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Gas-Phase Selective Etching of Native Oxide

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***Abstract*—A dry cleaning technology for ULSI process with regard to native oxide film on a silicon surface using gas-phase anhydrous hydrogen fluoride (AHF) has been developed at room temperature and at normal pressure. A fluorine passivated system for a corrosion-free condition and a continuous monitoring system for reaction mechanism are employed, where a strictly moistureless hydrogen fluoride (HF) gas is used, which is evolved by the generation method with low-temperature equilibrium. Gas-phase reaction of AHF gas with various kinds of silicon oxide films is investigated in detail. Gas-phase selective etching of native oxide film from other oxide films is achieved under the exact control of the concentration of HF and moisture.**

After etching of native oxide by HF gas, fluorine remains on the bare silicon surface in a chemically combined state, i.e., a fluorine terminated silicon surface. This fluorine terminated silicon surface gives a negative influence on succeeding processes. Then chemically combined fluorine must be removed from the bare silicon surface before each succeeding process. Elimination of chemically combined fluorine was examined using various treatments and has been achieved with Xe lamp irradiation.

The reaction mechanism of HF and silicon oxides is discussed in detail.

I. Introduction

GAS-phase selective etching of native oxide film formed on a silicon surface is the most essential requirement for ULSI process technologies in view of low contact resistance, low-temperature silicon epitaxy, high-quality thin oxide, and so on. Surface contamination is mainly caused by organic materials, metallic materials, and native oxide film. Dry cleaning of organic materials using ozone and dry removal of metallic materials using chlorine radicals are well known as feasible technologies. Ozone cleaning inevitably causes bare silicon surface oxidation. However, gas-phase selective etching of native oxide film has been considered as an impossible technology so far.

There have been several dry etching techniques of oxide films in the past, for example, pattern etching of silicon oxide film under a resist layer using HF vapor at 150–200°C [1]–[3] and overall etching of silicon oxide film using a gas mixture of HF and water vapor at room temperature [4]. The reaction of silicon oxide film and HF gas at room temperature has been recognized to proceed under the presence of water vapor so far. In such a case, all kinds of silicon oxide films, such as thermal oxide, CVD oxide, native oxide, and others have been etched away all at once without permitting selective etching. A gas mixture of HF and water vapor is too corrosive to the gas supply system and process chambers. Therefore, practical application of the gas mixture is difficult and not applicable for surface cleaning.

In this paper, ultraclean AHF gas and a corrosion-free system have been developed in order to realize gas-phase selective etching of native oxide [5], [6]. The reaction mechanism of silicon oxide film with moistureless HF has been investigated, and the selective etching conditions of native oxide have been developed [7], [8]. This paper describes the gas-phase selective etching of native oxide in an environment of strictly controlled AHF concentration in N_2.

The experimental apparatus is described in Section II. Section III describes experimental results of the selective etching, and elimination of chemically combined fluorine is given in Section IV. The reaction mechanism of silicon oxide films with moistureless HF is discussed in Section V. The conclusion is given in Section VI.

II. Experimental Apparatus

The "ultraclean surface dry cleaning system" is shown in Fig. 1. This system is characterized by a complete corrosion-free, moisture-free, contamination-free structure and a continuous monitoring system. The system consists of an all-metal structure without plastic materials in order to suppress the influence of the huge amount of out gas from plastic materials [9]. Additionally, the metal surface of the dry cleaning system is passivated by oxygen-free pure fluorine [6]. The fluorine-passivated metal surfaces are completely corrosion free even under an extremely corrosive environment such as HF gas and chlorine gas, including a huge amount of moisture. A dew point (DP) meter and infrared (IR) spectrometer are equipped for monitoring the system operation and analyzing the etching reaction.

The cross-sectional sketch of the chamber is shown in Fig. 2, where a single wafer is processed. N_2 gas flows between double O-ring seals to prevent both external leaks of HF gas and internal leaks of moisture.

Moistureless HF gas is obtained based on low-temperature gas–liquid equilibrium, where moisture concentra-

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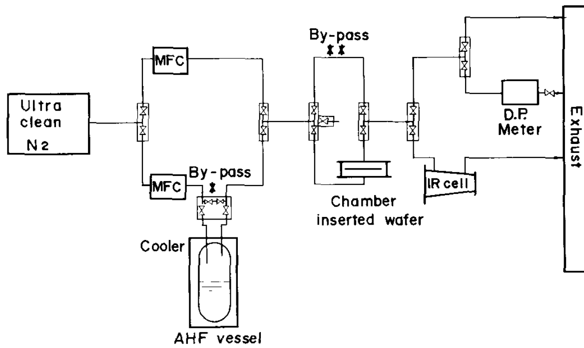

Fig. 1. Ultraclean surface dry-cleaning system using HF gas.

Drying flow : N_2 → Chamber → D.P. meter (H_2O).
Generation flow: N_2 → AHF → IR cell (HF).
Etching flow: N_2 → AHF → Chamber → IR cell (SiF_4).
Purge flow: N_2 → Chamber → IR cell (HF).

AHF: anhydrous hydrogen fluoride. DP meter: dew point meter, IR cell: infrared cell. MFC: mass flow controller.

