

Adsorption of (CH₃)₂S on c(10 × 2)Ag/Cu(100) Studied by S K-edge NEXAFS and XPS

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Received October 4, 2004; Accepted November 17, 2004

Adsorption structure and molecular orientation of dimethylsulfide [(CH₃)₂S] on c(10 × 2)Ag/Cu(100) surface at 85 K has been investigated by polarization dependent sulfur K-edge near-edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS) methods. The (CH₃)₂S molecule for submonolayer phase adsorbs on c(10 × 2)Ag/Cu(100) surface without dissociation of S-C bonds. The (CH₃)₂S molecule has an interaction with the surface Ag atoms through both sulfur and methyl group of the (CH₃)₂S. The orientation angle of two S-C bonds is estimated to be 22 ± 6° from the surface. This value is almost same as the (CH₃)₂S/Ag(111) adsorption system of 23 ± 5°. The adsorption behavior of the (CH₃)₂S molecule on c(10 × 2)Ag/Cu(100) surface is similar to the Ag(111) surface.

INTRODUCTION

Due to the industrial and environmental importance of sulfur-containing molecules, there have been a number of related studies on the adsorption and surface reactions on transition metal surfaces. The adsorption structure of the molecule is quite important to understand the surface reaction between the substrate and the adsorbed molecule from the viewpoint of desulfurization catalyst. A combined measurement Near-Edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS) are a smart technique for obtaining both adsorption structure and electronic information of the adsorbate [1-3]. From the NEXAFS spectrum we can achieve the information of an orientation angle for adsorbed molecule quantitatively. From the XPS analysis we can discuss about a chemical environment of the molecule and also decide an adsorbed species.

In many early studies, heteroepitaxial

metal-on-metal surface has been studied with paying attention to the unique catalytic, electronic and magnetic properties. For the metal-on-metal system of Ag thin layer on Cu(100), Ag atoms form with the super structure of c(10×2) pattern due to the large lattice mismatch of 13% between Ag (0.409 nm) and Cu (0.362 nm) [4-9]. The overlayer of Ag atoms form a close-packed hexagonal Ag(111)-like structure on Cu(100) surface.

Previously, we have studied the adsorption behavior of (CH₃)₂S molecule on clean Ag(111) and Cu(100) surfaces by sulfur K-edge NEXAFS and XPS measurements [10-11] and found that (CH₃)₂S molecule adsorbs molecularly on both surfaces without dissociation of the S-C bonds. For the (CH₃)₂S/Ag(111) system, we found that (CH₃)₂S molecule adsorbs with the molecular plane parallel to the surface [10]. On the other hand, the orientation angle of the S-C bonds of (CH₃)₂S molecule is estimated to be 38° from the surface for

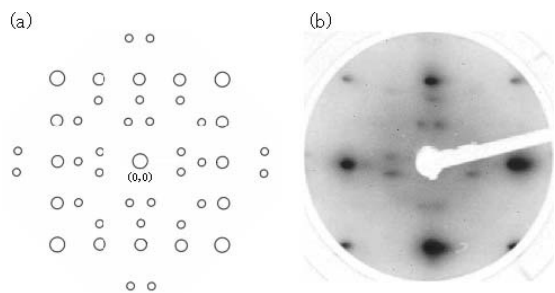


Fig. 1 Schematic view of (a) the LEED pattern of the c(10×2)Ag/Cu(100) surface and (b) the photographic view of the 110 eV electron energy.

(CH₃)₂S/Cu(100) system [11]. In this work, we have studied adsorption behavior of (CH₃)₂S molecule on c(10×2)Ag/Cu(100) surface by means of NEXAFS and XPS measurements at 85 K.

EXPERIMENTAL

A commercially available Cu(100) single crystal (7×7 mm², 2 mm thickness and oriented with a maximum deviation of ±0.5°) was mechanically polished using 0.05 μm Al₂O₃ to a mirror finish and electropolished in methanol solution of 7 vol% nitric acid at about 190 K with an electric current of 0.02 A for 2min. The Cu(100) crystal was cleaned by repeated cycles of Ar⁺ bombardment (2 keV) and heating up to ~923 K in an ultrahigh vacuum chamber (base pressure less than 2×10⁻⁸ Pa). The cleanliness and order of the Cu(100) surface were verified by XPS (S 2p, C 1s and O 1s) with use of MgKα (1253.6 eV) and LEED (Low Energy Electron Diffraction). This procedure resulted in a sharp (1×1) LEED pattern and in contaminant concentration lower than the XPS detection limit. Ag evaporation, equivalent to 0.9 ML coverage, was deposited in situ on the cleaned Cu(100) surface using resistive heating system by use of tungsten heater at room temperature. The c(10×2) LEED pattern was clearly observed, as shown in Fig. 1.

