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XPS guide for insulators: Electron flood gun operation and optimization, surface charging, controlled charging, differential charging, useful FWHMs, problems and solutions, and advice FREE

Special Collection: Reproducibility Challenges and Solutions II with a Focus on Surface and Interface Analysis

B. Vincent Crist

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Note: This paper is part of the Special Topic Collection: Reproducibility Challenges and Solutions II with a Focus on Surface and Interface Analysis.

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ABSTRACT

Current day x-ray photoelectron spectroscopy (XPS) instrument makers have made significant advances in charge compensation systems over the last 20 years, which makes it easier to analyze insulators, but samples still have many differences in chemistry, dielectric properties, sizes, surface roughness, etc. that force instrument operators to tweak flood gun settings if they want or need to obtain high quality chemical state spectra that provide the most information. This guide teaches which flood gun variables to check, and how to optimize electron flood gun settings by presenting high energy resolution, chemical state spectra that show the result of using a poorly aligned flood gun on modern XPS instruments equipped with a monochromatic aluminum K_{alpha} x-ray source. This guide is focused on the XPS measurement of insulators—nonconductive metal oxides and polymers. This guide shows that by measuring commonly available polymers (polypropylene and polyethylene terephthalate) or ceramic materials (SiO_2 and Al_2O_3), the operator can easily characterize the good and bad effects of XY position settings and other settings provided by modern electron flood gun systems. This guide includes many original, never-before-published XPS peak full width at half maximum (FWHM) that will greatly assist peak-fitting efforts. This guide reveals a direct correlation between electron count-rate and best charge-control settings. This guide discusses sample and instrument issues that affect surface charging and explains how to check the quality of charge control by measuring the FWHM and binding energy of C (1s) or O (1s) spectra produced from the sample currently being analyzed. A list of other charge-control methods is provided, along with advice and a best-known method. The availability of large extensive databases of actual spectra is extremely beneficial to users who need real-world examples of high quality chemical state spectra to guide their in-house efforts to collect high quality spectra and to interpret valuable information from the peak-fits of those spectra.

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I. INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is a chemical analysis technique that requires high vacuum and measures only the top 10 nm of any solid surface (see Fig. 1). XPS is trusted to provide reliable chemical state assignments[1–3] from many kinds of materials, especially insulating materials. More than 70% of all materials analyzed by XPS are insulators, which require charge compensation (control) when using a monochromatic x-ray source.

This publication is focused on the XPS measurement of insulators such as nonconductive metal oxides and polymers.

Modern XPS instruments can produce a focused beam (10–500 μm diam) of monochromatic aluminum x rays that excite the atoms within the surface of an electrically neutral sample causing photoelectrons [negative (−) particles] to be emitted from the surface (top 10 nm) of the sample into the vacuum of the analysis chamber which, in turn, means that the irradiated area now has

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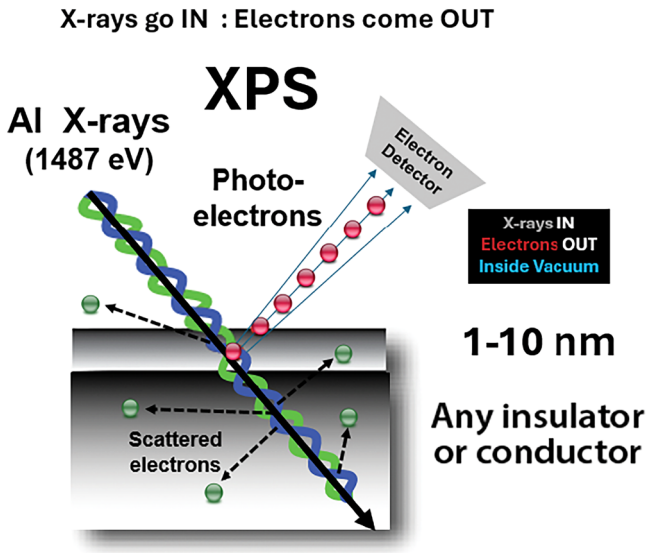


FIG. 1. Schematic of the fundamental physics of XPS. X rays IN and electrons OUT in high vacuum.

positive (+) charges, known as core-holes. These monochromatic XPS systems include electron flood guns to control/compensate for those positive core-holes. The example spectra provided in this report were measured by using aluminum K_{alpha} monochromatic x rays and different types of modern and older flood gun (FG) systems. The positive charge at the surface of an insulator is due to the many positive (+) core-holes that exist in the surface *before* the operator turns on the electron flood gun to neutralize the positive charge.

