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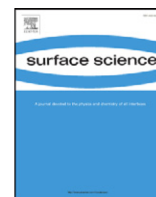

Monochromatic soft X-ray-induced reactions of CCl_2F_2 adsorbed on Si(111)-7×7 near the Si(2*p*) edge

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ABSTRACT

Continuous-time photoelectron spectroscopy (PES) and continuous-time core-level photon-stimulated desorption (PSD) spectroscopy were used to study the monochromatic soft X-ray-induced reactions of CCl_2F_2 molecules adsorbed on Si(111)-7×7 at 30 K (CCl_2F_2 dose $= 2.0\times10^{14}$ molecules/cm^2, ~0.75 monolayer) near the Si(2*p*) core level. Evolution of adsorbed CCl_2F_2 molecules was monitored by using continuous-time photoelectron spectroscopy at two photon energies of 98 and 120 eV to deduce the photolysis cross section as a function of energy. It was found that the photolysis cross sections for 98 and 120 eV photons are ~1.4×10^{-18} and ~8.0×10^{-18} cm^2, respectively. Sequential F^+ PSD spectra obtained by using continuous-time core-level photon-stimulated desorption spectroscopy in the photon energy range of 98–110 eV show the variation of their shapes with photon exposure and depict the formation of surface SiF species. The dissociation of CCl_2F_2 molecules adsorbed on Si(111)-7×7, irradiated by monochromatic soft X-ray in the photon energy range of 98–110 eV, is mainly due to dissociative electron attachment and indirect dipolar dissociation induced by photoelectrons emitted from the silicon surface.

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1. Introduction

High-resolution, anisotropic, dry etching of semiconductor materials is an important microfabrication technology [1,2]. Plasma etching techniques can cause damage to the semiconductor surface and result in degraded electrical and optical performance of the devices. In order to minimize the damage, photon-excited etching provides 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. Usually, excimer lasers or discharge lamps are employed as photon sources. The utilization of synchrotron radiation (SR) should significantly improve the spatial resolution and the efficiency of the photochemical reactions due to its shorter wavelength and higher photon energy, respectively.

Most experimental effort has been devoted to understanding the macroscopic process using nonmonochromatic light [3–8], but relatively little work has been undertaken to understand the process on microscopic level using monochromatic light [9–14].

Therefore, getting information about the reaction mechanisms and photolysis cross sections of the adsorbed molecules using monochromatic soft X-ray has become a very important research work [15–18], and development of advanced characterization techniques are crucial [19–21].

Photoelectron spectroscopy is a very important technique for the study of the electronic structure and chemical bonding of adsorbate and substrate. For high-intensity soft X-rays and/or molecules with high photolysis cross sections the decrease of the adsorbate concentration by the beam damage due to PES itself can not be neglected. As a result, marked change in PES spectra measured in series during irradiation of probe light will be observed [9–11,18,20]. Therefore, monochromatic SR can be employed as a soft X-ray light source in the photon-induced reactions of adsorbed molecules and also as a probe for investigating the chemical states of the adsorbed molecules and produced surface species. The series of PES spectra can be used to monitor changes in the surface chemical bonding structure during irradiation of soft-X-ray photons. In our previous work [20], we called this method continuous-time PES.

Photon-stimulated desorption is the desorption process of positive and negative ions and neutral species from surfaces caused by electronic transitions in the surface or adsorbate complexes resulting from photon irradiation.

It is well known that in the core-level PSD spectroscopy, the desorbed ion intensity versus incident photon energy can be measured, and a PSD spectrum is obtained. The spectral threshold and shape in a PSD spectrum can provide information on the basic excitation leading to the dissociation and desorption processes. It is generally assumed that the photon flux density is so low that only negligible

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beam damage of the adsorbate is caused by PSD during the time of obtaining a PSD spectrum. Therefore, the PSD spectrum is reproducible in further repeated PSD scans.

However, for high-intensity soft X-rays and/or molecules with high photolysis cross sections the decrease of the adsorbate concentration by PSD itself is not negligible. As a result, a great change in a series of PSD spectra, measured one by one via repeating the incident photon energy scan, will be observed. In our previous experiments [19], this series of PSD spectra was called continuous-time core-level PSD spectra, and the method to obtain these spectra was called continuous-time core-level PSD spectroscopy. Since a PSD spectrum can provide information on the local bonding and electronic structure of the surface, continuous-time core-level PSD spectroscopy can be used to monitor the variation of the surface chemical bonding structure–for example, the disappearance of a specific state and the formation of a new bonding structure–during irradiation of incident photons.

