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Characterization of $Si-SiO_2$ Interfaces Formed after Photo-Excited Cleaning

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Oxide films formed by thermal oxidation after photo-excited cleaning using chlorine radicals have been studied. The resulting $Si-SiO_2$ interface trap density was on the order of 10^9 $eV^{-1}cm^{-2}$ which is not attainable with conventional wet cleaning. The carrier recombination velocity at the $Si-SiO_2$ interface was also reduced. The dielectric breakdown field of MOS diode formed on photo-excited cleaned surface was over 11 MV/cm. Chlorine was not detected by Auger electron spectroscopy on a silicon surface just after photo-excited cleaning. These results promise an all dry cleaning process.

1. Introduction

In the manufacture of large scale integrated (LSI) circuits, the cleaning process for gate oxidation of silicon should completely eliminate harmful impurities such as heavy metals and alkalines, leave the silicon surface smooth and flat after cleaning, leave no residual active species, and not affect later processes. Thus in VLSI/ULSI production, it is more advantageous to use dry than wet cleaning.

The authors reported lately the photo-excited cleaning of silicon with photo-excited chlorine radicals.[1,2] This technique uses ultra-violet (UV) light and chlorine gas, and significantly reduces contaminants such as Na, Mg, Ca, Fe, and Cr. This paper describes how thermal SiO_2 films and their interfaces are improved with this technique.

2. Experiments

Four-inch boron-doped p-type silicon wafers in the experiments were with resistivity between 7.5 and 12.5 Ωcm and that were (100) oriented surface. All wafers were treated with $NH_4OH-H_2O_2-H_2O$ solution, HNO_3, and deionized water.[3] With this wet treatment, a 1.2 nm-thick native oxide was formed on the silicon. Just after the wet treatment, the wafer was set in the photo-excited cleaning chamber.

The cleaning equipment consisted of a quartz reaction chamber, a halogen lamp for wafer heating, and a microwave-excited mercury lamp for UV irradiation. The UV intensity between wavelengths of 200 and 300 nm was 22 mW/cm^2. The silicon wafer was kept at 150°C by heating from the reverse side. High-purity (99.999%) chlorine gas was used as the cleaning gas. The chlorine gas pressure was 2.7 kPa, and the flow rate was 50 ml/min. After photo-excited cleaning, we examined cleaning levels and residues on the surface.

Contaminant concentrations were measured by flameless atomic absorption spectrophotometry.[4] The native oxide on the cleaned surface was HF vapor etched, then the HF solution containing contaminants was analyzed. Surface residues were also evaluated by Auger electron spectroscopy, and surface roughness with Mirau optical profilometer. A gate oxide film was thermally grown on the photo-excited cleaned surface at 1000°C in dry oxygen. The 0.16 cm^2-aluminum electrodes were formed on the gate oxide film to measure C-V and C-t characteristics and dielectric breakdown voltage.

3. Results and discussion

3-1 Reduction of contaminants after photo-excited cleaning

Contaminant concentration after photo-excited cleaning is shown in Fig. 1. The sample surfaces were etched to a depth of 30 nm and 60 nm during photo-excited cleaning. The elements such as Fe, Ni, Cr, Al, Cu, Ca, Mg, and Na were analyzed. The amounts of Ni, Cr, Al, and Cu were too low to be detected. The amount of Fe after even 30 nm-etching was 1/10 that of a conventional wet treated surface. The amounts of Ca and Na were reduced to 1/3 and Mg was decreased gradually with depth. These elements were removed as chlorides as a result of reaction with chlorine radicals, or were removed with the silicon by etching. The latter case is what happened with Ca, because the vapor pressure of $CaCl_2$ is low.

The roughness of the silicon surface before and after photo-excited cleaning is shown in Fig. 2. R_{rms} is the root mean square of the height distribution. The R_{rms} of the reference was 0.48 nm. The R_{rms} was 0.50 nm for a 30 nm-depth etch and 0.65 nm for 60 nm. The surface roughness is increased slightly by photo-excited cleaning.

