行政院國家科學委員會專題研究計畫成果報告

CF₂Cl₂及CFCl₃在Si(111)(7x7)表面之光子及電子引發解離及脫附研究
Photon-Induced and Electron-Induced Dissociation and Desorption of CF₂Cl₂ and CFCl₃ on Si(111)(7x7) Surface

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中文摘要

本報告分析單色同步輻射光 (monochromatic synchrotron radiation) 引發吸附在半導體表面上的分子之光解作用 (photolysis)。我們研究的系統是吸附在 30K 溫度的疏半導體表面上之 CF₂Cl₂ 分子。我們使用的技術為光電子譜技術 (Photoemission Spectroscopy, PES) 以及電子激發脫附技術 (Photon-Stimulated Desorption, PSD)。從測得的受各種不同光照 (photons exposure) 影響的價層光電子譜 (valence-level photoemission spectra) 中，我們發現 98 eV 或 110 eV 能量的單色同步輻射光會引發吸附在表面的氣體分子產生光解作用。我們測得氣體分子與氟正離子之氣體分子產生光解所產生的氣體分子電離電子附著 (dissociative electron attachment, DEA) 與雙極解離 (dipolar dissociation, DD)。然而在光照光解作用很高時，氣體分子產生的主要機制是由於氟正離子的光電子捕獲 (electron capture) 反應。(b) 氟正離子的脱附主要是來自表面的 SiF 之鍵斷。而 SiF 的形成則是由於表面上的 CF₂Cl₂ 、CF₂Cl 或 CFCl 的 C-F 鍵之鍵斷所形成的中性氟原子及負電性氟離子與表面的氟原子形成鍵結。我們提出一個動力模型來解釋 CF₂Cl₂ 分子覆蓋的表面之光解作用。根據這個模型以及在 110 eV 光子照射下正/負氟離子信號的變化速率，我們得到 CF₂Cl₂ 分子在 110 eV 光子照射下的光解截面 (photolysis cross section) 大約是 2.9×10⁻¹⁷ cm²。我們也測得在 98-110 eV 能量範圍 (Si(2p)能量附近) 光解截面上射光子能量變化的數據。該資料顯示在 ~100 eV 的能量位置有一個能隙 (energy threshold)。此能隙與乾淨樣基材的總電子產量 (Total Electron Yield，TEY) 之能隙位置相同。此邊緣急增 (edge-jump) 顯示光解效益之增強是由於激發樣基材膜層 Si(2p) 電子而來的，並且確定了表面之光解作用的主要機制是樣材間接激發 (substrate-mediated excitation)。我們觀測到 SiF 是光解後唯一留在表面的氟化物。

關鍵詞：吸附，解離，脫附，光子引發解離，光子激發脫附，光子電子譜

Abstract

In this report, we present an analysis of the photolysis of an adsorbed molecule by monochromatic synchrotron radiation. The system studied was CF₂Cl₂ adsorbed on Si(111)(7x7) at 30 K, and the techniques employed were photoemission spectroscopy (PES) and photon-stimulated desorption (PSD). The valence-level photoemission spectra, under various photon exposures, show that the dissociation effect induced by the incident monochromatic photons (hv = 98 or 110 eV) occurs on this adsorbed gas-solid system. The PSD mass spectra indicate that F⁺ and F⁻ are the only...
desorbed ions for the surface with dose = 3 \times 10^{14} \text{ molecules/cm}^2 in the photon energies of 98-110 eV. Variations of the F and F$^+$ PSD ion yields were measured as a function of monochromatic (110 eV) photon exposure at the adsorbate coverage (0.3 \times 10^{15} \text{ molecules/cm}^2). The photon-exposure dependencies of the F$^-$ and F$^+$ yields show the characteristics: (a) at early stages of photolysis, the desorption of F$^-$ yields is mainly due to dissociative attachment (DA) and dipolar dissociation (DD) of the adsorbed CF$_2$Cl$_2$ molecules induced by the photoelectrons emitting from the silicon substrate, while at high photon exposure the F$^-$ formation by electron capture of the F$^+$ ion is the dominant mechanism; (b) the F$^+$ ion desorption is associated with the bond breaking of the surface SiF which is formed by reaction of the surface Si atom with the neutral fluorine atom or F$^-$ ion produced by scission of C-F bond of CF$_2$Cl$_2$, CF$_2$Cl, or CFCl species. A kinetic model was proposed for the explanation of the photolysis of the CF$_2$Cl$_2$-dosed surface. Based on this model and the variation rates of the F$^-$/F$^+$ signals during 110 eV photon bombardment, a photolysis cross section of \( \sim 2.9 \times 10^{-17} \text{ cm}^2 \) was determined. The photolysis cross section as a function of incident photon energy in the range 98-110 eV, near Si (2p), was also obtained, which shows a threshold at around 100 eV corresponding to the same rise as the total electron yield (TEY) spectrum of the clean silicon substrate. This edge-jump indicates an enhancement of the photolysis efficiency by indirect excitation of the substrate core-level (Si (2p)) electrons, and confirms the substrate-mediated excitation as the photolysis mechanism for the surface. The SiF is the only fluorosilyl product observed on the surface.

1. Introduction

Recent experiments have shown that reactions of molecules adsorbed on solid surfaces can be induced by irradiation with monochromatic synchrotron radiation photons [1-5]. Several reaction mechanisms other than substrate heating have been reported. 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. Generally, the absorption of incident photon in the adsorbed molecule may lead to excitation, which can result into dissociation through different pathways [6-9]. In contrast, the dissociation of adsorbed molecules can be mediated by the presence of photoexcited electrons of the substrate [10-14]. The photoelectron-induced dissociation in the adsorbed molecule AB, is similar to the dissociative electron attachment (DA: \( e^- + AB \rightarrow AB^* \rightarrow A + B^- \)), the dipolar dissociation (DD: \( e^- + AB \rightarrow AB^* + e^- \rightarrow A^+ + B^- + e^- \)) or the dissociative ionization (DI: \( e^- + AB \rightarrow AB^+ + 2e^- \rightarrow A + B^+ + 2e^- \)) of the adsorbate in the gas phase. It is generally believed that within the energy range of most secondary photoelectrons (i.e. 0-20 eV), DA and DD are the major processes responsible for the photodissociation of adsorbed molecules and the photodesorption of negative ions [13].

