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Continuous-time core-level photon-stimulated desorption spectroscopy for monitoring soft x-ray-induced reactions of molecules adsorbed on a single-crystal surface

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Continuous-time core-level photon-stimulated desorption (PSD) spectroscopy was proposed for monitoring the soft x-ray-induced reactions of molecules adsorbed on a single-crystal surface. Monochromatic synchrotron radiation was used as a soft x-ray light source in the photon-induced reactions of CF_3Cl adsorbed on a Si(111)-7×7 surface at 30 K and also as a probe for studying the produced fluorination states of the bonding surface Si atom in the positive-ion PSD spectroscopy. The F^+ PSD spectrum was obtained by monitoring the F^+ signal as a function of incident photon energy near the Si(2p) edge (98–110 eV). Sequential F^+ PSD spectra were measured as a function of photon exposure at four adsorbate coverages (the first dose$=0.3\times10^{15}$ molecules/cm^2, the second dose$=0.8\times10^{15}$ molecules/cm^2, the third dose$=2.2\times10^{15}$ molecules/cm^2, and the fourth dose$=3.2\times10^{15}$ molecules/cm^2). For the first and second CF_3Cl-dosed surfaces, the sequential F^+ PSD spectra show the variation of their shapes with photon exposure and indicate the formation of surface SiF species. The sequential F^+ PSD spectra for the third and fourth CF_3Cl-dosed surfaces also show the variation of their shapes with photon exposure and depict the production of surface SiF and SiF_3 species.

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I. INTRODUCTION

Photon-stimulated desorption (PSD) is the desorption process of positive and negative ions and neutral species from surfaces caused by electronic transitions in the surface or adsorbate complexes as a result of photon bombardment. Since the PSD of positive ions induced by synchrotron radiation (SR) photons was observed in 1979, research on PSD has shown rapid progress for over 20 years, and several photodissociation and photodesorption mechanisms have been proposed.[1–8]

Various PSD techniques have been developed. One of the most important and useful is the use of PSD in a spectroscopic mode. In the PSD spectroscopic mode, the desorbed ion yield versus incident photon energy is measured and the spectral threshold and shape provide the information on the basic excitation initiating the desorption process. For the PSD process via core-level excitation, the threshold energy corresponds to the photon energy required to excite a core-level electron of adsorbate or substrate atom. After exciting the electron, the following Auger decay process will lead to the rupture of chemical bonding and result in the ion desorption. The measurement of the PSD threshold energy for desorption gives insight into the chemical environment of the site from which the ion desorbed. For example, Yarmoff *et al.*[9–11] have employed core-level PSD spectroscopy to study the F^+ desorption from a fluorinated Si(111) surface, which contains different SiF_x species, and distinguished among F^+ originating from adsorbed SiF, SiF_2, or SiF_3 on the surface. Thus, core-level PSD spectroscopy is a powerful and useful method for studying the local electronic structure and chemical bonding of the adsorbed species.

In PSD spectroscopy, a PSD spectrum (ion intensity versus photon energy) is obtained during scanning the incident photon energy. It is generally assumed that the photon flux density is so small that only negligible beam damage of the adsorbate is caused by PSD during the time of measurement. Therefore, the PSD spectrum is reproducible in further repeated PSD scans. However, for high-intensity VUV and soft x rays, especially produced by third-generation synchrotron radiation sources, and/or the molecules with high photolysis cross sections—for example, some fluorine-containing molecules—the decay of the adsorbate concentration by PSD itself is not negligible. As a result, a dramatic change in a series of PSD spectra, which are measured one by one via repeating the incident photon energy scan, will be observed. This series of PSD spectra could be called continuous-time PSD spectra. Since a PSD spectrum can provide information on the local bonding and electronic structure of the surface, continuous-time PSD spectra can be employed to show the variation of the surface chemical bonding structure—the disappearance of a specific state and the formation of a new bonding structure during irradiation of incident photons. In the present work, we name this method continuous-time PSD spectroscopy.

On the other hand, photochemical processing via core-electron excitation is promising for the fabrication of future fine-structure microelectronic devices.[12–14] Because high-intensity soft x-ray synchrotron radiation can be used to cause site-specific chemical reactions on semiconductor surfaces by core-electron excitations of adsorbates or substrates, and its short wavelength nature may allow control of the photon-induced surface reactions to be done with extremely high spatial resolution, soft x-ray SR is considered to be a suitable photon source.[15–17] Several experiments on SR-stimulated processes[18–25] on semiconductor surfaces have been performed and shown that the SR-stimulated processing is a future prospective technology for low-temperature fabrication of semiconductor devices. Therefore, understanding the basic mechanisms responsible for the photochemical reactions of adsorbates on a semiconductor surface has become a very important research work.[26–32]

In order to gain insight into the monochromatic soft x-ray SR-excited reactions of adsorbed fluorochlorocarbon molecules with well-characterized semiconductor surfaces at the microscopic level, we have investigated in our previous experiments (Ref. 31) the photolysis of adsorbed molecules and the formed dissociation products present after monochromatic synchrotron radiation photon exposure for the system of CF_3Cl adsorbed on a Si(111)-7×7 surface as part of a general goal of developing an understanding of the photon-induced etching of semiconductor surfaces by using soft x-ray photons. We showed that CF_3Cl dissociation is activated primarily by low-energy photoelectron attachment and dipolar dissociation (DD) induced by higher-energy photoelectrons. The system of CF_3Cl adsorbed on Si(111) was chosen because CF_3Cl is used in the semiconductor etching process,[33–36] it has abundant experimental data of its interactions with electrons and photons in gas phase,[37–45] and silicon is the most important semiconductor material.

On the other hand, it is generally agreed that the fluorination of surface Si atom leading to the formation of SiF_x ($x=1-4$) species is the most important reaction process in the photoetching of silicon surface. From the experimental viewpoint, observation of the formation of SiF_x species during the irradiation of monochromatic soft x-ray near the core-level of adsorbate or substrate becomes very important in the core-electron excitation (site-specific) photoetching. Because in the continuous-time core-level PSD spectroscopy monochromatic soft x-ray SR is employed to induce reactions of adsorbates with surfaces and at the same time the desorption of ions induced by the incident photons is used to gain information on the variation of the chemical bonding of surface species, continuous-time core-level PSD spectroscopy can be used to study the reactions of the adsorbed etchant molecule with semiconductor surfaces. Therefore, in the present study we extended our previous work and employed continuous-time core-level PSD spectroscopy to monitor the soft x-ray SR-induced reactions of etchant molecules adsorbed on a silicon single-crystal surface. We focused on the observation of the fluorination of silicon surfaces during the irradiation of varying-energy monochromatic soft x-ray SR near the Si(2*p*) edge (98–110 eV) on the CF_3Cl/Si(111) system.

II. EXPERIMENT

The experiments were performed at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan using a 6-m low-energy spherical grating monochromator (6-m LSGM, bending magnet beamline) and a wide-range spherical grating monochromator (WR-SGM, bending magnet beamline). The experiments were performed in an ultrahigh-vacuum system (base pressure $<2\times10^{-10}$ Torr) equipped with a spherical sector electron energy analyzer (VG CLAM2) for synchrotron radiation photoemission spectroscopy (PES). The system is also equipped with an argon gun (VG AG5000) for sputtering, a quadrupole mass spectrometer (Balzers QMG421) for positive- and negative-ion PSD, and low-energy electron diffraction (LEED) optics (VG RVL900). A variable-temperature sample holder, connected to a closed-cycle refrigerated cryostat for cooling a sample down to 30 K and equipped with wires for passing current directly through the sample for heating it up to 1100 °C, was used for the sample cleaning and for the CF_3Cl adsorption measurements.

The Si(111) crystal (*p*-type, 9.6 Ω cm) surface was cleaned by cycles of argon-ion bombardment (800 eV) followed by direct resistive heating to 1100 °C. The surface structure was checked by LEED, and the cleanliness was checked by PES and evidenced by the characteristic surface states in the valence region.[46] Chlorotrifluoromethane (purity ⩾99.9%) was obtained from a commercial source and used without further purification. Gas exposure was made by dosing the clean Si(111)-7×7 surface with CF_3Cl gas from a gas-dosing system, composed of a miniature cross reservoir, a leak valve, and a stainless-steel tubing with a microchannel-plate doser head. It is equipped with two capacitance-pressure gauges (MKS-Baratron). The gas flux from the dosing system was calibrated by standard volumetric technique. We estimate the dose error to be ~20%. Measurements were performed for doses of 0.3, 0.8, 2.2, and 3.2×10^{15} molecules/cm^2. During the dosing of the gas and the PSD experiments the sample was kept at a temperature of 30 K.

Desorbing positive and negative ions were detected by a Balzers pulse-counting quadrupole mass spectrometer (QMS) (Balzers model QMG421 with off-axis secondary electron multiplier), which was positioned normal to the surface, and the incidence angle of the photon beam is 45° from the surface. The sample surface was located ~3 cm from the entrance of the QMS. During the measurement of positive and negative ions, the ionizer filament was turned off. A portion of positive and negative ions desorbed by photons impinging on the surface is focused by ion lenses at the entrance of the mass spectrometer. The angular acceptance of the QMS is ~10°.