While the x-ray source is turned on, the resulting various positive charges (core-holes in atoms) retard the kinetic energy of the photoelectrons, causing the kinetic energy of those photoelectrons to decrease. The positive charge within the surface is nonuniformly distributed in XYZ due to variations in the electrical, physical, and chemical nature of each surface, which distorts the shape of chemical state spectra (Table I). To obtain useful XPS spectra from an insulating material, the instrument operator needs to control/neutralize/compensate for that positive charge. The equipment, commonly used to control/neutralize/compensate for the positive charge at the surface of the sample, is a beam of low voltage electrons (0.1–20 eV) produced by an electron gun that is installed inside the XPS analysis chamber (see Fig. 2).

TABLE I. Electrical, physical, optical, and chemical properties that distort XPS spectra.

- Variations in chemical, electrical, and physical properties of the surface being analyzed.
- Dielectric nature of the material in the top 20 nm.
- Flux and shape of the focused x-ray beam.
- Depth distribution of the positive valence-holes (charges).
- Depth distribution of the positive core-holes (charges).
- Quality of the charge-control/compensation process.
- Electrical grounding of the sample stage.
- Differential charging that exists.

This beam of low voltage electrons, which is static (not rastered over the analysis area), can be a focused or defocused beam. Even though very modern electron guns produce an electron beam that is focused, most users refer to focused or flood type electron beams as a "flood gun (FG)"—a term that we use in this guide. This charge-control method is often called "charge compensation" or "charge neutralization," which are different from "charge control," also known as surface potential control.[4]

In various older monochromatic XPS systems, the electron flood gun (FG) needs to be manually moved into and out of the analysis chamber by the operator so that the electron FG beam is able to irradiate the area excited by the x-ray beam. In modern XPS systems, the electron gun is fixed inside the analysis chamber and is supplied with digital controls built into the instrument operating software that allows the operator to control the XY position and the other operating variables of the electron beam. Many modern charge compensation systems also include a built-in source of low voltage argon ions (+1 to +30 eV) that simultaneously irradiates the x-ray analysis area, while that same area is irradiated with low voltage electrons from the flood gun. When properly adjusted, the overlapping flood of low voltage argon ions and low voltage electrons produces a well-controlled surface charge (potential). One modern XPS instrument maker provides a repeller plate system that enhances the charge compensation produced by a coaxial source of FG electrons. The repeller plate system, when properly adjusted, produces a well-controlled surface charge without the use of argon ions.

The voltage of the positive charge from the x-ray induced core-holes within the surface analysis area will range between the

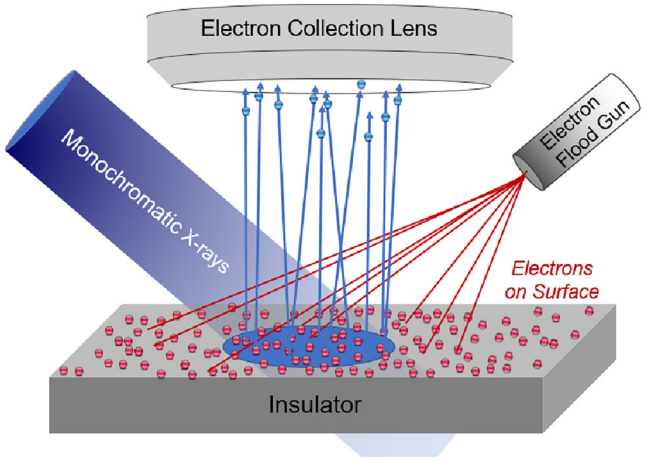


FIG. 2. Artistic depiction of idealized uniform charge control. The sample is a thick insulating film. Flood gun electrons fly straight. The surface has a uniform electrical field. Emitted photoelectrons fly straight with original KE values. A flood gun neutralizes all valence-hole charges.

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TABLE II. Contents of this publication include the following.

