FLUORINATION OF THE SILICON DIOXIDE SURFACE DURING REACTIVE ION AND PLASMA ETCHING IN HALOCARBON PLASMAS

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Surface sensitive spectroscopies were employed to investigate the surface modifications which occur on SiO₂ during actual reactive ion and plasma etching in CF₄ and CF₄/O₂ plasmas. Photoemission and electron energy loss spectroscopies were used to characterize the composition and bonding in the modified layer. Core level photoemission measurements indicated a reaction layer 10–15 Å thick with a mean composition of SiOF₂. Photoemission and EELS studies of the valence bands identified several features due to Si–F bonding. Comparisons with the SiO₂ valence bands and implications for bonding are discussed. Electron energy loss spectra were also used to determine if ion induced “defect” species formed during reactive etching persist in the reaction layer. A comparison of reactive ion etching samples with those exposed to plasma etching conditions (negligible ion bombardment) indicated that the ion bombarded surfaces exhibit a reduced level of fluorination during steady state etching. Low energy ion scattering was used to determine the composition of the outermost atomic layer. These measurements indicated a fluorine terminated surface with virtually no remaining surface oxygen.

1. Introduction

During reactive ion or plasma etching using CF₄ based plasmas, several processes are known to occur in parallel [1]. The fluorination and subsequent etching of the substrate competes with the deposition of CF₄ species and growth of carbonaceous films on the surface [2]. The predominance of one effect over the other depends on the plasma conditions and gas composition, and on the substrate which is interacting with the plasma. The addition of small percentages of O₂ to CF₄ leads to fluorine-rich plasmas and negligible carbon film deposition, while deposition is increased by the addition of H₂. This change is produced by the abstraction of fluorine in the form of HF and increased levels of CF₄ species in the plasma. Also, it has been shown that the amount of added H₂ necessary to promote the growth of CF₄ films on silicon dioxide is large compared to silicon, so that CF₄/H₂ will selectively etch silicon dioxide over silicon [3], while fluorine-rich CF₄/O₂ plasmas etch silicon over SiO₂. The importance of these two materials in Si technology makes an understanding of the details of etching in CF₄ plasmas of great interest.
Conceptually, therefore, an investigation of the etching of SiO₂ in CF₄ plasmas could be divided into two parts — one aimed at understanding the SiO₂-F reaction and determining the details of the fluorinated reaction layer, and the other composed of investigations of the formation of carbonaceous films on the surface. In reality these two effects exist in parallel under most plasma conditions and cannot be completely separated into two totally non-interacting processes. However, by performing investigations with conditions under which one or the other process dominates, useful information can be obtained. The results presented here represent part of a study employing surface sensitive techniques to investigate plasma and reactive ion etching of silicon dioxide in CF₄ based plasmas. The goal of this work is to investigate the surface modifications which occur during etching, providing insight into the processes which determine etch rates and selectivities. The experiments described below were designed to characterize the fluorinated layer which forms during actual reactive ion etching of SiO₂ and, because the etching of SiO₂ proceeds at negligible rates in the absence of energetic particle bombardment, to compare reactive ion etched surfaces with surfaces indicative of etching with reduced or negligible ion bombardment (plasma etching). Results pertaining to the deposition of C-F films will be presented elsewhere.

Previous investigations aimed at providing information on the etching of silicon dioxide in fluorine containing plasmas have employed a variety of approaches [4]. In situ electron spectroscopies (X-ray photoemission and Auger spectroscopy) were used to examine the surface reaction layer in some cases [5]. However, studies employing surface-sensitive techniques usually involved simulations of the plasma environment, using XeF₂, and simultaneous Ar⁺ ions, CF³⁺ ions, etc., due to the complex nature of the plasma. This work is unique in that it combined in situ surfaces studies with etching under actual reactive ion and plasma conditions. Furthermore, a variety of techniques were employed in order to gain as detailed a picture of the fluorinated layer as possible.

We will first briefly describe the experimental procedures and the apparatus employed. We will then present the results of our studies employing X-ray photoemission spectroscopy (XPS), electron energy loss spectroscopy (EELS), and low energy ion scattering spectroscopy (LEISS) to thoroughly investigate the surface characteristics of etched SiO₂.

2. Experimental details

The samples used in these studies were 1 inch Si(111) or Si(100) wafers which were oxidized to a thickness of approximately 5800 Å. In most cases no attempt was made to clean the accumulated hydrocarbon layer from the silicon dioxide surface prior to exposure to the etching environment. During
exposure, plasma or reactive ion etching typically led to the removal of at least 10-100 Å, rendering the initial surface conditions unimportant. Cleaning of the silicon dioxide surface by exposure to low power, high pressure oxygen plasmas for short periods was performed in some cases and proved very effective. As expected, this procedure had no effect on the characteristics of the surfaces after etching.

