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Reliability-Improvement of the MOS Structures Using Photo-Excited Dry Cleaning before Oxidation

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Photo-excited dry cleaning with Cl_2 greatly improved the reliability of MOS structures. The interface state density and flat band voltage shift of MOS diodes after Fowler-Nordheim current injection were estimated. At an etch depth of 6 nm, photo-excited dry cleaning resulted in much lower state density than conventional wet cleaning. We found that these improvements may be attributed to smoothing short-periodic rough surfaces and decreasing residual metals during photo-excited cleaning.

1. Introduction

As MOS devices become smaller, decreased reliability caused by hot carriers has been one of the most serious problems. It is reported that interface states at the Si/SiO_2 interface and traps in SiO_2 cause hot carrier induced degradation of MOSFET at high stresses.[1-3] Reducing interface states and traps in oxides is a key to making reliable MOS structures. Several methods to reduce interface state density and traps in oxides have been proposed. A low density of carrier traps in SiO_2 films was achieved using ultra-dry oxidizing atmosphere.[4] F and Cl in SiO_2 suppressed the generation of interface states.[5,6]

We already reported that damage-free photo-excited cleaning with Cl_2 improved the break-down field of SiO_2 and surface recombination velocity at a Si-etch depth of more than 30 nm. We found that metal contaminants such as Fe, Mg, Ca, Na on the silicon surface were eliminated during photo-excited cleaning, and we proposed a cleaning model where they react with chlorine radicals and the reaction-products were removed through vaporizing or lift-off.[7-10]

In this paper, we present the measured characteristics of the Si/SiO_2 interface obtained from high-frequency and quasi-static C-V curves before and after Fowler-Nordheim stress when silicon was etched by photo-excited cleaning before oxidation.

2. Experimental

Aluminum gate MOS capacitors were fabricated on P-type (100) oriented Si wafers with a resistivity of 10 Ωcm in a similar method to a previous paper.[9] All wafers were first treated by conventional RCA wet cleaning. In photo-excited cleaning, chlorine radicals were derived from 99.999% pure Cl_2 gas using ultraviolet(UV) light at 22 mW/cm^2 of wavelengths from 200 to 300 nm. The UV light was irradiated for 30 s on the wafer which was kept at 170°C. Chlorine gas pressure was 27, 270, and 2700 Pa and the etch depth of Si was 0, 6, and 44 nm. After photo-excited cleaning, Si was oxidized in dry oxygen for 10 min and was annealed in N_2 for 20 min continuously at 1000°C. Seventeennm-thick oxide films were obtained. Post-metal-annealing was done at 420°C for 30 min in forming gas(N_2-H_2).

We estimated the reliability of MOS capacitors with a flat-band voltage (V_{FB}) and interface state density (D_{it}) derived from high-frequency and quasi-static C-V curves before and after Fowler-Nordheim(F-N) stress. F-N carrier injection was done under the following conditions. A negative bias was applied to the gate electrode and the constant current was flowed. Current density was 2.6×10^{-5} A/cm^2, injection time was 500 s, and the injection carrier number was 8.1×10^{16}/cm^2. Applied voltage was more than 16 V.

The etch depth of Si during cleaning were estimated measuring the step-height between etched and non-etched regions masked by SiO_2 with a Talystep. Surface morphology was investigated with the scanning tunneling microscope (STM). The chlorine concentration at the Si surface after photo-excited cleaning and that in thermal oxide films were both analyzed by ion-chromatography. The native oxides and the thermal oxide films were etched by HF drops, and the HF solution containing chlorine was analyzed.

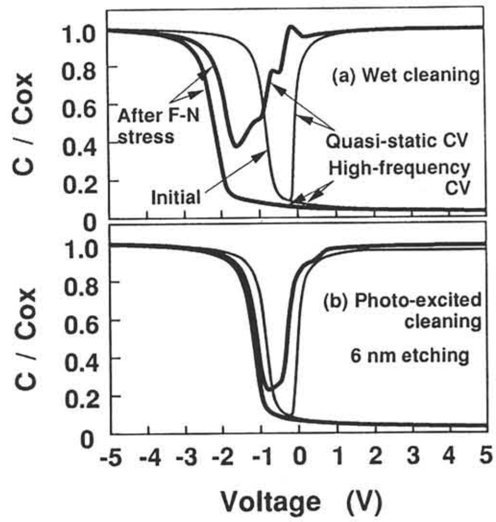

Fig.1. High-frequency and quasi-static C-V curves before and after Fowler-Nordheim current injection.

