SOLID STATE PHYSICAL CHEMISTRY

Annual Research Highlights

(1) "Development of a depth-resolved XMCD spectroscopy"

The magnetic depth profile of ultrathin films and multilayers has been extensively investigated, because the surface and interface often play important roles in the magnetic properties of actual materials we have developed a simple but effective depth-resolved XMCD technique according to the following principle.

In the soft x-ray region, the x-ray absorption spectrum is obtained generally by counting the Auger electrons (and secondary electrons caused by them) emitted at the core hole relaxation, the number of which is proportional to the x-ray absorption intensity. The electron escape depth changes depending on the direction of emitted electrons. An imaging type MCP detector allows us to record spectra with various probing depths simultaneously. By taking the absorption spectra with right and left helicities, we can obtain XMCD spectra. We applied this technique to Fe/Cu(100) and Fe/Ni/Cu(100). It was confirmed that the surface two layers of the 7 ML Fe/Cu(100) are ferromagnetically coupled, while the inner layers are in the spin density wave (SDW) state at 130 K. The technique enables to extract the XMCD spectra from the surface ferromagnetic (FM) and inner SDW regions separately, indicating that the FM/SDW interface has an antiparallel magnetic coupling, and that the SDW region has the bulk-like feature. For Fe/Ni/Cu(100), we have observed magnetically live surface layers and some thickness-dependent magnetic coupling between the Fe surface and Ni film.

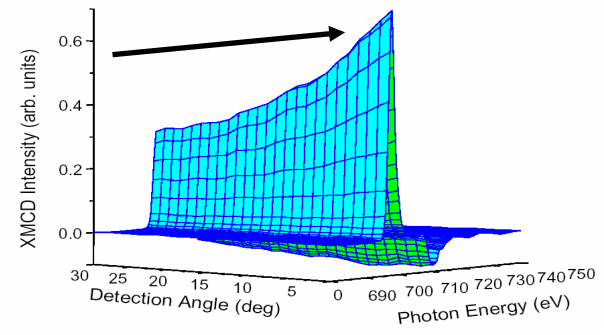

Fig. 1 Fe L-edge XMCD spectra from Fe(5 ML)/Ni(6ML)/Cu(100) films taken with various detection angles. The larger the angle is, the deeper the probing depth is. The spectra indicate that the interface couples to the Ni layers ferromagnetically and the surface couples anti-ferromagneitcally.

1.(1)-1) *Appl. Phys. Lett.*, **84**, 936-939 (2004)

(2) "Preparation and characterization of highly monodisperse FePd nanoparticles"

Magnetic nanoscale materials have attracted much attention owing to their potential applications in magnetic recording devices, medical diagnoses and magneto-optical systems. Until now, a great deal of effort has been devoted to prepare FePd nanocrystals via a wet chemical method with binary or multiple surfactants, such as trioctylphosphine oxide (TOPO)-TOP, hexadyl -amine (HDA) -TOPO-TOP, adamantanelcarboxylic acid (ACA)-HDA. However, the formation of highly mono-disperse FePd nanocrystals has been barely succeeded. We used a combination of ACA and alkylphosphine to stabilize FePd nanocrystals. The chemical synthetic route is based on the reduction of $Pd(acac)_2$ (acac=acetyl-acetonate) with hexadecanediol and thermal decomposition of $Fe(CO)_5$. The mean particles size can be varied from 11 to 16 nm by controlling the concentration and type of stabilizers and reaction conditions. High monodispersity of the FePd nanoparticles leads to the formation of two-dimensional (2D) superlattices consisting of hexagonal close-packed particles, which was confirmed by x-ray diffraction pattern and high-resolution transmission electron microscopic (HRTEM) images. This route provides a promising candidate for studying the magnetic properties of nanosized FePd materials.

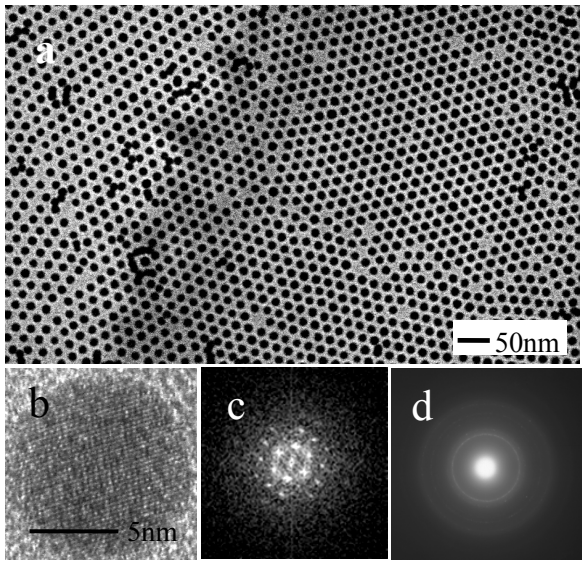

Fig. 2 (a) wide area TEM image, (b) high resolution TEM image, (c)Fast Fourier Transform (FFT) and (d) electron diffraction (ED) pattern of 11nm $Fe_{28}Pd_{72}$ nanoparticles.

