Visualization of buried interfacial nanostructures using photoelectron emission microscopy

Toshiyuki Taniuchi, Takanori Wakita, Motohiro Suzuki, Naomi Kawamura,
Masafumi Takagaki, Masato Kotsugi, Hiramichi Sato, Takayuki Wakayama,
Keisuke Kobayashi, Masaharu Oshima, Hiro Akinaga, Kanta Ono

[1]*Department of Applied Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan*
[2]*JASRI/SPring-8, Mikazuki-cho, Hyogo 679-5198, Japan*
[3]*HiSOR, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan*
[4]*National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8562, Japan*
[5]*High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 305-0801, Japan*

We have performed the visualization and nanospectroscopy (nano-XAFS) of buried interfacial Au nanostructures using hard x-ray photoelectron emission microscopy (PEEM). The hard x-ray PEEM has an advantage of relatively large probing depth with high spatial resolution. The hard x-ray experiments were performed at the undulator beamline BL39XU of the SPring-8. The 20 nm thick Au nanostructures covered by a Co capping layer, shown in Fig.1(a), were fabricated by electron beam lithography, Au sputtering, lift-off, and Co sputtering. Figure 1(b) shows the chemical contrast of the buried Au nanostructures with the 50 nm thick Co capping layer observed by hard x-ray PEEM near Au L-edge. The buried interfacial Au nanostructures were clearly imaged for Co capping layers of up to 200 nm. It should be noted that the probing depth of chemical contrast was estimated to be as large as 300 nm, while that of nano-XAFS was 25 nm.

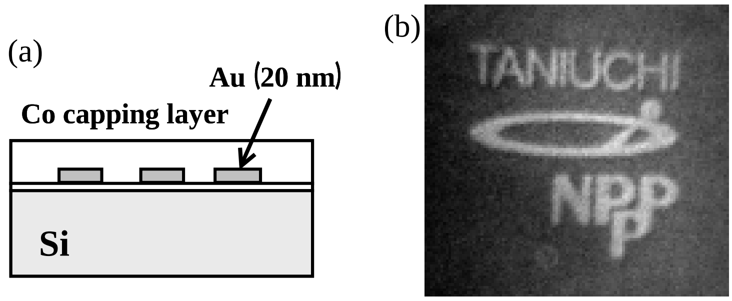


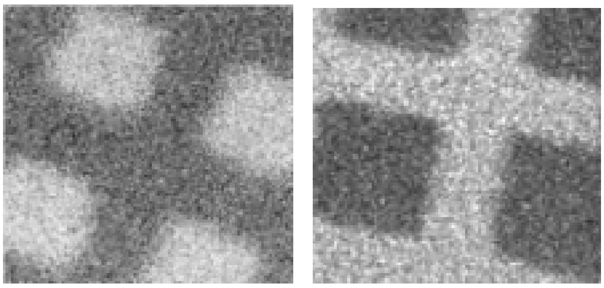
Fig. 1 (a) Cross-sectional schematic diagram of the buried interfacial Au nanostructures. (b) Hard x-ray PEEM image of buried Au nanostructure. The thickness of the Co capping layer is 50 nm.

Spectromicroscopic Characterization of Monomolecular Lithographic Patterns: the Effect of the Substrate

Mao-Lin Huang[1, 2], Chia-Hao Chen[1], Shih-Chieh Wang[1, 2], Ruth Klauser[1], and Michael Zharnikov[3]

[1]National Synchrotron Radiation Research Center, 101 Hsin-Ann Road,
Hsinchu 300, Taiwan
[2]Department of Materials Science and Engineering, National Tsing Hua
University, 101 Kuang-Fu Road Sec. 2, Hsinchu 300, Taiwan
[3]Angewandte Physikalische Chemie, University of Heidelberg, 69120
Heidelberg, Germany

Patterned self-assembled monolayers (SAMs) of alkanethiols (AT) on Au and Ag substrates were imaged and characterized by a scanning photoemission microscope (SPEM) setup. The patterns were prepared ex situ by electron irradiation of the pristine SAMs through a mask and subsequently exposed to ambient before their characterization in the SPEM chamber. The spectromicroscopic contrasts observed in the SPEM images resulted from a complex interplay of several competing processes [1]. On one hand, desorption of molecular fragments and chemical modification of the residual hydrocarbon layer occurred during the SAM irradiation. On the other hand, the fabricated patterns were further modified during their exposure to the ambient, which occurred through the adsorption of airborne molecules on the irradiated areas, possessing chemically active sites and enhanced surface roughness. Although the extent of the latter effect was assumingly the same for both Au and Ag substrates, the respective C 1s SPEM images showed opposite contrasts, which was attributed to the differences in the binding energy positions for the different carbon components in AT/Au and AT/Ag. The results for the electron-beam-patterned SAM resists will be compared with the analogous data for the monomolecular films patterned in situ by the focused X-ray beam.



