Hard X-ray Photoelectron Spectroscopy (HAXPES)

The basic principle of hard x-ray photoelectron spectroscopy is similar to that of general XPS, which irradiates excitation light on the sample surface and measures the kinetic energy of the photoelectrons emitted. While the photon energy of the monochromatic AlK α x-ray source most commonly used in traditional XPS instruments is 1486.6 eV, the photon energy of the excitation source used in hard x-ray photoelectron spectroscopy is 5 to 8 keV, more than triple. Therefore, the photoelectron spectrum achieved using hard x-ray contains a lot of information that was not available with general XPS.

Advantages of Hard X-ray Photoelectron Spectroscopy

Due to the high incident energy of hard x-ray, photoelectrons from a deeper core level can be excited compared to soft x-ray. For example, when the target is Si, soft x-ray can excite up to the 2s orbit only, but hard x-ray can excite up to the 1s orbit. Figure 1 shows an example of photoelectron excitation using AlK α x-ray source (hv=1486.6 eV) and CrK α x-ray source (hv=5414.8 eV).



Photoelectron excitation using AIK α X-ray source Photoelectron excitation using CrK α X-ray source

Figure 1. Diagram of photoelectron excitation on Si

While photoelectron excitation from the core is possible, when the excitation energy becomes high, photoionization cross-section decreases significantly. Photoionization cross-section is a physical quantity associated with the process of photoelectron excitation, and the strength of the spectrum is proportional to this value. Figure 2 plots the photoionization cross-section of Si and Ag by excitation energy. In the Si $2p_{3/2}$ and Ag $3d_{5/2}$ mainly measured with AlK α x-ray source, when the excitation energy increases from 1.5 keV to 5.0 keV, photoionization crosssection decreases by one to two digits. However, with Si 1s and Ag $2p_{3/2}$, which can be measured with CrK α X-ray source, the decrease in photoionization cross-section associated with excitation energy is small, and the ionization cross-section at excitation energy 1.5 keV and 5.0 keV are more or less the same.



Figure 2. Photoionization cross-section for excitation energy

Thus, since hard x-ray photoelectron spectroscopy can measure more core levels compared to soft x-ray, the most appropriate level can be measured depending on the objective by avoiding overlapped peaks or selecting deep core level.



Figure 3. Elements and energy level that can be excited by each X-ray source

Information from Deep Areas

The escape depth of a photoelectron is similar to the Inelastic Mean Free Path (IMFP) of an electron in materials, and the depth of the photoelectron information received as a signal is known to be around two to three times the IMFP. An advantage of HAXPES is that information from deeper areas can be obtained by using high-energy X-ray.

For example, in the case of AlK α and CrK α X-ray source, CrK α X-ray source can obtain information from a depth three times deeper than that of AlK α X-ray source. When measuring with CrK α X-ray source, the impact of contamination, absorbed species, and natural oxidation layer become relatively smaller, so a photoelectron spectrum closer to the original sample

information can be obtained. Additionally, nondestructive analysis of the surface where the sample is buried is possible, raising expectations for samples that were difficult to evaluate with AlK α X-ray source.



Figure 4. Difference in information depth between CrKa and AlKa X-ray source

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