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Site-Specific Ion Desorption of Methyl-Ester Terminated Biphenyl SAMs Induced by Core-Excitations

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1 Introduction

Possibility of site-specific (site-selective) ionic dissociation induced by core-excitation has been focused on research in soft X-ray induced chemical reaction. The site-specific dissociation is obviously observed on solid surfaces than in gas phase. We focus on this difference, and propose a hypothesis as follows. Holes with excess energy created by core-excitations delocalize and redistribution of such high internal energy can cause a variety of chemical reactions. In such case, reactions lose the memory of the sites of the primary excitations, and the probabilities of such reactions can be determined by statistical considerations. In the case of isolated gaseous molecules, the excess energy that diffuses over a molecule can lead statistical chemical reactions dominantly, thus the site-specific reactions is strongly hidden. On the other hand, in the case of solid surfaces, the excess energy that diffuses over a molecule rapidly flows into the solid or neighboring molecules, which does not contribute to chemical reaction. As a result, statistical reactions are suppressed and therefore site-specific reactions are emphasized at the solid surfaces [1].

Recently, remarkable site-specific ion desorption was observed in methyl ester terminated self-assembled monolayer (MHDA SAM: $Au-S(CH_2)_{15}COOCH_3$). In this study, we focus on the role of spacers (molecular chains) between functional groups and metal substrates of SAMs. So, we investigated ion desorption of methyl ester-terminated biphenyl SAM (M2P SAM; $Au-S(C_6H_4)_2-COOCH_3$) which has conductive biphenyl spacer (Fig. 1), in order to clarify whether the difference of conductivity of spacers affects site-specific reactions.

2 Experiment

Experiments were performed at the BL7A of KEK-PF. Near edge X-ray absorption fine structure (NEXAFS) was recorded in total electron yield (TEY) mode by measuring a sample drain current. The measured TEY spectra are normalized to the incident photon flux monitored with a gold-coated mesh. Partial ion yield (PIY) spectra of M2P were measured by using TOF-MS in the single-bunch operation of the PF ring.

M2P SAMs were prepared by immersing Au coated Si substrates into 1.0mM methyl ethyl ketone solution during 24h. SAMs were rinsed in methyl ethyl ketone immediately after removal from the solution and quickly inserted into the UHV chamber for analysis..

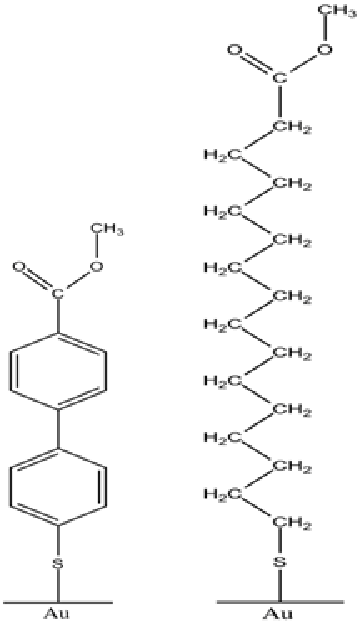

Fig. 1: Molecular structure of M2P (left) and MHDA (right) SAMs.

