

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

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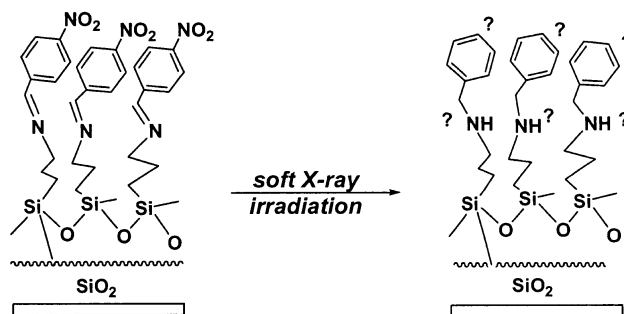
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I. Introduction

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.¹ 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

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

Previously, XPS analysis showed that the carbon–nitrogen 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.¹⁰ 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 $\Omega \cdot \text{cm}$) were purchased from MEMC Electronic Materials, Inc., and thoroughly cleaned by a procedure

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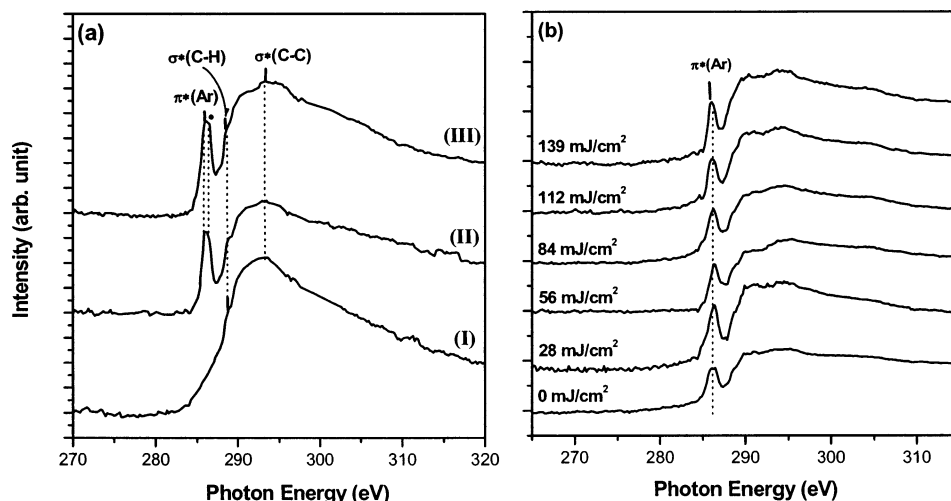


Figure 2. (a) C K-edge NEXAFS spectra of the aminosilylated surface (I), benzaldimine monolayer (II), and 4-nitrobenzaldimine monolayer (III). (b) Series of C K-edge NEXAFS spectra of the 4-nitrobenzaldimine monolayer irradiated by soft X-ray (energy, 550 eV); the raw spectra were divided by a gold-mesh 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 NO₂ 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 amine.

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).¹¹ 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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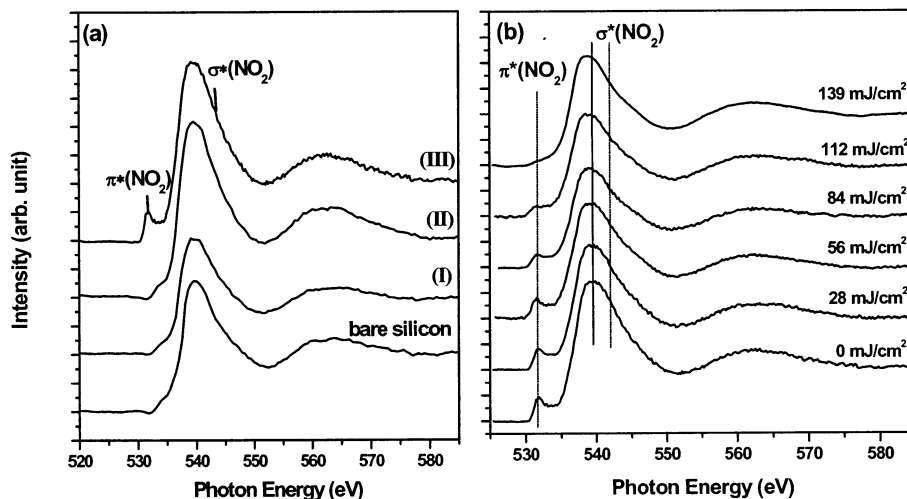


Figure 3. (a) O K-edge NEXAFS spectra of the bare silicon substrate, aminosilylated surface (I), benzaldimine monolayer (II), and 4-nitrobenzaldimine monolayer (III). (b) Series of O K-edge NEXAFS spectra of the 4-nitrobenzaldimine monolayer irradiated by soft X-ray (energy, 550 eV). All spectra were 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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