

X-ray Photoelectron Spectroscopy (XPS)

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X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

XPS BASICS ^[1]

X-Ray Photoelectron Spectroscopy (XPS), also called Electron Spectroscopy for Chemical Analysis (ESCA) is a surface analysis technique based on the photoelectric effect.

The photoelectric effect describes the ejection of a core electron from an atom, called the photoelectron, by impinging electromagnetic radiation. In the case of XPS the radiation is an X-ray beam. See Figure 1.

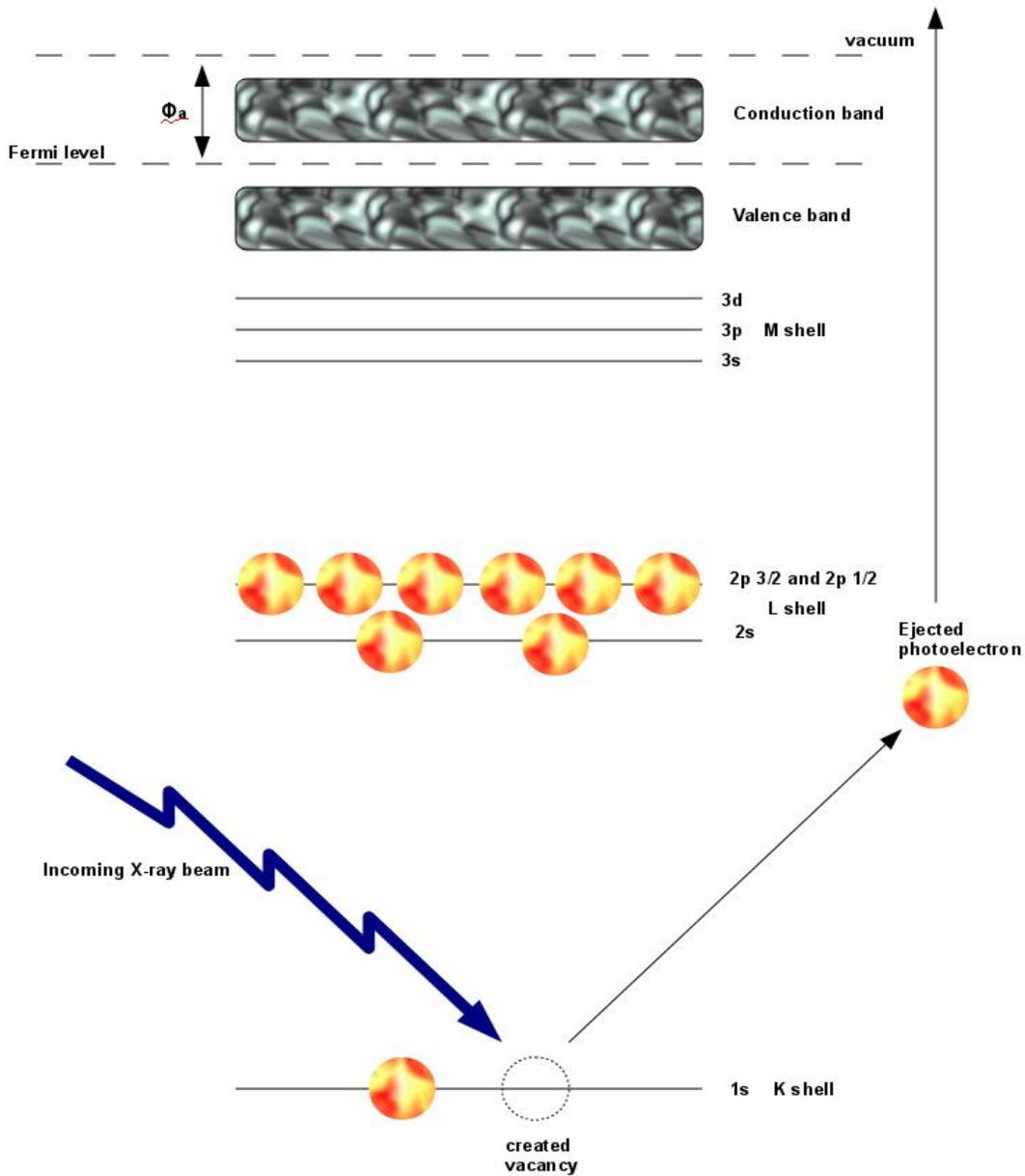


Figure 1: Schematic representation of the photoelectric effect

Once the photoelectron is ejected, it is guided through some magnetic fields until it hits a detector. The detector measures the kinetic energy of the photoelectron and the information is sent to the processor to calculate the binding energy, using the equation:

$$BE = h\nu - KE + F_{inst}$$

where BE is the binding energy of the photoelectron before being ejected, h is the Planck's constant, ν is the frequency of the X-ray beam, KE is the kinetic energy of the photoelectron, and F_{inst} is the work function of the instrument.

