

# Ultraviolet Photoelectron Spectroscopy

Usage and Applications

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## Ultraviolet Photoelectron Spectroscopy

The basic concept of photoelectron spectroscopy is that irradiated surfaces eject electrons which carry information about the surface from where it is being ejected.

Ultraviolet Photoelectron Spectroscopy is that branch of electron spectroscopy which uses low energy ultraviolet radiations to trigger changes in the molecule and study them in detail. The commonly used energy sources are :

Helium I (doublet) ----- 21.22 eV

Helium II ----- 40.81 eV

Neon I (doublet) ----- 16.7 eV

Neon II----- 26.9 eV

These energies are of the same order of magnitude as the binding energies for valence shell electrons of molecules and valence band states of condensed systems. As such UPS gives information about valence orbitals.

UPS can provide further information on the system if the emitted electrons are both energy and spatially analyzed. This is known as angle resolved UPS (ARUPS). Using ARUPS, the band structures of clean and adsorbate covered surfaces have been determined. By changing the angle of incidence and angle of detection, the electronic orbitals from which the photoelectrons are ejected can be identified. In addition, ARUPS provides detailed information on the surface chemical bond including the direction of the bonding orbitals and the orientation of the molecular orbitals of the adsorbed species on the surface.

The probability of photoemission varies with frequency approximately as  $\nu^{-3.5}$ . Hence excitation in the UV region is easier.

The flux of photons produced by the discharge lamps used in UV sources is intense in comparison to X-ray sources in XPS. Thus UPS is more sensitive and more suited to working with dilute samples.

Useful for delicate samples as there is less chance of radiation damage.

Varying the irradiated light allows one to see the frequency dependence of the various PES peaks. It can be shown on quantum mechanical bases that photoemission cross-section depends on size, number of nodes (angular) and localization of the orbital in question. This means that by repeating the measurement of the PE spectrum with many different exciting radiation energies, one can identify the "d-orbital character" of the orbitals involved. It is also important test of the bonding model which is being used to explain the band structure of the solid in question.

UPS can be employed to understand the molecular orbital picture of bonding in molecules.

UPS is most often used to study single crystals and to probe the molecular orbitals of chemisorbed molecules

In general UPS can be used to obtain the electronic structure of solids (complete band structure) and to study the adsorption of simple molecules such as CO and N<sub>2</sub> on metals. One can obtain information on chemisorption bonding by comparing the molecular orbitals of the adsorbed species with those of both the isolated molecule and with model calculations.

## Applications

### 1.) Study of adsorption of gases on metallic surfaces.

UPS can give information about the electronic structure of adsorption systems which can be used to deduce bonding schemes in adsorbed phase. However analysis of spectra of such systems is complicated because of the variations in the interaction between the adsorbate and the metals. A rare gas atom however can be used because of the weak interaction between the adsorbate and the metal surfaces. For example the UP spectra of xenon atoms on W (110) at various coverages shows two peaks in the region 5-8 eV.

In general the analysis can be done by comparing the spectra of a neat surface with a spectrum of the same surface with a gas adsorbed. Shift in ionization energies ( $\Delta I$ ), interaction energy of the ground state ( $\Delta E$ ) and ionic state ( $\Delta E^+$ ) and work function ( $\Delta\phi$ ) can be noted.

