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Invited

Progressive Technology of Fluoride Chemicals for ULSI Manufacturing

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Atomically clean and native oxide-free silicon surface is obtained by hydrogen fluoride gas treatment in fluorine passivated metallic system. Selective etching of native oxide from several silicon oxide films is achieved in extremely anhydrous environment. The terminated fluorine on silicon surface can be removed by the Xe or IR irradiation and the single crystalline of epitaxial silicon is performed on the bare silicon surface. The clean-up effect of surface impurities by hydrogen fluoride gas is recognized.

I.Introduction

The perfect cleaning technology of wafer surface is essential requirement for the progress of ULSI manufacturing. Surface contamination is mainly caused by organic materials, metalic materials and native oxide films. Dry cleaning of those materials have been developed except native oxide, though, the native oxide-free surface contributes to the progressive process technology. Selective etching of native oxide from several silicon oxide films was considered as impossible technology so far. The etching technology by hydrogen fluoride gas with water vapor has been used for surface cleaning of wafer.[1] However, this technology can not achieve the selective etching of native oxide, because all silicon oxide films such as thermal and CVD oxide are etched away with a native oxide at the same time. Furthermore, metallic system can not be used, because hydrogen fluoride gas with water vapor is too corrosive, and a plastic system can not be used due to the out-gassing property.

The new principle of selective etching of silicon oxides using extremely anhydrous hydrogen fluoride gas has been developed,[2)-4)] and the practical application is promoted here. The cleanliness of etching system must be absolutely improved. The fluorine passivation technology of metal surfaces has been developed for the corrosion-free, and out-gas-free metallic system.[5)-7)] The performance of clean silicon surface has been evaluated.

II.Selective Etching of Native Oxide and Various Silicon Oxide Films

Fig.1 shows the surface cleaning system based on the ultra clean technology mode[8)]. The system is constituted by a generating system of a ultra pure anhydrous hydrogen fluoride (HF), a supplying system of ultra pure nitrogen, a cleaning chamber and system monitors. The system was constructed by mirror-polished stainless steel (SUS 316), and all paths of HF were fluorine-passivated. The irradiation effects on the wafer surface can be examined by a cleaning chamber with a calcium fluoride crystal window. The generation principle of extremely anhydrous HF gas is based on the vapor pressure of HF and the gas-liquid equilibrium of HF/H_2O system. Nitrogen flows into the HF vessel which is cooled at the temperature from -50 to -80°C. The concentration of HF in N_2 is regulated exactly from 0.5 to 5.0% controlling the temperature of HF vessel, and the H_2O concentration in HF gas is suppressed less than 0.004 ppm due to the effect of the equilibrium of HF/H_2O. Fig.2 shows the HF critical concentration for various silicon oxides relating to H_2O concentration in gas phase. Each silicon oxide is etched away on the upper region of its HF critical concentration line, but is not etched at all under the line. the PSG film is etched away under the HF concentration of 0.1 vol%. Fig.3 shows the SEM of selective pattern-etching of multi-layer oxides films consisting of thermal oxide film (8900A), PSG film (6000A) and resist pattern. PSG film is pattern-etched by the HF gas containing 0.17% HF and 0.02 vol ppm H_2O and shows definite boundary without affect on thermal oxide film. The HF critical concentration changes with the surface structure of oxide films. Fig.4 shows the charactor change of native oxide by heat treatment where the HF critical concentration shifts to higher value due to the shift of Si_{2p} binding energy to higher value and the contact angle to hydrophobic side.

III.The Evaluation of Dry-Cleaning Surface

Fig.5 shows XPS spectra of the dry cleaned and wet cleaned surfaces of silicon. Spectrum around 103-104 eV is Si_{2p} of native

