Chapter 132
X-Ray Photoelectron Spectroscopy

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Keywords Photoelectron · Auger electron · Spectroscopy · X-ray
Surface analysis · Chemical state

132.1 Principle

When an X-ray is irradiated to a solid sample, electrons are emitted by photoelectric and Auger effects. The kinetic energy (E_{kin}) of these electrons is measured precisely using a concentric hemispherical analyzer (CHA). A characteristic X-ray of narrow energy width usually used as a probe. (e.g., Mg-Kα, Al-Kα) Fig. 132.1 shows the details of the photo- and Auger electron emission processes. The XPS spectra are usually indicated by electron intensity depending on binding energy (E_{bin}). When measuring the E_{kin} of a photoelectron, the following equation can be used.

$$E_{\mathrm{bin}} = h\nu - E_{\mathrm{kin}} - \Phi_{\mathrm{ana}}.$$

Here, $h\nu$ and Φ_{ana} are the probe energy and the work function of the analyzer, respectively. (The latter actually becomes the work function of the analyzer because the sample and the analyzer have the same potential at the XPS measurement though Φ is usually a work function of the sample.) We can assign sample constituent elements to measure the E_{bin} of a photoelectron peak because the XPS spectrum reflects the electron orbital of sample constituent elements directly. In addition, it is possible to guess the surface composition from the intensity of the detected peaks. The key feature of XPS is that it can presume the chemical state of

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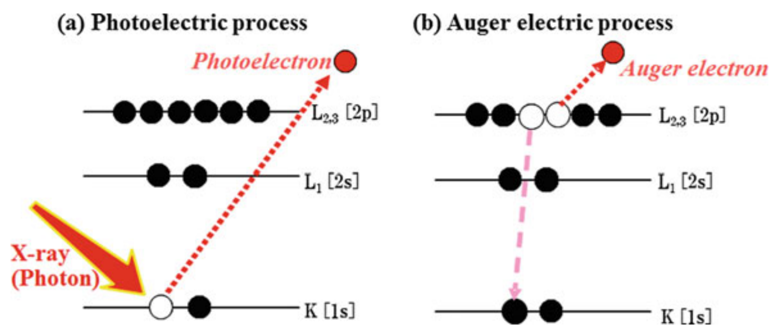

Fig. 132.1 Schematic diagram of the photo-electric and Auger electric processes. **a** the core electron receives the energy from irradiated X-rays, and this is emitted, **b** an outer electron transits to the hole, another electron receive the excess energy equals to the difference between two energy levels indicated by the pink dashed line, and this is emitted

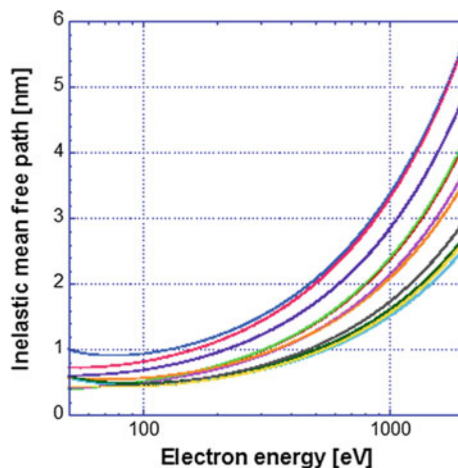

Fig. 132.2 IMFP of variable material depends on electron energy (calculation result using TPP-2 M [1])

the elements that comprise the sample surface. Here, the maximum kinetic energy of the electron measured with ordinary XPS is about 1400 eV or less. The electron in such an energy region easily loses energy through inelastic scattering in the solid. Therefore, information on the source atom, which one can obtain from the emitted electron, is easily lost. The distance that can be traveled through the solid by these electrons without energy loss is defined as the inelastic mean free path (IMFP). It is possible to estimate this using TPP-2 M [1] though the IMFP is different according to electron energy and the sample (Fig. 132.2). TPP-2 M is applicable to electrons of the energy of 30 keV or less [2]. For this reason, XPS only detects information on the surface of the solid sample.

