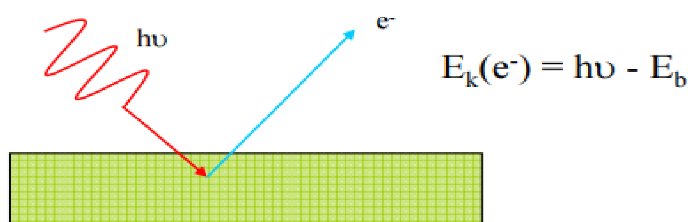
Module-5 Unit-5

XPS Principle and Instrumentation

Introduction

X-ray photoelectron spectroscopy (or XPS) belongs to the group of surface analysis methods wherein the sample under investigation is bombarded with photons/electrons/ion/etc. for exciting the emission of photons/electrons/ion/etc.

XPS involves irradiating the sample with low energy ((~1.5 keV) X-rays such that photoelectric effect is induced. An electron spectrometer with high resolution records the energy spectrum of emitted photoelectrons. Highest available vacuum conditions are required for XPS experiments. High vacuum assists photoelectron transport to the analyzer, and also avoids recontamination of clean samples. Contamination is an important concern in XPS, since it is a surface sensitive technique and the sampling depth is usually a few nm.



Principle

Surface analysis by XPS involved irradiation of the sample by low-energy (and mono-energetic) x-rays and the subsequent analysis of the energy of emitted electrons. Typically used x-rays are Kα lines of Mg (1.2536 keV) and Al (1.4866 keV). The penetration depth of these photons in solids is limited to a few microns. Thus, interactions take place between the incident photons are the surface atoms leading to the photoelectric emission of electrons. The kinetic energy (K.E.) of the emitted electrons is expressed as:

$$K.E. = h\nu - B.E. - \varphi_s \quad (1)$$

here hν is the energy of the photon, B.E. is the binding energy of the atomic orbital from which the electron is released, and φ_s, is the work function of spectrometer.

B.E. can also be described as the energy difference of the initial and final states when an electron is released from the atom. Electrons emitted from an ion possess different kinetic energies owing to the possibilities of different final states of the ion from each type of atom. Besides, there exists different probability or cross-section for each of thefinal state. **Figure 1** shows relative B.E. and ionization cross-sections for an atom.

Binding Energy

In a photoemission process, the total energy of the system, before emission, is equal to the sum of the energies of incident X-ray photon (hυ) and target atom in its initial state (E_i). After emission, total energy of the system equals the sum of the K.E. of the emitted electron (E_k) and energy of ionized atom in its final state (E_f). Equating the total energy before and after emission, and comparing with Einstein's equation gives the B.E. as the energy difference between the final and initial states of the target atom (i.e., $E_f - E_i$).

