SOLID STATE PHYSICAL CHEMISTRY

Annual Research Review

(1) "Structure and growth process of alkanethiolol self-assembled monolayer films on noble metals"

The structure and growth process of hexanethiolate SAMs on Cu(100) have been studied by STM and XAFS. Surface XAFS revealed that the thiolates gradually stand as the coverage increases, and finally they form a standing-up monolayer (ML) with the molecular axis tilted by 27±5º from the surface normal at saturated coverage. No 2D-ordered structure appears in the saturated ML just after adsorption. The saturated ML exhibits a slow evolution to a 2D-ordered phase with a c(2x6) periodicity, in which the S atoms form 1D zigzag rows along the close-packed Cu rows (Fig.1(a)). On the other hand, STM shows that spots are on a line.(Fig.1(b)). This discrepancy is reconciled by the structure, in which half of the S-C bonds stand normal, while another half tilt by 30º. (Fig.1(c)). This demonstrates that the combined use of XAFS and STM is very effective to the structure analysis of such a complicated system as a SAM film on Cu(100).

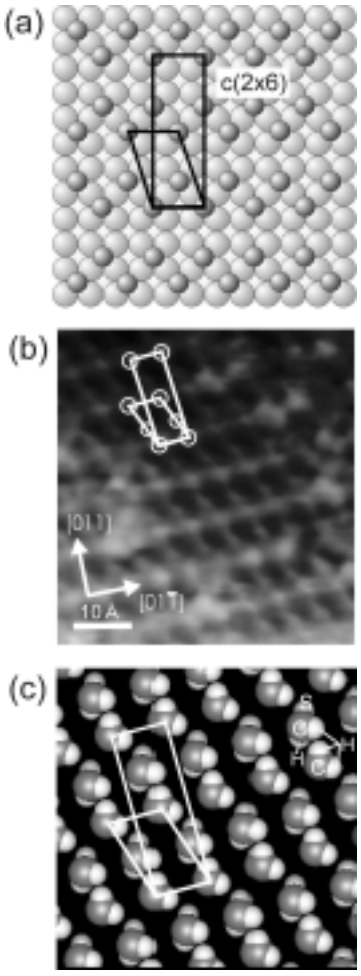

Fig. 1 (a) Structural model for arrangement of the S atoms of the thiolates on Cu(100) with saturated coverage. (b) Molecular image of a saturated ML on Cu(100). There exist two inequivalent molecular features; brighter protrusions (larger circle) and darker protrusions (smaller circle). The c(2x6) unit cell is also indicated. (c) 2D arrangement of the bottom part of the alkyl chains whose structure is optimized by force field calculations. The 2D arrangement of the S atoms and the methylene moieties that are directly bonded to the S atoms is shown in the form of the projected view along the surface normal.

A-12) *J.Phys. Chem.* **B195**, 12870-12878 (2001)
A-19) *Surf. Sci.* **489**, 20-28 (2001)

(2) "Development of a fast NEXAFS spectroscopy"

We have succeeded in measuring energy dispersive NEXAFS spectra in the soft x-ray region by combining a position sensitive electron analyzer with energy dispersed x rays obtained by a newly constructed beamline at the Photon Factory. By comparing the spectrum with the conventional NEXAFS one, the measuring time is shortened to 1/50 at C K-edge. The adsorption process of thiophene on Au(111) was traced *in situ* by continuously recording the C K-edge dispersive NEXAFS spectra with accumulation period of 30 s for each spectrum. It was revealed that thiophene adsorbs with its molecular plane parallel to the surface below ~7 L, and that it gradually stands up as exposure increases. No sudden change in the molecular orientation was observed during the adsorption process. We have demonstrated the availability of the energy dispersive NEXAFS technique for investigating surface chemical reactions.

