New application fields developed by Hard X-ray Photoelectron Spectroscopy："PHI Quantes"

Katsumi WATANABE[*1], Hiromichi YAMAZUI[*1] and Risayo INOUE[*2]

[*1] Department of Research and Development, ULVAC-PHI, INC., 370 Enzo, Chigasaki 253-8522, Japan
[*2] Analytical Laboratory, ULVAC-PHI, INC., 370 Enzo, Chigasaki 253-8522, Japan

A newly developed "PHI Quantes" is introduced, which enables both XPS(X-ray Photoelectron Spectroscopy) and HAXPES(Hard X-ray Photoelectron Spectroscopy) by using Al Kα and Cr Kα, respectively. HAXPES has advantages comparing with ordinary XPS, such as deeper analysis depth to several 10 nm, surface contamination free analysis, non-destructive interface analysis and chemical state analysis by measuring inner shell electron. Some latest applications are also demonstrated to show the capability of "PHI Quantes".

1. Introduction

X-ray photoelectron spectroscopy (XPS) is a method that analyzes the chemical composition and chemical state of a substance by measuring the electronic states of the elements contained in it. It only obtains information of the surface region up to a depth of a few nanometers because it measures the extremely small kinetic energy of photo-electrons. XPS is used for research and development ac-tivities in many different areas such as semiconductors, components of electronic devices, and chemical products. Typical XPS analyzers use soft X-rays such as Al Kα (1486.6 eV) and Mg Kα (1253.6 eV) as excitation sources, which give large photoionization cross sections.

In contrast, hard X-ray photoelectron spectroscopy (HAXPES) uses excitation sources of hard X-rays (5 to 10 keV). This method provides photoelectrons with kinetic energies several times larger than that of ordinary XPS to detect photoelectrons both from the surface and from deeper areas of a sample. Today, many reports on HAX-PES use synchrotron radiation[1, 2], attracting attention as a relatively new analysis method.

However, because using a synchrotron radiation facility imposes geographical and time restrictions, there has been a strong demand for equipment that can perform HAXPES analyses in the average laboratory. To meet this demand, we developed an equipment called "PHI Quantes" that uses both a conventional Al Kα source and Cr Kα (5414.9 eV) as a hard X-ray source.

This report describes the characteristics of HAXPES, features of "PHI Quantes", and its applications.

2. Characteristics of HAXPES

2.1 Information depth

Since HAXPES uses X-rays with energies of 5 keV or higher[3], it detects large kinetic energy photoelectrons with a long inelastic mean free path (IMFP) from inside the substance. A large IMFP corresponds to a large depth from the surface of a sample from which detectable pho-toelectrons are generated. Figure 1 shows IMFP values versus excitation energies calculated by Tanuma, et al[4]. Assuming the information depth is about three times the IMFP, the information depth is a few nanometers for soft X-rays such as Al Kα and Mg Kα that are used for general XPS analyses, while HAXPES provides information from a depth of tens of nanometers.

As the information depth is extremely small for the con-ventional XPS with its Al Kα or Mg Kα excitation source, a sample surface contaminated with dirt such as hydro-carbon will have a large impact on its measurements. For this reason, sometimes ion-etching or other treatments are used to remove surface contamination. However, ion etching alters the chemical states of some types of sam-ples preventing the analyzer from obtaining correct data. On the other hand, even when the surface is contaminat-ed, as HAXPES has an information depth of tens of nano-meters, it can analyze the electron states of the sample without interference from contaminants.
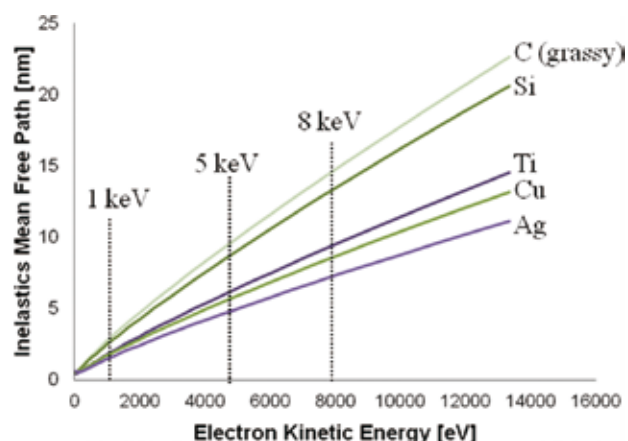

Figure 1　Inelastic mean free path for electron kinetic energies up to 13 keV, for grassy carbon, Si, Ti, Cu and Ag[11].