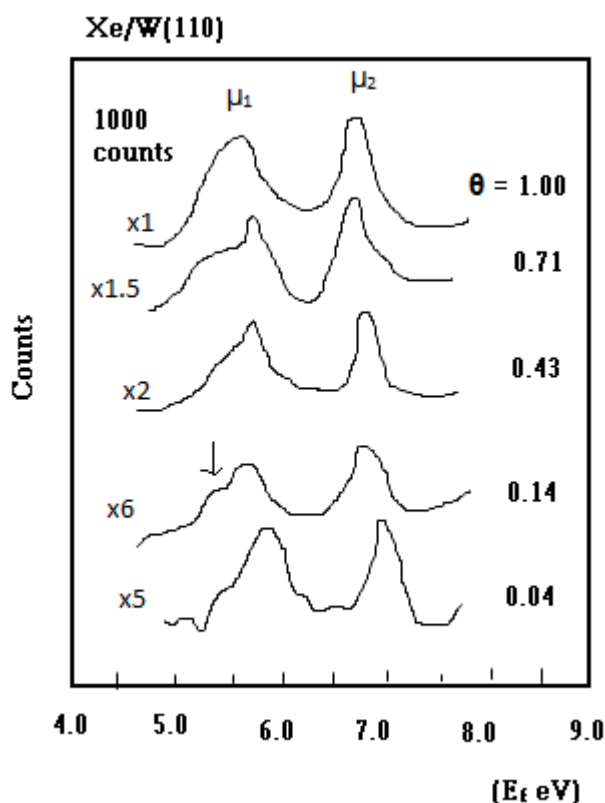


Figure 1 : UP spectra of Xenon on W(110) at various coverages.

### 2.) Adsorption of dinitrogen on metal surfaces.

The UP spectrum of physisorbed molecular nitrogen consists of three features due to  $3\sigma_g$ ,  $1\pi_u$  and  $2\sigma_u$  valence orbitals. All the energy levels are shifted to lower binding energies by 1.2 eV due to relaxation in the final state. The peak separations and their relative intensities however remain same as in the gas phase.

Substrate	$3\sigma_g$ eV	$1\pi_u$ eV	$2\sigma_u$ eV	$(1\pi_u - 3\sigma_g)$ eV	$(2\sigma_u - 1\pi_u)$ eV	T(K)
N <sub>2</sub> (gas)	15.6	17	18.8	1.4	1.8	-
Cu(N <sub>2</sub> )	11.1	12.5	14.3	1.4	1.8	20
Ni film	9.7	11	12.8	1.3	1.8	7
Ni(111)	9.2	10.5	12.3	1.3	1.8	45
Pd(111)	8.7	10.3	11.9	1.6	1.6	45

Al(111)	10.25	11.6	13.5	1.9	1.9	20
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Table 1 : UPS data for physisorbed nitrogen

In the chemisorptions of molecular dinitrogen on metal surfaces two states have been identified – the weakly adsorbed  $\gamma$  state (end-on orientation) and the strongly adsorbed  $\alpha$  state (side-on orientation)

Substrate	$3\sigma_g$ eV	$1\pi_u$ eV	$2\sigma_u$ eV	T(K)
$\gamma$ state				
Ni(100)	7.6	-	12.4	77
Ni(111)	9.0	-	13.0	70
Fe(111)	8.6	8.3	11.8-12.2	<77
W(110)	7.0	-	11.7	100
$\alpha$ state				
Fe(111)	8.4	7.5	12.3	110
Cr(110)	8.4	7.1	12.7	90

Table 2 : Data for chemisorption of molecular nitrogen

### 3.) Adsorption of CO on metallic surfaces.

Two peaks were observed in the spectrum for CO adsorbed on nickel at 7.5 eV and 11.0 eV with respect to the bare metal. Eastman and Cashion assigned these peaks for emission from  $3\sigma$  and  $1\pi$  molecular orbitals. This initial assignment was not correct.

The low peak is a composite peak due to emission from the  $3\sigma$  and  $1\pi$  molecular orbitals and the peak at 11.0 eV is due to the  $2\sigma$  level. It has been ascertained that in the adsorbed state the ordering of the orbitals is reversed and that the  $1\pi$  has a lesser binding energy as compared to the  $3\sigma$  level. In the gas phase CO the ordering of orbitals is reverse.

### 4.) Determination of the valence band structure of metals.

UPS can also be applied to determine the electronic structure and the valence band structure of metals. The key observations are :

- The nickel valence band spectrum shows the satellite emission in the energy range around 5 eV which is characteristic feature of this metal.
- The copper valence band spectrum shows a shoulder on the higher energy side namely around 3 eV.
- The valence spectrum of zinc also shows the high energy shoulder and the valence band appears at higher binding energies.
- The valence band spectrum of gold shows a split pattern which is also present in CsAu systems.

