Thermal and Ion-Induced Surface Reactions of 1,1-Difluoroethylene on Si(111)7×7 and Vitreous SiO_2

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Thermal and ion-induced reactions of 1,1-difluoroethylene (1,1-$C_2H_2F_2$ or *iso*-DFE) on Si(111)7×7 and vitreous SiO_2 surfaces have been investigated by vibrational electron energy loss spectroscopy and thermal desorption spectrometry. Like ethylene, *iso*-DFE predominantly chemisorbs via a [2 + 2] cycloaddition mechanism onto the 7×7 surface as a di-σ-bonded difluoroethane-1,2-diyl adstructure, which undergoes H abstraction and defluorination, producing hydrocarbon fragments and SiF_x ($x = 1-3$) upon annealing to >700 K. Ion irradiation of Si(111)7×7 in *iso*-DFE at 50 eV impact energy appears to substantially enhance the production of hydrocarbon fragments and SiF_x, leading to stronger SiF_4 desorption products over an extended temperature range (400−900 K). The observed SiC and SiF_x produced on the 7×7 surface by ion irradiation in *iso*-DFE are found to be similar to those obtained by ion irradiation in the fluoromethane homologues, CF_4 and CH_2F_2. The production of higher relative concentrations for the larger SiF_x and C_2-containing fragments is evidently favored on the 7×7 surface. On a vitreous SiO_2 surface, ion irradiation in *iso*-DFE, unlike that in CF_4 and CH_2F_2, appears to produce less SiF_x than that on the 7×7 surface, which indicates that surface O does not interact strongly with the C_2-containing fragments. The presence or absence of a C═C bond and the relative F-to-C ratio of the sputtering gas could therefore produce important effects on the resulting surface products obtained by low-energy ion irradiation.

1. Introduction

Recently, we have examined the surface products generated by ion irradiation in fluorinated methanes at 50 eV impact energy on clean and oxidized surfaces of Si(111)7×7 by using vibrational electron energy loss spectroscopy (EELS) and thermal desorption spectrometry (TDS).[1,2] These simple fluorinated methanes, CF_4 and CH_2F_2, with F-to-C ratios of 4 and 2, respectively, provide important benchmark systems for investigating surface reactions induced by low-energy ions. In particular, ion irradiation of the 7×7 surface in CF_4 and CH_2F_2 at 50 eV impact energy produces SiC and SiF_x ($x = 1-3$) as the primary surface products, while additional hydrocarbon species are found in the latter case of ion irradiation in CH_2F_2.[1,2] On a vitreous SiO_2 surface, ion irradiation by the same exposure of fluorocarbon ions appears to enhance the deposition of SiF_x but reduce the amount of SiC species, which suggests a plausible recombination reaction of the surface O with surface C (releasing CO and CO_2).[1,2] We now expand this study to ion irradiation in simple fluorinated ethylenes, particularly, 1,1- or *iso*-difluoroethylene (DFE, or $C_2H_2F_2$) with an F-to-C ratio of 1. Our goal is to further examine the effects of a smaller F-to-C ratio and the presence of a C═C double bond in the sputtering gas on the ion-induced surface processes. The present work is also of practical interest because *iso*-DFE is used as an additive to primary etchants such as CF_4 to control (reduce) the etching rates of oxidized Si surfaces in plasma semiconductor processing.[3−5] In these earlier studies,[3−5] the etching was normally conducted under high-pressure conditions, which makes the interrogation of the ion−surface interactions in the early adsorption stage difficult. Appropriately, the present work focuses on ion−surface processes under low-pressure (high vacuum) conditions in order to better explore the early chemisorption properties of these low-energy ions.

According to the gas-phase cracking pattern of *iso*-DFE,[6] the ion fragments for *iso*-DFE in the order of their relative abundances (indicated in parentheses) are $C_2H_2F_2^+$ (30%), $C_2H_2F^+$ (20%), CF^+ (15%), CH_2F^+ (12%), and C_2HF^+ (11%). For CF_4, CF_3^+ (estimated to be 78%) is the majority or base ion, with other smaller ions such as CF_2^+ (10%) and CF^+ (3%) present at lower proportions;[7] while for CH_2F_2, CH_2F^+ (38%) and CHF_2^+ (37%) are the majority ions, with CF^+ (11%), CHF^+ (4%), CH_2F^+ (3.8%), CH^+ (2%), and CF_2^+ (1%) as the minority ions.[6] When the ions collide with the surface, they may become neutralized and/or undergo further dissociation into other smaller fragments including C and F atoms. The resulting fragments and radicals may subsequently react with the substrate atoms and/or other predeposited surface species (e.g., O atoms in the case of the oxidized Si surface). Our study on ion irradiation in CF_4 and CH_2F_2 shows that their respective majority ions CF_3^+ and CH_2F^+/CHF_2^+ primarily undergo atomization upon low-energy impact on the surface.[1,2] The presence of the larger majority ions with a C═C double bond such as $C_2H_2F_2^+$ and $C_2H_2F^+$ in the present case is expected to generate different surface species, possibly with the C═C or C_2 intact, and different respective surface reactions.

To date, the surface spectroscopy of fluorinated ethylenes and their chemisorbed adspecies on Si surfaces is largely unknown. Given that the C−H bond (with a bond strength $\Delta H_B = 337$ kJ mol^{-1}) is generally weaker than the C−F bond ($\Delta H_B = 485$ kJ mol^{-1}),[8] we expect *iso*-DFE, like ethylene,[9] to chemisorb on the 7×7 surface at room temperature (RT) intact (likely as a [2 + 2] cycloaddition adspecies). However, the Si−F bond ($\Delta H_B = 552$ kJ mol^{-1}) is stronger than the C−F bond,

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which makes F abstraction quite thermodynamically plausible upon annealing. An early study on perfluoroethylene or C_2F_4 (and CF_3CH_2I) on Si(100)2×1 by Lin and Yates[10] shows that C_2F_4 physisorbs on Si(100) below 150 K, in contrast to ethylene that is found to chemisorb at 77−600 K.[11] The adsorption properties of *iso*-DFE, as an intermediate homologue between C_2F_4 and ethylene, on Si is therefore of particular interest to further our understanding of this fundamental chemisorption problem. The study of chemisorbed *iso*-DFE on Si surfaces at RT also provides an opportunity to characterize surface vibrations of simple CF_x (and SiF_x) species on Si surfaces not observed previously. To the best of our knowledge, no such study on the surface chemistry and spectroscopy of *iso*-DFE and their ion-induced processes on Si surfaces has been reported.