2.2 Signal intensity

Figure 2 shows the dependence of photoionization cross section on excitation energy for some elements[5]. As seen from the figure, the larger the excitation energy is, the smaller the photoionization cross section is. Therefore, for HAXPES, which uses an excitation source of high-energy X-rays, the photoionization cross section is extremely small. For example, for Si 2p3/2, the photoionization cross section with an excitation energy of 5 keV is smaller than that with an excitation energy of 1 keV by a factor of 100. Moreover, an excitation energy of 5 keV enables detection of Si 1s, which cannot be excited by 1 keV. Its photoionization cross section is equivalent to or larger than that of Si 2p3/2 at 1 keV. Thus, HAXPES can compensate for the decrease in photoionization cross section by measuring inner-shell electrons.

3. Hard X-ray photoelectron spectroscopy equipment: "PHI Quantes"

3.1 Outline of the system

Figure 3 shows an overview of "PHI Quantes". Figure 4 shows its optics. "PHI Quantes" is equipped with Al Kα and Cr Kα sources. This enables a single equipment to have the functions of both XPS and HAXPES and thereby to obtain electronic state information at different information depths. A single point in the vacuum chamber detects the photoelectron spectra induced by these two types of X-rays.

An ultra-high vacuum motor-driven five-axis sample stage moves a sample. The sample is transferred from a sample introduction chamber to the sample stage with a
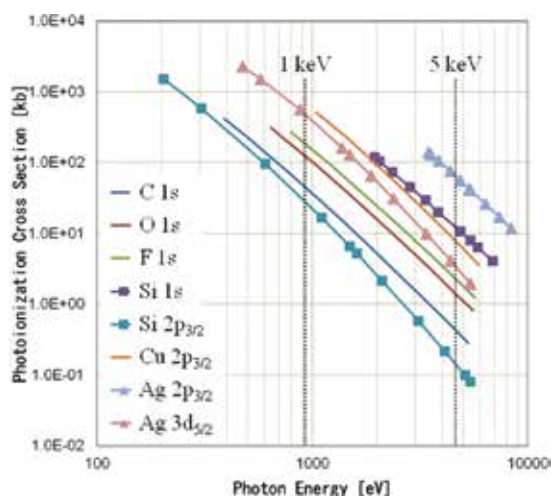

Figure 3　Overview of "PHI Quantes".

mechanism using UHV motors. The analyzer consists of a newly developed high-voltage resistant input lens with an input solid angle of about ±20 degrees and a 6-kV resistant hemispherical electrostatic analyzer. Also, this equipment is equipped with ion guns used for sputter ion etching and charge neutralization compensation, and a low-energy electron gun for charge neutralization compensation.

3.2 Scanning X-ray source

A scanning X-ray source generates both Al Kα and Cr Kα. A single scanning electron gun (with an acceleration voltage up to 20 kV) performs excitation of both X-rays. Al and Cr anode targets are automatically switched by an UHV motor-driven mechanism. As shown in Figure 4, each kind of X-ray is irradiated on a sample via the corresponding Johann-type monochromatic crystal. The monochromatic crystal for Al Kα is a common quartz plate (100) placed on a 200 mm diameter Rowland circle. The monochromatic crystal for Cr Kα is made of Ge (422). It is placed on a 300 mm diameter Rowland circle at 22 de-

Figure 2　Atomic subshell photoionization cross section of C 1s, O 1s, F 1s, Si 1s, Si 2p3/2, Cu 2p3/2, Ag 2p3/2, and Ag 3d5/2[12].

Figure 4　Schematic diagram of "PHI Quantes" optics.

grees from vertical.