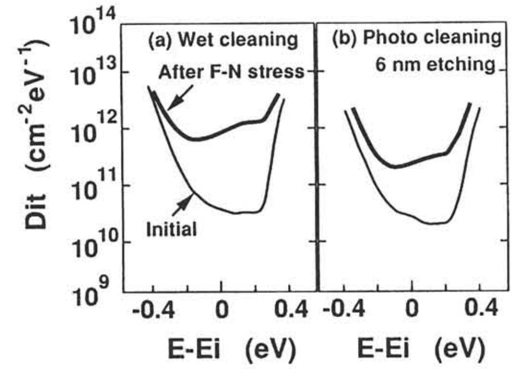

Fig.2. Interface state distribution before and after Fowler-Nordheim current injection for wet(a) and photo(b) cleaning.

3. Results and Discussion

Figure 1 shows high-frequency and quasi-static C-V curves before and after Fowler-Nordheim (F-N) current injection. Fig.1(a) shows curves for conventional wet cleaning and Fig.1(b) those for photo-excited cleaning process. There is little difference before F-N injection, but clear difference occurred after F-N injection. The shift to negative voltage of high-frequency C-V curves became small and the shape of quaisi-static C-V curves after injection changed. Figure 2 shows interface state distribution for wet(a) and photo(b) cleaning. The interface state density(D_{it}) in Si band gap decreased after photo-excited cleaning. Especially, the interface state peak at 0.2 eV above the mid-gap(Ei) for wet cleaning lowered after photo-excited cleaning. Figure 3 and Figure 4 show V_{FB} and the interface state density at the mid-gap as a function of etch depth. The shift of V_{FB} decreased to 1/5 after etching of 6 nm by photo-excited cleaning (Fig.3). D_{it} after F-N injection decreased to 1/3 from 8.7×10^{11}cm^{-2}eV^{-1} to 2.4×10^{11}cm^{-2}eV^{-1} by 6 nm photo etching. (Fig. 2,4) But after etching Si 44 nm, the V_{FB} shift and D_{it} both increased. The V_{FB} shift to negative voltage was due to generating positive fixed charges in oxide films and interface states. These fixed positive charge occur when holes generated in oxide films are trapped. Electrons were injected from the gate electrode during F-N stress because negative bias was applied. Electrons injected to oxide films obtain energy in high field oxide films, occur impact ionization, and generate the hole-electron pairs.[11] Impact ionization and hole trapping occur at defects in oxide films. Interface states are thought to induced by hole-trapping at the interface state sites of the Si-SiO_2 interfaces. The interface state sites exist at the broken Si-O bonds.

We thought that residual metal contaminants, surface morphology or chlorine atoms before oxidation affected V_{FB} shift and D_{it}. We already reported that metal contaminants such as Fe, Mg, Ca, Na on Si were eliminated by photo-excited cleaning.[7-10] Metal contaminants were thought to weaken the Si-O bonds in oxides and at the interface, and to make the hole-trapping sites and the interface state sites. However, there are other causes besides metals because there are more interface states (about 10^{11} $cm^{-2}eV^{-1}$) after F-N stress than metal contaminants for each element (less than 10^{10} cm^{-2}).

Figure 5 shows the surface morphology of Si. Si etching by 6 nm smoothed short periodical roughness after wet cleaning, but long periods of roughening occurred. As Si was etched deeper, the magnitude and period of the roughness increased. We thought that V_{FB} shift and D_{it} at 6 nm etching decreased because the short periodical roughening surface was removed, and that V_{FB} shift and D_{it} at 44 nm etching increased because the long periodical and local roughening proceeded. Short periods of rough surfaces had sharp surface edges, and enhanced the electric field in oxide films locally. Impact ionization occurs above 13 V, and it depends on applied field. We thought that the locally high field promoted impact ionization and hole-trapping, and increased the interface states at applied voltage above 16 V.