C1s SPEM images of electron-beam patterned hexadecanethiol SAMs on Au (left image) and Ag (right image). The images exhibit opposite contrasts, which are related to the interplay of several competing effects.

[1] R. Klauser, I.-H. Hong, S.-C. Wang, M. Zharnikov, A. Paul, A. Gölzhäuser, A. Terfort, and T. J. Chuang J. Phys. Chem. B 107 (2003) 13133.

X-ray Emission Spectroscopy and Electron Microscopy of Mechanically-ground Graphite using Electron Probe Microanalyzer

Michiru YAMASHITA, Kazutoshi YAMADA, Ayuko FUJIMOTO[**]
Yasuji MURAMATSU[*], Teruo TAKAHASHI, Muneyuki MOTOYAMA[**]

Hyogo Prefectural Institute of Technology, 3-1-12, Yukihira, Suma-ku, Kobe, Hyogo 654-0037, Japan.
[*] *Kansai Research Establishment, Japan Atomic Energy Research Institute (JAERI), 1-1-1 Kouto, Mikazuki, Sayo-gun, Hyogo 679-5148, Japan.*
[**] *University of HYOGO, 1-3-3 Higashi Kawasaki, Tyuou-ku, Kobe, Hyogo 650-0044, Japan*

Graphite is a material known very well as one form of the allotrope of carbons. Fine particles of graphite has been used as electrode material of the fuel cell or Li-ion battery. It is important to understand the character of the microcrystal graphite to achive lower internal resistance of the cell and to improve characteristic of the electrical charge and discharge cycle.

As start material, graphite powder on the market was prepared and was mechanically-ground in the argon atmosphere by Spex-8000 mixer mill which is usually used for mechanically-alloying. Processing time was up to 288 k seconds.

The shape of mechanically-ground graphite(MG Graphite) was investigated by a scanning electron microscope(SEM), and crystallinity was analyzed by a X-ray diffractmeter(XRD). The characteristics of chemical/electronic state was analyzed by an electron probe microanalyzer(EPMA). Carbon (C) K-emission spectra were excited by a 15 keV electron beam and analyzed by a lead stearate pseud multilayer monochromator. To improve the spectral resolution, 2nd order spectrum was measured.

X-ray emission spectra in CK region of MG graphite were shown in Figure 1. They were compared with those of highly oriented pyrolytic graphite(HOPG), carbon-black powder and fullerenes such as C_{60}. The shape of CK emission spectra of MG graphite obtained before processing time 32.4 ks was seemed to be simply broadened and the position of their peaks were not changed, and between 18.0 ks and 25.2 ks the spectra looked similar to that of carbon black powder. Details will be disscussed.

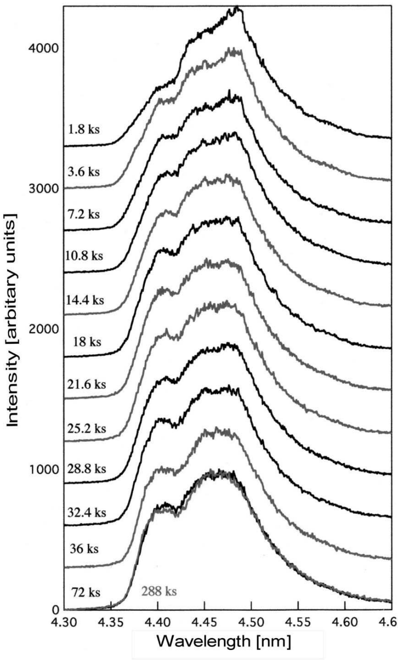


Figure 1: X-ray emission spectra in the CK region of mechanically-ground graphite.

References

1) Y. MURAMATSU, A. FUJIMOTO, M. YAMASHITA, K. YAMADA, M. MOTOYAMA: Soft x-ray emission and absorption spectroscopy of mechanically-milled graphite and carbon black using synchrotron radiation, The 31th annual meeting of the TANSO ZAIRYO Society, 1-3 December 2004.

