

IMAGING X-RAY PHOTOELECTRON SPECTROSCOPY

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Abstract

X-Ray photoelectron spectroscopy (XPS) provides surface sensitive chemical analysis of materials in vacuum, enabling the determination of atomic concentrations and chemical bonding within the first 50 nanometers of the sample surface. We will present progress on the design of an imaging XPS system with anticipated lateral resolution of 50 microns and 0.5 eV energy resolution. Sample illumination is accomplished using aluminum K-alpha X-rays. Scattered electron energy analysis is performed with the Physical Electronics 10-360 Spherical Energy Analyzer. The Sensor Sciences Cross Delay Line MCP detector provides position sensitive detection of scattered electrons. The case is also made for a low-power XPS instrument for in situ chemical analysis of extraterrestrial geologies.

Introduction

This work is aimed at non-destructive, chemical analysis of materials by x-ray photoelectron spectroscopy (XPS). In XPS, monochromatic x-rays incident upon a sample, eject core electrons from atoms within the sample (Siegbahn 1970). The ejected electrons will have kinetic energy equal to the energy of the incident photon less its binding energy and the spectrometer work function.

$$KE = h\nu - BE - \phi \quad (1)$$

Each element in the periodic table has well-defined, unique electronic energy levels. Therefore, we can use the kinetic energy spectrum of the electrons leaving the sample to investigate the atomic composition of the material. The relative abundance of each element is calculated from the ratio of integrated binding energy peaks. Differences in ionization cross sections and electron affinity are corrected using published sensitivity factors (Moulder, Stickle et al. 1992).

Surface sensitivity of this techniques arises because only elastically scattered electrons will exhibit the characteristic binding energy spectrum. The depth of origin for elastically scattered electrons is on the order of 50 nm. Consequently,

XPS measures the atomic composition within only the first 50-100 nanometers of the surface (Siegbahn 1970). Inelastically scattered electrons will have lost energy through multiple collisions and will thereby contribute to the background of the spectrum. The background gas within the chamber also limits the sensitivity of the XPS technique.

The gas within in the chamber is constantly bombarding the surface of your sample, possibly altering the material. We consider the time it takes to adsorb one monolayer of atoms on the surface, assuming that one hundred percent of the atoms that strike the surface stick. This "monolayer time" should be longer than the duration of the experiment to avoid the effects of contamination. We can establish a maximum base pressure in which to perform surface sensitive experiments based on the concept of monolayer time.

The minimum base pressure for monolayer time of one hour is $7E-10$ Torr. More strict requirements are required to publish the results of an experiment: less than $2E-10$ Torr. We use a variety of techniques to achieve these low pressures. Stainless steel vacuum chambers are sealed with Conflat flanges. In Conflat flanges, two circular knife edges press into annealed copper gaskets and are held tight with bolts forming an atomically perfect seal between the interior of the chamber and the atmospheric environment. Periodic baking of the chamber is performed to desorb water from the chamber walls. The air within the chamber is removed using a variety of pumps including mechanical, turbo-molecular, cryo, and sublimation pumps. The pressure within the chamber is measured and monitored using an ionization gauge.

Electrons leaving the sample are collected by an electrostatic lens. The lens focuses and decelerates the electrons to a pass energy that remains fixed across the scan of electron binding energies. This mode of operation is sometimes called Fixed Analyzer Transmission mode because