2. Experimental Details

The experimental apparatus and procedure used in the present work have been described elsewhere.[12] Briefly, the experiments were conducted in a home-built ultrahigh vacuum system with a base pressure better than 5×10^{-11} Torr. All of the EELS measurements were made under specular reflection scattering conditions of 45° from the surface normal and with the sample held at RT. A routine energy resolution of 12−17 meV (or 97−136 cm^{-1}) full-width at half-maximum with a typical count rate of 100 000 counts/s for the elastic peak could be achieved with our spectrometer typically operated at 5 eV impact energy. It should be noted that the calibration and tuning of the EELS spectrometer limit the reproducibility of the measured peak positions to ±2 meV (or ±16 cm^{-1}) in the present work. The TDS experiments were obtained by using a differentially pumped quadrupole mass spectrometer to monitor the ion fragments, along with a home-built programmable proportional-integral-differential temperature controller to provide a linear heating rate of 1 K s^{-1}. The TDS data have been smoothed by adjacent averaging. The respective monotonically increasing backgrounds with increasing temperature could be due to a somewhat low pumping speed in the ionization region of the mass spectrometer. The Si(111) sample (p-type boron-doped, 50 Ω cm, 8 × 6 mm^2, 0.5 mm thick) with a stated purity of 99.999% was purchased from Virginia Semiconductor Inc. The sample was mechanically fastened to a Ta sample plate with 0.25-mm-diameter Ta wires and could be annealed by electron bombardment from a heated tungsten filament at the back side of the sample. The Si(111) sample was cleaned by a standard procedure involving repeated cycles of Ar^+ sputtering and annealing to 1200 K until a sharp 7×7 LEED pattern was observed. The cleanliness of the 7×7 surface was further verified in situ by the lack of any detectable vibrational EELS feature attributable to unwanted contaminants, particularly the Si−C stretching mode at 800−850 cm^{-1}. The gaseous *iso*-difluoroethylene (99% purity) was purchased from Sigma−Aldrich and was exposed (without further purification) to clean Si(111) sample at a typical pressure of 1×10^{-5} Torr by use of a variable leak valve.

Ion irradiation was performed on a sample positioned 5 cm from the front face of the ion gun, by operating the ion gun with the chamber back-filled with the sputtering gas of interest to a working pressure of 2×10^{-5} Torr. The impact energy of the ion beam could be controlled by adjusting a floating voltage applied on the sample with respect to a preselected beam energy of the ion gun. The ion dose can be estimated by the product of the ion flux (estimated to be ~2 nA/mm^2) and the exposure time [obtained from the exposure in units of Langmuir (1 L = 1×10^{-6} Torr·s) and the working pressure]. Inside the ion gun, the sputtering gas was ionized by electrons with 180 eV kinetic energy, and only positive ions from the ion gun could reach the sample without mass selection. The concentration of each ion can be estimated from the cracking pattern of the corresponding molecule reported in the literature.[6]

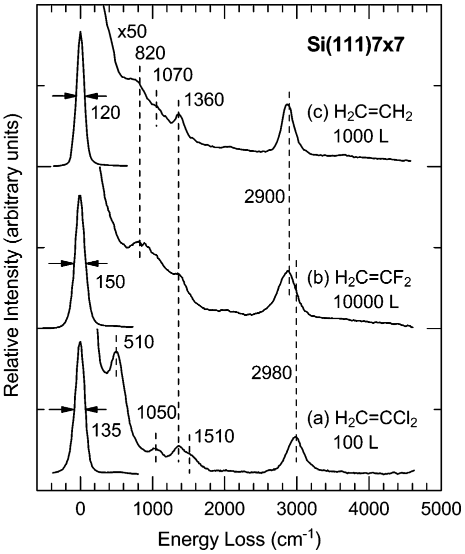

Figure 1. Vibrational electron energy loss spectra for saturation coverages of (a) *iso*-dichloroethylene, (b) *iso*-difluoroethylene, and (c) ethylene exposed to Si(111)7×7 at room temperature.

3. Results and Discussion

3.1. EELS Spectra of *iso*-DFE Adsorbed on Si(111)7×7.

Figure 1 compares the vibrational EELS spectra for saturation coverage [10 kL, where 1 kL = 1000 L, and 1 L (Langmuir) = 1×10^{-6} Torr·s] of *iso*-DFE with those for 1000 L of ethylene and 100 L of *iso*-dichloroethylene (DCE), all exposed to Si(111)7×7 at RT. It should be noted that the differences in the exposures required to reach saturation coverage for *iso*-DFE and other adsorbates could be due to differences in the sticking coefficients. The EELS spectra for *iso*-DFE (Figure 1b) and ethylene (Figure 1c) are found to be remarkably similar to each other, while the spectrum for *iso*-DCE is discernibly different. In particular, a prominent C−H stretch feature at 2900 cm^{-1} is observed for *iso*-DFE and ethylene, while the C−H stretch for *iso*-DCE is found at a higher frequency (2980 cm^{-1}). In the midfrequency region, all three adsorbates also exhibit a second common but weaker feature at 1360 cm^{-1}, which can be attributed to the CH_2 scissoring mode, indicating the presence of the CH_2 group in the corresponding adstructures. In the low-frequency region (<1200 cm^{-1}), only *iso*-DCE exhibits an intense EELS feature at 510 cm^{-1} that can be assigned to Si−Cl stretch (Figure 1a), in accord with the characteristic frequency for the Si−Cl stretching mode (467−600 cm^{-1}) commonly reported in the literature.[13,14] The presence of this Si−Cl feature at 510 cm^{-1} indicates dechlorination upon adsorption of *iso*-DCE at RT. Further details regarding chlorinated ethylenes and their surface chemistry have been given in our recent work.[15] In contrast, the intensities for the characteristic stretching frequencies for Si−F and Si−F_x (x = 2, 3) generally found at 825−850 cm^{-1} and 827−1015 cm^{-1}, respectively,[2] are considerably weaker relative to the C−H stretch at 2900 cm^{-1}. Given that other vibrational features are also found in this low-frequency region, the relatively low intensity of the band at 800−1200 cm^{-1} therefore suggests that defluorination plays only a minor role for *iso*-DFE.

