Thermal and Ion-Induced Surface Reactions of 1,1-Difluoroethylene on Si(111)7×7 and Vitreous SiO2

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Thermal and ion-induced reactions of 1,1-difluoroethylene (1,1-C2H2F2 or iso-DFE) on Si(111)7×7 and vitreous SiO2 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-diy1 adstructure, which undergoes H abstraction and defluorination, producing hydrocarbon fragments and SiFx (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 SiFx, leading to stronger SiF2 desorption products over an extended temperature range (400−900 K). The observed SiC and SiF2 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, CF4 and CH2F2. The production of higher relative concentrations for the larger SiFx is evident on the 7×7 surface. On a vitreous SiO2 surface, ion irradiation in iso-DFE, unlike that in CF4 and CH2F2, appears to produce less SiF2 than that on the 7×7 surface, which indicates that surface O does not interact strongly with the C2-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 and vitreous SiO2 surfaces have been investigated by vibrational electron energy loss spectroscopy and thermal desorption spectrometry (TDS).1,2 These simple fluorinated methanes, CF4 and CH2F2, 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 CF4 and CH2F2 at 50 eV impact energy produces SiC and SiF2 (x = 1−3) as the primary surface products, while additional hydrocarbon species are found in the latter case of ion irradiation in CH2F2.1,2 On a vitreous SiO2 surface, ion irradiation by the same exposure of fluorocarbon ions appears to enhance the deposition of SiF2 but reduce the amount of SiC species, which suggests a plausible recombination reaction of the surface O with surface C (releasing CO and CO2).1,2 We now expand this study to ion irradiation in simple fluorinated ethylenes, particularly, 1,1- or iso-difluoroethylylene (DFE, or C2H2F2) 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 CF3 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 C2H2F4+ (30%), C2H2F+ (20%), CF3+ (15%), CH2F+ (12%), and C2HF+ (11%). For CF4, CF3+ (estimated to be 78%) is the majority or base ion, with other smaller ions such as CF2+ (10%) and CF+ (3%) present at lower proportions;7 while for CH2F2, CH2F+ (38%) and CHF2+ (37%) are the majority ions, with CF+ (11%), CHF+ (4%), CH2F+ (3.8%), CH+ (2%), and C2F+ (1%) as the minority ions.8 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 CF4 and CH2F2 shows that their respective majority ions CF2+ and CH2F+/CHF2+ 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 C2H2F2+ and C3H2F+ in the present case is expected to generate different surface species, possibly with the C=C or C2 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 ΔHb = 337 kJ mol−1) is generally weaker than the C−F bond (ΔHb = 485 kJ mol−1),9 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 (ΔHb = 552 kJ mol−1) is stronger than the C−F bond,
which makes F abstraction quite thermodynamically plausible upon annealing. An early study on perfluorooethylene or C2F4 (and CF3CH2I) on Si(100)2 × 1 by Lin and Yates10 shows that C2F4 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 C2F4 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 CFx (and SiFx) 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 mm2, 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 7x7 LEED pattern was observed. The cleanliness of the 7x7 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/mm2) 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

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 coverages of (a) iso-dichloroethylene, (b) iso-difluoroethylene, and (c) ethylene exposed to Si(111)7 × 7 at room temperature.

![Figure 1](image_url)  
**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.

Given that other vibrational features are also found in this low-frequency region (<1200 cm−1), only iso-DFE 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-DFE 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−Fx (x = 2, 3) generally found at 825−850 cm−1 and 827−1015 cm−1, respectively, 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. 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, CH₂ 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 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-sp³ hybridization for the C atoms. Given the strong similarity in the EELS spectra between ethylene and iso-DFE (Figure 1c) and iso-DCE (Figure 1b), we therefore propose an analogous di-σ-bonded difluoroethane-1,2-diyl (H₂C=CF₂) 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 sp³ hybridization, while the weak band at 600–1300 cm⁻¹ could be assigned to a mixture of several modes including the C–C stretch, CH₂ 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). 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 absence 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. 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.

