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Adsorption structures of alkanethiols self-assembled monolayers on the Cu(100) surface studied by S-K EXAFS and C-K NEXAFS spectroscopies

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We performed S-K XAFS and C-K NEXAFS experiments for alkanethiols ($\text{CH}_3(\text{CH}_2)_n\text{SH}$; $n=6,12,16$) on Cu(100), and clarified the local structures around the S head groups and the orientation of alkyl chains; the S atoms were found to locate at a fourfold hollow site without surface reconstruction. These results are in clear contrast with the case of Cu(111), where the S atoms locate at a deep three-fold hollow site with significant lateral outward movements of the nearest neighbor Cu atoms. Such a structure difference might come from the different densities of the Cu atoms on these surfaces.

Keywords: NEXAFS, EXAFS, alkanethiol, SAM, Cu(100).

1. Introduction

Alkanethiols adsorbed on noble metals have attracted wide interest over the last decades partly because of their technological applicability to the fields of electrical devices or corrosion, and partly because of scientific importance of their self assembling 2D growth on the substrate. In self-assembled monolayer (SAM) films saturated hydrocarbon chains are close-packed due to the molecular-molecular interaction and form a brush-like structure [Ulman(1996)]. Recently, we studied the local structure of *n*-alkanethiols ($\text{CH}_3(\text{CH}_2)_n\text{SH}$, hereafter, denoted as *C_n*) on Cu(111) and found that the S atoms locate at a deep three-fold hollow site with significant lateral outward displacement of the nearest neighbor Cu atoms [Imanishi(1998)].

In the present work, we have studied the saturated state of C₆, C₁₂, C₁₆ on Cu(100) surface at 100 K. Cu surfaces are well-known as stronger interaction with S head group than Au or Ag substrates. In order to investigate the process of self-assembling, whether it involves reconstruction of the substrate or not is of great importance. By means of C-K NEXAFS and S-K EXAFS measurements we have revealed the competition of molecular-molecular and molecular-substrate interactions on SAM structures, comparing with our previous data of alkanethiols on Cu(111).

2. Experimental

A Cu(100) crystal was mechanically polished and electrolyzed in a methanol solution of nitric acid. The sample crystal was cleaned

by means of Ar⁺ sputtering (500 eV at ambient temperature) and annealing at 1000 K in the ultra high vacuum (UHV) chamber. All the XAFS experiments were done at Photon Factory, High Energy Accelerator Research Organization, Japan. The thiol SAM films on the Cu(100) surface were fabricated by evaporation (3–5 L dose; at 5×10^{-8} Torr) in vacuum ($< 1 \times 10^{-10}$ Torr base pressure) at 270 K. C-K NEXAFS spectra were recorded on at 100 K BL-7A for C₆, C₁₂, C₁₆ on Cu(100) by use of the partial electron yield mode with 200 eV retarding voltage. S-K EXAFS spectra were recorded at 100 K on BL-11B for C₁₂ on Cu(100) by use of the fluorescence yield mode. Spectra were taken at the incidence polar angle θ of 90° (normal x-ray incidence), 55° (magic incidence), and 15° (grazing incidence).

3. Results and Discussion

3.1 C-K NEXAFS

Figure 1 shows C-K NEXAFS spectra of saturated C₁₂ on Cu(100) at normal, magic, and grazing incidences. In the spectrum of randomly oriented multilayers, two peaks are prominent at 289 eV (peak A) and at 292 eV (peak B), which can be assigned to the C 1s-to- σ^* (C-H) and C 1s-to- σ^* (C-C) transitions, respectively. In the spectra of monolayers, peak A is most intense at normal incidence and almost disappears at grazing incidence, this implying that the C-H bond is parallel to the surface [Stöhr(1992)]. The position of peak B shifts higher in energy as the incidence angle gets larger. Curve fitting analysis derived that peak B consists of two peaks *B*₁ and *B*₂, whose transition moments are nearly perpendicular to each other. According to the theoretical calculation of C K-edge NEXAFS of propane, the lower energy peak *B*₁ can be assigned to the transition whose moment is vertical to the alkyl chain, while the higher energy peak *B*₂ is the one with the transition moment parallel to the chain [Stöhr(1987)].