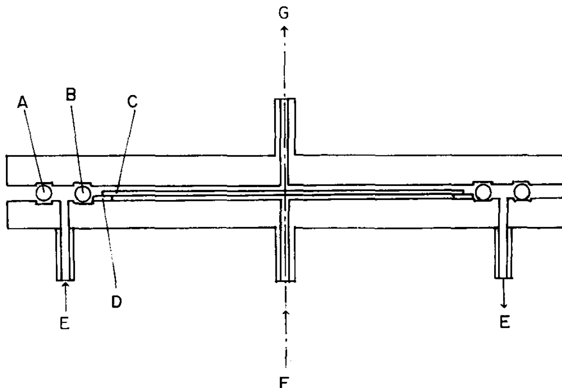

Fig. 2. Fluorine-passivated chamber. A: Polytetrafluoroethylene (PTFE) packing; B: nickel gasket; C: wafer; D: support; E: N_2 (seal gas); F: (N_2 + HF) gas inlet; G: exhaust gas.

tion in liquid AHF is guaranteed to be less than 0.1 ppm. Moisture concentration in HF gas decreases with decreasing vessel temperature. The vessel temperature is precisely controlled in the range of −70 to −40°C. The moisture concentration in generated HF gas is suppressed to a few parts per billion level, where this moisture concentration is limited by moisture level in the carrier gas N_2.

The dry-cleaning steps are as follows: The first step is an ultraclean N_2 flow through the chamber. A DP meter monitors the moisture in the chamber after introduction of the wafer. The second step is a generation flow of the diluted HF gas. The IR spectrometer strictly measures the HF concentration in N_2. The last step is the etching of oxide films by the diluted HF gas. The IR spectrometer continuously measures the exhaust-gas composition.

III. Selective Etching of Native Oxide

The reaction process of several oxide films is surveyed by an IR chart of SiF_4. The IR charts of exhaust gas for thermal and native oxide film at temperatures from 4 to 50°C are shown in Fig. 3, where time variation of IR transmittance for reaction product SiF_4 (1028 cm^{-1}) is illustrated. The start and end points of reaction are clearly recognized by the generation of reaction product SiF_4. The peak height of IR absorption is proportional to the surface area of the oxide film and the reaction rate, and the peak width is proportional to the thickness of the oxide film and inversely proportional to the reaction rate.

The reactivity of HF and silicon oxide film in relation to the temperature is elucidated from the peak pattern of IR chart. The reaction rate R_t of the thicker oxide film can be calculated by the reaction time measured from the IR chart, such as

$$R_t = \frac{\text{thickness of oxide film (Å)}}{\text{etching time (min)}}. \tag{1}$$

Native oxide shows a very sharp peak, because of its extremely thin thickness, on the order of angstroms, so that the reaction rate R_n of native oxide film is derived from the peak concentration of SiF_4, as follows:

$$R_n = C_p(\text{cm}^3/\text{l}) \times F(\text{l/min})/A(\text{cm}^2) = \frac{C_p \cdot F}{A}\,(\text{cm/min}) \tag{2}$$

where C_p is the volume concentration of SiO_2,[1] F is the flow rate of diluted HF gas, and A is the surface area of oxide film.

Temperature dependence of the reaction rates of several oxide films such as thermal oxide, CVD oxide, CVD BSG, and native oxide, is shown in Fig. 4. It is seen from Fig. 4 that the reaction rate of native oxide film is much smaller than those of other oxide films and that the reaction rates of thermal and CVD oxide films exhibit the highest around room temperature. The reaction rates of oxide films except native oxides decrease drastically with an increase of ambient temperature higher than room temperature.

Fig. 5 shows the relationship of the reaction rate and the HF concentration in N_2 for thermal and native oxide films. There exists a critical concentration of HF at which the reaction of HF gas with silicon oxide film occurs. Thermal oxide film does not react with HF having concentrations less than 4.7 percent and native oxide film less than 0.6 percent. Therefore, native oxide film is selectively etched away in the HF concentrations in the range of 0.6 to 4.7 percent without giving any influence on thermal oxide.

The relationship of the HF critical concentration and the H_2O concentration is studied for various oxide films, as shown in Fig. 6. Thermal oxide films have the highest HF critical concentration, while CVD oxide films and CVD BSG films have intermediate HF critical concentra-

[1]The volume concentration of SiO_2 (cm^3/l) is calculated from the peak concentration of SiF_4 (vol%) obtained by the IR transmittance (see Appendix A).

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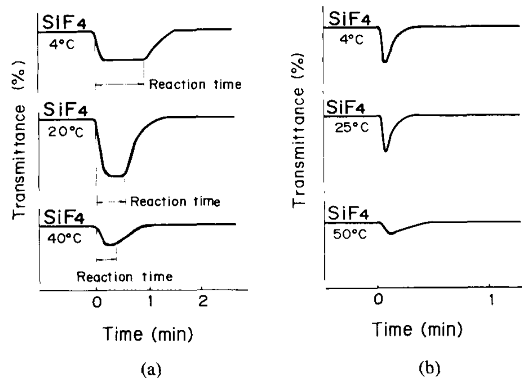

Fig. 3. IR chart of exhaust gas for thermal and native oxide film at 4–50°C. (a) Thermal oxide (wet O_2 oxidation): HF concentration: 4.7 vol%, H_2O concentration: 1.0 vppm. (b) Native oxide (hot air oxidation): HF concentration: 5.0 vol%, H_2O concentration: 0.01 vppm.