Our present EELS spectrum for ethylene on Si(111)7×7 (Figure 1c) is found to be in good accord with that reported earlier by Yoshinobu et al.[16] On the basis of the observation of the prominent C−H stretch feature at 2930 cm^{-1} and several weaker features in the 600−1300 cm^{-1} region, including the C−C stretch at 1090 cm^{-1}, CH_2 bending modes at 1235 cm^{-1} (wag), 940 cm^{-1} (twist), and 710 cm^{-1} (rock), and Si−C stretch at 625 cm^{-1} (symmetric mode) and 795 cm^{-1} (asymmetric mode), Yoshinobu et al. proposed that the adsorption of ethylene on Si(111)7×7 and Si(100)2×1 involves a [2 + 2] cycloaddition mechanism and the formation of a di-σ-bonded ethane-1,2-diyl adstructure with near-sp^3 hybridization for the C atoms.[16] Given the strong similarity in the EELS spectra between ethylene (Figure 1c) and *iso*-DFE (Figure 1b), we therefore propose an analogous di-σ-bonded difluoroethane-1,2-diyl ($H_2\dot{C}{=}\dot{C}F_2$) adstructure for *iso*-DFE on the 7×7 surface. In particular, like ethylene, the lower frequency of the C−H stretching mode at 2900 cm^{-1} for *iso*-DFE could be attributed to C sp^3 hybridization, while the weak band at 600−1300 cm^{-1} could be assigned to a mixture of several modes including the C−C stretch, CH_2 bending modes, and Si−C stretch, as well as the symmetric and asymmetric C−F stretching modes (found to be located at 926 and 1302 cm^{-1}, respectively, in the gas-phase spectrum of *iso*-DFE[17,18]). Furthermore, in contrast to *iso*-DCE (Figure 1a), the absence of the C═C stretching mode at 1510 cm^{-1} for *iso*-DFE (Figure 1b) [and ethylene (Figure 1c)] is consistent with the presence of the di-σ-bonded [2 + 2] cycloaddition product such as the difluoroethane-1,2-diyl adspecies. It should be noted that even for the C−F-containing molecules in the gas phase, the C−F stretching vibrations could extend over a wide frequency range of 1000−1360 cm^{-1}, while the C−F deformation vibrations correspond to the low-frequency bands at 520−830 cm^{-1}.[17,18] Given the complexities and the broadness of these EELS features, it is therefore not particularly fruitful to use these F-related vibrations to determine the nature of the corresponding adstructures.

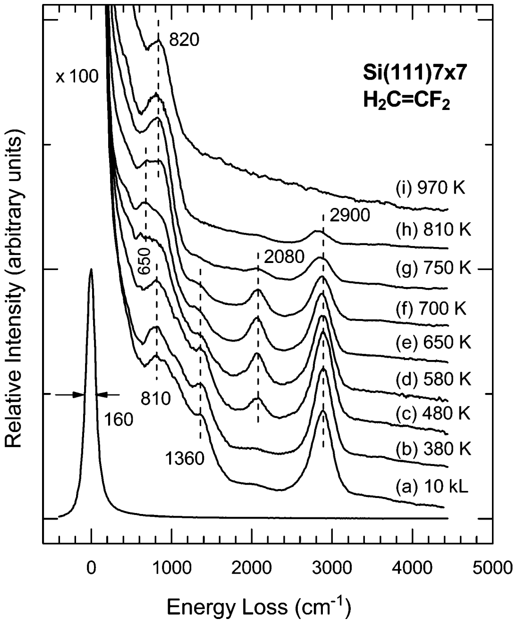

Figure 2. Vibrational electron energy loss spectra for (a) Si(111)7×7 exposed to 10 kL of *iso*-difluoroethylene at room temperature and upon annealing to (b) 380, (c) 480, (d) 580, (e) 650, (f) 700, (g) 750, (h) 810, and (i) 970 K.

To examine the thermal evolution of the proposed di-σ-bonded difluoroethane-1,2-diyl adspecies, we record EELS spectra for 10 kL of *iso*-DFE exposed to the 7×7 surface at RT followed by flash-annealing of the sample to successively higher temperatures. Upon annealing of the sample to 380 K, no discernible change from the RT spectrum (Figure 2a) is observed in the resulting spectrum (Figure 2b), which suggests that the adspecies are stable at 380 K. Furthermore, continuous reductions in the intensities of the CH_2 scissoring feature at 1360 cm^{-1} and of the prominent C−H stretch feature at 2900 cm^{-1} over the annealing temperature of 480−810 K (Figure 2c−h) appear to correlate with a concomitant increase in the intensity of the Si−H stretch at 2080 cm^{-1}. Such a correlation strongly suggests H abstraction of the predominant di-σ-bonded difluoroethane-1,2-diyl adspecies by the substrate Si atoms over 480−810 K. The H abstraction pattern for *iso*-DFE over this annealing temperature range is therefore similar to that observed for ethane-1,2-diyl adspecies in the case of ethylene on Si(111)7×7.[9,11] Moreover, the C−H stretch feature for the *iso*-DCE adstructure is found to undergo a red shift from 2980 to 2900 cm^{-1} upon annealing to 580 K, which could be attributed to the change in the immediate bonding environment, as expected from thermal evolution of the mono-σ-bonded chlorovinyl and di-σ-bonded vinylidene adspecies to vinylene.[15] In contrast, there is no corresponding red shift in the C−H stretch feature at 2900 cm^{-1} for *iso*-DFE over the same annealing temperature range, which suggests that the proposed difluoroethane-1,2-diyl adspecies for *iso*-DFE follows a similar evolution pattern involving C−C bond cleavage as that of ethane-1,2-diyl adspecies for ethylene.[9,11] Upon further annealing of the sample to 970 K (Figure 2i), the C−H stretch feature at 2900 cm^{-1} is found to disappear, which indicates total thermal breakdown of the adspecies into SiC. A reduction in the intensity of the Si−H stretch at 2080 cm^{-1} is also observed at 700−810 K (Figure 2f−h), which is in good accord with the desorption of H_2 above 700 K.[19] In addition, although the intensity of the weak low-frequency band at 600−1300 cm^{-1} appears to be relatively stable upon annealing to 480 K (Figure 2c), the nature and composition of this band (which has been previously attributed to a mixture of C−C stretch, CH_2 bending modes, and Si−C stretch, as well as the C−F stretch) may undergo complex changes. Upon annealing to 580−700 K (Figure 2d−f), a new feature attributed to Si−H bending mode is found to emerge at 650 cm^{-1}, which suggests the formation of monohydrides on the 7×7 surface.[20,21] Further annealing of the sample above 750 K diminishes this feature at 650 cm^{-1} with the emergence of a well-defined Si−C stretch feature at 820 cm^{-1} (Figure 2i). These spectral changes are consistent with the decomposition of the adspecies to SiC (and/or other hydrocarbon fragments) at these higher annealing temperatures.