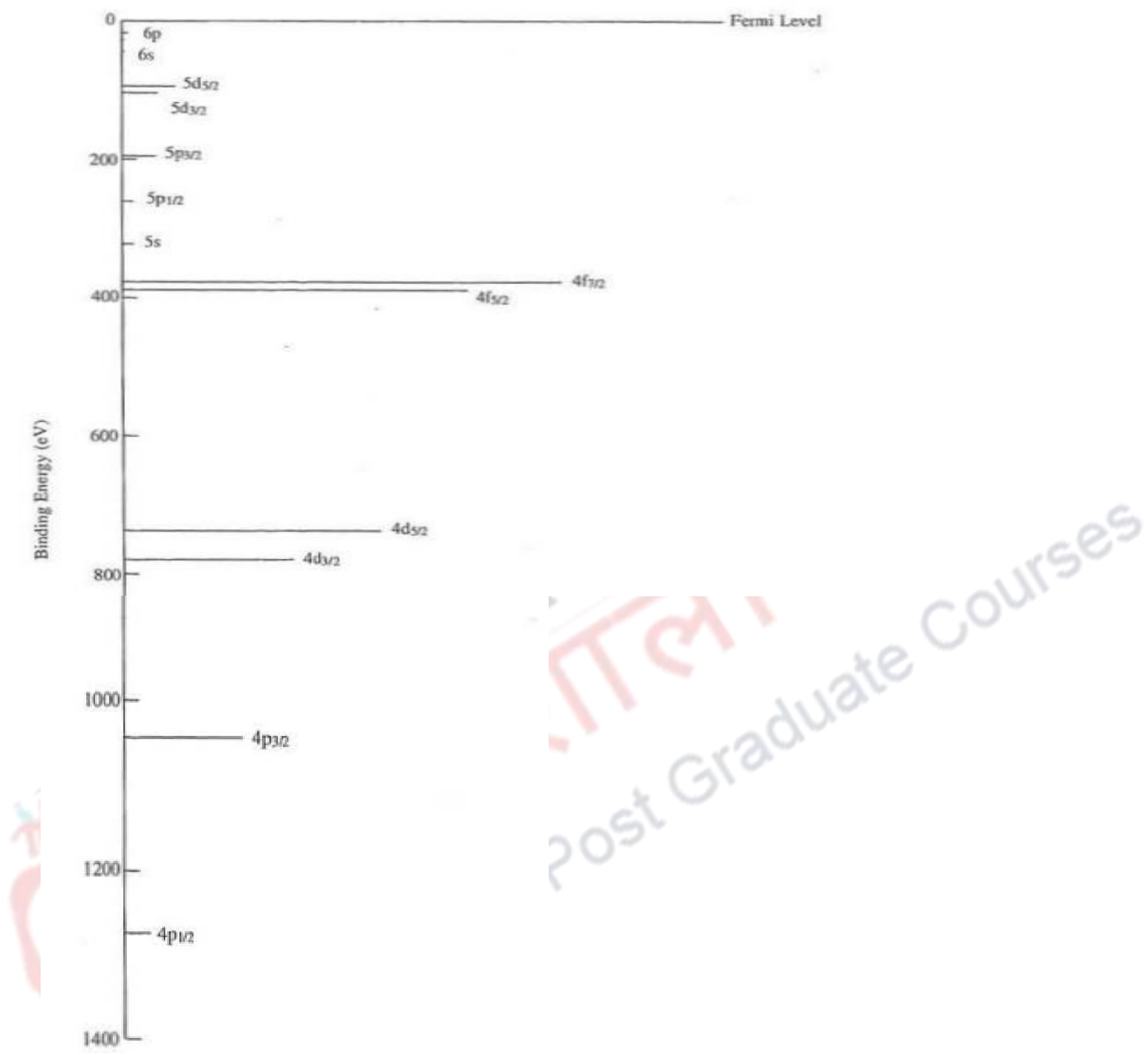


Figure 1: Relative B.E. and ionization cross-section for U. The B.E. is proportional to the distance below the line indicating the fermi levels, and the ionization cross section is proportional to the length of line.

In figure, Fermi level corresponds to zero B.E., and the depth below it reflects the relative energy of the ionized atom after emission, or simply B.E. of electron. Relative probabilities of different ionization processes are indicated by the length of the lines. Ionization causes splitting of the levels p, d and f, creating vacancies in $p_{1/2}$, $p_{3/2}$, $d_{3/2}$ $d_{5/2}$, $f_{5/2}$ and $f_{7/2}$.Thesplitting ratio of spin-orbit is 1:2 for p, 2:3 ford and 3:4 for f levels. For instance,**Figure 2**shows the spin-orbit splitting in Si 2p level.

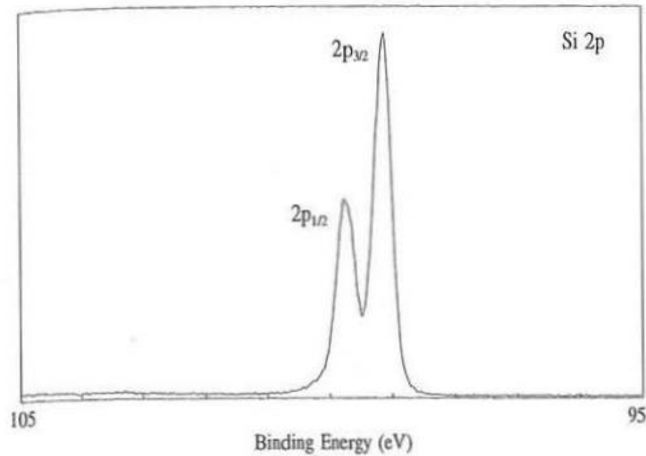
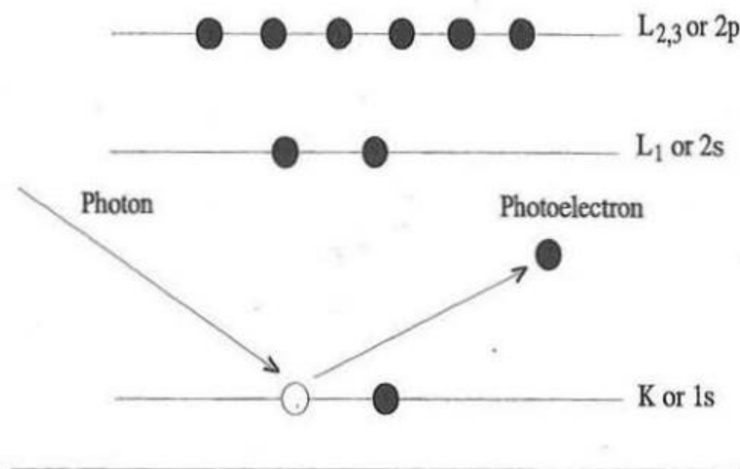


