Local electronic structure analysis using a photoelectron emission microscope (PEEM) with hard X-ray

M. Kotsugi†

Hiroshima Synchrotron Radiation Center, Hiroshima University,
2-313 Kagamiyama, Higashi-hiroshima, Hiroshima 739-8526, Japan,

T. Wakita

Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Mikazuki, Hyogo 679-5198, Japan,

T. Taniuchi

Graduate School of Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan,

K. Ono

High Energy Acceleration Research Organization, 1-1 Oho, Tsukuba, Ibaragi 305-0801, Japan

M. Suzuki, N. Kawamura, and M. Takagaki

Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Mikazuki, Hyogo 679-5198, Japan

M. Taniguchi

Hiroshima Synchrotron Radiation Center, Hiroshima University,
2-313 Kagamiyama, Higashi-hiroshima, Hiroshima 739-8526, Japan,

Graduate School of Science, Hiroshima University,
1-3-1 Kagamiyama, Higashi-hiroshima, Hiroshima 739-8526, Japan

K. Kobayashi

Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Mikazuki, Hyogo, 679-5198, Japan

M. Oshima

Graduate School of Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

N. Ishimatsu and H. Maruyama

Graduate School of Science, Hiroshima University,
1-3-1 Kagamiyama, Higashi-hiroshima, Hiroshima 739-8526, Japan

(Received 1 November 2005; Accepted 6 April 2006; Published 10 May 2006)

We demonstrate a new use for photoelectron emission microscopy (PEEM) in combination with hard X-ray synchrotron radiation. With this technique, an X-ray absorption fine structure spectrum can be acquired on each pixel in the observed image, thereby enabling analysis of the electronic properties in nanometer scale. Here, we report the local chemical composition and electronic structure of the Widmanstätten pattern in the Gibeon iron meteorite and clarify that the α lamella exhibits bcc structure with a spatially homogeneous Fe concentration.

Keywords: photoelectron emission microscope; hard X-ray synchrotron radiation; X-ray absorption fine structure; Gibeon iron meteorite; Widmanstätten pattern

I. INTRODUCTION

In the last decade, the photoelectron emission microscope (PEEM) has produced many fruitful results in the field of surface science [1–5]. PEEM is an electron microscope that can magnify the spatial information about secondary electrons photo-emitted from the surface with the lateral resolution power of several ten nanometers. For example, PEEM imaging associated with magnetic circular dichroism (MCD-PEEM) has been widely applied for magnetic multilayers as an element-selective visualization technique of magnetic domains [1–3]. On the other hand, few experiments have been carried out in combination with hard X-ray sources; Hwu, et al. have reported only one case on oxidized iron [12–14]. In that case, a satisfactory signal-to-noise ratio was not attained for local structure analysis. Therefore, a large number of unresolved issues still remain in the development of this technique. In this work, we report a successful result observed on the Gibeon iron meteorite, to which stable hard X-rays from BL39XU of SPring-8 have been applied for

*This paper was presented at 5th International Symposium on Atomic Level Characterizations for New Materials and Devices (ALC05), Hawaii, USA, 4-9 December, 2005.
†Corresponding author: kotsugi@hiroshima-u.ac.jp
the first time.

In conventional X-ray absorption fine structure (XAFS) analysis, the intensity of a photo-emitted secondary electron is proportional to the X-ray absorption intensity [6]. Because the spatial resolved intensity of secondary electrons is projected on the screen of PEEM, photon energy sweeping gives us the XAFS analysis on an arbitrary pixel of the projected image. The XAFS spectrum near the edge usually includes information about electronic structure, reflected in the excitation process from core level to an unoccupied state. The oscillatory fine structure in the extended region extracts interatomic distance as a radial distribution function [6]. The height of the absorption edge also represents the composition of the absorbing atom. Thus, this technique offers the opportunity to simultaneously analyze local electronic structure, local structure and chemical composition. The concept of this measurement technique is entirely different from common spatial-resolving XAFS techniques based on Fresnel’s Zone plates or microbeams. Furthermore, nanometer scale resolution power of PEEM is easily achieved. Consequently, we have named this technique "NanoXAFS" and are developing it as a new local structure analysis method for observation at the nanometer scale.

II. EXPERIMENTAL

Experiments were carried out on BL39XU at SPring-8 [10]. The hard X-ray synchrotron radiation is available in a range of photon energies from 5 to 37 keV. PEEM SPECTOR (Elmitec, Inc.) was installed inside the experimental hatch. A window of 250 μm in thickness was mounted on the upstream flange of the experimental system to introduce a hard X-ray beam without breaking ultra-high vacuum. The position of the experimental chamber, i.e. the position of the specimen relative to the synchrotron radiation, was fully controlled by a stepping motor from outside the shielding hatch to avoid irradiation [15].

