Photoelectron Spectroscopy (XPS) and its Applications

S S ACHARYA[†] and V R R MEDICHERLA

Dept. of Physics, Institute of Technical Education and Research, Siksha 'O' Anusandhan University, Bhubaneswar 751030

[†]corresponding author, email: acharyashakti@gmail.com

Abstract : X-ray photoelectron spectroscopy (XPS) is based on the principle of photo electric effect. XPS is suitable to study the electronic structure of metals and alloys. Apart from Identification of elements, chemical shift, core level shift, core disorder broadening and spin orbit splitting can be observed using XPS in bulk alloys and thin films.

Keywords: Photo-electric Effect, Chemical Shift, Spin orbit splitting

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1. Introduction

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a widely used technique to investigate the chemical composition of surfaces. XPS is based on the principle of photo electric effect. Photoelectric effect is a process in which electrons will be ejected out when a metal surface is irradiated with a light of suitable frequency. The energy of each constituting particle of light called photon is given as E = hν where E is the energy of the photon, h is Planck's constant and ν is the frequency. The frequency of each ejected photoelectron called threshold frequency should be smaller than the frequency of the photon. So the photoelectrons are

Fig. 1. represents photo electric effect.

ejected with a kinetic energy (KE) given by, KE = hν - Φ, where Φ is the work function. Photoelectric effect is shown in figure 1. In 1887, Heinrich Hertz suggested that ionization occurs when matter interacts with light of sufficient
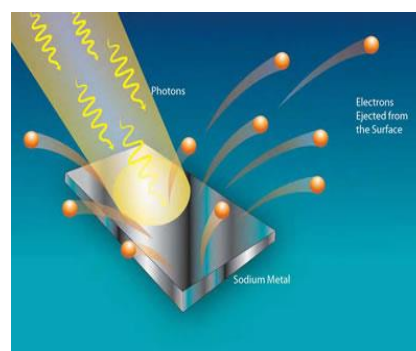
energy which is shown in figure 2 and is known as photo effect. Einstein explained Photoelectric effect quantum mechanically in 1905 for which he was awarded Nobel Prize in 1921.

Einstein's photoelectric equation is given as
$$1/2mv^2 = h\nu - \phi$$
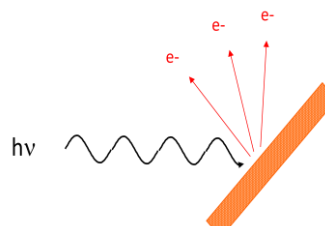$h\nu$ = Energy of incident photon
ϕ = Work function

Fig. 2. represents photo effect.

The Nobel Prize in Physics 1924 was awarded to Manne Siegbahn for his discoveries and research in the field of X-ray spectroscopy. In 1951, Kai Siegbahn developed theory of Electron Spectroscopy for Chemical Analysis (ESCA), i.e. XPS. The Nobel Prize in Physics 1981 was divided, one half to Kai M. Siegbahn for his contribution to the development of high-resolution electron spectroscopy [1]. (Other half to Nicolaas Bloembergen and Arthur Leonard Schawlow for laser spectroscopy.)

2. X-ray Photoelectron Spectroscopy (XPS)

XPS spectral lines are identified by the shell from

which the electron was ejected (1s, 2s, 2p, etc.).

The ejected photoelectron has kinetic energy:

$$KE = h\nu - BE - \phi$$

Figure 3 represents XPS process where one electron

from 1s core level is ejected out due to incident X-ray.

Source of excitation is X-ray.

Fig. 3. represents XPS process.

Most Commonly used X-ray sources are AlK_α (1486.6 eV) and MgK_α (1253.6 eV).

K_α X - ray is emitted due to the electron transition

from 2p to 1s state as shown in figure 4.
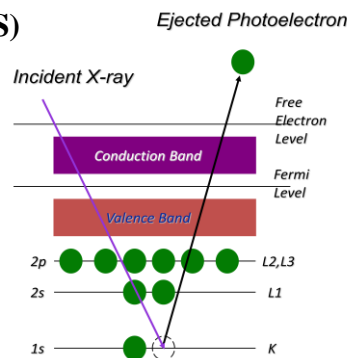
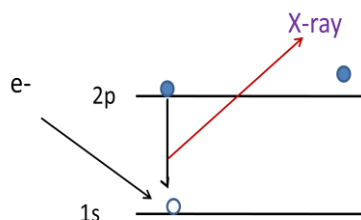For Al, 1s energy = 1559 eV, 2p energy = 72.4 eV.