Figure 2: High resolution spectrum of single crystal Si indicating the spin orbit splitting of 2p.

XPS analysis relies on the fact that each element possesses a unique set of B.E. Thus, the concentration of elements at the surface can by identified and determined. B.E. of elements vary (the chemical shifts) because of differences in the chemical potential and polarizability of compounds. These shifts lead to the identification of chemical state of the material under investigation.

The excited ions left after photoemission, may also eject Auger electrons. Auger emission typically occurs after 10^{-14} s of the photoelectric emission. Another competing emission of a fluorescent X-ray photon may also take place. Schematic illustration of Auger phenomenon is shown in **Figure 3**, where an electron from outer shell occupies the vacancy in the inner orbital by emitting a second electron in the process. This second electron carries the extra energy, and is called the Auger electron. The K.E. of Auger electron is the energy difference between the initial ion and the doubly charged final ion. Additionally, the K.E. of Auger electron does not depend on the mode of initial ionization. Therefore, photoionization often generates two electrons: one photoelectron and another Auger electron. The sum of the K.E. of theemitted electrons cannot be larger than that of the ionizing photons.



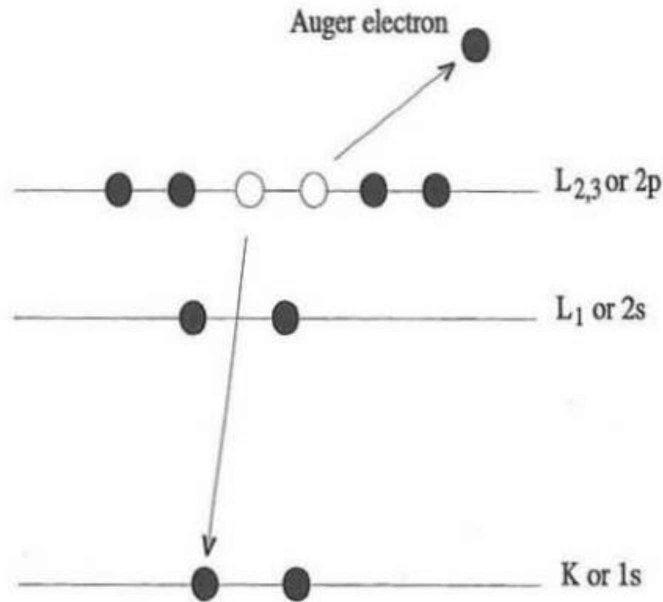


Figure 3: ***Top:*** **XPS emission for a hypothetical atom where an incident photon ejectsa photoelectron.** ***Bottom:*** **relaxation of the atomemitting a $KL_{23}L_{23}$ electron. The simultaneous two electron coulombic rearrangement results in a final state with two electron vacancies.**

Electrons undergo far more interactions with matter than photons, this results in extreme short path length of electrons (~ few angstroms) in comparison to photons (~ few microns). Therefore, when the depth of ionization is of the order of few microns, the electrons originating from deep into the bulk of solid (i.e., at a distance more than few angstroms from the surface), experience high energy losses. However, the electrons originating from the surface (or upto a depth of few angstroms from the surface) do not lose their energy, and cause peaks in the XPS spectrum. These electrons are crucial in XPS analyses. The deeper electrons experience elastic loss process before releasing from the background. **Figure 4**indicates the calculated inelastic mean free path (IMFP) of electrons in different materials.

