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A Mechanism of Particle Generation and a Method to Suppress Particles in Vapor HF/H_2O System

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A mechanism has been suggested to account for the particle generation and a method has been proposed to control them in the vapor HF/H2O system. During the etching process of the SiO2 films, the compounds such as SiO2 and H2SiF6 are produced and cause the particles. In order to decrease these products, it is important to shift the chemical equilibrium state ,changing the HF/H2O mole ratio and the wafer temperature.

INTRODUCTION

In the fabrication process of ULSI devices, the contaminations around the silicon surface induce the degradation of the junction and oxide properties [1]), so the surface cleaning technology must be developed. Especially in the fine trench and contact holes with high aspect ratio, it is difficult to clean the surface regions, using the ordinal liquid-phase system, because of the surface tension. Therefore, the vapor-phase cleaning system has been developed , using HF/H2O [2]) [3]) vapor, Cl radical [4]) and so on. In the vapor HF systems, many researchers indicated that it was effective to suppress the native oxide growth [2]), and recently Ohmi reported that it was possible to etch off the native oxide selectively [3]). However, the particle generation due to the reaction products becomes a serious problem in this system.

In this work, a mechanism of particle generation has been clarified and a method for suppressing particle generation has been proposed in the vapor HF/H2O systems.

EXPERIMENTAL PROCEDURE

Fig.1 shows the schematic drawing of the etching chamber used in this experiment. HF/N2 and H2O/N2 vapor were individually introduced into the etching chamber at the temperature of 40°C and SiO2 film was etched at atmospheric pressure. The sample was heated from the backside by irradiating the IR light from the tungsten halogen lamps.

The etching rate of the SiO2 film was evaluated by changing HF concentration, HF/H2O mole ratio and the sample temperature. Next, the thermal SiO2 film of 0.2 μm thickness was etched off with an over

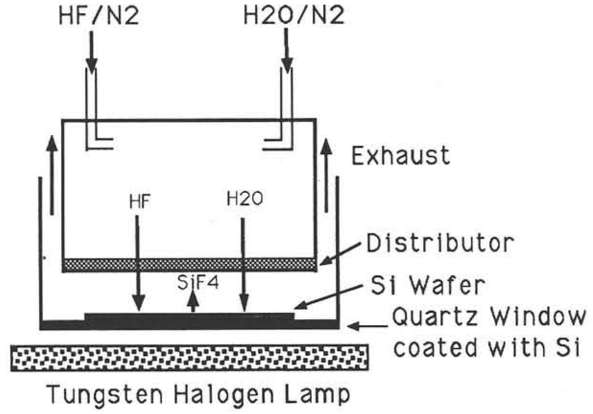

Fig.1 Schematic drawing of the etching chamber used in this experiment.

etch of about 50%. The number of the particles above 0.16μm in size was counted and the surface impurities were analyzed by SIMS.

RESULTS AND DISCUSSION

1) Mole ratio dependence of HF/H2O

Fig.2 shows the HF/H2O mole ratio dependence of the etching rate at the various HF concentration. Basically, the etching rate was determined by the HF concentrations, and it increased in proportion to the HF concentration. Also, the etching rate had a certain relationship with the water content above the critical concentration. The etching rate was increased in proportion to the water content at the HF/H2O mole ratio between 5 and 100, then it saturated at the HF/H2O mole ratio below 1. This behavior was obtained with the various HF concentrations.

Fig.3 shows the HF/H2O mole ratio dependence of the particle counts. It also indicates the HF concentration dependence of the particle counts. The particle counts were strongly dependent on the HF/H2O mole ratio. A large amount of particles of above 10,000 counts/wafer generated at the HF/H2O ratio below 1. When the water content was decreased and the HF/H2O mole ratio extended between 10 and 100, the particle counts abruptly decreased and the minimum value of about 80counts/wafer was obtained. However, when the water content decreased furthermore and approached around the critical concentration, the particle counts suddenly increased. In the case of the HF/H2O liquid-phase system, the particle counts were about 30 counts/wafer.

Fig.4 shows the relative intensity of ^{1}H, ^{19}F, ^{16}O atoms against ^{30}Si on the vapor-etched sample. For vapor HF/H2O system, the intensity of O, F atom indicated a large value in comparison with the sample etched in HF/H2O solution. And the sample with a higher HF/H2O mole ratio indicated less O and F intensity. This tendency had a good correlation with the particle counts. On the

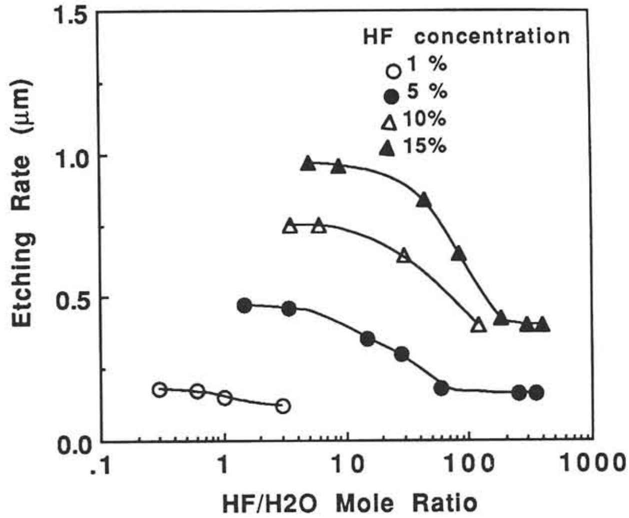

Fig.2 HF/H2O mole ratio dependence of the etching rate at various HF concentration