- Normal symmetrical peak-shapes of the C (1s), O (1s), Si (2p), and Al (2p) spectra produced by pure polymers, SiO_2, and Al_2O_3.
- Normal peak-shapes of spin–orbit pairs [e.g., Cr (2p), Zr (3d), Cd (3d) Si (2p), K (2p), Br (3d) Y (3d), S (2p)].
- Different types of peak-shape distortion caused by uncontrolled charging (aka differential charging).
- Effects of changing XY positions of the flood gun for a pure hydrocarbon polymer [polypropylene, C (1s)].
- Effects of adjusting the flood gun beam voltage, emission current, extractor voltage, and focus.
- List of typical FWHM for C (1s) and O (1s), and metal oxides that help you to decide if you have differential charging.
- List of charging problems and potential causes.
- Guidance on sample preparation.
- Other methods that can be used to enhance charge compensation.
- BKM for sample preparation and analysis.

aluminum x-ray energy (+1486 eV, upper limit) and valence-hole energies (+1 to +25 eV, lower limit). Because most materials have carbon as a surface contaminant or it is part of the bulk, the positive charge at the surface is due, in part, to the emission of the C (1s) electron, which is equal to the binding energy (BE) of the C (1s) electron, +285 eV. The loss of photoelectrons from oxygen atoms produces a corresponding +530 eV positive core-hole in the atom. The loss of photoelectrons from various electron orbitals of other elements in the sample produces positive core-holes and valence-holes with positive voltages that can range from +1 to +1486 eV. The resulting XYZ distribution and density of the positive charges trapped within the surface can be as deep as 1–5 μm, which corresponds to the depth of penetration of aluminum x rays. In comparison, the measured photoelectrons have escaped from the top 0–10 nm of the surface. Photoelectrons produced below the top 0–10 nm depth range do not produce intense XPS signals. Instead, those photoelectrons interact with some atoms to become scattered electrons that produce the background found in all spectra. The photoelectrons that are produced deep within the sample are trapped and never escape out of the bulk into the vacuum of the instrument.

The shape and usefulness of chemical state XPS spectra produced from the top 0–10 nm of the surface of insulating samples are affected by variations in chemical, electrical, and physical properties of the surface being analyzed. The variables that influence peak-shapes include items listed in Table I.

Within the deeper volume of the sample (below 10 nm, 100 Å), the aluminum K_{alpha} x rays produce core-holes, valence-holes, fluorescence, excitons, polaritons, phonons, electron-hole pairs, plasmons, isolated electrons, Auger transitions, trapped charges, infrared radiation, and other electronic states that form but do not normally affect the unscattered photoelectrons escaping from the top 10 nm (100 Å) of the surface. However, when any of these phenomena occur within the topmost 10 nm (100 Å) of the surface, they can and do influence the photoemission from the sample.

As mentioned earlier, to minimize or eliminate positive (+) surface charging at the analysis area of the surface of an insulator, the operator turns on a charge compensation or charge-control system (electron flood gun).

The major purpose of this paper is to provide guidance about many aspects of surface charging that occur when analyzing insulating materials by using monochromatic aluminum x rays. The major objective of this guide is to help the user to produce high quality XPS chemical state spectra from insulating materials. To simplify this learning, we present example spectra from simple pure materials [polypropylene, SiO_2, Al_2O_3, polyethylene terephthalate (PET)] that are commonly available in most laboratories. The high energy resolution, chemical state spectra from these specific insulators produce simple symmetrical chemical state peak-shapes that are easy to process when surface charging is fully charge controlled.

The high energy resolution, chemical state XPS spectra presented in this report were taken from the XPS International SpecMaster database of >70 000 monochromatic XPS reference spectra.[2,3]

The contents in the following part of this publication include high energy resolution, chemical state spectra having normal and abnormal peak-shapes listed in Table II.

After a basic, simple electron flood gun is turned on, the x-ray irradiated surface area of the insulating sample will soon develop a small negative charge (−1 to −5 eV) as long as the electron flux (emission current) is sufficient, and the direction of the electron beam directly overlaps the x-ray irradiated area of the surface.