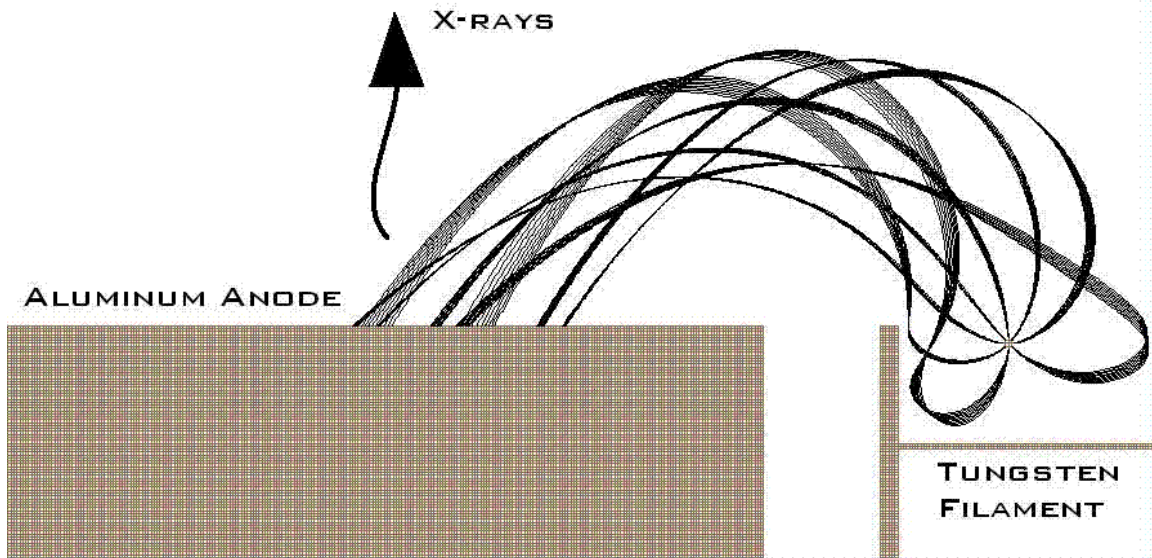


Figure 1. SIMION simulation of x-ray source configuration. Electrons leave the grounded filament with thermal energy at 2000K, 0.3 eV. They are attracted to the aluminum high voltage anode at +15kV. The electron hole pairs generated within the anode produce characteristic 1486.6 eV x-rays upon recombination.

it maintains constant transmission function and energy resolution across the spectrum (Physical Electronics 1984). Charged particles are dispersed by a deflection voltage across two concentric hemispherical plates. A narrow energy band is selected by the entrance and exit apertures (Roy and Tremblay 1990). The pass energy is the kinetic energy of the electrons that will pass through the spherical capacitor analyzer. Electrons with more or less energy will not be transmitted.

Upon leaving the hemispherical analyzer, the electrons pass through an ultra fine grid into a linear field region. The electrons are then accelerated in straight lines onto a triple stack of microchannel plates. The microchannel plates provide a factor of 10^7 gain to the electron signal. A cloud of electrons leaves the microchannel plates incident onto a cross delay line anode. The position of the electron cloud is determined from the time it takes the current from the electron cloud to reach each of the four edges of the detector. Using high resolution pulse sensing and timing electronics, spatial resolutions of 50 microns are possible (Siegmond, Jelinsky et al. 1999).

Low Power X-ray Source

Electron spectroscopy begins with the source of excitation within the sample. In XPS, we use monochromatic x-rays to illuminate the sample (Siegbahn 1970). X-ray guns are commercially

available in a variety of materials. Possible anode materials include aluminum, magnesium, chromium, copper, silver, and tungsten with aluminum and magnesium being the most popular due to their narrow line widths, approximately 0.7 eV and 0.9 eV respectively (Siegbahn 1970). The production of x-rays is accomplished when electrons are accelerated to a high voltage anode. The incident electron ionizes an atom within the anode by the ejection of an inner shell electron. Subsequently, a valence electron will transition to the inner shell to fill the hole and return the atom to its ground state. The transition of the electron to a lower energy level is accompanied by the emission of a photon. The photon will have energy equal to the energy of the electron transition to satisfy conservation of energy. In aluminum, the characteristic x-ray emitted by this process will have an energy of 1486.6 eV and a width of 0.7eV.

Chemical analysis in space is facilitated by low power instruments given the energy constraints on most spacecraft. Additionally, typical x-ray sources require active cooling of the anode by deionized water adding significant complexity to the system. The development of a low power x-ray source was motivated by these considerations. A copper anode was sputter coated with ten microns of aluminum at the University of Virginia Sputter coating facility. 1.7 Amps of current energize a thoriated tungsten filament.

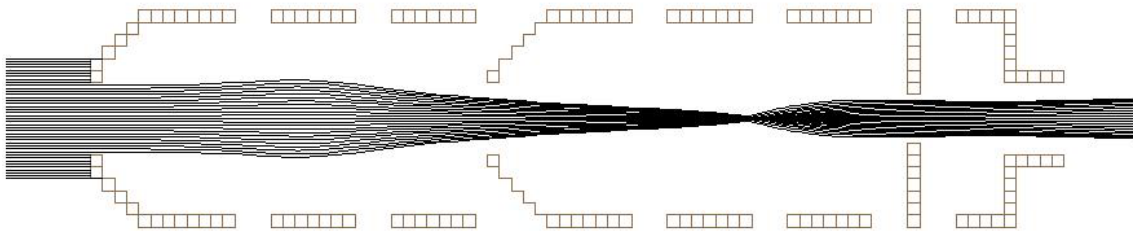


Figure 2: SIMION 7 model of the seven element electrostatic lens used to collect and focus electrons from the sample into the spherical capacitor analyzer.