The BE is characteristic of the atom from which the photoelectron was emitted.

A plot of intensity vs. BE is done by the computer. The energy of each peak identifies the element from which the photoelectron came, and the area under the peak is related to the relative amount of that element. The shape and precise position of the peaks give us information about the chemical state for that particular element.

Survey scans and high-resolution multiplex scans are the most common types of analyses within the XPS technique. Quantitation analyses are also feasible using XPS.

EXAMPLE OF XPS APPLICATION

Manso et al. [2] studied the changes in the surface properties of some polymers by implanting Ar and He ions; the surface analysis was done using several techniques, including XPS, which is the one I'll focus here.

Sample Preparation

They prepared poly(ϵ -caprolactone) (PCL) and poly(ethylene glycol) (PEG) films using spin coating at 2000 rpm for 45 seconds, the films were prepared from polymer solutions (PCL M_w = 10,000, PEG M_w = 6,000) onto Si(100) wafers.

After that, the polymers were implanted with ions with a DanFysik high current ion implanter. They were irradiated at doses up to 10^{14}cm^{-2} at room temperature, the chamber operating pressure was less than 10^{-5}Pa . Two current densities were used: 0.05 (labeled m) and 0.2 (labeled p) $\mu\text{A}/\text{cm}^2$.

The energies used were 25 and 100 keV for both He and Ar on PCL and PEG.

Experimental Details

XPS was used to analyze the modification of the chemical environment of O and C, and the general stoichiometry of the films. The instrument used was an Axis Ultra spectrometer XPS by KRATOS Analytical (UK), the source was a monochromatic Al K α with $h\nu = 1486.6 \text{ eV}$, power was 150 W. A base pressure of $\sim 6 \times 10^{-10} \text{ Torr}$ and an operating pressure of $\leq 2 \times 10^{-9} \text{ Torr}$ were used. A 90° take off angle and pass energy of 80 eV and 20 eV were used to obtain survey (0 - 1150 eV binding energy) and high resolution spectra, respectively.

The compensation of the surface charge was done by a flood gun with bias voltage of -3.2 V, referring all peak energies to the binding energy of the hydrocarbon peak at 285 eV.

For the high resolution spectra of C 1s and O 1s, a linear background subtraction was executed followed by peak fitting, with a G/L function using Vision 2 software by Kratos (UK).

The quantitative analysis was carried out by using element peak areas measured on survey spectra and software referenced relative sensitivity factors (RSF).

Results and Conclusions

The XPS analysis revealed a severe transformation of the PCL surfaces. There is a modification of the electronic structure of C 1s peaks compared with the untreated polymer. See Figure 2