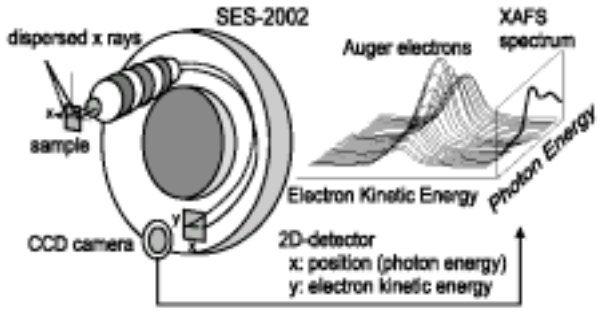

Fig.2 Schematic diagram of the energy dispersive NEXAFS method.

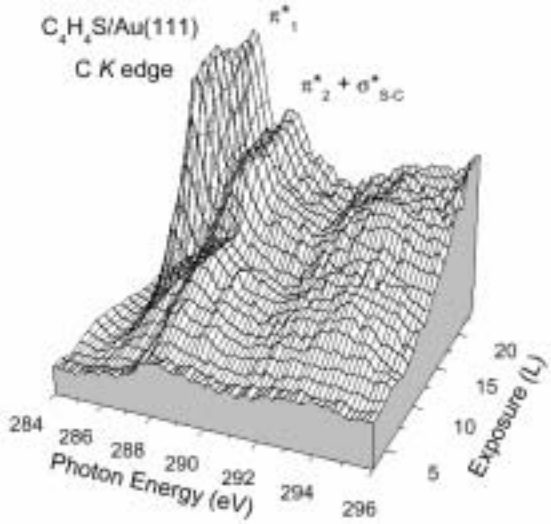

Fig.3 Coverage dependence of C-K NEXAFS from thiophene on Au(111).

A-11) *Jpn.J.Appl. Phys*. **40**, L718-L720(2001)

物性化学研究室

研究レビュー

(1)　貴金属基板上アルカンチオール自己組織化膜の成長過程と構造解析

Cu(100)面上に蒸着したヘキサンチオレイトの構造とＳＡM膜形成過程を表面 XAFS と超高真空 STM によって詳細に調べた．表面 XAFS の結果から，被覆率を増やしていくと，分子は寝た状態から次第に立ち始め，飽和時，分子軸を表面垂直から 27º傾いた構造をとる．飽和直後，二次元構造はランダムであるが，次第に規則性が増し，c(2x6)の周期構造をとる．このとき，S は 4-fold hollow site に吸着し，Cu 基板の最密充填列に沿って１次元ジグザグ構造をとることが分かった（図１(a)参照）．一方，観測される STM では，スポットは直線上にある．（図１(b)参照）．この食い違いは，S-C 結合の半分が立って，半分が大きく傾いた構造をとることによって説明される（図１(c)参照）．すなわち，ＳＴＭで観測されるスポットは S の位置ではなく，S-C 結合の位置を示すと考えられる．これらの結果は，ＳＴＭと XAFS を組み合わせることが複雑な構造解析に有効であることを示している．

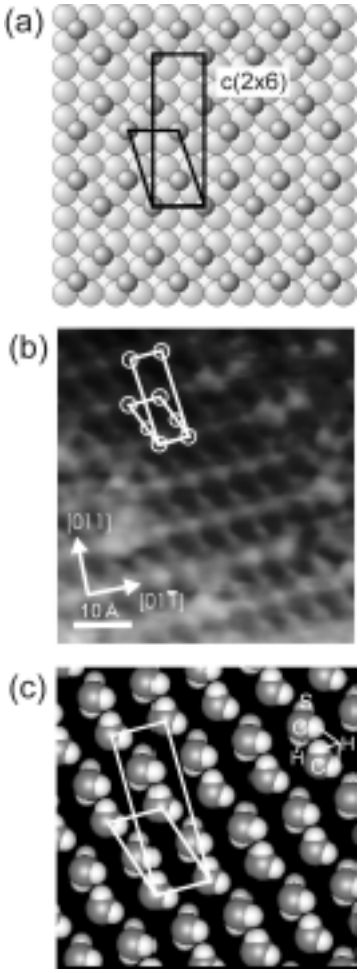

図 1(a) 飽和吸着時の S 原子配列の構造モデル
(b) STM 像．明スポットと暗スポットの２種類が観測される．(c)アルキル鎖の底部の二次元配列．半分は垂直に，半分は傾いた構造をとっている．

