SOLID STATE PHYSICAL CHEMISTRY

Annual Research Review

(1) "Structure of methylthiolate adsorbed on Au(111) studied by photoelectron diffraction"

The structure of the alkanethiolate SAMs has been an issue of controversy for long years, although the understanding of the structure is quite an important basis for the atomistic-level applications of SAMs.

We measured and analyzed scanned-energy and scanned-angle S2p photoelectron diffraction (PD) for CH_3S/Au(111), which is the simplest but one of the most thoroughly studied SAM systems both from experimental and theoretical points of view.

The PD experiments were performed at BL-7A of the Photon Factory with an ultrahigh vacuum end-station equipped with a high-resolution electron energy analyzer. Saturated methylthiolate monolayers on a single-crystal Au(111) surface with a commensurate ($\sqrt{3}$x$\sqrt{3}$)R30º super structure were used. PD spectra were simulated by using the multiple scattering calculation of diffraction package developed by Chen and van Hove.

We proposed from the PD analyses an unambiguous structure model as shown in Fig. 1, in which S atom is adsorbed on the atop site with the S-Au distance of 2.42 Å, and S-methyl bond is tilted by 50° preferentially along <211> and <121> directions. The present results will contribute to the fundamental understanding of the promising nano-material.

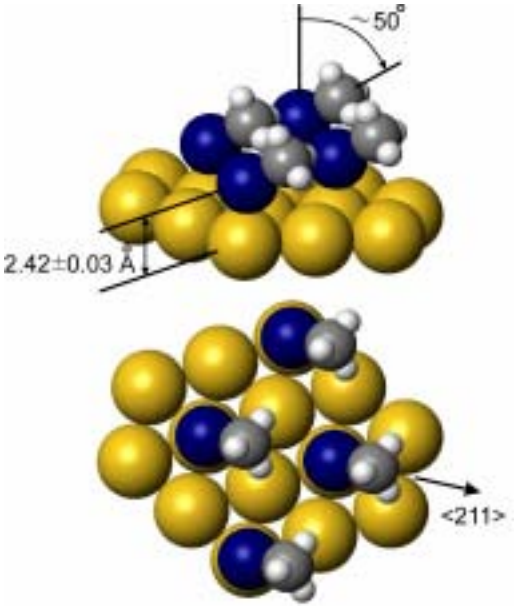

Fig. 1 Schematic side and top view of the best-fit adsorption geometry of methylthiolate adsorbed on Au(111). The hydrogen atoms are indicated at tentatively assumed positions.

A-4) *Phys. Rev. Lett.* ***90****, 066102 (2003)*

(2) "Water formation reaction on Pt(111): NEXAFS experiments and Monte Carlo simulations"

The catalytic water formation reaction was studied by a newly developed energy dispersive NEXAFS spectroscopy. Oxygen covered Pt(111) surfaces with a (2x2) structure were exposed to gaseous hydrogen (5.0×10^{-9} Torr) at constant surface temperatures (120 ~140 K). O K-edge NEXAFS spectra were measured during the reaction with a time interval of 35 s. From quantitative analyses for the spectra, the coverage changes of the adsorbed species (O, OH, and H_2O) were obtained. The reaction is composed of three steps, which are characterized by the induction period (I), fast increase in coverage of OH and H_2O with consuming oxygen (II), and slow conversion of OH to H_2O after the complete consumption of oxygen (III). It was also found that the maximum OH coverage becomes smaller at a higher temperature. The kinetic Monte Carlo simulation has reproduced the three characteristic reaction steps, from which the steps are explained as follows; in the first step OH domains are created through two-dimensional aggregation of H_2O (I), after the nucleation process the second step sets in where the OH domains propagate by the auto-catalytic cycle until they contact with each other (II), and finally the merged OH domains convert to H_2O (III). The Reaction Diffusion simulation has revealed that the density of H_2O nuclei decreases due to its high diffusion rate at a high temperature, which results in reduction of the OH coverage.