Thermal electrons are emitted by the filament due to resistive heating to temperatures between 1800 and 2700 Kelvin.

Ion optics simulations were performed in SIMION to study the performance of the x-ray anode configuration. SIMION accepts a user defined electrode geometry and the voltages applied to each surface. Laplace's equation is then solved iteratively to find the potential field everywhere. The trajectories of many electrons are calculated independently as they travel through the geometry, ignoring the effects of space charge. In the presence of a 15kV electric field, the electrons are rapidly accelerated to the aluminum anode. The simulated trajectories of 0.3eV electrons are shown in Figure 1. They are attracted to the aluminum high voltage anode at +15kV. The electron hole pairs generated within the aluminum anode produce characteristic 1486.6 eV x-rays upon recombination.

In addition to characteristic x-rays, continuum bremsstrahlung x-rays are also produced in the anode as the electrons decelerate. These low energy photons and secondary electrons are blocked by a two micron aluminum foil window capping the source. The window is 0.6 centimeters away and parallel to the anode surface. The window defines the solid angle of x-ray emission as 1.0 steradians. The value for x-ray production efficiency in aluminum by 15kV electrons is published to be 1.5E-3 photons per steradian per electron (Joy 1998). For operation at 0.5 milliamps the normal flux is 1.9E12 photons per cm² per second. Correcting for two 45-degree tilts between the sample surface and the x-ray source normal, the flux on the surface 9.3E11 photons per cm² per second. A monochromator is not used to achieve maximize sample brightness.

Lens and Electron Spectrometer

We use the Omni Focus II lens coupled with the Small Area lens to collect and focus the

electrons leaving the sample. Four apertures are available to define the acceptance area of the analyzer. The lens, simulated in Figure 2, is separated into two functional regions. The front section closest to the sample defines the analysis area using user defined magnification. High magnification results in a small analysis area and large solid angle, while low magnification results in the analysis of a larger area and a smaller solid angle (Physical Electronics 1984).

The conical electrode separating the front region from the back region serves to isolate the fields within the two regions. The rear section of the lens retards and focuses the electrons. Separation of the magnification from the focusing defines an analysis area that is independent of energy (Physical Electronics 1984). The lens accelerates the electrons to the pass energy of the analyzer for operation at fixed pass energy across the spectrum. This is done to keep the energy resolution constant across the spectrum of electron kinetic energies.

The Physical Electronics model 10-360 Spherical Energy Analyzer uses an energy dispersive electric field to select electrons within a narrow range of kinetic energies. This energy dispersive filtering is simulated in Figure 3 for 200 eV electrons. The pass energy is the kinetic energy of charged particles that will pass in a circular trajectory through the middle of the gap between the hemispheres. Charged particles with more or less kinetic energy will be deflected as shown and blocked from transmission by apertures. The energy resolution for this analyzer is stated by the manufacturer to be 1.5% of the pass energy (Physical Electronics 1984). Operation of the analyzer at lower pass energies permits finer energy resolution in the measurement. The gain in resolution is accompanied by a reduction in transmission and a loss of sensitivity (Roy and Tremblay 1990).

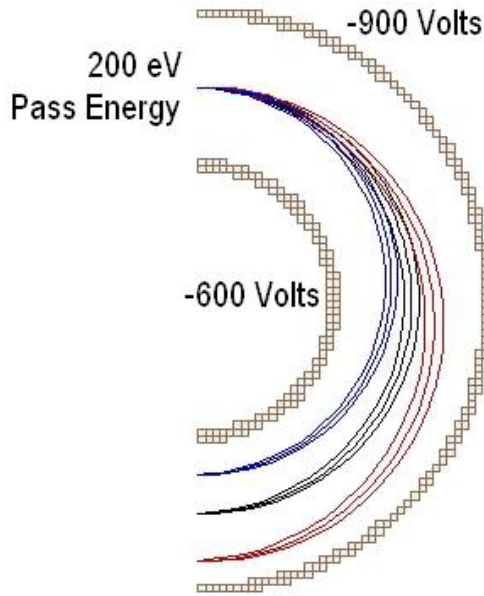


Figure 3. SIMION simulation of energy dispersive filtering for 200eV electrons. Voltages applied to the two hemispheres create an electrostatic field that curves the trajectories of the electrons. 200eV electrons pass through the center of the analyzer with a range of incidence angles. 180eV and 220eV electrons are dispersed in the radial direction to be deselected by apertures.