Using a scanning X-ray source, this equipment can obtain scanning X-ray images (SXI) by synchronizing the X-ray scan with the capture of secondary electrons from the X-ray irradiated point on the sample. Figure 5 shows SXI observations of a gold grid (200 LPI) using Al Kα and Cr Kα. The spatial resolution of the X-ray scan was 7.5 μm for Al Kα and 15 μm for Cr Kα, which were measured by using the 20-80% knife-edge method. The images in Figure 5 were obtained by switching these X-rays with a fixed sample position. They show that the central points of SXIs by excitations with Al Kα and Cr Kα agree well. The irradiation diameters of both X-rays can be arbitrarily adjusted within 100 μm and selected according to the application. Using the SXI ensures measurement of the correct positions on the sample and also makes it possible to analyze multiple points on a sample. In addition, it can obtain chemical mapping that reflects the chemical state of each point by capturing the spectrum at each point in the X-ray scanning area.

3.3 Measurement using charge neutralization compensation

As XPS is frequently used to measure insulators, accurate charge neutralization compensation is essential. Figures 6 (a) and (b) show F 1s and C 1s XPS spectra of PTFE measured by using Cr Kα.

A 1 eV low-energy electron beam and a 7 eV low-energy Ar$^+$ ion beam were simultaneously irradiated to carry out charge compensation[6]. Although these 1s peaks with relatively large natural widths make it difficult to use peak widths to evaluate the charge neutralization compensation, the peak positions for F 1s and C 1s are 689.1 eV and 292.1 eV, showing a good agreement with the values in the database[7]: 689.0 eV for F 1s and 292.0 eV for C 1s. Moreover, the fact that peak shapes with good symmetry unique to 1s peaks are obtained strongly suggests that the charge neutralization compensation is working correctly. These results show that the charge neutralization compensation used for conventional photoelectron spectroscopy equipment not only works for Al Kα but also for Cr Kα hard X-ray.

4. Applications of "PHI Quantes"

4.1 Assessment of information depth

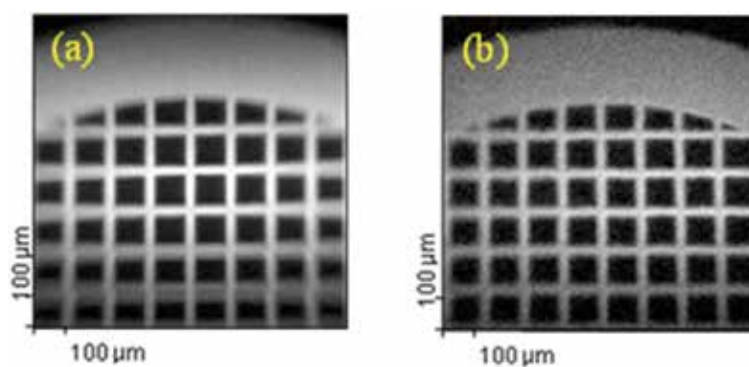The major advantage of installing a Cr Kα hard X-ray source is that it provides large analysis information

Figure 5   Scanning X-ray Image (SXI) of Au grid 200 LPI using Al Kα (a) and Cr Kα (b).
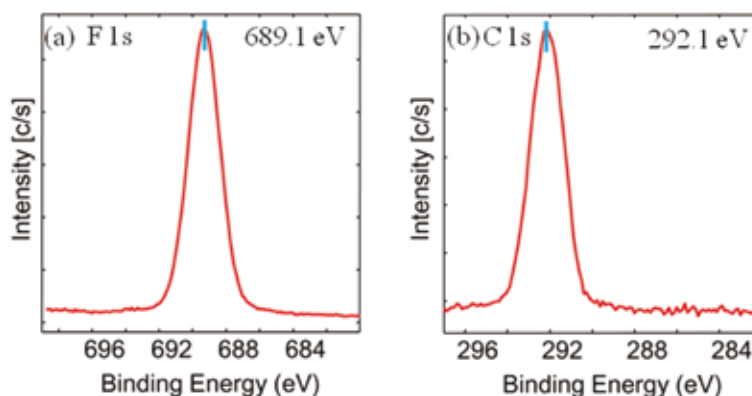

Figure 6   F 1s(a) and C 1s (b) XPS spectra of polytetrafuluoroethylene (PTFE) by Cr Kα XPS using automated charge neutralization.

depths. Presented here are measurement examples that compare the information depth for Cr Kα with that for Al Kα. Figure 7 shows measurements of two SiO$_2$/Si samples with different film thicknesses obtained by using Al Kα and Cr Kα, where the acceptance angle for the analyzer optical axis and the horizontal sample plane was set to 90 degrees. The SiO$_2$ film thicknesses were 10 nm and 30 nm. Figure 7 (a) and (b) are data obtained by using Al Kα, and Figure 7 (c) and (d) are by using Cr Kα.