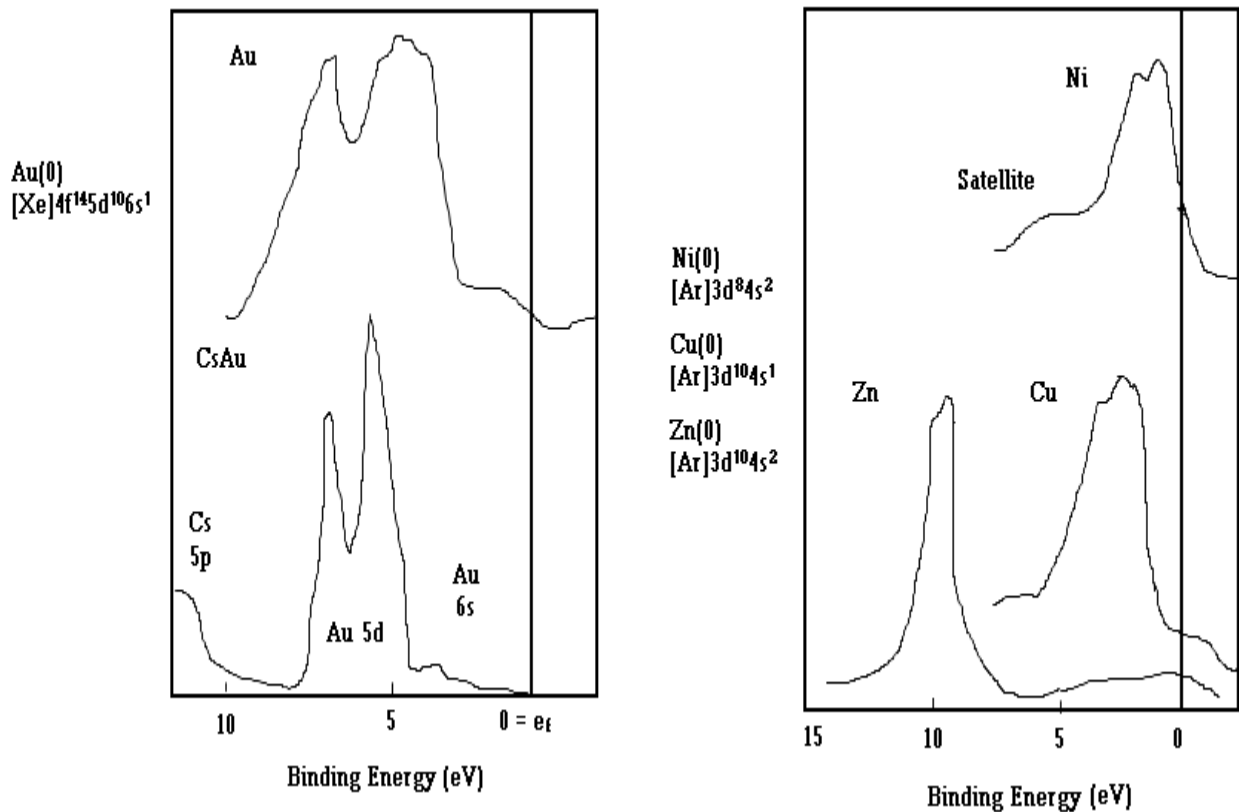


Figure 2 : UPS spectra of metals like ni, Cu, Zn, Au and CsAu

### Effect of He I and He II Radiation

In the photo excitation process using photons of two different frequencies with increase in final state energy an increase of overlap of the final state wave function with those of higher angular momentum initial states are expected (i.e., going from He I to He II radiation as shown in the Fig. the overlap of valence bands increases). This is a useful property which can be employed to analyze complicated spectra.