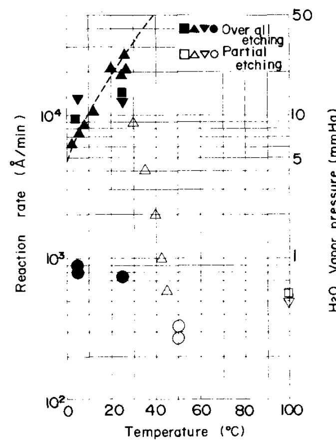

Fig. 4. Relation of reaction rate of several oxide films and temperature. △ Thermal oxide (wet O_2 oxidation): HF concentration: 4.7 vol%, H_2O concentration: 1.0 vppm. ○ Native oxide (hot air oxidation): HF concentration: 5.0 vol%, H_2O concentration: 0.01 vppm. ▽ CVD oxide: HF concentration: 1.0 vol%, H_2O concentration: 0.01 vppm. □ CVD BSG: HF concentration: 1.0 vol%, H_2O concentration: 0.01 vppm. ------ H_2O vapor pressure.

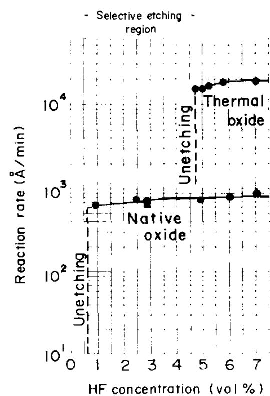

Fig. 5. Relationship of reaction rate and HF concentration at 25°C, where moisture level is kept at 0.01 ppm. Thermal oxide: dry O_2 oxidation. Native oxide: hot-air oxidation.

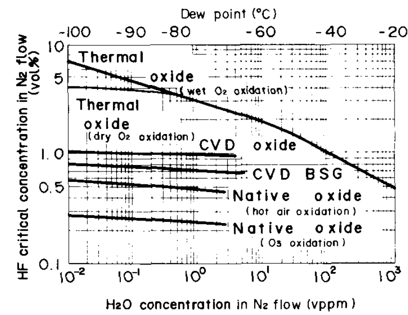

Fig. 6. Relationship of HF critical concentration and moisture level at room temperature for various oxide films, such as wet thermal oxide, dry thermal oxide, CVD oxide, CVD BSG, native oxide by hot-air oxidation, and native oxide by ozone oxidation.

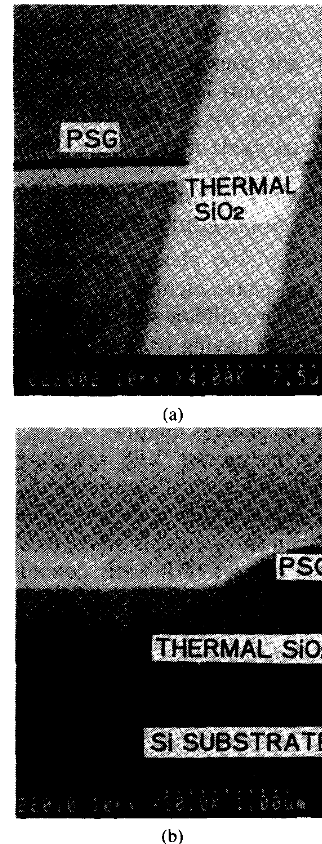

Fig. 7. SEM microphotograph of selective etching between CVD PSG and thermal oxide. (a) Plane view of CVD PSG pattern on thermal oxide. (b) Cross-sectional view.

tion. Two native oxides formed in hot air and ozone ambient have lower HF-critical concentrations. HF-critical concentrations of other native oxides formed by a wet-chemical cleaning procedure such as (H_2SO_4 + H_2O_2), (NH_4OH + H_2O_2), and HNO_3 treatment exhibit intermediate values between these two critical concentrations. CVD PSG film is not shown in Fig. 6 because it has the lowest HF-critical concentration of less than 0.1 percent.

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Therefore, it is recognized from Fig. 6 that the selective etching of native oxide film from other oxide films is possible except CVD PSG, under the condition that the HF concentration is kept from 0.6 to 0.8 percent at the H_2O concentration of 10 parts per billion (ppb). The HF concentration is completely controlled in these regions by adjusting the vessel temperature and utilizing the advanced gas-dilution system [10]. The HF-concentration region of selective etching becomes smaller at higher concentrations of H_2O. Therefore, the moistureless condition is strictly required for reliability of the selective etching.

Selective etching of multilayer oxide is obviously possible, as shown in Fig. 7, where multilayer oxide consists of CVD PSG and thermal oxide. Thermal oxide film with a 8900-Å thickness is formed on a silicon substrate, and CVD PSG film with a 6000-Å thickness is grown thereon. The multilayer oxide having a resist pattern is treated with the diluted HF gas containing 0.17-percent HF and 0.1 parts per million (ppm) H_2O, and then resist is stripped. It is clearly seen from Fig. 7 that CVD PSG film is etched away, and thermal oxide film remains unchanged.

