SOLID STATE PHYSICAL CHEMISTRY

Annual Research Review

(1) "The effect of molecular adsorption on spin orientation of magnetic thin films"

We have investigated spin reorientation transitions of Co and Ni thin films induced by surface chemisorption for CO-adsorbed Co/Pd(111) and CO- and H-adsorbed Ni/Cu(001) by means of Co $L_{III, II}$- and Ni $L_{III, II}$-edge x-ray magnetic circular dichroism (XMCD).

For 4 to 6 monolayer (ML) Co/Pd(111), a spin reorientation transition from surface parallel to perpendicular magnetization has been observed at 200K after CO dosage. The region of perpendicular magnetic anisotropy (PMA) becomes wider by about 3 ML at 200 K. It should be noted that the CO adsorption on the same system does not induce any spin reorientation at 300 K.

Effective spin magnetic moments were obtained by the analysis of the XMCD spectra by use of sum rules, as shown in Fig. 1. For Ni/Cu(001), similar transitions have been confirmed when the layers are covered with CO or H, and PMA range is also expanded by about 2 ML. The observed stabilization of PMA due to chemisorption is ascribed to quenching of the surface parallel magnetic orbital moment.

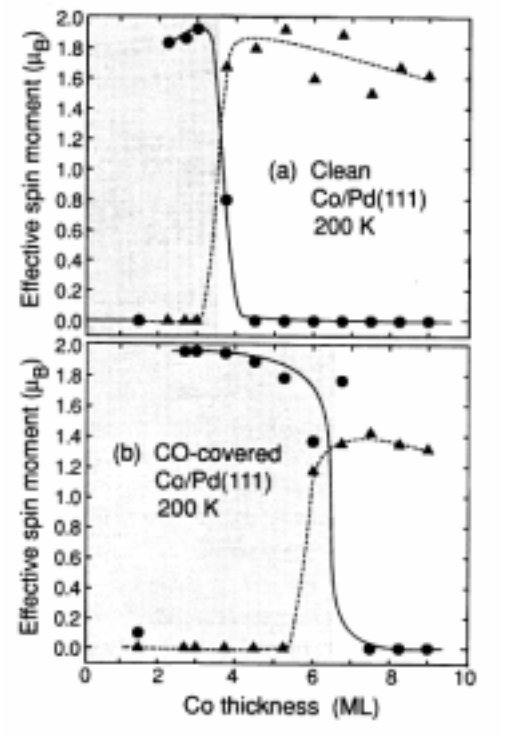

Fig. 1 Effective spin magnetic moments of (a) clean and (b) CO-covered Co films on Pd(111) at 200 K as a function of Co thickness. Circles and solid lines correspond to the surface normal direction, while triangles and dashed lines correspond to the surface parallel one. Hatched areas indicate the PMA regions.

A-14) *Phys. Rev.* **B 66** 24402 (2002)

(2) "Adsorption behavior of merocyanine dye on rutile TiO_2"

Merocyanine dyes that contain a carboxyl group and alkyl chain, like 3-carboxymethyl-5-[2-(3- alkyl-2-benzo thiazolinyldene)ethylidene]-2-thioxo-4-thiazolidinone (Mc2), enhance the efficiency of TiO_2 solar cells. Knowledge of the bonding of this dye molecule to the rutile TiO_2 surface will increase the understanding of the dye-semiconductor electron transfer responsible for the enhanced efficiency.

NEXAFS measurements and an *ab-initio* core-excited state molecular orbital calculation for the merocyanine dye were performed. From these results, it was found that the main molecular plane forms a 47° angle with the surface normal, and the carboxyl group that bonds to the TiO_2 surface is in alignment with the surface normal. STM experiments show that the dye molecules form aggregates on the TiO_2 surface