132.2 Features

- Surface analysis [<10 nm]. (usually)
- Qualitative and quantitative analyses of all elements except H and He. (Because the photoionization cross-section of H and He is extremely small.) Detection limit is about 0.1 A. C.%.
- The chemical state can be characterized. (peak position and shape.)
- Depth profiling using an ion to sputter away the surface during analysis, angle-resolved measurement and the background shape.
- The minimum analysis region is about 1 μm (the difference in the chemical state can be mapped).
- Thickness measurement of over layers of 10 nm or less on a substrate.

132.3 Instrumentation

A conventional XPS system is composed of an X-ray source, energy analyzer (CHA), manipulator, ion gun, and the sample introduction system by which the computer is controlled. These major components are enclosed in ultra-high vacuum (UHV) and magnetic shielding usually made of Mu-metal (Fig. 132.3). Recently, monochromators have come into widespread use as the X-ray source. Here, a low-energy electron gun serving as the neutralizer is essential to analyze the insulator sample using the monochromator. The use of the monochromator has the following advantage: high energy resolution, reduced background, no satellite peaks, and reduced irradiation damage. Recent developments include cluster ion beam [3] for reducing ion irradiation damage and high energy X-ray sources [4] for in-depth analysis to obtain more internal information. Moreover, a special type of XPS has recently become available that can be deployed without putting the sample in a UHV [5] enclosure.

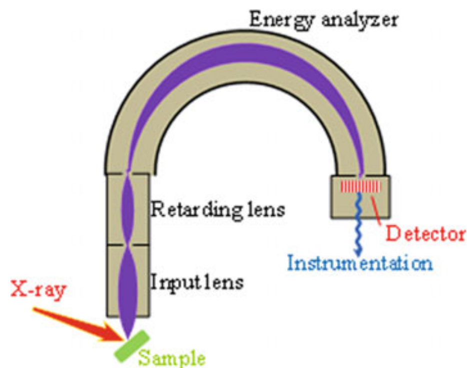

Fig. 132.3 Schematic diagram of XPS system

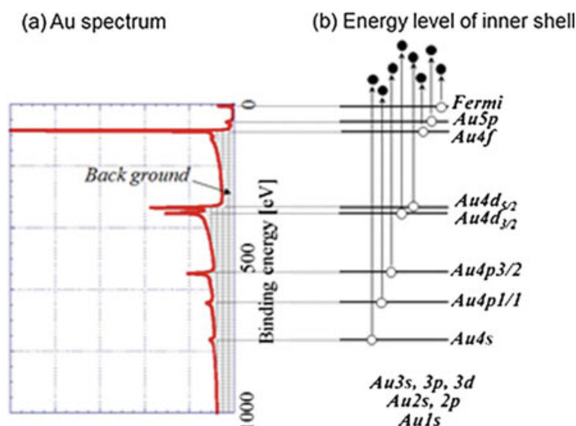

Fig. 132.4 Example of showing that XPS reflects electronic orbit directly. **a** survey spectrum of Au, **b** energy level of inner shell of Au

132.4 Applications

XPS is used in a multitude of fields including metals, catalysts, organisms, semi-conductors, and ceramics-related materials. It is used mainly for composition analysis and for the chemical state analysis of sample surfaces. XPS is widely used, with many documents published that standardize the measurement and calibration procedure. The International Organization for Standardization (ISO) list of documents concerning XPS is appended at the end of this paper. The survey spectrum and energy levels of the inner shell of Au are shown in Fig. 132.4. It is clear that the XPS spectrum reflects the electron state of the inner shell directly. (The background and Auger peaks are excluded.) The XPS qualitative analysis uses the fingerprint method (handbook or database). The surface composition is calculated from the peak area that originates in each element. As a general rule, presumption of the surface composition uses the relative sensitivity factor (RSF) method for the following equation.

$$C_i = \frac{[I_i/RSF_i]}{\left[\Sigma\left(I_j/RSF_j\right)\right]}$$

Here, C_i is the concentration of the element i. I_i and RSF_i correspond, respectively, to the peak area intensity and relative sensitivity factor of the element i. Moreover, j shows each element to use in the quantification. When the peak area and the peak position are measured with XPS, the background of the peak must be defined. The following 3 methods are usually used to define the background: (1) straight line type, (2) integration type (Shirley method [6] and the improved version), and (3) deconvolution type (a representative example is the Tougaard type [7]). It is necessary to understand the feature and to use it properly according to the intended purpose. There is a report that compares the methods of defining the background [8]. When the chemical state of the sample is presumed using XPS, it is

important to use the system with sufficient correction because the binding energy value is usually compared with a reference, and the chemical state is presumed. It should be noted that there is a possibility that the system used by the reference is not sufficiently corrected.