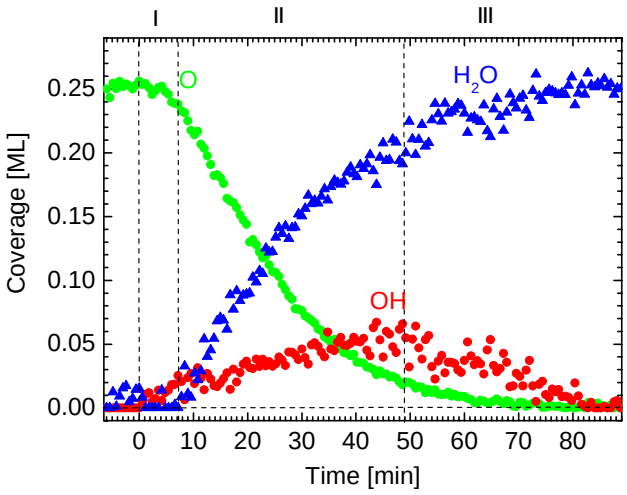

Fig. 2 Coverages of the adsorbed species (O, OH, and H_2O) as a function of time during dosing with gaseous H_2 (5.0×10^{-9} Torr) at 130 K. The O-covered Pt(111) surface started exposing to gaseous H_2 at 0 min. The reaction can be divided to three characteristic steps (I, II, and III).

A-9) *Chem. Phys. Lett.* **375**, 419-424 (2003).
A-11) *J. Chem. Phys.* **119**, 9233-9241 (2003).

物性化学研究室

研究レビュー

(1) Au(111)面上に吸着したメチルチオレイト吸着構造の光電子回折による解析

貴金属基板上のアルカンチオレイト自己組織化膜(SAM)の構造は, SAM の原子レベルでの応用の基礎として重要であることから，理論，実験の両面から様々な手法で研究されており，いろいろな構造モデルが提案されているが，まだ確定しているとはいえなかった。我々は最も基本的な SAM である CH_3S/Au(111)について，放射光を用いた光電子回折法を用いて構造解析を行った。実験は PF-BL7A ビームライン（東大スペクトル化学研究センター所属）で，高分解能光電子分光装置を用い，S2p スペクトルの方位角，極角依存性，光エネルギー依存性を調べることによって行った。解析は多重散乱電子回折プログラムを用いて行いった。そして，これまで提案されていた構造モデルがいずれも間違っていることを明らかにした。最終的に得られた構造モデルは図１に示すように，S が atop サイトで R(S-Au)=2.42 Å の位置にあり，S-CH_3 結合が 50º の傾きで，<211>, <121>方向に選択的に傾いた構造となっている。