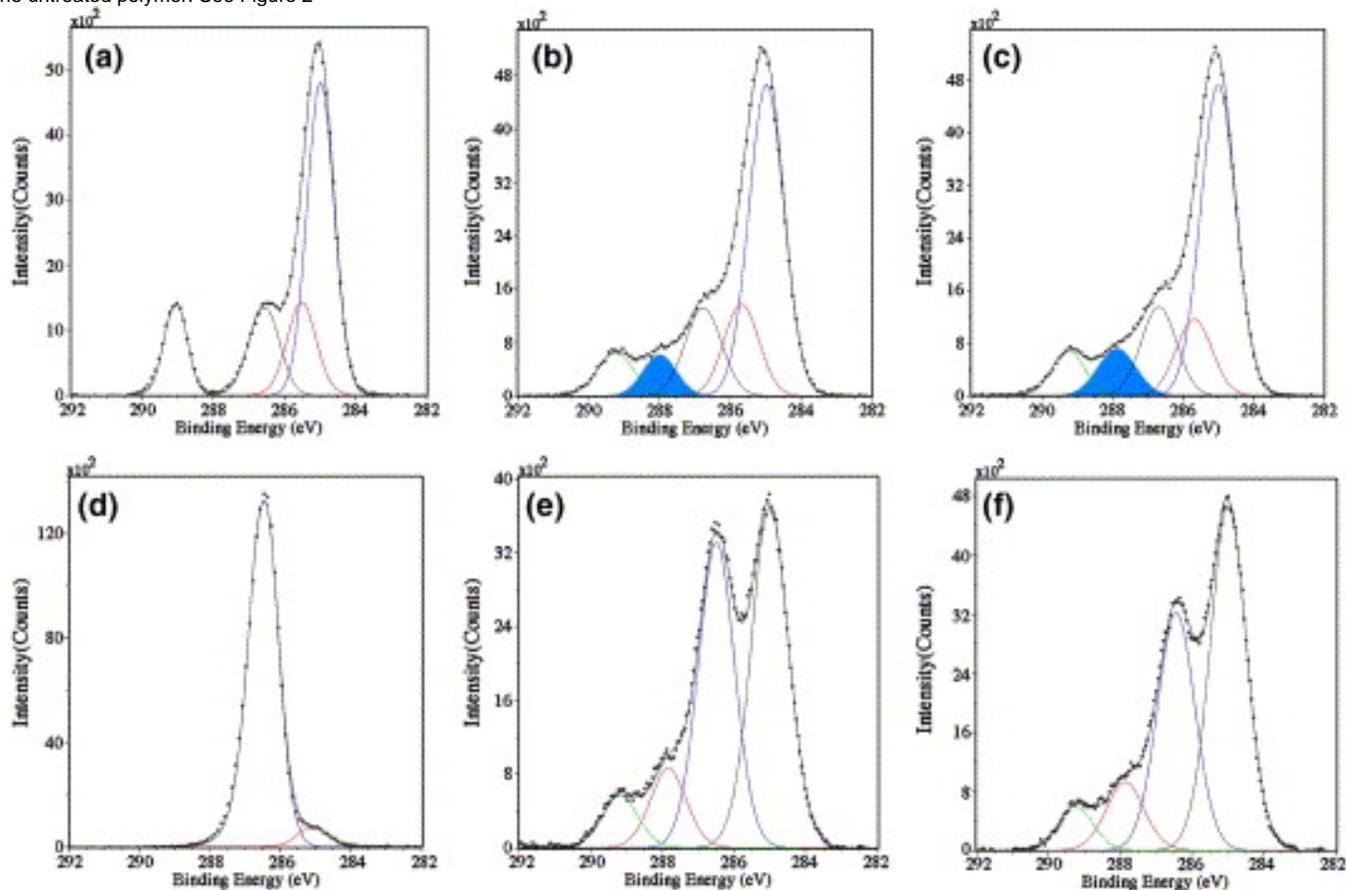


Figure 2: C 1s XPS spectra of (a) untreated PCL, (b) PCL-Ar100m, (c) PCL-Ar100p, (d) untreated PEG, (e) PEG-He25m, and (f) PEG-He25m after rinsing in deionized water.

The pure PCL spectrum shows four well defined components in agreement with standards. The same kind of modifications of the surface structure are achieved with either He or Ar. An additional feature appears in the PCL-Ar100m and PCL-Ar100p spectra at 287.9 eV. The original peaks are found at 285.0, 285.6, and 289.1 eV. This new peak is the result of the reordering after fragmentation of the COO lactone forming $\text{C}-(\text{C}=\text{O})-\text{C}$ or $\text{O}-\text{C}-\text{O}$ bonds. Analyzing this peak, with components of 6.8% for PCL-Ar100m and 8.7% for PCL-Ar100p, it can be concluded that the surface properties are not highly dependent on the current density.

Also, peak broadening was observed after implantation, more notably in the original COO peak at 289.1 eV; this is an indication of a mix of contributions with groups of the carboxylic type, i.e. $\text{O}=\text{C}-\text{OH}$.

When varying the energy from 25 to 100 eV, the effects of the implantations do not change considerably. The intensity of the new component was 5% C content for both PCL-Ar25m and PCL-Ar25p.

The analyses on PEG also showed dramatical changes in the surface properties of the polymer. Here the original component C 1s spectrum of PEG is transformed into a more complex four component structure. A new intense peak at 285.0 eV, which is related to the crosslinking of a stabilizing CH-network, is found for both He and Ar implantations at both energies. Figure 2e shows the spectrum of PEG-He25m.

The components at 287.8 and 289.2 eV are evidence of the formation of fresh $\text{O}-\text{C}-\text{O}$ / $\text{C}=\text{O}$ and COO complexes, respectively. These contributions are more intense for Ar and for 100 eV implantations, which might induce polar groups on the surface; this can disturb the highly hydrophilic character of PEG.

A slight decrease in all the contributions with respect to the stabilizing CH-network in the samples after rinsing in deionized water could be the result of the elimination of polymer fragments loose from the surface.

REFERENCES

- [1] ASM Metals Handbook, Ninth Edition, Vol. 10 - Materials Characterization
- [2] M. Manso, A. Valsesia, M. Lejeune, D. Gilliland, G. Ceccone, F. Rossi, Tailoring surface properties of biomedical polymers by implantation of Ar and He ions, Acta Biomaterialia, Volume 1, Issue 4, July 2005, Pages 431-440, ISSN 1742-7061, DOI: 10.1016/j.actbio.2005.03.003.