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Site-specific, synchrotron radiation induced surface photochemistry*

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This paper discusses recent research directed at understanding the nature of surface photochemistry driven by soft x-ray synchrotron radiation (SR). The research is motivated by the potential of x-rays for both high spatial resolution and site specificity. Although a number of systems indicate the potential for site specificity, we chose to study the system of SiF₄/Ge because the adsorbate's photoabsorption spectrum is rich in structure near the Si 2p threshold (106 eV) while that of the substrate is structureless. This allows us to differentiate substrate-induced effects from those of the adsorbate. By performing time-dependent measurements of the changes induced in the photoemission spectra by SR, we have found that this system's photochemistry is site-specific in the Si 2p region and have also determined the nature of the products produced by the reaction.

1. INTRODUCTION

Due to a rich variety of complex phenomena, adsorbate photochemistry has been the focus of considerable attention in recent years. Photochemistry driven by soft x-ray radiation excitation of core electrons has the potential for site specificity because the initial electronic state(s) are of sufficiently high binding energy to be well defined and atomically localized. The chemical consequences of these excitations are intriguing in that they offer the possibility of selective bond breaking, thereby influencing the final bonding configurations [1]. Also, from an applied viewpoint, the short wavelengths in the soft x-ray regime may allow control of the surface chemistry to be done with extremely high spatial resolution, regardless of the dissociation mechanism. The disappearance of a surface species, through the means of fragmentation and molecular desorption, is referred to as photolysis.

The dynamics of electronic excitations is of fundamental importance in the understanding of

photochemistry. In this, the substrate plays two important roles: (1) it inevitably adsorbs most of the incident radiation, and (2) its interaction with the adsorbate influences the evolution of adsorbate electronic excitation. These factors are common reasons given to explain that direct excitation of adsorbate electrons has not led to observable changes. When present, direct photochemistry is characterized by an absorption-induced dissociation (AID) mechanism. In contrast, most studies have postulated an indirect mechanism, where electron-induced dissociation (EID) is caused by photoelectrons from the substrate interacting with the adsorbate to cause fragmentation.

This work investigates the evolution of surface and gas phase species present before, during, and after photon exposure for the system of SiF₄ adsorbed on Ge(100) as part of the study of the potential for this system to exhibit an enhancement in photolysis by *resonant* excitation of the SiF₄ adsorbate Si 2p core electrons [2,3,4,5]. The objective is to determine if photoexcitation of

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adsorbate core-levels can directly lead to photolysis. This is part of a general goal to develop an understanding of the chemical changes possible by resonant core excitation. One aim is to identify physical properties and characteristics of adsorption systems that may be eligible for this phenomenon. The system of SiF_4 adsorbed on $\text{Ge}(100)$ at 30 K was selected because the photoabsorption cross section of Ge is structureless in the Si 2p absorption region (100–120 eV) while SiF_4 has many strong resonances [6]. Furthermore, adsorbed SiF_4 is a strong candidate for a significant photolysis cross section due to a highly polar Si-F bond and a low probability of dissociative precursor state quenching by the substrate because SiF_4 physisorbs weakly at 30 K. Silicon tetrafluoride has the highest F^+ desorption yield of all the fluoromethyl silanes [7] and the same molecular properties that lead to the high yield are suspected to play an important role in the photolysis process. Importantly, the SiF_4 dissociative electron attachment cross section is below $2 \times 10^{-18} \text{ cm}^2$ (the limit of detection in a recent gas phase study [8]) and its negative ions are known to be stable towards dissociation [9], so EID is not expected to play a significant role.

In this paper we review the results of recent SR-induced photolysis experiments on the SiF_4/Ge (30 K) system. Evidence is presented which shows that weakly adsorbed SiF_4 on $\text{Ge}(100)$ at 30 K exhibits photolysis by monochromatic 55–140 eV photons, a range which spans above and below the threshold for adsorbate Si 2p core electron excitation. Valence-level photoemission indicates fragmentation and desorption, both which lead to disappearance of the molecularly adsorbed species. Examination of gas phase species during irradiation confirms molecular desorption. Silicon 2p soft x-ray photoemission spectroscopy indicates that prior to dissociation anisotropic adsorption occurs leading to molecular species in different sites having different apparent Si 2p binding energies. Upon irradiation the molecular SiF_4 dissociates into SiF_n species (where $n = 0, 1, 2, 3$) and also desorbs as molecular SiF_4 . By measuring the photon energy behavior of the photolysis cross section, we are able to determine

that the photolysis mechanism is a direct AID type via adsorbate core electron excitations.

