Dramatic Improvement of Hot-Electron-Induced Interface Degradation in MOS Structures Containing F or Cl in SiO_2

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***Abstract*—The effects of F and Cl incorporated in SiO_2 on the susceptibility of metal/SiO_2/Si (MOS) interface to hot-electron damage have been studied. It has been found that, by introducing a very small amount of F or Cl in the thermal SiO_2, the generation of interface traps by Fowler-Nordheim (F-N) tunneled hot electrons can be greatly suppressed. In addition, the gate-size dependence of hot-electron-induced interface traps, which is normally observed in samples made of dry oxides, does not appear in such chlorinated or fluorinated samples. When excess amounts of F or Cl are introduced into SiO_2, however, the above mentioned benefits will diminish. The possible roles that F and Cl play that lead to the experimental observations will be discussed.**

I. Introduction

THE EFFECTS OF charged carrier injection on the degradation of the performance of metal/SiO_2/Si (MOS) devices have been extensively studied [1]-[4]. Of particular interest is the generation of the interface traps at the SiO_2-Si interface [1], [4], which are known to affect the electronic properties of the MOS transistors.

The use of chlorine in furnace tube cleaning and thermal oxidation is a widely accepted practice. More recently, it has been reported that by introducing small amounts of fluorine during thermal oxidation, significant improvement in the MOS properties can be accomplished [5]. The purpose of this study was to determine how the presence of Cl or F during thermal oxidation would affect the response of the MOS capacitor to hot-electron damage. It will be shown that, by introducing appropriate amounts of F or Cl, the generation of the hot-electron-induced interface traps can be significantly reduced.

II. Experimental

The MOS capacitors used in this study were fabricated on (100) oriented p-type Si wafers with a resistivity of 1–2 Ω·cm.

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Three types of oxides were investigated in this study: 1) oxides that do not contain Cl or F (hereafter designated the *control* samples; 2) oxides grown in the presence of F (hereafter designated the *fluorinated* sample); and 3) oxides grown in the presence of trichloroethane (TCA) (hereafter designated the *TCA* sample). Their growth processes are briefly described below.

A. Control Oxide

Wafers were cleaned by the RCA cleaning process, followed by rinsing thoroughly in DI water. They were then dried in N_2, and loaded into the dry oxidation furnace set at 1000°C. The oxidation times were adjusted to yield oxide thicknesses of 370–500 Å.

B. Fluorinated Oxide

After the RCA cleaning process, the wafers were immersed in an aqueous HF solution ($\leq$ 3 percent) for ~ 5 min before they were dried in N_2 and loaded into the oxidation furnace set at 1000°C. It has been shown that the above mentioned treatment in HF causes the Si surface to be covered with a layer of fluorine [6], which is consistent with the observation that the wafer surface remains hydrophobic for many minutes even after it is exposed to air. It has also been reported that subsequent oxidation causes the F to be incorporated in the SiO_2 network near both interfaces [5].

C. TCA Oxide

Thermal oxidation was performed at 1000°C in a dry O_2 + TCA ambient, and oxidation times were adjusted to produce 370-Å-thick oxides for TCA concentrations of 0.3 and 0.6 percent. Here the TCA concentration is defined as the volume flow ratio between TCA and dry O_2, and is adjusted by controlling the temperature (10–20°C) of the TCA bath while bubbling through it N_2 carrier gas. The flow rate of the N_2 carrier gas was 0.2 l/min, while that of the dry oxygen was 2.2 l/min. The total amount of Cl introduced was also controlled by the TCA purge time (ranging from 10 s to 20 min) during the initial stage of oxidation.