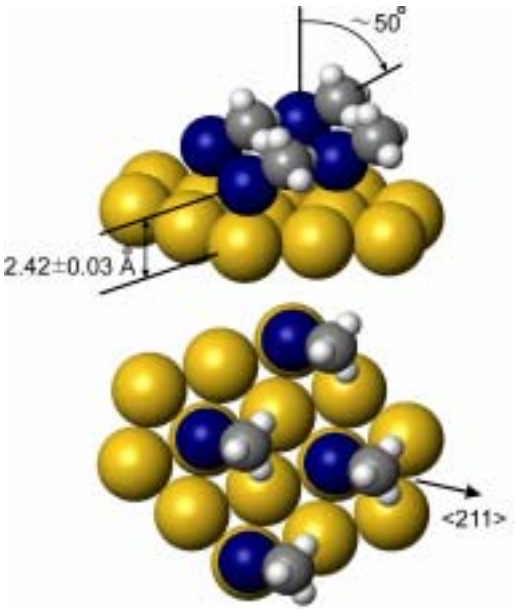

図１　Au(111)面に吸着したメチルチオレイトの構造モデル。上図：俯瞰図, 下図：平面図。メチル基は<211>, <121>方向に選択的に傾いている。

A-4) *Phys. Rev. Lett.* ***90****, 066102 (2003)*

(2)Pt(111)面上低温水生成反応：NEXAFS 実験とモンテカルロシミュレーション

水生成反応における白金の触媒作用は古くから知られており，燃料電池の機構としても重要であるが，最近，低温（<170 K）において，酸素を前吸着した Pt(111)表面上に水素ガスを流すと，自己触媒反応によって水が生成されることが STM の研究により報告されている。そこで，我々は最近開発したエネルギー分散型 NEXAFS 法を用い，O K-NEXAFS スペクトルの時間変化から Pt(111)表面上での吸着種（O, OH, H_2O）の被覆率の変化を追跡した。OH 種の同定は今回 NEXAFS を用いることによって初めて可能となった。その結果は図２に示すように，３段階で反応が進行することが分った。(I)誘導期，(II) O が減少し，OH, H_2O が増加する期間，(III) OH が H_2O に転換する期間。NEXAFS, STM, DFT 計算などから得られた素反応の速度定数，活性化エネルギーを用いてキネティックモンテカルロシミュレーションを行い，図２の被覆率の変化，STM の空間分布の変化を満足に再現することができた。

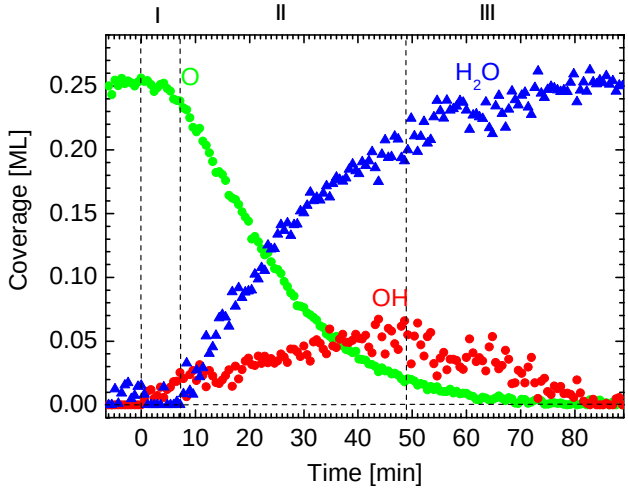

図２　酸素前吸着した Pt(111)表面を 130 K で H_2 (5.0×10^{-9} Torr)**にさらしたときの**表面吸着種(O, OH, H_2O)の被覆率時間変化。反応は３つのステップ(I, II, III)に分けられる。

A-9) *Chem. Phys. Lett.* **375**, 419-424 (2003).

A-11) *J. Chem. Phys.* **119**, 9233-9241 (2003).

1. Original Papers

(A) Refereed Jounals

(1) Y. Ogi, T. Endo and K. Tsukiyama, H. Kondoh, K. Tono, Y. Ogawa, Y. Hamada, T. Ohta and H. Kuroda, "Vibrational excitation of CO molecules by infrared free electron laser" *J.Electron Spectrosc*.**128,** 167-173 (2003)

(2) T.Yokoyama, D.Matsumura, K.Amemiya, S.Kitagwa, N.Suzuki and T.Ohta, "Spin reorientation transitions of ultrathin Co/Pd(111) films induced by chemisorption: x-ray magnetic circular dichroism study" *J.Phys. Condensed matter*, **15,** S537-S546 (2003)

(3) K.Amemiya, S. Kitagawa, D. Matsumura, T.Yokoyama and T.Ohta, "Development of a depth-resolved x-ray magnetic circular dichroism: Application to Fe/Cu(100) ultrathin films" *J.Physics:Condensed Matter*, **15,** S561-S571 (2003)

(4) H.Kondoh, M.Iwasaki, T.Shimada, K.Amemiya, T.Yokoyama, T.Ohta,, M.Shimomura, and S.Kono, "Adsorption of thiolate to singly coordinated sites on Au(111) evidenced by photoelectron diffraction" *Phys. Rev. Lett*. **90,** 66102 (2003).