In order to obtain a submonolayer phase, research grade (CH₃)₂S (>99.0%, Katayama Chemical), which was purified by a few freeze-pump-thaw cycles at ambient temperature, was introduced with an exposure of 1.0 L for submonolayer (2×10⁻⁸ Torr ×50 s) to the c(10×2)Ag/Cu(100) substrate and of 30 L for

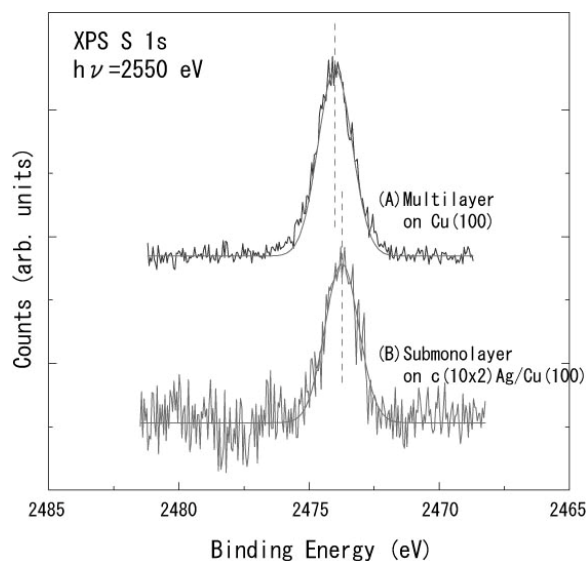


Fig. 2 S 1s XPS core level spectra using synchrotron radiation light of 2550 eV. (A) (CH₃)₂S molecule in the multilayer phase (30 L) at 85 K. (B) (CH₃)₂S molecule on c(10×2)Ag/Cu(100) surface in the submonolayer phase at 85 K.

multilayer (3×10⁻⁷ Torr ×100 s) via a leak valve (isotropic dosing) at a substrate temperature of 85 K.

The NEXAFS and XPS measurements were carried out at the soft X-ray double crystal monochromator beamline BL-3 on Hiroshima Synchrotron Radiation Center (HSRC) [12,13], which is located at Hiroshima University. The absolute photon energy was calibrated on the assumption that the first peak of K₂SO₄ appears at 2481.7 eV. The Sulfur-K fluorescence yield detection (FY) for submonolayer and multilayer phases was employed using an UHV-compatible gas-flow type proportional counter with P-10 gas (10% CH₄ in Ar). Polar angles of θ=90° (normal X-ray incidence, E vector parallel to the surface) and θ=20° (near-grazing incidence) were probed for the polarization dependent S K-edge NEXAFS measurement.

S 1s, S 2p and C 1s XPS spectra were recorded for the submonolayer and multilayer phases with a concentric hemispherical electron energy analyzer (ULVAC-OMNI-V) by using synchrotron radiation (SR) X-rays of 2550 eV and MgKα, respectively. Determination of core-level peak positions in XPS spectra were achieved by means of

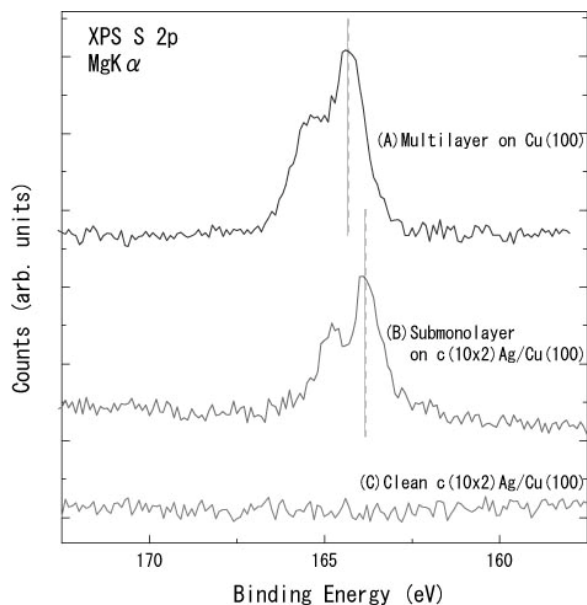


Fig. 3 S 2p XPS core level spectra using MgK α x-ray of 1253.6 eV. (A) (CH₃)₂S molecule in the multilayer phase (30 L) at 85 K. (B) (CH₃)₂S molecule on c(10 \times 2)Ag/Cu(100) surface in the submonolayer phase at 85 K. (C) clean c(10 \times 2)Ag/Cu(100) surface at 300 K.

