Two Dimensional Effect on Suppression of Thermal Oxidation Rate

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An oxidation model for silicon with geometrical nonplanarity is proposed considering the stress induced oxidation rate reduction effect. This effect dominates as the curvature radius at the edge of step decreases down to 500A. Observed retardation of thermal oxidation rate at the step edge is unifiedly explained for both convex and concave geometries. Morphology of oxidized step-shaped Si is experimentally investigated as a function of phosphorus concentration in Si. Appropriate phosphorus doping prevents the generation of " horn " at convex corner. Electrical properties of trench capacitors are studied. The break-down field strength of trench capacitors being determined by the oxide thinning at concave corner at trench bottom is suggested.

§1. INTRODUCTION

High density submicron VLSIs will be realized by introducing new device structures such as trench capacitor, BOX isolation, moat type isolation etc. as well as scaling down device dimensions. Therefore, accurate understanding and modeling of thermal oxidation for geometrical nonplanarity (e.g. curved Si surface and polysilicon gate edge) should be important as a basic knowledge for developement of these new structure devices. There are typically three examples of 2-D oxidation, which are (i) LOCOS (ii) gate oxide thinning at the isolation oxide wall¹⁾(iii) " horn " and " oxide thinning " of oxidized step-shaped Si²) and polysilicon³). For the LOCOS structures , a model including viscous flow of SiO_2 has been recently studied⁴⁾⁵⁾, but simulated shape slightly differs from experiment especially near the " bird's front neck ". For the latter two, the amount of oxide thinning and horn shape could not yet be well simulated $^{6)7)}$.

This paper describes a model including the oxidation rate reduction caused by the stress at the curved Si/SiO_2 interface and semiquantitative discussion. As for the device application, electrical properties of trench capacitors are examined in terms of our model.

§2. EXPERIMENTAL

Oxidation of shaped Si was examined as a function of phosphorus concentration in Si. P type

(100) wafers were doped with $POCl_3$ and annealed in N_2 ambient, followed by patterning and reactive ion etching to produce lum deep trench. The wafers were then oxidized in dry O_2 at 900°C or 1000°C. After depositing protective polysilicon, resulting morphology was investigated by SEM. Phosphorus concentration in Si controlled by changing N_2 annealing time was measured by Auger electron spectroscopy.

For trench capacitors, phosphorus was doped after trench formation and thin oxide was grown at 900° C in dry O₂.

§3. EXPERIMENTAL RESULTS

Figure 1 shows the observed " horn " structures after 900°C oxidation and their dependence on phosphorus concentration in Si. Ratio of oxide thickness at the corner with respect to the one on the flat surface is plotted in Fig.2 for two different oxidation temperatures, which clearly shows the existence of the critical phosphorus concentration . From these data, it can be derived that : (a) the oxidized Si shape and the oxide thickness at the convex corner depend on phosphorus concentration and oxidation temperature; (b) an appropriate phosphorus doping prevents the appearance of " horn ", but this doping level increases as the oxidation temperature decreases; (c) the retardation of oxidation at the convex corner occurs in a reaction controlled region in SiO_2 formation reaction.

Oxidized concave corners at the trench bottom are shown in Fig.3 with two different oxide thicknesses. Oxide thinning is clearly shown and this phenomenon occurs from very initial stage of oxidation(-100A) and becomes remarkable as the oxidation proceeds. In contrast to the oxidation of convex Si surface, oxide thinning can not be prevented by phosphorus doping. This will be related to the fact that $1150^{\circ}C$ oxidation is less effective to eliminate the generation of oxide thinning⁶.

§4. MODEL AND DISCUSSION

 ${\rm SiO}_2$ formation reaction is given by $^{8)}$

 $\mathbf{v}_{\mathrm{f}} + \mathrm{Si} + \mathbf{0}_2 \ddagger \mathrm{SiO}_2 \tag{1}$

where v_f is the free volume to grow SiO₂. The v_f depends on viscous flow of oxide, vacancies and interstitials in Si. Therefore, the retardation of oxidation occurs when substantial free volume is not supplied (e.g.there exists compressive stress at the Si/SiO₂ interface), because volume expansion of 125% is accompanied by this reaction. Figure 4 shows a stress relaxation time τ and grown strained oxide thickness in τ as a function of oxidation temperature, when spring and dashpot model is used for SiO₂. Obviously, it shows strained oxide of more than 200A thick is formed below 1050°C in dry O₂, and below 930°C in wet O₂ oxidation. During oxidation, stress will concentrate seriously with increasing oxide thickness.

MODEL

Our assumptions are as follows: (i) SiO_2 formation reaction follows the Arrhenius type equation;(ii) strain energy is included in free energy term when there exists stress and strain at the Si/SiO₂ interface,hence,activation energy is modified. Therefore, reduced reaction rate K_s is given by

$$K_{s} = K_{o} exp(-w/kT)$$
(2)

where k is Boltzmann's constant and w is the strain energy/atom and $K_{\rm o}$ is the intrinsic reaction rate.