(5) A.Nambu, H.Kondoh, I.Nakai, K.Amemiya and T.Ohta, " Film growth and X-ray induced chemical reactions of thiophene adsorbed on Au(111) " *Surf. Sci*. **530** 101-110 (2003)

(6) K.Tono, A.Terasaki, T.Ohta and T.Kondow, "Chemical control of magnetism: Oxidation induced ferromagnetism in the chromium dimer evidenced by photoelectron spectroscopy" *Phys. Rev. Lett*. **90**,133402 (2003).

(7) H.W.Yeom, J.W.Kim, K.Tono, I.Matsuda and T.Ohta, "Electronic structure of monolayer and double-layer Ge on Si(001)" *Phys. Rev*. **B67**, 85310(6pages) (2003)

(8) K.Okamoto, K.Kohdate, K.Nagai, J.Miyawaki, H.Kondoh, T.Yokoyama, A.Nojima and T.Ohta, "Development of light-modulated XAFS spectroscopy" *J. Synchrotron Radiation*, **10**, 242-247 (2003).

(9) K. Okamoto, K. Nagai, J. Miyawaki, H. Kondoh, and T. Ohta, "XAFS study on the photoinduced spin transition of $[Fe(2\text{-pic})_3]Cl_2 \cdot C_2H_5OH$" *Chem.Phys. Lett*., 371, 707-712 ,(2003)

(10) M. Nagasaka, I. Nakai, H. Kondoh, T. Ohta, and V. Carravetta, " Oxygen K-Shell Near Edge X-ray Absorption Fine Structure Study of O and OH Overlayers on Pt(111)" *Chem. Phys. Lett*. **375**, 419-424 (2003).

(11) K. Okamoto, J. Miyawaki, K.Nagai, D. Matsumura, A. Nojima, T. Yokoyama, H. Kondoh, and T. Ohta, "Structural Study on Highly Oxidized States of a Water Oxidation Complex $[Ru^{III}(bpy)_2(H_2O)]_2(\mu\text{-}O)^{4+}$ by Ruthenium K-edge X-ray Absorption Fine Structure Spectroscopy" *Inorganic Chemistry*, 42, 8682-8689 (2003)

(12) M.Nagasaka, H.Kondoh, K.Amemiya, A.Nambu, I.Nakai, T.Shimada, and T.Ohta, " Water formation reaction on Pt(111): Near Edge X-ray Absorption fine structure experiments and kinetic Monte Carlo simulations" *J. Chem. Phys*. **119**, 9233-9241 (2003).

(13) Y. Ichiyanagi, H. Kondoh , T. Yokoyama, K. Okamoto, K. Nagai and T, Ohta, "X-ray Absorption

Fine-Structure Study on the $Ni(OH)_2$ monolayer nanoclusters" *Chem.Phys. Lett*. **379**, 345-350 (2003).

(14) K.Tono, A.Terasaki, T.Ohta and T.Kondow, "Chemically induced ferromagnetic spin coupling: Electronic and geometric structures of chromium-oxide cluster anions, Cr_2O_n-(n=1-3), studied by photoelectron spectroscopy" *J. Chem. Phys*. **119**, 11221-11227 (2003)

(B) その他（Proceedings）

(1) H. Kondoh, M.Iwasaki, T.Shimada, K.Amemiya, T.Yokoyama, T.Ohta, M.Shimomura, and S. Kono, "Structure of Methylthiolate adsorbed on Au(111) studied by Photoelectron Diffraction" Photon Factory Activity Report Vol.20, (2003) Part A 14.

(2) A. Nojima, K. Nagai, K. Okamoto, J. Miyawaki, H. Kondoh, and T. Ohta, "Local structure of anisotropic copper hydroxide nanoparticles" Photon Factory Activity Report Vol.20, (2003) Part B 44.

(3) I. Nakai, H. Kondoh, T. Shimada, M. Nagasaka, and T. Ohta, "Effect of H atoms on sthylene adsorption on Pt(110) studied by NEXAFS spectroscopy" Photon Factory Activity Report Vol.20, (2003) Part B 55.