A-12) *J.Phys. Chem.* **B195**, 12870-12878 (2001)
A-19) *Surf. Sci.* **489**, 20-28 (2001)

⑵　高速 NEXAFS 分光法の開発

フォトンファクトリーに新しく建設したビームラインにおいて，エネルギー分散したＸ線と位置敏感検出器を備えた電子分光器を組み合わせることによってエネルギー分散型 NEXAFS 法を初めて成功させた．方法の原理図を図２に示す．この方法は，単分子層薄膜に適用するとき，従来の方法で５分要していた測定を数十秒に短縮した．応用例として Au(111)基板上にチオフェンをドースしたときの C-K NEXAFS スペクトル（直入射）の変化を図３に示した．最初基板に寝ていた分子が吸着量の増加と共に立ち上がっていく様子を実時間で観測したものである. このような高速 NEXAFS 法は表面での化学反応の追跡などに有効に利用することができ，将来の発展が期待される．

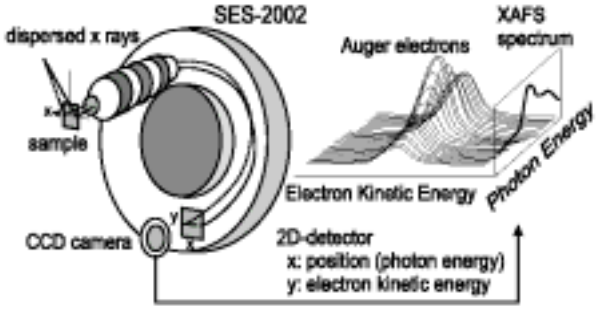

図２　エネルギー分散型 NEXAFS 法の原理図

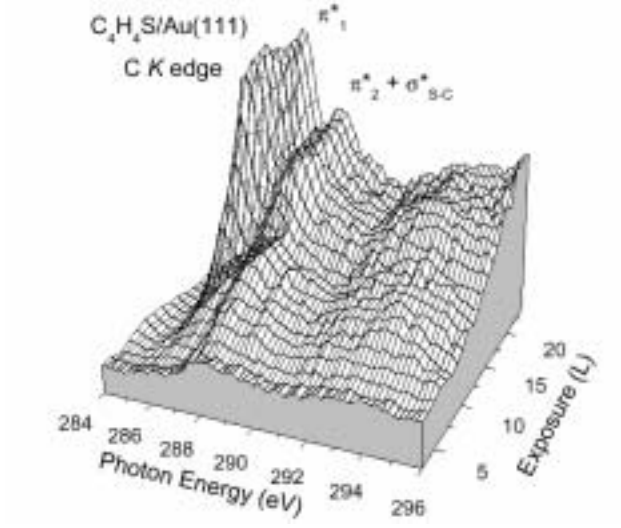

図３　Au(111)表面チオフェン吸着 C-K NEXAFS の吸着量依存性

A-11) *Jpn. J.Appl. Phys.* **40**, L718-L720 (2001

A. Original Papers

(1) (L. E.Griffiths), (M.Lee), (A. R. Mount), H.Kondoh, T.Ohta and (C. R. Pulham), "Low temperature electrochemical synthesis of titanium nitride" Chem. Comm. **2001**, 579-580.

(2) T.Yokoyama, K.Okamoto, K.Nagai, T.Ohta, (S. Hayami), (Z. Gu), (R.Nakajima) and (O.Sato), "Photo-induced magnetized state of Co(DTBSQ)(DTBCat)(phen)$C_6H_5CH_3$ studied by X-ray absorption spectroscopy" Chem.Phys. Lett. **345,** 272-276 (2001).

(3) H. Kondoh, I. Nakai, A. Nambu, and T. Ohta, (T. Nakamura), (R. Kimura), and (M. Matsumoto), "Dissociative and non-dissociative adsorption of selenophene on Au(111) depending on the preparation method" Chem.Phys.Lett**. 350,** 466-472 (2001).