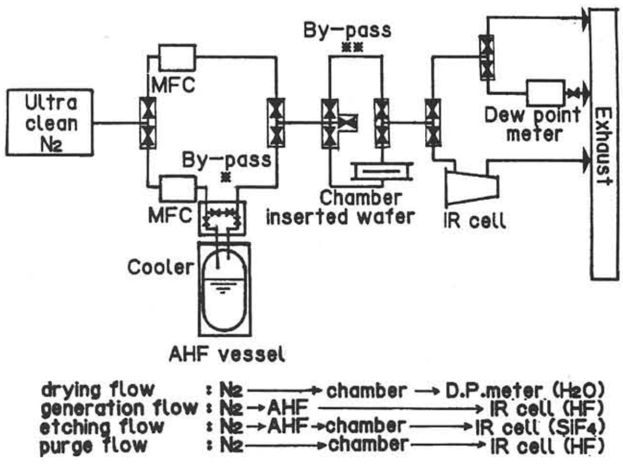


Fig.1. Dry Cleaning System for Ultra Clean Surface using HF Gas

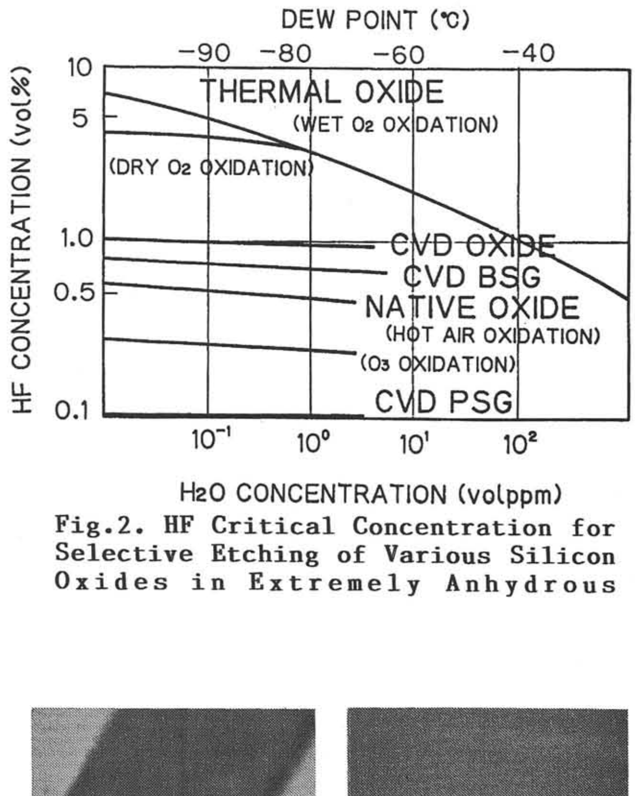
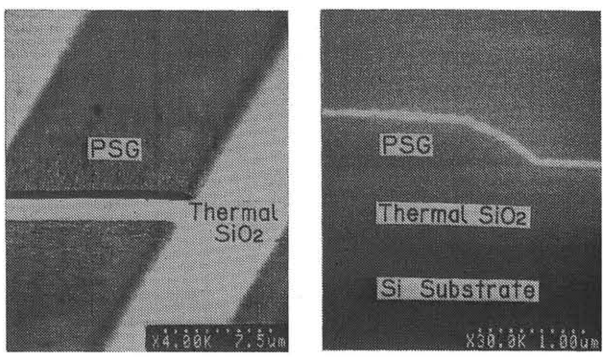


Fig.2. HF Critical Concentration for Selective Etching of Various Silicon Oxides in Extremely Anhydrous



plane **cross-section**

Fig.3. SEM of Selective Pattern Etching Surface of Multi Layer Silicon Oxide Films

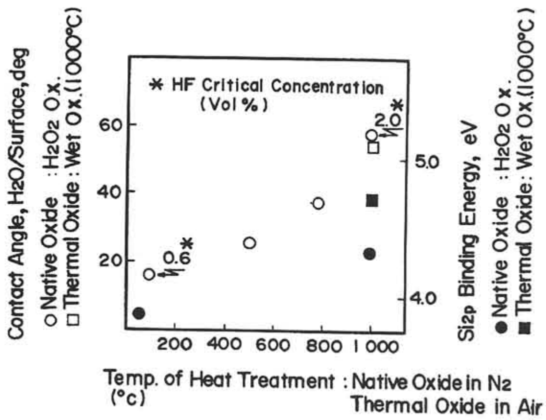


Fig.4. The Change of HF Critical Concentration in Heat Treatment of Native Oxide Film Relating Surface Properties

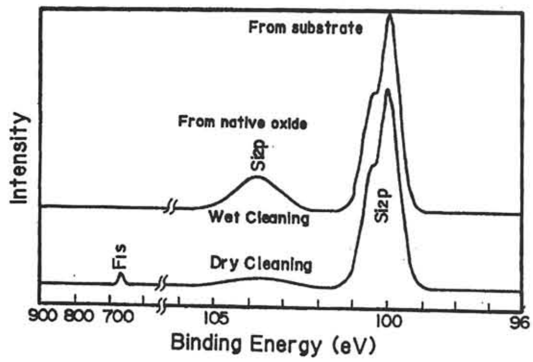


Fig.5. Si_{2p} and F_{1S} XPS Spectra on Wet and Dry HF Cleaning

Table I. Crystal Structure and Resistivity of Epitaxial Silicon on HF Cleaning Surfaces

Table I Resistivity of sputtering epitaxial silicon

Silicon Substrate 1)		Epitaxial Silicon	
HF cleaning	SiO_x 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.	$3{\sim}5\times10^6$