The experimental apparatus employed for studying the etched surfaces consisted of a multitechnique UHV surface analysis chamber (VG ESCALAB MK II, base pressure approximately 1 × 10⁻¹⁰ Torr) connected to an etching chamber (base pressure 5 × 10⁻⁷ Torr) which contained a flexible diode arrangement for reactive ion or plasma etching. Under reactive ion etching conditions, RF power (13.56 MHz, 0-1000 W) is applied to the bottom, or sample, electrode to maintain the discharge. The self-bias which forms between the plasma and the sample leads to ion bombardment of the sample in addition to exposure to reactive neutrals formed in the discharge. For plasma etching, the sample electrode is grounded and power is applied through the top electrode leading to much reduced ion bombardment.

Silicon dioxide etching was performed under a wide variety of plasma operating conditions, in both plasma and reactive ion modes. Pressures in the range of 5 to 100 mTorr and power densities between 0.06 and 0.47 W/cm² were employed, producing self-biases of the sample electrode (which is an indication of ion bombardment energies) which varied from approximately 100 to 800 V for different reactive ion etching conditions, and was close to 0 V for plasma etching. Etching with various gas compositions was also examined - CF₄, CF₄/O₂, and CF₂/H₂. Etch rates varied significantly - typically less than 20 Å/min for plasma conditions and from 100 to 600 Å/min for RIE conditions. Measurements of etch rates were performed using laser interferometry in the case of reactive ion etching and by in situ ellipsometry for much slower spontaneous etching.

Because the goal of this work is to investigate the fluorination and etching of silicon dioxide, both with and without ion bombardment, we will concentrate primarily on data obtained from CF₄/10%O₂ plasmas. This composition insured a fluorine-rich, CF₄ deficient plasma so that even under conditions of negligible ion bombardment no deposition of CF₄ species occurred. Also unless otherwise stated, 200 W of RF power was applied to maintain the discharge, producing a self-bias of approximately 400-500 V with the sample on a quartz electrode. The pressure was maintained at 25 mTorr with a constant flow rate of 50 sccm.

Exposures to the plasma without ion bombardment, i.e. spontaneous etching, were produced in two ways. One method was to convert to a plasma etching mode so that ion bombardment was confined to the top electrode. However, the asymmetry in the areas of the top and bottom electrodes and the need to use higher pressures to reduce sputtering of the upper Al electrode
onto the SiO₂ sample produces some uncertainty in the comparison with reactive ion etched samples. Therefore, samples were also placed in the chamber under reactive ion etching conditions, but were covered to prevent ion bombardment while allowing interaction with the neutral reactive species. A more direct comparison between etching with and without ion bombardment could be produced in this way. Both methods produced nearly identical surfaces.

After etching, the samples were passed into the analysis chamber, normally isolated from the reaction chamber by a gate valve. The pump-down of the etching chamber and transfer of the sample into the analysis chamber was typically accomplished in approximately 5 to 10 min. The wafers were placed on sample holders under stainless steel clips and transferred to a high precision rotatable xyz manipulator.

The analysis chamber contained facilities for performing a variety of surface spectroscopies. The instrumentation included a twin anode X-ray source (Al Kα and Mg Kα) and a hemispherical analyzer for X-ray photoelectron spectroscopy (XPS) and an additional monochromatized Al Kα X-ray source. Also included were an ion gun for low energy ion scattering spectroscopy (LEISS) and an electron gun for electron stimulated Auger spectroscopy or electron energy loss spectroscopy (EELS). The principal techniques employed in this study were Mg Kα XPS investigations of core and valence levels, along with EELS. Some LEISS measurements will also be discussed.

3. Results

Before beginning a detailed discussion of the results of the XPS measurements, we will first comment briefly on the effect of X-ray irradiation on the fluorinated samples. The primary effect consisted of the loss of surface fluorine by photon stimulated desorption (PSD). Concurrent with this loss of fluorine was accumulation of residual carbon on the surface, presumably due to the increased reactivity of the surface after fluorine desorption. Carbon accumulation was found to be negligible over periods of many hours for fluorinated samples not exposed to X-rays. These X-ray induced effects are large due to the high cross section for PSD of fluorine, and led to the necessity of keeping exposures on individual samples as low as possible to insure that an accurate characterization of the surface region was obtained.

3.1. Core level photoemission

We now turn to a detailed discussion of electron spectroscopy results. Unless otherwise indicated, the photoemission spectra were collected with an
Fig. 1. Wide energy range, low resolution MgKα photoemission survey spectrum of reactive ion etched (CF₄/10%O₂, 200 W) SiO₂. Plasma etching produces a similar surface but typically with an increased degree of fluorine incorporation.

electron emission angle of 75° from the normal to enhance the surface sensitivity. According to literature values [6] this angle of electron emission leads to effective mean free paths of about 5–6 Å for F(ls) and O(ls) levels and 8 Å for the Si(2p) level.