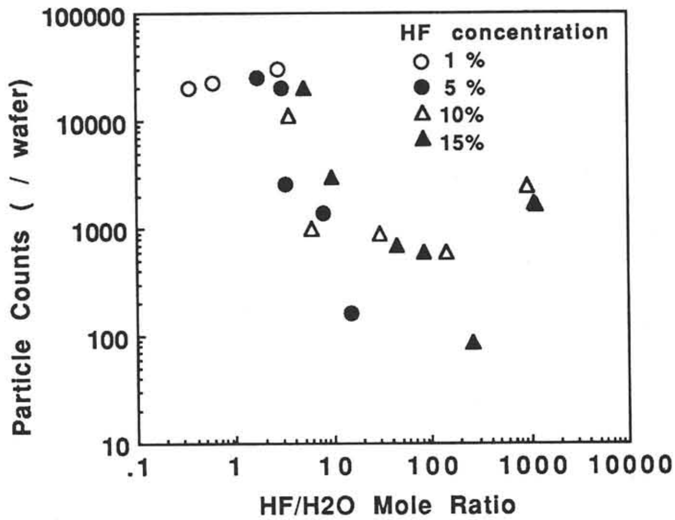

Fig.3 HF/H2O mole ratio dependence of the particle counts

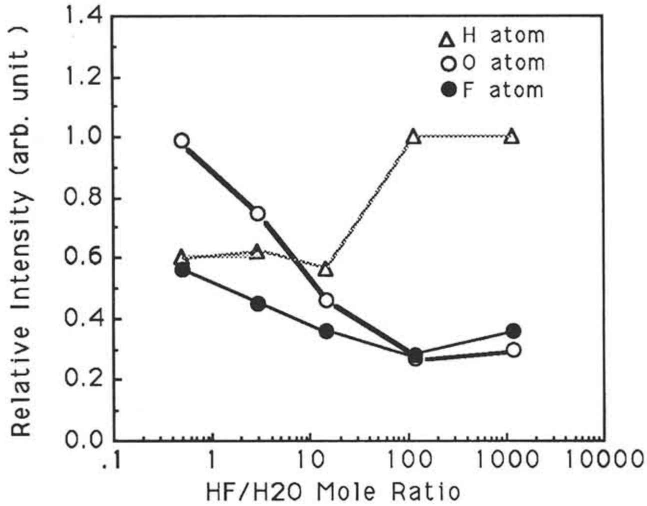

Fig.4 HF/H2O mole ratio dependence of H, O, F atom intensity

other hand, H intensity indicated a reverse tendency, that is, the sample with the higher HF/H2O mole ratio had larger H intensity. When the water content approached the critical concentration, F intensity increased. Also, it was confirmed by XPS that F and O atoms were chemically bonded to Si atoms.

2) A mechanism of particle generation

Fig.7 shows the reaction mechanism between SiO2 film and HF/H2O gas. SiH4 and H2O are produced by the reaction between HF and SiO2, and subsequently H2SiF6 are produced by the reaction between HF and SiF4. These reactions are principally reversible. Actually, the reaction seems to proceed by the hydration mechanism as shown in Fig.7 (2), (3) [5]. So, the etching process of SiO2 film suddenly proceeded at the water content above the critical concentration and the etching rate increased in proportion to the water content. However, with the existence of excess H2O, the etching rate did not appreciably increase because of the reverse reaction in equation(1). In this system, SiO2 and H2SiF6 are solid state compounds and are considered as the source of the particle generation. That is, during the etching process of the SiO2 film, SiF4 reacts with H2O or HF to produce SiO2 or H2SiF6 in the vapor phase.

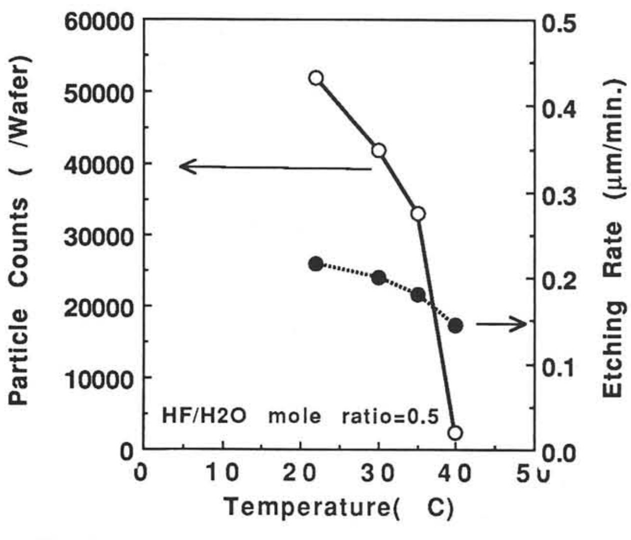

Fig.5 Wafer temperature dependence of particle counts

Considering the equilibrium constant[6] in equation (1), the following equation

$$Ka = \frac{(P_{H2O})^2 (P_{SiF4})}{(P_{HF})^4}$$

(P : Partial Pressure)