In these samples, the IMFP of Al Kα excitation is estimated to be 3.7 nm and 11.0 nm for Cr Kα excitation. The information depths calculated from these values are approx. 11 and 33 nm, respectively[8]. Figure 7 (a), the spectrum obtained with Al Kα, shows a peak attributed to the Si substrate, while Figure 7 (b) does not show such a peak. In contrast, Figure 7 (c), the spectrum obtained with Cr Kα, shows strong peaks attributed to the Si substrate, and furthermore, Figure 7 (d) also shows a peak from the Si substrate, indicating a good match with the calculated information depths. The data in Figure 7 support that the information depth for Cr Kα is substantially larger than that for Al Kα.

In Cr Kα excitation, an information depth of tens of nanometers is expected for light elements, and more than 10 nm even for heavy elements, which indicates that electron state information of areas deep inside the surface can be obtained non-destructively. In addition, as seen from Figure 7 (c), the structures[9] of Si$^+$ and Si^{3+} that are supposed to be sub-oxides are observed between the peaks of Si2p3/2 and SiO$_2$. These peaks probably suggest electron states of the buried region of the boundary surface.

4.2 Analysis of copper electrode pads

To analyze a more practical material, samples were made of a copper electrode pattern on a circuit board in a hard-disk drive. Figure 8 shows optical microscope images of copper electrode pads. Some color changes are observed on one of the copper electrodes. It is known that causes of color changes are differences in valence for Cu and differences in oxide film thickness[10]. General XPS analyzers often overlook these differences in color changes due to the small information depth. For this reason, discolored areas are sometimes analyzed by depth profile by ion etching. However, sputtering causes reduction of copper oxide, which can loose chemical state information.

Figure 8 (b) shows details of measured points. Heavily discolored areas (measurement points X and x) and lightly discolored areas (measurement points Y and y) were
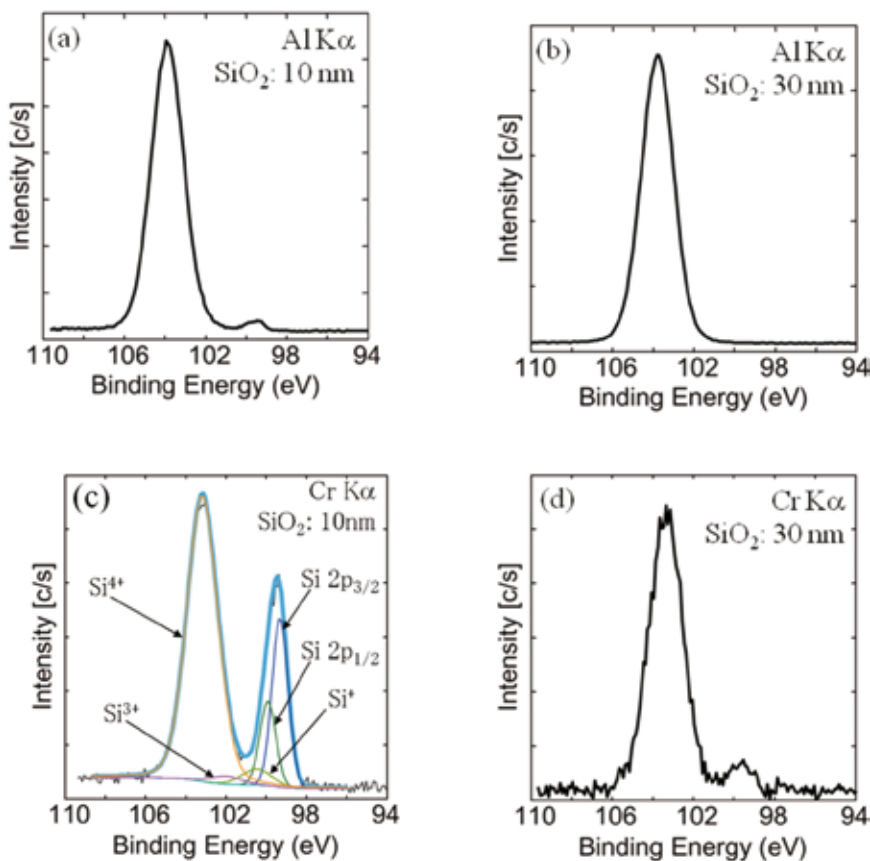

