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(REVIEW ARTICLE)

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Review: Electron Spectroscopy for Chemical Analysis of Macro and Nano size

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Abstract

Many methods were used to determined qualities and quantities of different materials, one of the most important techniques represent by X-ray photoelectron spectroscopy (XPS). This technique characterized by high Accuracy and precision for identify materials according to the nature of bonding and chemical environments. In this work the attentions concern with highly light with the theoretical and some practical information which depend to make the best identities for chemical compound in different and variance environments. The important for this work produce from explain the abilities for XPS analysis to decide the nature and properties with structure of different compound It even has the ability to distinguish between compounds that are very similar in their chemical composition.

Keywords: XPS; ESCA; Binding Energy; Relation Energy; Chemical Environments

1. Introduction

As we mention in our previous work X-ray play important roles in identification different chemical compound in macro and NANO size [1]. Electron spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy (XPS) is the most widely used for analysis and understand the nature of surface engineering. The important of ESCA as a surface analysis technique is due to its high information content, flexibility in handling a wide range of samples, and sound theoretical basis. XPS can measure elemental [2] composition as well as the chemical and electronic state of the atoms within a material.

1.1. The Basic ESCA (XPS) Experiment

The outer surface represents boundary between one phase and another, which responsible to the physical and chemical properties of the surface for the materials in Nano and macro size. As shown in figure 1, the main different between atomic layers can be related to orientation the atoms around each ether affect in addition to the outer layer of atoms is not surrounded by atoms on all sides, which makes it more reactive than atoms in the bulk[4].

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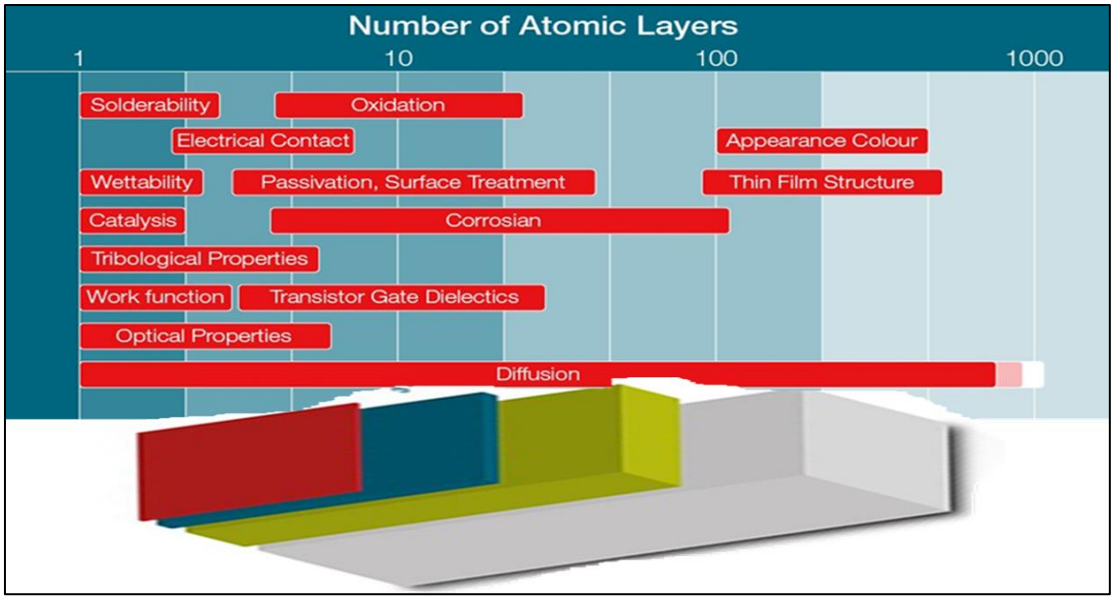


Figure 1 Skim for distribution number of atoms with identification by physical and chemical method

1.2. Principle of XPS

The process required only to the X-ray photoelectron which is ejected from the electron shell of an atom after photon absorbs by atom with an X-ray energy. An incident X-ray photon has enough energy (hv) to reject out an electron located in the inner shell, such as the K shell. With kinetic energy, we can calculate binding energy which leads to characteristic values of atomic electrons. From that we can identify what elements are present [4].

