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S K-edge X-ray absorption fine structure study of adsorbed alkanethiols on Ag(111)

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Introduction

Self-assembled monolayers (SAMs) of alkanethiols on noble metals have been extensively studied both from fundamental and technological points of view. Recently, Dooms et al. reported the total reflection XANES spectra from alkanethiols on Ag(111) and found an anomalous peak in octadecanethiol (C18) SAM, which might be associated with a specific adsorption structure [1]. However, our previous study of C18 on Ag(111) by using S K-edge XANES and SEXAFS indicated that this hypothesis is not correct. In this study, to clarify the adsorption structure of alkanethiolate on Ag(111) we investigated the simplest alkanethiolate (methylthiolate) SAM by the same approach.

Experiment

The experiments were performed at BL-7A and 11B. C K-edge NEXAFS spectra were measured at BL-7A by partial electron yield mode to check the orientation of alkyl chains. The S-K fluorescence-yield XAFS spectra were measured for the samples at 100 K by using a gas-flow proportional counter filled with the P10 gas. A mechanically and chemically polished Ag(111) surface was cleaned by repeated cycles of Ar^+ sputtering and annealing. Methylthiolate (C1) SAM was prepared by dosing dimethyl disulfide (CH_3-S-S-CH_3) to the Ag surface with more than 5L at room temperature.

Results and Discussion

Over 8h after dosing of dimethyl disulfide, (√7 x √7)R10.9° LEED pattern [2] was observed. Fig. 1 shows S K-edge NEXAFS spectra of C1 on Ag(111) at three different incident angles. The peak at 2473eV was assigned to the S1s → σ*(S-C) excitation. The tilt angle calculated from the polarization dependence of the σ*(S-C) peak is about 42±10° from the surface normal. $k^2\chi$ (k) functions and their Fourier transforms (Δk=2.3~8.7 Å^{-1}) for two incident angles, NI at 66° and GI at 38°, are shown in Fig. 2 (a) and (b), respectively. There are mainly three peaks at ~1.2 Å ascribed to the S-C and ~1.8 and 2.5 Å to the S-Ag contributions (Ramsauer- Tawnsend effect). The S-Ag bond length obtained is 2.57Å. From the effective coordination number analyses, we found that methylthiolate induces a surface reconstruction.

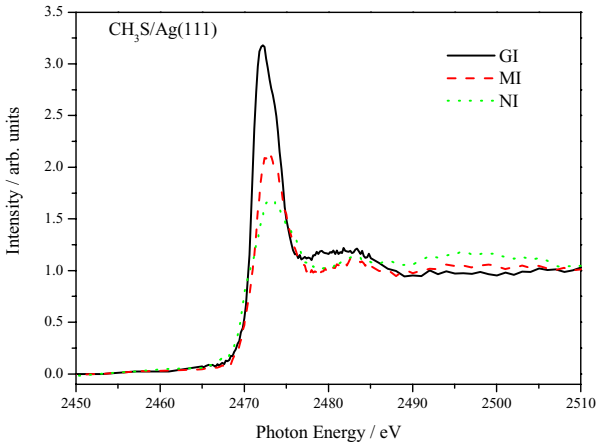

Fig.1 S K-edge NEXAFS spectra of C1/Ag(111)

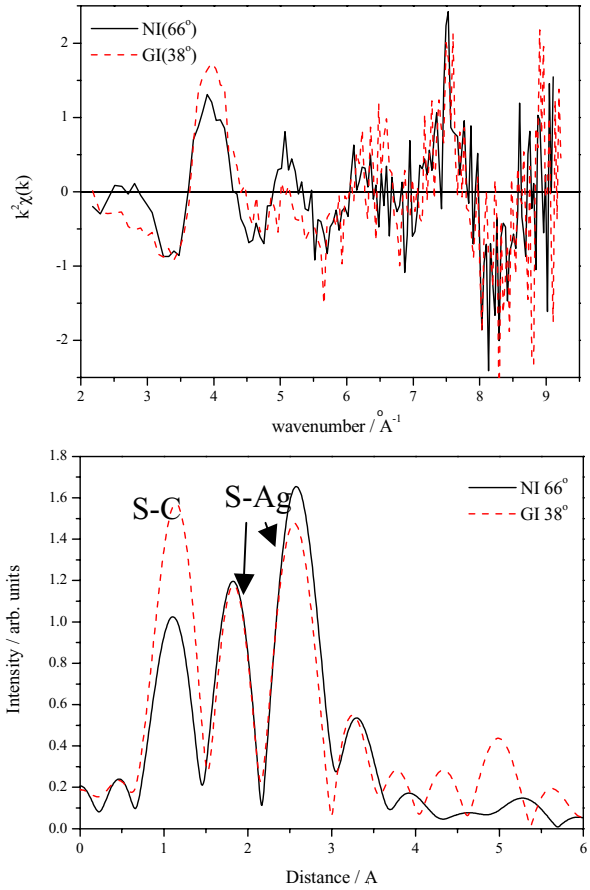

Fig. 2. S K-edge SEXAFS oscillation functions χk) (a), and Fourier transforms (b) of C1/Ag(111) .

References

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