is obtained. In this case, The amounts of SiF4 can be calculated from the etching rate of SiO2 film. The Ka value for HF/H2O=100 is 5 x 10^{-6} times smaller than that for HF/H2O=100, so the chemical equilibrium state for HF/H2O=1 was largely shifted to the right direction in equation(1) and the SiO2 generation can be largely suppressed in the vapor phase(Le Chaterier's Law). Also, the chemical equilibrium is shifted to the left direction in equation(4) because of the low concentration of SiF4 gas, then the formation of H2SiF6 could be suppressed. These phenomena caused the decrease of F and O atom intensity on Si surface and consequently particle generation could be suppressed. Also, considering that H atoms are stably terminated to the Si surface, it seems to be reasonable to contain a lot of H atoms on the clean Si surface with less particles.

When the HF/H2O mole ratio approaches infinity, H2O concentration is determined by the reaction products, so the etching rate was not appreciably changed in this regions. In this case, the amount of ionized $HF2^-$ species are less than that of HF amounts. So, the chemical equilibrium state was shifted to the right direction in equation(4) and H2SiF6 were largely produced in the vapor phase. So, the intensity of F atoms on Si surface increased and consequently the particles were generated.

(3) Temperature dependence

Fig.5 shows the wafer temperature dependence of the particle counts at the HF/H2O mole ratio of 0.5. It was observed that the particle counts largely decreased by raising the temperature from 25°C to 40°C. In this case, the etching rate decreased at the higher temperature. From the SIMS

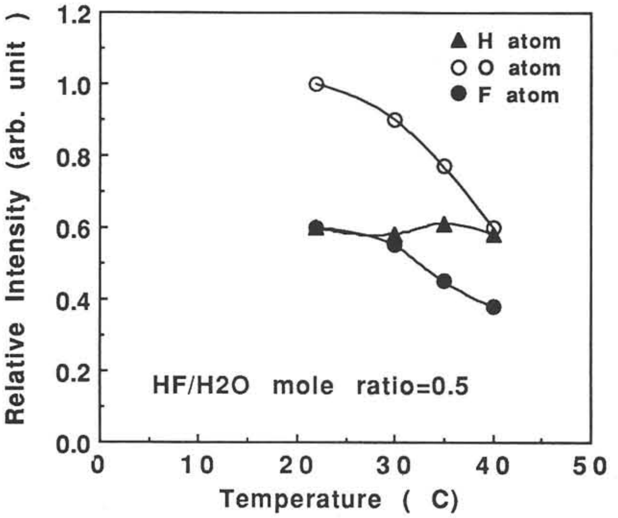

Fig.6 Wafer temperature dependence of relative intensity of H, O, and F atom

$$SiO_2 + HF \underset{}{\overset{H_2O}{\rightleftharpoons}} SiF_4 + 2H_2O \quad (1)$$

$$2HF + H_2O \rightleftharpoons H_3O^+ + HF_2^- \quad (2)$$

$$SiO_2 + 2H_3O^+ + 2HF_2^- \rightleftharpoons SiF_4 + 4H_2O \quad (3)$$

$$SiF_4 + 2HF \overset{H_2O}{\rightleftharpoons} H_2SiF_6 \quad (4)$$

Fig.7 Reaction mechanism between SiO_2 film and HF/H_2O gas

analysis(Fig.6), it was observed that the relative intensity of F and O atoms decreased by raising the sample temperature. The reaction shown in Fig.6(1) is exothermic, therefore it was believed that the etching rate decreased at the higher temperature. In this system, the sample was heated by using the tungsten halogen lamp, so the temperature of the surrounding ambient was not raised. The chemical equilibrium state was shifted to the right direction in equation(1)(Fig.7) and to the left direction in equation(2)(Fig.7), because the amount of SiF4 gas at 40°C is smaller than that at 25°C. As a result, the generation of SiO2 and H2SiF6 could be suppressed in the vapor phase, and the particles decreased.

CONCLUSION

The following conclusions are summarized in this experiment. In the etching process of SiO2 film by HF/H2O vapor system, the reaction products such as H2SiF6 and SiO2 were formed and consequently the particles were generated. The particles decreased by changing HF/H2O mole ratio and wafer temperature for the purpose of shifting the chemical equilibrium state. Especially, particle generation was largely affected by the HF/H2O mole ratio and the the adequate mole ratio regions existed for suppressing the particles. So, it becomes important to mix the HF and H2O gas fully and to keep good uniformity. Actually, the particle generation could be perfectly suppressed by raising miscibility and controlling the temperature.

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