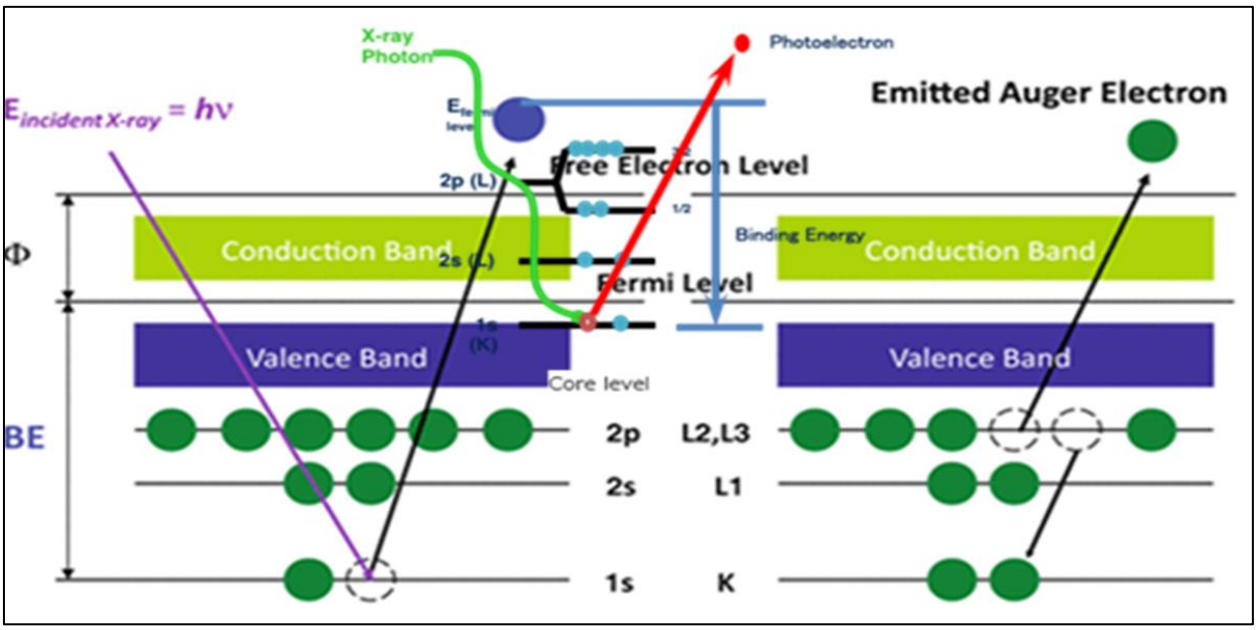


Figure 2 Skim for probabilities of interaction of X-ray with atoms in the surface

According to figure, When X-ray photon succeeded to reject out an electron located to outer atoms from the inner shell, which causing ionized the atom and convert to an excited state after steady state. Figure 2 shown that an electron located in the outer shell would refill the vacancy in the inner shell so that the atom can return to the normal state. the energy difference (kinetic energy), between the outer-shell electron and the inner shell which emission electron from inner to outer an electron shell which mention to binding energies. All the process can happened only if ''The X-ray photon transfers its energy to a core-level electron imparting enough energy for the electron to leave the atom' 'The

signals from Auger electrons are relatively weak compared with those of secondary electrons that have escaped from a solid surface[4-5].

$$E_{\text{incident X-ray}} = h\nu \quad \ldots\ldots\ldots \quad (1)$$

$$B_E = h\nu - K_E - \Phi_{spec} \quad \ldots\ldots\ldots\ldots \quad (2)$$

Where EB is the binding energy of the electron in the atom (a function of the type of atom and its environment), hν is the energy of the X-ray source (a known value), and KE is the kinetic energy of the emitted electron that is measured in the XPS spectrometer [4-6].

XPS analysis is a very informative method, a basic analysis of a surface will provide qualitative and quantitative information about all elements present (except hydrogen and helium). More sophisticated applications of this method yield a wealth [5-6] of detailed information about the chemistry, electronic structure, organization, and morphology of the surface. Therefore, XPS can be considered one of the most powerful analytical tools available.

XPS spectra are expressed as photoelectron intensity as Y-axis versus binding energy (EB) in X- axis. There are three types of peaks on an XPS spectrum background. The photoemission from core electron level peaks are the primary peaks for element analysis. The photoemission from valence levels peaks with low binding energy are useful for the analysis of material's electronic structure. The Auger emission excited by X-rays peaks are for chemical analysis. As mentions in figure 3, Each peak represents [7] the amount of electrons at a certain energy that is characteristic of some element. Figure 3 shows typical the first X-ray photoelectron spectrum which we obtained by digitizing the ''photometer scan in Robinson's paper generating 800 equally spaced points and then calculating the binding energy of each of these points from the *rH* values in the photometer scan using the CuKα1 X-ray energy''.