Two measurement methods of the PSD technique were employed. The first (method 1) fixed the mass of the quadrupole mass spectrometer at F^+ or F^- (mass=19) and monitored the signal versus time at some fixed incident photon energies near the Si(2*p*) edge. Because during the course of the experiment (about 1 h) the storage ring current decayed by about 5%, we therefore normalized the ion signal by continuously monitoring the incident photon flux. The incident photon flux was measured with a 90% transmission nickel mesh calibrated with a photodiode. The beam size on the sample surface is 0.1×0.6 mm^2. Typical photon flux densities employed for this study are $\sim1\times10^{15}$ cm^{-2} sec^{-1}.

The second (method 2) fixed the mass of the quadrupole mass spectrometer at F^+ or F^- (mass=19) and monitored the ion signal as a function of incident photon energy near the Si(2*p*) edge (98–110 eV). In order to reduce the uncertainty in the photon energy caused by a backlash of the grating movement, the photon energy was varied in one direction from high to low energy for each PSD measurement. In general, the second method is employed to study the positive- and negative-ion yields as a function of incident photon energy, assuming that there is no photon-induced change in the chemical state of the overlayer when the PSD spectrum is taken during varying-energy photon irradiation. However, due to the high photolysis cross section of CF_3Cl adsorbed on the Si(111)-7×7 surface, in the present study we intended to use the second method to examine the photon-induced changes in the chemical states of adsorbates by observing the variation of the spectrum shape in the series of F^+ PSD spectra, which were measured one by one via repeating the incident photon energy scan. For each PSD spectrum, after the photon mask was opened, the F^+-ion yield was measured during varying the energy of incident photons from 110 to 98 eV. When a PSD spectrum was finished, the photon mask was closed and the grating of the monochromator was moved back to a high-energy position for the next PSD scan. The photon exposure for each PSD scan is calculated by integrating the photon flux over various incident photon energies, and the accumulated photon exposure for each spectrum in a series of F^+ PSD spectra is the summation of the photon exposures of its present and previous PSD scans. A 900-line/mm grating and 100-μm slits were used, giving an energy resolution of ~0.04 eV for the working energy range of 98 to 110 eV.

III. RESULTS AND DISCUSSION

In our previous work (Ref. 31), the qualitative and quantitative nature of the photolysis of a $CF_3Cl/Si(111)$-7×7 system induced by fixed-energy SR photons near the Si(2p) edge in submonolayer coverage (dose=0.3×10^{15} molecules/cm^2, ~0.75 monolayer) has been established. We have shown that CF_3Cl dissociation is not due to direct photoexcitation of adsorbed CF_3Cl molecules; instead, it is activated primarily by low-energy photoelectron attachment and dipolar dissociation induced by higher-energy photoelectrons. The photoelectrons emitting from the silicon substrate are produced by incident photons. For higher coverage in the multilayer range (dose=0.8×10^{15} and 2.2×10^{15} molecules/cm^2) the qualitative nature of the photolysis of this system has also been studied.[31] The surface SiF was the only fluorosilyl product observed in the photolysis of $CF_3Cl/Si(111)$ at high exposure to fixed-energy photons and near completion of the reaction for all these three doses. The other surface fluorosilyl product SiF_x (x=2–4) was not observed.

In the present work, we focused on the continuous-time observation and analysis of the fluorosilyl products formed on the silicon surface during irradiation of varying-energy photons near the Si(2p) edge (98–110 eV). Continuous-time core-level PSD spectroscopy (method 2) was used. The goal was to measure the fluorosilyl products created in photolysis and, primarily, whether or not the highly fluorinated fluorosilyl products SiF_3 and SiF_4 are formed.

Although varying-energy photons instead of fixed-energy photons near the Si(2p) edge were used in the present work, the mechanisms responsible for CF_3Cl dissociation should be the same for both photons, because neither the valence level nor the core level of the CF_3Cl molecule is in the energy region of 98–110 eV. Therefore, the results and explanation established in our previous work (Ref. 31) for the study of the photolysis of CF_3Cl molecules adsorbed on the Si(111)-7×7 surface using fixed-energy photons can be employed to interpret the data measured in the present work and will be described briefly in the following Sec. III A.

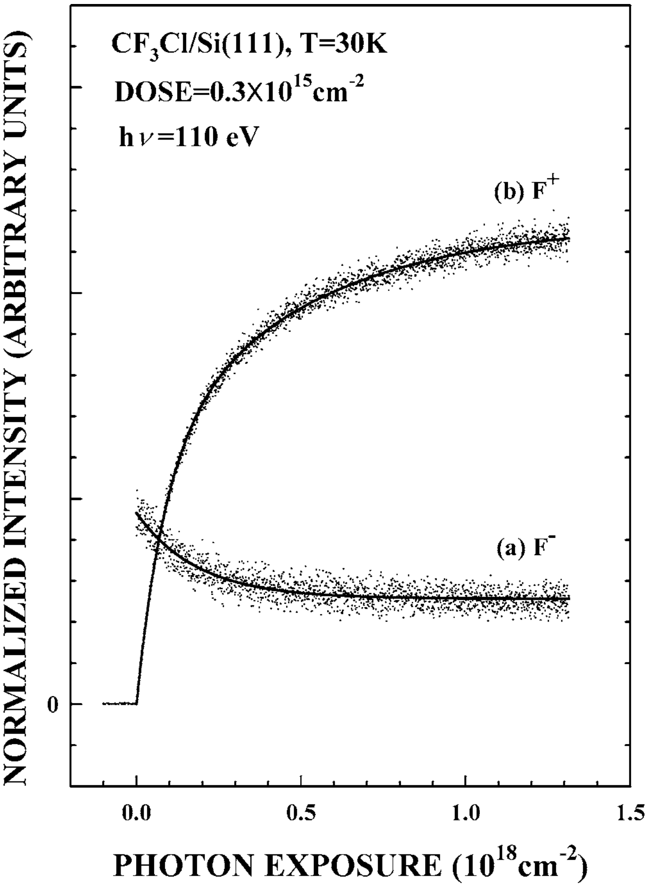

FIG. 1. Photon-exposure dependence of the photon-stimulated desorption yield of (a) F^- ions and (b) F^+ ions from CF_3Cl adsorbed on a Si(111)-7×7 surface at 30 K (CF_3Cl dose =0.3×10^{15} molecules/cm^2). The incident photon energy is 110 eV. The solid curve shown in (a) is the fitted double-exponential decay curve [Eq. (12) in Ref. 31], and that shown in (b) is the fitted curve of a double-exponential function [Eq. (1) in Ref. 31].

A. Surface photolysis induced by fixed-energy photons near the Si(2p) edge

1. Photon-exposure dependences of the F^- *and* F^+ *yields from the submonolayer-covered surface*

Briefly, we have monitored the variation of the intensities of F^-- and F^+-ion yields as a function of photon exposure by using the time-dependent measuring technique of positive and negative ions (method 1) (Ref. 31). Figures 1(a) and 1(b) show the photon-exposure dependences of the F^-- and F^+-ion yields from the submonolayer-covered surface (dose=0.3×10^{15} molecules/cm^2, ~0.75 monolayer) during 110 eV photon irradiation. The F^- desorption signal [Fig. 1(a)] immediately jumped to the maximum intensity after opening the photon shutter and decreased with further irradiation to a constant nonzero value. On the other hand, the F^+ desorption signal [Fig. 1(b)] was zero when irradiation started and increased with further irradiation to a roughly constant maximum intensity.

At the initial irradiation the maximum F^- yield should desorb from the physisorbed CF_3Cl molecules and indicates the highest desorption cross section during the photolysis, while the zero F^+ intensity indicates that the desorption cross section of F^+ ions from the adsorbed CF_3Cl molecules is very small. The detailed F^- desorption processes at the initial irradiation has been understood as follows. The 110-eV photons irradiating the silicon substrate generate photoelectrons from the substrate. Low-energy secondary photoelectrons can attach to the adsorbed CF_3Cl molecules to form a negative CF_3Cl^{*-} ion if the energy and incident direction of the electron upon a CF_3Cl molecule is in the range for a negative-ion resonance.[47] The negative ion at the surface can then either reemit the electron (autodetachment) and be quenched by the surface or dissociate to produce one excited CF_2Cl^{*-} and one neutral F fragment,[48–50]

$$e^- + CF_3Cl \rightarrow CF_3Cl^{*-} \rightarrow CF_2Cl^{*-} + F \quad (\text{DA: step } 1),$$

where a F atom will desorb from the surface for the case of a C–F bond oriented away from the surface or react with surface silicon atom to form surface SiF if the C–F bond is pointing toward the surface. The excited CF_2Cl^{*-} may further decay according to[48,50]

$$CF_2Cl^{*-} \rightarrow CFCl + F^- \quad (\text{DA: step } 2),$$

where a F^- ion will desorb from the surface and be detected by the quadrupole mass spectrometer as shown in Fig. 1(a) or subsequently release its negative charge back to the silicon substrate and attach to the surface to form surface SiF. On the other hand, photoelectrons with kinetic energies higher than 17 eV can excite the adsorbed CF_3Cl molecule to form an excited CF_3Cl^* which can then dissociate by the DD process[31]

$$e^- + CF_3Cl \rightarrow CF_3Cl^* + e^- \rightarrow F^- + CF^+ + Cl + F + e^-.$$

The F^- ion and the neutral F atom will either desorb from the surface or react with the surface silicon atom.