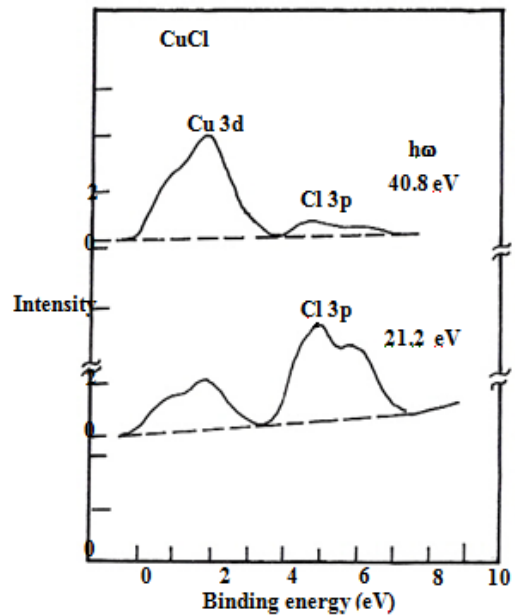


Figure 3 : Effect of He I and II on the UP spectra of CuCl

### Effect of Time on UP Spectra

It is still in doubt, whether this technique is non destructive or not. The spectrum of Cu (100) measured in equal time intervals between 0 and 10 hours after surface preparation with constant illumination of the sample during the time of the experiment, the signal increases in width and falls in intensity with time. This shows that the technique is in principle destructive. But at higher temperatures, there is no such deterioration of the signal with time; hence it is not clear whether it is due to radiation damage or due to the adsorption of residual gases.

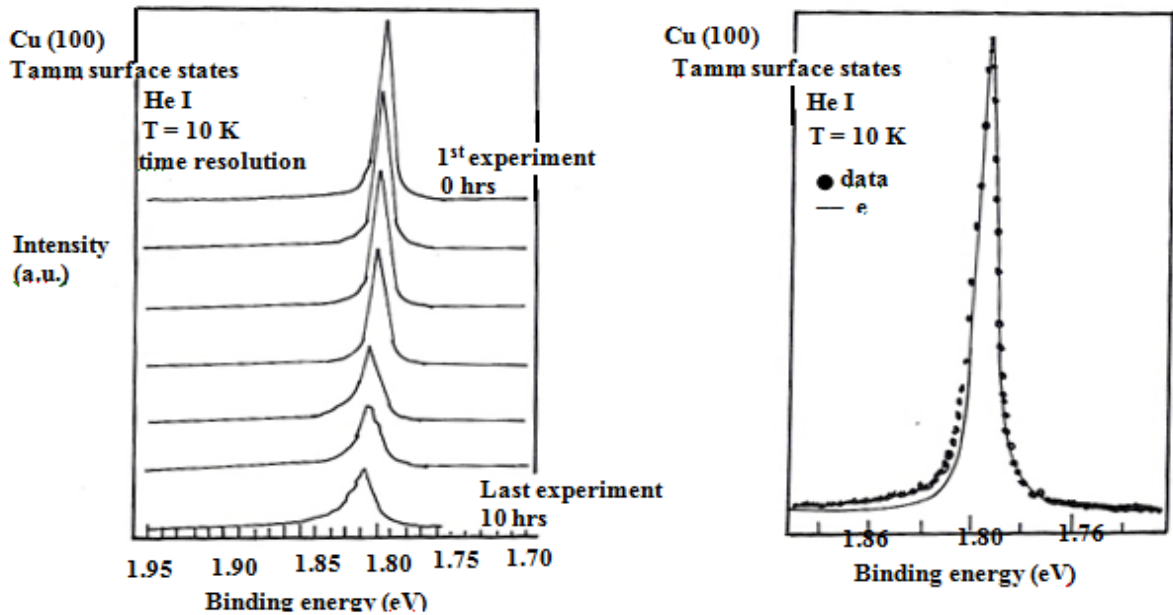


Figure 2 : Variation of UP spectra with time for Cu (100) at 10 K

### Comparison of XPS and UPS Spectra

#### (a) NiO

In the XPS spectrum, the O 2p contribution was estimated from a comparison of XPS spectra with that of the UPS of the transition metal oxide. In the UPS spectrum the O 2p band is visible. In both cases a distinct satellite is evident. It is assigned to a  $3d^7$  satellite peak (final state). The zero is the experimental Fermi energy, which is very close to the top of the valence band. So by comparison of UPS and XPS it is possible to estimate quantitatively the passive oxide layers formed on the surface.

