



The methanethiolate-induced pseudo-(100) reconstruction of Cu(111): A medium energy ion scattering structure study

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Abstract

The pseudo-(100) reconstructed surface of Cu(111) induced by adsorbed methanethiolate, CH₃S⁻, has been investigated by medium energy ion scattering (MEIS) using 91 keV incident H⁺ ions with the objective of establishing the number of reconstructed Cu layers. The results are shown to be consistent with a single reconstructed Cu surface layer containing 0.66 ML Cu atoms in an incommensurate or long-range coincidence net structure. Specifically, excellent fits to both the scattered ion energy spectra and the angular blocking curves are found for a model based on a single pseudo-(100) reconstructed Cu layer, the atomic density being consistent with that proposed in an earlier STM study (S.M. Driver, D.P. Woodruff, Surf. Sci. 457 (2000) 11).

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1. Introduction

A very substantial body of work has been conducted in the last 20 years or so on the interaction

of alkane thiols (CH₃(CH₂)_{n-1}SH) with noble metal surfaces, motivated particularly by their ability to form so-called self-assembled monolayers (SAMs) which can be used as the building blocks for molecular electronics and sensors (e.g. [1–4]). The bulk of this work has been performed on the Au(111) substrate, but other substrates, particularly of Ag and Cu, have been investigated. On all of these surfaces the thiol reacts with the substrate to detach the thiol hydrogen atom and

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form a thiolate which bonds to the surface through the S atom; for the shorter alkane chains, at least, the same adsorbed layers can be formed by reaction of the surface with alkane disulphides ($\text{CH}_3\text{-(CH}_2\text{)}_{n-1}\text{S-S(CH}_2\text{)}_{n-1}\text{CH}_3$) through S–S bond scission. Despite this activity, there have been rather few quantitative structure determinations of these surface phases and the thiolate-substrate interface. Alkanethiolate SAMs on Au(111) are generally assumed to involve little or no modification of the metal surface structure, although there have been suggestions that reconstruction may occur (e.g. [5,6]), while reconstruction has also recently been explicitly proposed for the system Ag(111)/methanethiol [7].

On Cu(111), the existence of a major reconstruction of the surface layer(s) is now well-established for both methanethiolate [8–11] and octanethiolate [12,13]. The structure of the adsorption phases formed by methanethiolate on Cu(111) have been particularly extensively studied, using near-edge and surface-extended X-ray absorption fine structure (NEXAFS and SEXAFS) [8,9] normal-incidence X-ray standing waves (NIXSW) [10], and scanning tunnelling microscopy (STM) [11]. At low temperatures the adsorbate-induced reconstruction is kinetically hindered, and an ordered ‘honeycomb’ adsorbate phase occurs which appears to involve both bridge and hollow site occupation [10,11,14]; this phase may also be metastable at room temperature under certain circumstances [11]. The equilibrium structure at room temperature, however, involves reconstruction of the outermost Cu atom layer(s) to a near-square ordering very similar to that of a Cu(100) surface. There are quite a number of other examples of this type of adsorbate-induced pseudo-(100) surface reconstructions on fcc(111) and (110) surfaces [15], although these other examples all involve atomic adsorbates. It appears that these are systems in which hollow site occupation on a (100) surface is so energetically favourable that even on other low index surfaces the outermost layer or layers reconstruct to form this type of surface, despite the strain energy cost of the substrate-reconstructed layer interface. On (111) surfaces it seems that these reconstructed layers are either incommensurate or have a rather long-range periodicity.

For methanethiolate on Cu(111) a model based on a commensurate $\begin{bmatrix} 4 & 3 \\ -1 & 3 \end{bmatrix}$ phase (defined relative to primitive translation vectors of the Cu(111) surface separated by the obtuse angle) has been proposed on the basis of STM images [11] (Fig. 1), but measurements of interatomic spacings and azimuthal angles are not sufficiently precise to be sure that the reconstructed surface is truly commensurate. Note that methanethiolate on Cu(100) does occupy four-fold coordinated hollow sites [16,17], although the pseudo-(100) reconstruction formed by this adsorbate on Cu(111) involves significantly larger Cu–Cu nearest neighbour distances than on the Cu(100) surface.

For such long-range commensurate or incommensurate structures a full quantitative structure determination is not really possible, but the SEXAFS and NIXSW data clearly demonstrate that a density-lowering reconstruction of at least one Cu layer occurs, and STM (and qualitative LEED) show that this reconstruction is of the pseudo-(100) type. What neither of these techniques can distinguish, however, is whether the reconstruction

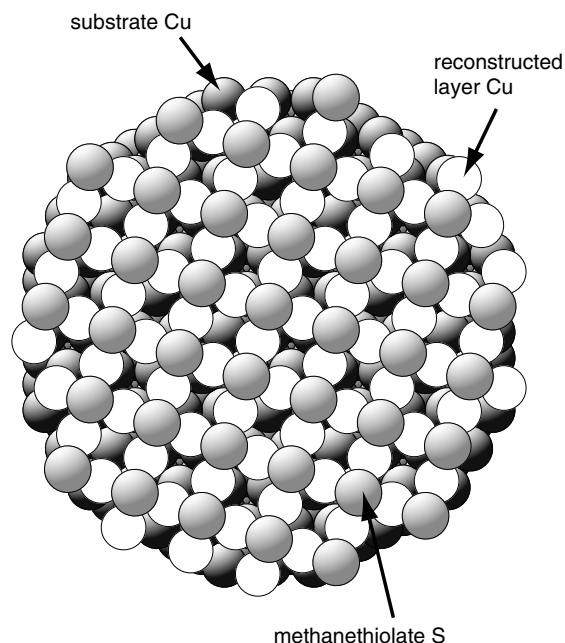


Fig. 1. Schematic plan view of the pseudo-(100) reconstructed Cu(111)/methanethiolate surface based on STM data [11].

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