X-ray Photoelectron Spectroscopy

Physics of XPS
X-ray Photoelectron Spectroscopy (XPS) is a technique to obtain qualitative or quantitative information of the elemental composition of surfaces. To be exact it can determine: chemical state of the elements in the sample, binding energy of electron states, thickness of layers of different materials near the surface, density of electronic states, uniformity of elemental composition across the top surface and uniformity of elemental composition as a function of depth. It can obtain data from 1 to 12 nanometers of depth. If data is required from deeper in the sample, then the surface must be physically or chemically removed.

XPS utilizes the photoelectric effect as its principle. An x-ray beam is pointed at the target surface. This beam will deliver photons with an energy of $E=\hbar\nu$ where $\hbar$ is Plank’s constant and $\nu$ is the frequency. As these photons travel through the sample with this energy a few of them will collide with the electrons in an atom and will cause these to jump as shown in Figure 1. Notice however that Auger electrons are being detected along with the x-rays that we want to detect.

![Figure 1. Diagram of X-ray Beam Hitting Sample.](image)

In this case the electrons that we want to detect are those that are jumping due to being hit by the photon. With this in mind, the kinetic energy that the electron will have will be related to the energy of the photon minus the binding energy that it originally had. This can be displayed in the equation $KE=\hbar\nu-BE$ where $BE$ is the Binding Energy. A diagram of this process can be seen in Figure 2.
Example of XPS
XPS was used to characterize silver nanoparticles that were doped onto a phosphate glass. In particular it was used to study the fundamental properties of the glass-embedded metallic particles in relation to quantum confinement effects with decreasing particle size. This data was then used to draw a connection with optical properties.

Sample Preparation
Silver NP-doped phosphate-based glasses of the P2O5 Al2O3 CaO SrO BaO type were prepared by melting and HT processes

Procedure
XPS measurements were performed with a Phi 5600 ESCA (electron spectroscopy for chemical analysis) System (Physical Electronics) with a monochromatic Al-Ka X-ray source (1486.6 eV) operating at 15 kV, 350W with the pass energy fixed at 58.7 eV. The operating vacuum was kept at ~10^{-9} Torr. Charge compensation was applied during spectra acquisition due to the insulating properties of the glass matrix

Data & Results
The experimental data for BE shows two peaks. The one with lower BE corresponds to ionic silver in relation to non-oxidized silver. The lack of peak deformation was interpreted as a loss of the ionic character of the silver in the glass matrix. High BE indicates the presence of small silver clusters for which a tendency to electronic quantum exists. While the low BE indicates a large particle size since in larger particles an increased core-hole screening by conduction electrons decreases the BE.
Figure 3. Illustration of silver XPS data and deconvolution into respective neutral and ionic contributions. Spectrum corresponds to the sample with SPR around 419 nm without BE correction. Experimental data represented by solid line.

References