

Configuration dependence of photon stimulated ion desorption from methyl ester compounds induced by core excitation

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Introduction

Recently, it was found that site-selective ion desorption is observed at resonant core excitations of C_{1s} , $O_{1s}(OCH_3) \rightarrow \sigma^*(O-CH_3)$ and $O_{1s}(OCH_3) \rightarrow \sigma^*(C-OCH_3)$ in methyl ester terminated self-assembled monolayer (MHDA-SAM, $CH_3OCO(CH_2)_{15}SH$) [1,2]. Selective chemical bond scission is achieved by core-electron excitation due to its localization and atomic selectivity. In addition, it was suggested that the site-selective ion desorption is closely related to inter- and intra-molecular configurations of reactive site [3].

In this work, photon-stimulated ion desorption (PSID) from methyl mercaptoacetate (MA, CH_3OCOCH_2SH) and MHDA-SAM on Ag surfaces has been investigated using soft x-ray around C and O K edges. MHDA has a long methylene chain $-(CH_2)_{15}-$, whereas MA has only one $-CH_2-$. Changes in site-selective ion desorption are expected to be observed due to positional difference of methyl ester groups with respect to the metal surface.

Experimental

Experiments were carried out at BL7A, whose details were described elsewhere [3]. Partial ion yield (PIY) spectra were measured by detecting selected ions using time-of-flight (TOF) mass spectrometer, respectively. Thin films were prepared by immersing Ag substrate into 1.0 mM ethanol solutions of MHDA and MA.

Results and Discussion

Figure 1 shows PIY spectra of CH_3^+ and OCH^+ for MA and MHDA obtained in C and O K-edge excitation regions. Ion yield exhibited enhancement at $C_{1s}, O_{1s}(OCH_3) \rightarrow \sigma^*(O-CH_3)$. Especially for MA, smaller ion yield were observed at $C_{1s}(OCH_3) \rightarrow \sigma^*(O-CH_3)$ as compared with that of MHDA. Moreover, OCH^+ ion intensity is also enhanced characteristically at $O_{1s}(OCH_3) \rightarrow \sigma^*(C-OCH_3)$ in MHDA, while the intensity in MA did not increase. The decrease of PIY at $C_{1s}(OCH_3) \rightarrow \sigma^*(O-CH_3)$ is induced by change of neutralization probability in desorbing ions. Figure 2 shows TOF spectra of CH_n^+ ($n:1-3$) in the C K-edge. The different fragment pattern in CH_n^+ ions at $C_{1s}(OCH_3) \rightarrow \sigma^*(O-CH_3)$ represents mass dependence of neutralization process, that is, heavier ions are neutralized easily for desorption reaction. In the O K-edge, the PIY for CH_3^+ in MHDA resembles that in MA, but not for OCH^+ . Though the peaks around 532 and 536 eV are observed for OCH^+ slightly, the site-selective ion desorption disappear in MA. This result can be interpreted as relaxation effect on ion desorption due to strong interaction with the metal surface.

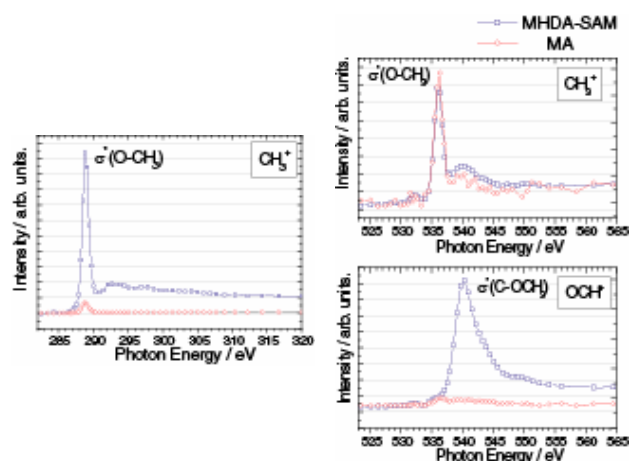


Fig. 1 Typical comparison of PIY spectra for MHDA-SAM and MA on Ag surfaces. Left: CH_3^+ in C K-edge. Right: CH_3^+ and OCH^+ in O K-edge.

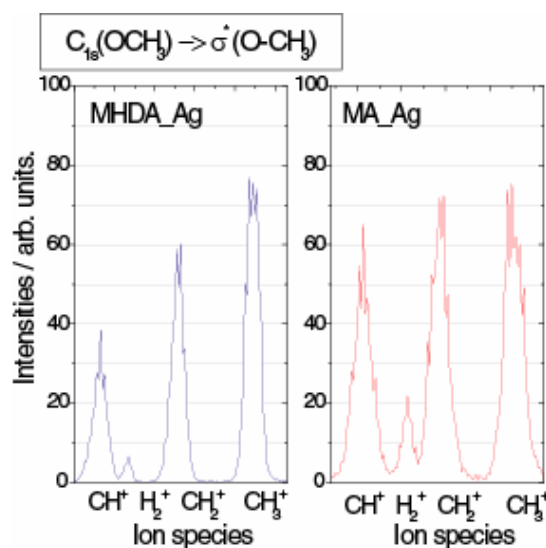


Fig.2 TOF spectra of CH_n^+ ($n:1-3$) for MHDA-SAM and MA in C K-edge.

References

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