Since the desorption of F^- ions at the initial irradiation has been explained by the substrate-mediated dissociation of adsorbed CF_3Cl molecules [dissociative electron attachment (DA)/DD], the decrease of the F^- signal with increasing photon exposure [Fig. 1(a)] has been attributed to the decrease in the concentration of adsorbed CF_3Cl molecules during irradiation. The more the surface was exposed to incident photons, the fewer parent CF_3Cl molecules were retained on the surface and fewer F^- ions were desorbed.

The variation of F^+ yield as a function of photon exposure [Fig. 1(b)] has also been explained (Ref. 31). As discussed earlier, the adsorbate of the Si surface before irradiation is the physisorbed CF_3Cl molecule and the direct excitation of this molecule is quenched by the substrate. The dissociation of this molecule is believed to be due to DA and DD by the photoelectrons. For further photon exposure, as shown in Fig. 1(b), the F^+-ion signal is seen to increase with photon exposure. Since the concentration of parent CF_3Cl molecules decreases with increasing photon exposure, the increase of the F^+ signal should appear to be associated with the buildup of dissociation products on the surface. Because the dissociation of CF_3Cl molecules will result in the desorption of neutral F atoms and negative F^- ions or the formation of surface SiF as mentioned previously, the buildup of this surface SiF should be responsible for the desorption of F^+ ions.

2. Surface fluorosilyl products at the near completion of photolysis for the submonolayer-covered surface

It is well known that excitation of the surface SiF by incident photons, above Si($2p$) binding energy (~101 eV), will result in the desorption of F^+ ions with high cross sections.[9,10] It is plausible that the cross sections for ejection of F^+ ions from other dissociation products are much lower than from surface SiF. Thus, the possible explanation for the increase of the F^+ signal for further photon exposure [Fig. 1(b)] is the increasing population of SiF species produced on the surface. This surface SiF is then subject to stimulated desorption, leading to the observed F^+ desorption. It is therefore very likely that the increasing signal of F^+-ion yield in Fig. 1(b) is from photon-stimulated desorption relating to SiF species on the surface.

In order to confirm the formation of surface SiF and identify the other possible fluorosilyl species retained on the surface, we have conducted a PSD experiment (method 2) in which we monitor the F^+-ion yield as a function of incident photon energy in the vicinity of the Si($2p$) absorption edge from the same surface of Fig. 1 at the near completion of photolysis (exposure $\sim 1.3 \times 10^{18}$ cm^{-2} to 110-eV photons). The observed F^+ PSD spectrum is shown in Fig. 2(a).

The threshold in Fig. 2(a) is most likely related to the Si($2p$) (~101-eV) core-level binding energy, indicated by an arrow in the figure. Such a threshold behavior is indicative of a desorption mechanism involving Auger decay of the core hole.[4–6] Yarmoff *et al.* have shown the coincidence of the thresholds in the F^+ PSD spectrum, observed near the Si($2p$) core level, with the fluorination states of the bonding surface Si atom.[9–11] Two surface preparations were employed in their studies. The first surface was prepared by exposure of a clean Si(111)-7×7 surface to 50 Langmuir (L) of XeF_2 at room temperature, and the second surface was produced by annealing of the first surface to ~300 °C. A threshold at ~101 eV near the Si($2p$) core level was observed in the F^+ PSD spectrum of the second surface and assigned to an excitation of the Si($2p$) core level in a SiF species to the conduction band minimum (CBM). For the first surface, in addition to the threshold at ~101 eV resulting from the desorption of F^+ from SiF species as observed in the second surface, there is also structure at higher photon energies. The threshold seen at ~103 eV was attributed to an excitation of the Si($2p$) core level in a SiF_3 species to a σ^* molecular orbital state. For comparison the F^+ PSD spectrum with a threshold at ~101 eV obtained for the second surface by Yarmoff *et al.* is included in Fig. 2(b).[9]

Comparing our F^+ PSD spectrum [Fig. 2(a)] with that observed by Yarmoff *et al.* [Fig. 2(b)], we find a strong resemblance of these two PSD spectra. Both spectra exhibit a similar shape of desorption curves. The small difference is

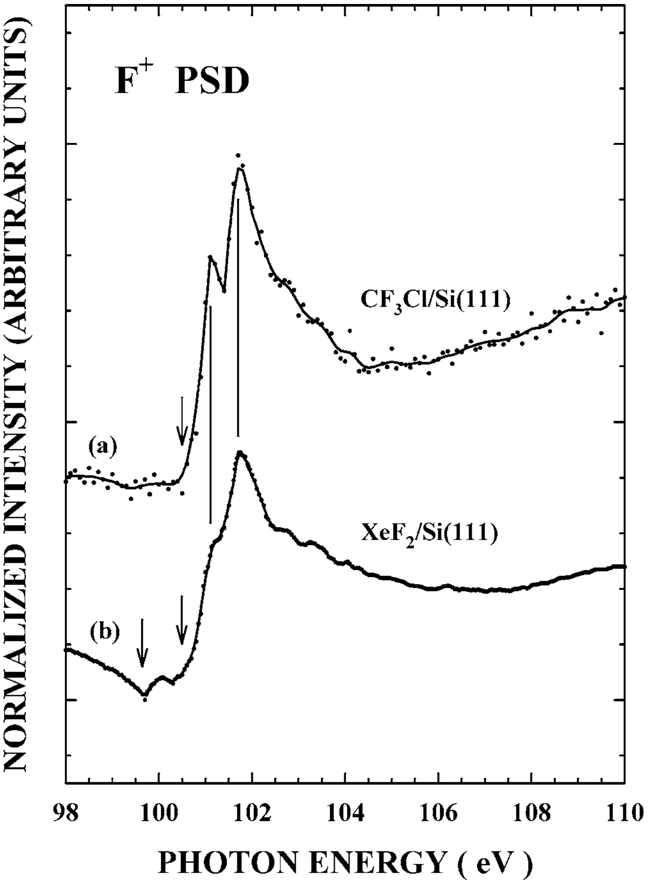

FIG. 2. (a) Photon-stimulated desorption spectrum of F$^+$ ions near the Si(2p) edge for a CF$_3$Cl/Si(111) surface (gas dose=0.3 $\times 10^{15}$ molecules/cm^2) at high exposure to 110-eV photons (1.3 $\times 10^{18}$ photons/cm^2) and near completion of the reaction. (b) F$^+$ photon-stimulated desorption spectrum of a Si(111) surface after exposure to 50 L of XeF$_2$ and annealing to 300 °C (Ref. 9).

that we observed two peaks in our spectrum, while their curve shows a shoulder followed by a peak at the same energy positions of 101.1 and 101.7 eV (shown with two vertical lines in Fig. 2). The shoulder and peak were assigned as due to spin-orbit splitting (0.61 eV) of the Si(2p) core level.[9] Although we observed two peaks, instead of one shoulder and one peak, the great resemblance indicates that these two peaks result from the same desorption process which is initiated by excitation of the $2p_{3/2}$ and $2p_{1/2}$ core levels of the bonding Si atom in SiF species.

Since the PSD curve near the core level is a convolution of the initial 2p core level and local density of final states above the CBM, the better resolution of the spin-orbit splitting observed as two peaks in our F$^+$ PSD spectrum indicates that there is less structure in the local density of final states at our surface than the annealed 50-L XeF$_2$/Si(111) surface. On the other hand, in addition to the threshold observed at ~101 eV for both Figs. 2(a) and 2(b), there is a threshold at lower energy (~100 eV) for Fig. 2(b), which was attributed to x-ray-induced electron-stimulated desorption (XESD) by Yarmoff and Joyce.[11] The difference of the structures in the local density of final states and the existence of the lower-energy threshold produced by XESD for Fig. 2(b) are possibly due to the different chemical environments of the SiF species of these two systems. Since it is well known that Si is spontaneously etched by XeF$_2$, the surface structure is believed to be quite different between XeF$_2$/Si(111) and SR-irradiated CF$_3$Cl/Si(111) in which etching effects may be very small. The etched surface of XeF$_2$/Si(111) is considered to be rough, and the number density of the SiF species of this surface should be greater than that of the SR-irradiated submonolayer CF$_3$Cl/Si(111) surface; thus, the local density of final electronic states is broadened for this surface.

In conclusion, the dissociation of CF$_3$Cl molecules adsorbed on a Si(111)-7×7 surface, irradiated by 110-eV photons, is attributed to DA and DD induced by the photoelectrons emitted from the silicon substrate, and the F$^+$ PSD spectrum [Fig. 2(a)] indicates that the surface fluorosilyl product formed by the photolysis of the submonolayer-covered surface with 110-eV photons is SiF. For the present work, the continuous-time PSD spectra were obtained from the CF$_3$Cl/Si(111) system irradiated by varying-energy photons in the energy range of 98–110 eV; since no valence level or core level of the CF$_3$Cl molecule is in the energy region of 98–110 eV, the dissociation of the CF$_3$Cl molecule observed in the present work should be due to the same mechanisms. The continuous-time F$^+$ photon-stimulated desorption spectra obtained from various CF$_3$Cl-covered surfaces will be discussed in the following sections.

