

Photolysis of Molecules Adsorbed on Single Crystal Surface

The studies in the VUV and soft-x-ray surface photophysics and photochemistry in the microscopic level using monochromatic synchrotron radiation is a new research category. In this article we employed the techniques of photon-stimulated desorption (PSD) of positive/negative ions and photoelectron spectroscopy (PES) to study the photolysis of molecules adsorbed on single crystal surface by monochromatic synchrotron radiation. The results obtained from this research will provide us a better understanding of the mechanisms of the photon-induced surface reactions.

High-resolution, anisotropic, dry etching of semiconductor materials is an important technology for highly integrated microelectronic devices. Plasma etching techniques can cause a significant amount of damage due to energetic particle bombardment of the semiconductor surface. In order to minimize the damage, photon-excited etching provided a possible route to achieve damage-free etching, because the etching reaction is obtained directly by the reaction of the adsorbed molecules with the semiconductor surface irradiated by the incident photons. Recent experiments have shown that reactions of molecules adsorbed on solid surfaces can be induced by irradiation with monochromatic synchrotron radiation photons. Generally, the absorption of synchrotron radiation photons can lead to excitation of valence-level and core-level electrons in both the adsorbate and the substrate. It is becoming well established that the mechanisms for photolysis of molecules adsorbed at surfaces can be classified into two categories: direct adsorbate photoexcitation and substrate-mediated excitation.

In order to gain insight into the photolysis of fluorochlorocarbon molecules adsorbed on well-characterized semiconductor surface by the monochromatic synchrotron in microscopic level; we have investigated the evolution of adsorbed molecules and the formed siliconfluoride species present before, during, and after monochromatic synchrotron radiation photon exposure for the system of CF_3Cl adsorbed on $\text{Si}(111)\text{-}7\times 7$ as part of a general goal of developing an understanding of the photon-induced etching of semiconductor surface by using soft X-ray photons.

The PES measurement technique was employed. It consisted of opening the photon mask and taking a series of PES spectra in time during continual irradiation until little visual difference was observed in the two most recent spectra. Desorbing

positive and negative ions were detected by a Balzers pulse-counting quadrupole mass spectrometer. Two measurement methods of 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. The second (Method 2) fixed the mass of the quadrupole mass spectrometer at F^+ or F^- (mass = 19) and monitored the signal as a function of incident photon energy near $\text{Si}(2p)$ edge (98 - 110 eV).

Results of the valence-level photoelectron spectroscopy measurement of the CF_3Cl -dosed surface (dose = $0.3 \times 10^{15} \text{ cm}^{-2}$) are shown in Fig. 1 which shows a series of spectra that differ only by the amount of time the surface was exposed to 98 eV photons. The topmost spectrum in Fig. 1, which was taken immediately following CF_3Cl adsorption, is very similar to the gas-phase spectrum, in both the relative energy position and intensities of the peaks, thereby indicating molecular adsorption. The presence of the Si surface state at ~ -0.2 eV for the CF_3Cl -dosed surface also suggests that the adsorbate is molecularly adsorbed. There is a dramatic change in the spectra as a result of exposure to the photon beam. The intensities of all the peaks decrease and their relative intensities also change. The changes observed in Fig. 1 are the result of photolysis of the Si- CF_3Cl surface complex due to exposure to the 98 eV photons from the synchrotron radiation source, which indicates a high cross section.

Because we have observed the variation in the series of PSD positive-ion mass spectra during 110 eV photon irradiation, it is important to directly monitor the variation of the intensities of main desorption ion yields (F^+ and F^-) as a function of photon exposure. In order to do this, the time-dependent measuring technique of positive and

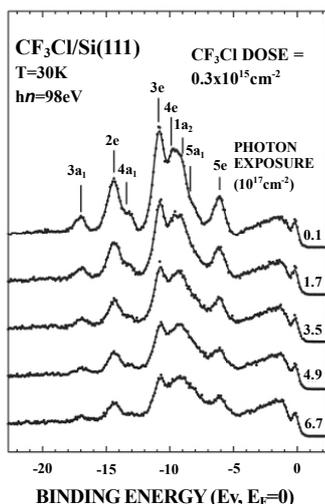


Fig. 1: Series of valence-level photoelectron spectra of CF_3Cl adsorbed on $\text{Si}(111)\text{-}7\times 7$ at 30 K as a function of photon exposure using 98 eV photons. The CF_3Cl exposure of the surface is 0.3×10^{15} molecules/ cm^2 . The total photon exposure for each spectrum is given in units of $10^{17}/\text{cm}^2$ and shown on the right of the figure. The orbital assignments and ionization energies (shifted to align the 3e orbital energy with the peak at -10.9 eV) of gas-phase CF_3Cl are given at the top.

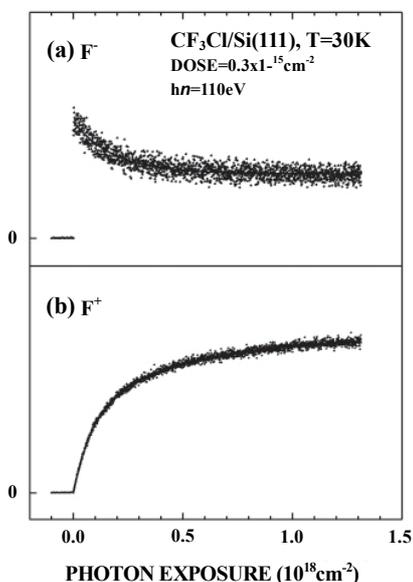
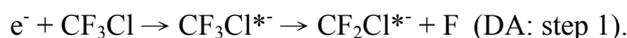


Fig. 2: Photon-exposure dependence of the photon-stimulated desorption yield of (a) F^- ions and (b) F^+ ions from CF_3Cl adsorbed on $\text{Si}(111)\text{-}7\times 7$ surface at 30 K (CF_3Cl dose = 0.3×10^{15} molecules/ cm^2). The incident photon energy is 110 eV.

negative ions (Method 1) was employed. In Figs. 2(a) and 2(b) are shown the photon-exposure dependencies of the F^- and F^+ ion yields from the CF_3Cl -closed surface during 110 eV photon irradiation. The F^- desorption signal [Fig. 2(a)] immediately jumped

to a 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. 2(b)] was zero when irradiation started, and increased with further irradiation to a roughly constant maximum intensity.

