

Magnetic Ordering effects as revealed from XPS

ASSIGNMENT -2

Submitted to :
Prof. B. Viswanathan
IIT Madras

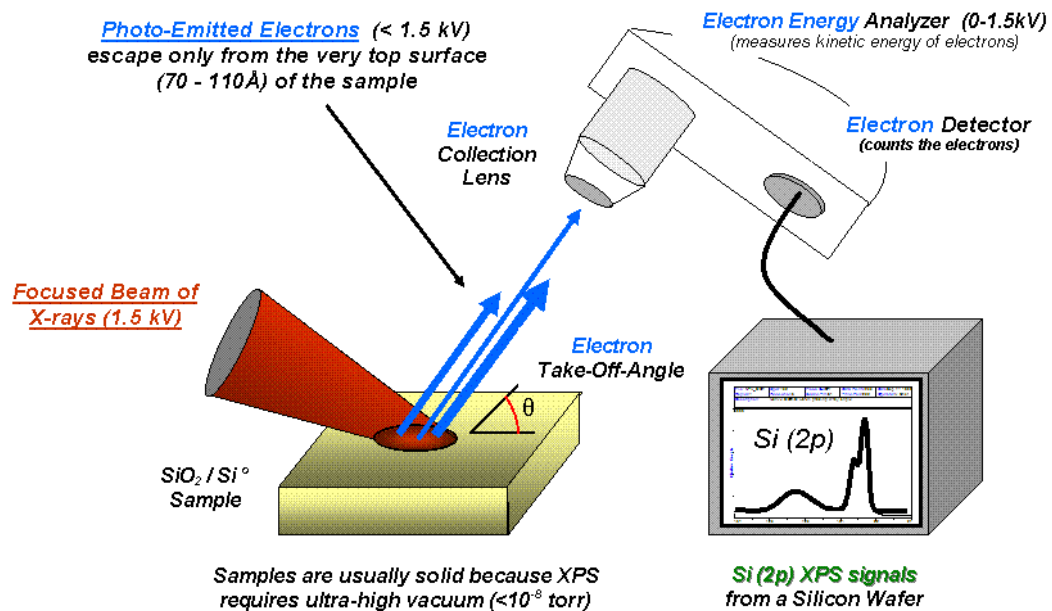
Submitted by :
Tapas Mahanand
Mtech Catalysis
Roll : CA20M005

INDRODUCTION

- X-Ray Photoelectron Spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique based on the photoelectric effect that can identify the chemical composition, chemical state and overall electronic structure, magnetic effects and density of the electronic states in the material.
- The change of the spin magnetic moment of the transition 3d metal atoms is studied in metal-containing nanoscale structures based on the relationship between the spin magnetic moment and the ratio of the intensities of multiplet splitting maxima in 3s spectra of metals.
- It is also known as Electron Spectroscopy for Chemical Analysis (ESCA).
- XPS is a powerful measurement technique because it not only shows what elements are present, but also what other elements they are bonded to.
- Photoemission can be used for :
 - 1)Determination of Surface geometry
 - 2)Measurement of Band Structure of solids

PRINCIPLE

- A mono-energetic x-ray beam emits photoelectrons A mono-energetic x-ray beam emits photoelectrons from the surface of the sample.
- The X-Rays either of two energies:
Al K_{1s} (1486.6eV)
Mg K_{1s} (1253.6 eV)
- The x-ray photons, the penetration about a micrometer of the sample.
- The XPS spectrum contains information only about the top 10 - 100 Å of the sample.
- The spectrum plotted by the computer from the analyser signal.
- The binding energies can be determined from the peak positions and the elements present in the sample identified.



Use of XPS for determining Magnetic Properties

One of the main characteristics of magnetic materials is the magnitude of the atomic magnetic moment. The methods known so far for the determination of this magnitude give an averaged value. Such investigations are informative for the materials with homogeneous crystalline structure. However, there are heterogeneous objects, the metals atoms of which have different surrounding; and they can differ in the value of the atomic magnetic moment.

It is obvious that it is necessary to conduct a detailed investigation of the interconnection between the electronic structure and varying magnetic characteristics of materials based on 3d transition metals at changing temperature and composition, using modern spectroscopy methods for structure investigations.

One of the most powerful direct methods for investigating electronic structure, chemical bond, nearest surrounding of the atoms of substances is X-ray photoelectron spectroscopy(XPS). The choice of an electron magnetic spectrometer is due to a number of advantages in comparison with electrostatic spectrometers, namely, its constant luminosity and resolution, which do not depend on the energy of electrons and high contrast of spectra.

In addition, the constructional separation of the energy analyser of magnetic type from the spectrometer vacuum chamber

allows using various ways of action on a sample in vacuum right at the moment of spectral measurements. Neither heating nor cooling of samples or mechanical cleaning of the sample surface from contaminations deteriorates the spectrometer resolution.

At present, the unique physical properties of nanoparticles are the subject of intensive studies. Special attention is paid to magnetic properties, in which the difference between massive material and nanoscale material is exhibited more clearly. By changing the size, form, composition and structure of nanoparticles, it is possible to regulate magnetic characteristics of the nanoparticle-based materials to a certain extent.

The main method of investigation was the method of XPS. The analysis was conducted on an electron magnetic spectrometer. The vacuum in the spectrometer chamber was 10^{-9} torr. The instrument resolution was 1.2 eV and the accuracy of the measurement of the peak positions was 0.1 eV.

Explaining XPS and magnetic moment with 3D metals

The XPS 3s spectra of transition metals are known to correlate with the magnetic moment of metal atoms. The interpretation of 3s spectra of transition metals within the single electron theory describes the $3s^{-1}$ multiplet in 3d metals as two groups of components well separated by energy, the relative intensities of which are associated with the total spin of the 3d sub-shell, and consequently, with the magnetic moment on an atom of a transition metal.

The presence of two maxima is characteristic of the 3s spectra of reference metals, in which multiplet splitting is reflected. Based on the model offered by Van Vleck, the values of atomic magnetic moments for the reference systems of 3d transition metals are obtained from the spectra parameters with the use of the approximation:

$$\frac{I_2}{I_1} = \frac{S}{(S+1)}$$

where S is spin quantum number.

The distance between the peaks determines the exchange interaction energy:

$$\Delta = (2S + 1)I_{SD}$$

where I_{SD} is intra atomic exchange integral between 3s and electrons depending on the overlapping of 3d and 3s shells.

The magnetic moment of atoms is determined from the expression:

$$\mu_S = 2 \mu_B \sqrt{(S+1)S}$$

where μ_B is Bohr magneton and S is the spin moment of unpaired 3d electrons.

The XPS spectra parameters are connected with the spin state or the atomic magnetic moment in the following manner:

1. The relative intensity of the 3s spectra multiplet maxima correlates with the magnitude of the magnetic moment of the atoms in the 3d metal systems.
2. The distance between the multiplet maxima yields information about the exchange interaction of 3s–3d shells, based on the changes taking place in the 3d shell, we obtain the information about the changes in the distance between neighbouring atoms.
3. The shape of the valence bands, which is the energy distribution of the density of d states, determines their localisation and presents the information about the nearest surrounding of the atoms.
4. The presence of variations in the 3s spectra shapes and the valence bands gives the information about the changes in the alloy structure.