After thermal oxidation, all wafers were *in situ* annealed in N_2 at the growth temperature for 30 min, followed by gate Al deposition, photolithography, and wet etching to define circular dots of 0.02, 0.05, and 0.08 cm in diameter. After removing the oxide from the back side and contact formation,

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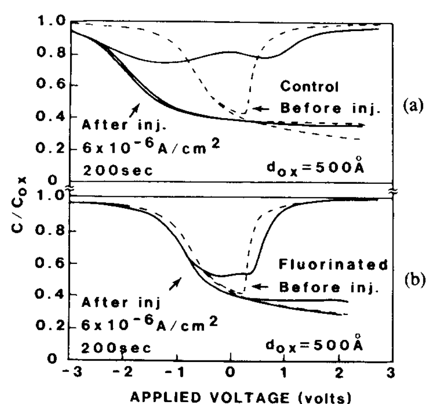

Fig. 1. High-frequency and quasi-static $C-V$ curves before and after constant-current electron injection (injected from Si substrate). (a) Dry oxide. (b) Fluorinated oxide.

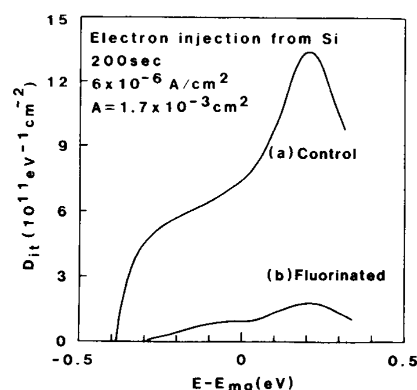

Fig. 2. Interface trap distribution after hot-electron injection in sample containing (*a*) dry oxide and (*b*) fluorinated oxide.

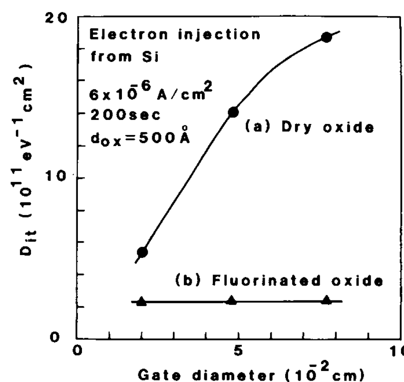

Fig. 3. Gate-size dependence of interface trap density after hot-electron injection in sample containing (*a*) dry oxide and (*b*) fluorinated oxide.

the wafers were subjected to a post-metal-anneal (PMA) at 400°C in forming gas (95-percent N_2, 5-percent H_2) for 30 min.

Constant-current Fowler–Nordheim (F–N) electron injection was done using a HP 4145 Semiconductor Parameter Analyzer. In this study, electrons were always injected from the Si substrate (gate biased positively) to eliminate the effects of nonuniform electron injection from the gate edges of the capacitors [4].

The density and energy distribution of the interface traps before and after the hot-electron injection were analyzed by measuring the high-frequency and quasi-static capacitance-voltage ($C-V$) curves, at a ramp rate of 0.01–0.05 V/s. The low ramp rate was essential for the quasi-static $C-V$ measurements, otherwise large errors would occur in the interface trap distribution, due to the nonequilibrium effect resulting from the long minority-carrier response time.

III. Results and Discussion

Fig. (a) and (b) shows high-frequency and quasi-static capacitance-voltage ($C-V$) curves for a control and a fluorinated sample measured after F–N electron injection from the Si substrate at a constant current density of 6×10^{-6} A/cm^2 for 200 s. It is obvious that the sample with fluorinated oxides sustained much less hot-electron induced damage, both in terms of the voltage shift of the high-frequency curves and the distortion of the quasi-static curves.

The dramatic improvement in the resistance to hot-electron damage for the fluorinated sample is also illustrated in Fig. 2, where the interface trap densities for the two samples after the same amount of electron injection are compared. Note that a broad peak appears above midgap for both samples. This peak has been found to be characteristic of all our samples after hot-electron injection, and the magnitude of this peak will be used as a convenient measure of the degree of damage, as it was used previously in the study of radiation effects [7].

Another interesting phenomenon is that the gate-size dependence of interface traps generated by F–N electron injection, which normally occurs in nonfluorinated samples [4], disappeared for the fluorinated samples (see Fig. 3, where D_{it} is the magnitude of the characteristic peak above midgap). This suggests that the effect of gate-induced stress on the generation of interface traps [4], [7] has been minimized in samples containing fluorinated oxides. Similar effects as described above have been observed in samples fluorinated by adding small amounts of NF_3 in dry O_2 during oxidation [8].