(4) M. Nagasaka, H. Kondoh, K. Amemiya, A. Nambu, I. Nakai, T. Shimada, and T. Ohta, "Kinetics of water formation reaction on Pt(111) studied by dispersive NEXAFS" Photon Factory Activity Report Vol.20, (2003) Part B 56.

(5) T. Shimada, H. Kondoh, K. Amemiya, I. Nakai, M. Nagasaka, and T. Ohta, "Adsorption of NO Pt (110): X-ray photoelectron diffraction study" Photon Factory Activity Report Vol.20, (2003) Part B 57.

(6) D. Matsumura, T. Yokoyama, K. Amemiya, S. Kitagawa, and T. Ohta, "XPS and XMCD studies on spin reorientation transition of Co/Pd(111) induced by surface CO chemisorption" Photon Factory Activity Report Vol.20, (2003) Part B 58.

(7) K. Nakatsuji, S. Ohno, T. Iimori, H. Miyaoka, M.Yamada, Y. Takagi, K. Yagyuu, K. Amemiya, D. Matsumura, S.Kitagawa, T. Yokoyama, and T.Ohta, "X-ray magnetic circular dichroism on Co/N/Cu(001) surfaces" Photon Factory Activity Report Vol.20, (2003) Part B 59.

(8) H. Abe, K. Amemiya, D. Matsumura, S. Kitagawa, H. Watanabe, T. Yokoyama, and T. Ohta, "X-ray magnetic circular dichroism study on spin reorientation transition of Ni/Cu(001) induced by Fe deposition" Photon Factory Activity Report Vol.20, (2003) Part B 60.

(9) H. Watanabe, K. Amemiya, D. Matsumura, S. Kitagawa, H. Abe, T. Yokoyama, and T. Ohta, "XMCD study of spin reorientation transitions of Co/Pt(111) induced by CO adsorption" Photon Factory Activity Report Vol.20, (2003) Part B 61.

(10) A. Imanishi, T. Hayashi, H. Suzuki, K. Amemiya, T. Ohta, and Y. Nakato, "H-terminated Si(111) surfaces immersed in HI solutions studied by Si 2p core-level photoelectron spectroscopy" Photon Factory Activity Report Vol.20, (2003) Part B 92.

(11) J. Miyawaki, D. Matsumura, A. Nojima, T. Yokoyama, and T. Ohta, ”Structural study of Co ultrathin films on Pd(111) by Surface EXAFS” Photon Factory Activity Report Vol.20, (2003) Part B 95.

(12) K. Amemiya, S. Kitagawa, D. Matsumura, H. Abe, H. Watanabe, T. Yokoyama, and T. Ohta, “Layer-resolved magnetic structure of Fe/Cu(100) ultrathin films observed by the depth-resolved x-ray magnetic circular dichroism” Photon Factory Activity Report Vol.20, (2003) Part B 270.

２．**Reviews**

(1) 太田俊明, 雨宮健太, 近藤　寛「エネルギー分散型表面ＸＡＦＳ法」, 放射光　16, 34-40 (2003)
T.Ohta, K. Amemiya, and H.Kondoh, “Energy dispersive surface XAFS method” Houshako **23**, 345-350 (2002)

(2) 登野健介,　寺崎　亨, 太田　俊明,　近藤　保,「バナジウム炭化物クラスター負イオンの構造」　豊田研究報告　56, 55-65 (2003)
K. Tono, T. Terasaki, T. Ohta, and T. Kondow, “Negative ion structures of vanadium carbide clusters” Toyota Research Report 56, 55-65 (2003)

(3) 近藤　寛、岩崎正興、島田透、雨宮健太、横山利彦、太田俊明、下村勝、河野省三,「光電子回折による Au(111)上メチルチオレートの吸着構造解析」表面科学　24 巻 8 号 448-454 (2003).
H. Kondoh, M. Iwasaki, T. Shimada, K. Amemiya, T. Yokoyama, T. Ohta, M. Shimomura, and S. Kono, “Structure analysis of methyl thiolate adsorbate on Au(111) by photoelectron diffraction” Surface Science 24, 448 - 454 (2003)