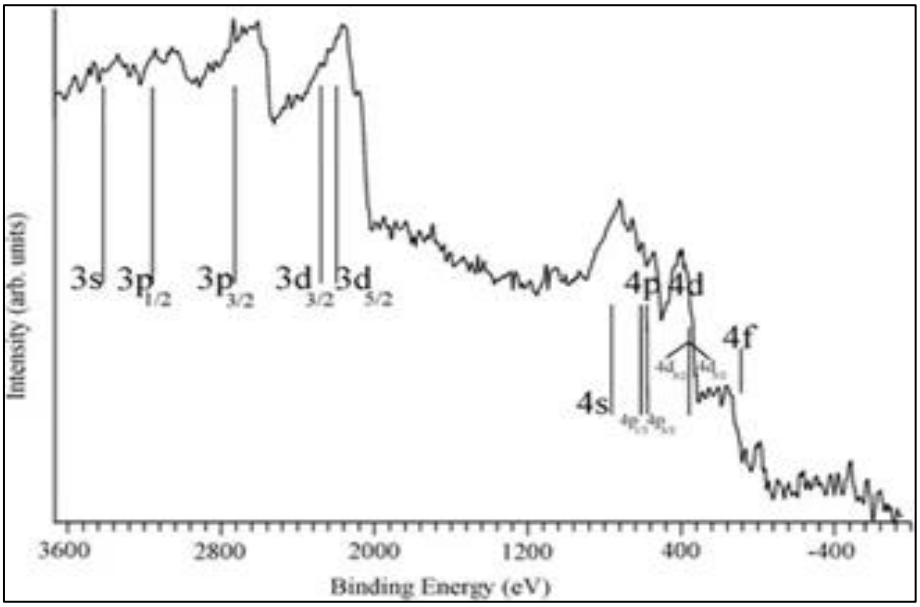


Figure 3 Skim for typical XPS spectrum, X- axis refers to intensity of photon with specific energy, while Y- axis include the binding energy according to orbitals of elements

2. Information Derived from an XPS or ESCA Experiment

three thinks we can get it by using XPS analysis Qualitative analysis, Quantities analysis and nature of Bonding with change the nature of chemical environments. However, it should be mentions that this technique is Non-destructive elemental with depth 10nm into surface of sample and that used assessment by angular-dependent XPS and photo electrons with differing escape depths [8].

2.1. Qualitative Analysis

XPS is powerful tool for surface chemical analysis. They can identify chemical elements in the layer within several nanometers from the outermost 10nm of a surface. If Binding Energy (EB) is displayed, XPS peaks are [9-10]

independent of incident x-ray energy. All elements could identification except H and He with precision reach to concentrations >0.1 atomic %.

2.2. Quantitative Analysis

Peak identification in AES spectra is straightforward. After the spectrum is plotted you can look for the designated [9-10] value of the peak energy from the graph and find the element present on the surface. Peak identifications in XPS spectra are more complicated because of the Auger peaks. So we need to use two different X-ray sources to distinguish the Auger peaks from photoelectron peaks. The ability for quantitative determination of the elemental surface composition reach to error < ±10%, and spatial resolutions down to 5 μm for laboratory instruments and spatial resolutions down to 40 nm for based instruments.

2.3. Chemical shifts

The important of chemical shifts of binding-energy peaks for an element are caused by the surrounding chemical state of the element. When an atom bonds to a more electronegative atom, it becomes slightly positive and the BE of its remaining electrons increases. So the detailed spectra which determine the chemical environment of individual elements include the following.

a- the molecular oxidation state, covalently and bonded atoms. B-
b- identification aromatic which may unsaturated structures or paramagnetic ($\pi* \rightarrow \pi$) transitions.
c- characterized of organic groups using derivatization reactions.
d- valence band spectra and bonding orbitals represent Finger printing for materials.

3. Binding Energy and the Chemical Shif

In order to understand the relation between EB and chemical shift, it should be start with Koopmans theorem, whose explain that the different between initial state Ei(n) and final state Ef(n-1) refers to EB of [11-12] an emitted electron by X-ray energy. The mathematical equation for this relation was EB = Ef(n-1) - Ei(n) , according to the physical behavior of materials if there is no rearrangement of the electrons during photoemission process in the surface of atoms which means negative value for orbital banding energy EB. The last cases were representing by value $-\varepsilon k$ and that for reject photoelectron which can be make approximation by Koopmans theorem to be

