

## Polarization-dependent dissociation selectively induced by core-electron excitation in methyl ester terminated self-assembled monolayer using rotatable TOF-MS

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### Introduction

Polarized nature of SR has hardly been utilized for photon stimulated ion desorption (PSID) experiments, although PSID in inner-shell region reveals specific phenomena. When the localization character of core electron is memorized in the excitation of core electron to  $\sigma^*$ ,  $\pi^*$ , and Rydberg states, it is possible to break a bond in the vicinity of the excited atom: this phenomenon is called site-selective ionic dissociation.

In this paper, polarization-dependent PSID induced by core-excitation of methyl ester terminated self-assembled monolayer ( $\text{CH}_3\text{OCO}(\text{CH}_2)_{15}\text{S}/\text{Au}$ , MHDA-SAM) has been investigated [1]. It is expected that SAM has an advantage to observe polarization dependence in surface-sensitive ion desorption because SAM can be prepared with highly oriented functional group on the topmost surface. The results indicated different dependence on incident angle between the site-selectively and non-selectively desorbing ions.

### Experimental

Measurements of polarization-dependent PSID in core-excited MHDA-SAM were carried out at the beamline BL11A. Time-of-flight (TOF) spectra were measured to obtain partial ion yield (PIY) spectra for each desorbing ion at various incident angles of SR light using the rotatable TOF mass spectrometer (MS) [2]. The incident angle was changed by rotating both the sample holder and the TOF-MS device simultaneously, which were kept at a right angle. All measurements were performed with the spectral resolving power ( $E/\Delta E$ ) of about 1000. MHDA-SAM was prepared by immersing Au coated quartz substrate (Tanaka Kikinzoku Kogyo corp.,  $\geq 99\%$  of Au(111) surface) into 1.0 mM ethanol solutions of MHDA (NARD institute ltd.) during 72 hours.

### Results and Discussion

Fig.1 shows SR incident angle dependence of representative PIY spectra for  $\text{CH}_n^+$  ( $n=1-3$ ) ions in the C K-edge region, and  $\text{CH}_n^+$  ( $n=2,3$ ) and  $\text{OCH}^+$  ions in the O K-edge region. An incident angle is defined as an angle from the surface, that is an angle of electric field vector of SR from the surface normal. It is clearly seen that the yields is enhanced at the shallower incident angle for

$\text{CH}_n^+$  ions in the  $\text{C1s}(\text{OCH}_3) \rightarrow \sigma^*(\text{O}-\text{CH}_3)$  excitation, and  $\text{CH}_n^+$  and  $\text{OCH}^+$  ions in the  $\text{O1s}(\text{OCH}_3) \rightarrow \sigma^*(\text{O}-\text{CH}_3)$  and  $\sigma^*(\text{C}-\text{OCH}_3)$ , respectively, while the ion yields induced by non-selective dissociation in the other excitations hardly depend on the angle. In addition, such independence of ion yields is also seen in non-selective  $\text{C}_2\text{H}_m^+$  desorption. The clear polarization dependence in the  $\text{CH}_n^+$  and  $\text{OCH}^+$  ionic dissociation reactions indicates that initial memory of site-selective excitations is conserved during subsequent Auger decay and ionic dissociation.

### References

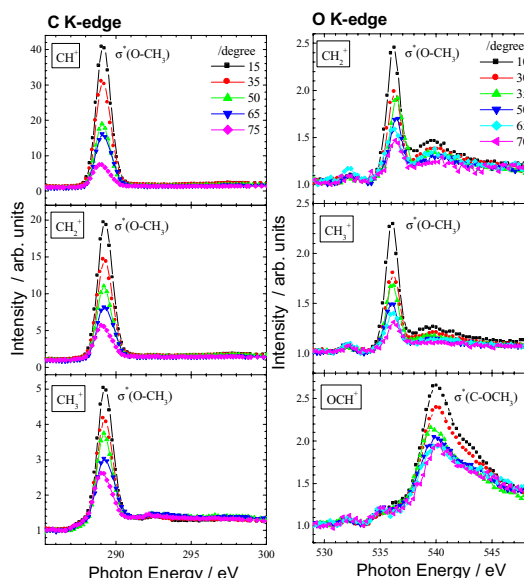


Fig.1 Typical PIY spectra for MHDA-SAM were measured at various incident angles of SR from the surface. The graphs show PIYs for  $\text{CH}_n^+$  ( $n=1-3$ ) in C K-edge, and  $\text{CH}_n^+$  ( $n=2,3$ ) and  $\text{OCH}^+$  in O K-edge. Spectra were normalized in the pre-edge region to exclude variation of irradiation area due to the change of incident angle.

[1] H. Kizaki et al., J. Electron Spectrosc. Relat. Phenom. 144-147 (2005) 447.

[2] T. Sekiguchi et al., Appl. Surf. Sci. 169-170 (2001) 287.

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