NEXAFS Studies on the Soft X-ray Induced Chemical Transformation of a 4-Nitrobenzaldimine Monolayer

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I. Introduction

SAMs are closely packed molecular assemblies that are formed spontaneously by the immersion of an appropriate substrate (e.g. metal, metal oxide, mica, etc.) into a solution of an active surfactant. Monolayers of this type are employed not only to control surface properties,² such as wettability, adhesion, and lubrication, but also to fabricate new functional materials³ including catalysts and supports for biomolecules. Recently, there are a few reports regarding the bond cleavage or damage of SAMs induced by X-ray or soft X-ray irradiation while taking X-ray photoelectron spectra. $^{4-6}$ Whitesides et al. investigated damage to CF₃CO₂- and CF₃CONH-terminated monolayers and demonstrated that photoelectrons ejected from the surfaces, rather than incident X-ray photons, were largely responsible for the damage.⁵ Sagiv et al. applied Fourier transform infrared (FT-IR) spectroscopy to obtain a sensitive assessment of damage to hydrocarbon monolayers. 6 Monolayer damage caused by X-ray irradiation is likely to be selective for a particular functional group. In that case, X-ray irradiation damage would be associated with specific chemical reactions that transform functional

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groups into new ones. Such transformations can also be used to tailor surface properties with spatial resolution.⁷

Previously, XPS analysis showed that the carbonnitrogen bond of nitro-substituted aromatic imine monolayers was cleaved selectively upon soft X-ray irradiation,8 and GC-mass spectrometry coupled with a solid-phase microextraction (SPME) method implied that the imine functionality was transformed into a nonhydrolyzable one.8d Recently, we have successfully generated a sub-100-nm pattern on the surface through these chemical transformation.9 However, the detailed chemical structure of the irradiated monolayers by soft X-ray still remains unclear, owing to the lack of proper analytical tools.

We noticed that near edge X-ray absorption fine structure (NEXAFS) spectroscopy is the most suitable method to examine these structural changes, in particular, of organic functional groups because it provides detailed information about the bonding nature of the individual groups. NEXAFS spectra are dominated by resonances arising from transitions of the 1s core level to unoccupied molecular orbitals of π^* and σ^* symmetry. Of Since such states are specific to the bonding within different functional groups, NEXAFS can be used to probe the chemical structure of surfaces.¹¹ In this study, we characterized unambiguously the structural changes of the 4-nitrobenzaldimine monolayer induced by soft X-ray irradiation using the spectroscopic method.

II. Experimental Section

General. The polished prime Si(100) wafers (dopant, phosphorus; resistivity, $1.5-2.1~\Omega$ ·cm) were purchased from MEMC Electronic Materials, Inc., and thoroughly cleaned by a procedure

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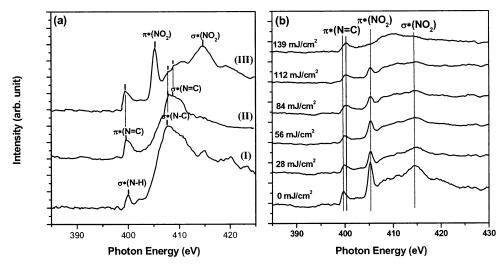


Figure 1. (a) N K-edge NEXAFS spectra of the aminosilylated surface (**I**), benzaldimine monolayer (**II**), and 4-nitrobenzaldimine monolayer (**III**). (b) Series of N K-edge NEXAFS spectra of the 4-nitrobenzaldimine monolayer irradiated by soft X-ray (energy, 550 eV); the raw spectra were divided by a gold-mesh signal (I_0) measured concurrently to remove beam fluctuation, and the resulting spectra were subtracted by the spectrum of a bare silicon surface to remove the substrate contribution.

described elsewhere. 12 4-Nitrobenzaldimine and benzaldimine monolayers used in this study were prepared by treating the aminosilylated silicon wafers with 4-nitrobenzaldehyde and benzaldehyde, repectively. 8,12

NEXAFS Measurements. NEXAFS spectroscopy was performed at the 2B1 SGM (spherical grating monochromator) and 4B1 PEEM (photoemission electron microscopy) beamlines of the Pohang Accelerator Laboratory¹³ (Korea). Absorption spectra were taken at the C K-edge, N K-edges, and O K-edge in total electron yield mode, measuring the sample current. 10 All spectra were recorded at an incidence angle of 45° to the surface normal and normalized to a gold-mesh signal (I_0) measured concurrently to remove beam fluctuations. The result of this has then been subtracted by the spectrum of the bare silicon surface to eliminate the substrate contribution. However, in the case of O K-edge spectra, the background signal was reasonably flat, and this correction was unnecessary. Energy calibration was performed by recording spectra of several known transition metal oxides such as TiO_2 and LiV_3O_8 . ^{10b} The energy resolution was 0.2-0.3eV. During the experiments, the base pressure of the experimental chamber was kept around 1×10^{-10} Torr.