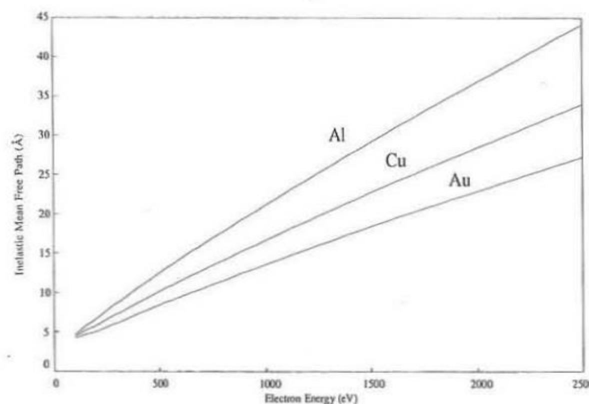


Figure 4: Calculated IMFP for electrons in different metals from the methods of S. Tanuma, C.J. Powell and D.R. Penn, Surf. Interface Anal.17,911 (l99l).

An electron spectrometer detects the electrons emitted from the sample as a function of their K.E. The analyzer works as an energy window, termed as pass energy, and accepts only the electrons with energy within the range of this window. The pass energy is usually fixed for maintaining a constant energy resolution. Incoming electrons are adjusted to the pass energy before entering the energy analyzer. A variable electrostatic field is used before the analyzer in order to scan the different energies. This is called retardation voltage and can be varied from zero to more than the energy of the photon. Electrons are detected as discrete events, and the number of electrons for a given detection time and energy is stored and displayed.

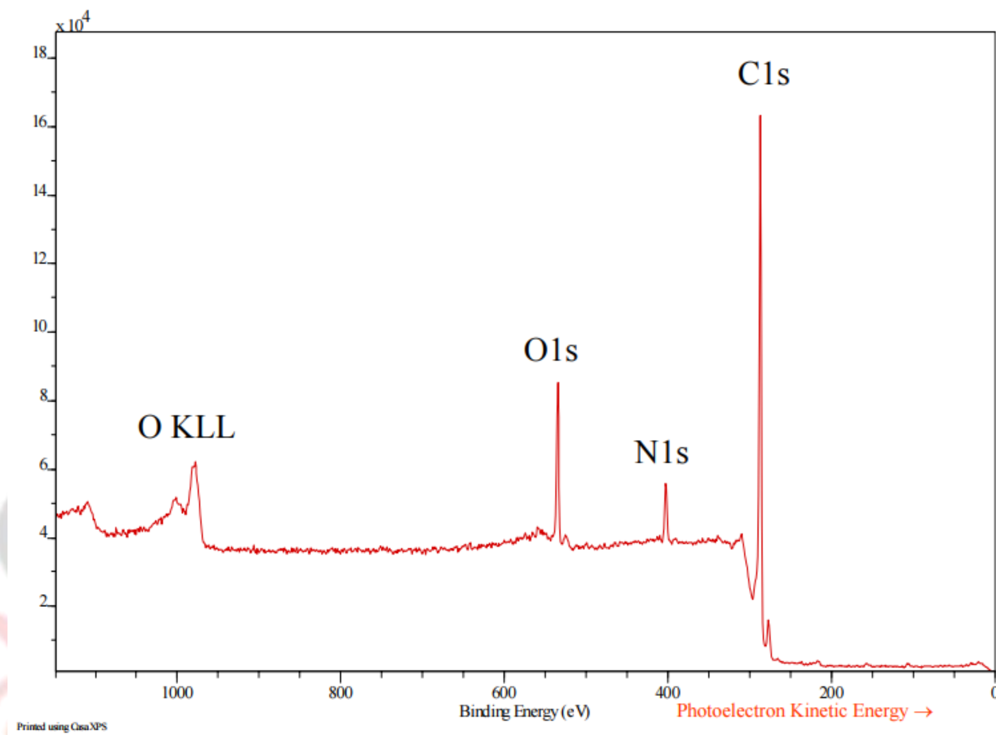


Figure 5: XPS spectrum of polystyrene.

Figure 5 shows XPS spectrum of polystyrene sample which was pre-treated with nitrogen plasma. The spectrum was recorded by exciting the sample by Al Kα rays. The B.E. scale is drawn from right to left and thus, the K.E. of the photoelectrons increase in reverse direction.

The spectrum contains three photoemissions (electrons emitted from 1s orbitals of C, N, and O atoms in the sample surface), and one Auger emission (O KLL). The background of these peaks resultsdue to the electrons excited by X-ray Bremsstrahlung radiation at low B.E., and from inelastically scattered photoelectrons at higher B.E. (to the either side of C-1s peak).

The energy of Auger electrons does not depend on the energy of X-ray. Thus, whenever Auger peaks overlap with photoelectron peaks, Auger peaks are displaced on the B.E. scale by altering the X-ray energy (such as using Mg Kα instead of Al Kα, etc.).