IV. Influence of Fluorine-Terminated Surface on Succeeding Process

Characteristics of the clean bare silicon surface obtained in this gas-phase etching technology are investigated. Since the bare silicon surface is immediately oxidized in the ambient having oxygen and moisture even at room temperature [11]–[13], native oxide must be removed just before starting each subsequent process in order to improve the process quality.

Fig. 8 shows the precise XPS spectra from the wet-cleaned and the dry-cleaned silicon surfaces. The Si_{2p} XPS spectrum from native oxide is clearly recognized on the wet-cleaned silicon surface. This native oxide comes from final rinsing in deionized (DI) water containing dissolved O_2 of 0.6 ppm. On the dry-cleaned silicon surface, the Si_{2p} spectrum peak from the native oxide is very weak while a F_{1s} spectrum appears. This indicates that the bare silicon surface is covered by chemically combined fluorine, i.e., fluorine-terminated silicon surface. It is well known that Si–F bond energy is much higher than Si–H bond energy. Thus, chemically combined fluorine is considered to give a definite influence on succeeding processes. Therefore, as a next step an influence of chemically combined fluorine on the bare silicon surface is investigated. The effect of fluorine-terminated silicon surface on succeeding processes was evaluated by the sputtering epitaxy and the oxidation.

Table I summarizes the results of low-temperature sputtering silicon epitaxy [14]–[19] on three different silicon surfaces such as fluorine-terminated silicon surfaces, native oxide surfaces having a thickness of 7 Å, and wet-cleaned silicon surfaces having 0.4-Å native oxide. In this sputtering epitaxy, single-crystalline silicon is obtained on the wet-cleaned silicon surface at a substrate temperature of 300°C, where the sheet resistivity of grown film having a thickness of 0.2 μm is 100 Ω. On the other hand,

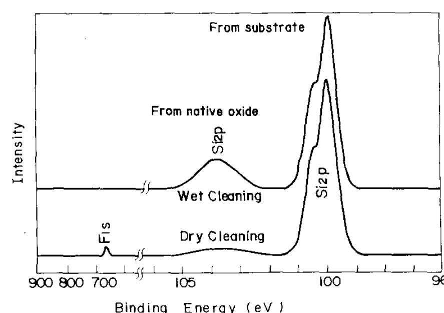

Fig. 8. Si_{2p} and F_{1s} XPS spectra from wet and dry HF-cleaned silicon surface. Cleaning condition:

1) Pretreatment: $H_2SO_4:H_2O_2$ (4:1 vol) 5 min.
   Wet cleaning: 0.5% HF aq. solution 1 min.
   Over flow rinse: Ultra Pure DI water 10 min.
2) Pretreatment: $H_2SO_4:H_2O_2$ (4:1 vol) 5 min.
   Dry cleaning: 1.0% HF gas (D.P. −100°C).

TABLE I
Resistivity of Sputtering Epitaxial Silicon

Silicon Substrate [1]		Epitaxial Silicon	
HF cleaning	SiOx film thickness (Å) (x>0.5)	Crystal structure [2]	Sheet resistivity [3] (Ω)
Before cleaning	7	Poly-crystal	5×10^6
Wet cleaning	0.4	Single-crystal	100
Dry cleaning	0.3	Amorphous	$3\sim5\times10^6$

1) Pretreatment
$H_2SO_4:H_2O_2$(4:1vol) Deionized water
Isopropyl alcohol (IPA) vapor drying
2) Crystal structure : Reflection electron diffraction
3) Sheet resistivity : Four point probe method

the grown films become polycrystalline silicon having the sheet resistivity of 5×10^6 Ω on the native oxide surface and amorphous silicon having the sheet resistivity of 3–5 $\times 10^6$ Ω on the fluorine-terminated silicon surface, when all process parameters are kept at the same conditions. Thus fluorine-terminated silicon surfaces have been confirmed to exhibit similar characteristics to native oxide surfaces for film depositions.

MOS capacitance–voltage curves for oxide films formed on p-type substrates after the wet and dry cleaning are shown in Fig. 9, where the oxide thickness is about 200 Å. It is seen from Fig. 9 that an inversion layer is formed quickly in an MOS diode on the dry-cleaned silicon surface compared to that on the wet-cleaned silicon surface. Thus, it is concluded that chemically combined fluorine degrades the generation lifetime of carriers after the high-temperature treatment in oxidations. This shortening of the generation lifetime is caused by the remaining fluorine.

These two experimental results strongly indicate that terminating fluorine must be removed before succeeding processes. The elimination procedures of terminating fluorine have been investigated. Fig. 10 shows the F_{1s} XPS spectra from the fluorine-terminated surface after 1-h thermal treatment up to 930°C in N_2 at atmospheric pressure.