When curved Si(radius r_o) with conformal oxide (oxides surface radius R) as shown in Fig.5 are oxidized to grow new oxide (thickness t_{ox}) in the absence of any stress relief mechanism,the strain energy (W) and stress (σ_{rr}) are given by

$$W \propto (t_{ox}/r_o)^2 [(r_o/R)^{en} - 1]^2 \sigma_{rr} \propto (t_{ox}/r_o) [(r_o/R)^{en} - 1]$$
(3)

where n = 2,3 for the cylindrical and the spherical geometry respectively; e = 1,-1 for the convex and

the concave surfaces respectively. Eqs.(3) are given by solving equilibrium eq. $\partial \sigma_{km} / \partial x_m = 0$, with dynamical boundary conditions (i.e. $\sigma_{rr} = 0$ at the oxide surface and σ_{rr} is continuous at r_{o}) and geometrical condition related to volume expansion; isotropic body is also assumed. It is clearly shown that the strain energy and the stress concentrate seriously as the radius ro decreases. Figure 6 shows the normalized reaction rate and the stress as a function of the curvature radius of convex Si, where eq.(2) and w = W/N (N is the number of Si in a unit volume) are used for calculation. It shows the retardation of oxidation rate are remarkable as the radius decreases down to 500A. Using eqs.(2) and (3), the shape of oxidized curved Si at 900°C oxidation are calculated as a function of the oxide thickness on the plane surface in Fig.7. These results well explain the experimental features of " horn " and " oxide thinning " formation. This model contains no arbitrary parameters, therefore it can provide a strong tool for prediction of oxidized structure for future devices.

PHOSPHORUS DOPING EFFECT

There are three different contributions by phosphorus doping which explains our experiment: (i) Characteristic oxidation time separating the reaction and the diffusion controlled region decreases as phosphorus concentration increases⁹. Thus, the stress does not concentrate and the horn is not generated owing to shorter period for reaction controlled region, which is similar to that of high temperature oxidation.

(ii) Introduced vacancies relax the stress at the SiO_2/Si interface. Therefore, the reduction factor is smaller than in eq.(2), and the retardation is not so enhanced.

(iii) Viscosity of SiO₂ is reduced by phosphorus doping. This will contribute to free volume supply. <u>DIFFUSION LIMITED REGION</u>

As oxidation proceeds, SiO_2 formation reaction is limited by O_2 diffusion. Therefore, for convex Si, diffusion window becomes wider and horn formation will not be enhanced. On the other hand, for concave Si, diffusion window becomes narrower and oxide thinning will be enhanced. This explains the observed data²⁾⁷⁾.

§5. ELECTRICAL PROPERTIES OF TRENCH CAPACITORS

Trench capacitors with rounded convex top edge by phosphorus doping were fabricated and their break-down voltage was measured as shown in Fig.8. The break-down voltage of trench capacitor is still lower than that of plane capacitors, however, both break-down voltage would become equal when the oxide thickness was less than 100A . This indicates that the break-down voltage is determined by the thinned oxide at the concave corner of trench bottom for our trench capacitors. Simple calculation of field strength also supports the experimental data. Moreover, the difference of slopes indicates the difference of oxidation rate. Oxide thinning at the trench bottom can only be prevented by decreasing oxide thickness and/or depositing thin CVD film. Oxide/nitride/oxide structures give high break-down voltage comparable to plane capacitors as shown in Fig.8.

§6. CONCLUSION

The oxidation model which can describe the nonplanar Si oxidation including stress and strain concentration effect is proposed. The model can well explain the observed phenomena. It is shown that appropriate phosphorus doping in Si can prevent the generation of " horn " at the convex Si corner. The concave Si corner at the trench bottom determines the electric break down field strength of trench capacitors. Limitation of using thin



PHOS. CONC. 2.7x10²⁰cm⁻³



PHOS. CONC. 6.7x10²⁰cm⁻³



0.5µm PHOS. CONC 3.9x10²⁰cm⁻³

Fig.1

SEM cross sections of thermally oxidized shaped Si prediffused with phosphorus at different concentrations

OXIDATION 900°C DRY 02 5hr. thermal oxide should become significant in the future submicron device era, which may reveal the importance of thin CVD film for future device fabrications.

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Fig.2 Oxide thickness ratio as a function of surface concentration of phosphorus





PHOS.CONC. 6.5 x $10^{20}/\text{cm}^3$ OXIDATION 900°C DRY 0₂ 3min.

OXIDATION 1000°C DRY 02 3hr.

Fig.3 SEM cross sections of thermally oxidized concave Si surface at trench bottom



1000Å

Fig.5 Geometrical configuration of the model for oxidation of Si with nonplanar surface. The solid line at r_o is the original interface and the dashed lines represent the boundaries of the newly produced oxide



Fig.4 Stress relaxation time and strained oxide thickness as a function of oxidation temperature



Fig.6 Normalized reaction rate and magnitude of stress as a function of curvature radius of convex Si



Fig.7 Calculated geometry of 2 - D oxidation of curved Si surface



Break-down voltage of trench and plane capacitors vs. oxide thickness on plane Si