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 CH₂ 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. 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. 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. 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 H₂ above 700 K. 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, CH₂ 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. 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 Ion-Irradiated in iso-DFE. Figure 3 shows typical vibrational EELS spectra of Si(111)×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, while the Si–F stretching mode usually occurs at 825–850 cm⁻¹. For Si–Fₓ (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. 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 [SiFx] (x = 1–3) surface species. Furthermore, a second new feature attributed to Si–H stretching mode of surface silicon hydrides is observed at 2100 cm⁻¹ (Figure 3b–e). Unlike the fluorosilyl
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 exposure suggests that ion irradiation in 2 kL of iso-DFE were different.

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\(_2\)F\(_2\).\(^{1,2}\) In our earlier work on ion irradiation in CF\(_4\), the emergence of the bending modes of SiF\(_2\) \((x = 2, 3)\) 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 3c).

However, the small but discernible blue shift of the Si–F\(_2\) 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\(_2\) symmetric and asymmetric stretching modes of the larger SiF\(_2\) and SiF\(_3\) species (with the higher characteristic vibrational frequencies). The observed blue shift \((\sim 40 \text{ cm}^{-1})\) for the iso-DFE ion-irradiated sample, like that for ion irradiation in CH\(_2\)F\(_2\),\(^2\) is found to be smaller than the corresponding blue shift \((\sim 105 \text{ cm}^{-1})\) 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\(_2\)F\(_2\) 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\(_2\)F\(_2\) (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.

Further annealing of the sample to above 810 K, all hydrogen-related features including the Si–H stretch at 2100 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 hydrocarbon fragments are desorbed from the sample, while the intensity reductions in the CH\(_2\) scissoring mode at 1360 cm\(^{-1}\) and Si–H stretch at 2100 cm\(^{-1}\) indicate that the corresponding SiF\(_2\) and SiH surface species are being desorbed from the surface, and 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 the sample to above 810 K, all hydrogen-related features including the Si–H stretch at 2100 cm\(^{-1}\) and 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)$\times$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$\times$7 surface upon ion irradiation in iso-DFE (not shown) are found to be similar to those for ion irradiation in CF$_4$ or CH$_2$F$_2$.$^{1,2}$ In particular, ion irradiation in a low exposure (1–2 kL) of iso-DFE at 50 eV impact energy changes the 7$\times$7 LEED pattern of Si(111)$\times$7 to a 1$\times$1 pattern, which could be reverted back to a weak and diffuse 7$\times$7 pattern by annealing to 900 K. However, no discernable LEED spots could be observed upon ion irradiation with a higher ion-irradiation exposure (10 kL), and a 1$\times$1 followed by a diffuse 7$\times$7 pattern could only be recovered upon annealing of the sample to 900 and 1000 K, respectively. In accord with our EELS data (Figure 4), the observed changes in the LEED patterns during thermal evolution are consistent with the gradual desorption of SiF$_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)$\times$7 surface held at 700 K. The resulting vitreous SiO$_2$ layer (estimated to be 5 Å thick by Ibach et al.$^{30}$) is found to exhibit a weak 1$\times$1 LEED pattern. As shown in Figure 5a, such a vitreous SiO$_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 oxidation 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$_2$. 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$_2$F$_2$ 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$^{-1}$. 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$\times$7 surface (Figure 3). The intensity increase in the fluorosilyl stretch near 810 cm$^{-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$\times$7 sample (2100 cm$^{-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$\times$7 sample (2900 cm$^{-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}$