3.2. EELS Spectra of Si(111)7×7 Ion-Irradiated in *iso*-DFE. Figure 3 shows typical vibrational EELS spectra of Si(111)7×7 as a function of ion-irradiation exposure in *iso*-DFE at 50 eV impact energy at RT. In comparison with the EELS spectrum for the RT adsorption of *iso*-DFE (i.e., without ion irradiation) on the 7×7 surface (Figure 3a), a new prominent feature at 810−850 cm^{-1} is found to increase in intensity with increasing ion-irradiation exposure. According to the reported literature data, the Si−C stretching mode is commonly observed at 750−950 cm^{-1},[11,13] while the Si−F stretching mode usually occurs at 825−850 cm^{-1}.[22,23] For SiF_x ($x = 2, 3$) species, the bending (rocking) and symmetric and asymmetric stretching modes are generally found at 300−380, 827−870, and 920−1015 cm^{-1}, respectively.[22−25] The new EELS feature found at 810−850 cm^{-1} can therefore be attributed to the stretching modes of both silicon carbides (SiC) and fluorosilyl [SiF_x ($x = 1-3$)] surface species. Furthermore, a second new feature attributed to Si−H stretching mode of surface silicon hydrides[13] is observed at 2100 cm^{-1} (Figure 3b−e). Unlike the fluorosilyl

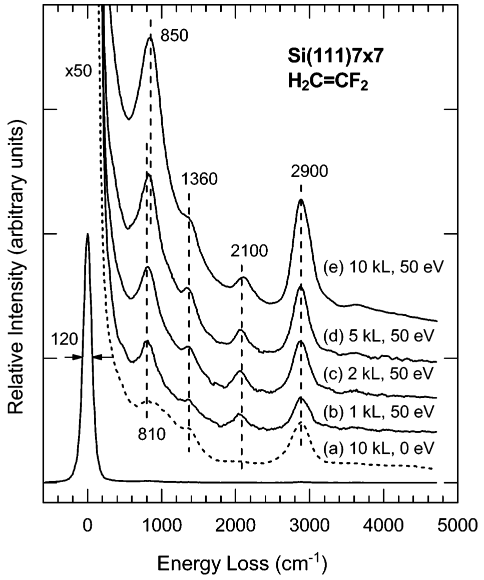

Figure 3. Comparison of vibrational electron energy loss spectra for Si(111)7×7 (a) exposed to 10 kL of *iso*-dichloroethylene with those for Si(111)7×7 ion-irradiated at 50 eV impact energy in (b) 1, (c) 2, (d) 5, and (e) 10 kL of *iso*-difluoroethylene.

stretching feature at 810−850 cm^{-1}, the Si−H stretch at 2100 cm^{-1} appears to become saturated after ion irradiation in 2 kL of *iso*-DFE (Figure 3c). The stronger propensity of the Si substrate for F attack than H attack suggests that the F atoms are more reactive and that the formation of fluorosilyl products, unlike silicon hydrides, does not depend on the availability of the Si dangling bonds. In addition, all the EELS spectra for ion irradiation (Figure 3b−e) also exhibit a prominent feature at 2900 cm^{-1} and a weak shoulder at 1360 cm^{-1}, which could be assigned to the C−H stretching modes and CH_2 scissoring modes of the adsorbed hydrocarbon species,[26,27] respectively, as previously observed for *iso*-DFE exposure without ion irradiation (Figure 3a). Furthermore, the C−H stretch feature at 2900 cm^{-1} apparently continues to strengthen with increasing ion-irradiation exposure, which suggests that ion irradiation could promote the formation of hydrocarbon adspecies and the growth of a carbonaceous layer on the 7×7 surface.[28]

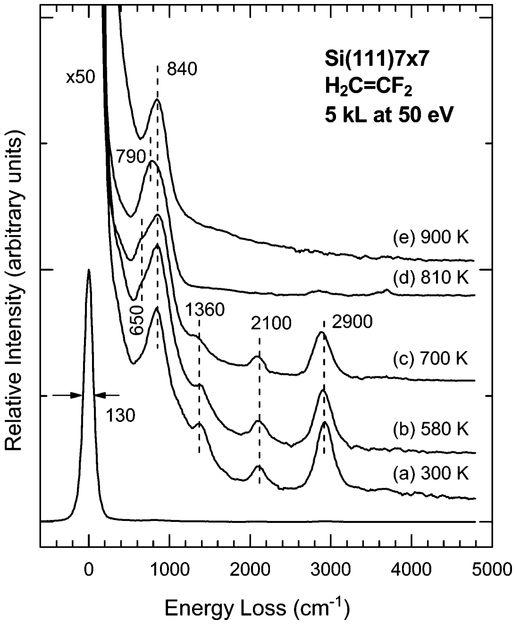

Figure 4. Vibrational electron energy loss spectra for (a) Si(111)7×7 ion-irradiated at 50 eV impact energy in 5 kL of *iso*-difluoroethylene at 300 K, followed by annealing to (b) 580, (c) 700, (d) 810, and (e) 900 K.