Figure 7   Si 2p Spectra of SiO$_2$(10 nm)/Si and SiO$_2$ (30 nm) / Si, by using Al Kα and Cr Kα.
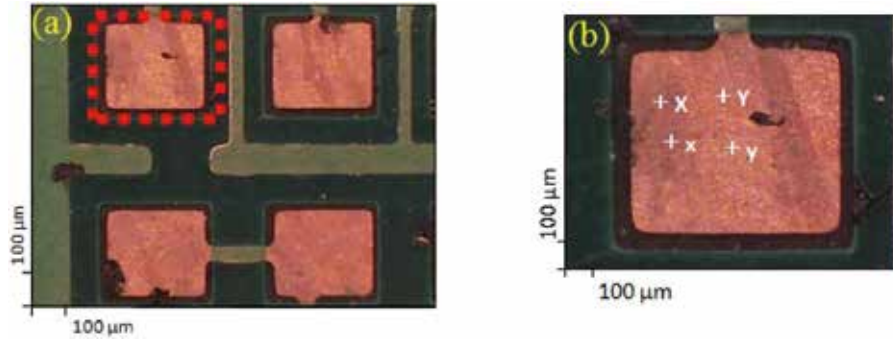
Figure 8　Cu pads on a pattern circuit board (a). The left upper pad in (a) is enlarged in (b). XPS spectra were measured on the points of (X and Y) and (x and y) using Al Kα and Cr Kα, respectively.
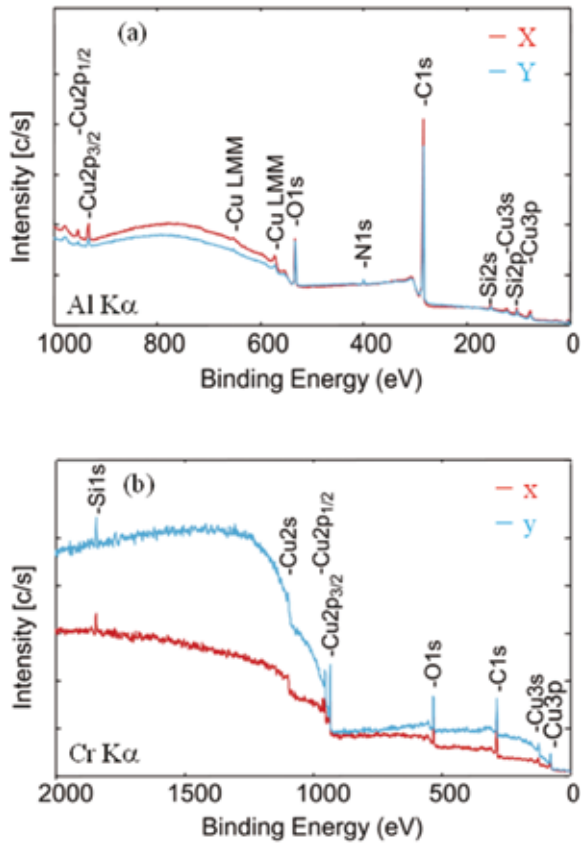

Figure 9　XPS survey spectra by Al Kα (X and Y) and Cr Kα (x and y). The measurement positions of X, Y, x, and y are indicated in Figure 8.

selected. X and Y were measured by using Al Kα, and x and y, by Cr Kα. Charge neutralization was used in these measurement procedures.