In comparison with the spectral changes for ion irradiation of a vitreous SiO$_2$ surface in CF$_4$ and CH$_2$F$_2$ 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
At the annealing temperature of 810 K (Figure 5f), the Si significant change to the observed spectral features (Figure 5e). Upon annealing of the sample to 730 K, there is no energy. Upon annealing of the sample to 730 K, there is no - is therefore similar to those found for ion irradiation in CF\textsubscript{4} and CH\textsubscript{2}F\textsubscript{2},\textsuperscript{2} suggesting that common surface species (including species produced by ion irradiation in surface, thermal evolution of the EELS features for the surface iso \textsuperscript{37%}) for CH\textsubscript{2}F\textsubscript{2}.\textsuperscript{6} Unlike the smaller ion fragments such as CF\textsubscript{3}+, CF\textsubscript{2}+, CH\textsubscript{3}F\textsuperscript{+},\textsuperscript{2} and CH\textsubscript{2}F\textsubscript{2}+ that could atomize upon impact with the substrate, the larger ions C\textsubscript{2}H\textsubscript{2}F\textsubscript{5}+ (with a C=C double bond) are more likely to produce smaller C\textsubscript{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\textsubscript{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\textsuperscript{-1} and C–H stretch at 2920 cm\textsuperscript{-1} appear to be largely removed, while a notable increase in the spectral feature near 770 cm\textsuperscript{-1} is observed. The reduction of the Si–H stretching feature at 2185 cm\textsuperscript{-1} above 730 K is consistent with the recombinative desorption of H\textsubscript{2} (with desorption maxima commonly observed at 650–710 K for dihydrides and at 770–810 K for monohydrides\textsuperscript{19–21}). The apparent extinction of the C–H stretching mode at 2920 cm\textsuperscript{-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\textsuperscript{-1}, which can be assigned as the Si–C stretching mode of the SiC surface species. In the case of the vitreous SiO\textsubscript{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\textsubscript{4} and CH\textsubscript{2}F\textsubscript{2},\textsuperscript{2} suggesting that common surface species (including the fluoroaryl 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\textsubscript{2} Ion-Irradiated in iso-DFE. Figure 6 compares the TDS profiles of mass 85 (SiF\textsubscript{5}+) and mass 66 (SiF\textsubscript{2}+) for Si(111)-7×7 and the vitreous SiO\textsubscript{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\textsubscript{2} surface at RT (i.e., without ion irradiation) are also shown in Figure 6. Evidently, the TDS profiles of mass 85 (SiF\textsubscript{5}+) are generally different from those of mass 66 (SiF\textsubscript{2}+), while those for mass 47 (SiF\textsubscript{4}+) (not shown) are found to be similar to those of mass 66 (SiF\textsubscript{2}+). In accord with the gas-phase cracking patterns, mass 85 (SiF\textsubscript{5}+) corresponds to the base mass of SiF\textsubscript{4} and could therefore be used to indicate the presence of the etching product, SiF\textsubscript{4}. Because the TDS profiles for mass 66 (SiF\textsubscript{2}+) and mass 47 (SiF\textsubscript{3}+) are similar, they could be attributed to the same parent species, most likely SiF\textsubscript{3}\textsubscript{2}.\textsuperscript{2} We also monitored other fragments, including mass 69 (CF\textsubscript{4}+), mass 50 (CF\textsubscript{2}+), and mass 31 (CF\textsuperscript{+}), during the TDS experiments. The absence of any desorption feature for these masses confirms that no substantial amount of CF\textsubscript{4} species is formed for thermal desorption on the Si(111)-7×7 or vitreous SiO\textsubscript{2} surface with or without ion irradiation in iso-DFE.

It has been shown by Engstrom et al.\textsuperscript{33} and Winters and Coburn\textsuperscript{34} that the coverage of F atoms on a Si surface controls the relative concentrations of the fluoroaryl surface species. In particular, at low F coverage, the production of only the smaller SiF species is favored, which leads to SiF\textsubscript{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\textsubscript{3} and SiF\textsubscript{4}, which result in SiF\textsubscript{2} 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-difluoroethylene at 50 eV impact energy. The vitreous SiO\textsubscript{2} surface was obtained by exposing 10 kL of O\textsubscript{2} to Si(111)-7×7 held at 700 K.