The hot-electron-induced interface traps have also been studied for samples with oxides grown in dry O_2 + TCA. Fig. 4 shows the hot-electron-induced interface trap peak density as a function of the TCA purge time during oxidation, and a minimum clearly emerges from such a plot. The existence of such a minimum has been confirmed by several different runs, and further experimentation is underway to reduce the TCA flux to achieve a broader minimum occurring at longer purge times, so as to establish a more practical process.

For samples processed with TCA purge times near the minimum shown in Fig. 4, we also observed almost no gate-size dependence, very similar to the result for the fluorinated sample shown in Fig. 3.

The interface traps in all the samples studied (including the control) have been found to change with time at room temperature after the termination of electron injection. This effect has been reported elsewhere [9]. The interesting thing is that, compared with the control, samples with fluorinated

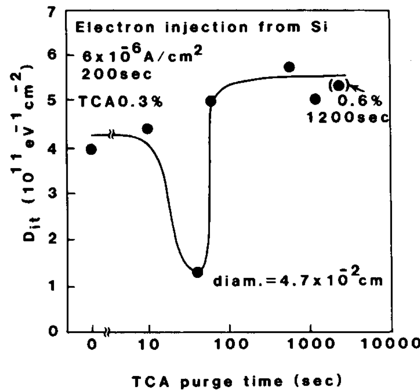

Fig. 4. Hot-electron-induced interface trap density as a function of the duration that the TCA was turned on during oxidation.

oxide or grown with very small amounts of TCA exhibit much smaller changes with time.

From the results presented above, it is apparent that the fluorinated sample behaves very similarly to the TCA sample (the one grown with small amounts of TCA), and that both exhibit significantly improved resistance to hot-electron damage.

The lack of gate-size dependence in the hot-electron-induced interface traps for the fluorinated and the TCA samples suggests that the effects due to the interfacial stress [4], [7] are suppressed in these samples. One possibility is that the incorporation of F or Cl in the oxide substantially reduces the as-grown bond strain gradient near the SiO_2–Si interface to a point that it is overcome by the Al-gate induced strain gradient (which is in the direction opposite to the as-grown gradient [7]). According to the Bond Strain Gradient model [10], this would mean that the nonbridging oxygen defect, which could form interface traps when it migrates to the SiO_2–Si interface, would tend to move in the direction away from the SiO_2–Si interface. Therefore, one would not expect to see any dependence on the gate size as long as the gate-induced stress is sufficiently large for all the gate sizes studied. This model would also be consistent with the reduced interface trap density after hot-electron injection and weaker subsequent time dependence in the fluorinated and the TCA samples (the ones grown with small amounts of TCA).

The fact that excess amounts of TCA during oxidation cause the samples to become less resistant to hot-electron damage may be due to the hydrogen species in the TCA ($= C_2H_3Cl_3$) that are incorporated into the oxide, and that are known to enhance the hot-electron induced interface degradation.

IV. Summary

By introducing very small amounts of F or Cl in SiO_2 during the initial stage of thermal oxidation, we have been able to dramatically alter the interface properties of MOS capacitors subjected to hot-electron injection. More specifically, the hot-electron-induced interface trap density is significantly reduced, the gate-size dependence is greatly suppressed, and the post-injection time dependence of the interface traps is slowed down considerably.

These results are consistent with a model that suggests that the bond strain distribution near the SiO_2–Si interface may be modified by the presence of F or Cl in the SiO_2 network.

We have also demonstrated that, to realize the benefit of TCA, one must exert caution to control its amount. Excess amounts of TCA may cause the oxide to be more susceptible to hot-electron damage, perhaps due to the incorporation of hydrogen into the oxide.

Whatever the mechanisms may be, we believe our findings are of significant technological importance, especially for applications where hot-electron damage is of concern.

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