

**Literature Report
For
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**Experimental approaches to the study of
insulating materials by electron spectroscopy**

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Abstract: This report reviews various experimental approaches to obtain useful spectra for insulator using electron spectroscopy. Charging mechanisms are discussed and successful application of electron spectroscopy is given.

Keywords: electron spectroscopy, insulator, experimental approach

The category of the electron spectroscopy includes: X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) and High-resolution Electron Energy Loss Spectroscopy (HREELS). They are so called because during the analysis, electrons are used as incident or detected particles.

The immediate section briefly describes principles of electron spectroscopy which provides how these spectrometers work.

1 Principles and the information provided by electron spectroscopy^[1]

XPS

For XPS, it uses photon source in the X-ray energy range to irradiate the surface. The atoms in the surface emit electrons (photoelectrons) after direct transfer of energy from photon to the core-level electron. These emitted electrons are then separated and counted. The energy of the photoelectrons is related to the atomic and molecular environment from which they originated. The number of electrons emitted is related to the concentration of the emitting atoms in the sample.

Much useful information can be provided by these electron spectra: Identification of elements; Semi-quantitative determination of surface composition; Information about the molecular environment (oxidation state, bonding atom); Non-destructive elemental depth profiles.

AES

AES is a very important tool for chemical surface analysis. For typical AES, it uses electron beam with about 3-30 keV energy to bombard the sample, the emitted Auger electrons from the first few monolayers because of their restricted kinetic energy. Thus, by the analysis the Auger electrons obtained, AES can provide useful quantitative and qualitative surface information.

HREELS

HREELS perhaps is more sensitive than other techniques because it bases on an extremely precise measurement of electron energies (within a few eV) and because of its exceptional

surface sensitivity. In HREELS, low energy, well-monochromatized electron beam is used to excite vibrations from a material surface. Electrons backscattered are then collected and analyzed to provide the molecular vibrations of species adsorbed on the sample surface or intrinsic collective phonon vibrations from a solid material.

2 Problem occurred when analyzing insulators

Many materials which researchers are interested in are insulators, such as minerals, ceramics, fibers, polymers, glasses, halides and biological materials and so on. In addition, many metals and semiconductors are spontaneously oxidized when exposed to air and are thus coated by insulating layers (e.g. Fe_2O_3 , SiO_2) of varying thickness. During their surface analysis, the corresponding specimens are submitted to incident irradiation (such as electrons in AES, X-ray photons in XPS or low energy electrons in HREELS) and electrons emitting are collected and analyzed. During this process, insulating samples are subjected to charging effects because of their insulating nature. Since the early development of the surface analytical techniques, these effects have been widely observed and reported in a variety of papers. ^[2,3]

The effect of charging

In electron spectroscopy, surface is either positive or negative charged and the surface charging leads to general four kind of problems:

- 1) General instability leading to spectral noise making analysis impossible and
- 2) Shifting of spectra on the energy scale which leading to difficulties in interpreting chemical states. Different charging in different regions of the surface may cause a given peak to broaden or to split into more than one peak. In AES, where the shift on the energy scale may be 50 or 100 eV, spectral intensity decreases. In HREELS, when surface potential is over 10 eV, charge repels incoming electrons. As a consequence, no electron energy loss will be recorded.
- 3) May lead to chemical reaction on sample surface. In AES, electron-stimulated desorption (ESD) leads to creation of oxygen vacancies and a loss of oxygen in the surface region when surface are highly charged. ^[4]
- 4) Excessive charge may damage sample. Under high electrical field, delicate samples such as polymers may be destroyed.

Owing to the detrimental effects mentioned above, it is important to avoid, or at least reduce charging by suitable experimental methods.

3 Mechanism of charging

Surface charging brings difficulties in obtaining correct information about sample, various ways are provided helping to eliminate these notorious effects. Before evaluate these methods, knowledge about charging mechanism will be very helpful in finding and evaluating those methods.

Because charging mechanisms are slightly different for three kind of electron spectroscopy, mechanisms are discussed individually:

XPS

When the conductivity of the sample is large enough, the charge thus resulted from the electron process is immediately neutralized by an electron flux. On the contrary, with insulators, neutralization is only partial and a significant net positive charge accumulated at the surface.