A low resolution, wide energy range X-ray photoemission survey spectrum of silicon dioxide after reactive ion etching (CF₄/10%O₂, 25 mTorr, 200 W) is given in fig. 1. Etching under identical plasma conditions, but without ion bombardment, produced similar spectra. Both types of surfaces show a significant incorporation of fluorine, indicated by a large F(ls) intensity at approximately 687 eV. The only one features observed under these conditions are attributed to either oxygen or silicon core and valence levels. Surfaces protected from ion bombardment typically displayed a larger F(ls) (15%–20%) intensity along with a reduced O(ls) intensity. As will be discussed more fully below, this was the only observable difference between the reactive ion and plasma etched samples. All other aspects of photoemission features – binding energies and widths – were the same. Thus, the following discussion of core level binding energies and peak shapes will apply equally to reactive ion and plasma etched surfaces.

Higher resolution photoemission spectra were collected for Si(2p), O(ls), and F(ls) core levels. The hemispherical analyzer supplied a resolution of about 0.2 eV, so that the total resolution of approximately 1 eV was de-
determined by the MgKα source linewidth. Spectra were also collected using monochromatized Al Kα X-rays, but the large loss of intensity at grazing electron emission angles made the collection of high resolution, surface sensitive spectra impractical.

The use of thick oxide samples led to sample charging and binding energy shifts in the photoemission measurements. To overcome this problem, an internal binding energy calibration was employed. The O(1s) peak from fluorinated samples showed no significant broadening or splitting as a function of the electron emission angle, indicating that the oxygen core level binding energy in the fluorine-rich surface region is the same as that in the silicon dioxide substrate. Because the fluorinated layer has a thickness of about 10 Å, a large fraction of the O(1s) intensity for grazing emission angles originates from oxygen in this layer. Hence, the lack of measurable change in the peak shape is not due to a lack of sensitivity to oxygen in the modified surface layer. Thus, the O(1s) core level can be used as a reference to correct for sample charging effects. In the following, all binding energies are referenced to this level, which was determined to have a binding energy of 532.9 eV using a low energy flood gun for charge compensation. This value is also consistent with other studies of SiO₂ [7].

A comparison of the O(1s) level for a heavily fluorinated sample, prepared by reactive ion etching, with that from a clean silicon dioxide sample is shown in fig. 2. The two spectra were normalized to the same area to allow a comparison of the peak shapes. The absolute binding energy is found to be 532.9 ± 0.3 eV for both the clean and fluorinated surfaces. The width of the O(1s) peak is 1.6 eV. The only difference between the two spectra is very slight broadening in the peak width of the fluorinated sample. The insensitivity of the O(1s) level to fluorine incorporation indicates the absence of direct oxygen–fluorine bonding – oxygen in the fluorinated reaction layer is still bound exclusively to silicon. The replacement of a next-nearest neighbor oxygen–silicon bond with a fluorine–silicon bond does not produce a significant binding energy shift in the O(1s) level.

Photoemission from the F(1s) region is given in fig. 3. Using the O(1s) as a reference, the binding energy is determined to be 687.0 ± 0.3 eV. Fluorine bound to silicon in SiO₂ has all next-nearest neighbors of high electronegativity, either oxygen or fluorine. This produces a F(1s) binding energy somewhat higher than that found for a silicon substrate (686.0 to 686.4 eV), where next-nearest neighbor Si–Si bonds exist. An identical binding energy is obtained for low coverages of fluorine on SiO₂, indicating that the initial bonding does not change with increased coverage and reaction.

The observation of oxyfluoride species on sputtered SiO₂ exposed to XeF₂ has recently been reported [5b]. Joyce et al. observed an asymmetric F(1s) peak which they fit with two peaks, producing a major component at 686.1 eV and a smaller component (about \( \times 1/3 \)) at about 684 eV. They assigned the
Fig. 2. MgKα O(1s) photoemission spectra for clean and heavily fluorinated SiO₂, taken with an electron emission angle of 75° from the normal. No changes were observed in the fluorinated spectrum as a function of the emission angle indicating that the oxygen bonding is not influenced by fluorination at other sites.