In our previous experiments [15–21], we have employed various techniques to study the monochromatic soft X-ray photochemistry of Freon-13 ($CClF_3$) molecules adsorbed on Si(111)-7×7. The results were of interest because they showed that $CClF_3$ dissociation is activated mainly by low-energy photoelectron attachment and dipolar dissociation induced by higher-energy photoelectrons in the photon energy range of 98–110 eV. In the present work, continuous-time photoelectron spectroscopy and continuous-time core-level PSD spectroscopy were employed to study the photon-induced dissociation and desorption of Freon-12 (CCl_2F_2) molecules adsorbed on Si(111)-7×7 at low temperature, using monochromatic soft X-ray from a synchrotron as the photoexcitation source. The CCl_2F_2 molecule was used as a model halogenated hydrocarbon molecule to gain insight into the etching mechanism(s), because it has adequate experimental data of its interactions with electrons and photons in gas phase [22–32] and condensed phase [31–35]. Furthermore, CCl_2F_2 is an environmentally important halocarbon.

On the other hand, the Si(111) surface was employed as a model surface, because this surface has abundant experimental data of its interactions with fluorine-containing molecules [36–43].

2. Experiment

The experiments were performed at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan using a 6-m low-energy spherical grating monochromator (6-m LSGM, 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 for photoelectron spectroscopy, an argon-ion gun for sputtering, a quadrupole mass spectrometer for positive- and negative-ion PSD measurements, and low-energy electron diffraction (LEED) optics. A variable-temperature sample holder allows the sample to cool to $-243\,^\circ$C and heat to $1100\,^\circ$C during measurements.

The Si(111) crystal (p-type, 9.6 $\Omega\cdot$cm) surface was cleaned by cycles of argon-ion bombardment followed by direct resistive heating to $1100\,^\circ$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 [44]. Dichlorodifluoromethane (purity≥99.9%) was obtained from a commercial source and used without further purification. Gas exposure was made by dosing a clean Si(111)-7×7 surface with sample gas from a gas-dosing system. The gas flux from the dosing system was calibrated by standard volumetric method and the dose error was estimated to be 20%. During the dosing of gas and the PES/PSD experiments the sample was kept at a temperature of 30 K.

The continuous-time PES technique was employed. Emitted photoelectrons were detected by a spherical sector electron energy analyzer, which was positioned normal to the surface, and the incidence angle of the photon beam was 45° from the surface. The sample surface was located about 3.8 cm from the entrance of the electron energy analyzer. A portion of photoelectrons emitted by photons impinging on the surface was focused by electron lenses at the entrance of the electron energy analyzer.

Generally, PES is used to measure the emitted electron yield as a function of electron kinetic energy, assuming that there is no photon-induced change in the chemical state of the sample when the PES spectrum is taken during incident photon irradiation.

However, due to the high photolysis cross section of CCl_2F_2 adsorbed on the Si(111)-7×7 surface, in the present study we intended to use PES to examine the photon-induced changes in the chemical state of the adsorbate by observing the variation of the spectral structure in the series of PES spectra, which were measured one by one via repeating the emitted kinetic energy scan. In other words, after the beam shutter was opened, a series of PES spectra was taken in time during continual irradiation until little difference was observed in the two most recent spectra.

The incident photon flux was measured with a 90% transmission nickel mesh calibrated with a photodiode. The beam size on the sample surface is ~0.2×0.4 mm^2. Typical photon flux density is $\sim7\times10^{14}$ cm^{-2}s^{-1}. Because during the course of the experiment the storage ring current decayed, we therefore normalized the PES spectra by the incident photon flux. The photon exposure for each PES scan is calculated by integrating the photon flux over the irradiation time, and the accumulated photon exposure for each spectrum in a series of PES spectra is the summation of the photon exposures of its present and previous PES scans. The sample was moved to a new unirradiated position for each series of PES spectra or new measurement in time.

The positive and negative ions desorbing from the surface were detected by a pulse-counting quadrupole mass spectrometer (QMS), which was positioned normal to the surface. The sample surface was located ~3 cm from the entrance of the QMS. During the measurement of positive or negative ions, the ionizer filament was turned off. A portion of positive or negative ions desorbed by photons impinging on the surface was focused by ion lenses at the entrance of the mass spectrometer. The angular acceptance of the QMS is ~10°.

Three PSD measurement methods were used. The first (method 1) consisted of opening the beam shutter and taking a series of PSD positive- or negative-ion mass spectra in time during the continual irradiation of some fixed-energy photons until little difference was observed in the two most recent spectra. The second (method 2) 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(2p) edge. Because during the course of the experiment (about 2 h) the storage ring current decayed by about 5%, the time-dependent incident photon flux density $f(t)$ was obtained by continuously monitoring the Ni mesh current and used to normalize the ion signal. Therefore, the photon flux density $f(t)$ in this work can be represented as a multiplication of a proportionality constant and the nickel mesh current in time for each measured data point. This $f(t)$ is then numerically integrated to achieve the transformation to the photon-exposure ϕ (photons cm^{-2}). The measured time-dependent data of F^+ and F^- PSD yields will thus be transformed into photon-exposure dependent data.

The third (method 3) fixed the mass of the quadrupole mass spectrometer at F^+ (mass = 19) and monitored the ion signal as a function of incident photon energy near the Si(2p) 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 third 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

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