3 Results and Discussion

Fig. 2(a) shows TEY spectrum of M2P in the C K-edge region. The dotted lines are the peak element of each excitation state obtained from peak fitting analysis. The black-painted peak is the excitation of $C1s(O-CH_3)$ to the $\sigma^*(O-CH_3)$ antibonding orbital extracted from the conjugated and obscure NEXAFS spectrum by peak fitting procedure. Fig. 2(b) shows the PIY spectrum of CH_3^+. The site-specific ion desorption can be seen at this σ^* excitation as a pronounced desorption of CH_3^+ ion, as seen in other methyl ester terminated SAMs [1]. PIY spectra include site-specific component and non-specific one. In other words, ionic desorption induced by core-excitations is promoted by different two mechanisms, direct (specific) and indirect (non-specific) processes. The non-specific component in the PIY spectrum appear with intensity in proportion to the drain current, TEY. On the other hand, a specific desorption via a direct process should occur only at a specific resonant state. To estimate the non-specific component, TEY and PIY spectra are normalized at the pre-edge (280 eV) and the ionization threshold (292 eV) where TEY includes less specific component. In this manner, the normalized TEY can be regarded as non-specific component. The thick line in Fig. 2(b) shows normalized TEY. At the σ^*(O-CH_3) excitation, the site-specific component of CH_3^+ is estimated to be more than 97% of CH_3^+ ion yield. This value is higher than that for MHDA SAM, where site-specific component at σ^*(O-CH_3) is estimated to be 90-95% in the previous study [1]. This result indicates that a conductive spacer, biphenyl, is more efficient to memorize a localization character of core-excitations than the insulating spacer, methylene long chain. This effect is also related to relaxation speed of holes created by Auger decay process. The holes diffused over the molecule after Auger decays would rapidly flow into the metal surface via its conductive spacer. This consideration supports our hypothesis mentioned above.

References

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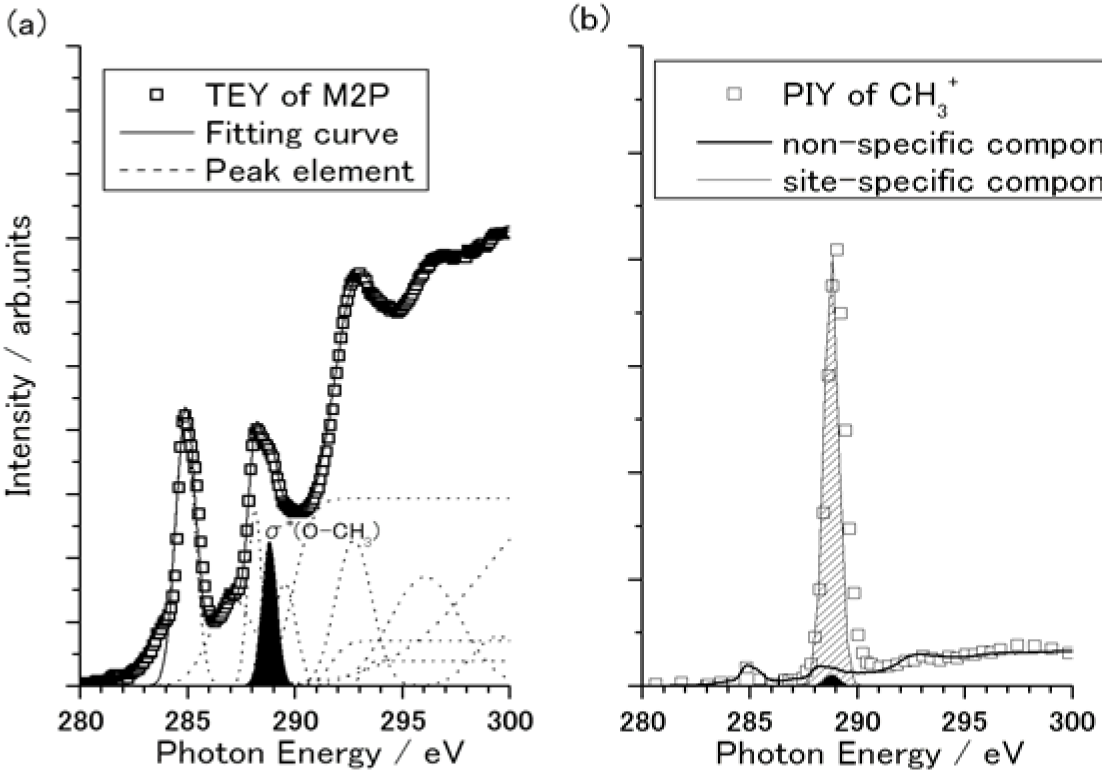

Fig. 2: (a) TEY spectrum of M2P SAM and fitted curves as resonant excitations. (b) PIY spectrum of CH_3^+ and normalized TEY. The black-painted peak shows non-specific component of σ^*(O-CH_3) excitation.