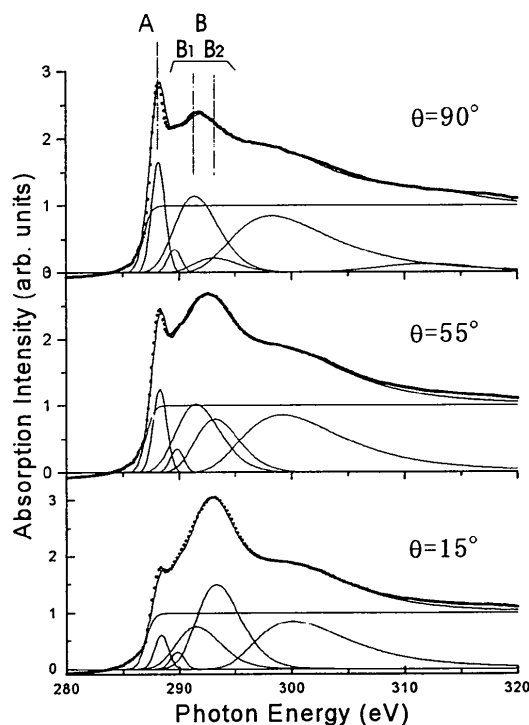


Figure 1
Curve-fitting analysis of C-K NEXAFS spectra for C₁₂ on Cu(100)

The analysis of peak *A* and peak *B*₂ gives C-H, C-C average angles from surface normal, respectively. It reveals that thiols adsorb on Cu(100) more tilted than that on Cu(111) (see Table1).

Table 1

The orientations of the $\sigma^*(\text{C-H})$ and $\sigma^*(\text{C-C})$ transition moments (angles to the surface normal) compared with those of the Cu(111) case.

polar angle(°)	Cu(100)		Cu(111) [*]	
	C-H	C-C	C-H	C-C
C6	67±10	22±10	78±10	12±10
C12	61±10	27±10	78±10	12±10
C16	65±10	30±10		

^{*}) Imanishi et al.(1998)

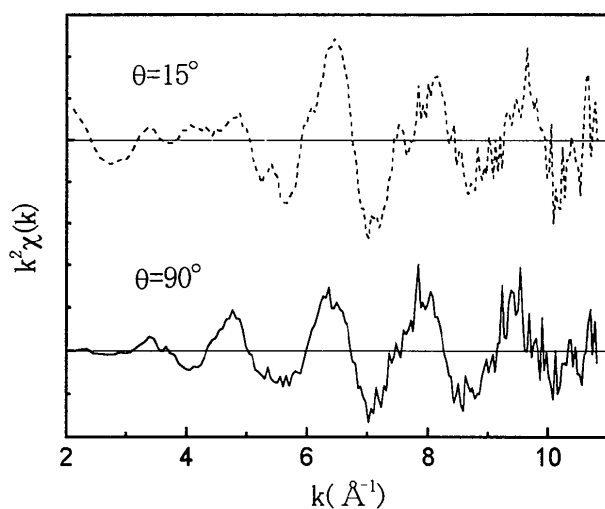


Figure 2

$k^2\chi(k)$ functions of S-K EXAFS spectra for C12 on Cu(100) at grazing(15°) and normal (90°) incidence angles.

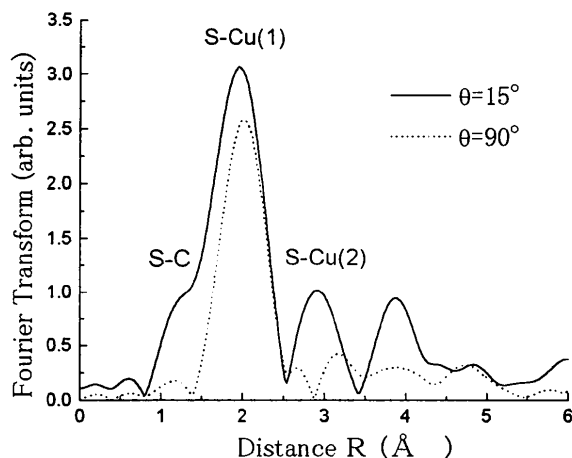


Figure 3

Fourier-transforms of S-K EXAFS spectra for C12 on Cu(100).