In order to gain insight into the monochromatic synchrotron radiation-excited reaction of adsorbed fluorochlorocarbon molecules with well-characterized semiconductor surfaces 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$_2$Cl$_2$ adsorbed on Si(111)(7x7).
2. Experiment

The experiments were performed at the Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan using the 6-m low-energy spherical grating monochromator (6m LSGM, bending magnet beam line). The experiments were performed in an ultrahigh vacuum system (base pressure $< 2 \times 10^{-10}$ 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, and a quadrupole mass spectrometer (Balzers QMG421) for electron-stimulated desorption (ESD). A LEED optics (VG RVL900). A variable-temperature sample holder, connected to a continuous-flow He cryostat for cooling sample down to 30 K, and equipped with wires for passing current directly through sample for heating it up to 1100°C, was used for the sample cleaning and for the CF$_2$Cl$_2$ adsorption measurements. The Si (111) crystal 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. CF$_2$Cl$_2$ was obtained from a commercial source and used without further purification. Gas exposure was made by dosing the clean Si (111)(7x7) surface with the CF$_2$Cl$_2$ gas from a gas-dosing system. The gas-dosing system is made out of a miniature cross reservoir, a leak valve and a stainless steel tubing with 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 techniques. During the dosing of the gas and the PSD measurements, the sample was kept with a temperature of 30 K. The results presented in this paper are for exposures in the range of submonolayer.

3. Results and Discussion

The results of the valence-level photoelectron spectroscopy of the surface (dose = $0.3 \times 10^{15}$ cm$^{-2}$) were obtained. They show a series of spectra that differ only by the amount of time the surface was exposed to 98 eV (or 110 eV) photons. The incident photon energy of 98 eV (or 110 eV) was employed because its energy is just below (or above) the ionization energy of Si (2p) core-level ($\sim$ 100 eV). The topmost spectrum in the series of the spectra, which was taken immediately following CF$_2$Cl$_2$ 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 $\sim$ -0.2 eV for the CF$_2$Cl$_2$-dosed surface also suggests that the adsorbate is molecularly adsorbed and that it does not strongly perturb the Si surface. 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. These changes are not a result of contamination, as subsequent PES of an area of the sample that had not been previously exposed to the photon beam resulted in a spectrum that was identical to the top spectrum. The changes are the result of photolysis of the Si-CF$_2$Cl$_2$ surface complex due to exposure to the 98 eV (or 110 eV) photons from the synchrotron radiation source, which indicates a high cross section.

In order to gain insight into the photoinduced dissociation, the PSD mass spectrum technique was employed to study the positive and negative ion desorption yields, and series of PSD positive- and negative-ion mass spectra were measured. These series of PSD mass spectra were measured in the mass range 0-106 amu and at an incident photon energy of 110 eV. The positive-ion mass spectra in the PSD series indicate that F$^+$ is the only desorbed ions for all photon exposure range, and the intensity of the F$^+$ yield increases with increasing photon exposure. The series of PSD
negative-ion mass spectra was also measured. In these series, the only observed desorbing ion for all photon exposure range, and the intensities of F⁻ signal vary with photon exposure. The photon-exposure dependencies of the F⁻ and F⁺ ion yields from the surface (dose = 0.3 x 10¹⁵ molecules/cm²) during 110 eV photon irradiation were measured. The F⁻ desorption signal 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 was zero when irradiation started, and increased with further irradiation to a roughly constant maximum intensity. These photon-exposure dependencies of the F⁻ and F⁺ yields are explained by the characteristics: (a) at early stages of photolysis, the desorption of F⁻ yields is mainly due to dissociative attachment (DA) and dipolar dissociation (DD) of the adsorbed CF₂Cl₂ molecules induced by the photoelectrons emitting from the silicon substrate, while at high photon exposure the F⁺ formation by electron capture of the F⁺ ion is the dominant mechanism; (b) the F⁺ ion desorption is associated with the bond breaking of the surface SiF which is formed by reaction of the surface Si atom with the neutral fluorine atom or F⁻ ion produced by scission of C-F bond or CF₂Cl₂, CF₃Cl, or CFCl₃ species.

A kinetic model was proposed for the explanation of the photolysis of this CF₂Cl₂-dosed surface. Based on this model and the variation rates of the F⁻/F⁺ signals during 110 eV photon bombardment, a photolysis cross section of ~ 2.9 x 10⁻¹⁷ cm² was determined. The photolysis cross section as a function of incident photon energy in the range 98-110 eV, near Si (2p), was also obtained, which shows a threshold at around 100 eV corresponding to the same rse as the total electron yield (TEY) spectrum of the clean silicon substrate. This edge-jump indicates an enhancement of the photolysis efficiency by indirect excitation of the substrate core-level (Si (2p)) electrons, and confirms the substrate-mediated excitation as the photolysis mechanism for the surface. In order to identify the possible fluorosilyl species retained on the surface, we have conducted PSD experiment in which we monitor the F⁻ and F⁺ ion yields as a function of incident photon energy in the vicinity of the Si(2p) absorption edge at the near completion of photolysis. The observed F⁻ and F⁺ PSD spectra indicate that the SiF is the only fluorosilyl product observed on the surface.

4. References