

MSE 310 Lecture 15

X-ray Photoelectron Spectroscopy

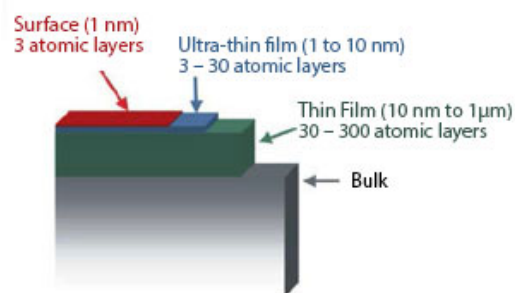
27/3/2021

Introduction

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a technique for analyzing the surface chemistry of a material. XPS can measure the elemental composition, empirical formula, chemical state and electronic state of the elements within a material.

XPS is a powerful measurement technique because it not only shows what elements are present, but also what other elements they are bonded to. The technique can be used in line profiling of the elemental composition across the surface, or in depth profiling when paired with ion-beam etching. It is often applied to study chemical processes in the materials in their as-received state or after cleavage, scraping, exposure to heat, reactive gasses or solutions, ultraviolet light, or during ion implantation.

A surface layer is defined as being up to three atomic layers thick (~1 nm), depending upon the material. Layers up to approximately 10 nm are considered ultra-thin films, and layers up to approximately 1 μm are thin films. The remainder of the solid is referred to as bulk material. This terminology is not definitive however, and the distinction between the layer types can vary depending upon the material and its application.



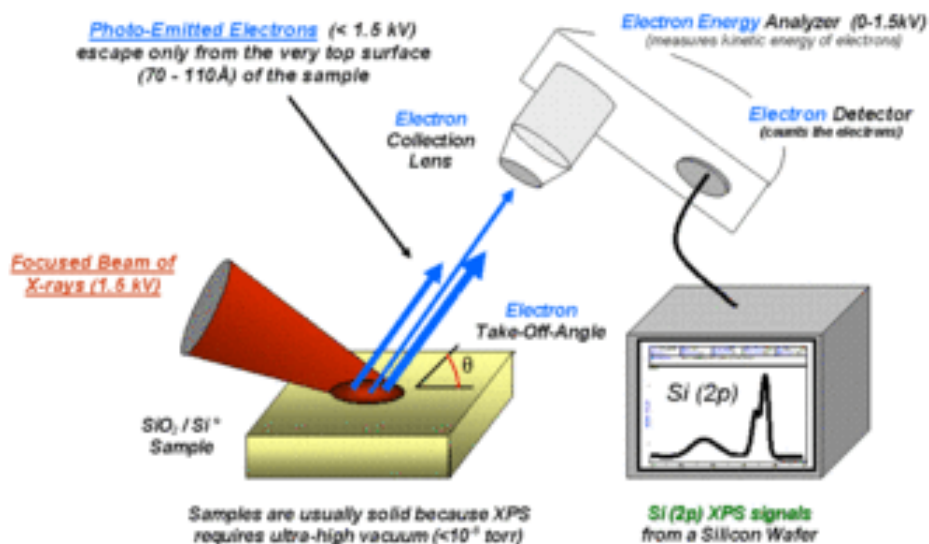
The surface represents a discontinuity between one phase and another and, therefore, the physical and chemical properties of the surface are different from

those of the bulk material. These differences affect the topmost atomic layer of the material to a large extent. In the bulk of the material, an atom is surrounded on all sides in a regular manner by atoms composing that material. Because a surface atom is not surrounded by atoms on all sides, it has bonding potential, which makes the surface atom more reactive than atoms in the bulk.

Photoemission principle: When an **x-ray** bombards a sample, some electrons become excited enough to escape the atom.

Instrumentation

The main components of an **XPS** system are the source of **X-rays**, an ultra-high vacuum (UHV) chamber with metal magnetic shielding, an electron collection lens, an electron energy analyzer, an electron detector system, a sample introduction chamber, sample mounts, a sample stage with the ability to heat or cool the sample, and a set of stage manipulators.



Working

It is a relatively simple technique where the sample is illuminated with X-rays which have enough energy to eject an electron from the atom. These ejected electrons are known as photoelectrons. The kinetic energy of these emitted electrons is characteristic of the element from which the photoelectron originated.