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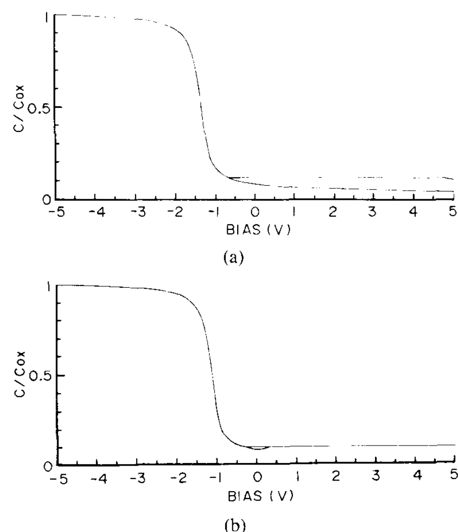

Fig. 9. MOS capacitance-voltage curves for oxide films having a thickness of 200 Å after wet and dry cleaning, where frequency is set at 1 MHz. (a) Wet cleaning. (b) Dry cleaning.

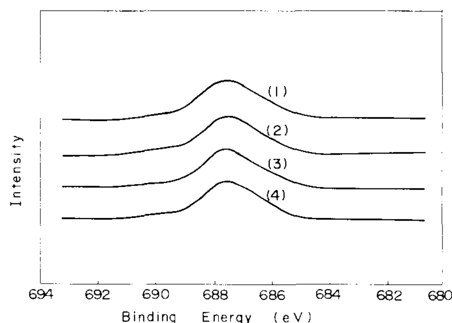

Fig. 10. F_{1s} XPS spectra from fluorine terminated surfaces heated up to various temperatures in N_2 environment. Treatment conditions are (curve 1) room temperature at 760 torr; (curve 2) 80°C for 1 h at 760 torr; (curve 3) 630°C for 1 h at 760 torr; and (curve 4) 930°C for 1 h at 760 torr.

It is worthwhile to note that F_{1s} spectra peak intensity does not change even after heating the substrate to 930°C. Terminiating fluorine could not be eliminated by heating silicon wafer up to 930°C.

The surface-cleaning technology with low kinetic energy Ar ion bombardment has been introduced to remove terminating fluorine, which has been confirmed to be very effective to remove adsorbed impurities on the bare silicon surface, particularly adsorbed moisture [15]. F_{1s} XPS spectra from the fluorine-terminated silicon surface are shown for the different bombarding Ar ion energies in Fig. 11, where the effect of the thermal treatment in an ultrahigh-vacuum environment is also given. The peak height of F_{1s} spectra decreases with an increase in Ar ion energy, but the elimination of terminating fluorine is not sufficient even when Ar ion energy is increased up to 10 eV, as shown in curve 4.

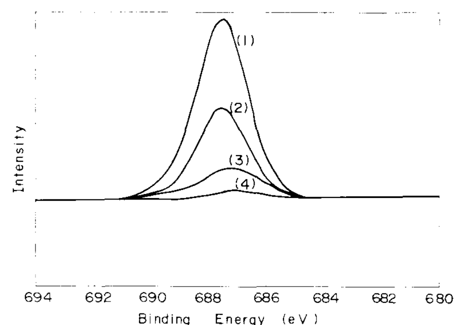

Fig. 11. Variation of F_{1s} XPS spectra from fluorine-terminated surface by low-energy Ar bombardment. Bombardment conditions are (curve 1) no bombardment (dry cleaned surface); (curve 2) no bombardment (substrate temperature 300°C, base pressure 5×10^{-9} torr); (curve 3) substrate temperature 300°C, Ar gas pressure 8×10^{-3} torr, bombarding Ar ion energy of ~3 eV; and (curve 4) substrate temperature 300°C, Ar gas pressure 8×10^{-3} torr, bombarding Ar ion energy of ~10 eV.

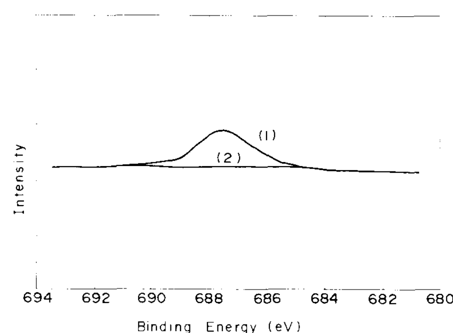

Fig. 12. Variation of F_{1s} XPS spectra from fluorine-terminated surface by an irradiation of Xe lamp: (curve 1) before irradiation and (curve 2) after irradiation. Xe lamp energy: 1.13–4.13 eV. Irradiated condition: 1 min, 10 W/cm^2 1×10^{-8} torr.

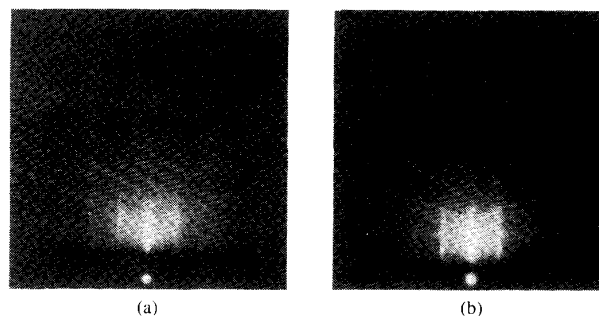

Fig. 13. Reflection electron diffraction pattern of epitaxial silicon on dry and wet cleaned surface. (a) Epitaxial silicon on wet cleaned surface and (b) epitaxial silicon on dry-cleaned surface having a Xe lamp irradiation as a pretreatment of fluorine removal.

