What is XPS?

X-ray photoelectron spectroscopy (XPS) is a surface analytical technique, which is based upon the photoelectric effect. Each atom in the surface has core electron with the characteristic binding energy that is conceptually, not strictly, equal to the ionization energy of that electron. When an X-ray beam directs to the sample surface, the energy of the X-ray photon is adsorbed completely by the core electron of an atom. If the photon energy, h , is large enough, the core electron will then escape from the atom and emit out of the surface. The emitted electron with the kinetic energy of E_k is referred to as the photoelectron. The binding energy of the core electron is given by the Einstein relationship:

$$E_b = h\nu - E_k - \phi$$

Where h is the X-ray photon energy (for monochromatic Al Ka, h = 1486.6eV);E_k is the kinetic energy of photoelectron, which can be measured by the energy analyzer; and Φ is the work function induced by the analyzer, about 4%7e5eV. Since the work function, Φ, can be compensated artificially, it is eliminated, giving the binding energy as follows:

$$E_b = h\nu - E_k$$

For insulating samples, once the photoelectrons are emitted out of the sample surface, a positive charge zone will establish quickly in the sample surface. As a result, the sample surface acquires a positive potential (varying typically from several volts to tens of volts) and the kinetic energies of core electrons are reduced by the same amount,C.

$$E_b = h\nu - (E_k - C)$$

It can be seen that the surface charging results in the shift of the XPS peaks to higher binding energy. In this case, the binding energy has to be calibrated with an internal reference peak. The C 1s peak from the adventitious carbon-based contaminant, with the binding energy of 284.8eV, is commonly used as the reference for calibration. In order to neutralize the surface charge during data acquisition, a low-energy electron flood gun is used to deliver the electrons to the sample surface. The electron flood gun can be tuned to provide the right current to push the XPS peaks back to the real position.

The core electron of an element has a unique binding energy, which seems like a "fingerprint". Thus almost all elements except for hydrogen and helium can be identified *via* measuring the binding energy of its core electron. Furthermore, the binding energy of core electron is very sensitive to the chemical environment of element. The same atom is bonded to the different chemical species, leading to the change in the binding energy of its core electron. The variation of binding energy results in the shift of the corresponding XPS peak, ranging from 0.1eV to 10eV. This effect is termed as "chemical shift", which can be applied to studying the chemical status of element in the surface. Therefore, XPS is also known as electron spectroscopy for chemical analysis (ESCA).

Since the number of photoelectron of an element is dependent upon the atomic concentration of that element in the sample, XPS is used to not only identify the elements but also quantify the chemical composition. After the value of peak intensity (the peak area after background removal) is obtained, the atomic concentration of an element, C_i, can be expressed as:

$$C_i = \frac{I_i / S_i}{\sum_i I_i / S_i}$$

Where I_i is the peak intensity for element i, and S_i is the sensitivity factor for the peak i.

[Reference: Surface analysis method in materials science, edited by D. J. O'connor, B. A. Sexton, R. St. C. Smart, Springer-Verlag, Heidelberg, (1992).]