III. Result and Discussion

The aminosilylated surface (I) (thickness, about 8 Å) was prepared by allowing silicon wafers to react with (3-aminopropyl)diethoxymethylsilane in toluene, and subsequent condensation with benzaldehyde and 4-nitrobenzaldehyde gave benzaldimine (II) and 4-nitrobenzaldimine (III) monolayers, respectively. The thickness of thus prepared imine monolayers was typically 10-12 Å, and the absolute density of the imines on the surface was determined to be ~ 4 imines/nm² for each monolayer. 12c

To scrutinize the structural transformation of the 4-nitrobenzaldimine monolayer caused by soft X-ray, the

monolayer was exposed to synchrotron soft X-rays of 550 eV with 6.6×10^{10} photons/cm²·s, and the NEXAFS spectra were taken at the carbon K-edge, nitrogen K-edge, and oxygen K-edge with a dosage interval of 28 mJ/cm². ¹⁴ For the exact assignment of the peak associated with the particular functionality of the 4-nitrobenzaldimine monolayer (III), NEXAFS spectra of the aminosilylated surface (I) and the benzaldimine monolayer (II) were also obtained.

N K-Edge NEXAFS Spectra Figure 1a shows the nitrogen K-edge NEXAFS spectra of the monolayers I, II, and III. The raw spectra were divided by a gold-mesh signal (I_0) measured concurrently to remove beam fluctuation. The resulting spectra were subtracted by the spectrum of the bare silicon surface to remove the substrate contribution. The absorption spectrum of the aminosilylated surface (I) is dominated by two main peaks at 400.0 eV and at 407.5 eV corresponding to the N-H σ^* and N-C σ^* resonances, respectively. 15 In the absorption spectrum of the benzaldimine monolayer (II), a new peak appeared at 399.2 eV, and the peak was also present in the spectrum of the 4-nitrobenzaldimine monolayer (III). We assigned this peak to the C=N π^* resonance. 16 Meanwhile, the peak at 407.5 eV associated with the N-C σ^* resonance became broad compared with that of the aminosilylated surface, which must be due to the peak originated from the C=N σ^* resonance (at 408.4 eV). The sharp peak at 405.2 eV and the broad peak at 414.3 eV appeared only in the spectrum of the 4-nitrobenzaldimine monolayer (III). This suggests that these peaks correspond to the NO₂ π^* and NO₂ σ^* resonances, respectively, and

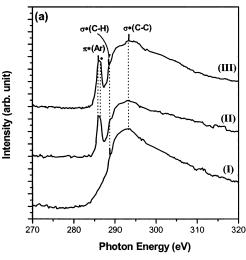
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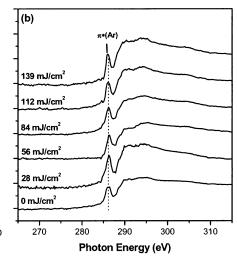


Figure 2. (a) C K-edge NEXAFS spectra of the aminosilylated surface (I), benzaldimine monolayer (II), and 4-nitrobenzaldimine monolayer (III). (b) Series of C K-edge NEXAFS spectra of the 4-nitrobenzaldimine monolayer irradiated by soft X-ray (energy, 550 eV); the raw spectra were divided by a gold-mesh signal (I_0) measured concurrently to remove beam fluctuation, and the resulting spectra were subtracted by the spectrum of a bare silicon surface to remove the substrate contribution.

the peak position and the gap between the π^* resonance and the σ^* resonance are consistent with the literature value. 17

In Figure 1b is shown the change of the nitrogen K-edge spectra of the 4-nitrobenzaldimine monolayer under continuous soft X-ray irradiation (0–139 mJ/cm²). The intensity of the peaks corresponding to the NO₂ π^* and NO_2 σ^* resonances diminished as X-ray irradiation progressed, while the peak associated with the C=N π^* resonance is shifted to higher photon energy by 0.6 eV. The former observation is well in harmony with the XPS result reported previously, 8 and it confirms that the nitro group on the 4-nitrobenzaldimine monolayer is cleaved selectively upon soft X-ray irradiation. Meanwhile, the latter observation clearly indicates that the imine functionality of the monolayer is transformed into a new chemical species, and this chemical transformation also exactly coincides with the previous wet analysis.8d On the basis of the fact that the final peak position (at 400.2 eV) is very close to that of the N-H σ^* resonance of the aminosilylated surface, it is quite reasonable to conclude that the imine bond of the monolayer is reduced to an