Fig. 12 shows F_{1s} XPS spectra from a fluorine-terminated silicon surface before and after irradiation by the Xe lamp, which has a power density of about 10 W/cm^2 under the reduced pressure of 1×10^{-8} torr. It is confirmed in Fig. 12 that the Xe lamp irradiation removes terminating fluorine from the silicon surface within 1 min.

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The single-crystalline silicon epitaxy has been obtained on the dry-cleaned substrate at 700°C by the Si_2H_6 CVD procedure, where terminating fluorine has been removed by an irradiation of the Xe lamp [20], [21]. Crystallinity of grown film has been evaluated by reflection electron diffraction analysis, as shown in Fig. 13, where the reflection electron diffraction pattern of the grown film on the dry-cleaned silicon surface shows clear Kikuchi lines, the same as those of the wet-cleaned silicon surface.

V. Mechanism of Gas-Phase Etching of Silicon Oxide Film

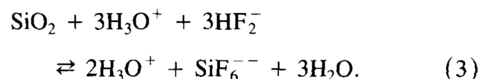
It has been considered so far that the reaction of silicon oxide with HF gas proceeds at temperatures higher than room temperature where the reaction mechanism has been well defined [22], [23]. However, the reaction of the silicon oxide film with the HF gas at room temperature has not been considered to proceed without coexistence of moisture [4].

In this work, the moistureless HF gas has been established, resulting in a discovery of various new phenomena.

The rapid initiation of reaction for silicon oxide film with moistureless HF gas is the first experimental demonstration. The HF critical concentration shifts to the lower value due to an increase in the moisture level of diluted HF gas, as shown in Fig. 6. For example, the HF critical concentration for thermal oxide film (wet O_2 oxidation) is 6.5-percent HF at 10 ppb H_2O but shifts to 3.0-percent HF at 1 ppm H_2O and to 1.0-percent HF at 100 ppm H_2O in the diluted HF gas.

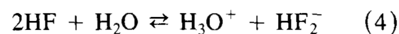
On the other hand, the decrease of flow rate of diluted HF gas shifts the critical HF concentration to the lower value even if the moisture level in diluted HF gas is kept constant, as shown in Fig. 14, where the HF critical concentration for thermal oxide is illustrated as a function of flow velocity of diluted HF gas having a moisture level of 100 ppb. It is seen from Fig. 14 that the decrease of HF critical concentration becomes remarkable at a flow velocity less than 40 cm/s.

The reaction mechanism is discussed as follows: In the liquid phase reaction, hydrofluoric acid ionizes and reacts with silicon oxide to result in the formation of hydroflurosilicic acid. This is a well-known reaction process and is widely used in industrial production:

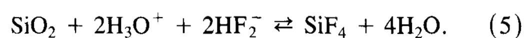


$$SiO_2 + 3H_3O^+ + 3HF_2^- \rightleftarrows 2H_3O^+ + SiF_6^{--} + 3H_2O. \quad (3)$$

On the other hand, an HF molecule does not ionize in a completely moisture-free gas-phase environment. However, the reaction can be considered to be triggered by HF molecule ionization at the oxide film surface due to remaining adsorbed moisture molecules. Thus, a keynote reaction is proposed as follows:



$$2HF + H_2O \rightleftarrows H_3O^+ + HF_2^- \quad (4)$$



$$SiO_2 + 2H_3O^+ + 2HF_2^- \rightleftarrows SiF_4 + 4H_2O. \quad (5)$$

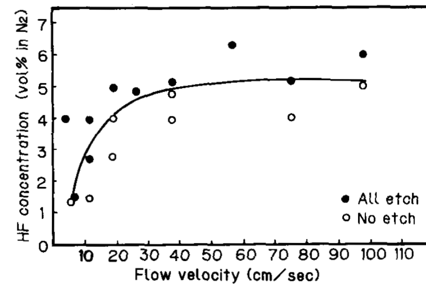
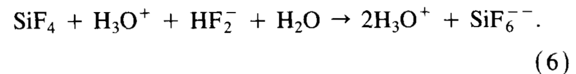


Fig. 14. Flow velocity dependence of HF critical concentration.

The presence of H_2O on silicon oxide surfaces initiates the ionization of the HF molecule, and silicon oxide reacts with the generated HF_2^- ion, which leads to a generation of more H_2O, as shown in (5). The generated H_2O enhances the ionization reaction of HF molecules, resulting in an increase of HF_2^- ions. This positive feedback mechanism causes rapid initiation of oxide film etching, as shown in Fig. 5, where the rapid rise in the reaction rate is observed at the HF critical concentration.

