid-like layer and solid-like layer in  $\text{SiO}_2$ , shows good agreement with the experimental results.

#### REFERENCES

- 1) B.E.Deal and A.S.Grove; *J.Appl.Phys.* 36, (1965) 3770.
- 2) C.P.Ho and J.D.Plummer; *J.Electrochem.Soc.* 126, (1979) 1516.
- 3) C.P.Ho and J.D.Plummer; *J.Electrochem.Soc.* 126, (1979) 1523.
- 4) H.Z.Massoud; *Appl.Phys.Lett.* 53, (1988) 497.
- 5) E.A.Irene and D.W.Dong; *J.Electrochem.Soc.* 125, (1978) 1146.
- 6) F.Gualandris, G.U.Pignatello and S.Rojas; *J.Vac.Sci.Technol.B3*(1985) 1604.
- 7) T.Yamaji and F.Ichikawa; *J.Appl.Phys.* 59, (1986) 1981.
- 8) R.N.Ghoshtagore; *Thin Solid Films* 25, (1975) 501
- 9) W.Kern and G.L.Schnable; *RCA Review* 43, (1982) 323.