Chemistry of fluorine in the oxidation of silicon

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The chemical environment of fluorine in the oxide layer of metal-oxide-semiconductor (MOS) structures has been examined by surface analytical spectroscopies. HI treatment of Si(100) results in subsurface SiF formation. Upon oxidation, oxyfluoride moieties are formed with a significant accumulation of fluorine throughout the oxide layer. These changes are correlated to the electrical integrity of MOS interfaces by performing Fowler–Nordheim electron injection studies.

Metal-oxide-semiconductor (MOS) structures with a fluorinated gate oxide layer provide improved radiation hardness, lower interface degradation from hot-electron effects, and better breakdown characteristics. Fluorine incorporation into the oxide layer has been accomplished in several ways and the effects of varying fluorine concentrations, its distribution, and varying the size of the metal gate have also been examined. It appears that controlled incorporation of fluorine into the gate oxide may enhance reliability and performance in future ultralarge scale integrated (ULSI) device technology.

In situ surface analytical spectroscopies are used to study the bonding environments of fluorine atoms on the HF-treated Si(100) surface and that same surface when undergoing subsequent oxidation. Al-gate MOS structures have been prepared and subjected to high-field stressing by Fowler–Nordheim electron injection. Clear correlation between MOS interface quality and fluorine chemistry is observed for the first time.

The experiments were carried out in a multichamber ultrahigh vacuum (UHV)-based integrated processing system; details of the system and the experimental procedures have been described elsewhere. Wafer pretreatment involved one of the following types, (i) a modified RCA clean, i.e., with no HF treatment (MRCA), (ii) a standard RCA clean (SRCA), and (iii) a RCA clean followed by a final 10% dilute HF dip (FHF). For MOS structures, dry thermal oxidation was carried out ex situ in a conventional hot-wall furnace at 950 °C, followed by evaporation of the gate electrodes and post-metallization forming gas anneals. Oxide samples for surface analysis were prepared by in situ thermal oxidation (120 Å), in situ low-temperature UV/O₂ oxidation (12–50 Å), and RCA clean.

Figure 1 shows the changes in the flatband voltage (V₉₀) and the density of interface traps in the midgap region (Dₙ) as a function of injected electron fluence for the different samples. Constant-current Fowler Nordheim electron injection from the gate with fields ranging from 6 to 7 MV/cm was carried out for several periods of 10 s each. V₉₀ and Dₙ were sampled after one and three injection periods, respectively, by high-frequency and quasi-static capacitance-voltage (C-V) measurements. As illustrated in Fig. 1 (top), MRCA, RCA, and FHF samples show decreasing shifts in V₉₀ upon stressing. While for the midgap Dₙ values, FHF samples show the least amount of interface trap generation and the SRCA and MRCA samples behave similarly. These results are similar to previously published data.

High-resolution electron energy loss and thermal desorption spectroscopy (HREELS, TDS) have identified the presence of SiH and SiH₂ groups on the HF-treated Si surface. While C and O contamination levels are below the detection limits of XPS and TDS. Figure 2 shows, by XPS, the amount and chemical character of fluorine for a HF-dipped surface and for that surface subsequently treated by UV/O₂ for various times. Measurements at time (t) = 0 (Fig. 2) show the presence of ~0.2 monolayers (ML) of F within the surface region (~25 Å), angle-dependent data suggesting primarily subsurface distribution. Upon a short 2 min oxidation at 250 °C by the UV/O₂ process, the F 1s intensity increases and the peak shifts towards a higher binding energy oxyfluoride [(F)-(O)-Si] position from the initial SiF₄ bonding arrangement. Continued oxidation results in increasing fluorine concentration in the near-surface region with the peak maximum at the oxyfluoride B.E. position. Oxidation of a HF-treated surface always results in the formation of oxyfluoride complexes, independent of the oxidation procedure employed. This has been verified with oxides grown by thermal (high temperature, gas phase), UV/O₂ (low temperature, gas phase), and RCA oxidations (low temperature, liquid phase).