A tentative model for the temperature gradient snow metamorphism and its validation on X-ray microtomographic data

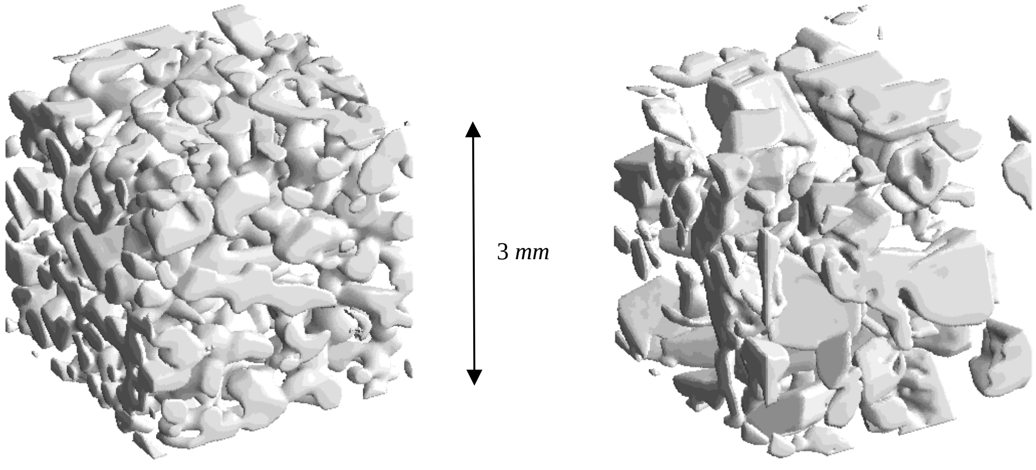
Frédéric Flin[1], Jean-Bruno Brzoska[2], Romeu André Pieritz[2], Bernard Lesaffre[2], Cécile Coléou[2], Yoshinori Furukawa[1]

[1]*Institute of Low Temperature Science, Hokkaido University, Japan*
[2]*Snow Research Center, Météo-France, Grenoble, France*

A simple physical model describing the temperature gradient metamorphism of snow is presented in this work. This model, based on Kelvin and Langmuir-Knudsen equations, is close to a previously developed model of isothermal metamorphism (see [1]), but takes into account the variation of the saturating vapor pressure with temperature. It can determine locally whether the ice is condensing or sublimating, just depending on both temperatures in the snow matrix and local mean curvatures of the ice/air interface. This model can also explain the formation of facets that occurs during the metamorphism (see figure).

Thanks to X-ray microtomographic images of snow samples obtained under different temperature gradient conditions, the validity of this model has been verified. This offers interesting outcomes for the numerical simulation of the temperature gradient metamorphism.

Snow samples after 3 weeks of temperature gradient metamorphism (Météo-France/CEN - Grenoble, France).
Experimental images obtained by absorption X-ray microtomography (ESRF/ID19 - Grenoble, France).
E=18 keV, image size: 300^3 voxels.



Temperature gradient: ~3 K/m

Temperature gradient: ~16 K/m

Reference:

[1]. F. Flin, J. B. Brzoska, B. Lesaffre, C. Coléou and R. A. Pieritz, “Full three-dimensional modelling of curvature-dependent snow metamorphism: first results and comparison with experimental tomographic data”, Journal of Physics D: Applied Physics, vol. 36, pp. A49-A54, 2003.

Quantitative analysis of environmental biofilms with STXM

*James J. Dynes, *Adam P. Hitchcock, **John R. Lawrence, ***Gary G. Leppard

**Chemistry and BIMR, McMaster University, Hamilton, ON Canada L8S 4M1*
***National Water Research Institute, 11 Innovation Blvd., Saskatoon, SK, S7N 3H5, Canada*
****National Water Research Institute, 867 Lakeshore Rd., Burlington, ON, L7R4A6, Canada*

Biofilms are a complex mixture of cells and extracellular polymeric substances (EPS). The EPS serve many functions, including: (i) sorption of organic (e.g., antimicrobial agents) and inorganic (e.g., metals) compounds; (ii) trapping of particulates such as organic debris, humic substances, clays and other minerals; (iii) compound transformations. X-ray absorption spectroscopy using synchrotron light sources can identify and quantify chemical species in wet, complex matrices at a spatial resolution of better than 50 nm. We present STXM images, spectra and derived quantitative chemical maps (Ca, K, Fe, Mn, Ni, protein, lipid, carbohydrate, nucleic acid, etc) of wet riverine biofilms [1,2]. The biofilms are grown in annular reactors using South Saskatchewan river water as the inoculant. The biofilms are examined after exposure to controlled amounts of trace metal ions (e.g. Ni^{2+} at 1-10 ppm) [2] or after growth in the presence of organic antimicrobial compounds (e.g. chlorhexidine, at 100 ppb). The methods to detect and quantify the trace amounts will be described. Typical results will be presented and compared to complementary studies of the same sample (in some cases the same regions) by confocal laser scanning microscopy and transmission electron microscopy. These studies are contributing to research projects on:

(1) applications of biofilms for trace metal remediation (see **Fig 1)**
(2) understanding antimicrobial resistance of biofilms
(3) Ca biomineralization (**Fig. 2**).