The Auger electron spectroscopy of the silicon surface after 60 nm of etching with

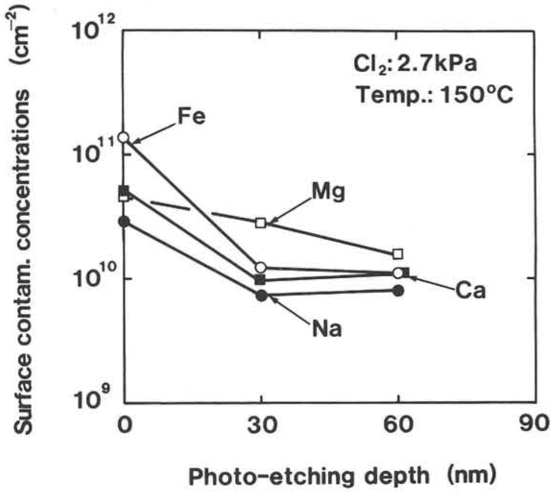

Fig. 1. Dependence of contaminant concentrations on etching depth

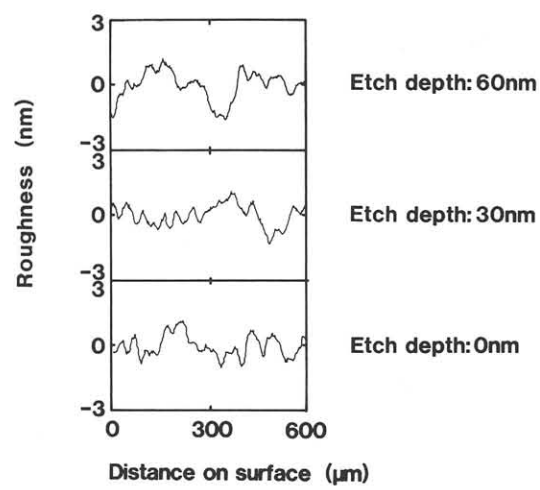

Fig. 2. Surface roughnesses measured with a Mirau optical profilometer

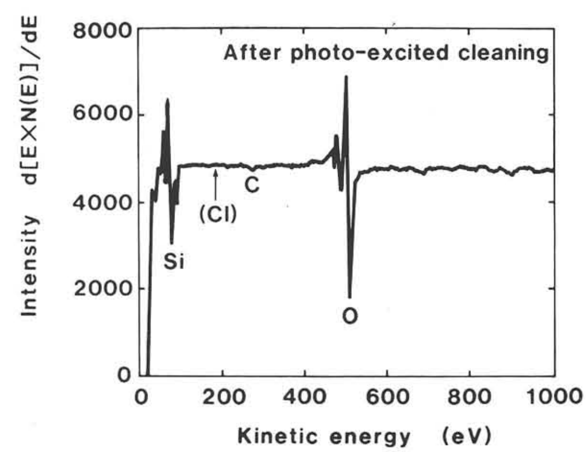

Fig. 3. Auger electron spectrum of a 60 nm etched silicon surface after photo-excited cleaning

photo-excited cleaning is shown in Fig. 3. Si, C, and O were found from this spectrum. Chlorine was, however, not found on the surface. There is also less carbon in photo-excited cleaning than in the conventional method.

3-2 Electrical characteristics of Si-SiO_2 interface

Figure 4 shows a capacitance-voltage curve of the aluminum gate MOS diode. The diode was made on silicon etched 60 nm with photo-excited cleaning. The curve shows no hysteresis which indicates that no carrier traps are generated and that there is no ion contamination after the cleaning process. The flatband-voltage V_{FB} is -0.91 V which is exactly the same as that of the conventional wet cleaned one.

Interface trap densities D_{it} at Si-SiO_2 interfaces were measured with quasi-static C-V. The voltage sweep was 0.05 V/s. Figure 5 compares the energy distribution of D_{it} among the samples. The density after photo-excited cleaning with 30 nm-etch has a very low value (on the order of 10^{10} $eV^{-1}cm^{-2}$) and is comparable with the reference. However, after 60 nm, the D_{it} decreased significantly. The the minimum D_{it} is on the order of 10^9 $eV^{-1}cm^{-2}$ which is not attainable with the conventional wet process.

Figure 6 shows the carrier recombination velocity at the Si-SiO_2 interface. The data was taken by the Zerbst plot made with a C-t technique at 50°C.

Dielectric breakdown voltages are greatly influenced by metal contamination.[5] Figure 7 shows improvement of the breakdown voltage distribution over a wafer after photo-excited cleaning. The conventional sample shows some initial short dots and