This rapid reaction accompanies the generation of huge amounts of H_2O, resulting in the suppression of generation of SiF_4 according to an irreversible hydration mechanism such as



$$SiF_4 + H_3O^+ + HF_2^- + H_2O \rightarrow 2H_3O^+ + SiF_6^{--}. \quad (6)$$

Therefore, the reaction rate is kept almost constant for HF concentrations greater than the critical concentration, as shown in Fig. 5.

The proposed ionization trigger mechanism is further proved by the following experiments. The thermal oxide film etching has been confirmed to continue even at 1.2-percent HF concentration due to the existence of H_2O as a reaction product, once the reaction is initiated in the environment of 5-percent HF, which is higher than the critical concentration of 4.7 percent at a moisture level of 100 ppb. The thermal oxide film, CVD oxide, and CVD BSG film do not react with liquid AHF (H_2O concentration less than 0.04 ppm), while CVD PSG film is etched immediately with AHF. The AHF has the strongest affinity for H_2O so that it immediately absorbs moisture completely from the silicon oxide surface. In this circumstance, the surface does not behave as the trigger of HF ionization, so the thermal oxide, CVD oxide, and CVD BSG film survive in the liquid AHF. In the case of CVD PSG film, the difference is caused by the highly hygroscopic nature of CVD PSG film.

These experiments are considered to make clear the existence of an ionization trigger mechanism of gas-phase oxide film etching. This ionization trigger mechanism of gas-phase oxide film etching suggests that the difference of the HF critical concentrations for various oxide films comes from the difference of the amount of adsorbed moisture molecules on these oxide surfaces. The mois-

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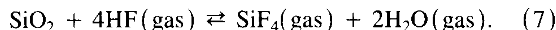
tureless environment is the key point of selective etching because of the trigger effect of trace H_2O.

This mechanism also explains the temperature dependence of reaction rates at temperatures lower than 25°C. It is recognized that the reaction rates of various silicon oxide films become the highest at around 25°C and decrease with a decrease of temperature, as shown in Fig. 4. The decrease of reaction rate with a decrease of temperatures is a well-known phenomenon [22]–[24], but the decrease below 25°C cannot be explained by conventional equilibrium constant theory.

Before going to the discussion on the temperature dependence of reaction rates, the molecular state of hydrogen fluoride in gas phase is surveyed. HF molecules are known to associate in the gas phase at low temperature, like 3.0 molecules at 20°C and 4.6 molecules at 0°C [25]. However, the association of HF molecules in diluted gas is not confirmed so far. A degree of association of HF molecules in N_2 is determined, as shown in Fig. 15 (Appendix B). It is clearly seen from Fig. 15 that the association of HF molecules in N_2 below 5 vol% is not recognized in the temperatures from 0 to 25°C, it is concluded that the reaction rate is not affected by the association of HF molecules.

HF molecules have been confirmed to form complexes with SO_2, CO_2, COS (carbonyl surfide), and so on, in the gas phase by IR spectrometry [26]. IR spectra of HF molecules diluted in inert gas are measured, as shown in Fig. 16. It is demonstrated in Fig. 16 that HF molecules do not form any complex with N_2, Ar, or He molecules.

Further consideration must be directed to the formation of H_2O as a factor affecting on the reaction rate. The increase in H_2O concentration in the reaction system increases the hydration degree due to the reversible equilibrium expressed by (7):



$$SiO_2 + 4HF(gas) \rightleftarrows SiF_4(gas) + 2H_2O(gas). \quad (7)$$

The increase of this hydration degree due to the increase of H_2O as a reaction product clearly explains the dependence of the reaction rate on the flow rate of diluted HF gas. This flow-rate dependence is shown in Table II. The reaction rate increases with the increase of the flow rate. The releasing speed of H_2O from the reaction surface becomes faster in proportion to the flow rate because of the higher vaporization speed of H_2O. The release of H_2O from the reaction surface promotes the reaction expressed by (7) toward the right direction.

The release of H_2O from the reaction system is a necessity for the reaction to proceed. The releasing speed of H_2O depends on the vapor pressure of H_2O at a reaction temperature. The decrease of the reaction rate below 25°C is considered to result from the decrease of the vapor pressure of H_2O at the reaction surface. This estimation is confirmed from the fact that the slope of the relation between the reaction rate and temperature coincides as well with the slope of the relation between H_2O vapor pressure and temperature below 25°C in the dashed line, as shown in Fig. 4.

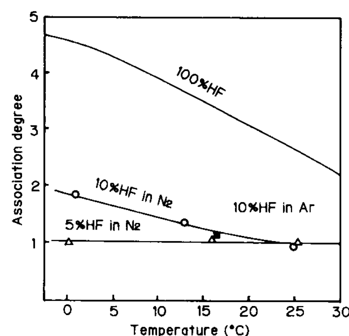


Fig. 15. Temperature dependence of association degree of HF molecules in N_2.

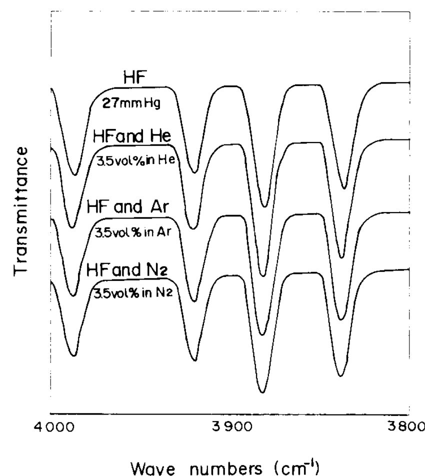


Fig. 16. IR spectra of HF and diluted HF in inert gases such as He, Ar, and N_2.