$$EB = -\varepsilon k \quad \ldots\ldots\ldots \quad (3)$$

and that as mention without rearrangement for the electrons. According to Hartree-Fock method the εk can be estimated within range 10-30 Ev for banding energy EB [13]. The different and variance between EB and εk with negative values can be related to incomplete the accounts for the two theorem Koopmans and Hartree-Fock [14]. It should be referring to important section which is after emission of the photoelectron that is not meaning the other electrons will be frozen without any reactivity, because there is ionization process for atoms. The rearrangement of electrons which caused by reduction energy is identify value '' relaxation energy'' Er(k) and that represent [12-15] the final steps accorded for two electrons in core hole with neighboring atoms which means extra relaxation with the outer atoms. The other physical properties that play important activities in XPS analysis is electronic correlation and relativistic effect $\delta\varepsilon corr$, $\delta\varepsilon rel$ respectively which neglected in the two theorem due to their small value, after additions this two values the equation would be

$$(EB= -\varepsilon k- Er(k) - \delta\varepsilon corr - \delta\varepsilon rel) \quad \ldots\ldots\ldots \quad (4)$$

If the energy of the atom's initial state is changed, for example, by formation of chemical bonds with other atoms, then the EB of electrons in that atom will change. The change in EB, is called the chemical shift. To a first approximation all core-level E_{BS} for an element will undergo the same chemical shift (for example, if a silicon atom is bound to a chlorine atom, i.e. a Si—Cl bond, the chemical shift for the Si_{2P} and Si_{2s} Si—Cl peaks relative to the position of the Si^0 state for each peak will be similar).

4. Chemical environment of Bond

The nature of atoms influence with the oxidation state of materials and that responsible to make shift in value of bending energy, thus XPS technique able to recognized this variance. This assumption which depend on effect of oxidation state

with final state after changed such relaxation energy thus the change in binding energy when change chemical environment can be calculated ΔE_B which is (ΔE_B = - Δk)

Many examples can be depend on it to showon the relation for initial state with bending energy ΔE_B . For example, carbon in organic materials C1s when shown increase with increases the ability for connections atoms towards higher oxidation value thus the arrangement was: C-C < C-O < C=O < O-C=O < O-(C=O)-O . This arrengement is [15-16] aggrement with the nature of oxgyen atomes which is more negativitty as compare with carbon atoms in addition to increase the oxgyen atomes which bonded with carbon atoms the value of EB with be identifyed due to increase the postive charge for carbon atoms. The other parameter which should take care was the oxidation state and the value of ΔE_B in addition to changes the density of electrons and distributions on the atoms which is not necessary shown straight line relation, but that did not prevent to be mentions and understood it.

The degree of ionic with covalent bond ratios can variance with the chemical environments, thus XPS analysis shown not typical only but ideal method for decided and determined the nature of bonded between the atoms which make it the best in this sections. Finally we mentions for some tables which reported the vales of bending energy ΔE_B for C_{1s} with different atoms as shown in table (1) in addition to table (2) which reported the nature of bonding with types of chemical compounds.

Table 1 Typical values of C_{1s} binding energy for specific atoms in organic compound.

Functional group		Binding energy (eV)
Hydrocarbon	C—H, C—C	285.0
Amine	C—N	286.0
Alcohol, ether	C—O—H, C—O—C	286.5
Cl bound to carbon	C—Cl	286.5
F bound to carbon	C—F	287.8
Carbonyl	C=O	288.0
Amide	N—C=O	288.2
Acid, ester	O—C=O	289.0
Urea	N—C(=O)—N	289.0
Carbamate (urethane)	O—C(=O)—N	289.6
Carbonate	O—C(=O)—O	290.3
2F bound to carbon	—CH_2CF_2—	290.6
Carbon in PTFE	—CF_2CF_2—	292.0
3F bound to carbon	—CF_3	293–294

Table 2 Typical values for O1s bending energy in organic compound

Functional group		Binding energy (eV)
Carbonyl	C=O, O—C=O	532.2
Alcohol, ether	C—O—H, C—O—C	532.8
Ester	C—O—C=O	533.7

5. Conclusion

As mentions in details about XPS analysis, this technique represents the best method and the best efficiency process for qualitative and quantitate analysis. The important of this apparatus not only identified different materials but also it is able to be the best judgment to decide the identities of chemical compounds without needed for more examinations or analysis by other methods which is exceptional quality compared to many methods. The review concern with electron binding energies, chemical shifts, and related phenomena in electron spectroscopy for the emission photoelectrons

which variance in the same compound with different atoms. thus we mention that is techniques able to provide the researchers for huge amount of information for organic or inorganic compound with different state.

Compliance with ethical standards

Disclosure of conflict of interest:

No conflict of interest to be disclosed.

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