C K-Edge NEXAFS Spectra. Parts a and b of Figure 2 show the carbon K-edge NEXAFS spectra of the monolayers (**I–III**) and the spectral change of the 4-nitrobenzaldimine monolayer upon soft X-ray irradiation, respectively. The raw spectra were normalized by the same method used for the nitrogen K-edge spectra. The two peaks at 288.4 eV (shoulder) and 293.3 eV were observed in all spectra (**I–III**) and were assigned to the C–H σ^* and C–C σ^* resonances, respectively, on the basis of the literature data (Figure 2a). In spectra for **II** and **III**, a peak originated from the characteristic aromatic π^* resonance was observed at 286.1 eV. 10a,11b,c The slightly broad shape of this peak may be caused by overlapping with the π^* resonance peak (a shoulder marked with •) attributed to the imine bond (C=N). 16

Analysis of the spectra along the X-ray irradiation showed that the phenyl unit remained intact on the monolayer surface. As shown in Figure 2b, the intensity of the aromatic π^* resonance peak was not reduced by soft X-ray irradiation. However, the peak became somewhat sharp as the soft X-ray irradiation went on. This result must be due to the disappearance of a C=N π^* resonance peak, which is well consistent with the result obtained from nitrogen K-edge spectra.

O K-Edge NEXAFS Spectra. The oxygen K-edge NEXAFS spectra of the monolayers (I–III) are shown in Figure 3a. The spectra of the aminosilylated surface (I) and the benzaldimine monolayer (II) have two broad peaks around 539 and 563 eV, which originate from the silicon oxide layer of the bare silicon substrate. 18 Also, the distinguishable peak at 531.8 eV was observed. We assigned this peak to the π^* resonance attributed to the nitro group (NO2). It was not straightforward to distinguish the NO2 σ^* resonance peak because it was buried in the signal of the bare silicon substrate. However, the peak at 542.1 eV could be located and assigned to the NO2 σ^* resonance when the spectra were subtracted by the spectrum of the bare silicon substrate.

In Figure 3b, we can see that the intensity of the π^* resonance peak corresponding to the nitro group becomes reduced upon soft X-ray irradiation and that the vertex of the broad band around 539 eV is slightly shifted to the lower energy region, owing to decrease of NO₂ σ^* resonance peak. These results are strong evidence supporting the selective cleavage of the nitro group.

In the previous XPS study, we could not retrieve any information from O(1s) photoemission spectra upon soft X-ray irradiation, because oxygen peaks from siloxane and the silica layer overwhelm that of the nitro group. Also, the possibility of forming a hydroxyphenyl moiety along with the cleavage could not be examined because of the same reason. In the oxygen K-edge absorption spectra as well as the carbon K-edge spectra of the X-ray irradiated 4-nitrobenzaldimine monolayer, we could not find any new peaks attributed to the hydroxyphenyl moiety. ¹⁹ Therefore, we can eliminate the possibility that

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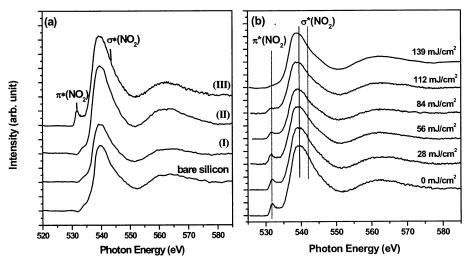


Figure 3. (a) O K-edge NEXAFS spectra of the bare silicon substrate, aminosilylated surface (I), benzaldimine monolayer (II), and 4-nitrobenzaldimine monolayer (III). (b) Series of O K-edge NEXAFS spectra of the 4-nitrobenzaldimine monolayer irradiated by soft X-ray (energy, 550 eV). All spectra were normalized against a gold-mesh signal (I_0) measured concurrently to remove beam fluctuation.

the nitro group is replaced by an oxygen containing functional group. In this respect, the hydrogen group is most likely to be positioned at the para position of the phenyl group after the cleavage. Obviously, the current NEXAFS analysis is more diagnostic than XPS analysis to monitor the structural change of the organic functionality on the surface.

IV. Conclusion

Structural transformation of a 4-nitrobenzaldimine monolayer induced by soft X-ray irradiation was investigated successfully using near edge X-ray absorption fine structure (NEXAFS) spectroscopy. NEXAFS analysis at the C K-edge, N K-edge, and O K-edge clearly characterizes the chemical structure of the organic surfaces that undergo selective transformation with soft X-ray irradiation. The spectroscopic study provides unambiguous evidences for the previous tentative conclusion that the nitro group is

cleaved selectively, leaving the phenyl unit intact on the monolayer surface and transforming the imine functionality into a new chemical species. Despite the limited availability of synchrotron facilities, NEXAFS spectroscopy is so diagnostic for the characterization of organic functional groups on the surface that fast growing popularity is expected.

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