It is of interest to compare the EELS spectra obtained by ion irradiation in *iso*-DFE (Figure 3) with those in CF_4 and CH_2F_2.[1,2] In our earlier work on ion irradiation in CF_4, the emergence of the bending modes of SiF_x ($x = 2, 3$) at 340 cm^{-1} has been used as evidence for the formation of the larger fluorosilyl surface species.[1,2] The absence of these bending features at 340 cm^{-1} in the present case involving ion irradiation in high *iso*-DFE exposure suggests that the formation of these larger SiF_x ($x = 2, 3$) species is not dominant even at 10 kL (Figure 3e). However, the small but discernible blue shift of the $Si-F_x$ stretch feature from 810 to 850 cm^{-1} with increasing *iso*-DFE ion-irradiation exposure (Figure 3d) suggests that there are increasing contributions from the $Si-F_x$ symmetric and asymmetric stretching modes of the larger SiF_2 and SiF_3 species (with the higher characteristic vibrational frequencies). The observed blue shift (~40 cm^{-1}) for the *iso*-DFE ion-irradiated sample, like that for ion irradiation in CH_2F_2,[2] is found to be smaller than the corresponding blue shift (~105 cm^{-1}) for the CF_4 ion-irradiation case,[1] which is also consistent with the lower relative surface concentration of F atoms (and therefore of the larger SiF_x species) produced by ion irradiation in the larger fluorocarbons. This difference in the relative F surface concentration at higher ion-irradiation exposure may be related to the different F-to-C ratios of the sputtering gases (4 for CF_4 versus 2 for CH_2F_2 and 1 for *iso*-DFE). Since the stretching mode for SiC has also been reported to be near 820 cm^{-1},[11,13] the increase in intensity found for the feature at 810−850 cm^{-1} could be argued as an indicator of SiC buildup during ion irradiation. However, the intensity increase in this feature found for ion irradiation in *iso*-DFE (with two C atoms) is similar to that for ion irradiation in CH_2F_2 (with one C atom).[2] The apparent lack of dependence on the C stoichiometry of the sputtering gas in the observed intensity change further supports that the stretching vibrations from the fluorosilyl species should provide a greater contribution to the feature at 810−850 cm^{-1} than those from the SiC species. Furthermore, a notable difference between the EELS spectra for ion irradiation in *iso*-DFE and that in CH_2F_2[2] is the presence of the CH_2 scissoring modes at 1360 cm^{-1} in the former case (Figure 3). This difference could be due to the different relative surface concentration and composition of the hydrocarbon fragments produced in ion irradiation.

Figure 4 illustrates the effects of annealing the resulting surface species obtained by ion irradiation of Si(111)7×7 in 5 kL of *iso*-DFE (shown in Figure 3d). In particular, with the exception of the emergence of a weak shoulder at 650 cm^{-1} that is attributable to SiH bending,[26] no significant spectral change is observed upon annealing of the sample to 580 K (Figure 4b). Further annealing to 700 K appears to generally reduce the intensities of all features, and the weakening of the feature at 840 cm^{-1} has evidently helped to better expose the new feature at 650 cm^{-1} (appearing as a shoulder in Figure 4c). The intensity reductions in the $Si-F_x$ stretch at 840 cm^{-1} and Si−H stretch at 2100 cm^{-1} indicate that the corresponding SiF_x and SiH surface species are being desorbed from the surface, while the intensity reductions in the CH_2 scissoring mode at 1360 cm^{-1} and C−H stretch at 2900 cm^{-1} further suggest dehydrogenation of the surface hydrocarbon fragments. Upon further annealing of the sample to above 810 K, all hydrogen-related features including the Si−H stretch at 2100 cm^{-1} and the C−H stretch at 2900 cm^{-1} are essentially extinct (Figure 4d), which is in good accord with the total breakdown of the hydrocarbon fragments and the recombinative desorption of H_2 from silicon monohydrides above 700 K.[29] The breakdown of the hydrocarbon fragments is also consistent with the spectral evolution of the broad peak near 790 cm^{-1} as a result of changing contributions from the SiH bending and fluorosilyl stretch (reduction) and SiC stretch (enhancement). This broad peak evolves into a sharp feature at an annealing temperature of 900 K (Figure 4e), suggesting the formation of carbon cluster and other precursor surface species for SiC alloy. We have also collected the temperature-dependent EELS spectra for ion irradiation of Si(111)7×7 in a higher exposure (10 kL) of *iso*-DFE. The resulting spectral features (not shown) are found to exhibit similar temperature dependence to those shown in Figure 4, which suggests that, except for the increased amounts obtained with the higher ion-irradiation exposure, the nature of the surface species generated at different ion-irradiation exposures are similar.

During the annealing experiment, the changes in the LEED pattern for the 7×7 surface upon ion irradiation in *iso*-DFE (not shown) are found to be similar to those for ion irradiation in CF_4 or CH_2F_2.[1,2] In particular, ion irradiation in a low exposure (1−2 kL) of *iso*-DFE at 50 eV impact energy changes the 7×7 LEED pattern of Si(111)7×7 to a 1×1 pattern, which could be reverted back to a weak and diffuse 7×7 pattern by annealing to 900 K. However, no discernible LEED spots could be observed upon ion irradiation with a higher ion-irradiation exposure (10 kL), and a 1×1 followed by a diffuse 7×7 pattern could only be recovered upon annealing of the sample to 900 and 1000 K, respectively. In accord with our EELS data (Figure 4), the observed changes in the LEED patterns during thermal evolution are consistent with the gradual desorption of SiF_x and hydrocarbon fragments from the surface in the temperature range of 400−900 K, leaving SiC as the predominant surface product above 900 K.