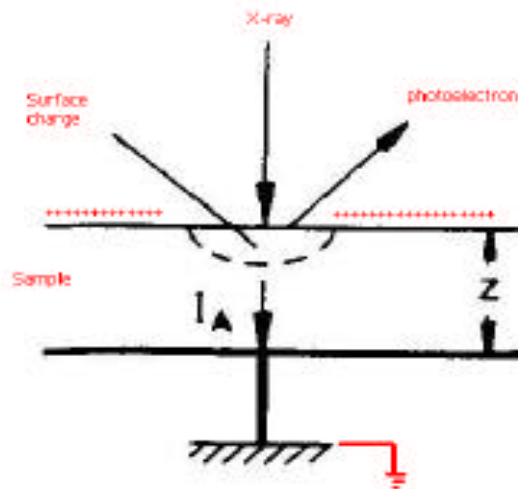


Figure 1 Schematic of XPS charge mechanism

As shown in Figure 1, sample surface acquires a positive potential which varies from several volts to several tens of volts and the kinetic energies of the photoelectrons are decreased by the electronic field. This means that the Fermi levels of the sample and spectrometer are no longer in equilibrium, resulting an unknown surface potential. This is a kinetic phenomenon and in most cases the magnitude of the charge reaches a stable value within a few seconds when turning on the X-ray.

AES

A schematic of the “capacitor model” of the sample is shown below:^[5]

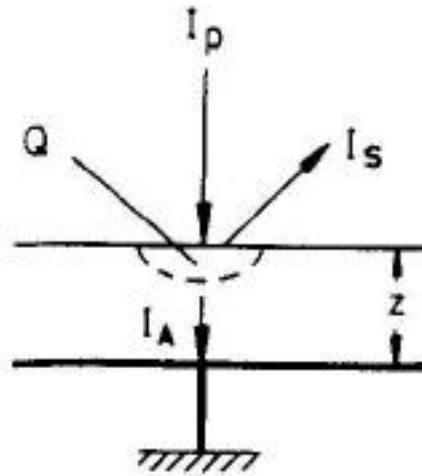


Figure 2 Schematic of XPS charge mechanism

I_s : total secondary emission current, j_p : Primary electron current density, z : sample thickness, Q : surface charge

Charging of insulator is a bit more complex than that in XPS. It is believed that the buildup of charge occurs quickly and is the result of the mismatch of the incident electron beam current and the emitted electron emission current.

According to Hofmann^[6], surface charge potential in AES can be expressed:

$$U_c = (I_b - I_e) \times R$$

$$U_c = b \times z \times \lambda_b (I - \alpha)$$

where

U_c : Surface charge potential; I_p : beam current; I_s : total secondary emission current; R : resistivity of insulator; z : sample thickness; j_p : Primary electron current density; α : secondary emission coefficient

Surface charge can be either positive or negative in AES depending on the total secondary electron emission coefficient. If $\alpha > 1$, the sample surface charges positively. Since the emitted electrons constituting the secondary electron emission are mainly of energies below 50 eV, a small positive charge is sufficient to attract them back to the sample. Thus, a positive charge of about 10eV may greatly reduce the overall emission such that the total emission and the incident beam current exactly balance. Thus, if $\alpha > 1$ the sample surface will charge positively and

stabilized by a small amount in the range 0-20 eV. Element peaks are shifted down in energy by some 10 eV but are still easily identified.

On the other hand, if $\sigma < 1$, sample charges negatively. As the beam energy falls, σ increases to unity, the surface potential becomes stable. In general, this will cause the surface charge of the sample to be about the order of kilovolts. In this case, the Auger electron peaks are shifted up in the energy by this amount and may not be measurable.

So, it is important to make sure that $\sigma > 1$. σ relates to the incident beam energy and incident angle.

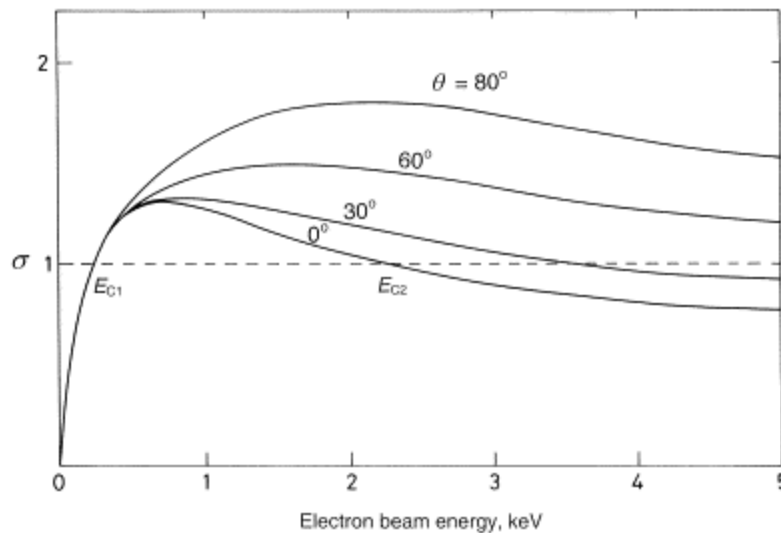


Figure 3. Schematic dependence of the σ , on the primary electron energy, E , and the angle of incidence, q , in the range $0-80^\circ$. The energies $EC1$ and $EC2$ at which σ is unity, are shown for the 0° curve.