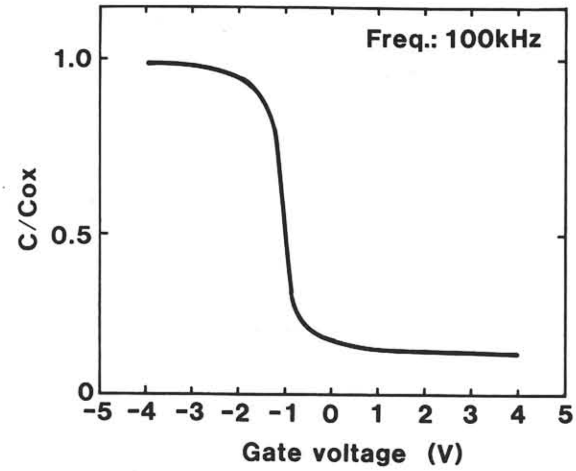

Fig. 4. Typical C-V curve of MOS diode made with photo-excited cleaning

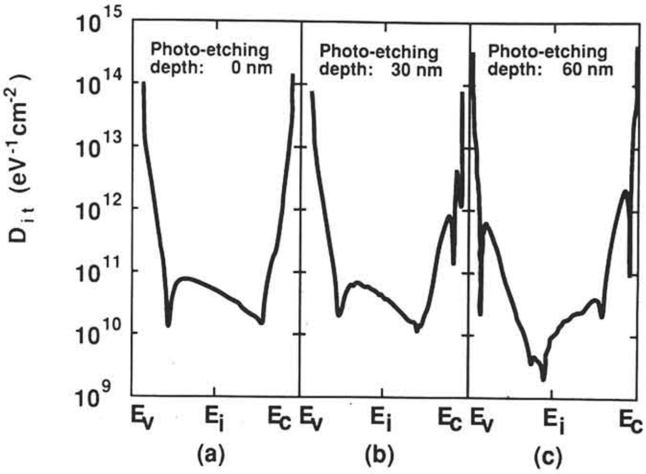

Fig. 5. Interface trap densities Dit using quasi-static C-V method (a) wet cleaned (0 nm etched), (b) 30 nm etched, (c) 60 nm etched

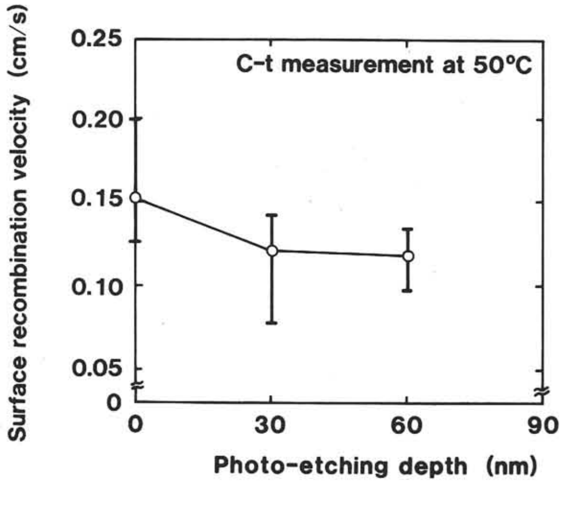

Fig. 6. Etch depth dependence of surface recombination velocity

tailing near the intrinsic value. The former one surely is due to particle contamination. The last one is due to metallic contamination. In samples that were photo-excited cleaned both defects were removed, resulting in showing very sharp distributions for both 30 nm and 60 nm etched samples. The peak value of these samples exceeded 11 MV/cm compared to the 9.5 MV/cm of the reference.

4. Conclusion

Si-SiO_2 interfaces formed after thermal oxidation with photo-excited cleaned surfaces were investigated. Contaminant concentrations on silicon surfaces such as Fe, Ca, Na, Mg were reduced by the photo-excited cleaning. Although the surface roughness was increased by photo-excited cleaning, surface residues such as chlorine and carbon atoms were not detected by Auger electron microscopy. The minimum Si-SiO_2 interface trap density was on the order of 10^9 $eV^{-1}cm^{-2}$ which is not attainable with conventional wet cleaning. The carrier recombination velocity at the Si-SiO_2 interface decreased gradually with photo-excited cleaning. The dielectric breakdown fields of MOS diodes formed after photo-excited cleaning exceeded 11 MV/cm. These results make it possible to utilize the newly developed dry cleaning by substituting the conventional wet one.

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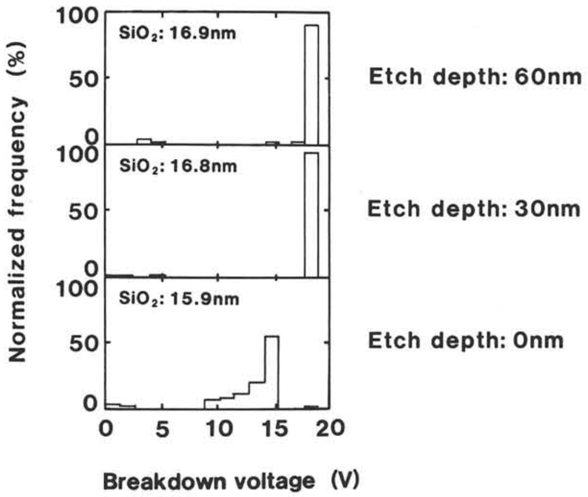

Fig. 7. Distribution of dielectric breakdown voltage in oxide film

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