2. EXPERIMENTAL

Details of the experimental procedure have been described previously[2,4]. Briefly, radiation from a 6m toroidal grating monochromator (TGM) at the Synchrotron Radiation Center, University of Wisconsin-Madison, was used for the measurements. Due to its high transmission and small spot size, the transmitted beam on this beamline has a very high flux density ($\sim 5 \times 10^{14} \text{ sec}^{-1} \text{ cm}^{-2}$ is typical for the measurements reported here). A measurement consisted of taking a series of valence level (VL) or core level (CL) photoelectron spectroscopy (PES) scans in time at a given photon energy. The photon energy was then changed and the sample moved to a new position for another series of measurements. A total electron yield (TEY, electron yield as a function of photon energy) measurement was made on a previously unexposed region as well. The photolysis cross section, σ , was extracted from the decay constant after fitting the normalized intensity of a well-resolved feature in the PES spectra to a single exponential function. The CL data was analyzed by curve fitting the spectra to sums of Si 2p spin-orbit split pairs of peaks as detailed elsewhere.

3. RESULTS AND DISCUSSION

Figure 1 shows representative Si 2p (a) and valence level (b) PES spectra for SiF_4 adsorbed on Ge at 30 K. Also shown in (a) is a proposed model for the initial adsorption structure which will be discussed later. The Si 2p data were obtained for a dose of $2.8 \times 10^{15} \text{ cm}^{-2}$ (~ 4 monolayers, ML, assuming unity sticking coefficient) and following significant photolysis. The impact of photolysis on the valence-level PES data is illustrated in the series shown in (b) for a dose of $1.4 \times 10^{15} \text{ cm}^{-2}$.

Figure 1. Representative Si 2p PES spectroscopy (a) and valence-level spectroscopy (b) from ref. [2] for SiF₄ adsorbed on Ge(100). In (a), the peak assignments are shown and the molecular species sites are illustrated above the lineshape analysis results of Spectrum 5 in Fig. 3 of ref. 11. In (b), a series of VL spectra for 106 eV photon energy illustrates the effects of photolysis. The assignment of the peaks to SiF₄ molecular orbitals is shown. The intensity of the 5a₁ valence peak versus exposure time is shown in the inset, where the time is in 100 second units.

3.1 Mechanisms

The equation used to infer the photolysis cross section (σ , cm²) from time-dependent VL PES is $n(t) = n(0)e^{-\sigma ft}$ where $n(t)$ is the surface number density (cm⁻²) of adsorbate. Once the photon flux density (f , cm⁻² s⁻¹) is known, the value for σ can be extracted from the decay constant of a fit to the PES signal (which is proportional to n) versus time.

The objective of this work is to determine if photo excitation of adsorbate core-levels can directly lead to photolysis. Our main goal is to develop an understanding and thus a framework of the chemical changes possible by resonant core excitation. The system chosen is to be considered a model one and a starting point as a means to identify physical properties and characteristics of molecules that may be eligible for this phenomenon. Our approach is to compare σ at photon energies above and below the threshold (~106 eV) for adsorbate core-level excitation to the total electron yield (TEY). The criterion for a direct mechanism is the ratio $R = R_{\sigma}/R_T$ where $R_{\sigma}(\epsilon) = \sigma(\epsilon)/\sigma(100)$ and $R_T(\epsilon) = \text{TEY}(\epsilon)/\text{TEY}(100)$ are the increases in σ and TEY relative to the pre-threshold (100 eV) values, respectively. Then, the occasion of $R > 1$ is evidence of direct photolysis following core-level excitation.

The ratio R is plotted versus photon energy in Fig. 2 and shows a dramatic increase in photolysis upon core excitation of the adsorbate. If the photolysis were strictly due to secondary electrons, then the ratio should be near unity. Therefore, for this system, we can conclude that direct excitation is a dominant driving force in the photolysis for the photon energy region 106-117 eV.

R also depends on dose. R is highest for the lowest and highest dose and at a minimum for the intermediate doses. The reason that R decreases following the lowest dose is due to intermolecular quenching of the initial excitation by neighboring molecules. This quenching is still active at the highest dose; however, the excitations that are not quenched are more effective at causing a reaction. This is probably due to secondary reactions of

photo products with surrounding molecules which become more probable at higher coverages.

Figure 2. The relative increases in the total electron yield (R_T) and photolysis cross section (R_σ) for doses of 1.4 and $2.8 \times 10^{15} \text{ cm}^{-2}$ SiF_4 . For each, the TEY of the clean $\text{Ge}(100)$ substrate is shown. In both cases, the photolysis is enhanced more than the TEY after passing the Si 2p threshold, showing they are not directly correlated. The error relative to the 100 eV data is shown.