Position Sensitive Detector

Upon leaving the hemispherical analyzer, the electrons pass through an ultra fine grid into the cross delay line position sensitive detector by Sensor Sciences Inc. Within the detector the electrons are accelerated by a linear electric field onto a triple stack of microchannel plates that provide a factor of 10^7 gain to the electron signal. The microchannel plate stack is 25mm in diameter and consists of an array of 12 micron pores inclined at 13 ± 2 degrees to the normal axis. The interior of the pores is treated to encourage secondary electron emission from the surface such that the collision of one electron with the wall will result in the emission of tens or hundreds of secondary electrons. 5kV across the three microchannel plates ensures an unidirectional flow of charge through the plates.

Upon leaving the microchannel plates the electron cloud is accelerated through a linear field region onto a cross delay line anode. The anode, shown in figure 4, consists of two layered copper zigzag patterns, positioned orthogonally and isolated with alumina. Two separate conducting paths are used to localize the electron cloud in the

X and Y directions (Siegmond, Jelinsky et al. 1999). The extension of the serpentine conduction path outside the active area of the detector creates a time delay in the signals from neighboring strips. The charge pulse is collected at the four points shown in the figure as white circles. The time delay between detection of charge on the left side and the detection of charge on the right side is used to localize the charge in the X direction. Similarly, the time difference between when the top side of the detector receives a pulse and when the bottom side receives the pulse determines the Y location. The cross delay line electronics have achieved 30 micron FWHM spatial resolution (Siegmond, Jelinsky et al. 1999).

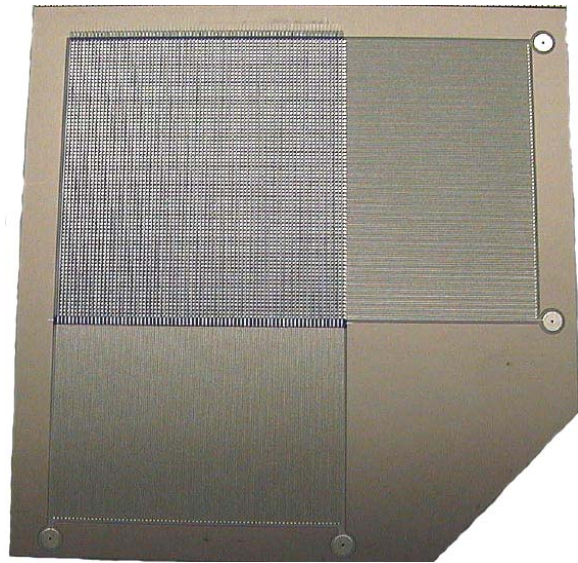


Figure 4: Ceramic/metal multilayer XDL anode with ~50ns delay and 0.5mm periods

Summary

In this paper, we have described the working design of an imaging electron spectrometer. The low power aluminum x-ray source provides sample illumination with 1486.6eV photons. The photon bombardment ejects electrons from within the sample. By measuring the kinetic energy of the elastically scattered electrons we can calculate their binding energy and determine their elemental origin. We use the Omni Focus II lens coupled with the Small Area lens to collect and focus the electrons leaving the sample. The lenses accelerate the electrons to the analyzer pass energy independent of magnification for analysis in fixed transmission mode. The position sensitive detector amplifies the electrons using microchannel plates and then locates the XY position of the cloud with

delay line electronics. The anticipated resolution of this system is 0.5eV and 50 microns spatially. Image acquisition software remains to be written as we complete integration testing.

References

- Joy, D. C. (1998). "The Efficiency of X-ray Production at Low Energies." Journal of Microscopy **191**(1): 74-82.
- Moulder, J., W. Stickle, et al. (1992). Handbook of X-ray Photoelectron Spectroscopy. Eden Prairie, Minnesota, Perkin-Elmer Corporation.
- Physical Electronics, Ed. (1984). Model 10-360 Precision Energy Analyzer: Technical Manual. Eden Prairie, MN, Perkin Elmer.
- Roy, D. and D. Tremblay (1990). "Design of Electron Spectrometers." Reports on Progress in Physics **53**: 1621-1674.
- Siegbahn, K. (1970). "Electron Spectroscopy for Chemical Analysis." Philosophical Transactions of the Royal Society of London, Series A **268**: 33-57.
- Siegmund, O., P. Jelinsky, et al. (1999). "High-Resolution cross delay line detectors for the GALEX Mission." SPIE **3765**: 429-440.