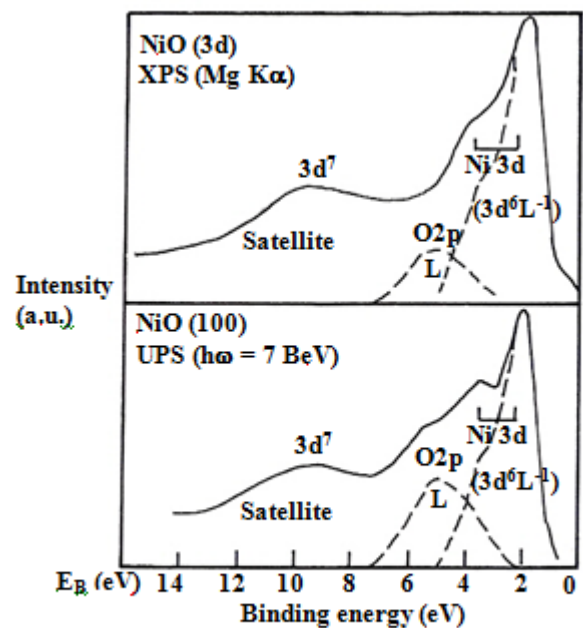


Figure 3 : Comparison of UPS and XPS of NiO

## (b) CuO and Cu<sub>2</sub>O

A comparative study of valence bands of polycrystalline samples of Cu<sub>2</sub>O and CuO taken with He I, He II, Mg-K<sub>α</sub> shows that in Cu<sub>2</sub>O, O 2p and Cu 3d states are separated and with Mg-K<sub>α</sub> in the XPS only metal 3d density of states are predominant. With UV sources, the spectrum gives a fair representation of the combined O 2p and Cu 3d density of states. In the case of CuO valence band studies in a similar way shows that the separation between the O 2p and Cu 3d orbitals is no longer so pronounced, indicating a stronger hybridization between the ligands and the metal d electrons.