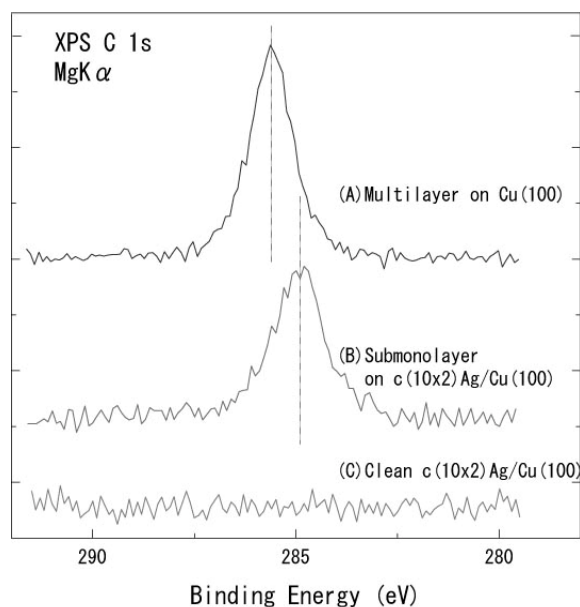


Fig. 4 C 1s XPS core level spectra using MgK α x-ray. (A) (CH₃)₂S molecule in the multilayer phase (30 L) at 85 K. (B) (CH₃)₂S molecule on c(10 \times 2)Ag/Cu(100) surface in the submonolayer phase at 85 K. (C) clean c(10 \times 2)Ag/Cu(100) surface at 300 K.

subtraction Shirley's background and fitting by a combination of Gaussian and Lorentzian curves in order to separate overlapping peaks with use of CASA XPS program.

RESULTS AND DISCUSSIONS

XPS of S 1s, S2p

Figure 2 shows S 1s XPS spectra with use of SR light for multilayer and submonolayer on c(10 \times 2)Ag/Cu(100) at 85 K. Both peak shapes are single peak and there is no peak at around 2470 eV, which means atomic sulfur. These results indicate that (CH₃)₂S molecule for submonolayer phase adsorbs molecularly without dissociation on c(10 \times 2)Ag/Cu(100) surface. The S 1s binding energies for submonolayer and multilayer phases are found to be 2473.7 eV and 2474.0 eV, respectively. The S 1s peak for submonolayer is observed to lower binding energy side in comparison with the multilayer phase. This result suggests that a small amount of charge transfer from the substrate to the adsorbed molecule has occurred. For the adsorption system on Ag(111) and Cu(100) surfaces, the S 1s binding energies for submonolayer are observed at 2473.6 eV and 2473.3 eV, respectively. These results imply that the reactivity for c(10 \times 2)Ag/Cu(100) surface is nearly equal to Ag(111) surface.

Figure 3 shows S 2p XPS spectra with use of MgK α for clean, submonolayer and multilayer phases on c(10 \times 2)Ag/Cu(100) surface at 85 K. For submonolayer phase, the spectrum can deconvolutes with single adsorbate parameter and there is also no peak at around 162 eV. This result indicates that (CH₃)₂S molecule does not dissociate, adsorbs molecularly and there is one adsorbate phase on the surface. This corresponds with the S 1s XPS results.