Figure 9 shows survey spectra by Al Kα and Cr Kα. The measurement results by Al Kα show strong C 1s peaks, which clearly indicates that the surface is contaminated. Similarly, the spectra obtained with Cr Kα also show strong C 1s, O 1s, and Si 1s peaks, which indicates contamination on the surface. However, the detected elements were the same except for N 1s, and these survey spectra found no large differences among the measure-

ment points.

Figure 10 shows Cu 2p3/2 spectra obtained with Al Kα and Cr Kα. The Cu 2p3/2 spectra obtained with Al Kα show Cu^+ and Cu^{2+} peaks at all points, with a larger amount of Cu^+ being detected. However, these spectra show little difference in chemical state and composition ratio among measurement points, providing no information on the causes of the color changes. Meanwhile, Cu^+ and Cu^{2+} peaks are also included in the Cu 2p3/2 spectra obtained with Cr Kα, and a relatively larger amount of Cu^{2+} was detected from point x, which is heavily discolored. From the theoretical IMFP values[11] of Cu 2p3/2 photoelectrons for these X-ray types, the analysis depth of Cr Kα is estimated to be about five times larger than that of Al Kα.

These measurement results show that the copper electrode pad contains much Cu^+ near the surface regardless of color changes, and that discolored areas contain a relatively larger amount of Cu^{2+} in the regions deeper than the surface.

4.3　Analysis of silicon-on-insulator (SOI)

The preceding section showed examples in which different analysis results were obtained from different information depths by using the two X-ray sources of "PHI Quantes". Next, this section shows the results of analyzing an SOI sample, which provides clearer differences of the results caused by differences in information depth. The sample was provided by Bio-Nano Electronics Research Centre, Toyo University.

Figure 11 shows the layered structure of this sample. A 100 nm thick SiO_2 insulation layer and a 10 nm Si layer are deposited on a silicon substrate. A natural oxide layer exists on the outermost surface because the sample had been in the atmosphere.
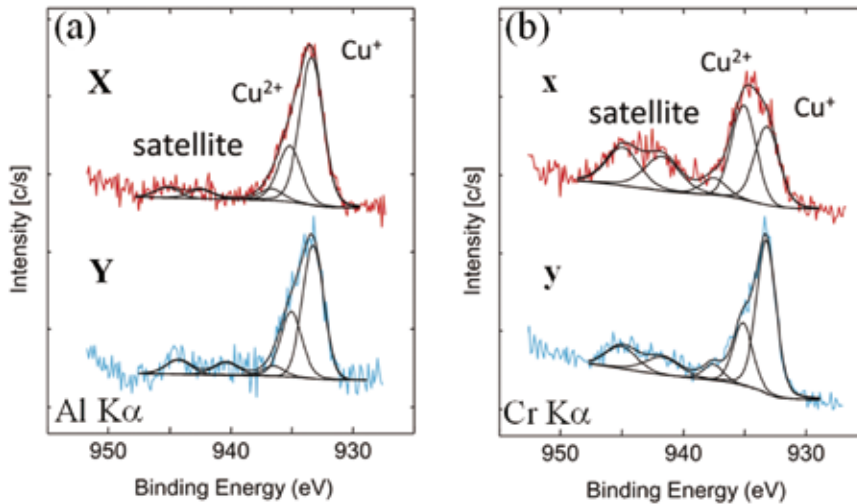
Figure 12 shows angle resolved measurement results