B. Continuous-time F$^+$ photon-stimulated desorption spectra from various CF$_3$Cl-covered surfaces

In the present work, four surface preparations were employed for the demonstration of soft x-ray-induced surface photochemical reactions using continuous-time PSD spectroscopy. The first surface was prepared by exposure of a clean Si(111)-7×7 surface to 0.3×10^{15} molecules/cm^2 of CF$_3$Cl at 30 K, the second surface was produced by a dose of 0.8×10^{15} molecules/cm^2, the third surface was prepared by a dose of 2.2×10^{15} molecules/cm^2, and the fourth surface was produced by a dose of 3.2×10^{15} molecules/cm^2. In our previous valence-level photoemission spectroscopy studies of CF$_3$Cl adsorbed on a Si(111)-7×7 surface we have assigned one monolayer (1 ML) to a dose of approximately 0.4×10^{15} molecules/cm^2 by measuring the variation of the work function with dose.[46] Therefore, the first, second, third, and the fourth surfaces correspond to 0.75 ML, 2 ML, 5.5 ML, and 8 ML, respectively.

1. Continuous-time F$^+$ *PSD spectra from the first surface* (dose $=0.3\times10^{15}$ molecules/cm^2)

In order to gain insight into the formation of the fluorination states of the bonding surface Si atom via the photon-induced dissociation of adsorbed CF$_3$Cl molecules on a Si(111) surface using soft x-ray SR near the Si(2p) edge (98–110 eV), continuous-time core-level PSD spectroscopy (method 2) was employed to study the F$^+$ desorption yields and a series of F$^+$ PSD spectra was measured. Figure 3 shows the series of F$^+$ PSD spectra of CF$_3$Cl adsorbed on

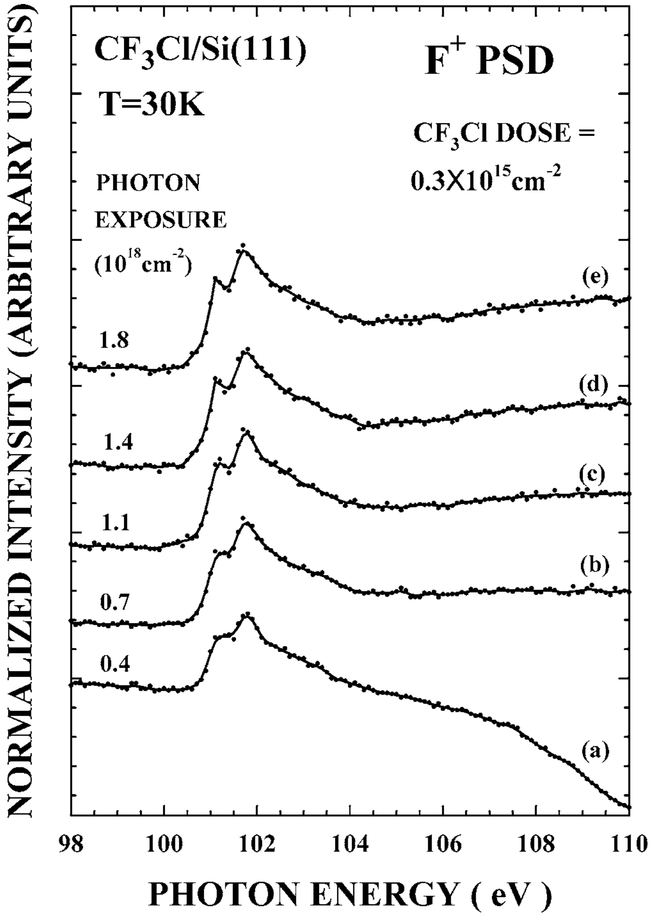

FIG. 3. Continuous-time F^+ photon-stimulated desorption spectra of CF_3Cl adsorbed on a Si(111)-7×7 surface at 30 K as a function of photon exposure using 98–110-eV photons. The CF_3Cl dose of the surface is 0.3×10^{15} molecules/cm^2. The total photon exposure for each spectrum is given in units of 10^{18} photons/cm^2 and shown on the left of the figure.

Si(111)-7×7 at 30 K for various photon exposures using 98–110 eV photons. The CF_3Cl dose of the surface is 0.3 $\times10^{15}$ molecules/cm^2 (~0.75 monolayer). The total photon exposure for each spectrum is given in units of 10^{18} photons/cm^2 and shown on the left of each curve. Figure 3(a) indicates the first F^+ PSD spectrum in this series.

As mentioned earlier, each F^+ PSD spectrum was measured after the photon mask was opened and the photon energy was varied from high to low energy. Figure 3(a) shows that the F^+-ion signal increases from photon energy at 110 eV toward lower photon energy (104 eV). This increase is similar to that observed in Fig. 1(b), in which the F^+ signal increases with photon exposure at $h\nu=110$ eV. Therefore, it can be explained by the same mechanism described in Sec. III A.

At early stages of photolysis, the damage of the adsorbed CF_3Cl molecules is mainly due to DA and DD induced by the photoelectrons emitting from the silicon substrate, which is excited by incident photons at fixed energy (110 eV) for Fig. 1(b) and by photons with varying energy (110–104 eV) for Fig. 3(a). Although the photon with fixed energy was employed for Fig. 1(b) and that with varying energy was used for Fig. 3(a), they should have the same effect for the dissociation of the adsorbed CF_3Cl molecules, because the binding energies of the molecular orbitals of CF_3Cl molecule are not located in the energy range of 104–110 eV. As mentioned previously, F^+-ion desorption is associated with bond breaking of the surface SiF species, which were formed by reactions of the neutral fluorine atom or F^- ion produced by scission of C–F bonds of CF_3Cl in the DA or DD processes. Since the concentration of the parent CF_3Cl molecules decreases with increasing photon exposure, the increase of the F^+ signal is associated with the increasing population of SiF species produced on the surface.

On the other hand, Fig. 3(a) shows a structure in the energy region 101–104 eV, which increases its intensity with photon exposure as shown in Figs. 3(a)–3(e). Because the F^+ PSD spectrum with the highest photon exposure [Fig. 3(e)] has the largest structure in the energy range 101–104 eV, it will be discussed. Comparing Fig. 3(e) with the F^+ PSD spectrum observed from the surface irradiated by photons of fixed energy (110 eV) at the near completion of photolysis [Fig. 2(a)] we find a strong resemblance of these two PSD spectra. Both spectra exhibit almost the same shape of desorption curves, which has a structure with two peaks at the energy positions of 101.1 and 101.7 eV. Therefore, we concluded that both methods of irradiation will result in the same formation of surface SiF species. The observation of this structure in Fig. 3(a) indicates that detectable damage of the adsorbed CF_3Cl molecules will occur and the surface SiF species is produced even during taking the first F^+ PSD spectrum.

We would like to point out that the F^+ PSD spectrum does not change its spectrum shape and intensity in further PSD scans (at least in the 15 further PSD scans, not shown in Fig. 3). This fact indicates that comparing to the photolysis cross section of CF_3Cl, the photolysis cross section of SiF is very small and the beam damage of SiF species is negligible in our F^+ PSD experiments.

It is interesting to roughly estimate the photolysis cross section of CF_3Cl from Fig. 3. Since the feature with two peaks at 101.1 and 101.7 eV is attributed to F^+ desorption from the SiF species via the excitation of the $2p_{3/2}$ and $2p_{1/2}$ core levels of the bonding Si atom, the intensity of this feature (obtained by subtracting the intensity just before the edge from the intensity at the 101.7-eV peak) should be proportional to the density of SiF on the surface. Therefore, we can obtain the relative density of SiF versus photon exposure from Figs. 3(a)–3(e). These data points (not shown) can be fitted with a function, which has the character of an exponential rise to maximum, $a(1-e^{-\sigma\phi})$, where σ is the decay constant and ϕ is the photon exposure. If we simply assume that the photolysis of CF_3Cl produces F and that the F reacts with the Si surface to form SiF species; then, the photolysis cross section of CF_3Cl adsorbed on Si(111)-7×7 can be extracted from the decay constant and found to be ~3.6 $\times10^{-18}$ cm^2.

