

NEXAFS study of 1-butanethiol adsorbed on Cu(111) and $\sqrt{7} \times \sqrt{7}$ R19.1° S/Cu(111)

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The adsorption of 1-butanethiol on Cu(111) and $\sqrt{7} \times \sqrt{7}$ R19.1° S/Cu(111) surfaces has been studied by S *K*-edge near edge X-ray absorption fine structure (NEXAFS) spectroscopy and thermal desorption spectroscopy. Upon adsorption on clean Cu(111) surface at room temperature, butanethiolate as well as atomic sulfur is formed. For the butanethiolate, the S–C bond is found predominately perpendicular to the surface as revealed by polarization analysis. In contrast, on $\sqrt{7} \times \sqrt{7}$ R19.1° S/Cu(111) surface, the S–H and S–C bonds of the butanethiol stay intact, resulting in a weakly chemisorbed butanethiol.

Keywords: near edge X-ray absorption fine structure (NEXAFS); 1-butanethiol; Cu(111).

1. Introduction

Ultrathin organic thin films of self-assembled monolayers have been the subject of intense research due to their potential applications in areas of lubrication, corrosion inhibitors, gas sensors (Ulman, 1991). In contrast with the extensively studied system of alkanethiols adsorbed on Au surfaces, there have been only a few reports of alkanethiols adsorption on Cu surfaces (Laibinis *et al.*, 1991; Rieley *et al.*, 1997; Hutt *et al.*, 1998; Imanishi *et al.*, 1998; Loepp *et al.*, 1999; Floriano *et al.*, 2000), presumably due to the difficulty of maintaining a clean Cu surface in the solution phase. In anticipation of the wider adoption of Cu-based interconnecting technology in the future generation of IC circuitry, an enhanced understanding of Cu-liquid interface and the corrosion protection of Cu metal becomes much more necessary. In the present study, we employed NEXAFS and TDS to study the adsorption of 1-butanethiol on both clean Cu(111) and $\sqrt{7} \times \sqrt{7}$ R19.1° S/Cu surfaces. The aims are focused on understanding the adsorption geometry, comparing the relative chemical bonding strength between two systems, and exploring the possibility of synthesizing the disulfide bond on the surface.

2. Experimental

The experiments were carried out in a 12" mu metal sphere equipped with a sputtering ion gun, a LEED, an energy analyzer, and a microchannel plate (MCP). A Cu(111) single crystal was cut from a single crystal boule with a miscut angle determined *via* x-ray diffraction to be less than 0.5°. Standard sample sputtering/anneal cycle was repeated until a sharp LEED pattern for the clean Cu surface was obtained and no contaminant was found with XPS. The partial electron yield detector was constructed from the MCP in conjunction with three Au meshes. For S *K*-edge NEXAFS measurements, a bias potential of 1900 V was chosen to retard the signals from Cu substrate and yet retain S

Auger contribution. The measurements were performed at a DCM beamline (BL 15A) at SRRC, Taiwan (ring energy 1.5 GeV). The beamline resolution was better than 0.4 eV at the S *K*-edge. The polar angle of the incident x-ray was varied between 0° (normal incidence) and 70° (grazing incidence). The photoelectric current generated by a Cu mesh situated before the sample was used as the intensity of incident x-ray (I_0) for normalizing x-ray absorption spectrum.

The 1-butanethiol was obtained from Aldrich Chemical Co and, after cycles of freezing/thawing pretreatment, the purified 1-butanethiol was vacuum-dosed onto the surface. The dosage was measured in term of Langmuir (1 Langmuir = 10^{-6} Torr x sec). The sample could be heated to 800 K by means of resistive heating and cooled down to 100 K by heat conduction to a liquid nitrogen reservoir external to the chamber.

3. Results and Discussion:

Fig. 1 shows a series of S *K*-edge NEXAFS spectra acquired at two different x-ray incidence angles for 1-butanethiol adsorbed onto different surfaces. The curves labeled C_{4ad} refer to the spectra taken for 20 L butanethiol adsorbed at room temperature onto the clean Cu(111) surface. At grazing incidence condition ($\theta = 70^\circ$), a peak at 2469.9 eV is clearly noted. High-resolution synchrotron based S2*p* XPS data show that at room temperature the chemisorption of the butanethiol leads to coadsorbed thiolate and atomic sulfur species on the surface (Yang *et al.*, 2000). The similar coexistence of thiolate and atomic sulfur species for methanethiol chemisorbed on Cu(111) has also been observed (Jackson *et al.*, 2000). A previous XAS study unambiguously assigns the peak at 2469.9 eV to the atomically-adsorbed sulfur and the corresponding transition is originated from S *1s* state to unfilled *p*-derived hybrid state of S and metal atoms (Stöhr *et al.*, 1985).