3.3. EELS Spectra of Vitreous SiO_2 Ion-Irradiated in *iso*-DFE. We also investigate the effects of ion irradiation in *iso*-DFE on a vitreous SiO_2 surface, prepared by following a procedure similar to that used by Ibach et al.;[30] that is, exposing 10 kL of O_2 to a Si(111)7×7 surface held at 700 K. The resulting vitreous SiO_2 layer (estimated to be 5 Å thick by Ibach et al.[30]) is found to exhibit a weak 1×1 LEED pattern. As shown in Figure 5a, such a vitreous SiO_2 surface is characterized by three energy loss features at 385, 690, and 1050 cm^{-1}, corresponding to, respectively, rocking (350−480 cm^{-1}) and symmetric (690−840 cm^{-1}) and asymmetric stretching modes (1050−1180 cm^{-1}) of the Si−O−Si radical.[30] It should be noted that, in contrast to the Si−Si separation in a native oxide layer that is essentially the same as that in crystalline silicon (2.35 Å), the Si−Si separation found in vitreous SiO_2 in silica (3.05 Å) is considerably larger. The native oxide layer formed at RT therefore has a more “compressed” structure with a smaller angle between the two Si−O bonds than the vitreous SiO_2, which can be obtained by annealing the sample after and/or during oxidization to 700 K (as used in the present work) or by ion-bombarding the sample in O_2 at RT.[28] The vitreous SiO_2 can be distinguished from the native SiO_2 formed at RT by the characteristic blue shifts of approximately 10−130 cm^{-1} in their vibrational features from those of the native SiO_2.[30] Figure 5b−d illustrates the effects of increasing ion-irradiation exposure of *iso*-DFE at 50 eV impact energy on a vitreous SiO_2 surface (Figure 5a). In our early study of increasing ion-irradiation exposure of CH_2F_2 and CF_4 (to 10 kL) at 50 eV impact energy, the rocking mode of the Si−O−Si radical of vitreous SiO_2 is found to evolve into a better-defined shoulder at 385 cm^{-1} due to additional contribution from Si−F_x bending modes, while the features corresponding to the Si−O stretching modes (of vitreous SiO_2) and the Si−C and Si−F_x stretching modes have evidently merged into a single broad band with a maximum near 950 cm^{-1}.[1,2] Similar observations about these EELS features below 1500 cm^{-1} can also be made for increasing ion-irradiation exposure of *iso*-DFE. In particular, ion irradiation of the vitreous SiO_2 surface in increasing exposure of *iso*-DFE at 50 eV impact energy (Figure 5d) appears to generally broaden the characteristic EELS features for the vitreous SiO_2. The apparent blue shift of the Si−O symmetric stretching mode from 690 cm^{-1} (Figure 5a) to 770 cm^{-1} (Figure 5d) with increasing ion-irradiation exposure could be due to the emergence of a new Si−F_x ($x = 1-3$) stretch feature near 810 cm^{-1}, as observed earlier for the 7×7 surface (Figure 3). The intensity increase in the fluorosilyl stretch near 810 cm^{-1} appears to correlate with a similar increase in the intensities of the Si−H stretch feature at 2185 cm^{-1} and the C−H stretch feature at 2920 cm^{-1} with increasing ion-irradiation exposure of *iso*-DFE (Figure 5b−d). It should be noted that the Si−H stretching mode for the vitreous SiO_2 sample evidently occurs at a slightly higher energy loss (2185 cm^{-1}) than the corresponding feature for the 7×7 sample (2100 cm^{-1} shown in Figure 4). A minor difference in the C−H stretch frequency is also observed for the vitreous SiO_2 sample (2920 cm^{-1}) relative to the 7×7 sample (2900 cm^{-1}). Both of these spectral changes could be due to the change in the electronegativity of the Si atoms in the presence of their O neighbors.[31]

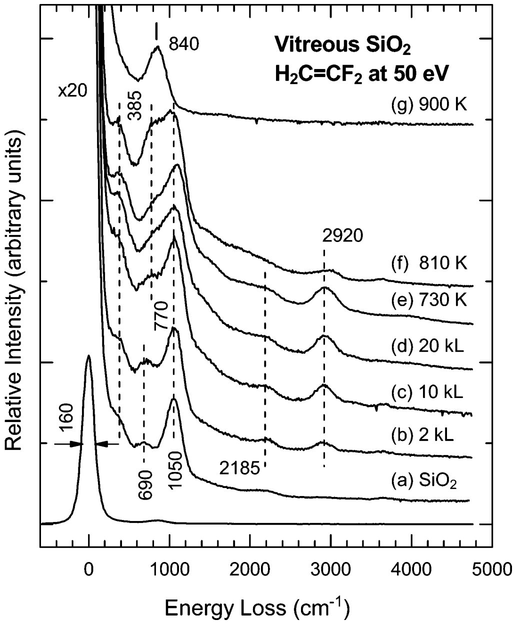

Figure 5. Vibrational electron energy loss spectra for (a) vitreous SiO_2, ion-irradiated at 50 eV impact energy in (b) 2, (c) 10, and (d) 20 kL of *iso*-difluoroethylene, followed by annealing to (e) 730, (f) 810, and (g) 900 K. The vitreous SiO_2 surface was obtained by exposing 10 kL of O_2 to Si(111)7×7 held at 700 K.

In comparison with the spectral changes for ion irradiation of a vitreous SiO_2 surface in CF_4 and CH_2F_2 with increasing ion-irradiation exposure (Figures 5 and 6 of ref 2), the intensity increases for the *iso*-DFE ion-irradiation-induced features (including the fluorosilyl stretch near 810 cm^{-1}, the Si−H stretch at 2185 cm^{-1}, and the C−H stretch at 2920 cm^{-1}) appear to be considerably less for the same amount of ion-irradiation exposure. For example, even with a 20-kL ion-irradiation exposure of *iso*-DFE, the corresponding fluorosilyl stretch feature near 810 cm^{-1} has not overtaken the nearby symmetric and asymmetric Si−O stretching modes of the oxidized surface, in marked contrast to the emergence of a single broad peak near

950 cm^{-1} in the case of CF_4 and CH_2F_2 with just half the corresponding ion-irradiation exposure.[2] According to the respective cracking patterns, the major ions for *iso*-DFE are $C_2H_2F_2^+$ (30%), $C_2H_2F^+$ (20%), CF^+ (15%), CH_2F^+ (12%), and C_2HF^+ (11%),[6] while the corresponding major ions are CF_3^+ (78%) and CF_2^+ (10%) for CF_4 and CH_2F^+ (38%) and CHF_2^+ (37%) for CH_2F_2.[6] Unlike the smaller ion fragments such as CF_3^+, CF_2^+, CH_2F^+, and CHF_2^+ that could atomize upon impact with the substrate, the larger ions $C_2H_2F_2^+$ and $C_2H_2F^+$ (with a C=C double bond) are more likely to produce smaller C_2-containing fragments. This difference in the nature of the ions (i.e., with or without a C=C double bond) produced from different sputtering gases in the ion irradiation process may therefore account for the different spectral evolution so observed.

Figure 5 also depicts the effect of annealing a vitreous SiO_2 surface ion-irradiated in 20 kL of *iso*-DFE at 50 eV impact energy. Upon annealing of the sample to 730 K, there is no significant change to the observed spectral features (Figure 5e). At the annealing temperature of 810 K (Figure 5f), the Si−H stretch at 2185 cm^{-1} and C−H stretch at 2920 cm^{-1} appear to be largely removed, while a notable increase in the spectral feature near 770 cm^{-1} is observed. The reduction of the Si−H stretching feature at 2185 cm^{-1} above 730 K is consistent with the recombinative desorption of H_2 (with desorption maxima commonly observed at 650−710 K for dihydrides and at 770−810 K for monohydrides[19−21]). The apparent extinction of the C−H stretching mode at 2920 cm^{-1} indicates that the destruction of the hydrocarbon adspecies either by dissociation or desorption occurs above 730 K (Figure 5e) and proceeds to completion above 810 K (Figure 5f). Further annealing of the sample to 900 K (Figure 5g) reduces the spectrum to a single EELS feature at 840 cm^{-1}, which can be assigned as the Si−C stretching mode of the SiC surface species. In the case of the vitreous SiO_2 surface, thermal evolution of the EELS features for the surface species produced by ion irradiation in *iso*-DFE (Figure 5e−g) is therefore similar to those found for ion irradiation in CF_4 and CH_2F_2,[2] suggesting that common surface species (including the fluorosilyl adspecies and silicon hydrides) are produced by ion irradiation in all three sputtering gases.