2. *Continuous-time* F^+ *PSD spectra from the second surface* (dose$=0.8\times10^{15}$ molecules/cm^2)

Figure 4 shows a series of F^+ PSD spectra of CF_3Cl adsorbed on Si(111)-7×7 at 30 K for various photon expo-

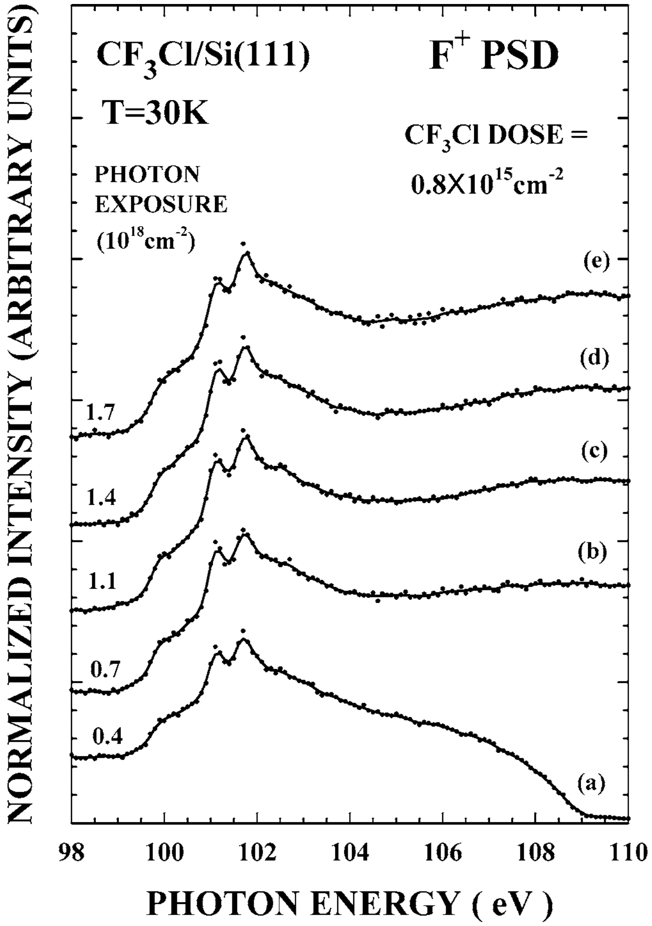

FIG. 4. Continuous-time F^+ photon-stimulated desorption spectra of CF_3Cl adsorbed on a Si(111)-7×7 surface at 30 K as a function of photon exposure using 98–110-eV photons. The CF_3Cl dose of the surface is 0.8×10^{15} molecules/cm^2. The total photon exposure for each spectrum is given in units of 10^{18} photons/cm^2 and shown on the left of the figure.

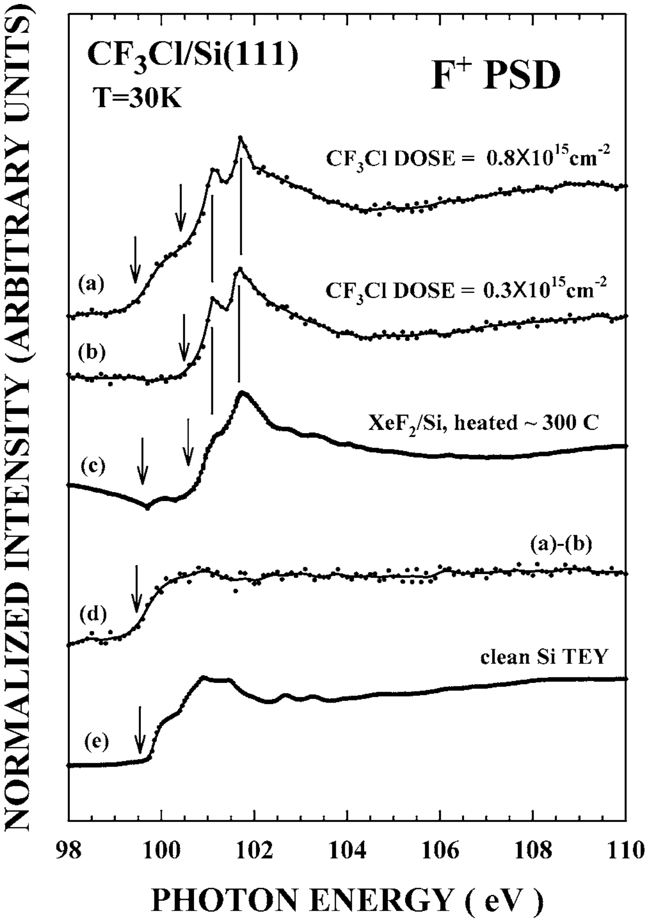

FIG. 5. (a) The last spectrum in the series of F^+ photon-stimulated desorption spectra of CF_3Cl adsorbed on a Si(111)-7 ×7 surface at 30 K as a function of photon exposure using 98–110-eV photons. The CF_3Cl dose of the surface is 0.8 $\times 10^{15}$ molecules/cm^2 (photon exposure$=1.7 \times 10^{18}$ photons/cm^2) [the same as Fig. 4(e)]. (b) The last spectrum in the series of F^+ photon-stimulated desorption spectra of CF_3Cl adsorbed on a Si(111)-7×7 surface at 30 K as a function of photon exposure using 98–110-eV photons. The CF_3Cl dose of the surface is 0.3 $\times 10^{15}$ molecules/cm^2 (photon exposure$=1.8 \times 10^{18}$ photons/cm^2) [the same as Fig. 3(e)]. (c) F^+ photon-stimulated desorption spectrum of a Si(111) surface after exposure to 50 L of XeF_2 and annealing to 300 °C (Ref. 9). (d) The difference curve obtained by subtracting (b) from (a) (see text). (e) Total electron yield (TEY) spectrum at the Si(2*p*) edge of clean Si(111)-7×7.

sures using 98–110-eV photons. The CF_3Cl dose of the surface is 0.8×10^{15} molecules/cm^2 (~2 monolayers). The total photon exposure for each spectrum is given in units of 10^{18} photons/cm^2 and shown on the left of each curve.

All spectra in Fig. 4 exhibit two peaks at the energy positions of 101.1 and 101.7 eV and a shoulder at ~100 eV. Comparing the spectra in the series of Fig. 4 with those in the series of Fig. 3, we find a resemblance of these two series of PSD spectra. Both series of spectra exhibit two peaks at the energy positions of 101.1 and 101.7 eV. However, the spectra shown in Fig. 4 indicate an additional shoulder at the energy position of ~100 eV.

In order to identify the possible fluorosilyl species retained on the surface and the possible mechanisms responsible for the F^+ PSD in Fig. 4, the last spectrum [Fig. 4(e)] with one shoulder at ~100 eV and two peaks at 101.1 and 101.7 eV in the series of F^+ PSD spectra (Fig. 4) is shown in Fig. 5(a) and the last spectrum [Fig. 3(e)] with only two peaks at 101.1 and 101.7 eV in the series of F^+ PSD spectra (Fig. 3) is shown in Fig. 5(b). As evident by comparison of Figs. 5(a) and 5(b), the two peaks at 101.1 and 101.7 eV are due to the same PSD mechanism, which is responsible for the F^+ desorption from the same surface SiF species. However, the additional shoulder (at ~100 eV) observed in Fig. 5(a) may be due to a new type of PSD mechanism. In order to gain further insight into this new feature it is helpful to plot the difference curve of Figs. 5(a) and 5(b), which shows the change of the F^+ PSD spectrum due to this new mechanism. The difference curve is shown in Fig. 5(d).

It is well known that the secondary electrons created by absorption of photons in the substrate can induce ions desorbing from the surface (XESD).[51] For the XESD near the substrate core level, a photon-energy dependence of the positive-ion PSD yield which scales with the photoabsorption of the substrate is expected. Our approach is to compare the difference curve [Fig. 5(d)] to the total electron yield (TEY) from a clean silicon substrate at photon energies near the Si(2*p*) core level for substrate core-level excitation. Core-level TEY spectra have been shown to be proportional to photoabsorption spectra.[52] Measurement of the total electron yield from a clean Si(111)-7 × 7 surface was carried out and plotted in Fig. 5(e). Comparing Figs. 5(d) and 5(e), we find that the difference curve resembles the photoabsorption cross-section curve of bulk Si. This excellent correlation between the difference curve and the TEY curve is strong evidence for a photoinduced process driven by substrate excitation. Therefore, we conclude that the additional F^+ PSD shoulder in Fig. 5(a) is due to XESD, in which the secondary electrons created by absorption of photons at the bulk Si(2*p*) edge induce the dissociation of surface SiF species and result in the desorption of F^+ ions.

By comparing the intensities of the indirect and direct F^+ PSD edges in Fig. 5(a), the indirect excitation has the same order of magnitude for inducing F^+ desorption near the Si(2*p*) core level as the direct excitation of the bonding Si atom. The indirect process (XESD) responsible for the F^+ desorption from surface SiF species has also been observed by Yarmoff *et al.*[9–11] In Sec. III A the F^+ PSD spectrum obtained from the second surface by Yarmoff *et al.*[9] has been described and shown in Fig. 2(b). This spectrum shows a small structure at ~100 eV and a much larger edge at ~101 eV. The small structure was attributed to XESD, and the large edge was assigned to the direct excitation of the bonding Si atom.[11] For comparison Fig. 2(b) is included here and indicated as Fig. 5(c). Comparing our F^+ PSD spectrum [Fig. 5(a)] with the spectrum obtained by Yarmoff *et al.* [Fig. 5(c)], we find that the intensity of the indirect PSD edge is much less than that of the direct PSD edge (by about an order of magnitude) in their spectrum, while in our spectrum these two intensities have the same order of magnitude. The difference of these two spectra in the intensity ratio of indirect excitation to direct excitation is possibly due to the different chemical environments of the SiF species of these two systems. The chemical environment of the SiF species of the annealed 50-L XeF_2/Si(111) surface has only Xe, while that of the SiF species of the photolyzed CF_3Cl/Si(111) surface has surface species containing C and Cl. In conclusion, the continuous-time F^+ PSD spectra (Fig. 4) indicate that the surface fluorosilyl product formed by the photolysis of the second CF_3Cl-dosed surface with 98–110-eV photons is also SiF.