The position and intensity of the peaks in an energy spectrum provide the desired chemical state and quantitative information. The surface sensitivity of XPS is determined by the distance that that photoelectron can travel through the material without losing any kinetic energy. These elastically scattered photoelectrons contribute to the photoelectron peak, whilst photoelectrons that have been inelastically scattered, losing some kinetic energy before leaving the material, will contribute to the spectral background.

The chemical environment of an atom alters the binding energy (BE) of a photoelectron which results in a change in the measured kinetic energy (KE). The BE is related to the measured photoelectron KE by the simple equation;

$BE = hv - KE$ where hv is the photon (x-ray) energy. The chemical or bonding information of the element is derived from these chemical shifts.

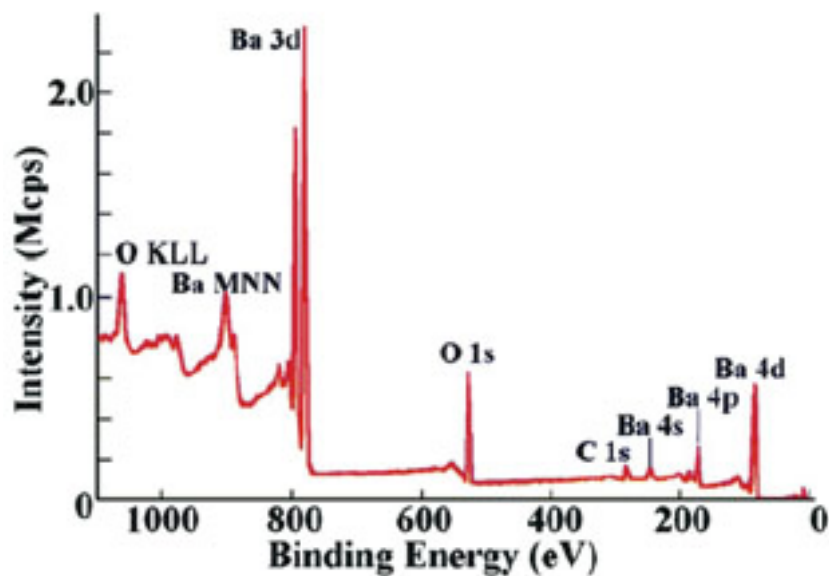
XPS involves irradiating the sample with low energy (~ 1.5 keV) X-rays such that photoelectric effect is induced. An electron spectrometer with high resolution records the energy spectrum of emitted photoelectrons. Highest available vacuum or ultra high vacuum conditions are required for XPS experiments. High vacuum assists photoelectron transport to the analyzer, and also avoids recontamination of clean samples. Contamination is an important concern in XPS, since it is a surface sensitive technique and the sampling depth is usually a few nm.

XPS spectrum

A typical XPS spectrum is a plot of the number of electrons detected at a specific [binding energy](#). Each element produces a set of characteristic XPS peaks. These peaks correspond to the [electron configuration](#) of the electrons within the atoms, e.g., $1s$, $2s$, $2p$, $3s$, etc. The number of detected electrons in each peak is directly related to the amount of element within the XPS sampling volume. To generate atomic percentage values, each raw XPS signal is corrected by dividing the intensity by a *relative sensitivity factor* (RSF), and normalized over all of the elements detected. Since hydrogen is not detected, these atomic percentages exclude hydrogen.

To demonstrate an XPS spectrum, a survey spectrum of barium oxide was produced using a wide energy range. The spectrum shows various barium and

oxygen peaks as well as a carbon peak, which is a surface impurity. The barium oxide spectrum can be collected in approximately 10 seconds with a modern XPS spectrometer. Because barium oxide is an insulator, a low energy electron beam was directed onto the specimen during analysis to control specimen charging. There is a significant background beneath the peaks in the spectrum, which is caused by electrons that are inelastically scattered before leaving the sample surface. Such scattering reduces the kinetic energy of the electrons and reduces intensity from the peaks. The background must be removed from the spectrum before quantifying the spectrum.



XPS easily detects all elements except [hydrogen](#) and [helium](#). Hydrogen has no core electrons and, therefore, core-electron XPS is impossible. The H 1s electrons are valence electrons and as such participate in chemical bonding. And also the diameter of these orbitals [H (1) and He (2)] is so small, reducing the catch probability to almost zero.