1.(1)-2) *Chemistry of Materials*, **16**, 5149 (2004)

物性化学研究室

研究ハイライト

(1) 深さ分解 X 線磁気円二色性分光法の開発

磁性薄膜や多層膜の磁性が深さ方向にどのように変わるかを調べることは長年の課題であった。これを解決する目的で，我々は簡単で，かつ，有効な深さ分解 X 線磁気円二色性（XMCD）法の開発を行なった。３ｄ遷移金属表面の X 線吸収分光(XAS)スペクトル測定には，オージェ電子収量法が用いられているが，オージェ電子の出射角度によって飛び出す電子の深さが異なることから，その出射角度依存性をイメージング型の MCP 検出器で同時に測定することによって，検出深度の異なる XAS が得ることができる。したがって，左右ヘリシティの円偏光を用いた XAS の測定から深さ分解 XMCD スペクトルが得られる。具体的な応用としては，Fe/Cu(100), Fe/Ni/Cu(100)系の Fe 磁性薄膜の深さ分解 XMCD を測定し，解析を行った。そして，7 ML Fe/Cu(100)系では，表面第二層までが面直の強磁性であり，内部層は 130 K までは SDW 状態，それより高温では非磁性状態であること，また，Fe/6 ML Ni/Cu(100)系では，界面の Fe 層は Ni と強磁性的にカップルしているが，表面 Fe 層は厚さによって大きく振動していることが明らかになった。

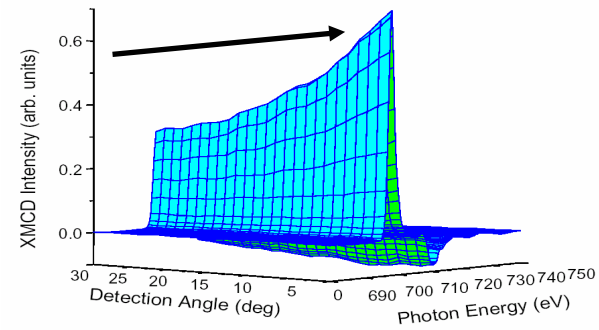

図１　様々な出射角度での Fe(5 ML)/Ni(6 ML)/Cu(100)の Fe L-吸収端 XMCD スペクトル。大きい出射角度はバルクが強調され，小さい出射角度は表面が強調される。このスペクトル形状の変化から，界面層は Ni と強磁性的に，表面層は反強磁性的にカップルしていることが分る。

1.(1)-1) *Appl. Phys. Lett.*, **84**, 936-939 (2004)

(2) 高度に単分散した FePd ナノ粒子の合成と評価

磁性ナノ粒子は磁気記憶素子，医学診断，磁気光学系などへの応用の観点から大きな注目を集めている。これまでさまざまな方法で FePd ナノ結晶の合成の報告がある。特に，湿式法によって，トリオクチルフォスフィン　オキサイド（TOPO）-TOP，ヘキサディルアミン(HAD)-TOPO-TOP，アダマンタネルカルボン酸（ACA）-HDA などの表面活性剤を用いて合成が行なわれているが，必ずしも高分散のナノ結晶合成は成功していない。今回，我々は ACA とアルキルフォスフィンの組み合わせを用いた。そして，$Pd(acac)_2$ をヘキサデカンディオールで還元し，$Fe(CO)_5$ を熱分解することを行なった。合成した FePd ナノ粒子は 11 から 16 nm であり，そのサイズは安定剤の濃度や反応条件によって制御することができる。高単分散したナノ粒子は二次元六方最密充填超格子を形成する。この結晶形は X 線回折パターン，高分解能電子顕微鏡で観測し，その磁性は SQUID によって調べた。室温では超常磁性，２K では 350 Oe, 50 K で 150 Oe の保磁力を持つ強磁性粒子であることが分った。

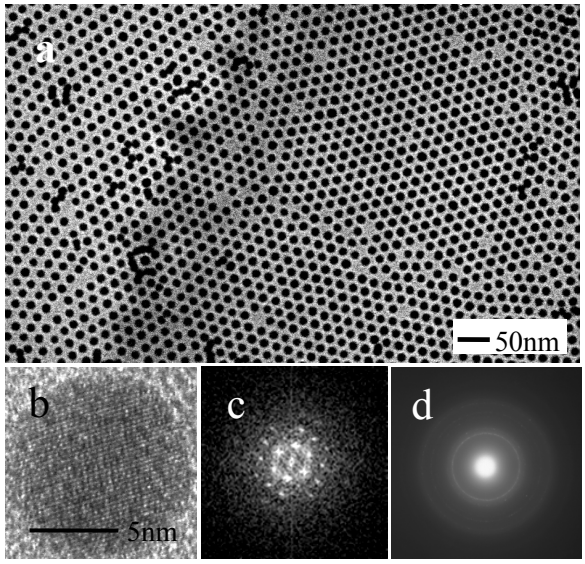

図２　11nm $Fe_{28}Pd_{72}$ ナノ粒子試料の (a) 広領域電顕像, (b) 高分解能電顕像, (c) 高速フーリエ変換パターン, (d) 電子回折パターン