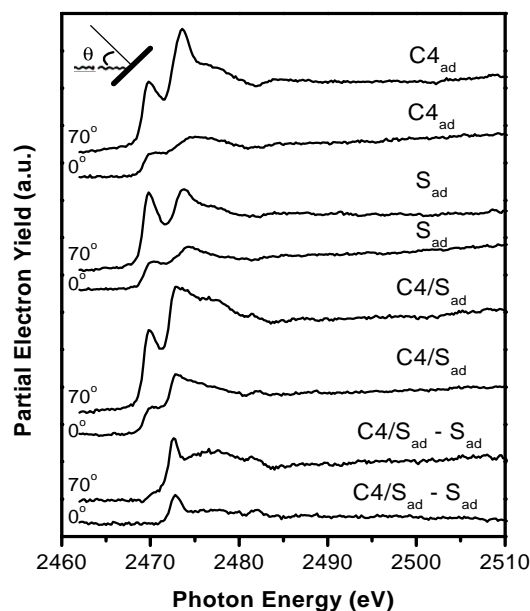


Figure 1 Polarization-dependent S *K*-edge NEXAFS spectra for (1) butanethiol/Cu(111); (2) $\sqrt{7} \times \sqrt{7}$ R19.1° S_{ad}; (3) butanethiol/ $\sqrt{7} \times \sqrt{7}$ R19.1° S_{ad}/Cu(111); (4) = (3) - (2).

The second peak at 2473.7 eV in $C_{4,ad}$ spectra becomes more visible at grazing incidence condition and is assigned to $S\ 1s$ to $\sigma^*(S-C)$ transition. In comparison, for physisorbed 1-butanethiol, there exists an intense peak at 2472.6 eV, which is attributed to the transition from $S\ 1s$ to both $\sigma^*(S-C)$ and $\sigma^*(S-H)$ transitions (Rieley *et al.*, 1997; Imanishi *et al.*, 1998). The spectra for physisorbed butanethiol are shown in Fig. 2. For the chemisorbed butanethiol, the shift of the peak toward higher photon energy indicates that S-H bond scission occurs and the thiolate is formed (Imanishi *et al.*, 1998). The broad resonance at ~ 2484 eV, insensitive to the x-ray incidence angle, is attributed to the substrate scattering effect (Rieley *et al.*, 1997). As the x-ray incidence angle is changed to the normal direction, the $\sigma^*(S-C)$ resonance at 2473.7 eV almost disappears completely. The detailed polarization analysis, including several more incident angles, indicates that butanethiolate is ordered on the Cu surface with the S-C bond aligned predominately toward the surface normal.

A layer of atomic sulfur exhibiting $\sqrt{7} \times \sqrt{7}$ R19.1° LEED pattern can be formed on the Cu(111) surface by means of thermal decomposition of the butanethiol. However, the detailed atomic arrangement of $\sqrt{7} \times \sqrt{7}$ R19.1° structure remains unsettled (Foss *et al.*, 1997). Separate thermal desorption study shows that, as the thiolate is heated to above 550 K, the thiolate desorbs as well as decomposes completely into isobutene *via* β -hydrogen elimination pathway (Yang *et al.*, 2000). The island formation of atomic sulfur is noted because of the appearance of $\sqrt{7} \times \sqrt{7}$ structure in the low coverage regime. Three cycles of butanethiol adsorption followed by thermal decomposition were performed to yield a saturated $\sqrt{7} \times \sqrt{7}$ structure with a coverage of 0.43 ML (Foss *et al.*, 1997), where one ML of the adsorbate was set equal to the same substrate density. The S K -edge NEXAFS spectra for such a structure are shown in two curves labeled as S_{ad} in Fig. 1. Again, the peak at 2469.9 eV is attributed to $S\ 1s$ to p -derived unfilled state between S and Cu metal and the observation of higher intensity at grazing incidence angle is consistent with a predominate vertical orientation feature of Cu-S bond in the $\sqrt{7} \times \sqrt{7}$ structure. The similar edge jumps for butanethiol and $\sqrt{7} \times \sqrt{7}$ S/Cu indicate that the coverage for saturated butanethiol at room temperature is close to 0.43 ML too.