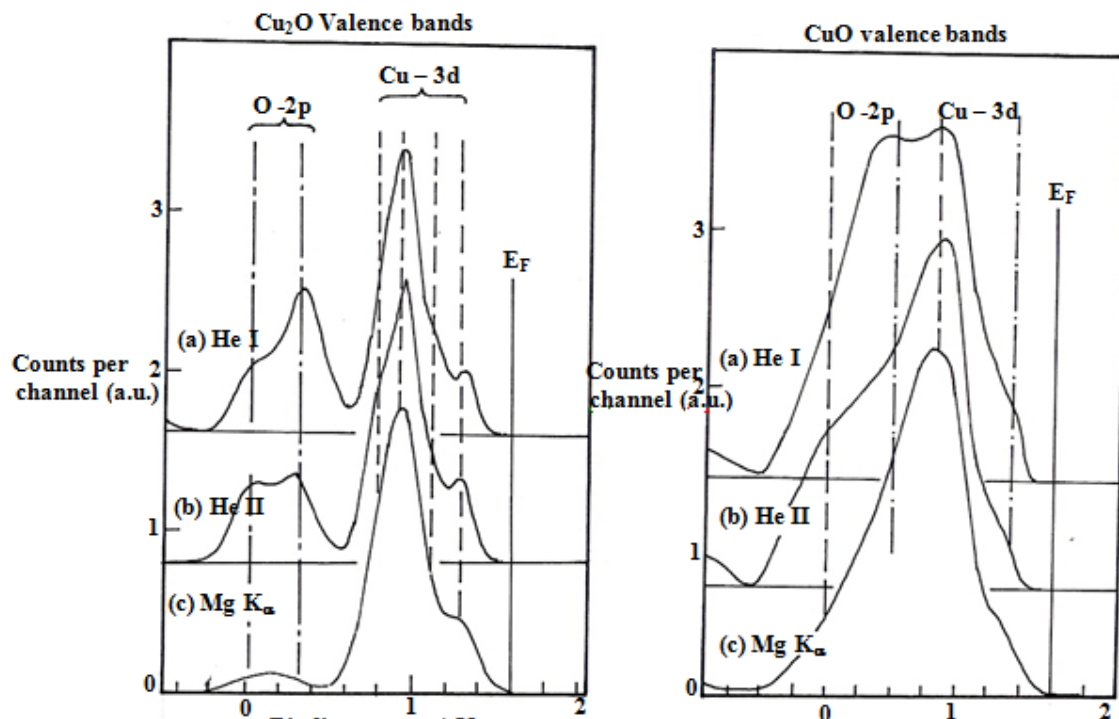


Figure 4 : Comparison of photo electron spectra of Cu<sub>2</sub>O and CuO with He I, II and Mg K<sub>α</sub> as the sources

## (c) XPS and UPS of Ni- Zr alloys

### XPS

The XPS studies on the oxidized amorphous Ni<sub>64</sub>Zr<sub>36</sub> alloy revealed that the oxidation in air at elevated temperatures resulted in a significant enrichment of zirconium due to the formation of a zirconia layer on the surface. Similarly the oxidized sample followed by reduction enhances the Ni on the alloy surface. From the XPS we can understand that the oxidized sample is showing higher peak area for Zr than that of Ni.

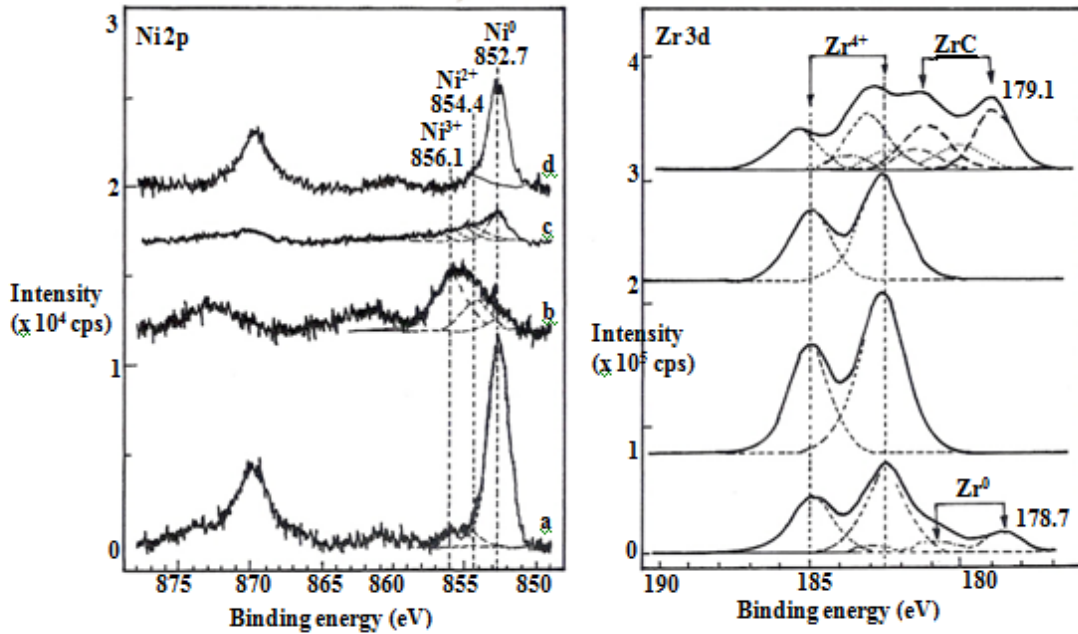


Figure 5 : Zr3d and Ni2p XPS data of Ni-Zr alloys. (a) As-quenched amorphous Ni<sub>36</sub>Zr<sub>64</sub> alloy; (b) sample (a) oxidized in 500 mbar O<sub>2</sub> at 523 K for 30 min. ; (c) as-quenched amorphous Ni<sub>24</sub>Zr<sub>76</sub> alloy oxidized under the same condition as (b); (d) sample (b) annealed at 773 K for 20 min.