Fig. 3. F(1s) photoemission for an etched, fluorinated SiO₂ surface. The binding energy is about 1 eV higher than fluorine in a fluorinated layer on Si.
lower binding energy feature to SiO–F bonding. No such asymmetric peak was observed in our work using thick SiO₂ samples, either for reactive ion etching or fluorination by exposure to the plasma without ion bombardment. Fluorination of sputtered samples also did not produce an asymmetric F(1s) core level. However, experiments using thin oxide samples (20–30 Å) did produce broadened, asymmetric F(1s) peaks very similar to those displayed in fig. 2 of ref. [5b]. In our case this apparent shoulder is due to charging effects across the oxide layer and/or changes in the apparent binding energy near the interface. The lower binding energy “feature” was found to be located more toward the Si–SiO₂ interface by examination of the angular variation of the F(1s) peak shape. There may also be a discrepancy in the F(1s) binding energies reported by Joyce et al. and in our work. We find a shift of roughly 1 eV between fluorine bound to Si in SiO₂ and the analogous species on a Si surface, while fig. 3 of ref. [5b] suggests that the binding energies are the same. Thus, while the changes observed by Joyce et al. upon heating (the lower binding energy feature is removed) and the differences in the two experimental situations (species which are unstable and easily desorbed may not survive in an actual plasma environment) support an explanation in terms of oxyfluoride species, it is clear that some care must be exercised in examining possible alternate interpretations.

In the case of fluorine etching of silicon by XeF₂, a wealth of information can be obtained from examination of the Si(2p) core level, which shows distinct shifts due to different fluorinated species, SiFₓ. This information was used to obtain a detailed idea of the make-up of the reaction layer. For silicon dioxide, however, the oxide shift of approximately 3.5 eV compared with the shift of approximately 4.5 eV for the SiF₄ species makes it impossible to separate Si(2p) contributions due to increasing fluorine–oxygen substitutions, since shifts of only about 0.2–0.3 eV per fluorine atom occur. The observed shift can, however, be used to obtain some information. A comparison between Si(2p) photoemission spectra for silicon dioxide and a reactive ion etched sample is given in fig. 4. The etched sample shows a broadened Si(2p) as well as a shift of the peak centroid. Some care must be exercised in the interpretation of these changes. It is known that ion bombardment can also lead to significant broadening of the 2p core level in SiO₂. However, identical Si(2p) features are obtained for silicon dioxide fluorinated under plasma conditions without ion bombardment, indicating that the changes evident in fig. 4 are primarily chemically induced.

A least-squares fit performed using one peak for the silicon dioxide component, with its peak position and width determined from clean silicon dioxide, and a single broad peak to encompass the fluorinated components is presented in fig. 4 as the dotted curves. The results indicate a mean shift for the fluorinated species of 0.66 eV from silicon dioxide. This fit is included to give a rough idea of the degree of fluorination, and is consistent with an average composition of approximately SiOF₂.
Fig. 4. Spectra of the Si(2p) core level for clean and fluorinated SiO₂. The fluorinated surface exhibits a Si(2p) level shifted by about 0.6–0.7 eV. Also shown are the results of a least-squares fit to the fluorinated peak, using one component to represent unmodified SiO₂ (with the peak parameters fixed by a fit to the clean surface peak) and another component to represent the distribution of fluorinated species.

Although plasma etched samples displayed an increase in the F(1s) intensity of about 15%, no detectable difference in the Si(2p) spectra for the two cases was observed. This high degree of similarity in the plasma etched and reactive ion etched Si(2p) lineshapes might be due in part to the inability to resolve the peaks corresponding to different SiFₓ species. The higher level of fluorination in the plasma etching case could be incorporated without measurably affecting the overall lineshape, due to the large degree of overlap for the different components.

Further information can be obtained by examining the core level intensities, and the dependence of these intensities on the photoelectron emission angle. The simplest picture of the reaction layer is one in which oxygen atoms are removed from the silicon dioxide lattice and replaced by two fluorine atoms. In this case, the change in intensity in the O(1s) peak from silicon dioxide to the fluorinated sample, ratioed to the F(1s) intensity and corrected for relative cross sections and mean free paths – i.e., the change in the number of oxygen atoms over the change in the number of fluorine atoms – would be 0.5. Differences from this value could indicate the existence of species such as Si–Si bonds, Si dangling bonds, etc. in this layer. Such species can be formed in ion bombarded silicon dioxide, and their existence and concentrations could provide information on ion enhancement effects on the etch rate. The value of
the ratio obtained experimentally, using cross sections from Scofield [8] and mean free paths adjusted according to Ashley and Tung [6], is $-0.52 \pm 0.04$. This is consistent with core level spectra which produced no detectable evidence of species other than Si–F bonds and Si–O bonds.

The angular dependence of the core intensities can be used to obtain the mean stoichiometry of the reaction layer. The photoemission intensities measured for the O(1s) and F(1s) levels as a function of angle are illustrated in fig. 5 for a plasma etched sample (200 W, CF$_4$/10%O$_2$), and for a reactive ion etched sample with identical conditions. The data presented in this figure are the $I(F)/I(Si)$ and $I(O)/I(Si)$ ratios as a function of angle. The Si(2p) intensities did not change upon fluorination from values measured for the angular dependence for clean silicon dioxide (to within 4%). This suggests that no significant changes in the Si density and photoelectron mean free paths in the near-surface region occur upon fluorination and etching. Forming these ratios normalizes the F(1s) and O(1s) intensities to the density of Si atoms and removes instrumental effects as a function of angle. These data were then fit to a simple model which assumed a homogeneous layer characterized by a fluorine density, $\rho$, corresponding to an average stoichiometry SiO$_x$F$_y$ and thickness, $d$. Thus,