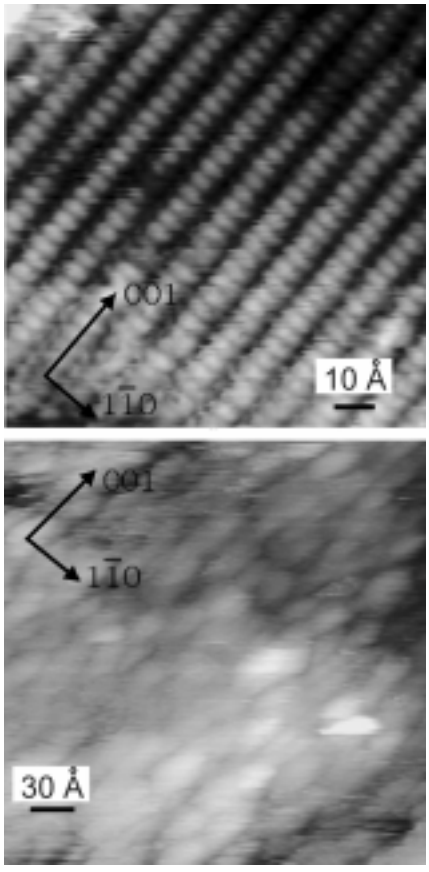

Fig.2 STM images of clean TiO_2(110) surface (upper 100 x $100Å^2$ image) and Mc2 covered TiO_2 surface (lower 300 x $300Å^2$ image). Dimer rows can be seen along the (001) direction on the clean surface. Dye aggregates form along the (001) direction in the lower image.

A-3) *Chem.Phys. Lett.* **360** 133-138 (2002)

物性化学研究室

研究レビュー

(1) 磁性薄膜のスピン配向に対する分子吸着の効果

Pd(111)単結晶上に作成した Co 磁性薄膜表面に CO を化学吸着させたとき，また，Ni/Cu(001)表面に CO や H2 を吸着させたときスピン配向転移が誘起されるかどうかを調べた。実験は放射光実験施設，BL-7A(スペクトル化学研究センター所属)軟 X 線分光ステーションで行い，軟 X 線円偏光を用いた Co, Ni-$L_{III,II}$X 線磁気円二色性(XMCD)の測定を行い，総和則を用いて，スピン磁気モーメント，軌道磁気モーメントの膜圧依存性を調べた。その結果，200K で CO を 4〜6ML Co/Pd(111)に吸着させると，面内磁化から面直磁化に転移することが分かった。面直磁化の領域は約 3 ML 広がる。一方，Ni/Cu(001)に CO や H2 を吸着させても，同様に面直磁化の領域が約 2 ML 広がることがわかった。このような面直磁化の安定性は化学吸着が面内の軌道磁気モーメントを下げることによるとして説明できる。

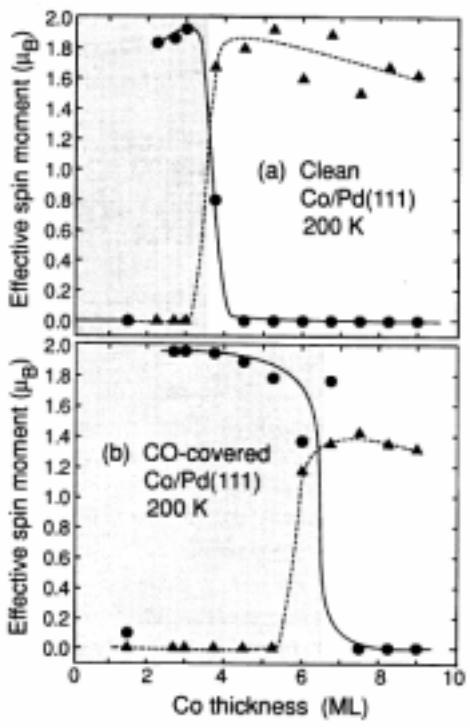

図 1　(a)清浄表面，(b) CO 吸着表面の有効スピン磁気モーメント　●，実線は垂直磁化，▲，点線は面内磁化を表す。ハッチした領域が垂直磁化

A-14) *Phys. Rev.* **B 66** 24402 (2002)

(2) 酸化チタン上のメロシアニン色素の吸着様式

カルボキシ基とアルキル鎖を含むメロシアニン色素，３－カルボキシメチル-5-[2-(3-アルキル-2-ベンゾチアゾリニリデン)エチリデン]-2-チオキソ-4-チアゾリジノンは酸化チタン太陽電池の効率を高めることが知られている。この色素分子が酸化チタン表面とどのような結合をしているかを知れば，高効率の原因である色素―半導体電荷移動の理解を深めることが期待される。そこで，ここでは偏光依存 NEXAFS 測定と非経験的内殻励起分子軌道計算を組み合わせて，メロシアニン色素の配向角を調べた。その結果，カルボキシ基で吸着して表面垂直に立ち，主分子面は表面垂直から 47° 傾いていることが明らかになった。一方，STM の測定から，色素は酸化チタン表面で集合体を作り，(001)方向に配向していることが分かった。