Factors affecting the intensity of peaks in the spectrum

Consider a volume element of the sample with thickness dz at a depth z underits surface. The photoelectrons emitted at an angle θ with respect to the normal to the sample surface (the “photoemission angle”) enter the detector and contribute to the spectrum. Usually, X-rays’reflection and refraction induced photoelectrons are significant only at a grazing angle φ < 5º, and may be ignored in other cases.

1) The intensity of the x-rays at depth z

$$\gamma(1-r)\frac{\sin\phi}{\sin\phi'}e^{\frac{-z}{\lambda_{h\upsilon}\sin\phi'}}$$

γ = incident X-ray flux
r = coefficient of reflection
$\lambda_{h\nu}$ = attenuation length of X-ray photons

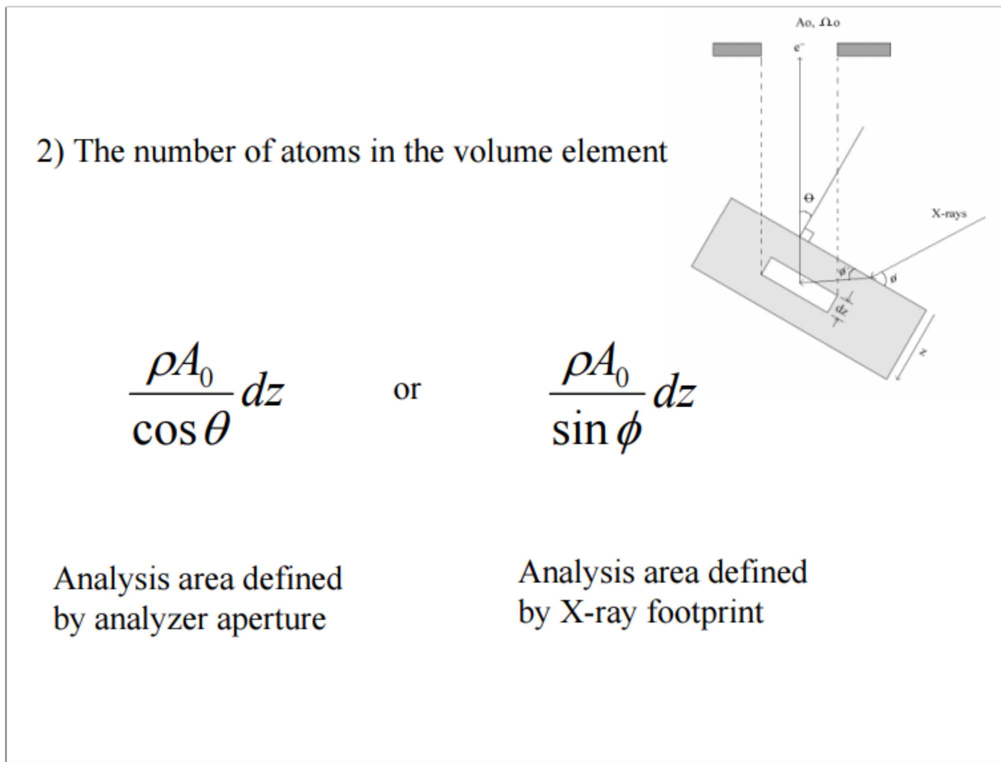
X-ray flux is not usually known.Therefore, this factor is not considered and peak intensity ratios or composition of the sample in terms of atom percent (considering one peak from each chemical element) is taken into account. The extent to which volume element generates counted photoelectrons is influenced by the particulargeometry of the experimental setup. The following cases may normally arise:

1) More surface is irradiated by X-rays than detectable by the analyzer optics (e.g., a non-monochromated X-ray source may have been used)

2) Less surface isirradiated by X-rays than observed by the analyzer optics (using a monochromated X-ray source)

Both these cases must be considered carefully and sometimes a transition between the two cases may be observedwhen there is a change in photoemission angle θ. However, these geometrical factors can be cancelled by evaluating sample composition as atomic percentage.

The analyzer acceptance angle Ω0 is a function of the lens programs and aperture settings, and is unknown. This is also cancelled byevaluating sample composition as atomic percentage(consideringpeak intensityratios).



The attenuation of emitted photoelectrons flux gives XPS its surface sensitivity. The inelastic mean free path is the average distance between collisions where the photoelectron loses its energy. If a photoelectron loses K.E. in a collision, it will contribute to the background rather than to the characteristic "no-loss" peak in the spectrum.