(4) (H. Orita), H. Kondoh, and (H. Nozoye), "Decomposition of PF_3 on Ni(755) and Coadsorption with Ethylcyclohexane: Comparing Results of PF_3 with CO", J. Catal. **197**, 244-250 (2001).

(5) (K. Sakamoto), (M. Hirano), (H. Takeda), (S. T. Jemander), I. Matsuda, K. Amemiya, T. Ohta, (W.Uchida), (G. V. Hansson), (R. I.G. Uhrberg), "Interaction of metastable molecular oxygen with the dangling bonds of a Si(111)-(7x7) surface" J. Electron Spectrosc. , **114-116,** 489-494 (2001).

(6) T.Yokoyama, K. Amemiya, Y. Yonamoto, D. Matsumura and T.Ohta, "Anisotropic magnetization of CO adsorbed on ferromagnetic metal thin films studied by x-ray magnetic circular dichroism" J.Electron Spectrosc.**119,** 207-214 (2001).

(7) (D.Kondo), (K.Sakamoto), (H.Takeda), F.Matsui, T.Ohta, K.Amemiya, (W.Uchida), and (A.Kasuya), "Thermal effect in unoccupied molecular orbitals of C60 molecules adsorbed on a Si(001)-(2x1) surface studied by NEXAFS" J. Synchrotron Rad**. 8,** 505-507 (2001).

(8) K.Okamoto, (T.Takahashi), K.Kohdate, H.Kondoh, T.Yokoyama, and T.Ohta, "Characterization of ruthenium-dinitrogen tetramine complexes by XAFS spectroscopy" J. Synchrotron Rad. **8,** 689-691 (2001).

(9) H.Katsumata, (T.Miyanaga), T.Yokoyama, (T.Fujikawa), and T.Ohta "Quantum statistical approach to Debye-Waller factor in EXAFS: application to monatomic fcc systems" J. Synchrotron Rad**. 8**, 226-228 (2001).

(10) T.Yokoyama, K.Okamoto, D.Matsumura, T.Ohta, (S.Ohkoshi), and (K.Hashimoto), "Characterization of relaxed photo-excited magnetized states in Prussian-blue analogous magnets" J. Synchrotron Rad. **8,** 913-915 (2001).

(11) K.Amemiya, H.Kondoh, A.Nambu, M.Iwasaki, I.Nakai, T.Yokoyama and T.Ohta, "Energy dispersive NEXAFS in the soft x-ray region: a new technique to investigate surface reactions" Jpn.J.Appl. Phys. **40,** L718 - L720 (2001).

(12) H.Kondoh, N.Saito, F.Matsui, T.Yokoyama, H.Kuroda and T.Ohta, "Structure and growth process of alkanethiol monolayers on Cu(100) studied by STM and XAFS" J. Phys. Chem. B **105,** 12870-12878 (2001).

(13) H.Kondoh, F.Matsui, Y.Ehara, T.Yokoyama and T.Ohta, "Surface-Monolayer-Controlled Molecular Alignment in short *n*-alkane multilayers" Langmuir, **17 ,** 8178-8183 (2001).

(14) (K.Seki), (R.Mitsumoto), (E.Ito), (T.Araki), (Y.Sakurai), (D.Yoshimura), (H.Ishii), (Y.Ouchi),

(T.Miyamae), (T.Narita), (S.Nishimura), (Y.Takata), T.Yokoyama, T.Ohta, (S.Suganuma), (F.Okino), and (H.Touhara), "High-energy spectroscopic studies of the electronic structures of organic systems formed from carbon and fluorine by UPS, vacuum-UV optical spectroscopy, and NEXAFS: Poly(hexafluoro-1,3-butadiene)[$C(CF_3)=C(CF_3)]_n$, fluorinated graphites(CF,C_2F, and C_6F), perfluoroalkanes n-C_nF_{2n+2}, poly(tetrafluoroethylene)$(CF_2)_n$, and fluorinated fullerenes($C_{60}F_x$ and $C_{70}F_x$)", Mol.Cryst. Liq. Cryst. **355,** 247-274 (2001).