TABLE II

RELATIONSHIP BETWEEN CONCENTRATION OF PRODUCED MOISTURE IN N_2 AND ETCHING RATE

Run No.	Flow rate (l/min)	Water area (cm²)	HF gas concentration (vol%)	Etching rate (Å/min)	concentration of produced moisture in N_2 (vol%)
1	1.0	2.4	5.0	15071	0.043
2	1.0	10.0	5.0	14525	0.18
3	0.24	0.36	5.0	16559	0.012
4	0.25	2.4	5.0	13912	0.06
5	0.26	3.6	4.3	14354	0.25
6	0.11	2.4	5.4	9936	0.39
7	0.11	15.0	5.4	4564	2.39
8	0.11	30.0	5.0	3845	2.30

Thermal oxide film thickness : 9640 Å
Saturated vapor : 2.3 vol%

VI. CONCLUSION

Gas-phase selective etching of native oxide film, thermal oxide film, CVD oxide film, and so on by a gas mixture of moistureless HF and N_2 has been investigated. A dry-cleaning process in this research is carried out in a complete corrosion-free system using fluorine-passivated metal components and an IR spectrometer.

The reaction rates of several silicon oxide films in diluted HF gas are surveyed in detail as a function of re-

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action temperature, gas flow rate, HF concentration, and moisture level. It has been demonstrated experimentally that there exists an HF critical concentration in N_2 to react with oxide film, and this HF critical concentration is different for various oxide films, such as thermal oxide, CVD oxide, CVD BSG, CVD PSG, and native oxide. The selective etching of native oxide film is attained by its low critical concentration of HF compared with other oxide films except CVD PSG.

Oxide films are perfectly removed from silicon surfaces by diluted HF gas etching, but bare silicon surfaces are covered by chemically combined fluorine. The fluorine-terminated silicon surface behaves similarly to the native oxide surface in succeeding film depositions and degrades the generation lifetime of carriers in succeeding high-temperature processes such as oxidation. The chemically combined fluorine must be removed from the silicon surface before succeeding processes. Xe lamp irradiation in reduced pressure environments eliminates fluorine from the fluorine-terminated silicon surface.

Native oxide is very well known to degrade contact resistance, where the contact resistance increases its significance with a decrease in pattern dimension, particularly for high-speed processor and analog devices such as imaging devices. This newly developed gas-phase selective etching technology makes it possible to remove native oxide films just before each processing.

The mechanism of gas-phase etching of oxide film is discussed based on the dependence of reactions on moisture level, gas flow rate, and temperature. The gas-phase oxide film reaction is initiated by HF molecule ionization at the oxide surface due to adsorbed H_2O molecules. The ionized molecule HF_2^- reacts with oxides resulting in an appearance of reaction product H_2O, which enhances HF molecule ionization. This is a newly proposed ionization trigger mechanism for gas-phase oxide film etching.

Appendix A
SiF_4 Concentration Measuring Method

The volume concentration of SiO_2 (C_{SiO_2}) is calculated from the following equation. The peak concentration of $SiF_4(V)$ can be determined from peak heights of IR absorption at room temperature T (in degrees Celsius):

$$C_{SiO_2} = \frac{V}{\rho} \times \frac{M}{22.4} \times \frac{273}{273 + T}$$

where M is the molecular weight of SiO_2 (60 g), and ρ is the density of SiO_2 (2.2 g/cm^3).

Appendix B
The Association Degree Measuring Method

The measuring method of association degree is as follows: The HF molecule forms aggregated molecules such as cyclic hexamer $(HF)_6$ and chain polymers $(HF)_n$. These molecules have similar gas-phase behavior to monomolecules (HF). For example, the number of aggregated molecules is 2.46×10^{19} cm^{-3} under the same conditions, such as a temperature of 298 K and a pressure of 1 atm.

The gas mixture of N_2 and HF decreases its volume by contact with DI water owing to a dissolution of $(HF)_\alpha$ into the water, where α is an association degree. Cyclic hexamer and chain polymers dissolve in DI water to form monomolecules. The volume decrease (ΔV) of mixture gas is measured. The HF weight (W) dissolved into the water can be observed by an alkalimetry method of the solution. Thus, the association degree (α) is calculated from the following equation:

$$\frac{\Delta V}{22400} \times \frac{273}{273 + T} = \frac{W}{\alpha \cdot w}$$

where V is the volume decrease of the gas mixture in cubic centimeters, W is the HF weight in the solution in grams, w is the HF molecular weight (20.01), and T is the temperature in degrees Celsius.

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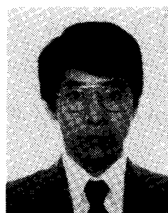

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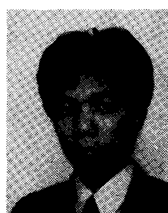

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