An example of detecting the chemical state difference using XPS on the sample surface is shown in Fig. 132.5. This is the C1s spectrum after removing silicon oxide deposited on the silicon substrate by reactiveness ion etching (RIE) with CHF_3 gas plasma. By etching silicon oxide with fluorocarbon gas plasma, silicon is exposed, the fluorocarbon polymer is deposited on the silicon surface, and the etching stops in a high selective ratio. The peak detected on the high binding energy side in Fig. 132.5 depends on the amount of fluorine.

Figure 132.6 shows a result of XPS analysis using Mg-kα after a native oxide on the silicon wafer is removed with diluted hydrogen fluoride solution. It is not well known that the peak exists in the negative binding energy region. These peaks correspond to Si-KLL Auger electrons excited by bremsstrahlung X-rays from a Mg target, and the peaks are about 1610 eV in E_{kin} mode. When the chemistry is presumed, the Auger peak in a negative binding energy region is useful [9, 10]. The result of comparing the photoelectron with an Auger electron peak excited by

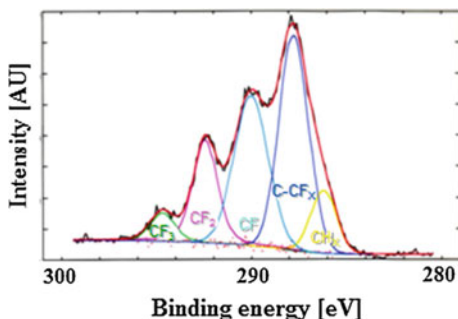

Fig. 132.5 C1 s spectrum on Si surface after SiO_2 is removed using RIE

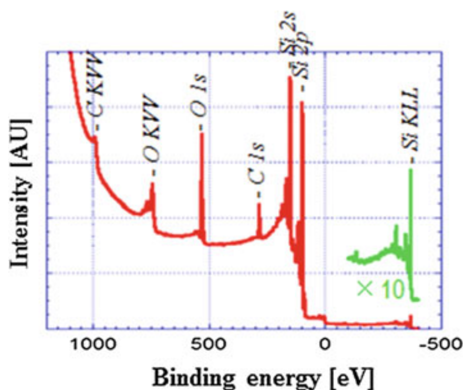

Fig. 132.6 XPS analysis result of Si wafer after natural oxide is removed by d-HF

X-rays is shown in Fig. 132.7 [9]. Here, the sample used is thin silicon nitride [5 nm] that is deposited on the silicon wafer using low-pressure chemical vapor deposition (LPCVD). The difference between the silicon oxide and the silicon nitride can be clearly distinguished by using the Si-KLL peak which appears in negative binding energy region (Fig. 132.6). The Auger peak excited by the bremsstrahlung X-rays has extremely small background with very low intensity. As a result, a nitride and interfacial oxide film thickness were estimated, and the process was optimized.

The background can be greatly decreased by using the grazing incidence (GI) X-ray as a probe. As a result, it becomes possible to lower the detection limit. (The detection limit of a Si wafer surface using conventional XPS measurement is about 1×10^{13}–1×10^{14} atoms/cm^2.) [11] It is reported that the detection limit can be improved using the total reflection (TR-) XPS [11]. (The detection limit of Fe and Cu improved 1×10^{11}, 9×10^{10} atoms/cm^2, respectively.) Reduction of the background using GI-XPS was attempted using a commercially available XPS system [12]. Figure 132.8 shows the geometric diagram of the GI-XPS measurement. The lower half of the flux of X-rays from the monochromator was cut with the sample and the sample holder, and the high angle incidence flux of the upper half was able to be cut with the adjustable shutter. As a result, only parallel X-rays are irradiated to the sample. Figure 132.9 shows the result of measuring the silicon wafer from which the native oxide is removed using a diluted hydrogen fluoride solution by conventional XPS and GI-XPS. It is clear that the background can be dramatically reduced using GI-XPS and the background is equivalent with TR-XPS.