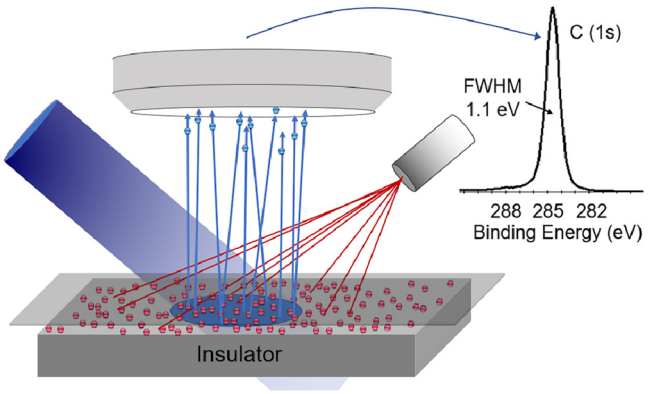


FIG. 3. Example of well-controlled charging of polypropylene. The peak is symmetrical. FWHM is <1.2 eV. No distortions. No sloping tails. No shoulder. The electrical field is flat as depicted by a flat mesh.

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When the surface charging of the analysis area is uniform, balanced, and steady, it is considered to have "controlled charging." An example of controlled charging is shown in Fig. 3. If that surface area has charging that is not uniform, not balanced, or unsteady, then that surface area has "uncontrolled charging," also known as "differential charging." Examples of these two types of charging are presented later.

The various chemical and electrical properties of the surface volume being analyzed can cause distortions in the resulting negative (−) electrical field in the surface and just above the physical surface protruding into the vacuum outside of the sample surface. Distortion of the uniformity of the electric field within the surface and above the analysis area can distort the shape of high energy resolution, chemical state spectra. These distortions can appear as anomalous shoulders at the low BE side, sloping charge tails at the low BE side, false doublets, or peaks with broad full width at half maximum (FWHM). Charging can and often does produce peaks with unexpected binding energies, which, in turn, degrades the reliability of the binding energies, BEs, used to make chemical state assignments.[1]

As mentioned above, the information interpreted from peak-fitting high energy resolution chemical state spectra of insulators is used to make valuable decisions in major industries, government labs, and universities toward product development, process improvement, and materials characterization. For these reasons, it is extremely important to produce XPS spectra from insulators that are free from the adverse effects of surface charging that can be horizontal, vertical, uniform, nonuniform, positive (+), or negative (−).

Surface charging is a phenomenon that is normally associated with true insulators, but, in fact, surface charging also occurs for semiconductors, very thin insulating films on metals, side-by-side structures made of conductors and insulators, native oxides, and conductors that are deliberately isolated from the grounding. In fact, >70% of all the materials analyzed by XPS can suffer from various forms of surface charging (− or +). Please note that surface charging is different from bulk charging due to differences in physical structure as well as the electrical and chemical nature of the bulk. Sample charging is the sum of surface charging plus bulk charging, but in this guide, we focus only on surface charging effects.

This guide discusses the sample, surface, and instrument variables that affect the production of a uniform, low voltage, negative electrical field which, in turn, influences the peak-shapes of high energy resolution, chemical state XPS spectra.

Insulating materials are regularly analyzed by XPS for many different applications (Table III). For this reason, the operator must use a charge compensation system (e.g., electron flood gun) to collect reliable[5] and meaningful chemical state spectra from: polymer films, paint films, semiconductors, topological materials, catalysts, unknown contaminations, ceramics, paper, dental implants, medical implants, 3D printed plastics, nonconductive metal oxides, hydroxides, carbonates, sulfides, sulfates, minerals, glasses, glass coatings, laser parts, cosmetics, medicines in tablets, and more.

Also, each surface is different from the last surface, so the operator needs to learn and practice how to optimize the electron flood gun and how to recognize or determine if the current sample is suffering from unexpected differential charging. This guide addresses those variables and shows that the XY position of the flood gun is the main variable.

TABLE III. Real-world XPS applications that require reliable high quality charge control.

• Chemical state identification
• Heat, oxidation, or plasma treatments
• Quality control
• Contamination analysis
• Chemical structure of multilayered films
• Stoichiometry of the bulk material
• Thickness of thin films

Practical real-world experience teaches each operator that the BE, FWHM, and expected Gaussian shape of the O (1s) and the C (1s) signals are the main indicators of the quality of charge control for the current sample. A single, nearly symmetrical O (1s) peak-shape is available from many different materials. The shape of the O (1s) signal can be discerned by using the unscanned mode spectra, Snap-shot™ mode spectra, or normally scanned mode spectra. The optimum beam voltage to use depends on the flood gun design and the surface, but the usual range is between −0.1 and −4.0 eV.

In this guide, you will read about electron flood gun optimization, differential charging, charge control, problems, solutions, useful FWHMs, BEs, and special terminology.