Figure 10　Cu 2p3/2 spectra by Al Kα (X and Y) and Cr Kα (x and y) and results of curve fitting. X, Y, x and y are shown in Figure 8.
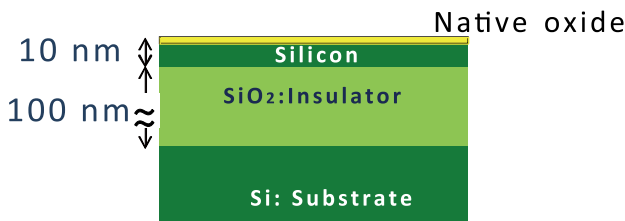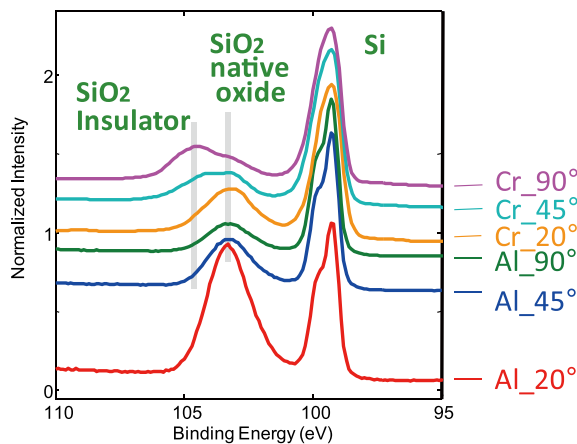

Figure 11　Schematic of SOI sample.

Figure 12　Angle resolved results of shown in Figure 11 by Al Kα and Cr Kα.

by Al Kα and Cr Kα. The take-off angle (angle of the analyzer axis to the sample surface) was set to 20, 45, and 90 degrees for each X-ray source. The larger the take-off angle, the larger the information depth on a sample surface.

The results in Figure 12 show that using Cr Kα helped obtain information on the SiO_2 insulation layer that Al Kα cannot detect. These results show that this analyzer can non-destructively analyze deeper layers and boundary surfaces of a thin-film multilayer structure, which until now could only be analyzed by ion sputter etching.
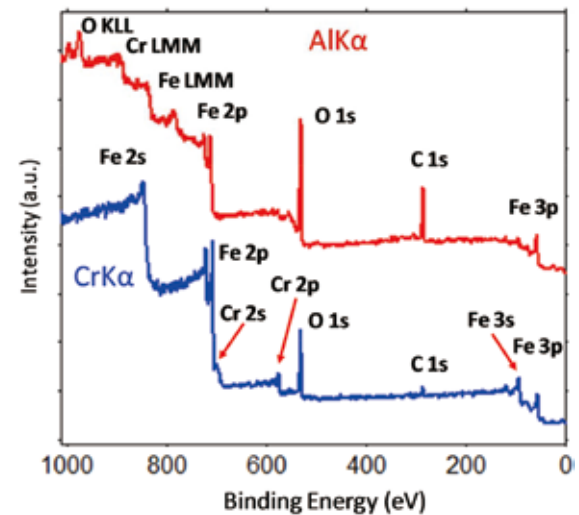
Figure 13　XPS survey spectra of Fe-Cr alloy sample by Al Kα and Cr Kα.

4.4　Metal surface analysis

In the analysis of metallic elements, photoelectron peaks are often superimposed with X-ray-excited Auger transition peaks. This sometimes makes analysis difficult. Figure 13 shows survey spectra of an Fe-Cr alloy obtained by using the two X-ray sources. The spectra obtained with Al Kα include superposition of Auger electrons of oxygen, chromium, iron, and other elements on the high binding energy side as mentioned above. This makes the details of the photoelectron peaks less clear. On the other hand, in the analysis using Cr Kα, Auger electrons that have kinetic energies unique to each element move to an even higher binding energy range, leaving no superposition of peaks as are observed in the spectra obtained with Al Kα. Thus, HAXPES, which uses high-energy X-ray sources, can avoid superposition of Auger transition peaks.

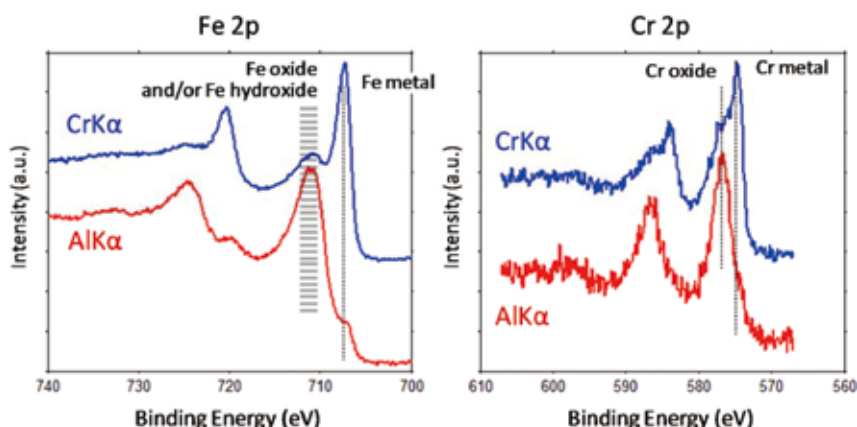Figure 14 shows details of Fe 2p and Cr 2p spectra.

