7A/2002G273

Polarization-dependent ionic dissociation of methyl ester terminated self-assembled monolayers by core-electron excitations

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Introduction

Polarization dependence of near edge X-ray absorption fine structure (NEXAFS) spectroscopy using linearly polarized SR is one of powerful tools especially to investigate orientation and structure of adsorbed molecules on surfaces conveniently [1]. As opposed to abundant spectroscopic NEXAFS studies, however, polarization dependence of photon stimulated ion desorption (PSID) induced by core excitations has rarely been carried out because of much experimental difficulties. Recent our studies have found the site-selective ion desorption reactions of methyl ester compounds, such as polymer thin film and self-assembled monolayers (SAMs) [2]. The purpose of this study is to measure polarization dependence of each PSID in core excitations of methyl ester-terminated SAMs as an oriented molecular system and to investigate whether the polarization dependence is conserved even in ion desorption phenomena and what information about desorption dynamics can be derived from the dependence.

Experimental

Measurements of NEXAFS and polarization-dependent PSID were carried out at the beamline BL7A. Although the polarization dependence of NEXAFS can be measured by rotating a sample holder, time-of-flight mass spectrometer (TOF-MS) is generally installed in a chamber at a fixed direction. So, if the surface normal direction deviates from the TOF direction, detection yield of desorbing ions falls down rapidly. In this study, the rotatable sample holder is equipped with additional correction electrodes at 2 mm away from the each side of the sample to apply appropriate gradient of electrical potential for the desorbing ions in the off-normal arrangements between the sample and TOF-MS. As there is limitation of off-normal angle range measurable by the correction electrodes, two equivalent TOF devices are installed in the chamber at 30° and 70° (30° and 70°-TOFs) from the incident SR to make measurements possible in wide incident angle range (10 - 80°) [3].

Results and Discussion

Typical results obtained for deuterated methyl ester-terminated SAM ($CD_3OCO(CH_2)_{15}S/Au$) in the C K-edge region are shown in Fig. 2. Intensities of CD_3^+ and D^+ ions in the $\sigma^*(O-CD_3)$ excitation obviously depend on the incident angle of SR. On the other hand, H^+ desorption is independent of the angle in whole excitation region. Ions
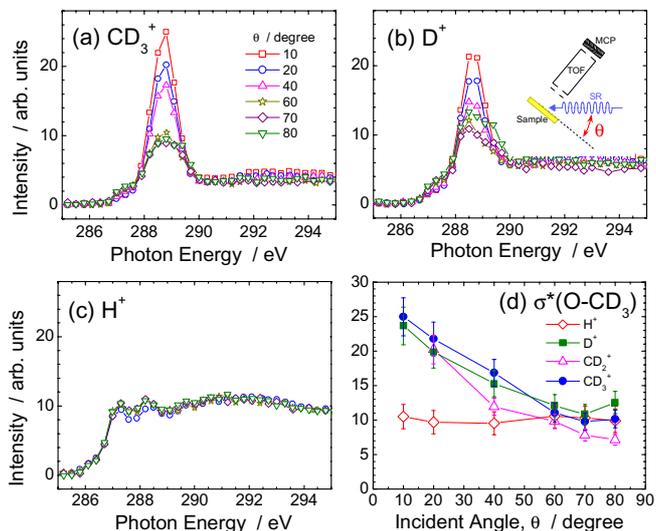

Fig. 1 (a)-(c) Normalized PIY spectra of CD_3^+, D^+, and H^+ ions measured at different incident angles of SR. Spectra at 10-40° and 60-80° were measured using 70°-TOF and 30°-TOF, respectively. (e) Incident angle dependence of integrated PIY intensities of H^+, D^+, CD_2^+, and CD_3^+ ions for the net $\sigma^*(O-CD_3)$ excitation.

which desorb site-selectively indicate significant polarization dependence, but non-selective ions rarely show the dependence. These findings indicate that site-selective ion desorption takes place only within the functional group where core electron is excited and the initial memory of the core excitation is effectively conserved during desorption.

Trends of the incident angle dependence of the net $\sigma^*(O-CD_3)$ intensities depicted in Fig. 2(d) differ in desorbing ions as well as resonant excitations. Variation of the dependence can be understood by the different superiority of dissociation/desorption mechanisms: direct dissociation induced by core excitation and indirect dissociation caused by rapid energy relaxation and X-ray-induced electron stimulated desorption.

References

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