Current day XPS instrument makers have made significant advances in charge-control systems over the last 20 years that make it easier to analyze insulators, but samples still have many differences that force instrument operators to tweak flood gun settings if they want or need to obtain high quality chemical state spectra that provide the most useful information. The latest development in charge control involves the simultaneous use of argon ions (5–10 eV) and electrons (0.1–10 eV) (see Fig. 4).

Before starting any analysis, the operator should optimize the flood gun beam at that exact same location with the x rays turned ON and by varying the XY position of the flood gun beam until the lowest BE for the O (1s) [or C (1s)] signal has been produced. This is best done by using the snapshot or unscanned mode of data collection. Scanned mode also works but takes more time.

II. TERMINOLOGY

Specialized terms are used when describing XPS of insulating materials. In the general literature and the ISO 18115 (Vocabulary of XPS), there are three terms that seem to describe the exact same thing.

In this guide, those three terms are given more exact definitions that make them distinct from each other, i.e., charge control, charge neutralization, and charge compensation.

A. Charge control (surface potential control)

This publication: Charge control occurs when a steady flow of particles (electrons) produces charge neutralization of valence-holes,

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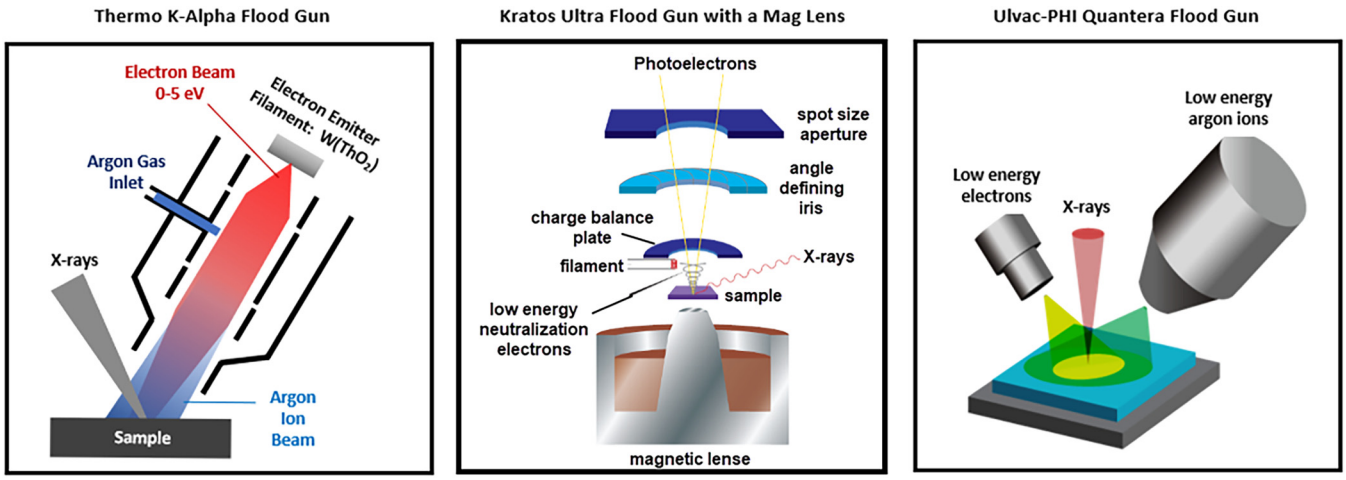


FIG. 4. Schematic drawings of modern electron flood gun systems. Two systems use simultaneous beams of low voltage electrons and low voltage argon ions. The other system uses a charge-balance plate (an electron repeller). All three systems provide significant improvements in charge compensation/control. Reprinted with permission from The XPS Library website (https://xpslibrary.com, last accessed, January 2020.

charge-balance, or a steady potential. The resulting potential of the irradiated area can be either positive or negative.

B. Charge neutralization

As defined by ISO 18115:[6] Maintenance at a fixed potential, usually near neutrality, of a surface under bombardment by primary particles of photons, by compensating any accumulating surface charge with a particle of the opposite charge

This publication: Charge neutralization is an active process where positive or negative electrical charges continuously neutralize each other. As an example: When an x-ray beam is turned on, positive (+) core-holes form due to photoemission, which is followed by the intra-atomic cascading of outer level electrons that neutralize the inner level core-holes.

