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Development of a laboratory system hard X-ray photoelectron spectroscopy and its applications

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ABSTRACT

Development of a laboratory hard X-ray photoelectron spectrometer using excitations by monochromatic Cr Kα X-rays of 5.4 keV and a high energy analyzer with a wide acceptance angle resolved objective lens is introduced. Wide applicability of the system as a powerful tool for the investigations of electronic and chemical states of materials are demonstrated by various examples including bulk sensitive valence band and core level spectroscopy, overlayer thickness determination by photoelectron take off angle dependence measurements, buried layer analysis, bulk sensitive photoelectron diffraction to determine surface polarity of compound single and poly crystalline films, interface state spectroscopy in MOS structures by applying voltage bias, and environmental cell for high pressure photoelectron spectroscopy. These results evidently show the laboratory HXPES system is going to be indispensable in wide varieties of targets. It also opens up opportunities of the analysis of materials which are not accessible to beamlines due to limitations by safety control regulation and avoidance of risks to the beamlines.

1. Introduction

In this article, we introduce development of a laboratory hard X-ray photoelectron spectrometer using excitation by monochromatic Cr Kα X-rays. We also report results of our extensive efforts to explore the wide applicability of the system as a powerful tool for the investigations of electronic and chemical states of materials. Basing upon the results of these efforts, the laboratory HXPES system has been authenticated to be not only a complementary to the beamline HXPES, but also indispensable in the advanced researches and developments in wide varieties from the basic to industrial science and technology.

Since the first successful experiments of hard X-ray photoelectron spectroscopy (HE-PES, HX-PES, HXPES, HXPS, HIKE or HAXPES) using undulator synchrotron X-rays at SPring-8 [1,2], HXPES has grown as a versatile tool for the studies of bulk electronic structures of materials [3–5]. It is widely used not only for solid state physics, but also for materials science, analytical science and technology, and researches and developments in advanced devices. Now the demands from the users exceed supply of the beamtime. Thus the restriction of beamtime resources is becoming a limiting factor for further development. Another essential drawback is impossibility of the prompt turnaround on-site experiments, which is very often the key to the advanced researches and developments. If laboratory HXPES system with practical throughput and energy resolution is realized, above mentioned problems are solved, and the utilization of HXPES will spread more widely from basic research to the industrial researches and developments, and even to the monitoring of the production lines. It also will provide ways to free the restrictions at beamlines due to the safety control rules, thus will opens further opportunities of HXPES applications.

Motivated by the above consideration, we have conducted development of a laboratory HXPES system, High Energy Angle Resolved X-ray Photoelectron Spectrometer for Laboratory (HEARP Lab) [6].

The developed system is devised with a compact monochromatic Cr Kα (5.4 keV photon energy) X-ray source, a wide acceptance objective lens, and a high energy hemispherical electron analyzer with large (200 mm) mean radius. The Cr Kα X-ray source was designed based upon the compact Al Kα X-ray source of PHI 500 *VersaProbe* of ULVAC PHI [7], and fabricated by ULVAC PHI. The wide acceptance objective lens was designed by H. Matsuda and H. Daimon of NAIST [8–11], and tested at NIMS contract beamline group at

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SPring-8. Assembly of the system and basic performance tests were done at NIMS contract beamline group at SPring-8. Development of applications and introduction of new measurement techniques were performed in collaboration with NIMS internal, and external users. Some of these results are introduced in this article.

As a counter part of this project, a development of a scanning photoelectron microscopy system combining a K-B mirrors and a high energy analyzer with the same wide acceptance objective lens that used in HEARP Lab, for the 3D analysis of the electronic structures and chemical states has been conducted at BL47XU, which is also introduced by Ikenaga et al. in this issue [12].

We first introduce the HEARP Lab system with descriptions of basic performance. Then we show examples of applications involving bulk sensitive valence band and core level spectroscopy of advanced materials, overlayers-thickness determination in the thickness range of up to 25 nm [13], investigation of buried layers, bulk sensitive X-ray photoelectron diffraction [14] and its applications to surface polarity determinations [15], interface state spectroscopy of MOS structure by electric field application, and environmental cell developments. All these examples verify potentials of HEARP lab system to open up wide opportunities of applications, which have never been realized using conventional laboratory photoelectron spectrometers. It should also be noticed that these opportunities have never been realized by beamline HXPES alone as efficiently as shown in this article due to inherent inconvenience of the synchrotron beamline experiments by limited beamtime with binding to medium term schedules, and incompatibility of sample environment and so on.

2. System and components

One of the crucial keys in the laboratory HXPES system development is to devise a monochromatic X-ray source of 5–6 keV photon energy with high-flux and small spot size on a sample surface. The second important requirement is to accept photoelectrons effectively into a high energy electron analyzer with angular resolution capability for the measurements of takeoff angle dependence and X-ray photoelectron diffraction. In order to satisfy these requirements, we constructed a system consists of a focused Cr Kα source, a wide acceptance objective lens, and a high energy version of VG SCIENTA R4000 analyzer [16], as schematically shown in Fig. 1.