To develop NanoXAFS technique, we used the Gibeon iron meteorite as a standard specimen. Gibeon is a typical iron meteorite exhibiting a characteristic micrometer-sized structure known as the Widmanstätten structure [7]. Iron meteorites have been well studied in the field of planetary science to investigate the history of the solar system [9]. However, in keeping with the terminology of materials science for describing certain crystallographic features, the Widmanstätten structure can be considered a mixed multi-crystal composed of bcc-FeNi and fcc-FeNi. The fine structure in the Widmanstätten structure is characterized by the acicular-shaped single crystal, or "lamella", that are several tenths of a μm in width [8]. This microstructure should show spatially different chemical compositions and lattice structures, and this size of microstructure is comparable to the field of view of a PEEM analyzer; therefore, the iron meteorite is an appropriate specimen for the evolvement of NanoXAFS.

The Gibeon iron meteorite was sliced almost parallel to the (001)bcc plane. The surface was roughly polished by diamond slurry of 3 μm in diameter and then by diamond slurry of 1 μm. Finally the surface was etched by an aqueous solution of FeCl₃ for 20 min to expose the Widmanstätten structure.

III. RESULTS AND DISCUSSION

NanoXAFS images were continuously recorded by scanning the photon energy from 7.1 to 7.16 keV at an interval of 1 eV for the Fe K-absorption edge, and from 8.38 to 8.315 keV for the Ni K-edge. Field of view was set 500 μm in diameter and exposure time for an image was 4 sec. The XY slit of x-ray was set to nearly equal as the field of view to reduce the stray electrons from the outside of field of view. The estimated photon flux in this condition was approximately 1 \( \sim 2 \times 10^{12} \) photons/s. From the total 127 images, we assigned pre-edge and center at the Fe K-edge to the photon energies of 7.104 and 7.128 keV, and in the case of the Ni K-edge to energies of 8.319 and 8.346 keV. The raw images at the pre-edge and the center at the Fe K-edge are displayed in Figs. 1(a) and 1(b). Brightness of the images is proportional to the absorption intensity, and the red-hot color scale in Figs. 1(a) and 1(b) is fixed to demonstrate the difference between pre-edge and edge. The microstructure of the Widmanstätten pattern is observed at the center of the image, although fine structure is still not clarified. Total intensity drastically changes between the images at the pre-edge and the center. The spatial intensity profile is identified as stronger in the middle of the image; it is ascribed to the sum of the X-ray beam profile and the transmission of the PEEM analyzer.

Normalized spatial distributions for Fe and Ni composition are shown in Figs. 1(c) and 1(d), respectively. These images were subjected to the following procedure: First, to extract the net contribution of the absorbing atom, the raw image exposed on the center of edge was subtracted by the image at pre-edge; second, the extracted image was divided by the image at pre-edge to cancel out the transmission function of the analyzer and beam profile; finally, the image intensity was normalized. The raw image at pre-edge does not include the photoelectron emitted from the adsorbing atom and is therefore a proper background image. This procedure was applied for both Fe and Ni constituents.

In Figs. 1(c) and 1(d), the information at the verge of the image is emerged, and the irregular intensity distribution of the X-ray beam or analyzer transmission has been successfully canceled out. Here, the three different regions are clearly recognized on the specimen: chemically and spatially homogeneous broad lamellae of 200 μm in width with higher Fe concentrations, thin 10 μm lamellae with lower Fe concentrations, and uneven thick triangular lamellae. The Ni distribution in a thick γ lamella is spatially non-homogeneous. Ni in γ lamellae is highly condensed at the interface, and the intensity profile is the reversal between both images for Fe and Ni; it should be caused by the binary system of iron meteorite mainly composed of Fe and Ni. The intensity profile of Ni extracted along the line on A-A’ in Fig. 1(a) is indicated in Fig. 1(b). The α lamella shows spatially homogeneous Ni composition; in contrast, the Ni composition in γ lamella rapidly increases approaching the interface. Thin γ lamellae and uneven thick γ lamellae are separated by thick α lamellae. This is likely the result of interatomic diffusion of Fe and Ni in the core of a mother body when an asteroid
FIG. 1: Spatial distribution of XAS intensity in the Gibeon iron meteorite, (a) at pre-edge, (b) at center of the Fe K-absorption edge and (c) the normalized image for Fe composition, which is compared with (d) the normalized image for Ni composition. e) Extracted intensity profile along A-A’ in Fig. 1(d). The normalization provides the qualitative chemical map of the absorbing atom. It is evident that the α lamella shows spatially homogeneous content and the γ lamella shows uneven distribution. The Ni content in γ lamella increases approaching the interface.

has been cooled at an extremely slow rate, as postulated by planetary scientists [7]. Thin γ lamellae exhibit spatially homogeneous Ni distributions derived from strong segregation. The irregular bump in the middle of thick γ lamella is reflected by the embossing surface formed by chemical etching.