The above graph^[7] gives the relationship of σ and electron energy E , angle of incident beam, θ . By increasing incident angle or increase the energy of beam ($EC1 < E < EC2$), it is possible to control σ to be more than unity. In experiment, it can be easily realized by rotating the sample to increase the incident angle of the electron beam.

Also caution should be taken that this simple charge model does not take into account that the in-depth and lateral distribution of the induced charge in the sample. This situation is considered in detail by some authors.^[8]

HREELS

When an electronically insulating material is bombarded by a low energy (0-10eV) electron beam, it will charge up electrostatically. Low energy electrons are trapped on the material surface, resulting in an electrostatic potential that repels all further incoming particles. One thing should

be noted that as in HREELS, the surface charge is always negative. As a consequence, no electron energy loss spectrum can be recorded. The sole signal that is detected comes from electrons that are reflected far from the material surface by electrostatic force. It contains only so-called "elastic" peak at zero loss energy, i.e. at maximum (incoming) kinetic energy.

The difference that HREELS from the AES is that in a poorly conducting material will either present a normal HREELS spectrum or no spectrum at all. And in HREELS the charged state of the material surface (i.e. electrostatic mirror state) is reached almost instantaneously, or within a few minutes at the most.

4 Critical parameters that affect the surface charging in XPS and AES

Several factors contribute to sample charging in the XPS are reviewed in detail.^[9] These factors include:

1) Influence of the thickness of the specimen and substrate effects:

For a specimen homogeneous in composition it shows that surface potential is expected to decrease when sample thickness is decreased and this fact has been experimentally established for a long time^[10].

Also, when sample thickness is less than penetration depth of the incident X-rays, an additional contribution to charging mechanisms may be issued from the substrate. The penetration depth of incident X-rays being larger than the thickness of the specimen, a part of the incident photons generate photoelectrons and Auger electrons which are injected from the substrate into the specimen.

2) Influence of the lateral surroundings

Illumination of sample has been supposed to be uniform over a large surface of the specimen so that the surface potential is considered as being a constant as a function of the lateral coordinates when the specimen is homogeneous in its bulk composition and thickness. In fact surface potential is a function which changes obviously, with the lateral inhomogeneities of the specimen composition leading then to lateral changes of the local electron energy affinities and to changes of the local density of secondary electron emission. The distortions and shifts of the measured spectra correspond to the variations of surface potential integrated over the projected area of the field aperture of the analyzer on the specimen surface so that the decrease of this field aperture decreases the peak broadening.

3) Influence of the incident angle

When XPS or AES is operated at oblique incidence angle i , the incident flux, *Error! Unknown switch argument.*, on the specimen surface is *Error! Unknown switch argument.* $\cos i$ where *Error! Unknown switch argument.* is measured on a plane perpendicular to the direction of incident X-rays. Surface charge density is proportional to *Error! Unknown switch argument.* $\cos i$ and then a shift of the surface potential varying like $\cos i$ may be expected, when the incident angle is changed.

4) Time dependence

The initial time evolution of surface charge potential is proportional to the fluence of the irradiation, and to the secondary yield of the uncharged insulator. The surface potential changes as function of the irradiation time.

5 Solutions to the Charging in electron spectroscopy

Since the very beginning of the application of electron spectroscopy on insulator, various methods to obtain useful spectra have been put forward. Broadly speaking, these methods can be divided into two categories: one is charge reference in which a known bond energy (BE) material is used to calculate surface charge potential and thus to calibrate sample spectra. The other is charge-elimination which uses various methods to decrease surface charge.

5.1 Charging reference

The principle of charging reference is that the reference materials truly reflect the steady-state static charge exhibited by the specimen surface and that they contains an element peak of known binding energy.

This kind of method is applicable to XPS and AES. For HREELS, however, because the energy of the probe electrons is so low that the slightest charge which is tolerable for XPS and AES may be disaster for HREELS. One practical method for HREELS is charge elimination.