## UPS

The changes of the valence band structures of the amorphous Ni<sub>36</sub>Zr<sub>64</sub> alloy due to different treatments have been studied by UPS. The valence spectrum of the as-quenched Ni<sub>36</sub>Zr<sub>64</sub> exhibited a dominant peak at about 6 eV below the Fermi level (trace a). Similar peaks have been observed in UPS investigations of transition metal oxides, and have been attributed to emission from O 2p states interacting with the d-bands of metals. Combined with the corresponding XPS results, the main peak in trace 'a' can be assigned to surface ZrO<sub>2</sub>. The shoulder centered at about 11 eV can be correlated with surface OH or C-related species, which are commonly present on untreated metal surfaces. Annealing to 773 K, however, gave rise to significant changes of the valence band spectrum, such as the emergence of the Fermi edge and a peak at about 3 eV below the Fermi level. Additionally, the intensity of the peak at 6 eV decreased strongly. The appearance of the Fermi edge

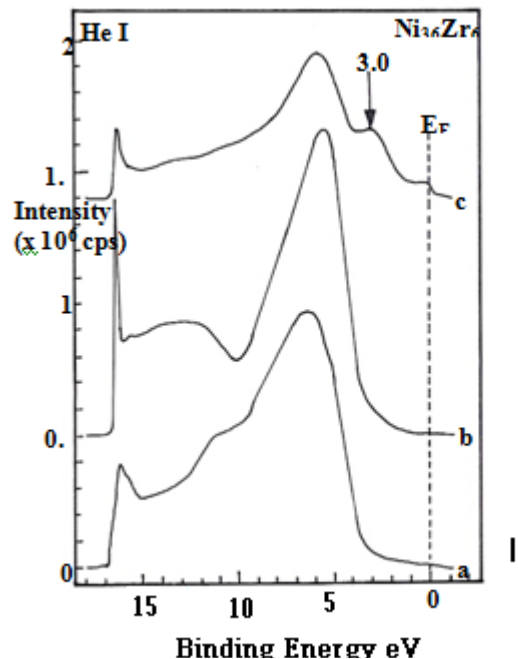


Figure 6 : . (a) As-quenched amorphous alloy; (b) sample (a) oxidized in 500 mbar O<sub>2</sub> at 523 K for 30 min; (c) sample (b) annealed at 773 K for 20 min



proves the metallic character of the annealed surface. Both the Fermi edge and the peak at 3 eV below the Fermi level can be assigned to ZrC at the surface. In the valence band spectrum of clean ZrC, a Fermi edge and a large structure distribution distributed between 0 and 5 eV were observed originating from hybridized Zr 4d and C 2p states.

## **Conclusion**

The surface of solids plays an overriding part in a remarkably large number of processes, phenomena and materials of technological importance. These include not only catalysis but also corrosion, passivation, adhesion, tribology, metals, ceramics, micro electronics, composites, polymers, protective coatings, semiconductors, superconductors, interfaces and even grain boundaries. Photoelectron spectroscopy is one of the exciting and rapidly growing branches in solid state physics, chemistry and biology contributing its maximum for the study of these solid surfaces. Photoelectron spectroscopy can give information on the Fermi energies and the density of states in the valence bands of metals, alloys and semiconductors and to detect the chemisorption levels which are of vital importance in understanding the nature of chemisorption which is responsible for the surface reactions.

It is clear that the photo electron spectroscopy can be suitably exploited for studying a variety of processes in catalysis. These include (I) Identification of the active sites (II) The mode of generation of active sites (III) the pores present in active systems (IV) the mode of deactivation of a catalyst and the activation procedures required for the degeneration of the catalysts and so on. It should also be mentioned that many other properties of the catalyst solids, like their magnetic behaviour, electrical conduction, and extent of ionicity or covalency can also be deduced by suitable and appropriate photoelectron spectroscopic measurements.

## **References**

**Catalysts and Surfaces – Characterization Techniques**

**B. Viswanathan, S Kannan, R.C. Deka**