XPS of C 1s

Figure 4 shows C 1s XPS spectra with use of MgK α for submonolayer and multilayer phases. For submonolayer phase there is no shoulder structure and atomic carbon peak at around 283.5 eV, which is originate with the surface contamination or molecular dissociation. The C 1s peak for submonolayer phase also shifts towarded to the lower binding energy side in comparison with the spectrum for multilayer. It is

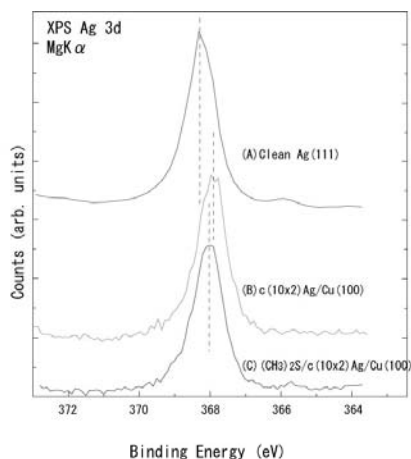


Fig. 5 Ag 3d(5/2) XPS core level spectra using MgK x-ray. (A) clean Ag(111) surface. (B) c(10x2)Ag/Cu(100). (C) (CH₃)₂S/c(10x2)Ag/Cu(100) system in the submonolayer phase at 85 K.

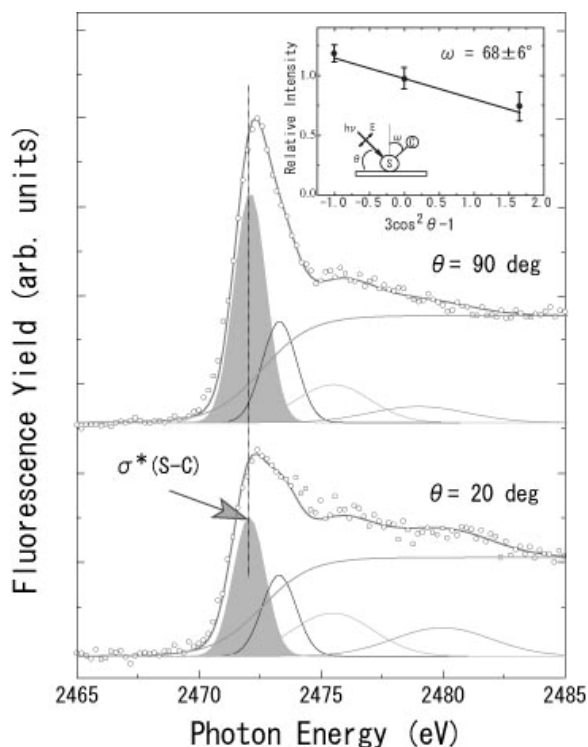


Fig. 7 Curve-fitting results of S K-edge NEXAFS spectra. Inset is a relative intensity of the $\sigma^*(S-C)$ peak as a function of the incident angle of $(3\cos^2\theta - 1)$ together with a least-squares fitted line.

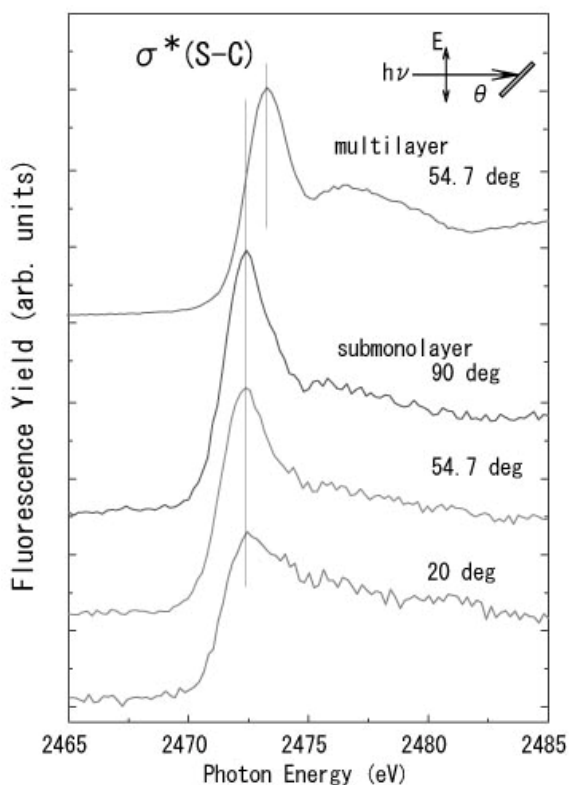


Fig. 6 Polarization dependent S K-edge NEXAFS spectra of (CH₃)₂S submonolayer and multilayer phases.

found that (CH₃)₂S molecule does not dissociate, two methyl groups have an equal chemical condition and interact with the overlayer Ag atoms. The interaction between the methyl group and the overlayer Ag atoms is caused by the charge transfer from the Ag atom to the methyl group. Therefore (CH₃)₂S molecule adsorbs through both the sulfur and the methyl groups on c(10x2)Ag/Cu(100) surface. This result is same as (CH₃)₂S/Ag(111) system [10].