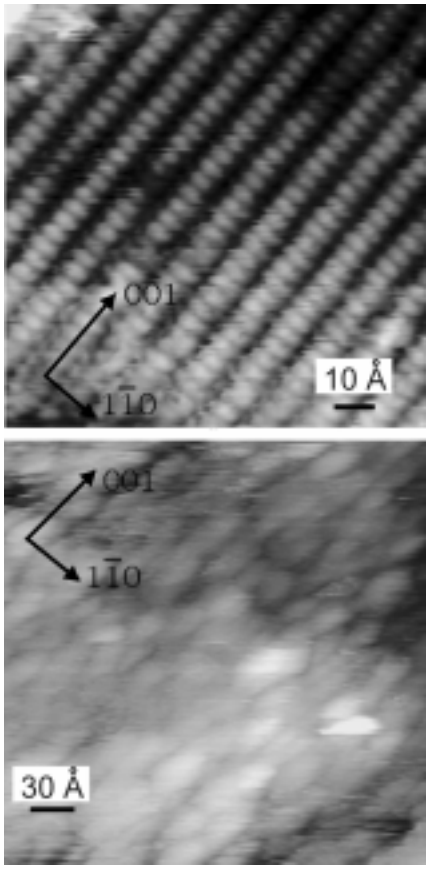

図 2　清浄 TiO_2 表面（上図 100 x 100Å^2），および色素吸着表面（下図 300 x 300Å^2）の STM 像。 二量体列が清浄表面の(001)方向に配列している。

A-3) *Chem.Phys. Lett.* **360** 133-138 (2002)

A. Original papers

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(4) (T.Nakamura), (S. Yasuda), (T. Miyamae), (M.Matsumoto), H.Kondoh, I.Nakai, and T.Ohta, "Self-oxidized monolayers using organic ditellurides" *J.Am.Chem.Soc.* **124,** 12642-12643 (2002).

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(11) I.Matsuda, T.Ohta, and (H.W.Yeom), "In-plane dispersion of the quantum-well states of the epitaxial silver films on silicon" *Phys. Rev.* **B 65,** 85327 (2002).

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B. Reviews

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(4) 近藤　寛:「有機材料の XAFS」放射光　**15**, 245-249 (2002).
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C. Proceedings

(1) H. Kondoh and T. Ohta, "Molecular Self-Assembly Studied by XAFS" Photon Factory Activity Report Vol.19, (2002) Part A 10-11.

(2) K. Amemiya, H. Kondoh, I. Nakai, A. Nambu, M. Iwasaki, T. Shimada, M. Nagasaka and T. Ohta, "Observation of a Surface Chemical Reaction with Soft X-ray Energy Dispersive Surface NEXAFS" Photon Factory Activity Report Vol.19 (2002) Part A, p.12

(3) (T. Yokoyama), (H. Tokoro), (S. Ohkoshi), (K. Hashimoto), K. Okamoto and T. Ohta, "Local structures of $RbMnFe(CN)_6$ studied by EXAFS: The photoinduced phase and the high- and low-temperature phases" Photon Factory Activity Report Vol.19 (2002)　Part B, p.13

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(1) T.Ohta: "Surface XAFS applied to atomic and molecular adsorbates" in "Chemical applications of synchrotron radiation" edited by T.K.Sham (World Scientific, Singapore, 2002) pp.665-706

(2) T.Ohta, K.Tsukiyama, and H.Kuroda edited, "Infrared Free Electron Laser and its Application" Jpn. J Appl.Phys. Vol. 41(2002) Suppl. 41-1, p.1-154.

(3) 太田俊明編："Ｘ線吸収分光法―XAFS とその応用" IPC 出版(2002)

(4) 雨宮健太,（北島義典）："Ｘ線吸収分光法―XAFS とその応用" IPC 出版(2002) 太田編, 第 4 章 6 節 p.115 – 127 「軟 X 線領域の XAFS」

(5) 近藤 寛,（関 一彦）："Ｘ線吸収分光法―XAFS とその応用" IPC 出版(2002) 太田編, 第 5 章 4 節 「有機材料」p.203 - 207