1.(1)-2) *Chemistry of Materials,* **16**, 5149 (2004)

１．原著論文

（１）Refereed Journals

(1) K. Amemiya, S. Kitagawa, D. Matsumura, H. Abe, T. Yokoyama and T. Ohta, “Direct observation of magnetic depth profiles of thin Fe films on Cu(100) and Ni/Cu(100) with the depth-resolved x-ray magnetic circular dichroism” *Appl. Phys. Lett.,* **84**, 936-939 (2004)

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(3) K. Tono, T. Terasaki, T. Ohta and T. Kondow, “Electronic structure of Mn2O-: ferromagnetic spin coupling stabilized by oxidation” *Chem. Phys. Lett.*, **388**, 374-378 (2004)

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(5) I. Nakai, H. Kondoh, K. Amemiya, M. Nagasaka, A. Nambu, T. Shimada and T. Ohta, “Reaction-path switching induced by spatial-distribution change of reactants: CO oxidation on Pt(111)” *J. Chem. Phys. (Comm.)*, **121**, 5035-5038 (2004)

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(10) Y. Nakayama, H. Kondoh and T. Ohta, “Structure-dependent mixed valence of Sm on Cu(111) studied by XPS and STM ” *Surf. Sci*., **552**, 53-62 (2004)

(11) P. Zhu, T. Shimada, H. Kondoh, I. Nakai, M. Nagasaka, and T. Ohta, “Adsorption structures of NO on Pt(111) studied by the Near Edge X-ray Absorption Fine Structure Spectroscopy” *Surf. Sci.*, **565**, 232-242 (2004)

(12) Y. L. Hou, S. Gao, T. Ohta, T. Kondoh, “Fabrication of anisotropic magnetic nanostructures by soft chemical approach” *Trans. Mater. Res. Soc. Japan*, **49**, 123-126 (2004).

（2）その他

(1) M. Nagasaka, H. Kondoh, K. Amemiya, A. Nambu, I, Nakai, T. Shimada and T. Ohta, “Water formation reaction on Pt(111) studied by time-resolved NEXAFS and kinetic Monte Carlo simulation” *Photon Factory Activity Report*, Vol. 21 Part A, 8 (2004)

(2) A. Nojima, J. Miyawaki, M. Shimojo, T. Ohta, S. S. Astaputre and S. Kulkarni, “XAFS study if Eu doped xinc oxide nanoparticles” *Photon Factory Activity Report*, Vol. 21 Part B, 19 (2004)

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(6) D. Matsumura, T. Yokoyama, K. Amemiya, H. Abe, T. Shimada and T. Ohta, “CO adsorption structure on Co/Pd(111) magnetic thin film studied energy-scannin photoelectron diffraction” *Photon Factory Activity Report*, Vol. 21 Part B, 49 (2004)

(7) H. Abe, K. Amemiya, D. Matsumura, S. Kitagawa, H. Watanabe, T. Yokoyama, and T. Ohta, “Depth-resolved XMCD study on spin reorientation transitions of Fe/Ni/Cu(001)” *Photon Factory Activity Report*, Vol. 21 Part B, 79 (2004)

(8) K. Tono, J. Ikeuchi, H. Kondoh, and T. Ohta, “Surface electronic structure of the carbon-adsorbed W(110) surface” *Photon Factory Activity Report*, Vol. 21 Part B, 87 (2004)

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(12) J. Miyawaki, D. Matsumura, A. Nojima and T. Ohta, ”Structures of Co ultrathin films on Pd(111) studied by Surface EXAFS” *Photon Factory Activity Report*, Vol. 21 Part B, 77 (2004).

(13) K. Amemiya, D. Matsumura, H. Abe, S. Kitagawa, T. Yokoyama, and T. Ohta, “Direct observation of an oscillatory surface magnetization in Fe/Ni/Cu(100) films” *Photon Factory Activity Report*, Vol. 21 Part B, 80 (2004)

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２．総説・解説

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H. Kondoh, “Surface chemical reactions observed by the Energy dispersive surface XAFS method” *Shokubai*, **46**, 589-594 (2004)

３．著書

(1) 太田　俊明「X 線吸収分光法（ＸＡＳ）と X 線発光分光法（ＸＥＳ）」
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