3.2 S-K EXAFS

Extraction of the EXAFS function $\chi(k)$ (k is the photoelectron wave number) was carried out according to the well-established procedures[Koningsberger(1988)]. The extracted $k^2\chi(k)$ functions and their Fourier transforms for C₁₂ on Cu(100) are shown in Figs.2 and 3. For both of the S-C and S-Cu first shells the $\chi(k)$ of CH₃SH adsorbed on Cu(100) was used as the standards, where the coordination number of S-Cu(1) shell is $N=4$ and the S-Cu(1) distance is $R=2.29$ Å[Imanishi(1997)]. The results of curve-fitting analysis were listed in Table2, where γ and ω are the polar angles of S-C and S-Cu estimated by the ratio $N_r = N^*(90^\circ)/N^*(15^\circ)$ (N^* is the effective coordination number). $\gamma(\text{S-C})$ for Cu(100) could not be estimated because the S-C peak was too small at normal incidence. In the case of C12 on Cu(100), calculated N_r values without involving surface reconstruction are 0.848 (hollow), 0.246 (bridge), and 0 (atop). The experimental one is 0.829, indicating that the S atoms locate at a fourfold hollow site without any reconstruction of the first layer Cu atoms. Moreover, the S-Cu second shell analysis gives $R(\text{S-Cu}(2))=3.23\pm 0.03$ Å, which is in good agreement with the S-Cu(2) distance without reconstruction (3.21 Å).

Table 2

The structure parameters of C12 on Cu(100) and Cu(111) derived from S-K EXAFS analysis

	Cu(100)	Cu(111) [*]
R(S-C) (Å)	1.81±0.04	1.76±0.05
$\gamma(\text{S-C})$ (°)	--	27±12
R(S-Cu) (Å)	2.28±0.03	2.31±0.02
$\omega(\text{S-Cu})$ (°)	53±2	55±2
d (Å)	0	0.48

^{*}) Imanishi et al.(1998)

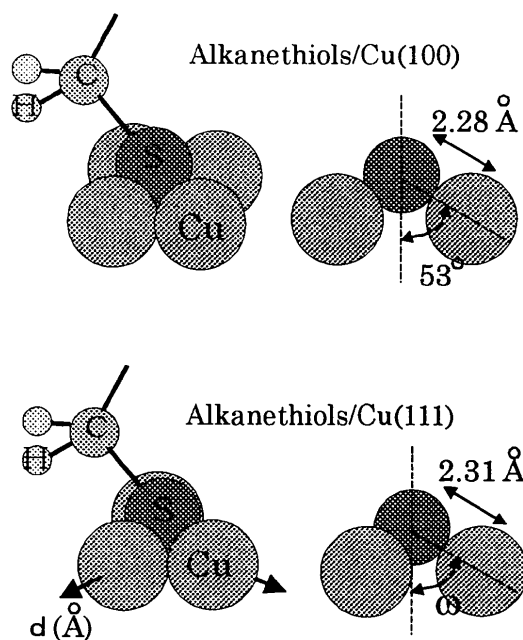


Figure 4

Illustrated local structures around S atoms of saturated alkanethiols on Cu(100), Cu(111) surfaces.

On the other hand, for C12 on the Cu(111) surface the experimental Nr value was 1.06 ± 0.05 . This is much larger than the calculated Nr values for the non-reconstructed surface; 0.365 (hollow), 0.237 (bridge), and 0 (atop). The corresponding polar angles ω are 39° (hollow), 33° (bridge), and 0° (atop). Larger Nr values imply that the S atoms locate at a deeper position compared with the three-fold hollow site. Assumed that the nearest neighbor Cu atoms displace only in lateral directions to the surface, the lateral outward displacement d was estimated about 0.5 Å from the experimental value of ω (see Fig.4).

4. Conclusions

Main conclusions from above results and discussion are follows:
(1) Alkanethiols on Cu(100) adsorb more obliquely than those on the Cu(111) surface.

(2) S atoms locate at a fourfold hollow site without reconstruction for the case on Cu(100), in clear contrast with the case on Cu(111), where they locate at a deeper three-fold hollow site with drastic displacement of the surface Cu atoms.

The second result is due to the larger density of the first layer Cu atoms on Cu(111) ($0.18 \text{ atoms}/\text{Å}^2$) than Cu(100) ($0.15 \text{ atoms}/\text{Å}^2$). At the saturation stage (about 0.3 ML), the distance between each S atom in the stable site is smaller even with the surface reconstruction.

Thus, alkanethiols are closer packed and assembled with a smaller tilt angle on Cu(111) than that on Cu(100). That explains the result (1) well.

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