$$
\rho_F(z) = \rho_F, \quad 0 < z < d,
$$

$$
\rho_F(z) = 0, \quad z > d.
$$

(1)
The angular dependence of these photoemission intensity ratios can then be calculated following standard treatments [9]. Measured values for the \( I(0)/I(\text{Si}) \) ratios for silicon dioxide were used to obtain the relative instrumental sensitivity between the Si(2p) and the O(1s) or F(1s) energies. The results of this procedure are given by the solid lines in fig. 5 for the plasma etched sample. Similar quality fits were obtained for reactive ion etched samples. The values obtained are \( d = 10 \) Å and a mean stoichiometry of SiO\(_{0.9}\)F\(_{2.2}\) for the plasma etched sample and \( d = 11 \) Å with SiO\(_{1.1}\)F\(_{1.8}\) for the reactive ion etched sample. A model assuming an exponential profile of fluorine incorporation expressed as \( \rho_F(z) = \rho_F(0)e^{-z/d} \), was also employed. Fits using this model give \( d = 8 \) Å and SiO\(_{0.5}\)F\(_{3.0}\) for the plasma etched sample and \( d = 9 \) Å with SiO\(_{0.7}\)F\(_{2.6}\) for the reactive ion etched case. Here the stoichiometry given is not the average value, but is instead the level of fluorination at the outermost layer, \( z = 0 \).

An analogous procedure could be performed for the \( I(\text{O})/I(\text{Si}) \) angular intensity dependence. However, this leads to the same values as those determined from the fluorine intensities. This is due to the connection between the removal of oxygen and the uptake of fluorine atoms. The good fit achieved to both sets of intensities with the same values of \( d \) and average stoichiometry is an indication that the loss of one oxygen is compensated by the incorporation of two fluorine atoms throughout the reaction layer.

### 3.2. Valence band photoemission

Photoemission spectra of the valence region were also collected using the Mg K\(\alpha\) source. In this case, the mean free path is on the order of 10 Å. Again, it proved impractical to obtain monochromatic spectra at grazing electron emission angle.

Before discussing the changes induced in the valence band region by fluorination, we must first discuss the photoemission features observed for clean silicon dioxide, given by the dotted spectrum in fig. 6a. Many theoretical and experimental investigations of these features have been presented in the literature [10]. For our purposes it will suffice to give a brief synopsis of the results of these studies. The photoemission structure consists of three main features. The upper band, extending from about 5 to 10 eV in binding energy, is made up almost exclusively of O(2p) orbitals. The upper edge of this band consists of nonbonding O(2p) lone pair states while the lower part of the band has some weak bonding to Si states. This band is followed by a pseudo-gap, more pronounced in crystalline forms, separating the strong bonding states. These bonding states show two main features which have been assigned to O(2p)–Si(3p) and O(2p)–Si(3s) bonding, at about 12 and 15 eV, respectively. The peak at 25 eV is the O(2s) core level which has only a very slight participation in the bonding and can be considered core-like.
Fig. 6. Photoemission spectra of the valence bands obtained using MgKα X-rays. (a) Valence bands for fluorinated SiO₂ (line) compared to clean SiO₂ (dotted). The spectra are normalized to the Si(2p) intensity in each case. (b) Difference spectrum, fluorinated – clean.

The line spectrum in fig. 6a is the photoemission from the same region for a fluorinated sample, in this case a plasma etched sample. Identical features are observed for samples subjected to reactive ion etching but with a lower intensity of the fluorine induced features. The clean and fluorinated samples have been normalized to the intensity in the Si(2p) core level, which does not change upon fluorination as discussed previously. This procedure then provides the valence electron density per silicon atom for clean and fluorinated SiO₂.

Several changes are seen to occur upon fluorination. The growth of the F(2s) photoemission peak at 32 eV is accompanied by a reduction in the O(2s) peak at about 25 eV. The most obvious changes in the 2p valence band region are the growth of a new feature at about 10 eV, in the pseudo-gap of silicon dioxide, and an increase in the intensity in the region of the strong bonding states in silicon dioxide.