The photon energy scanning provides a local XAFS spectrum. The averaged X-ray absorption intensities for Fe extracted from the square in Fig. 1(d) are shown in Fig. 2(a) as a red line with filled circles, and a spectrum for Ni extracted from same region is also shown in Fig. 2(b) as a red line with filled triangles. The XAFS spectra obtained on a reference specimen of bcc-Fe foil is also displayed in Fig. 2(a) as a blue line with filled squares. The sharp crest is recognized at the Fe K absorption edge of the iron meteorite. However, the spectrum of synthetic bcc-Fe also shows similar behavior. The shape of the crest in the synthetic Fe$_x$Ni$_{1-x}$ system is reported to commonly show a single peak when the crystallographic structure takes bcc below 25 at.% Ni [11]. Therefore, the sharp crest in iron meteorite suggests that the α lamella takes the bcc structure. From the results of chemical mapping, the α lamella assumes the bcc structure with spatially homogeneous composition. Unfortunately, because the surface in γ lamella has been embossed resulted from chemical etching, we were not able to perform local spectroscopic anal-
FIG. 2: (a) Averaged XAS intensity in the iron meteorite (red line with circle), which is extracted from the squared region in Fig. 1(d). The Fe absorption spectrum on a reference specimen of Fe foil (blue line with square). (b) XAS spectrum at the Ni K-edge, observed on α lamella in iron meteorite. The crest shows similar behavior as being a single peak, suggesting that α lamella takes the bcc structure in comparison with synthetic FeNi.

ysis of γ lamellae. As a result, mirror polishing would be a more appropriate treatment for iron meteorites. However, we successfully resolved the spatial electronic structure at the flat region of lamella of Widmanstätten structure in conjunction with hard X-ray synchrotron radiation and PEEM. The accumulation of further experience will be essential in establishing the quantitative analytical technique of NanoXAFS.

IV. SUMMARY

We demonstrated for the first time a new use of PEEM combined with the XAFS. The microstructure of FeNi lamellae in the Gibeon iron meteorite was investigated and the bcc crystallographic structure of α lamellae with spatially homogeneous composition has been clarified. Further accumulations of technical know-how will help develop NanoXAFS for local structure investigations.

Acknowledgments

The authors thank M. Funaki of the National Institute of Polar Research (NIPR) for useful discussions and E. Bauer of Arizona State University for helpful advice. The synchrotron radiation experiments were performed at the SPring-8 with approval from the Japan Synchrotron Radiation Research Institute (JASRI), supported by the Nanotechnology Project of Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan (Proposal No. 2004B0738-NXa-np and 2004A0371-NSc-np-Na).

[1] J. Stöhr, H. A. Padmore, S. Anders, T. Stammler and M. R. Scheinfein, Surf. Rev. Lett. 5, 1297-1308 (1998).
[2] W. Kuch, L. I. Chelaru, F. Offi, J. Wang, M. Kotsugi, et al., Phys. Rev. Lett. 92, 17201-17204 (2004).
[3] F. Nolting, A. Scholl, J. Stöhr, J. W. Seo, J. Forpeyrine, et al., Nature 405, 767-769 (2000).
[4] M. Kotsugi, W. Kuch, F. Offi, L. I. Chelaru, and J. Kirschner, Rev. Sci. Instrum. 74, 2754-2758 (2003).
[5] T. Taniuchi and M. Oshima, H. Akinaga, K. Ono, J. Electr. Spec. and Relat. Phenom. 144, 741-744 (2005).
[6] J. Stöhr, NEXAFS Spectroscopy, Springer Verlag (Berlin).
[7] V. F. Buckwald, Handbook of Iron Meteorites, Univ of California, Berkeley, 1975.
[8] H. J. Bunge, W. Weiss, H. Klein, L. Wcisak, U. Garbe, et al., J. Appl. Cryst. 36, 137-140 (2003).
[9] T. Nagata and M. Funaki, Mem. Natl. Inst. Polar. Res. 46, 245-262 (1987).
[10] H. Maruyama, M. Suzuki, N. Kawanaka, M. Ito, E. Arakawa, et al., J. Synchrotron Rad. 6, 1133-1137 (1999).
[11] H. Sakurai, F. Itoh, H. Maruyama, A. Koizumi, K. Kobayashi, et al., J. Phys. Soc. Jpn. 62, 459-463 (1993).
[12] Y. Hwu, W. -L. Tsai, D. Y. Noh, J. H. Je, G. H. Fecher, M. Bertolo, H. Berger, G. Margaritondo, Jpn. J. Appl. Phys. 38, 646 (1999).
[13] Y. Hwu, W. -L. Tsai, B. Lai, J. H. Je, G. H. Fecher, M. Bertolo, G. Margaritondo, Surf. Sci. 480, 188 (2001).
[14] G. H. Fecher, Y. Hwu, W. Swiech, Surf. Sci. 377-379, 1106-1111 (1997).
[15] T. Wakita, T. Taniuchi, K. Ono, M. Suzuki, N. Kawanaka, et al., Jpn. J. of Appl. Phys., accepted for publication.

http://www.sssj.org/ejssnt (J-Stage: http://eijssnt.jstage.jst.go.jp)