When a low voltage beam of electrons is turned on, the process of charge neutralization is supplied with free electrons that cascade into the outer level valence-holes.

C. Charge compensation

Charge compensation is a process that partially controls (compensates) the positive or negative charges.

D. Charge-control mesh-screen

A grounded, conductive metal mesh-screen, having 90% transmission, supported on a grounded, conductive metal base that can be adjusted in Z height such that the mesh-screen is 0.2 to 1.0 mm above the surface of the insulating sample.

Because the x-ray beam is usually located at a 30–35 deg angle from the surface plane, the metal mesh-screen is normally out of view of the electron collection lens, which is normally at 90 deg with respect to the x-ray beam.

E. Controlled charging

Controlled charging is an active and ongoing state that produces a steady state potential (+ or −). The recorded BEs can be larger or smaller than the "true" BEs. The instantaneous charge on this type of surface region can be negative or positive. The main phenomenon that defines "controlled charging" is that the voltage is stable and uniform over the surface area being measured. For example, the C (1s) of polypropylene appears as a single symmetrical peak because controlled charging exists and because differential charging is absent.

F. Differential charging (uncontrolled charging)

Differential charging is a nonuniform surface potential that produces distortion in XPS peak-shapes. As an example, when the C (1s) of polypropylene appears as an asymmetric peak having a sloping tail or shoulder at slightly lower BE, this is due to the presence of a nonuniform distribution of negative or positive charges on or within the surface of the sample.

G. Capacitor

A capacitor is a device that accumulates and stores electrical energy in an electric field. A nonconducting dielectric acts to increase the capacitor's charge capacity. The capacitor is a component that has the ability or "capacity" to store energy in the form of an electrical charge producing a potential difference much like a small rechargeable battery. Depending on the proposed application, the dielectric can be air, gas, paper, organic film, mica, glass, or ceramic.

H. Sample charging

As defined by ISO 18115:[6] Accumulation of electrical potential in the sample or on the sample surface caused by particle or photon bombardment.

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Note: Sample charging is the sum of surface charging and bulk charging.[7–11]

I. Surface charging

Accumulation of electrical potential on the surface of the sample caused by particle or photon bombardment that produces either a net negative or positive surface charge.

Surface charging, which we focus on in this paper, is localized to the top 10 nm. Surface charging involves surface effects such as: space charge, image potential, field states, virtual states, the Tamm state, and more.

III. CHARGE NEUTRALIZATION—TWO STEPS

Charge neutralization is a complex active and ongoing process where positive electrical charges and negative electrical charges continuously cascade and neutralize each other while both the x-ray beam and electron flood gun beam are turned on. The process of charge neutralization of positive (+) core-holes starts when core-holes attract and capture electrons from the same-level, mid-level, or valence-level electron orbitals that have lower BEs (see Figs. 5 and 6). The process of charge neutralization for individual atoms comes to an end when a photoionized atom no longer has a positive charge in a core-level or valence-level.

The process of charge neutralization is a 2-step process where one step of the process is: (1) due to intra-atomic cascading of electrons within an atom while the other process is; (2) due to the capture of flood gun electrons into valence-hole(s).

A. Charge neutralization of core-holes—Step 1

The initial photoionization of an atom produces either a core-hole or a valence-hole, which initializes the charge neutralization process.

In Sec. III A, we focus on core-holes and the process that neutralizes core-holes.

Immediately after a single core-hole is produced, the atom starts to rebalance the Coulombic fields of the atom, which shrinks slightly due to the change in the screening of the core. The core-hole immediately collects a bound electron from various potential intra-atomic sources such as: (a) the same orbital, (b) the same shell, or (c) orbitals that have BEs lower than the positive energy of the core-hole. This process is called the "electron cascade." See Fig. 5 for an artistic depiction of charge neutralization of core-holes.

The lifetime of core-holes is extremely short, typically 10^{-16}–10^{-18} s, because the atom undergoes extremely fast intra-atomic processes where electrons cascade from filled lower energy orbitals (core-level, mid-level, or valence-level) into empty higher energy (core) holes, in turn producing lower energy holes.

This cascade process can be viewed as either an electron cascade or a core-hole cascade, but the outcome is the production of valence-holes in the valence bands.