TDS was used to probe in the gas-phase species desorbed from the HF-treated and UV/O₂ surfaces; indirectly the molecular structure of surface moieties are studied. Figure 3 shows TDS spectra recorded in the desorption temperature range 300–700 °C, using a heating rate of ~5 °C/s. Peaks are shown for m/e ratios of 47 [Fig. 3 (top)] and 63 [Fig. 3 (bottom)] and are assigned to desorbing SiF and SiOF species, respectively. SiF surface moieties are detected for the HF treated surface (t = 0) whereas no peak is observed for SiOF, in agreement with the XPS data of Fig. 2. The relative intensity of the SiF
peak to that for \( m/e = 2 \) (HF treatment results in \( \approx 1.5 \) ML of surface hydrogen\(^{11} \)) suggests that the surface F coverage is \( < 0.2 \) ML. Upon UV/O\(_2\) treatment, the F bonding changes from (SiF) to (SiOF) in agreement with the XPS data in Fig. 2. This is reflected in the peak intensities, with attenuation of \( m/e = 47 \) and growth of \( m/e = 63 \). Isotopic labeling experiments using \(^{18}\)O gas in the UV/O\(_2\) oxidation process (30 s procedure) shifted the SiOF desorption peak to \( m/e = 65 \) while a weak SiF peak (\( m/e = 47 \)) was still present; this supports our mass assignments.

Three features in Fig. 3 need mention. (i) SiOF detected by TDS can originate either (a) from surface groups where fluorine is still attached to a Si atom but there is a neighboring oxygen atom, or (b) from groups where fluorine is directly bonded to an O atom. The exact origin cannot be unambiguously stated from our measurements. Both classes of moieties could exist on the surface with the latter species being predominant (Fig. 2). (ii) The peak desorption temperature for SiF is found to increase slightly upon oxidation. This could be due to the growth of a thin oxide layer which could trap the SiF groups at the interface. (iii) The complete disappearance of the SiF peak after 5 min of oxidation may not imply that such species have been completely quenched during oxidation. During the conversion of SiF to SiOF, there is also rapid oxidation of the substrate with the formation of a thin (15–20 Å in 30 s) oxide layer. Interfacial SiF can remain trapped under the oxide undetected by TDS.

Assuming that the photoelectrons originate from the same depth in both the H-terminated Si and SiO\(_2\) samples, it is interesting that the absolute fluorine concentration increases significantly (> \( 10 \times \)) in the near-surface region during oxidation (Fig. 2). Since the final oxide thickness for the process conditions in Fig. 2 is \( \approx 45–50 \) Å, the photoelectrons must originate primarily from the oxide layer suggesting constant fluorine migration towards the interface and incorporation into the growing oxide. It also im-
The sequence of chemical changes during the oxidation by the RCA and UV/O₂ methods show distinct energy
losses related to the vibration of the O-H bond. Indeed, HREELS measurements on oxides prepared
in MRCA samples, even though both samples show comparable generation of midgap level traps, FHF samples
are resistant to both fixed-charge and trap generation possibly due to sufficient F content, both in the bulk oxide and at
the interface.

These results show clearly that the oxidation of Si is generally accompanied by the motion of any F in the Si surface region into the oxide with the formation of oxyfluoride species. Since F-based chemistries are common in precleaning oxidation, some F-related reliability enhancement may already be present in today’s MOS devices. Further optimization for reliability will depend on the ability to control the depth profile and bonding of oxyfluoride moieties in ultrathin MOS structures.

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However, the cross section for conversion of SiF⁺ species to SiOF groups will bear some correlation to the actual availability of H, bridging oxygen atoms, and other moieties and will therefore not be unity. F atoms which are not converted into —OF groups may end up terminating Si dangling bonds at the interface (the first unreacted silicon layer), resulting in what has been called “pile-up of fluo-
rine at the interface.” A unique fluorine distribution profile in the SiO₂/Si structure can be expected from each sample pretreatment. The profile can influence the reliability of the MOS structure in different ways. F in the bulk oxide could influence the fixed-charge generation under stress and thereby V₉FP, while F at the interface can influence trap generation and thereby V₉IT. Such a differential F atom distribution between the oxide bulk and the interface can explain some features in Fig. 1. For example, the shift in V₉FP is somewhat less pronounced in SRCA samples than in MRCA samples, even though both samples show comparable generation of midgap level traps. FHF samples are resistant to both fixed-charge and trap generation possibly due to sufficient F content, both in the bulk oxide and at the interface.

FIG. 4. Schematic representation of the atomic level rearrangements in the outer region of a Si surface after (a) HF treatment, (b) 1 min UV/O₂ oxidation, and (c) extended oxidation.