1) J. R. Lawrence et al., Appl. Environ. Microbiol. 69 (2003) 5543
2) J.J. Dynes et al, Environ. Sci. Tech. (2005) .
3) Research supported by NSERC, Environment Canada, AFMNet, the Canada Research Chair program. ALS is supported by DoE (DE-AC03-76SF00098).

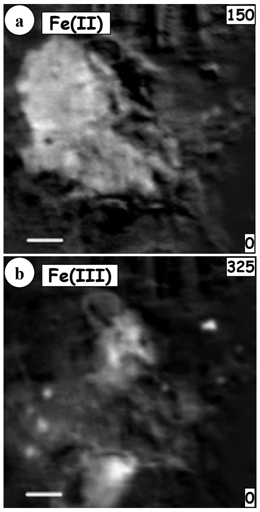


Fig 1 Distributions of (a) Fe^{2+} and (b) Fe^{3+} in a metal-rich, bio-mediated deposit in a riverine biofilm.Ni and Mn are also present in this region [2]. Scale bar is 1 micron (ALS STXM-11)

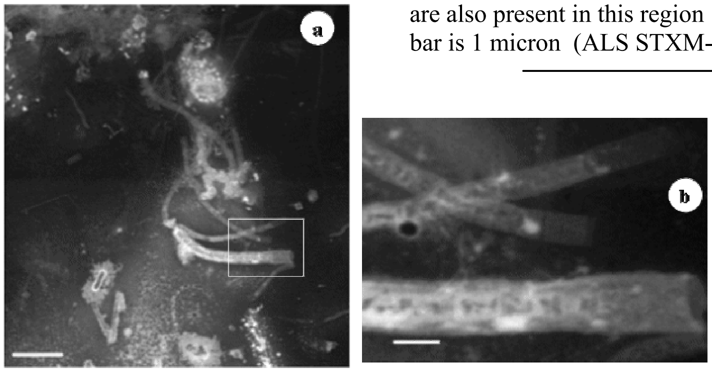


Fig. 2 STXM-derived map of Ca (on/off 2p resonance) in a riverine biofilm. (a) Scale bar is 5 micron. (b) Expansion of the box region. Scale bar is 1 micron. (ALS STXM5.3.2)

Soft X-ray STXM study of clay-salt interactions

Will P. Gates[1] and Adam P. Hitchcock[2]

[1] *Department of Primary Industries, RMB 1145 Chiltern Valley Rd, Rutherglen, VIC 3685 Australia*
[2] *Brockhouse Institute for Materials Research, McMaster University, Hamilton, ON L8S 4M1 Canada*

The exchange and re-distribution of cations between clays and the adjacent aqueous environment has been studied using scanning transmission X-ray microscopy (STXM) at ALS beamlines 5.3.2 and 11.0.2 with the goal of identifying mechanisms responsible for structural degradation of salt-affected soils and sediments. Images and spectra of thin films (<5 μm) of nontronite, sodium bicarbonate and their mixtures were measured at the C 1s, Ca 2p, O1s, Fe 2p and Na 1s edges. Both dry, and fully hydrated samples in wet cells, were examined. The anion components of the bicarbonate–nontronite system could be identified from O 1s NEXAFS spectra (Fig.1). Chemical component maps (fig. 2) created from differences of images on/off resonance lines specific to each chemical species, of a dried sample after mixing Ca-saturated clay with 1 M $NaHCO_3$ indicate that cations and salt species are considerably redistributed. Bicarbonate and Ca^{2+} are associated strongly with the edges of clay platelets, but Na^+ is uniformly distributed throughout the clay particle (probably also on its surface) indicating essentially complete exchange of Ca^{2+} by Na^+ at the charge complex of the clay. Upon re-wetting of the sample, Ca^{2+} was found to be uniformly dispersed throughout the particle and to have lost its prior association with clay platelet edges, indicative of dissolution of a Ca precipitate.