(15) I.Matsuda, (H.W.Yeom), (T.Tanikawa), K.Tono, (T.Nagao), (S.Hasegawa) and T.Ohta, "Growth and electron quantization of metastable silver films on Si(001)" Phys.Rev. **B63**, 125325-125333 (2001).

(16) Y.Yonamoto, T.Yokoyama, K.Amemiya, D.Matsumura, and T.Ohta, "Magnetism of an ultrathin Mn film on Co(100) and the effect of oxidation studied by x-ray magnetic circular dichroism", Phys. Rev. **B63,** 214406-1-7 (2001).

(17) K.Amemiya, T.Yokoyama, Y.Yonamoto, D.Matsumura and T.Ohta, "O K-edge x-ray magnetic dichroism of atomic O adsorbed on an ultrathin Co/Cu(100) film: Comparison with molecular CO on Co/Cu(100)" Phys.Rev. **B64,** 132405-1-4 (2001).

(18) (T.Koide), (H.Miyauchi), (J.Okamoto), (T.Shidara), (A.Fujimori), (H.Fukutani), K.Amemiya, (H.Takeshita), (S.Yuasa), (T.Katayama) and (Y.Suzuki), "Direct determination of interfacial magnetic moments with a magnetic phase transition in Co nanoclusters" Phys. Rev.Lett. **87,** 25701 (2001).

(19) H.Kondoh, H.Tsukabayashi, T.Yokoyama and T.Ohta, " S K-edge X-ray absorption fine structure study of vacuum-deposited dihexyldisulfide on Ag(100) " Surf.Sci.**489**, 20-28 (2001).

(20) (K.Sakamoto), (D.Kondo), (H.Takeda), (T.Sato), (S.Suga), F.Matsui, K.Amemiya, T.Ohta, (W.Uchida), and (A.Kasuya), "Thermal-dependent unoccupied electronic structure of a C_{60} monolyaer film adsorbed on a Si(111)-(7x7) surface" Surf. Sci. **493,** 604-609 (2001).

B. Reviews

(1) 近藤、太田,「アルカンチオール自己組織化への基板効果」豊田中研報告 No.**54** ,51-59 (2001).

H.Kondoh and T.Ohta, " The effect of substrates on the formation mechanism of alkanethiol self-assembly monolayer films" Report of Toyota Central Research Laboratory **54** , 51-59 (2001).

(2) 近藤 寛「XAFS で観る分子の自己組織化」, PHOTON FACTORY NEWS 19 巻 3 号, 29-35 (2001).

H.Kondoh, "Molecular self-assembled monolayer films observed by XAFS", PHOTON FACTROY NEWS 19-3, 29-35 (2001).

(3) 松田 巌, (Hang Woog Yeom), (谷川 雄洋), 登野健介, (長谷川修司), 太田俊明, 「半導体表面上金属超薄膜の量子井戸状態の研究」PHOTON FACTORY NEWS 19 巻 2 号, (2001) 26-31.

I.Matsuda, (H. W. Yeom), (T.Tanigawa), K.Tono, (S.Hasegawa), T.Ohta, "Study of quantum well states of ultra-thin metal films on a semiconductor" PHOTON FACTORY NEWS 19-2, 26-31 (2001).

C. Proceedings

(1) F.Matsui, (H.W.Yoem), T.Ohta, "Initial oxidation of a Si(111) 7x7 surfaces studied by O K-edge NEXAFS" KEK Progress Report 2001-1 p.17-18.

(2) T.Yokoyama, K.Okamoto, T.Ohta, (S.Ohkoshi), (K.Hashimoto), "Local structure of a photo-induced magnet of CoW cyanide studied by EXAFS" KEK Progress Report 2001-2 p.24 (2001).

(3) T.Yokoyama, K.Okamoto, T.Ohta,(S.Ohtoshi), and (K.Hashimoto), "Electrinic state of a photo-induced magnet of CoW cyanide studied by XANES" KEK Progress Report 2001-2 p.25 (2001).

(4) S.Kitagawa, D.Matsumura, K.Amemiya, T.Yokoyama, T.Ohta, (S.Ohkoshi), and (K.Hashimoto), "XMCD study on Prussian blue analogues" KEK Progress Report 2001-2 p.30 (2001).