To obtain a clearer picture of the changes, a difference spectrum is given in fig. 6b. The loss of intensity in the O(2s) level along with the increase of the F(2s) intensity again indicates that the loss of one oxygen atom is compensated by the addition of two fluorine atoms. As in silicon dioxide, the fluorine induced band consists of three main features. The shift of 2.8 eV between the upper edge of the silicon dioxide bands (corresponding to the O(2p) nonbonding lone pairs) and the upper edge in the fluorine spectrum is
consistent with the shift of 3.1 eV calculated for the O(2p) and F(2p) atomic levels [11]. This lowest binding energy feature thus consists of the F(2p) nonbonding lone pair orbitals for fluorine bound to silicon and is somewhat narrower than the corresponding oxygen feature in SiO$_2$, probably due to the lack of the weak bonding features at the bottom of this band in SiO$_2$. The additional structure, by further analogy with silicon dioxide, corresponds to F(2p)–Si(3p) bonding and F(2p)–Si(3s) bonding states at about 11.9 and 14.4 eV, respectively. While, the non-bonding F(2p) levels are shifted from the corresponding levels in SiO$_2$ by approximately the value expected from the atomic levels, the Si(3s, 3p)–F(2p) and Si(3s, 3p)–O(2p) bonding states occur at approximately the same energies.

An interesting comparison can be made between these photoemission results and those obtained by Gruntz et al. for fluorinated amorphous silicon [12]. Their samples were prepared by sputtering crystalline Si in an argon–SiF$_3$ atmosphere. There is very strong similarity between fig. 6b and the bands displayed in fig. 4 of ref. [12] which have a similar triangular structure with peaks observed at 9.0, 11.3, and 13.3 eV for a sample containing 28 at% F. Gruntz et al. also observed the F(2s) level at 31.3 eV as compared with a value of 32 eV shown in fig. 6b, so that a rigid shift of about 0.7 eV in fig. 6b would produce a spectrum nearly identical to that displayed in their fig. 4. This also agrees with the shift observed in the F(1s) level, which occurs at about 686.4 eV for Si–F bonds on Si, but 687.1 eV for silicon dioxide. The features observed in the photoemission spectra for fluorinated SiO$_2$ are expected to have the strongest similarity to a heavily fluorinated Si surface, with a predominance of SiF$_3$ species, than to a less fluorinated sample retaining a large number of Si–Si bonds. This is seen by examining photoemission from fluorinated amorphous Si with 5 at% F versus 28 at% F in ref. [12] – the valence bands in fluorinated SiO$_2$ are much closer to those displayed in the 28% F sample. These results indicate the similarity in the Si–F bonding in the two systems.

3.3. Electron energy loss

Electron energy loss measurements were performed with incident electron energies between 100 and 1000 eV. The measurements were performed with a pass energy of 5 eV, giving an analyzer contribution to the resolution of about 100 meV. The total resolution was approximately 500 meV, determined by the full width at half maximum of the elastic peak. The off-axis electron gun was located at an angle of 40° from the analyzer, and nearly in the plane containing the axis of rotation of the sample, allowing the use of grazing incidence and emission angles. Care was taken to keep the beam current and exposure times low to avoid beam induced changes.
Fig. 7. EELS spectra of (a) clean SiO$_2$ and (b) fluorinated SiO$_2$. Spectra for both reactive ion etched (dotted) and plasma etched (line) are presented in (b). The primary electron energy was 100 eV.

The information contained in the electron loss spectra is complementary to that obtained from photoemission valence band spectra, and has the added advantage that much higher surface sensitivity can be obtained. The range of incidence and emission angles available allowed sampling with effective mean free paths from about 2–5 Å at a primary energy of 100 eV. Using the information gained from the valence band photoemission results, EELS then can provide information on the empty conduction band states. Electron loss measurements also offer the possibility of detecting empty and filled states in the band gap, providing a more direct means of investigating the existence of "defect" species at the surface.

Fig. 7a displays an EELS spectrum of clean silicon dioxide. Silicon dioxide has been studied using EELS previously by Lieske and Hiezel [13], who assigned the transitions based on optical and X-ray data and the results of molecular simulations (SiO$_4$ tetrahedra) of silicon dioxide. The agreement with these previous measurements is very good and we will not discuss the details of the assignment of all the observed transitions here. In the following, we will be most interested in the region including the band gap and states relatively close to the valence band edge, which are the easiest to interpret. The optical band gap, measured from the center of the elastic peak to the leading edge of the Si(2p) non-bonding valence states, is found to be 9.8 eV. The threshold is formed by transitions from the O(2p) non-bonding states at the valence band.
maximum to the lowest unoccupied levels which are mainly Si(3s) and Si(3p) states. The features beyond this point have been discussed and given several different interpretations. Based on the similarity between the structure observed for excitation of the valence bands and from the Si(2p) core level, an explanation in terms of excitations to several different low-lying final states seems most reasonable.

