11B/1999G078

STRUCTURAL ORDERING OF ALKANETHIOLATE MONOLAYER ADSORBED ON CU(100)

Hiroshi KONDOH*, Akira NAMBU, Masaoki IWASAKI, Toshihiko YOKOYAMA and Toshiaki OHTA
Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Tokyo 113-0033, Japan

Introduction

Ordering process of self-assembled monolayers of alkanethiolate on Au(111) has been extensively studied to understand the self-assembly mechanism. It is widely known that the S-Au interface structure is very similar to that of the (001) surface of bulk single-crystal alkane. In case of Cu(100), however, there is an obvious difference in symmetry between the Cu(100) surface and the bulk alkane structure. STM observations for hexanethiolate monolayers adsorbed on Cu(100) indicated that two-dimensionally (2D) ordering process needs a much longer time (more than 10 hours) compared to that on Au(111). During the 2D-ordering process, no significant change of molecular orientation was observed by C-K NEXAFS. In this work, time-dependent change of interface structure for a hexanethiolate monolayer on Cu(100) has been investigated by means of S K-edge XAFS.

Experimental

The hexanethiolate monolayer was prepared by exposing a clean Cu(100) surface to gaseous hexanethiol at room temperature to the saturation. The saturation coverage was estimated by XPS to be 0.30 ± 0.03 with respect to the surface Cu atoms. LEED measurements revealed that this monolayer has the c(2x6) unit cell, indicating that one unit cell contains four thiolates. S-K XAFS spectra were measured at BL-11B using the fluorescence detection method for the hexanethiolate monolayer just after adsorption and 36 hours after adsorption.

Results and discussion

Figure 1 shows Fourier transforms of S-K EXAFS oscillations for the hexanethiolate monolayer measured just after adsorption (a) and 36 hours after adsorption (b). Although no drastic change was observed after 36 hours, it is appreciable that a new peak appears at around 3.2 Å in the normal incidence curve, which is associated with contribution from the nearest-neighbor (NN) sulfur atoms. Curve-fitting analysis for this peak reveals that the NN sulfur atoms are located at a distance of c(2x2). Furthermore the analysis for S-Cu shells indicated that the sulfur atom of the thiolate is located at the four-fold hollow site of the unreconstructed Cu(100) surface as shown in Fig.2 (top). Considering the coverage and the unit cell, we propose a structure model for 2D arrangement of the sulfur atom of the thiolate as shown in Fig.2 (bottom). They form zigzag chains along the close-packed Cu rows. At the initial stage (Fig.1(a)) the sulfur atoms also occupy the four-fold hollow sites with almost the same local structure as those in the ordered surface. The absence of the Fourier transform peak contributed from the NN sulfur atoms indicates that there is no ordering at the S-Cu interface. Thus, surface thiolates rapidly form a well-oriented but 2D-disordered monolayer with randomly occupying the hollow sites. This rapid process is followed by slow evolution of the 2D-ordered structure via. surface diffusion. Force field calculations revealed that a large lattice mismatch between the c(2x6)-S layer and the alkyl layer is effectively reduced by tilting of the S-C bonds that bridges the two layers.

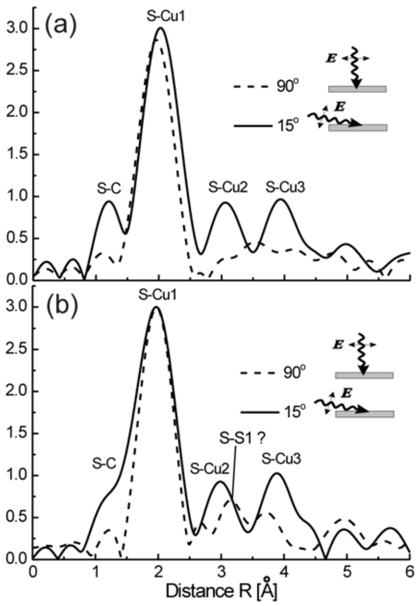

Figure 1: Fourier transforms of S-K EXAFS oscillation for the hexanethiolate monolayer on Cu(100). (a) just after adsorption, (b) 36 hours after adsorption.

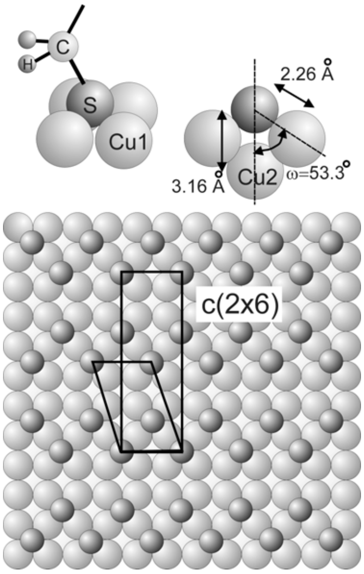

Figure 2: Model for local structure around the sulfur atom of the hexanethiolate and 2D arrangement of the sulfur atom.

* kondo@chem.s.u-tokyo.ac.jp