Fig. 4. represents production of X-ray.

So energy difference = 1486.6 eV.

For Mg, 1s energy = 1303 eV, 2p energy = 49.4 eV

So energy difference = 1253.6 eV.

3. Applications

(a) Identification of elements:

Photoelectrons ejected out from core levels as well as from valence shells possess different kinetic energy thus represent features at different energy levels as shown in figure 5. Survey scan of Fe, $Fe_{0.6}Ni_{0.4}$ and Ni at low temperature excited by AlKα monochromatic radiation is shown in figure 5. Absence of oxygen and carbon features indicate the purity of the samples. Spectrometer was calibrated using Ag 3d spectrum recorded at low temperature (10 K) and the kinetic energy of the recorded spectra was subtracted from the energy of AlKα source to estimate the binding energy of the ejected photoelectrons. Different values of binding energy given in figure 5 represents the electrons ejected out from different levels.

(b) Spin orbit splitting:

s level does not split where as p, d and f etc. levels split into two. The splitting of p, d and f levels were clearly observed in spectrum of various elements and was known as spin orbit splitting (SOS). Figure 6 represents SOS of Ag 3d. The energy difference observed from the spectrum of Ag was 6 eV and was calculated and estimated to be 5.8 eV theoretically using the following equation.

$$\Delta E_{s.o.} = \frac{e^2 h^2 Z^4 (10^{-7})}{8\pi^2 m^2 a_0{}^3 n^3 l(l+1)} J$$

Z = Effective atomic no. for the given orbital.

 Ag 3d

(1s)	(2s,2p)	(3s,3p)	(3d)
2 x 1	8 x .85	8 x .35	9 x .3 = 14.3

Z = 47 – 14.3 = 32.7

47 = Atomic No. of Ag.

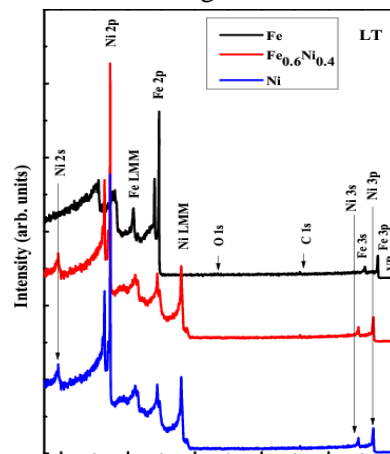Similarly, the intensity ratio of $3d_{5/2}$ and $3d_{3/2}$

Fig. 5. represents survey scan of Fe, $Fe_{0.6}Ni_{0.4}$ and Ni at low temperature excited by AlKα monochromatic radiation.

peaks was observed to be 0.69:1 experimentally which was in accordance with the theoretical estimation of about 2:3.

4.   Conclusion

X-ray photoelectron spectroscopy is the most widely used technique to identify the elements, observe the chemical shift, estimate spin orbit splitting, observe core level shift as well as core disorder broadening in bulk alloys and thin films. So XPS is the most suitable technique to study the electronic structure of strongly correlated system in which many body effects occur[2].

Fig. 6. represents spin orbit splitting in Ag 3d.

References

[1] C. Nordling E. Sokolowski and K. Siegbahn, Phys. Rev. **105**, 1676 (1957)

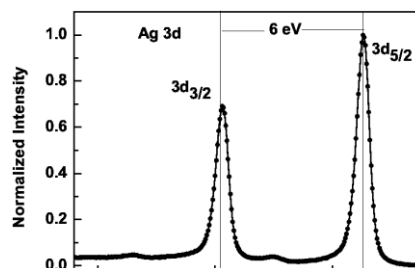[2] S. Hufner, *Photoelectron Spectroscopy, Principles and Applications*.