Following are several methods widely used in XPS and AES^[1]

1) Reference via adventitious carbon-based contamination

Samples in the spectrometer may be contaminated by the adsorption of the residual gases. These contamination layers can be used for referencing purpose.

Carbon is the element that is most commonly detected in contamination layers and C1s photoelectrons are those most generally adopted for referencing purpose. A binding Energy of 285.0 ± 0.2 eV is often used for this level and the difference between its measured position in the

energy spectrum and the above value gives the charging value according to the following equation

$$E_B = E_B' - C$$

where: E_B is the known BE and E_B' is the BE acquired in the experiment. C is the surface charge.

The main disadvantage of this technique is the uncertainty caused by the spread of BE values from 284.8 to 285.2 eV ^[11]

Despite the apparent limitations and uncertainties associated with adventitious carbon referencing, it is the most convenient and commonly applied technique.

2) Deposited surface layers

In this method, organic compounds and metal are used instead of carbon as they can often be reliably condensed onto surface under UHV conditions.

This technique is not applicable for the powder samples. Actual charge correction depends on the surface coverage according to the detail study. ^[12]

3) Implanted noble gas ions

Kohiki et al ^[13] used argon implantation at 1 keV at low doses into insulators. A binding energy of 242.3 ± 0.2 eV is granted for argon ions. They found this technique is quite flexible in determine the insulators' charging. Care must be taken to keep the ion flux sufficiently low for the sample not be damaged.

4) Internal standard

This technique lies in the use of an internal standard which depends on the invariance of the binding energy of a chosen chemical grouping in different molecules. The referencing species is now “locked” into the unknown material and thus reflect the static charge of the system if it is uniform over the surface. This method is particular useful for carbon-containing materials, esp. polymer systems. However, it requires to know the molecular formula of the material studied and the binding energy of the chemical grouping employed must be know to be invariant in a range of environment by some independent method.

Insulators tend to cause more of a problem in AES than in XPS as the electron current densities involved are much higher. All the referencing method mentioned is applicable for the AES, however it is important to consider the charging situation before using it.

5.2 Charge elimination

For charge-elimination, it can be subdivided into two main categories: one kind treats the sample to improve its conductivity thus eliminates surface charge. The other is a more widely used method which use external or so-called secondary particle source to neutralize surface charge.

5.2.1 Increasing sample conductivity (applicable to XPS, AES and HREELS)^[14,15]

- (1) Blend sample with impurities. When insulator mixes with conductive impurities, the conductivity of sample will increase. Thus, the charge can be easily eliminated. The disadvantage of this method is that it introduces impurities which might interfere with the spectra obtained.
- (2) Heating sample to improve the electrical conductivity of insulators. However, considering this method may induce conflicting electron emission and/or electric fields which will perturb data acquisition. To circumvent this problem, heating must be pulsed.
- (3) Use very thin films. If the material growth process allows, it is the easiest way to alleviate the charging problem. When the sample is thin enough, electrons from metallic substrate can enter into dielectric insulating layer. Thus the positive charge in the surface is reduced. The main problem for this method is that whether structure of the thin film can reflect that of thicker layers.

5.2.2 Charge neutralization with charge particles

Using charged particles to neutralize surface charge is one of the easiest and most widely used solution to charging problems. Because the surface charge mechanisms have slight difference, the charge neutralization methods are discussed individually:

XPS

As discussed above, surface charge in XPS is always positive. For XPS, it simply adopts a beam of low energy electrons to irradiate at surface and contribute to the neutralization of the surface positive charge. The main difficulty of this method is to adjust the flood gun voltage to exactly balance positive charge without getting an excess of electrons including negative sample charge. This is usually done by tuning the voltage for minimum core level line width.^[16] Also should be cared is that the electron beam does not modify the chemical state of the atoms or induce electron-stimulated decomposition. For example, silicon oxide decomposition induced by an electron is a well-known phenomenon.

Furthermore, combination of electron guns and internal reference has been proposed.^[17]

AES

From charging mechanism, charge status in AES depends on secondary electron yield, γ . When $\gamma > 1$, surface is positively charged and thus can use method in XPS to neutralize surface charge. So, various efforts should be done to increase γ .^[18]

When $\gamma < 1$, surface is negatively charged. It is proposed to use high-energy electron beams (Auger gun) to increase the yield of Auger electron, thus neutralize surface charge. Another straightforward method is using light noble ion gun with high current density ($>10^3$ A/cm²) to neutralize negative surface charge. It is not recommended, however, to use this method because ions are introduced to sample surface and might add complexity of spectra and at mean time, high current density of ion gun may damage sample surface.