Figure 6. Thermal desorption profiles of (a) mass 66 (SiF\textsubscript{2}+) and (b) mass 85 (SiF\textsubscript{5}+) for Si(111)-7×7 and vitreous SiO\textsubscript{2} with and without ion irradiation in 10 kL of iso-difluorocarbene at 50 eV impact energy. The vitreous SiO\textsubscript{2} surface was obtained by exposing 10 kL of O\textsubscript{2} to Si(111)-7×7 held at 700 K.
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 CF4 and CH3F2.1,2 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 SiF4 (corresponding to mass 85 or SiF4+) 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 SiO2 sample in iso-DFE are quite different from those obtained by ion irradiation in either CF4 or CH3F2.1,2 Evidently, desorption of SiF3 from the iso-DFE ion-irradiated vitreous SiO2 sample is observed at a higher temperature (700–920 K). Furthermore, ion irradiation in 10 kL of iso-DFE generally generates less SiF4 and SiF3 desorption products on vitreous SiO2 than on Si(111)7×7. In contrast, ion irradiation in 10 kL of CF4 or CH3F2 produces more SiF4 and SiF3 desorption products on the vitreous SiO2 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 SiO2 surface. Given the F-to-C ratios of 1:1, 2:1, and 4:1 for iso-DFE, CH3F2, and CF4, 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 CH3F2 and CF4 (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 CH3F2 suggests that ion irradiation in either iso-DFE or CH3F2 could generate a comparable amount of F-containing ions. Therefore, the different behavior for ion irradiation in iso-DFE on vitreous SiO2 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 C2-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 CF4 or CH3F2, the observation of more SiF4 and less SiC formed on vitreous SiO2 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 C2-containing fragments.

4. Summary

Thermal and ion-induced reactions of iso-DFE on Si(111)7×7 and vitreous SiO2 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 adsorbate similar to that found for ethylene.3,11 The resulting di-σ-bonded difluoroethylene-1,2-diyld structure undergoes H abstraction and defluorination upon annealing, producing hydrocarbon fragments and SiF4, which evolves as SiF3 and SiF2 desorption products above 700 K. In contrast, ion irradiation of Si(111)7×7 in iso-DFE generates more hydrocarbon fragments and SiF3, resulting in stronger SiF4 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 SiO2 surfaces induced by ion irradiation in iso-DFE at 50 eV impact energy with those by ion irradiation in CF4 and CH3F2.1,2 Our results reveal very similar behavior for species produced by ion irradiation in either iso-DFE or CH3F2 on the 7×7 surface but not on the vitreous SiO2 surface. In particular, our vibrational EELS data shows that SiC and SiF3 (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 SiF3 adspecies is produced by ion irradiation in iso-DFE relative to that in CF4. The difference between the case of CH3F2 and iso-DFE may be due to different surface concentrations and compositions of the corresponding hydrocarbon fragments. For example, the presence of the CH2 scissoring mode in the EELS spectra for Si(111)7×7 indicates the formation of CH2-containing hydrocarbon fragments in the case of ion irradiation in iso-DFE, while its absence in the case of ion irradiation in CH3F2 shows that CH2-containing hydrocarbon surface products play only a minor role. On the vitreous SiO2 surface, ion irradiation in CF4 or CH3F2 produces more SiF4 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 SiO2 surface is not significantly affected by ion irradiation in a high exposure of iso-DFE at 50 eV impact energy, which evidently produces less SiF4 on the oxidized surface than on the 7×7 surface. Our TDS data also shows that, unlike the case of vitreous SiO2 ion-irradiated in CF4 or CH3F2, the desorption product SiF4 from the iso-DFE ion-irradiated vitreous SiO2 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 SiO2 ion-irradiated in the three sputtering gases. The absence of selectivity of SiO2 over Si observed for ion irradiation in iso-DFE may suggest that surface O could not effectively remove surface carbon clusters or C2-containing species. Appropriate mixing of iso-DFE with either CF4 or CH3F2 as the sputtering gas could therefore be used to manipulate the etching efficiency of SiO2.

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References and Notes