Since we have confirmed the formation of surface SiF species at the second CF_3Cl-dosed surface during SR irradiation, it is reasonable to believe that the adsorbed SiCl species could be formed from dissociation of the CF_3Cl layer in a similar way as surface SiF. Yarmoff *et al.* have obtained a Cl^+ PSD spectrum in the photon energy range of 98–110 eV from SiCl species at the chlorinated silicon surface [Cl_2-saturated Si(111)-7 × 7], which mimics the TEY spectrum of a clean Si substrate and shows a threshold at ~100 eV.[54,55] This Cl^+ PSD spectrum was assigned to indirect XESD, which is due to an excitation of the Cl(3*s*) core level by the secondary electron emitting from the surface as a consequence of photon absorption in the substrate.[55] The Cl^+ desorption is not attributed to direct excitation of the Si(2*p*) core level of the bonding Si atom in SiCl species. However, we would like to point out that the desorption of Cl^+ ions was not observed in the photon energy range of 98–110 eV in the present experiment. On the contrary, the desorption of F^+ ions from SiF species at the fluorinated silicon surface by directly exciting the Si(2*p*) core level of the bonding Si atom was observed in our present and previous experiments[31,53] and those reported by Yarmoff *et al.*[9–11] We will explain the reason why the desorption of Cl^+ ions was not observed in the present experiment as follows.

Yarmoff *et al.* have obtained a kinetic-energy distribution of F^+ ions desorbed from the surface SiF species irradiated with 109.2-eV photons for the XeF_2/Si(111) surface, which shows a maximum at ~2.2 eV.[11] On the other hand, the kinetic-energy distributions of Cl^+ ions desorbed from surface SiCl species of a Cl_2-saturated Si(111)-7 × 7 surface, all peaked at ~0.4 eV, were measured by Durbin *et al.* using various incident photon energies in the energy range of 21–125 eV.[55] Because the kinetic-energy distribution of Cl^+ ions is small enough that it overlaps the minimum energy which is necessary to overcome the surface potential, the kinetic-energy distribution is asymmetric and shows a cutoff. It is well known that F and Cl atoms are very electronegative; the adsorbed F/Cl should be in a F^-/Cl^- oxidation state [Si^+-X^-(X=F,Cl)]. The desorption of F^+ ions from the SiF species at the fluorinated silicon surface via direct excitation of the Si(2*p*) core level of the bonding Si atom[11] and the desorption of Cl^+ ion from the SiCl species at the chlorinated silicon surface via indirect excitation of the Cl(3*s*) core level by the secondary electron[55] indicate that for a surface with only one type of monohalide SiX (X=F,Cl) species, the desorbed positive X^+ ion has sufficient energy to overcome the surface potential contributed by a single type of Si^+-X^- dipoles.

Since F has a larger electronegativity than Cl, the dipole contribution to the surface potential by Si^+-F^- should be greater than that by Si^+-Cl^-. Therefore, for a surface with both SiF and SiCl species as in the present experiment the surface potential contributed by both Si^+-F^- and Si^+-Cl^- should be lower than that contributed by only Si^+-F^- for a surface with only one type of SiF species and higher than that by Si^+-Cl^- for a surface with only SiCl species. Since the F^+ ion has sufficient energy to overcome the surface potential contributed by only one type of Si^+-F^- [kinetic-energy distribution peaked at ~2.2 eV for the desorbed F^+ ions from the surface with only one type of SiF species for XeF_2/Si(111)], it should be able to overcome the surface potential contributed by both Si^+-F^- and Si^+-Cl^- for the SR-irradiated CF_3Cl/Si(111) surface and observed in the present experiment. On the contrary, although the Cl^+ ion has sufficient energy to overcome the surface potential contributed by only Si^+-Cl^- [asymmetric kinetic-energy distribution peaked at ~0.4 eV for the desorbed Cl^+ ions from the surface with only SiCl species for Cl_2-saturated Si(111)-7 × 7], it may not have sufficient energy to overcome the surface potential contributed by both Si^+-F^- and Si^+-Cl^- for the present surface. As a result, the Cl^+ ion is difficult to desorb from the SR-irradiated CF_3Cl/Si(111) surface and not observed in the present experiment.

As described in the previous paragraphs, the F^+ PSD feature with two peaks at 101.1 and 101.7 eV shown in Fig. 5(a) is due to the direct excitation of the Si(2*p*) core level of the bonding Si atom in surface SiF species and the F^+ PSD shoulder at ~100 eV is attributed to indirect excitation, in which the secondary electrons created by the absorption of photons at the bulk Si(2*p*) edge induce the dissociation of SiF and result in the desorption of F^+ ions. It is generally believed that secondary electrons which cause ion desorption via this indirect process do so through excitation of lower-lying core levels or valence states of SiF species.[11] If this is the only excitation mechanism induced by the secondary electrons leading to the desorption of F^+ ions, it would be difficult to explain the large difference between the intensity ratio of indirect excitation to direct excitation in our F^+ PSD spectrum [Fig. 5(a)] (~1) and the intensity ratio in the spectrum obtained by Yarmoff *et al.* [Fig. 5(c)] (~0.1), because the flux density of the photoemitted secondary electrons versus the incident photon flux density is the same for both systems. On the other hand, it would be even more difficult to explain the reason why there is no F^+ PSD shoulder at ~100 eV in Fig. 5(b) for the SR-irradiated lower CF_3Cl-dosed surface. Since the difference curve [Fig. 5(d)] scales with the TEY spectrum of a clean Si substrate and the Cl^+ PSD spectrum which was obtained from SiCl species at the chlorinated silicon surface [Cl_2-saturated Si(111)-7×7] (Ref. 55) mimics the same TEY spectrum, we speculated that the desorption mechanism responsible for the F^+ PSD shoulder at ~100 eV could be related to the excitation of SiCl species (we have both SiF and SiCl species on the surface). A new PSD mechanism responsible for the F^+ PSD shoulder at ~100 eV is proposed as follows.

In the XESD for the desorption of Cl^+ ion from the SiCl species at the Cl_2-saturated Si(111)-7×7 surface, the secondary electron photoemitted from the surface induces a transition of the Cl(3*s*) core-level electron to an unoccupied level (Cl antibonding orbital).[55] The decay of this excited state, which occurs via an intra-atomic Auger process, creates two holes on the Cl atom, thereby producing a Cl^+ ion. Subsequent Coulomb repulsion between the Cl^+ ion and the Si cation leads to Cl^+ desorption. However, in the previous paragraph we have pointed out that for the SR-irradiated $CF_3Cl/Si(111)$ surface the desorption of Cl^+ ions from SiCl, induced by similar processes, could be quenched by the surface potential which is contributed by both Si^+-F^- and Si^+-Cl^-. Because the suppressed Cl^+ ion is in the vicinity of the F^- of Si^+-F^-, it could be attracted by and move towards the F^-. Thus, it is highly possible for the electron associated with the F atom to "jump" to the Cl^+ ion. The released energy in this process is tramsmitted in a radiationless process to a second electron, which may then leave the F atom. This process, like the Auger transition, creates a two-hole state on the F atom, thus changing the oxidation state from −1 to +1. Coulomb repulsion between the F^+ ion and the Si cation results in the desorption of F^+ ions. Since the desorption of F^+ ions follows the excitation of Cl in SiCl via the secondary electrons created by absorption of photons at the bulk Si(2*p*) edge, the F^+ PSD spectrum should mimic the TEY spectrum of a clean Si substrate. Hence, the aforementioned mechanism can be employed to explain the resemblance between the difference curve [Fig. 5(d)] and the TEY spectrum [Fig. 5(e)]. As a result, this mechanism is responsible for the F^+ PSD shoulder at ~100 eV. Because the Auger-transition-like process is induced by the positive Cl^+ ion in the neighborhood of the SiF species, it could be called the positive-ion-induced Auger process. The desorption caused by the positive-ion-induced Auger process could be called the positive-ion-induced Auger-stimulated desorption.

Therefore, the reason why there is no F^+ PSD shoulder at ~100 eV in Fig. 5(b) for the SR-irradiated lower-CF_3Cl-dosed surface can be explained as follows. Since the CF_3Cl dose of this surface is 0.3×10^{15} molecules/cm^2 (~0.75 monolayer), which is less than one monolayer, we speculated that the distance between the created SiF and SiCl species during SR irradiation is not short enough for the positive-ion-induced Auger process to occur. As a result, there is only a feature with two peaks at 101.1 and 101.7 eV in the F^+ PSD spectrum [Fig. 5(b)], which is due to the direct excitation of the Si(2*p*) of the bonding Si atom in SiF species.

3. *Continuous-time* F^+ *PSD spectra from the third surface* (dose=2.2×10^{15} molecules/cm^2)

A sequence of F^+ PSD spectra near the Si(2*p*) edge as a function of photon exposure is shown in Fig. 6. The CF_3Cl dose of the surface is 2.2×10^{15} molecules/cm^2 (~5.5 monolayers). The total photon exposure for each spectrum is given in units of 10^{18} photons/cm^2 and shown on the left of each curve.