3.4. TDS Profiles of Selected Surface Products for Si(111)-7×7 and Vitreous SiO_2 Ion-Irradiated in *iso*-DFE. Figure 6 compares the TDS profiles of mass 85 (SiF_3^+) and mass 66 (SiF_2^+) for Si(111)7×7 and the vitreous SiO_2 surface upon ion irradiation in 10 kL of *iso*-DFE at 50 eV impact energy. The TDS profiles of mass 85 and mass 66 for 10 kL of *iso*-DFE exposed to Si(111)7×7 and a vitreous SiO_2 surface at RT (i.e., without ion irradiation) are also shown in Figure 6. Evidently, the TDS profiles of mass 85 (SiF_3^+) are generally different from those of mass 66 (SiF_2^+), while those for mass 47 (SiF^+) (not shown) are found to be similar to those of mass 66 (SiF_2^+). In accord with the gas-phase cracking patterns,[6,7] mass 85 (SiF_3^+) corresponds to the base mass of SiF_4[7] and could therefore be used to indicate the presence of the etching product, SiF_4. Because the TDS profiles for mass 66 (SiF_2^+) and mass 47 (SiF^+) are similar, they could be attributed to the same parent species, most likely SiF_2.[32] We also monitored other fragments, including mass 69 (CF_3^+), mass 50 (CF_2^+), and mass 31 (CF^+), during the TDS experiments. The absence of any desorption feature for these masses confirms that no substantial amount of CF_x species is formed for thermal desorption on the Si(111)7×7 or vitreous SiO_2 surface with or without ion irradiation in *iso*-DFE.

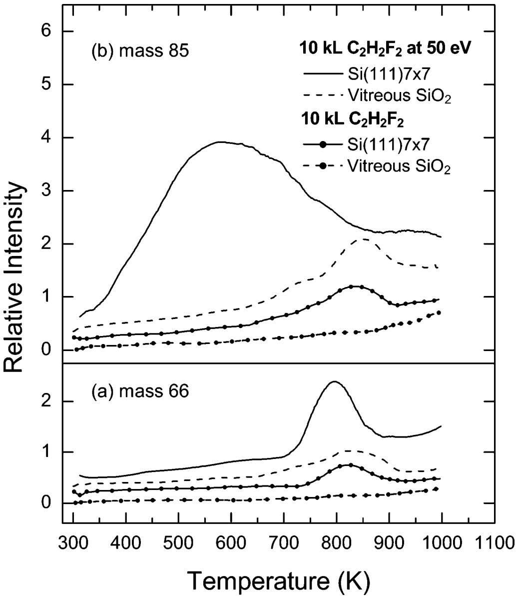

Figure 6. Thermal desorption profiles of (a) mass 66 (SiF_2^+) and (b) mass 85 (SiF_3^+) for Si(111)7×7 and vitreous SiO_2 with and without ion irradiation in 10 kL of *iso*-difluoroethylene at 50 eV impact energy. The vitreous SiO_2 surface was obtained by exposing 10 kL of O_2 to Si(111)7×7 held at 700 K.

It has been shown by Engstrom et al.[33] and Winters and Coburn[34] that the coverage of F atoms on a Si surface controls the relative concentrations of the fluorosilyl surface species. In particular, at low F coverage, the production of only the smaller SiF species is favored, which leads to SiF_2 as the major desorption product above 700 K. On the other hand, at a higher F coverage, the predominant surface products are the larger SiF_2 and SiF_3, which result in SiF_4 as the major desorption product with a maximum at 600 K. The mass-85 TDS profile for Si(111)7×7 ion-irradiated in 10 kL of *iso*-DFE, shown in Figure 6b, exhibits a broad feature with maximum at 600 K (corresponding to SiF_4 desorption), which is considerably more intense than the corresponding TDS feature at 750−950 K for the *iso*-DFE ion-irradiated vitreous SiO_2 sample. The observed difference for the mass-85 TDS profiles therefore suggest that the relative surface concentration of F atoms is considerably higher for the *iso*-DFE ion-irradiated 7×7 sample than the *iso*-DFE ion-irradiated SiO_2 sample. The higher relative F surface concentration is contributing to the higher relative concentrations of SiF_2 and SiF_3 surface species for the *iso*-DFE ion-irradiated 7×7 sample, in good accord with our temperature-dependent EELS data (Figure 4). Furthermore, the corresponding mass-66 feature with maximum at 800 K (corresponding to SiF_2 desorption) for the *iso*-DFE ion-irradiated 7×7 sample is also more intense than the broader feature at 700−900 K for the ion-irradiated vitreous SiO_2 sample (Figure 6a), which is also consistent with the generally higher relative F surface concentration found for the ion-irradiated 7×7 sample than the vitreous SiO_2 sample. In addition, for the 10 kL exposure of *iso*-DFE to Si(111)7×7 without ion irradiation, both the mass-85 TDS feature at 700−900 K and the mass-66 feature at 750−900 K are found to be even weaker than the respective features for the ion-irradiated vitreous SiO_2 sample (Figure 6), which suggests that ion irradiation is responsible for enhancing the production of the surface F atoms in good accord with our EELS data shown in Figure 3a,e. In the case of 10 kL exposure of *iso*-DFE to the vitreous SiO_2 surface (without ion irradiation), no TDS features for either mass 85 or mass 66 are observed, confirming the general lack of adsorption of *iso*-DFE on the (passivated) oxidized surface.