A subsequent readsorption of 2.5 L butanethiol onto $\sqrt{7} \times \sqrt{7}$ R19.1° S_{ad} /Cu(111) at 100 K produces two NEXAFS spectra designated as C_4/S_{ad} in Fig. 1. TDS result shows that no physisorbed multiplayer is formed at this dosage (Yang *et al.*, 2000). At first glance, the strong polarization dependence characteristic of the butanethiolate and S_{ad} adsorption is removed. NEXAFS spectra intrinsic to the butanethiol adsorbed on S_{ad} /Cu(111) can be obtained by subtracting the raw spectra from the corresponding spectra of S_{ad} . As-treated spectra are presented in the bottom two curves of the Fig. 1. It is noted that to facilitate the spectra subtraction, no height adjustment of the edge jump for different incident angles was attempted. However, when comparing the peak intensity variation for different incidence angles, the height of edge jump was always normalized to unity. For the butanethiol adsorbed on ordered sulfur overlayer, several new findings appear. The intense peak now shifts from 2473.7 to 2472.6 eV where $\sigma^*(S-C)$ and $\sigma^*(S-H)$ transitions occur (Rieley *et al.*, 1997; Imanishi *et al.*, 1998). Moreover, the atomic absorption peak at 2469.9 eV disappears and the small remnant in $\theta = 70^\circ$ curve is mostly likely due to an incomplete cancellation between two raw data sets. Taken together, it is suggested that both S-H and S-C bonds of the butanethiol are not broken on sulfur overlayer-covered Cu surface. Therefore, only weak van

der Waals interaction is in place and the butanethiol is at most weakly chemisorbed on the S_{ad} /Cu surface. This reasoning corroborates with the TDS result in which the first monolayer of butanethiol on S_{ad} /Cu is found to desorb almost completely below room temperature.

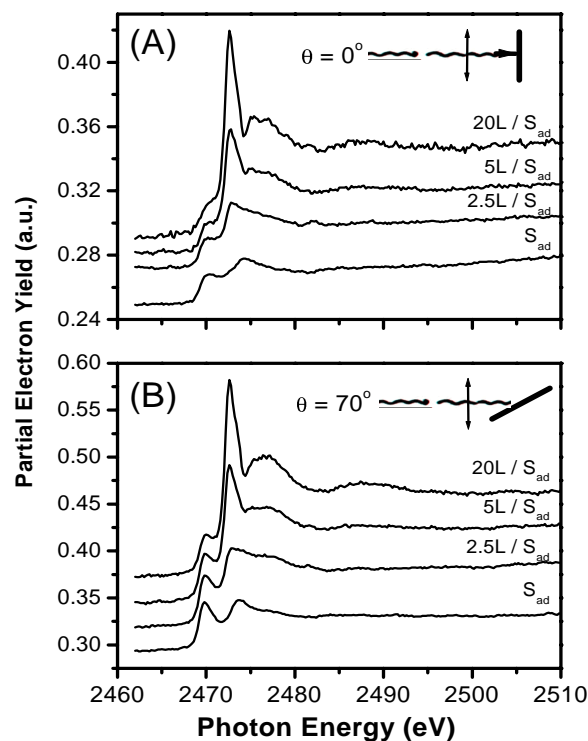


Figure 2
Dosage-dependent S K -edge NEXAFS spectra for butanethiol adsorbed on $\sqrt{7} \times \sqrt{7}$ R19.1° S_{ad} /Cu(111) at 100 K.

Fig. 2 shows a sequence of dosage-dependent S K -edge NEXAFS spectra for the butanethiol adsorbed on $\sqrt{7} \times \sqrt{7}$ R19.1° S_{ad} /Cu(111). The spectra for 2.5 L dosage of butanethiol have been shown in Fig. 1. As the dosage is increased to 20 L, the sharp resonance at 2472.6 eV and two broad resonances at ~ 2477 and ~ 2488 eV become more pronounced. After subtracting the contribution from S_{ad} layer, the spectrum difference between normal and grazing incidences for thick butanethiol multilayer is removed, suggesting the presence of the random adsorption nature for the multilayer.

In summary, we found that 1-butanethiol adsorbed dissociatively on clean Cu(111) surface at room temperature, forming thiolate and atomic sulfur species. For the thiolate species, S-C bond is found to orient perpendicular to the surface. In comparison, the adsorption of 1-butanethiol on $\sqrt{7} \times \sqrt{7}$ R19.1° S/Cu surface does not lead to a breaking of the S-H and S-C bonds; as a result, the butanethiol can only weakly chemisorb on sulfur-precovered Cu surface and the thiol molecules completely desorb from the surface at room temperature. Therefore, it seems reasonable to conclude that the chemically inert nature of S_{ad} surface cannot be used to assist the formation of disulfide bond.

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