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

oxide. The peak of dry cleaning is smaller than that of wet cleaning. In the wet cleaning, SiO_2 is considered to be formed by rinsing in D.I water. A quantity of SiO_2 is small in the dry cleaning, but F_{1s} spectrum of fluorine is recognized on the surface. It is elucidated that fluorine terminates on the silicon surface dry-cleaned by hydrogen fluoride gas. The effect of fluorine terminated silicon surface on succeeding process was evaluated. Epitaxial silicon films on the silicon substrate treated by three kinds of pretreatments were evaluated [9]. From the reflection electron diffraction pattern on the three experiments, single crystal silicon is obtained on the wet cleaned surface, but is not obtained on the dry cleaned surface and a no-treated surface. Table I shows the crystal structure and sheet resistivity of silicon films. The sheet resistivity of film on the wet cleaned surface is 100Ω/□, but it is 3-5 x 10^6 Ω/□ on the dry cleaned and the no-treated surface. The film on the dry cleaned surface has been confirmed to exhibit similar characteristics to native oxide with 7 A thickness on the substrate. The terminated fluorine must be eliminated before succeeding processes. It is confirmed that the irradiation of Xe lamp or IR lamp for 1 min under the reduced pressure of 1 x 10^{-8} torr can remove the terminated fluorine from the dry cleaned silicon surface [10], as shown in Fig.6. The epitaxial silicon on the eliminated surface is confirmed to be the single crystal structure by the refection electron diffraction pattern as shown in Fig.7. The cleanliness of the bare silicon surface after cleaning of native oxide is examined by Total Reflection X-Ray Fluorescence (TREX), compared with several wet cleaning such as RCA, H_2O_2/HF cleaning[11] and HF drain-cleaning. The

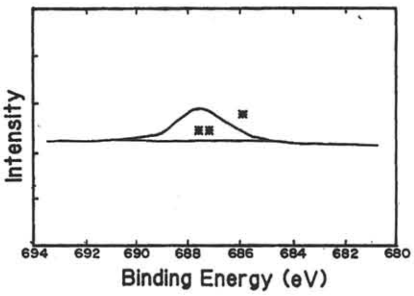


Fig.6. F_{1S} XPS Spectra of Fluorine Terminated Surface after Xe or IR Lamp Irradiation

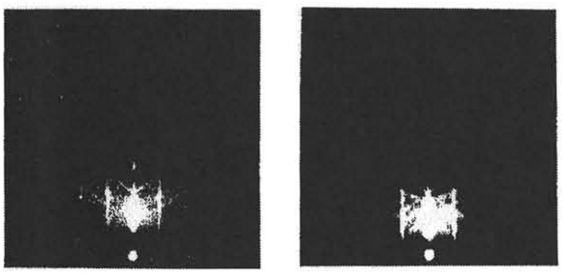


Fig.7. Refection Electron Diffraction Patterns of Epitaxial Silicon on HF Cleaning Surfaces

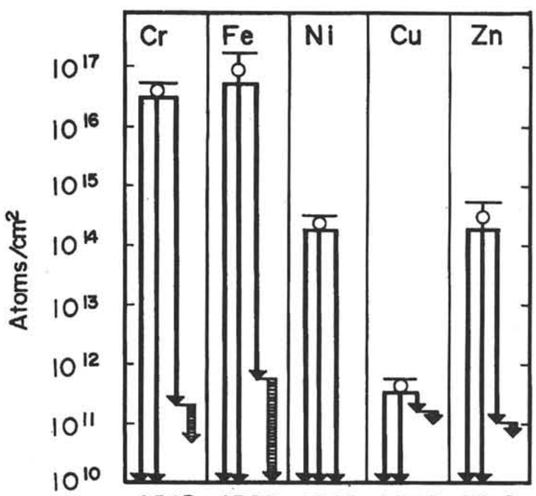


Fig.8. Evaluation of The Clean-up Effect on Surface Impurities by TREX After Cleaning of Native Oxide

clean-up effect at the atoms level from 10^{14}-$10^{17}/cm^2$ to $10^{11}/cm^2$ regarding Cr, Fe, Ni, Cu and Zn by hydrogen fluoride gas treatment is recognized as shown in Fig.8.

IV.Conclusion

The selective etching of native oxide has been performed by high purity and extremely anhydrous hydrogen fluoride and the fluorine passivation technology realized the clean metallic system for the surface cleaning. The bare silicon surface was evaluated by the sheet resistirity and crystal structure of epitaxial silicon. The cleaning effect of metallic contamination by hydrogen fluoride gas was recognized at the atoms level of $10^{11}/cm^2$.

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