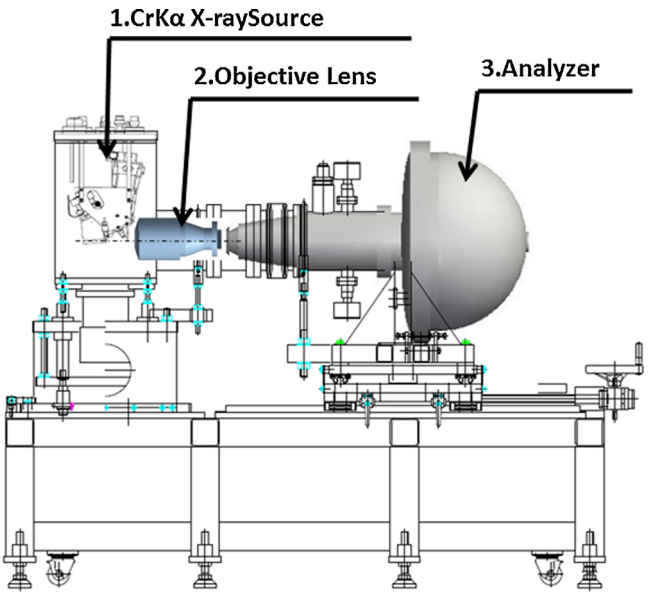

Fig. 1. Configuration of HEARP Lab system.

Regarding to the X-ray source, we adopted a flange mounted design as shown in Fig. 2. A water cooled Cr target is bombarded by a focused electron beam with the maximum acceleration energy of 20 keV. The emitted Cr Kα (5.4 keV) X-rays are monochromatized, and focused onto a sample surface by a compact bent crystal monochromator with a 300 mm Rowland circle as shown in Fig. 2. The X-ray beam can be scanned on the sample by moving the focused electron beam on the target as schematically shown in Fig. 2(b). The X-ray spot size is variable from 10 μm (1.25 W) to 200 μm (50 W) by defocusing or raster scanning of the electron beam. Fig. 2(c) shows a scanning image of the secondary electron of a copper mesh grid. A minimum X-ray spot size was confirmed as 9.9 μm × 8.3 μm by measurement of the edge steepness analysis of the mesh image.

In order to collect photoelectrons efficiently, we inserted a wide acceptance objective electrostatic lens in front of the high energy analyzer. We adopted a lens design with an ellipsoidal mesh electrode in the first stage reported by Matsuda and Daimon [8–11]. A new design with specifications as follows was made by them for our purpose; ±45° acceptance angle, ±9° exit angle with angular resolution of 0.5°, magnification factor of 5, spot size at the exit point 0.5 mm or less, and working distance of 11 mm from the aperture. We have manufactured several prototypes to achieve the high voltage operation up to 10 kV, improving the electrodes shapes and their configuration to reduce the micro-discharges. The high-precision fabrication of an ellipsoidal metal mesh electrode in the first stage of the lens is an important key to this objective lens development.

The state of art objective lens is shown in Fig. 3. Fig. 3(a) and (b) are photographs of the lens and the mesh electrode, respectively. Fig. 3(c) is cross-sectional drawing of the lens with simulated electron trajectories, and Fig. 3(d) is a spot image on a fluorescent screen placed at the exit focus point of the wide acceptance objective lens and its line profile. In this measurement, divergent electron beam, which is generated by quasi-elastic scattering of focused electron beam spot of 100 μm diameter at kinetic energy of 5 keV from a Au plate was used. The coincidence between lens parameter sets determined experimentally to minimize the focus spot and those obtained by simulation was excellent.

In order to evaluate the angular dependence of the transmission of the objective lens, we have constructed test equipment, using a compact fine parallel beam electron gun on a rotatable mount installed in front of the lens. Retractable fluorescent screen-Faraday cup assemblies are also set up at the front and rear focus points of the lens to measure the electron beam image and current. The parallel electron beam size is ca. 100 μm. The absolute transmission of the final version of the prototype objective lens evaluated by this equipment was 70% in average with flat angle dependence within ±45°. About ±10% of fluctuation was observed due to the shadowing by mesh wires. The details of the objective lens characterization will be reported elsewhere [17].

The objective lens is installed in front of a VG SCIENTA R4000 10 KV hemispherical analyzer, and controlled synchronously by VG SCIENTA software. Angle acceptance of the input lens of the analyzer is ±7°. This restricts the angle acceptance of the combined objective lens and the analyzer system to ±35°. The magnification factor of the analyzer input lens is 5, thus the total magnification factor is 25. To increase the photoelectron signals on the detection plane of the analyzer, we usually use the glancing angle incidence geometry of the X-rays to the sample surface. The analyzer is set up to have the configuration of the entrance slit parallel to the elongated footprint of the X-rays on the sample surface to accept photoelectrons as effectively as possible.

The system has an analysis chamber, which is facilitated with a five axis goniometer (2 rotation axis and *x*, *y*, *z* axis), a preparation chamber, and a load lock for sample introduction. All the