Valence-selective photoelectron holography and cutting-edge two-dimensional angular-distribution analyzer

OHiroshi Daimon^{1,2}, Hiroyuki Matsuda², Hiroki Momono², László Tóth³

 ¹ Toyota Physical and Chemical Research Institute 41-1, Yokomichi, Nagakute Aichi 480-1192, Japan
Phone: +81-561-57-9517 E-mail: daimon@toyotariken.jp
² Nara Institute of Science and Technology (NAIST), 8916-5 Takayama, Ikoma Nara, 630-0192 Japan
Phone: +81-743-72-6020 E-mail: daimon@ms.naist.jp
³ University of Debrecen H-4032 Debrecen Egyetem ter 1, Hungary
Phone: +36 52-512900 E-mail: tothla@tigris.unideb.hu

Abstract

The analysis of atomic structure around local non-periodic active-site atoms has become possible recently by several atomic-resolution holographies developed in Japan. The characteristic of these methods is that it can reveal the structures around specific atomic species, even around individual valence-state atoms. The development of effective cutting-edge two-dimensional angular-distribution analyzer is also explained.

1. Atomic-resolution holographies

3D local atomic structure around specific active-site atom plays crucial role in functional materials such as high temperature ferromagnetic semiconductors or superconductors. The 3D atomic structure around this kind of local specific atoms, however, has not been able to be analyzed by a standard structure analysis method of electron diffraction (ED) or x-ray diffraction (XRD) because this kind of active site has no translational symmetry. Recently several techniques have been developed to investigate the 3D atomic structure around this kind of specific atoms with no translational symmetry. One method is the photoelectron holography, where the obtained angular distribution pattern includes the interference between the direct photoelectron wave from the emitter and the scattered waves from surrounding atoms. Because the phase difference information between the direct wave and the scattered waves are recorded, the diffraction pattern is considered as a hologram [1], and the real-space atomic arrangement is easily obtained directly. Fig. 1 shows an example of the reconstructed structure for K doped graphite intercalation superconductor [2]. A similar technique which uses fluorescent xray is called "fluorescent x-ray holography" [3]. Recently their accuracy improved dramatically by the development of new analysis code [4] and a sensitive detector [5]. A new technique of direct 3D atomic structure analysis method "stereography of atomic arrangement" has also been developed [6]. These techniques received renewed attention recently. Hence we started a project of "3D active-site science" [7] in



Fig. 1 Example of photoelectron holography [2]

order to open a new field of "Local 3D active-site functional materials science". The target materials in this project are ranging from inorganic materials to bio-materials. Recent results of dopant As in Si [8] and others are presented.

2. Cutting-edge two-dimensional angular-distribution analyzer

In order to obtain photoelectron hologram it is required to measure 2π str angular distribution of core-level photoelectrons from specific atoms. The acceptance angle of commercial analyzer is small (about 0.0007 of hemisphere). Hence it takes a long time to measure 2π str angular distribution. So far we have used a display-type spherical mirror analyzer called DIANA [9] which can display the angular distribution of 1π str (0.5 of hemisphere) at once. DIANA has been effectively used to obtain holograms such as seen in Fig. 1 [2]. Although DIANA has an advantage of widest acceptance angle, its energy resolution is not high enough to separate corelevel chemical shift of about 1 eV at several hundred eV. Hence we have developed DELMA (display-type ellipsoidal mesh analyzer) [10] (Fig. 2) by combining a wide acceptance angle electrostatic lens (WAAEL) [11] and commercial hemispherical analyzer (R4000 from VG-Scienta Co.). WAAEL



Fig. 2. Display-type ellipsoidal mesh analyzer (DELMA) [10]

can converge the electrons emitted to $\pm 50^{\circ}$ to one point, and the following lens system introduce these electrons to R4000. Although R4000 can analyze small solid angles determined by the entrance slit, this system can measure solid angles of $\pm 50^{\circ}$ by using deflectors at the exit of the lens system. One example of the result obtained by this system is site-selective photoelectron spectroscopy for Fe₃O₄ [12]. The scanning time is several times shorter than the commercial one and the merit is the sample is not necessary to rotate, but the measurement time is still long. The size of this system is large $(1 \text{ m} \times 2.5 \text{ m})$ m). Hence we have developed a new high-energy-resolution display-type analyzer Compact-DELMA [13](Fig. 3). The WAAEL used here can decelerate the electron energy down to 1/100 with the divergence angle of $\pm 7^{\circ}$. By combining with CMA-type analyzer this system can display the angular distribution of electrons of $\pm 50^{\circ}$ at once on the screen with a high energy-resolution of 0.01%.



Fig. 3. Compact DELMA [13]

Support by the JSPS Grant-in-Aid for Scientific Research on Innovative Areas "3D Active-Site Science": grant No. 26105001, 26105007, and 26105013. is gratefully acknowledged.

- A. Szöke: AIP Conference Proceedings, No.147, AIP New York 1986.
- [2] F. Matsui, R. Eguchi, S. Nishiyama, M. Izumi, E. Uesugi, H. Goto, T. Matsushita, K. Sugita, H. Daimon, Y. Hamamoto, I. Hamada, Y. Morikawa, Y. Kubozono, Scientific Reports 6, 36258 (2016).
- [3] M. Tegze, G. Faigel: Europhys. Lett. 16, 41 (1991).
- [4] T. Matsushita, A. Yoshigoe, and A. Agui: Europhys. Lett. 71, 597 (2005).

- [5] K. Hayashi, N. Happo, S. Hosokawa, W. Hu, and T. Matsushita: J. Phys. Condens. Matter 24, 093201 (2012).
- [6] H. Daimon: Phys. Rev. Lett. 86, 2034 (2001).
- [7] URL: http://www.en.3d-activesite.jp/
- [8] K. Tsutsui, T. Matsushita, K. Natori, T. Muro, Y. Morikawa, T. Hoshii, K. Kakushima, H. Wakabayashi, K. Hayashi, F. Matsui, and T. Kinoshita, Nano Letters, 17, 7533 (2017).
- [9] H. Daimon, Rev. Sci. Instrum. 59, 545 (1988).
- [10] H. Matsuda, K. Goto, L. Tóth, M. Morita, S. Kitagawa, F. Matsui, M. Hashimoto, C. Sa-kai, T. Matsushita, H. Daimon, Journal of Electron Spectroscopy and Related Phenomena 195, 382 (2014).
- [11] H. Matsuda, H. Daimon, M. Kato and M. Kudo, Phys. Rev. E 71, 066503 (2005).
- [12] Y. Hashimoto, M. Taguchi, S. Fukami, H. Momono, T. Matsushita, H. Matsuda, F. Matsui, and H. Daimon, Surf Interface Anal., 51, 115 (2019).
- [13] H. Matsuda, L. Tóth, and H. Daimon, Rev. Sci. Instrum. 89, 123105 (2018).