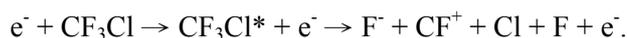
The detailed F^- desorption processes at the initial irradiation can be understood as follows. The 110 eV photons irradiating the silicon substrate generate photoelectrons from the substrate. The low energy secondary photoelectrons can attach to the adsorbed CF_3Cl molecules to form a negative CF_3Cl^* ion. 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 through dissociative electron attachment (DA),



The excited CF_2Cl^* may further decay according to



where F^- will desorb from the surface and be detected by the quadrupole mass spectrometer as shown in Fig. 2(a). On the other hand, the 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 dipolar dissociation (DD) process



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

Now, we consider the decay of F^- yields with increasing photon exposure [Fig. 2(a)]. Since the desorption of F^- ions at the initial irradiation has been explained by the substrate-mediated dissociation of the adsorbed CF_3Cl molecules (DA/DD), the decrease of the F^- signal with increasing photon exposure [Fig. 2(a)] can be attributed to the decrease in the concentration of adsorbed CF_3Cl molecules during irradiation. The more the surface was exposed to incident photons, the less the parent CF_3Cl molecules were retained on the surface, and the less F^- ions were desorbed.

We now turn to the variation of F^+ yield as a function of photon exposure [Fig. 2(b)]. 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/DD by the photoelectrons. For further photon exposure, as shown in Fig. 2(b), the F^+ ion signal is seen to increase with photon exposure. Since the concentration of the parent CF_3Cl molecules decreases with increasing photon exposure, the increase of F^+ signal should appear to be associated with the build-up of dissociation products on the surface. Because the dissociation of CF_3Cl molecule will result in the desorptions of neutral F atom and negative F^- ion, or the formation of surface SiF , the build-up of this surface SiF could be responsible for the desorption of F^+ ions.

It is well known that excitation of the surface SiF by incident photons, above $\text{Si}(2p)$ binding energy (~ 101 eV), will result in the desorption of F^+ ion with high cross sections. It is plausible that the cross sections for ejection of F^+ ions from other dissociation products are much lower than from the surface SiF . Thus, the possible explanation for the increase of F^+ signal for further photon exposure [Fig. 2(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.

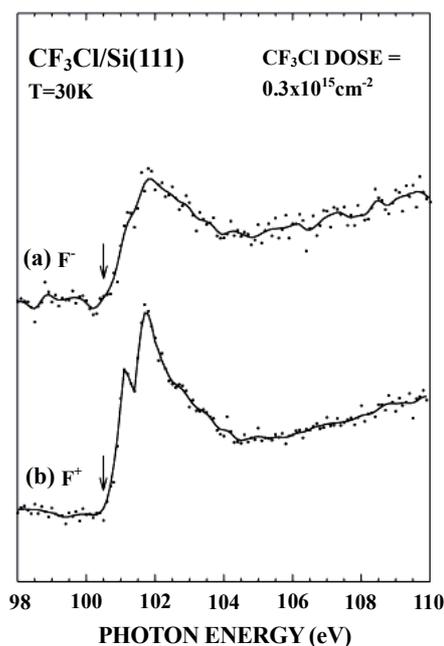


Fig. 3: Photon-stimulated desorption spectrum of (a) F^- ions and (b) F^+ ions near the $\text{Si}(2p)$ edge for a $\text{CF}_3\text{Cl}/\text{Si}(111)$ surface (gas dose = 0.3×10^{15} molecules/ cm^2) at high exposure to 110 eV photons (1.3×10^{18} photons/ cm^2) and near completion of reaction.

In order to confirm the formation of surface SiF , we have conducted PSD experiment (Method 2) in which we monitor the F^- and F^+ ion yields as a function of incident photon energy in the vicinity of the $\text{Si}(2p)$ absorption edge from the same surface of Fig. 2 at the near completion of photolysis (exposure $\sim 1.3 \times 10^{18}$ cm^{-2} to 110 eV photons). The observed F^- and F^+ PSD spectra are shown in Figs. 3(a) and 3(b), respectively. The threshold in Fig. 3(b) is most likely related to the $\text{Si}(2p)$ (~ 101 eV) core-level binding energy, indicated by arrow in the figure. Such threshold behavior is indicative of a desorption mechanism involving an excitation of the $\text{Si}(2p)$ core-level in a SiF species to the conduction band minimum (CBM). Therefore, the F^+ PSD spectrum [Fig. 3(b)] indicates that the surface fluorosilyl product formed by the photolysis of the CF_3Cl -dosed surface with 110 eV photons is SiF .

In the present experiment, the time-dependent variation of the adsorbed molecules on single crystal surface was studied by PES and two PSD methods. The experimental results clearly show that the photolysis of molecules adsorbed on a single crystal surface can be induced by monochromatic synchrotron radiation. These results are crucial for the photoetching of semiconductor surfaces by using monochromatic synchrotron radiation.

BEAMLINES

08A Low Energy SGM beamline
24A Wide Range SGM beamline

EXPERIMENTAL STATION

Photon-stimulated Desorption end station

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PUBLICATIONS

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