Instrumentation

The instrumentation of XPS system can be explained using the experimental set up shown in fig. 10. In a typical set up, when the sample kept in ultra-high vacuum is illuminated by the photons with energy (hν); soft x-rays, then after direct transfer of energy from the photons to the core level electrons their atoms on the surface emit electrons or sp called photoelectrons. The process can be explained as follows:

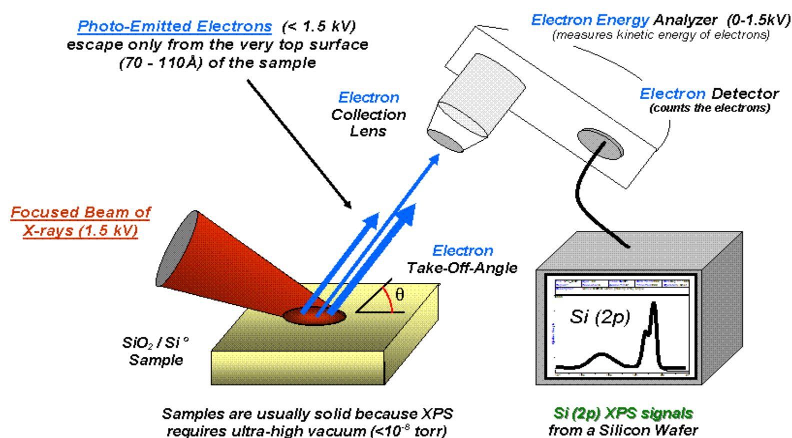


Figure 5: Monochromatic XPS system

1. A bound electron adsorbs a photon and converts part of the energy to kinetic energy.
2. While leaving the atom, some energy of the electron is consumed in overcoming the Coulombic attraction of nucleus, thereby decreasing its kinetic energy.
3. At this time the outer orbitals readjust, reducing the energy of the final state which is being created and delivering this extra energy to the outgoing electron.
4. Then the XPS spectrum is obtained by determining the K.E. and number of electrons escaping from upper 0 to 10 nm of sample under investigation.
5. XPS may be routinely employed to study inorganic compounds including metal alloys, semiconductors, polymers, glasses, ceramics, ion-modified materials, etc.

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Review your learning:

Q1. The kinetic energy of the photoelectron energies is dependent on _________ of the atom, which makes XPS useful to identify the oxide state.

a) Mass
b) Charge
c) Chemical environment
d) Volume

2. Ion etching techniques provides the depth profiling from the surface.
a) True
b) False

3. Electron spectroscopy is based on the ionization phenomenon.
a) True
b) False

4. The kinetic energy of the ejected photoelectron is dependent upon the energy of which of the following?
a) Ions around
b) Photons around
c) Material
d) Impinging photon

5. ESCA gives sufficient chemical information up to a depth about ________ armstrong in metals.
a) 5-20
b) 15-40
c) 40-100
d) 100-200

6. ESCA gives sufficient chemical information up to a depth about ________ armstrong in polymers.
a) 5-20
b) 15-40
c) 40-100
d) 100-200

7. ESCA gives sufficient chemical information up to a depth about ________ armstrong in oxide.
a) 5-20
b) 15-40
c) 40-100
d) 100-200

8. ESCA can identify elements in the periodic table above which of the following?
a) Carbon
b) Boron
c) Helium
d) Potassium

9. These characteristic peaks correspond to the ________ of the electrons within the atoms, e.g., 1s, 2s, 2p, 3s, etc.

a) Electron configuration

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b) Hydrogen

c) Noble Gas

d) Oxygen

10. ESCA focusses on which of the following information?
a) Mass of the electron
b) Charge of the electron
c) Binding energy of the electron
d) Mass of atoms

11. In the spectrum, two main peaks at _________ and ________ are observed.
a) 284.6, 532.5
b) 248.6, 523.5
c) 264.8, 535.2
d) 246.8, 553.2

12. 284.6 eV matches which of the following specific atom type?
a) Carbon
b) Oxygen
c) Nitrogen
d) Argon

13. Which of the following is the detection limit of ESCA?
a) 0.1% monolayer
b) 0.5% monolayer
c) 1% monolayer
d) 2% monolayer

14. By studying which of the following can we determine if the surface corresponds to C-O or C=O chemical form?
a) Mass of the electron
b) Energy of the carbon peak
c) Binding energy
d) Charge of electron

15. 532.5 eV matches which of the following specific atom type?
a) Carbon
b) Oxygen
c) Nitrogen

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