3.2 Reaction Kinetics

The molecular and surface fragment species have been determined with Si 2p PES at $140 \text{ eV}^{[24]}$. A typical spectrum is shown in Fig. 1a with the results of the lineshape analysis. Inset to this figure is a schematic of an adsorbate structure, with four distinct sites, which is consistent with the observed chemical shifts. The molecular species were assigned as follows: α -

SiF_4 to lone molecules on the surface; β - SiF_4 in the base of islands and in contact with the Ge substrate, δ - SiF_4 within the outer island layer or "skin," and γ - SiF_4 residing within the island interior. Also, SiF_n ($n = 0, 1, 2, 3$) fragments were found, where n decreased with increasing dose (D). Here, we focus on the amount of these species present as a function of photon exposure (ξ). A kinetic model is developed which is consistent with the observed behavior during irradiation. Cross sections for the generation and depletion of surface species are then derived by application of the model to the data.

Kinetic data for the highest two doses is shown in Fig. 3. The results of photolysis on these plus the lower two ($D = 0.4$ and $0.7 \times 10^{15} \text{ cm}^{-2}$, not shown) coverages, may be summarized as follows. First, the molecular species all exhibit either decaying (δ, γ) or transient (β) behavior, characterized by the value of photon dose at which they reach steady state (δ, γ) or maximum (β) values. As the SiF_4 dose is lowered, these situations are attained at lower photon exposure, likely due to (1) lower interadsorbate quenching and (2) less of an overlayer to desorb away. The features ascribed to SiF_n increase monotonically, which indicates that the photolysis products are not further decomposed by additional excitation. From these observations and some additional postulates, the following reaction pathways may be identified:

Application of kinetic modeling to the data leads to the following set of equations:

$$\text{decay: } y(\xi) = y(0) + \Lambda e^{-\sigma(\xi-\xi_0)} \quad (1)$$

$$\text{transient: } y(\xi) = y(0) + \Lambda_1 e^{-\sigma_1(\xi-\xi_0)} - \Lambda_2 e^{-\sigma_2(\xi-\xi_0)} \quad (2)$$

$$\text{asymptotic growth: } y(\xi) = y(0) + \Lambda [1 - e^{-\sigma(\xi-\xi_0)}] \quad (3)$$

Figure 3. Variation of Si 2p component area versus photon exposure for the two greatest doses, $D = 2.8$ and $1.4 \times 10^{15} \text{ cm}^{-2}$. The component data area is represented by symbols while fitted functions are plotted as solid curves over the range of data points used in the fitting. Dashed lines are drawn as a guide to the eye for data not considered during the fit analysis

The cross section values obtained from fitting these functions to the kinetic data are plotted in Fig. 4. There is a general trend of all cross sections decreasing with greater dose. This is attributed to excitation quenching by adsorbate-adsorbate interactions. An electronic excitation is quenched if it relaxes to a stable, lower energy state before bond cleavage occurs. This behavior is also observed in the photolysis cross section about the Si 2p threshold measured with valence level PES, where the values decrease monotonically with SiF₄ dose by almost an order of magnitude from $D = 0.4$ to $D = 2.8$ [^{2,3,4}].

Figure 4. Kinetic cross sections from analysis of Si 2p component areas as a function of photon exposure. For the sake of clarity, error bars are not shown. The relative error among the cross section values is estimated to be $\sim 20\%$.

4. Conclusions

Due to its potential for submicron parallel processing of materials and site specificity, numerous groups have embarked on studies of SR-induced photochemistry. Our emphasis has been to try to understand the role that SR can play in site selective bond breaking. Evidence was presented to demonstrate surface specificity in the system of SiF_4/Ge at 30 K. From time-dependent PES measurements, cross sections were determined at various photon energies. Comparison of the photolysis cross sections to the electron yield showed that the photolysis was due primarily to direct excitation of Si 2p electrons in adsorbed SiF_4 . The various reactants and products were determined from Si 2p core level PES. Kinetic modeling of the photon energy dependence of these species points out the importance of interadsorbate quenching in this system.

Due to the relatively weak flux densities available from present day SR sources, studies of energy-dependent x-ray photochemistry have been limited to systems with high cross sections for photolysis. With the advent of third-generation light sources such as the ALS, APS, Spring8, and ESRF, systems with much lower cross sections will be amenable to study. The next generation of light sources will allow research into systems with cross sections as low as 10^{-21} cm^2 in reasonable times (~ 15 min). Furthermore, the long penetration lengths of high-energy x-rays from facilities such as the APS, ESRF, and Spring8 will allow the extension of these studies to bulk phenomena,

thereby opening up many new avenues of basic and applied research.

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