The TDS profiles for Si(111)7×7 ion-irradiated in *iso*-DFE shown in Figure 6 are found to be similar to those of the respective masses for Si(111)7×7 ion-irradiated in CF_4 and CH_2F_2.[1,2] Ion irradiation of the 7×7 surface in all three sputtering gases studied by us therefore appears to generate similar desorption patterns. For example, desorption of SiF_4 (corresponding to mass 85 or SiF_3^+) is observed over a wide temperature range with the maximum near 600 K for the 7×7 surface ion-irradiated in all three sputtering gases. On the other hand, the TDS profiles of the respective masses for ion irradiation of the vitreous SiO_2 sample in *iso*-DFE are quite different from those obtained by ion irradiation in either CF_4 or CH_2F_2.[1,2] Evidently, desorption of SiF_4 from the *iso*-DFE ion-irradiated vitreous SiO_2 sample is observed at a higher temperature (700−920 K). Furthermore, ion irradiation in 10 kL of *iso*-DFE generally generates less SiF_4 and SiF_2 desorption products on vitreous SiO_2 than on Si(111)7×7. In contrast, ion irradiation in 10 kL of CF_4 or CH_2F_2 produces more SiF_4 and SiF_2 desorption products on the vitreous SiO_2 sample than on the 7×7 surface. There are two possible factors that could account for the different behavior found for ion irradiation of 10 kL of *iso*-DFE on the vitreous SiO_2 surface. Given the F-to-C ratios of 1:1, 2:1, and 4:1 for *iso*-DFE, CH_2F_2, and CF_4, respectively, the amount of F atoms or F-containing fragments produced by ion irradiation in *iso*-DFE is expected to be less than those produced by ion irradiation in CH_2F_2 and CF_4 (assuming similar electron-impact ionization cross sections for the three sputtering gases). However, the similarity between the TDS profiles for ion irradiation of Si(111)7×7 in 10 kL of *iso*-DFE and those in CH_2F_2 suggests that ion irradiation in either *iso*-DFE or CH_2F_2 could generate a comparable amount of F-containing ions. Therefore, the different behavior for ion irradiation in *iso*-DFE on vitreous SiO_2 could not be explained just by the different relative amounts of F generated from the three sputtering gases. Indeed, the nature of the different hydrocarbon ions produced in the three sputtering gases may play a more important role. For example, ion irradiation in 10 kL of *iso*-DFE may produce carbon clusters or C_2-containing fragments on the surface upon impact (although our EELS data could not be used to clearly identify the vibrational features of the carbon clusters). For ion irradiation in 10 kL of CF_4 or CH_2F_2, the observation of more SiF_x and less SiC formed on vitreous SiO_2 than on Si(111)7×7 has led us to propose that the presence of surface O helps to remove C, thereby enabling more F to react with the Si surface. The absence of similar phenomena found for ion irradiation in *iso*-DFE is therefore consistent with the fact that surface O does not appear to react well with carbon clusters or C_2-containing fragments.

4. Summary

Thermal and ion-induced reactions of *iso*-DFE on Si(111)7×7 and vitreous SiO_2 surfaces have been investigated by using vibrational EELS and TDS. In the case of the RT adsorption and thermal evolution of *iso*-DFE on Si(111)7×7, the strong similarity of the EELS spectra for *iso*-DFE and ethylene indicates that *iso*-DFE predominantly chemisorbs on the 7×7 surface molecularly with di-σ-bonding in a [2 + 2] cycloaddition adstructure similar to that found for ethylene.[9,11] The resulting di-σ-bonded difluoroethane-1,2-diyl adstructure undergoes H abstraction and defluorination upon annealing, producing hydrocarbon fragments and SiF_x, which evolves as SiF_4 and SiF_2 desorption products above 700 K. In contrast, ion irradiation of Si(111)7×7 in *iso*-DFE generates more hydrocarbon fragments and SiF_x, resulting in stronger SiF_4 desorption over an extended temperature range (400−900 K) with a maximum at 600 K. This difference clearly demonstrates the higher efficiency in producing surface species by ion irradiation than by thermal dissociation of a sputtering gas on Si surfaces.

To study the effect as a result of the change in the F-to-C ratio of the sputtering gases, we also compare the surface processes on Si(111)7×7 and vitreous SiO_2 surfaces induced by ion irradiation in *iso*-DFE at 50 eV impact energy with those by ion irradiation in CF_4 and CH_2F_2.[1,2] Our results reveal very similar behavior for species produced by ion irradiation in either *iso*-DFE or CH_2F_2 on the 7×7 surface but not on the vitreous SiO_2 surface. In particular, our vibrational EELS data shows that SiC and SiF_x ($x = 1-3$), along with other hydrocarbon fragments, are the primary surface species on Si(111)7×7 produced by ion irradiation in *iso*-DFE at high exposure. Our exposure-dependent EELS spectra also indicate that a lower relative concentration of larger SiF_x adspecies is produced by ion irradiation in *iso*-DFE relative to that in CF_4. The difference between the case of CH_2F_2 and *iso*-DFE may be due to different surface concentrations and compositions of the corresponding hydrocarbon fragments. For example, the presence of the CH_2 scissoring mode in the EELS spectra for Si(111)7×7 indicates the formation of CH_2-containing hydrocarbon fragments in the case of ion irradiation in *iso*-DFE, while its absence in the case of ion irradiation in CH_2F_2 shows that CH_2-containing hydrocarbon surface products play only a minor role. On the vitreous SiO_2 surface, ion irradiation in CF_4 or CH_2F_2 produces more SiF_x than on Si(111)7×7, which is consistent with the hypothesis that surface O facilitates the removal of surface C (and hydrocarbon fragments), leaving more fluorine to react with silicon. On the other hand, our EELS data show that the vitreous SiO_2 surface is not significantly affected by ion irradiation in a high exposure of *iso*-DFE at 50 eV impact energy, which evidently produces less SiF_x on the oxidized surface than on the 7×7 surface. Our TDS data also shows that, unlike the case of vitreous SiO_2 ion-irradiated in CF_4 or CH_2F_2, the desorption product SiF_4 from the *iso*-DFE ion-irradiated vitreous SiO_2 sample is only observed at higher temperature (>700 K). The role of the relative F content (as reflected by the F-to-C ratio) is therefore clearly illustrated by the changes in the TDS data for the vitreous SiO_2 ion-irradiated in the three sputtering gases. The absence of selectivity of SiO_2 over Si observed for ion irradiation in *iso*-DFE may suggest that surface O could not effectively remove surface carbon clusters or C_2-containing species. Appropriate mixing of *iso*-DFE with either CF_4 or CH_2F_2 as the sputtering gas could therefore be used to manipulate the etching efficiency of SiO_2.

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