

## Development of high lateral and wide angle resolved hard X-ray photoemission spectroscopy

Hard X-ray photoemission spectroscopy (HAXPES) has become a powerful tool to investigate the chemical states and electronic structures of various materials using third generation high-brilliance synchrotron radiation sources. The most advantageous feature of HAXPES is that it enables intrinsically bulk sensitive electronic structures and buried interface profiles to be measured. The variable depth analysis of electronic properties by HAXPES has realized various applications both in basic and applied research fields [1]. Such research is targeting nanoscale-microscale materials, leading to more requests for observations in this area. Hence, it is important to investigate the electronic states, including edge structures and cross sections with depth profiles, over the nanometer to micron scale. Anticipating demands from rapidly developing nanoscale- micronscale science and technology, the 2D scanning of a sample with finer micro-focused X-rays is necessary to obtain a higher lateral resolution. We have targeted the 3D analysis of chemical states by utilizing the large probing depth of HAXPES together with the variable takeoff angles provided by a wide-angle lens. Our development approach on the HAXPES scanning microscope combines the Kirkpatrick-Baez focusing mirrors (K-B) and a wide-acceptance-angle

electrostatic lens (WAAELs) with angular resolving capability at beamline **BL47XU** [2].

By installing the K-B mirrors, we achieved a beam size of 1.10 (H)  $\times$  0.98 (V)  $\mu$ m<sup>2</sup> at photon energy of 7.94 keV as a lateral resolution. Both the vertical and horizontal focusing mirrors are elliptical, and the lengths of both mirrors are 100 mm. The working distance of the K-B system is 350 mm. The magnification is 0.35/50=1/143 to locate K-B system at a position 50 m from center of the undulator. In other words, the divergence is 143 times. Development of a WAAEL with an angular resolution capability is also necessary to realize 3D chemical analysis via angleresolved X-ray photoelectron spectroscopy. Details of the simulation results for this WAAEL are described elsewhere [2,3]. The total magnification factor increases 25 times by combining the objective and the analyzer lenses. This means that the effective view field on the sample with the entire analyzer system is 5 times smaller compared to the analyzer without a WAAEL. The efficiency of the electron detection thus increases while decreasing the X-ray spot size on the sample surface. Thus, the combination of a WAAEL and the  $1-\mu m^2$ focusing of the K-B mirror effectively increases the throughput of the photoelectron measurements. The result of the evaluation of acceptance angle is shown in Fig. 1. Figure 1(a) shows the 2D image record of the Au valence band spectrum near the Fermi edge region in the angular mode. The number of slice peaks can be directly indicated by acceptance angles larger than ±32°, because the period of the multi-slit is 2.8°. The magnified profile of one slice is shown by red circles in Fig. 1(b). The blue curve in Fig. 1(b) is the derivative of the edge shape of the slice profile. The angular resolution is estimated to be 1.32° from the FWHM of the derivative. The spherical aberration is apparent in high emission angles (Fig. 1(c)). The aberration of 22 meV at the maximum is remarkably small for the total energy resolution of 265 meV. It is thought that this aberration originates in the accuracy of an ellipsoidal mesh, in which the gap from a mesh-shaped design is currently about 50  $\mu$ m. The high-precision fabrication of an ellipsoidal mesh is the most important point, and much research and development was conducted to remove this aberration.



Fig. 1. Test results for the angular acceptance and resolution of the WAAELs obtained using a test device composed of a Au plate, in front of which a combination of a cylindrical multi-slit (the period of the multi-slice is 2.8°) was mounted. (a) 2D image recorded in the Au Ef region in angular mode. Right and bottom show the integrated profiles of the slit image along with the kinetic energy and the Au Ef spectrum along with emission angle, respectively. (b) Magnified profile of one slice (red circles) and the differential curve in the edge shape of this slice profile (blue line). (c) Raw plot of Fermi level of Au for binding energy at each acceptance angle (red circles) and after correcting for energy (blue circles).

Here, some of the results that combine K-B mirrors with a WAAEL are described. All the experiments were measured at a photon energy of 7.94 keV. The performance of this scanning depth analysis was evaluated by carrying out core spectra measurements of a typical multilayered sample of Ir (8 nm)/HfO<sub>2</sub> (2.2 nm)/ thickness-graded (TG) SiO<sub>2</sub> (0-10 nm)/Si (001), schematically shown in Fig. 2(a). By scanning the position of the TG sample surface along the SiO<sub>2</sub> thickness and varying the direction stepwise in 50um increments, the Si 1s and O 1s spectra are found to exhibit the features shown in Figs. 2(b) and 2(c), respectively. The Si 1s from the SiO<sub>2</sub> layer loses intensity and shifts towards a lower binding energy as the thickness decreases. In addition, the depth profile of the structure has been mapped along the SiO<sub>2</sub> thickness varying direction with the TOA dependence of these core spectral intensities. These results directly indicate that band bending depends on thickness due to the charge trap of interlayer band diagram [4]. This charge trap mechanism proposes that positive charges are trapped on the HfO<sub>2</sub> surface, while negative charges are trapped in the HfO<sub>2</sub> film along thickness of SiO<sub>2</sub>.

Furthermore, the scanning and angle-resolved results of 2D mapping applied to micro-dots of (Fe<sub>2.5</sub>Mn<sub>0.5</sub>)O<sub>4</sub> ferromagnetic oxide (thickness: 20 nm) on Nb0.5wt%-SrTiO<sub>3</sub> substrates are shown in Fig. 3. This (Fe<sub>2.5</sub>Mn<sub>0.5</sub>)O<sub>4</sub> system is a typical magnetic semiconductor exhibiting strong electron correlation effects [5]. The valence band spectra revealed that the DOS near  $E_F$  of (Fe<sub>2.5</sub>Mn<sub>0.5</sub>)O<sub>4</sub> thin films systematically decreased as the Mn concentration increased. The band shift due to changing the electron correlation was observed in a wide substitution range and is interpreted



Fig. 2. (a) Schematic structure of the Ir  $(8 \text{ nm})/\text{HfO}_2$ (2.2 nm)/SiO<sub>2</sub> (0–10 nm)/Si multi-layer. (b) and (c) Position dependence of Si 1s and O 1s along the TG direction by increments of 50 µm, respectively.

by the change on the basis of the Mott-Hubbard model [5]. The dot size is 50 × 50  $\mu$ m<sup>2</sup> in the optical image of Fig. 3(a). In Figs. 3(b) and 3(c), the 2D mapping image of integral intensity for the Fe 2*p*<sub>3/2</sub> and Sr 3*p*<sub>3/2</sub> shows mapped with 1- $\mu$ m steps, respectively. The micro-dot is well resolved using a 1- $\mu$ m beam size. This lateral-resolved investigation of a micro-dot thin film suggests that this material system has potential to develop advanced spin electronics. Through a combination of the K–B mirrors and the WAAEL, chemical state mapping will provide important information about the electronic properties of various materials crucial to basic science, industry and technology.



Fig. 3. Results of 2D mapping via sample scanning applied to a rectangular micro-dot of  $(Fe_{2.5}Mn_{0.5})O_4$  ferromagnetic oxide (thickness, 20 nm) on a Nb0.5wt%–SrTiO<sub>3</sub> substrate. (a) Dot size is  $50 \times 50 \ \mu\text{m}^2$  in the optical image. (b) and (c) 2D mapping image of the integral intensity for Fe  $2p_{3/2}$  and Sr  $3p_{3/2}$ , respectively.

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