Fig. 7b presents spectra for both a reactive ion etched sample and a plasma exposed sample. These spectra were taken with grazing incident and emission angles and a primary energy of 100 eV, giving an effective mean free path of about 3 Å. The most prominent change is the peak which appears at a loss energy of 12.8 eV, shifted 3 eV from the valence band maximum of silicon dioxide. The most reasonable interpretation of this feature involves transitions from the F(2p) non-bonding states previously observed in the valence band spectra. A second peak due to F(2p)-Si(3p) bonding states is then observed 1.8 eV lower, as in the photoemission, and a broad feature at approximately 17.0 eV can be assigned to transitions from the F(2p)-Si(3s) states at the bottom of the photoemission valence bands. An alternative explanation of these features in terms of transitions to different final states of the F(2p) non-bonding levels might be suggested in view of similar explanations of the structure in EELS spectra of SiO₂, however, the similarity of these features with the valence bands is suggestive of the above interpretation. Regardless of the interpretation of the higher energy loss features, it is clear that the most prominent peak at 12.8 eV loss involves transitions from the F(2p) non-bonding states into the lowest empty states and it should be noted that this level is approximately 1 eV closer to the edge of the oxygen levels (the O(2p) non-bonding states) in the EELS spectra than in the photoemission spectra of the valence bands. This indicates that the final states involved in this fluorine transition – presumably Si(3s, p)-F(2p) antibonding states by analogy with silicon dioxide – are about 1 eV lower than the corresponding oxygen states.

Both the reactive ion etched and plasma etched samples show a high degree of fluorination of the surface, with only a small remnant of the O(2p) band edge states still visible. The level of fluorination is apparently much higher than indicated in the photoemission spectra due to the shorter mean free path and increased fluorination level at the surface. However, it is difficult to quantitatively compare the photoemission and EELS results since the transition matrix elements are very different. The higher fluorine incorporation in the plasma sample is also evident.

Electron energy loss spectroscopy was also used to investigate states in the band gap of silicon dioxide. Lieske and Hiezel [13] identified two states in the band gap of clean silicon dioxide at 3.2 and 6.5 eV loss energies. They attributed the features to transitions involving Si–Si bonds. We also observe a feature at 6.8 eV and find some evidence of intensity at lower loss energies for clean silicon dioxide. The peak at 6.8 eV occurs at the same energy for which a
large peak grows upon the adsorption of hydrocarbon species from background gas over a period of hours. This feature is effectively removed by exposure to O$_2$ plasmas, although a small residual sometimes remained. We attribute the peak at 6.8 eV to small amounts (much less than one monolayer) of carbon not removed by our O$_2$ plasma cleaning procedure. It was also shown in the studies of ref. [13] that ion bombardments produces prominent states in the band gap that are observable with EELS. Transitions were seen at loss energies of 5 and 7 eV, and attributed to broken Si–O bonds. An EELS spectrum of an argon bombarded silicon dioxide sample displaying these transitions is presented in fig. 8a. An explanation of these features in terms of broken, relaxed Si–O bonds is questionable since ion bombardment in the energy range employed would be expected to primarily yield displacement damage giving O vacancies [14]. This is also consistent with the experimentally observed reduction of the oxide surface by preferential sputtering of oxygen [15]. However, the exact nature of these defect states is still controversial. In any case, the observation of these features by EELS provides the means to determine if the species giving rise to these transitions persist in the reaction layer. This is of interest since a probable mechanism for the increased etching of silicon dioxide with ion bombardment involves the break-up of Si–O bonds to allow more efficient fluorination.
Examination of the spectra in fig. 7b indicates that none of the damage induced features observed in fig. 8a are found in these reactive ion etched samples. However, some etched samples did exhibit clear features in this region. An example is given in fig. 8b for SiO₂ etched in pure CF₄ under reactive ion etching conditions. A small peak is observed at a loss energy of 6.8 eV. This energy does not coincide with either of the prominent peaks due to ion bombardment observed in fig. 8a for clean SiO₂. This could be due to a shift incurred because of the fluorine incorporation, but comparison with the results for clean silicon dioxide indicates that this feature occurs at the same energy as that assigned to Si–Si bonds by Lieske and Hiezel and to carbon adsorption in our case. Intensity in this region generally occurred for samples etched in less fluorine-rich plasmas – pure CF₄ or CF₄/H₂ – and additionally can be seen for both reactive ion etched samples and plasma etched samples. Furthermore, a feature is seen to grow at this energy after prolonged exposure to X-rays, when not present initially. Our previous studies on the effects of X-ray exposure then suggest that this feature is due to the adsorption of carbon containing species. In the absence of X-ray exposure or prolonged periods in the vacuum chamber, this feature arises from CF₄ groups adsorbed from the plasma. Samples which exhibited this feature usually also exhibited a small C(1s) photoemission peak.