There were more than 10^{14} chlorine atoms cm^{-2} in the native oxides after photo-excited cleaning at every condition of photo-excited cleaning. We do not have clear data

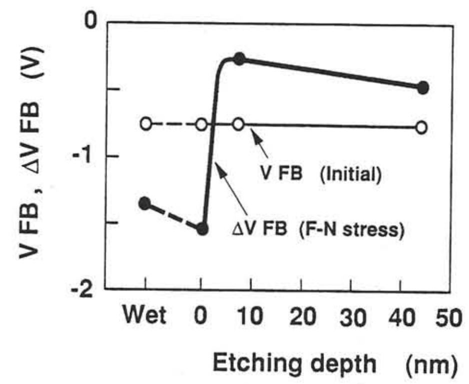

Fig.3. Photo etching depth dependence of flat band voltage (V_{FB}) at the initial state and flat band voltage shifts (ΔV_{FB}) during Fowler-Nordheim injection.

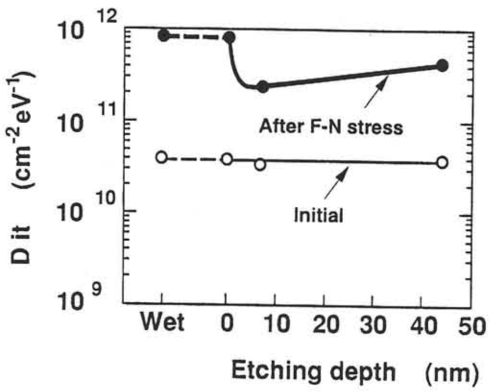

Fig.4. Photo etching depth dependence of interface state density (D_{it}) before and after Fowler-Nordheim injection.

(a)

(b)

(c)

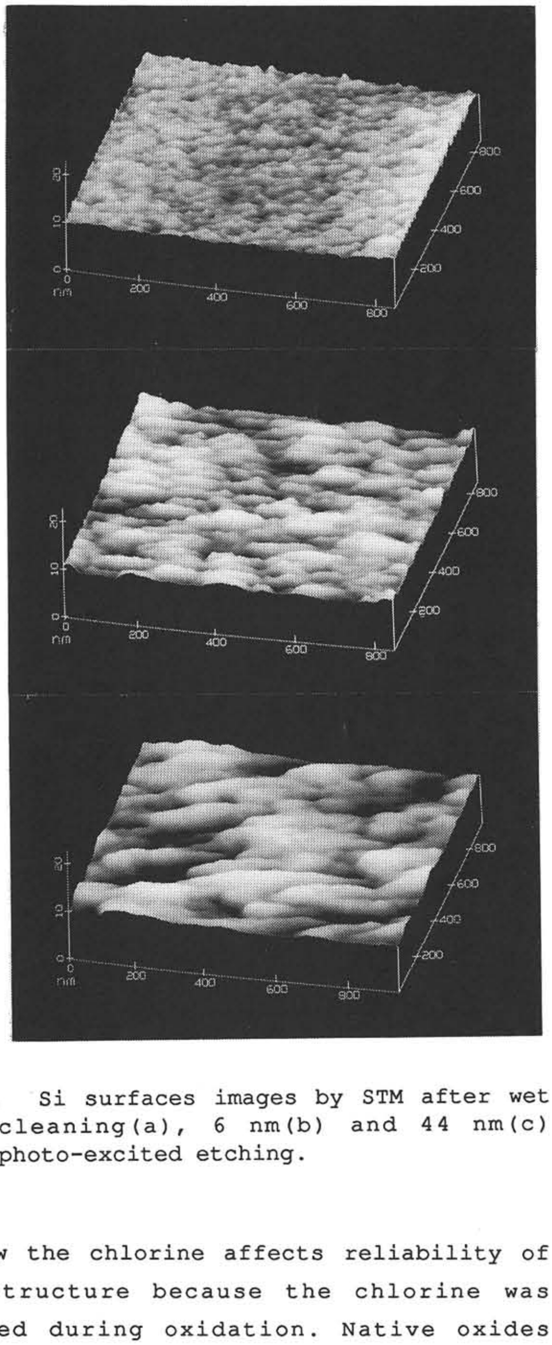

Fig.5. Si surfaces images by STM after wet cleaning(a), 6 nm(b) and 44 nm(c) photo-excited etching.

on how the chlorine affects reliability of MOS structure because the chlorine was reduced during oxidation. Native oxides formed after photo-excited cleaning might also affect properties of thermal SiO_2 films and Si/SiO_2 interfaces.[12]

4. Conclusion

We have shown that photo-excited dry cleaning with Cl_2 greatly improved reliability of MOS structures with etching depth of only 6 nm. This improvement may be attributed to smoothing the short range roughness and decreasing amount of residual metals during photo-excited cleaning.

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