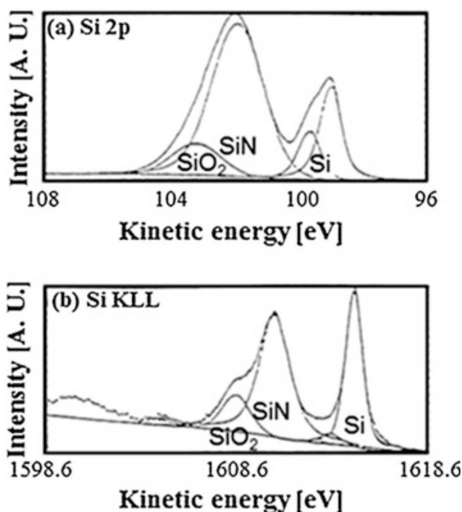

Fig. 132.7 The Auger peak detected in the negative binding energy region is a useful example in evaluating the chemical state analysis. **a** Si 2p spectrum, **b** Si-KLL spectrum

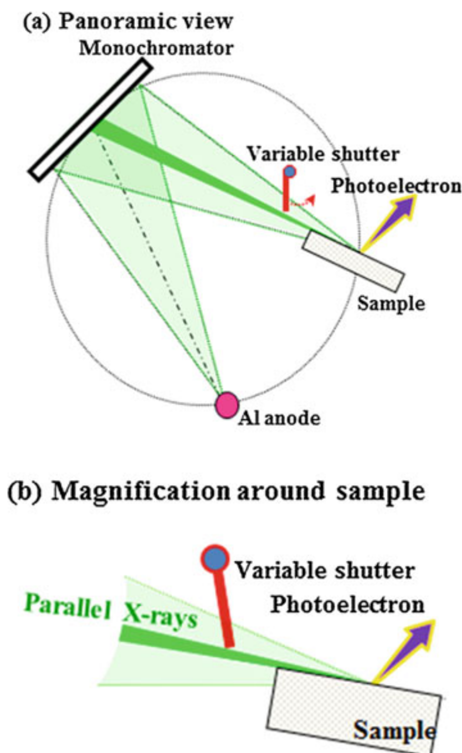

Fig. 132.8 Schematic diagrams of GI-XPS. **a** panoramic view, **b** magnification around sample

The principle and the features of XPS were clearly recorded, and some analysis examples were introduced though there was a lot of XPS application. For instance, a thin film thickness measurement [13], a chemical depth profile using cluster ions [14–16], a nondestructive depth profile using angle-resolved XPS [16–20], a chemical mapping [21] a work function measurement [19, 22, 24, 25], HA-XPS [23] and a band gap measurement [19, 24, 25], etc. There is a good textbook available [26–28] which describes XPS analysis.

Appendix: List of ISO Documents Concerning XPS (Aug. 2016)

Terminology	
ISO 18115-1	Surface chemical analysis—Vocabulary—Part 1: General terms and terms used in spectroscopy
ISO 18115-2	Surface chemical analysis—Vocabulary—Part 2: Terms used in scanning probe microscopy

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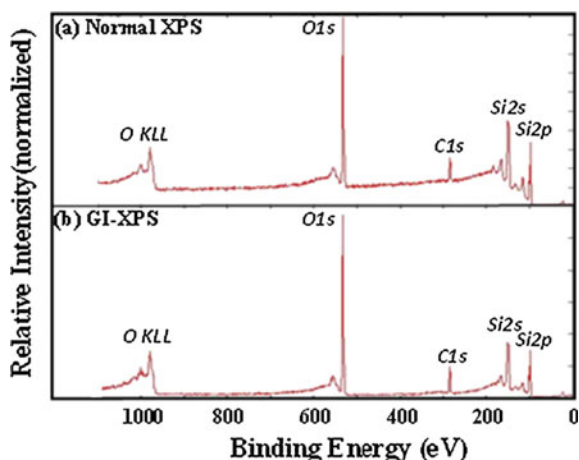

Fig. 132.9 Survey spectra of Si wafer. **a** conventional XPS measurement, **b** GI-XPS measurement