3.4. Low energy ion scattering results

Because the adsorption processes leading to reaction and etching are strongly influenced by the conditions at the outermost atomic layers, it is important to have a probe which is sensitive to this region. Low energy ion scattering is well suited for investigations of the outer monolayer of the sample. A monoenergetic beam of He⁺ ions is scattered from the surface and the deflected ions are energy analyzed using the hemispherical analyzer. For a fixed scattering angle, the energy of a detected ion depends on the mass of the surface atom from which it scattered, thus providing essentially a mass spectrum of the surface. The high neutralization rates for the ions lead to extremely short sampling depths on the order of one monolayer. LEISS spectra of clean and etched, fluorinated SiO₂ surfaces are given in fig. 9. Both spectra were acquired under identical conditions. The fluorine intensity from the fluorinated sample is about 1.8 times that of the oxygen in SiO₂, consistent with the expected substitution. However, a lack of detailed knowledge of scattering cross sections and of changes in ion neutralization probabilities as a function of surface fluorination makes a quantitative comparison uncertain. Fluorinated surfaces obtained by reactive ion and plasma etching were essentially identical. A possible experimental difficulty arises in the case of reactive ion etching. Some fluorination of the surface layer will continue to occur after the plasma is extinguished, due to the finite lifetime of F radicals. This could
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Fig. 9. Low energy ion scattering intensity from clean and fluorinated SiO$_2$ using 1 keV He$^+$ ions. The fluorinated sample shows almost no scattering from surface oxygen.

obscure any differences that might be observed in LEISS between reactive ion and plasma etched samples. At this time, the extent of this effect is not known.

The most prominent aspect of the LEISS data is the almost total absence of oxygen scattering from the fluorinated surface. This indicates that nearly all of the surface oxygen has been replaced by fluorine, producing a saturated outer layer. The Si surface scattering peak is also much less prominent on the fluorinated surface. Oxygen in Si–O–Si bridge bonds at the surface might be more parallel to the surface than fluorine, leading to less shadowing of the Si than in the case of Si–F bonds. With the increased number of fluorine atoms compared to the number of oxygen atoms at the SiO$_2$ surface, this could explain the less well defined Si surface scattering peak.

4. Discussion

From the above results, we can arrive at a reasonably clear picture of the composition and bonding in the reaction layer during SiO$_2$ etching. This layer is formed by the substitution of fluorine for oxygen leading to a mean composition with approximately two fluorine atoms per silicon and a steady state thickness on the order of 10–15 Å. No species which could be interpreted as intermediates in the etching reaction were found. This suggests that the
initial step of the reaction, in which a Si–O bond is broken to allow the formation of a Si–F bond, limits the process, and that additional steps leading to the final configuration, consisting of the removal of the oxygen and incorporation of an additional fluorine atom, are fast. The displacements and broken bonds formed during a collision cascade could enhance this process as suggested previously [4b]. Electron energy loss measurements indicate a significant gradient in this layer, indicating more highly fluorinated species in the outermost layer. This high concentration of fluorine at the surface is particularly evident from LEISS measurements. This aspect could also have bearing on etching processes since additional fluorine would be less likely to adsorb on this saturated surface. Again, ion enhanced reaction/diffusion, leading to more efficient penetration and fluorination of the SiO₂ lattice, could explain the observed ion induced etch rate enhancement. Reduction of the level of fluorination of this outer layer by sputtering could also produce a surface on which additional fluorine adsorption would occur at an increased rate.

The only observable difference between reactive ion etched and plasma etched samples was a higher level of fluorination in the plasma case. A possible explanation of this result could be increased sputtering of incompletely fluorinated species (chemically enhanced sputtering). This would lead to differences in the composition of the fluorinated layer in terms of SiFₓ species for the two etching modes. This could not be determined since sequential substitutions of fluorine for oxygen, creating more highly fluorinated SiFₓ species, do not produce observable spectral changes. Thus, an extraction of contributions due to different SiFₓ species, as performed in ref. [12], was not possible. Another possible explanation would simply be increased ion induced loss of fluorine, leading to an overall reduction in the steady state level of fluorine that is incorporated in the reaction layer.

5. Summary

We have used a variety of surface sensitive spectroscopies to investigate the modified layer formed upon SiO₂ during etching in fluorine containing plasmas. X-ray photoemission and EELS were employed to study the composition and bonding in this layer through investigations of the core levels and valence bands and also of the band gap region. The photoemission measurements indicate a reaction layer approximately 10–15 Å thick with a mean composition of about SiOF₂ for both reactive ion and plasma etched samples. The fluorine induced valence bands can be understood by analogy to the structure observed in silicon dioxide and indicate the formation of Si–F bonds. These valence features are also reminiscent of those observed in fluorinated amorphous silicon. Strong fluorine induced features in very surface sensitive EELS measurements indicate a heavily fluorinated surface layer, with a high
ratio of fluorine to oxygen. EELS measurements were also used to investigate states in the band gap. A feature due to carbon adsorption was identified, but no evidence was found for the persistence of ion bombardment induced features in the reactive ion etched surface layer. Low energy ion scattering was used to study the outermost atomic layer of etched samples. The measurements indicate a fluorine terminated surface with virtually no surface oxygen remaining.

References