Figure 14　Fe2p and Cr2p spectra of shown in Figure 13.

There are peaks that derive from oxides and hydroxides for both X-ray sources, while they are more conspicuous especially for Al Kα. In contrast to the spectra obtained with Al Kα, peaks that derive from metallic elements are stronger for Cr Kα. These data suggest that there exist large amounts of oxides and hydroxides of Fe and Cr on the Fe-Cr alloy, and the metallic state is maintained in the region deep inside the surface (a little over 10 nanometers).

5.　Conclusion

In contrast to conventional XPS, this report described an outline of the new product "PHI Quantes" that newly features HAXPES, including application examples.

HAXPES is an analysis method with great capabilities and potential. It can analyze regions deep inside the surface, perform non-destructive analysis without being affected by surface contamination, and analyze inner-shell electron states, which is impossible with conventional XPS. In addition, equipped with two types of X-ray sources, it can make use of both of their features when evaluating materials. Until now, HAXPES has only used synchrotron radiation. The authors hope the laboratory-type "PHI Quantes" will be used enough to make HAXPES a "household name" (albeit in laboratories), and that it will prove useful for preliminary analysis before using synchrotron radiation.

Part of this paper includes some content from the authors' article "Laboratory Hard X-ray Photoelectron Spectroscopy," Journal of the Surface Science Society of Japan[12].

References

1)　T. Ishikawa, K. Tamasaku and M. Yabashi: Nucl. Instrum. Methods Phys. Res., Sect. A, 547, 42 (2005).

2)　K. Kobayashi, M. Yabashi, Y. Takata, T. Tokushima, S. Shin, K. Tamasaku, D. Miwa, T. Ishikawa, H.Nohira, T. Hattori, Y. Sugita, O. Nakatsuka, A. Sakaiand S. Zaima: Appl. Phys. Lett., 83, 1005 (2003).

3)　M. Kobata, K. Kobayashi: Journal of Vacuum Society Japan: 58 (2), 43 (2015).

4)　H. Shinotsuka, S. Tanuma, C. J. Powell and D. R. Penn: Surf. Interface Anal. 47 (9), 871 (2015).

5)　M. B. Trzhaskovskaya, V. I. Nefedov and V. G. Yarzhemsky: At. Data Nucl. Data Tables 82, 257 (2002).

6)　P. E. Larson, M. A. Kelly: J. Vac. Sci. Technol. A16, 3483 (1998).

7)　J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben: "Handbook of X-ray Photoelectron Spectroscopy" ed. by J. Chastain, R. C. King, Jr. (Physical Electronics, Inc., 1995).

8)　H. Ishii, S, Mamishin, K. Tamura, W. G. Chu, M. Owari, M. Doi, K. Tsukamoto, S. Takahashi, H. Iwai, K. Watanabe, H. Kobayashi, Y. Kita, H. Yamazui, M. Taguchi, R. Shimizu and Y. Nihei: Surf. Interface Anal. 37, 211 (2005).

9)　Y. Takata: The Japanese Society for Synchrotron Radiation Research 17, 66 (2004).

10)　Y. Haijima, A. Matsumura, T. Sugiyama, S. Tomonaga, M. Dobashi and I. Koiwa: Journal of The Surface Finishing Society of Japan, 59-12, 920 (2008).

11)　S. Diplas, J. F. Watts, P. Tsakiropoulos, G. Shao, G. Beamson and J. A. D. Matthew: Surf. Interface Anal. 31, 734 (2001).

12)　H. Yamazui, R. Inoue, N. Sanada, K. Watanabe: J. Surf. Sci. Soc. Jpn., Vol.37, No.4, p150, 2016. (in Japanese).