The first spectrum [Fig. 6(a)] shows no structure near the Si(2*p*) edge. It means that the desorption of F^+ ions is not from the surface fluorosilyl product. The F^+ ion desorption is due to the direct photodissociation and photodesorption of CF_3Cl molecules.[31] However, there is a structure observed in Figs. 6(b)–6(f). The intensity of this structure increases with photon exposure [from Fig. 6(b) to 6(f)]. Because the last spectrum in Fig. 6 [Fig. 6(f)] indicates the most clear structure, we will discuss this spectrum.

Figure 6(f) exhibits two thresholds at the energy positions of ~100 and ~101 eV. Comparing Fig. 6(f) with Fig. 4(e), we find a strong resemblance of these two PSD spectra. Both spectra exhibit two thresholds at the energy positions of ~100 and ~101 eV. The main difference is that the spectrum shown in Fig. 4(e) indicates a spin-orbit splitting at the energy positions of 101.1 and 101.7 eV, while Fig. 6(f) shows only one peak at ~102 eV. As discussed previously, the threshold at ~101 eV indicates that the surface fluorosilyl product is SiF and the threshold at ~100 eV is due to XESD via the positive-ion-induced Auger-stimulated desorption. The increase of the intensity of the structure with photon exposure, observed in Figs. 6(b)–6(f), indicates an increase of the number density of the SiF species on the surface during irradiation.

One possible explanation for the worse resolution of spin-orbit splitting observed in Fig. 6(f) from the third surface and the better resolution observed in Fig. 4(e) from the second surface is that there is greater structure in the local density of final states at the third surface than the second surface. Be-

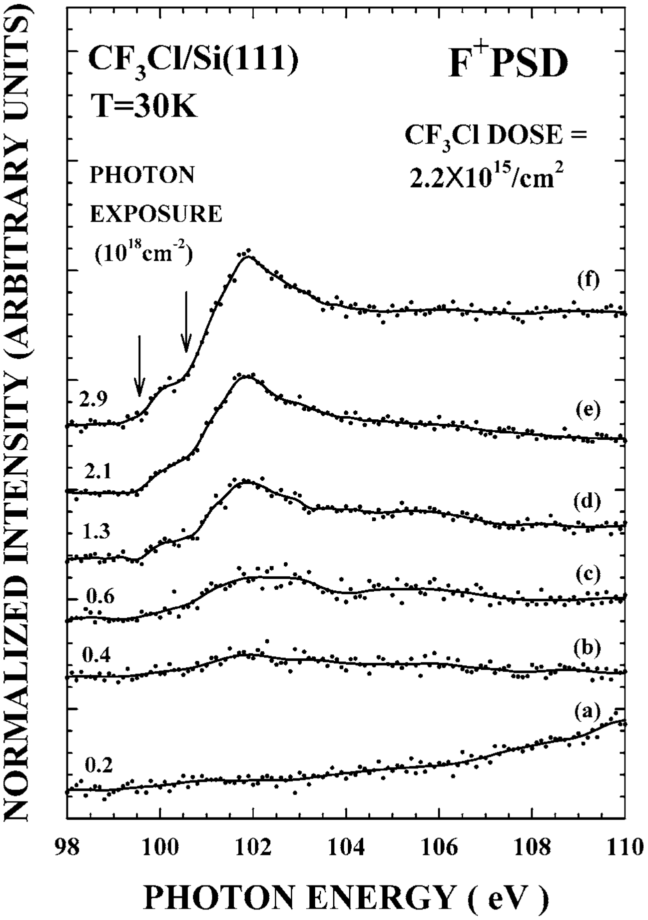

FIG. 6. Continuous-time F^+ photon-stimulated desorption spectra of CF_3Cl adsorbed on a Si(111)-7×7 surface at 30 K as a function of photon exposure using 98–110-eV photons. The CF_3Cl dose of the surface is 2.2×10^{15} molecules/cm^2. The total photon exposure for each spectrum is given in units of 10^{18} photons/cm^2 and shown on the left of the figure.

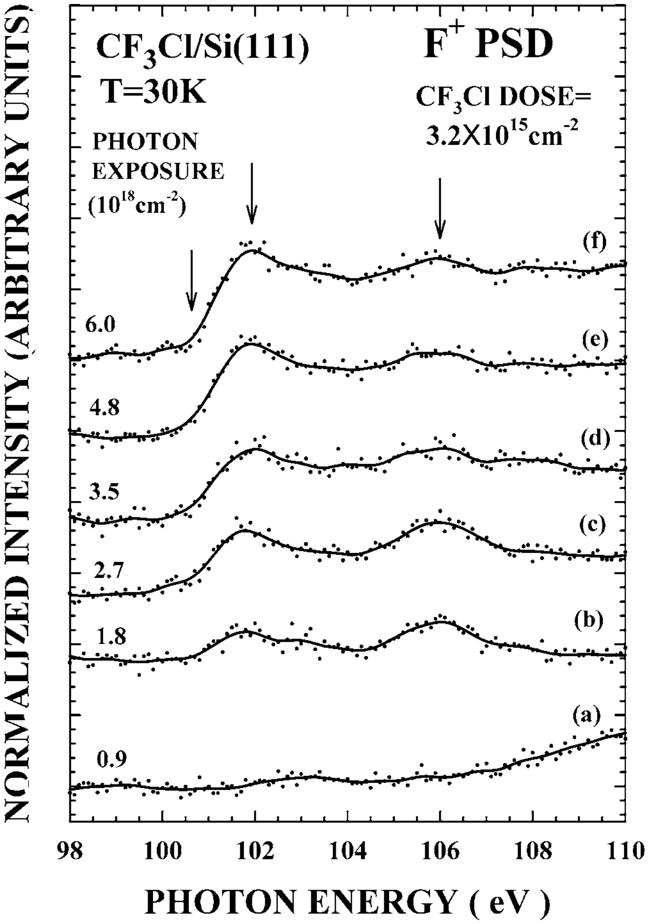

FIG. 7. Continuous-time F^+ photon-stimulated desorption spectra of CF_3Cl adsorbed on a Si(111)-7×7 surface at 30 K as a function of photon exposure using 98–110-eV photons. The CF_3Cl dose of the surface is 3.2×10^{15} molecules/cm^2. The total photon exposure for each spectrum is given in units of 10^{18} photons/cm^2 and shown on the left of the figure.

cause the third surface has more adsorbed CF_3Cl molecules than the second surface, the third surface after soft x-ray SR irradiation is considered to be more inhomogeneous due to more coadsorptions of carbon and chlorine. This inhomogeneity could cause a broadening of the valence electronic states of SiF and result in greater structure in the local density of final states.

Another possible explanation for the worse resolution of spin-orbit splitting in Fig. 6(f) is that the broadening of the SiF-derived features could be related to ions traveling through the CF_3Cl layer on the way out. Because the third surface has a thicker CF_3Cl layer than the second surface, the resolution of spin-orbit splitting should be worse in Fig. 6(f). Therefore, we believe that the worse resolution of spin-orbit splitting in Fig. 6(f) is due to a combination of the effect of the greater structure in the local density of final states and the effect of ions traveling through the CF_3Cl layer on the way out.

In Sec. III B 1, we have pointed out that SiF-induced features were observed in the first PSD spectrum [Fig. 3(a)] for the first surface. It is noted that for the second surface SiF-induced features were also shown in the first PSD spectrum [Fig. 4(a)]. However, for the present surface the first PSD spectrum [Fig. 6(a)] does not show SiF-induced features. This is probably because the SiF species are buried beneath the CF_3Cl layer, which attenuates the F^+ ions both by scattering and by neutralization. As the layer is thinned by the PSD process, the ions can escape and will be observed as shown in the following PSD spectra [Figs. 6(b)–6(f)].

4. Continuous-time F^+ *PSD spectra from the fourth surface* (dose=3.2×10^{15} molecules/cm^2)

A series of F^+ PSD spectra near the Si($2p$) edge as a function of photon exposure is shown in Fig. 7. The threshold at ~101 eV (which peaks at ~102 eV) is clearly observed in Figs. 7(b)–7(f), which indicates the transition from Si($2p$) of an adsorbed SiF species to CBM as discussed in the aforementioned lower-coverage surfaces. In addition to this edge, a broad feature which peaks at ~106 eV is seen. This feature depicts that a new fluorosilyl species was produced in the surface.

