

# Site-specific ion desorption of methyl ester-terminated self-assembled monolayer (SAM) induced by core excitation

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## Introduction

Site-specific bond scission following core excitation has been studied for the aim of controlling chemical reactions. It was found that poly-methylmethacrylate (PMMA) thin film indicates remarkable site-specificity in the photon stimulated ion desorption (PSID) [1]. Self-assembled monolayer (SAM) is expected to be useful to get direct information about the effect of the functional group and molecular environment to the PSID reaction; because it is close-packed structure with the headgroup of adsorbate covalently bonds to a substrate and the terminated functional group are aligned on the topmost surface. In this study, the PSID reactions following core-excitation have investigated using the SAM of methyl 16-mercapto hexadecanate (MHDA: HS-(CH<sub>2</sub>)<sub>15</sub>-COOCH<sub>3</sub>) on gold.

## Experiment

The experiments were performed at the soft X-ray beamline BL-7A and 11A of the Photon Factory (KEK-PF). Total electron yield (TEY) spectra were obtained by measuring the sample drain-current. Desorbed ions were detected using a time-of-flight mass spectrometer (TOF-MS) combined with pulsed SR (single bunch mode) at an angle of 60° with respect to the SR beam (30° from to the sample surface). Total ion yield (TIY) spectra were measured by detecting non-select ions. In the measurement of the desorbed ions, the sample surface is located at the normal direction and 12~15 mm away from the TOF-MS.

## Results and Discussion

In the TEY spectrum, the absorption for methyl ester group is similarly observed with PMMA and for methylene chain is observed with typical alkanethiol SAM. The ion desorption efficiency (IDE) which obtained by dividing TIY by TEY, was enhanced at 289.4 eV, C 1s →  $\sigma^*$  (O-CH<sub>3</sub>) excitation. Similar enhancement was observed for PMMA, but the enhancement of the MHDA is larger than PMMA. Fig. 1 show the partial ion yield (PIY) spectra of typical ions, H<sup>+</sup>, CH<sub>n</sub><sup>+</sup> (n=1, 2, 3), C<sub>2</sub>H<sub>3</sub><sup>+</sup>, and C<sub>2</sub>H<sub>5</sub><sup>+</sup> together with the TEY spectrum of MHDA in the carbon core excitation region. From this figure, CH<sub>n</sub><sup>+</sup> (n=1, 2, 3) ions are observed selectively at the resonant transition of C 1s to  $\sigma^*$  (O-CH<sub>3</sub>) orbital. The spectra of other ions do not have such a specific feature.

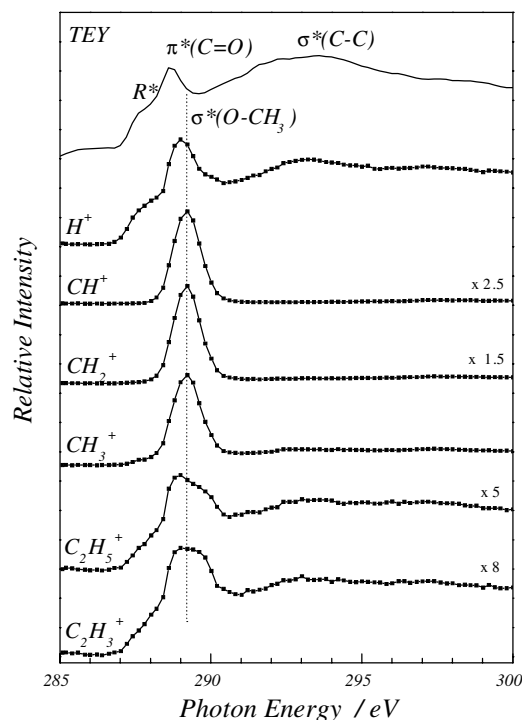


Fig. 1. TEY and PIY spectra of H<sup>+</sup>, CH<sub>n</sub><sup>+</sup> (n=1-3), C<sub>2</sub>H<sub>3</sub><sup>+</sup> and C<sub>2</sub>H<sub>5</sub><sup>+</sup> of MHDA in the C K-edge

For example, the PIY spectrum of H<sup>+</sup> ion follow the features of the TEY spectrum, therefore the indirect photo desorption is dominant mechanism in the H<sup>+</sup> desorption.

The site-specificity of CH<sub>3</sub><sup>+</sup> ions are more clear than that of PMMA in the point of the decrease of the ion yields of indirect reaction. These results indicate that the molecular environment affect strongly the site-specific reaction.

## References

- [1] K. Tanaka *et al.*, J. Electron Spectrosc. Relat. Phenom. 119, 255 (2001).

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