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General procedures	
ISO 16243	Surface chemical analysis—Recording and reporting data in X-ray photoelectron spectroscopy (XPS)
ISO 18116	Surface chemical analysis—Guidelines for preparation and mounting of specimens for analysis
ISO 18117	Surface chemical analysis—Handling of specimens prior to analysis
ISO 18516	Surface chemical analysis—Determination of lateral resolution and sharpness in beam-based methods
ISO 19319	Surface chemical analysis—Fundamental approaches to determination of lateral resolution and sharpness in beam-based methods
ISO 20579-1	Surface chemical analysis—Sample handling, preparation, and mounting—Part 1: Guidelines for handling of specimens prior to analysis
ISO 20579-2	Surface chemical analysis—Sample handling, preparation, and mounting—Part 2: Guidelines for preparation and mounting of specimens prior to analysis
ISO 20579-3	Surface chemical analysis—Sample handling, preparation, and mounting—Part 3: Biomaterials
ISO 20579-4	Surface chemical analysis—Sample handling, preparation, and mounting—Part 4: Nanomaterial reporting requirements, analysis challenges, and solution extraction methods
Data management and treatment	
ISO 14975	Surface chemical analysis—Information formats
ISO 14976	Surface chemical analysis—Data transfer format
ISO 22048	Surface chemical analysis—Information format for static secondary ion mass spectrometry
ISO 28600	Surface chemical analysis—Data transfer format for scanning probe microscopy

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Depth profiling	
ISO 14606	Surface chemical analysis—Sputter depth profiling—Optimization using layered systems as reference materials
ISO 15969	Surface chemical analysis—Depth profiting—Measurement of sputtered depth
ISO 16531	Surface chemical analysis—Depth profiling—Methods for ion beam alignment and the associated measurement of current or current density for depth profiling in AES and XPS
ISO 17109	Surface chemical analysis—Depth profiling—Method for sputter rate determination in X-ray photoelectron spectroscopy, Auger electron spectroscopy, and secondary-ion mass spectrometry sputter depth profiling using single and multilayer thin films
ISO 22335	Surface chemical analysis—Depth profiling—Measurement of sputtering rate: mesh replica method using a mechanical stylus profilometer
Electron spectroscopies	
ISO 10810	Surface chemical analysis—X-ray photoelectron spectroscopy—Guidelines for analysts
ISO 13424	Surface chemical analysis—X-ray photoelectron spectroscopy—Reporting of results of thin film analysis
ISO 14187	Surface chemical analysis—Characterization of nanostructured materials
ISO 14701	Surface chemical analysis—X-ray photoelectron spectroscopy—Measurement of silicon oxide thickness
ISO 15470	Surface chemical analysis—X-ray photoelectron spectroscopy—Description of selected instrumental performance parameters
ISO 15472	Surface chemical analysis—X-ray photoelectron spectrometers—Calibration of energy scales
ISO 16129	Surface chemical analysis—X-ray photoelectron spectroscopy—Procedures for assessing the day-to-day performance of an X-ray photoelectron spectrometer
ISO 18118	Surface chemical analysis—Auger electron spectroscopy and X-ray photoelectron spectroscopy—Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials
ISO 18392	Surface chemical analysis—X-ray photoelectron spectroscopy—Procedures for determining backgrounds
ISO 18554	Surface chemical analysis—Electron spectroscopies—Procedures for identifying, estimating, and correcting for unintended degradation by X-rays in a material undergoing analysis by X-ray photoelectron spectroscopy
ISO 19318	Surface chemical analysis—X-ray photoelectron spectroscopy—Reporting of methods used for charge control and charge correction
ISO 19668	Surface chemical analysis—X-ray photoelectron spectroscopy—Estimation of detection limits
ISO 19830	Surface chemical analysis—Electron spectroscopies—Minimum reporting requirements for peak fitting in X-ray photoelectron spectroscopy
ISO 20903	Surface chemical analysis—Auger electron spectroscopy and X-ray photoelectron spectroscopy—Methods used to determine peak intensities and information required when reporting results

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ISO 21270	Surface chemical analysis—X-ray photoelectron and Auger electron spectrometers—Linearity of intensity scale
ISO 24237	Surface chemical analysis—X-ray photoelectron spectroscopy—Repeatability and constancy of intensity scale

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