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In this talk we report on the kinetics of thermal oxidation of silicon in the case where HCl is added to dry O₂ during the high temperature oxidation. It has been reported by Kriegler¹⁾ that the oxidation rate and the diffusivity of Na⁺ ions in the oxide are considerably increased in the presence of HCl. The increase of the oxidation rate cannot be explained only by the presence of H₂O molecules, formed by the reaction,



N-type 10 ohm-cm (111), (100), (311) and (110) oriented wafers were used. Slices were oxidized at 1100°C for various HCl/O₂ mole ratios below 10%.

The oxide thickness, X, as a function of oxidation time, t, was fitted to the following linear-parabolic relationship,

$$Bt = X^2 + AX, \quad (2)$$

by the least square method. B increases with the HCl/O₂ mole ratio. The values of B for 0, 2, 5 and 10 percent are 4.0, 6.1, 6.5 and 7.2 x 10⁻⁴ μ²/min, respectively. A is strongly dependent on the orientation, and decreases with increasing the HCl/O₂ mole ratio. The increase of B/A with the HCl/O₂ mole ratio is approximately linear in the range of the ratio below 5%.

The above results suggest that the increase of the oxidation rate is caused by three reasons: The first is enhanced diffusion of O₂ and H₂O molecules in the HCl oxide. The second is enhanced reactions at the Si-SiO₂ interface, resulting from a catalytic action of HCl. The third is the contribution of H₂O to the oxidation.

In order to determine the diffusivity of O₂ and H₂O molecules in the HCl oxide, wafers of the (100) orientation were oxidized initially in the 1:10 mixture of HCl and O₂ to obtain the oxide thickness, X₀, and then oxidized in the dry or wet oxygen.

The theoretical relationship between the oxide thickness, X, and the oxidation time, t, in the dry or wet oxygen is expressed as

$$Bt = (X - X_0)(X + X_0 + A'), \quad (3)$$

where
$$A' = A + 2(D/D_0 - 1)X_0 \quad (4)$$

A and B are determined independently by the oxidation of bare silicon wafers. D and D₀ are the diffusivity of the oxidizing molecules in the growing oxide and the HCl oxide, respectively.

In Eqs. (3) and (4), it is assumed that the equilibrium concentration of oxidizing molecules in the oxide is not changed in the presence of HCl. The diffusivity of O₂ in the HCl oxide is approximately 1.6 times larger than in the dry oxide. The diffusivity of H₂O was determined by the analysis of the oxidation in the wet oxygen, where the bubbler temperature is 90 °C. The diffusivity of H₂O in the dry oxide is approximately 1.5 times larger than that in the wet oxide. The diffusivity of H₂O in the HCl oxide is approximately 1.7 times larger than that in the dry oxide. By using these values of the diffusivity, it is concluded that the partial pressure of H₂O is 0.0075 atm, which is approximately half of the equilibrium value for the reaction (1) for the HCl/O₂ mole ratio of 10 %.

If the HCl/O₂ mole ratio is sufficiently small, we get

$$B/A = C_0(k_0 + k' \gamma_0)/N, \quad (5)$$

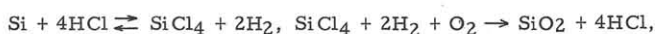
where C₀ and γ₀ are the equilibrium concentration of O₂ and HCl, respectively, in the oxide. N is the number of O₂ incorporated in a unit volume of oxide. k₀ is the reaction constant for the dry oxygen. From the experimental values of B/A, it is concluded that

$$k_0(100) < k_0(111) < k_0(311) < k_0(110),$$

and

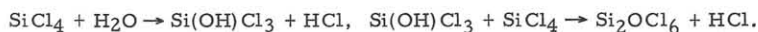
$$k'(111) < k'(100) < k'(311) < k'(110).$$

The latter relation is the same as for the gaseous etching of silicon. The following reactions are important,



If the rate of each pair of reactions is larger than the rate of the direct reaction, Si + O₂ → SiO₂, the hydrogen chloride may be considered as a catalyst.

The results of the infrared spectroscopy of the output gas from the furnace and the observation of the Si-SiO₂ interface through a microscope and secondary electron microscope verify these reactions. The deficiency of O₂ leads to the etching. The infrared absorption spectra were assigned to H₂O, HCl, Si₂OCl₆, SiH₂Cl₂, SiHCl₃ and SiCl₄. Si₂OCl₆ is formed by the reactions,



The observation of the wafers through the microscope revealed triangle-shaped etch pits for (111), square-shaped pits for (100) and line-shaped pits for the (110) orientation. The shape of the etch pits is reasonable since the etch rate is largest in the <110> direction.

1) R. J. Kriegler, Thin Solid Films 13 (1972) 11.