HREELS

As surface charge is always negative in HREELS, the desirable way is to use secondary high-energy beam (e.g. Auger gun) and adjust incident energy and angle to let the secondary electron emission yield higher than unity. The surplus electron on sample surface can be eliminated.^[3]

Using Auger electron beam may only suitable for inorganic samples. For organic samples such as polymers, middle energy technique was brought forward to circumvent the problems mentioned above by Apai et al.^[19,20]

Recently, these authors^[21] developed this method to lower energies in the range of 130 to 170 eV. Desirable charge elimination has been achieved on thick polystyrene and polytetrafluoroethylene (PTFE).

6 Successful example of application of electron spectroscopy on insulators

Electron spectroscopy can provide rich information of surface and/or interface properties of sample. During three methods of electron spectroscopy, HREELS is a very promising technology in analyzing polymers due to its high surface sensitivity and wide spectral range allowing a probe of both vibronic and electronic excitation compared with IR and Raman spectroscopy.

Until recently, this method is restricted in its application to thick insulating polymers because of poor resolution and difficulty with charge neutralization and data processing methods to improve the resolution of HREELS spectrum. The authors^[20,21] successfully applied Medium Energy Technique on 0.1mm thick polystyrene. This method allow them to get stable, reproducible spectra from the insulating material at effective resolution of ~ 6 meV at relative high loss intensity. (The secondary gun was operated at 170 eV beam energy and <5 nA beam current)

The key of this technique is the use of a defocused beam that illuminates both the sample and the metallic sample holder. This stable surface potential maybe of two possible mechanisms: induced surface conductivity and enhanced secondary electron emission near the vacuum level.

Figure 4 shows spectra they got in different spectrometers: (a) is obtained from Model LK2000 with 6 eV impact energy. (b) is obtained form Model ELS3000 with 4.5 eV impact energy. This two spectra are almost the same which shows that the flexibility of middle energy technique.

With the combination of IR and Raman spectra of the sample, they successfully assign the 18 vibration models of the sample.

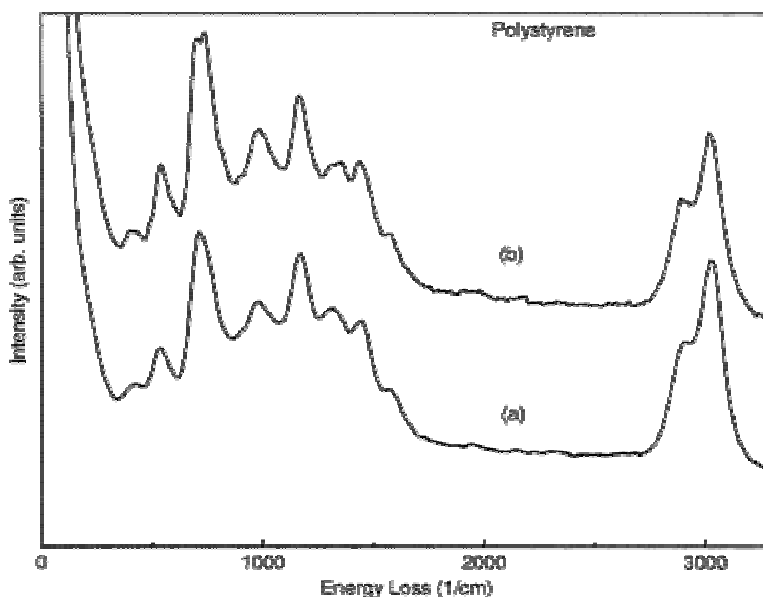


Figure 4 (a) HREELS at 6 eV impact energy taken with the LK2000 spectrometer. (b) 4.5 eV impact energy taken with the ELS3000.

Summary

Various methods to obtain useful spectra are reviewed. Charge reference is simple and convenient and is proved liable in some cases. But it might introduces errors because of uncertainty of reference's BE under experiment conditions and results are not comparable for different spectrometers. When reference materials are not stable under analysis condition, it will lead to wrong interpret of spectra.

For charge compensation (most neutralization), it is easy to be realized (use flood gun) and is flexible for many kinds of insulators and often desirable results can be obtained.

However, it is very hard to completely neutralize surface charge and sometimes might lead to chemical reaction on surface thus destroyed sample.

Recently, several workers^[7,9,22] have demonstrated their extensive researches on charging mechanism of insulators. Their works cast light on ways of finding more effective methods to obtain useful electron spectra of insulators.

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