(5) K.Nagai, K.Okamoto, H.Kondoh, T.Yokoyama and T. Ohta, "Electronic state and local structure of Mn oxide nanoparticle synthesized by microemulsion method" KEK Progress Report 2001-2 p.33 (2001).

(6) M.Iwasaki, H.Kondoh, I.Nakai, A.Nambu, K.Amemiya, T.Yokoyama, and T.Ohta, "Energy dispersive NEXAFS measurement: Decomposition of methxy on Ni(111)" KEK Progress Report 2001-2 p.46 (2001)

(7) H.Kondoh, A.Nambu, M.Iwasaki, T.Yokoyama, and T.Ohta, "Structural ordering of alkanethiolate monolayer adsorbed on Cu(100) "KEK Progress Report 2001-2 p.47 (2001)

(8) I.Nakai, A.Nambu, M.Iwasaki, H.Konodoh, K.Amemiya, T.Yokoyama and T. Ohta, "Two distinct adsorption states of selenophene monolayer on Au(111)" KEK Progress Report 2001-2 p.48 (2001)

(9) A.Nambu, H.Kondoh, M.Iwasaki, I.Nakai, and T.Ohta, "A core-level spectroscopic study of thiophene film deposited on Au(111): Structural change at initial stage of film growth" KEK Progress Report 2001-2 p.49 (2001)

(10) D. Matsumura, T.Yokoyama, K.Amemiya, Y.Hamada, S.Kitagawa, and T.Ohta, "XMCD study on spin reorientation transition of nickel thin films induced by adsorption of H_2 and CO" KEK Progress Report 2001-2 p.52 (2001)

(11) Y.Nakayama, H.Kondoh, K.Amemiya, T.Yokoyama and T.Ohta, "Trivalent Sm on Cu(111) at and above room temperature" KEK Progress Report 2001-2 p.53 (2001).

(12) (K.Sakauchi), (N.Ozawa), (T.Kodama), (I.Ikemoto), (K.Kikuchi), K.Kohdate, D.Matsumura, T.Yokoyama and T.Ohta, "XANES study of metalofullerenes" KEK Progress Report 2001-2 p.59 (2001).

(13) O.Endo, (M.Nakamura), T.Ohta and (K.Ito), "Non-situ XAFS study of the alkali on the noble metal surface" KEK Progress Report 2001-2 p.81 (2001).

(14) Y.Yonamoto, T.Yokoyama, K.Amemiya, D.Matsumura, S.Kitagawa, Y.Hamada, T.Ohta and (T.Koide), "Magnetic interaction between adsorbed NO and *fcc* Co(001) thin films studied by X-ray magnetic circular dichroism" KEK Progress Report 2001-2 p.95 (2001).

(15) (Y.Kishigami), (I.Shimoyama), (J.Zhaohui), (M.Tanaka), (K.Nakagawa), K.Amemiya and T.Ohta, "S1 exciton formation yield in anthracene single crystal under excitation with 250 – 800 eV photons" KEK Progress Report 2001-2 p.115 (2001)

(16) K.Kohdate, D.Matsumura, T.Yokoyama, T.Ohta, (K.Sakaguchi), (N.Ozawa), (T.Kodama),

(I.Ikemoto) and (K. Kikuchi), “Tm L-III EXAFS study of Tm@C82” KEK Progress Report 2001-2 p.149 (2001)

(17) K.Okamoto, K.Kohdate, K.Nagai, H.Kondoh, T.Yokoyama, (S.Emura), and T.Ohta, “Development of light-modulated XAFS spectroscopy” KEK Progress Report 2001-2 p.293 (2001)

D. Books

(1) T.Ohta edited, “Chemical Applications of Synchrotron Radiation” J. Electron Spectroscopy and related phenomena **119** (2001) special issue 107-274

(2) T.Ohta and (M.Nomura), edited, “Proceedings of the Eleventh International Conference on X-ray Absorption Fine Structure” J, Synchrotron Radiation **8** (2001) 47-1014.