Wen, Frigo, and Rosenberg have investigated the interaction of SiF_4 with Si(111)-7×7 at 30 K using PES and angle-

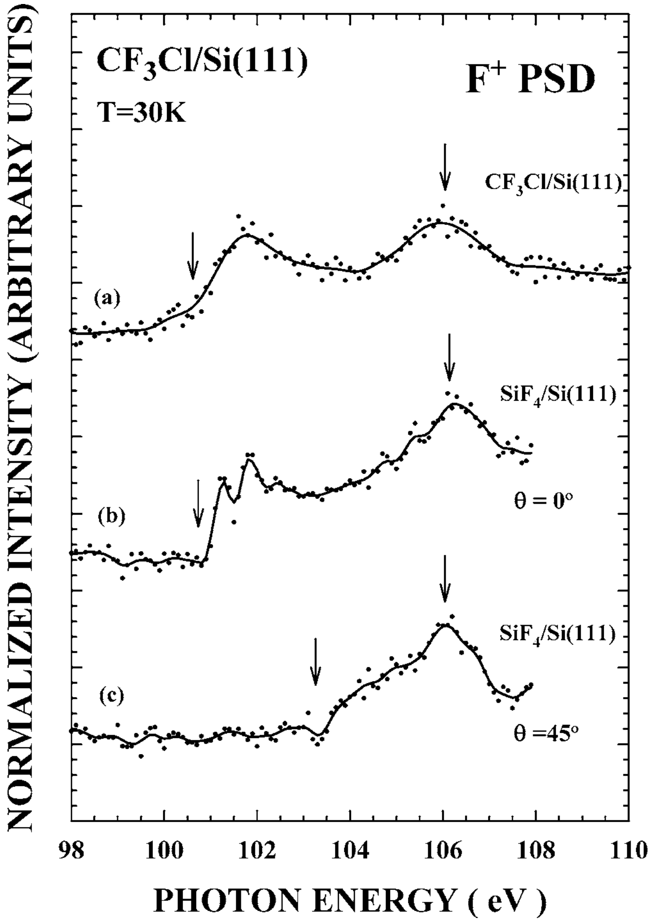

FIG. 8. (a) The third spectrum [Fig. 7(c)] (photon exposure $=2.7\times10^{18}$ photons/cm^2) in the series of F$^+$ photon-stimulated desorption spectra of CF$_3$Cl adsorbed on a Si(111)-7$\times$7 surface at 30 K as a function of photon exposure using 98–110-eV photons. The CF$_3$Cl dose of the surface is 3.2×10^{15} molecules/cm^2. (b) F$^+$ photon-stimulated desorption spectrum of the low-temperature dosed (icy SiF$_4$ covered at $T=30$ K), warmed-up ($T>100$ K) SiF$_4$/Si(111) surface, observed along the surface normal (Ref. 53). (c) F$^+$ photon-stimulated desorption spectrum observed at an angle of 45° from the same surface as Fig. 8(b) (Ref. 53).

dependent photon-stimulated desorption.[53] For very high-dosed surface, they observed that SiF$_4$ ice was formed. Subsequent warming of the SiF$_4$-covered surface to a temperature >100 K, the angle-dependent F$^+$ PSD spectra near the Si($2p$) core level were measured. Figure 8(c) shows the F$^+$ PSD spectrum taken with the QMS analyzer at an observation angle of 45° from the surface normal.[53] This spectrum indicates that there is a threshold at $\sim$103 eV (which peaks at $\sim$106 eV) near the Si($2p$) core level. This threshold was assigned to an excitation of the Si($2p$) core level in a SiF$_3$ species.[53] For the F$^+$ PSD spectrum measured along the surface normal [shown in Fig. 8(b)],[53] in addition to the threshold at $\sim$103 eV resulting from the desorption of F$^+$ from SiF$_3$ species as observed at an angle of 45°, there is also structure at lower photon energy. The threshold seen at $\sim$101 eV was attributed to an excitation of the Si($2p$) core level in a SiF species to the CBM.

For comparison the F$^+$ PSD spectrum measured in the present study [Fig. 7(c)] is shown in Fig. 8(a). Comparing the F$^+$ PSD spectrum [Fig. 8(a)] with Fig. 8(b), we find a resemblance of these two spectra. Both spectra exhibit one feature in the energy range of 101–103 eV and another feature in the energy range of 104–107 eV. The small difference is that Wen *et al.* observed two peaks at the energy positions of 101.1 and 101.7 eV in their spectrum [Fig. 8(b)], while our present spectrum [Fig. 8(a)] shows a broad peak at the same energy region. The two peaks observed at the energy positions of 101.1 and 101.7 eV in Fig. 8(b) were assigned to the desorption processes which are initiated by excitation of the $2p_{3/2}$ and $2p_{1/2}$ core levels of the bonding Si atom in SiF species.[53] As discussed in the previous section, the CF$_3$Cl/Si(111) surface after SR irradiation is considered to be more inhomogeneous due to carbon and chlorine contaminations and also possibly by etching (SiF$_3$ formation means the Si–Si bond is broken by F atoms), and this inhomogeneity could cause a broadening of the valence electronic states of SiF and result in greater structure in the local density of final states. In the previous section, we have pointed out that the worse resolution of spin-orbit splitting could also be due to ions traveling through the CF$_3$Cl layer on the way out. Therefore, we believe that the worse resolution of spin-orbit splitting in Fig. 8(a) is due to a combination of the effect of the greater structure in the local density of final states and the effect of the ions traveling through the CF$_3$Cl layer on the way out.

Since the feature in the energy range of 104–107 eV in our present spectrum [Fig. 8(a)] has the same spectrum shape as those shown in Figs. 8(b) and 8(c), we attribute this feature as due to an excitation of the Si($2p$) core level in a SiF$_3$ surface species to a σ^* molecular orbital state in the quasi-molecular SiF$_3$.[11,53] Therefore, the F$^+$ PSD spectrum [Fig. 8(a)] indicates that the surface fluorosilyl products formed in the photolysis of the fourth CF$_3$Cl-dosed surface are SiF and SiF$_3$.

It is noted that the SiF$_3$ species is also formed in the third surface, because a small 106-eV peak is observed in Figs. 6(c) and 6(d). So the spectra in Fig. 6 show that small quantity of SiF$_3$ is once formed and decomposed by the following SR irradiation. However, we would like to emphasize that the SiF$_3$ species is not produced at the lower-CF$_3$Cl-dosed surfaces [the first (0.75 ML) and second (2 ML) surfaces]; it is formed at the higher-CF$_3$Cl-dosed surfaces [the third (5.5 ML) and fourth (8 ML) surfaces]. The formation of the SiF$_3$ species at the higher-CF$_3$Cl-dosed surfaces can be explained as follows. The F atom or F$^-$ ion created by the bond-breaking of C–F via DA and DD processes will move towards the silicon surface for the C–F bond pointing toward the surface or travel through the CF$_3$Cl layer on the way out for the C–F bond oriented away from the surface. The outgoing F/F$^-$ could be scattered backward to the surface by the CF$_3$Cl layer. These backscattered F/F$^-$ and inward-moving F/F$^-$ have the possibility to reach the silicon surface and react with the surface to form SiF$_3$ species. This reaction may be similar to the reaction of F with Si during plasma etching or reactive ion etching (RIE). The main difference could be that the incident kinetic energy of F/F$^-$ in the present experiment is much lower than that in the plasma etching or RIE. The fact that the SiF_3 species is not produced at the lower-CF_3Cl-dosed surfaces (0.75 and 2 ML) shows that the density of the F/F^- reaching the surface is not great enough to produce SiF_3 species. On the contrary, the formation of SiF_3 species at the higher-CF_3Cl-dosed surfaces (5.5 and 8 ML) indicates that the density of the F/F^- is great enough to produce SiF_3 species, because there are more adsorbed CF_3Cl molecules to produce F/F^- and a thicker CF_3Cl layer to scatter the F/F^- backward to the surface.

IV. CONCLUSIONS

Continuous-time core-level PSD spectroscopy can be used for an investigation of soft x-ray-induced reactions of adsorbate with the surface in core-electron-stimulated surface photochemistry. In the present study, monochromatic synchrotron radiation was employed as a soft x-ray light source, which induced the reactions of CF_3Cl adsorbed on Si(111)-7×7, and also as a probe in the positive-ion PSD technique for monitoring the formation and identifying the characteristics of the produced fluorination states of bonding surface Si atom.

The F^+ PSD spectrum was obtained by monitoring the F^+ signal as a function of incident photon energy near the Si(2p) edge (98–110 eV). Sequential F^+ PSD spectra were measured as a function of photon exposure at four adsorbate coverage. For the first and second CF_3Cl-dosed surfaces, the sequential F^+ PSD spectra show the variation of their shapes with photon exposure and indicate the formation of surface SiF species. The sequential F^+ PSD spectra for the third and fourth CF_3Cl-dosed surfaces also show the variation of their shapes with photon exposure and depict the production of surface SiF and SiF_3 species.

The dissociation of CF_3Cl molecules adsorbed on a Si(111)-7×7 surface, irradiated by varying-energy photons in the energy range of 98–110 eV, is mainly due to DA and DD induced by photoelectrons emitted from the silicon substrate. The feature with two peaks at 101.1 and 101.7 eV in the F^+ PSD spectra of the first and second CF_3Cl-dosed surfaces was assigned to the excitation of the $2p_{3/2}$ and $2p_{1/2}$ core levels of the bonding Si atom in SiF surface species to the CBM. The broadening of these two peaks to form as one peak at 102 eV for the third and fourth CF_3Cl-dosed surfaces is attributed to a combination of the effect of the greater structure in the local density of final states and the effect of ions traveling through the CF_3Cl layer on the way out. The additional shoulder at the energy position of ~100 eV in the F^+ PSD spectra of the second and third CF_3Cl-dosed surfaces is ascribable to XESD via positive-ion-induced Auger-stimulated desorption. The peak at ~106 eV in the F^+ PSD spectra of the third and fourth CF_3Cl-dosed surfaces was assigned to an excitation of the Si(2p) core level of the bonding Si atom in SiF_3 surface species to a σ^* molecular-orbital state in quasimolecular SiF_3.

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