XPS of Ag 3d(5/2)

Figure 5 shows Ag 3d(5/2) XPS spectra with use of MgK α for clean Ag(111), c(10x2)Ag/Cu(100) and (CH₃)₂S/c(10x2)Ag/Cu(100) of submonolayer phase. There Ag 3d(5/2) peaks appear at 368.5 eV, 367.8 eV and 368.0 eV, respectively. The Ag 3d(5/2) peak for the c(10x2)Ag/Cu(100) system shifts to the lower binding energy side in comparison with clean Ag(111) surface. This indicates that the charge transfer from the Cu(100) surface to the overlayer Ag atoms has been occurred. For submonolayer (CH₃)₂S molecule adsorbed system on c(10x2)Ag/Cu(100),

the Ag 3d(5/2) peak slightly moves to the higher binding energy side comparing with the c(10×2)Ag/Cu(100) system. This implies that the charge transfer from the overlayer Ag atoms to the adsorbed (CH₃)₂S molecule has been occurred. It seems that these charges work on the interaction between the sulfur and the methyl group of (CH₃)₂S molecule and the overlayer Ag atoms.

Polarization dependence of S K-edge NEXAFS

Figure 6 shows the submonolayer sulfur K-edge NEXAFS spectra of (CH₃)₂S for different X-ray incidence angles together with that of multilayer phase. The multilayer spectrum, as a standard spectrum, of solid (CH₃)₂S prepared by depositing 30 L on c(10×2)Ag/Cu(100) surface at 85 K is taken at =54.7° by means of the fluorescence yield detection. The submonolayer spectra are taken at normal(=90°), 54.7°(magic angle), and grazing(=20°). By comparing the edge-jump between the submonolayer and atomic sulfur adsorption system (c(2×2)S/Ni(100), the sulfur coverage is 0.5 ML), the sulfur amount of the submonolayer phase is determined to be ~0.2 ML.

A small polarization dependence can be seen in figure 6; for normal X-ray incidence (= 90°) the first feature at around 2472.5 eV is enhanced. On the other hand, the intensity of the first feature is slightly smaller for grazing X-ray incidence (=20°) than for normal incidence. Comparing the gas phase [14] with multilayer spectra, the first feature can be ascribed to the $\sigma^*(\text{S-C})$ resonance. This result indicates that the orientation angle of the (CH₃)₂S plane is qualitatively slant to the surface. In order to estimate the molecular tilt angle quantitatively, the angular dependence of the $\sigma^*(\text{S-C})$ resonance intensity was examined by a curve-fitting analysis of the NEXAFS spectra [15, 16]. Figure 7 shows the curve-fitting results of both the normal and grazing incident NEXAFS spectra. In the curve-fitting result the observed peak at around 2472.5 eV is assigned to the $\sigma^*(\text{S-C})$ resonance. Inset is a relative intensity of the $\sigma^*(\text{S-C})$ peak as a function of the incident angle of $(3\cos^2\theta-1)$, together with a least-squares fitted line, whose gradient gives the orientation angle of the S-C bond. The threshold energy of S 1s (2473.7 eV) is determined from the S

1s XPS measurement. The orientation angle of the S-C bonding axis with respect to the surface is estimated to be $22\pm 6^\circ$. The estimated tilt angle of the S-C axis for submonolayer is similar to that for submonolayer coverage of (CH₃)₂S molecule on Ag(111) surface [10].

CONCLUSION

We have investigated the adsorption behavior of (CH₃)₂S molecule on c(10×2)Ag/Cu(100) surface at 85 K by sulfur K-edge NEXAFS and XPS. (CH₃)₂S molecule adsorbs molecularly on c(10×2)Ag/Cu(100) surface with the molecular orientation angle of ~22° from the surface. The (CH₃)₂S molecule has an interaction with the overlayer Ag atoms through both sulfur and methyl groups. This adsorption behavior is nearly same as (CH₃)₂S/Ag(111) system.

ACKNOWLEDGEMENTS

The authors are grateful for the financial supported of a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 15360358) and a Grant-in-Aid on Research for the Future "Photoscience" (JSPS-RFTF-98P-01202) from Japan Society for the promotion of science (JSPS). This work was performed under the approval of HSRC Program Advisory Committee (No. 02-A-5 and 03-A-3).

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