Research supported by Soil and Water Platform of DPI-PIRVic (Australia), NSERC (Canada), and the Canada Research Chair program (APH). ALS is supported by US DoE under contract DE-AC03-76SF00098.

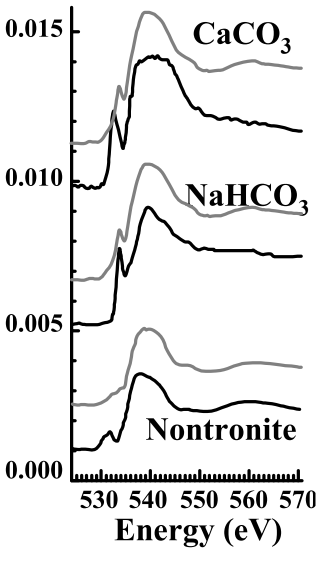


Fig. 1 O 1s spectra of reference minerals (black) compared to spectra from saline clay sample (grey).

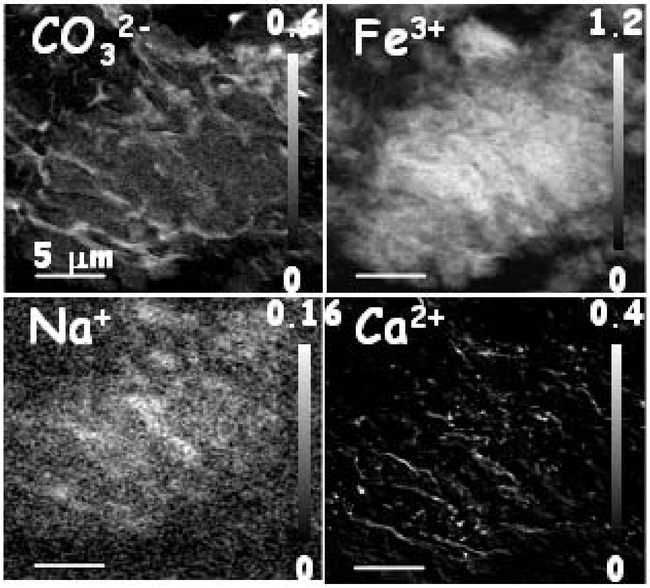


Fig. 2 Maps of carbonate, clay and cations in dry salt-clay mixture from image differences (on/off resonance) at C 1s, Fe 2p, Na 1s and Ca 2p edges. Gray scale limits are difference optical density.

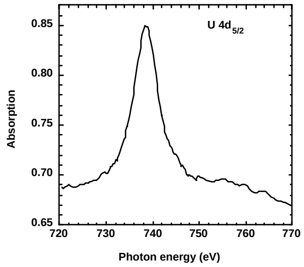
Prospects for Actinide STXM

T. Tyliszczak,[1] H. J. Nilsson,[1,2] L. Werme,[2,3] and D. K. Shuh[1]

[1]*Chemical Sciences Division, Lawrence Berkeley National Laboratory,*
MS 6-2100, One Cyclotron Road, Berkeley, CA 94720 USA
[2]*SKB, Box 5864, S-102 40, Stockholm, Sweden*
[3]*Dept of Physics, Uppsala University, Box 530, S-751 21, Uppsala, Sweden*

In assessing the migration behavior of actinides and other radionuclides in the environment it is of great importance to have detailed knowledge of the chemical interactions between the migrating actinide species with surrounding minerals, as well as with particulates present in transporting groundwater. There are several methods used to experimentally gain such information such as laboratory sorption experiments and hard x-ray absorption fine structure (XAFS). Recently, scanning transmission x-ray microscopy (STXM) has been utilized with actinides and shows the ability to give spatially-resolved chemical information from high-resolution near-edge XAFS (NEXAFS) on the 25 nm length scale. The STXM atmospheric working pressure and requirements for very small amount of samples greatly simplifies the handling of radioactive materials.

The results from the initial studies of the common uranium, neptunium, and plutonium oxides will be presented, demonstrating the capabilities and limitations of soft x-ray STXM spectromicroscopy for the investigations of actinide systems. The actinide 4d edges are employed for both imaging and for oxidation state determination. Additional information can be obtained from light element edges, such as the oxygen K-edge. The results from the initial investigation of actinide colloids and actinide sorption on particles will be shown. Actinide sample preparation methods, as well as sample radiation damage considerations, will be described and discussed. The prospects for future actinide investigations by STXM will be critically evaluated.



NEXAFS spectrum collected at the U $4d_{5/2}$ edge from a 35 nm edge region of a UO_2 particle.