Because carbon and oxygen atoms are present in surface contaminants, we use them as a simple example. The carbon and oxygen atoms in those contaminants produce +285 eV C (1s) positive core-holes and +530 eV O (1s) positive core-holes. Many insulators are composed of three or more elements, so the other elements will produce positive (+) core-holes with energies ranging from as small as +20 eV to as high as +1486 eV. These core-holes undergo intra-atomic cascade, and valence-hole neutralization shown in Figs. 5 and 6.

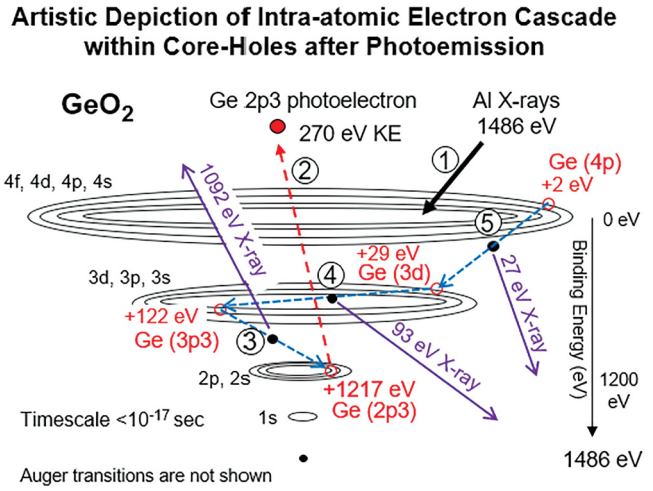


FIG. 5. Artistic schematic of core-hole-electron cascade for an insulator (e.g., GeO_2). The sequence of actions is 1–5. Internal electrons are the source of the neutralization. The time scale for the electron cascade to produce a valence-hole is $<10^{-17}$ s. This depiction uses a simple Bohr orbital model to simplify the display.

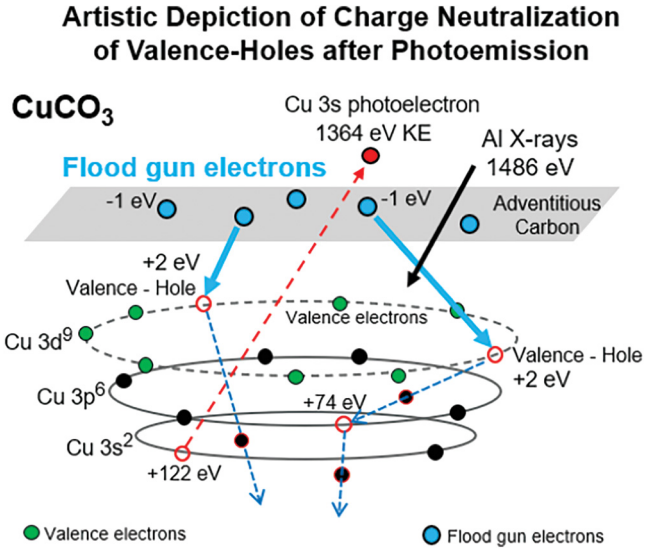


FIG. 6. Artistic schematic of charge neutralization of valence-holes for an insulator (e.g., $CuCO_3$). Flood gun electrons are the source of neutralization of valence-holes. The timescale for this charge neutralization process is 10^6 times slower than intra-atomic electron cascade shown in Fig. 5. This depiction uses a simple Bohr orbital model to simplify the display.

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The resulting total positive charge in any insulator will vary across the x-ray irradiated surface due to spatial XY variations in the intensity of the Gaussian shaped x-ray beam, the XY variations in the electrical, chemical, and physical nature of the sample surface, and the influx of the flood gun electrons. These voltages may or may not develop a uniform positive or negative voltage over the XY area of the sample. The resulting voltages at the surface can vary by ±50%. For example, if the flood gun voltage is set to −2 eV, the voltages across the surface can range from −1 to −3 eV. This range of voltages is a major reason for the broadening of XPS signals and the shift in the BEs of the XPS signals.

B. Charge neutralization of valence-holes—Step 2

The other half to the charge neutralization process is due to the charge neutralization of the valence-holes. Positive holes in valence orbitals attract and capture low voltage flood gun electrons that are loosely capacitively attached to the topmost surface. The rate of charge neutralization of valence-holes by flood gun electrons is roughly 10^6 slower than the extremely fast intra-atomic electron cascade mechanisms (10^{-17}–10^{-18} s) that neutralize deep core-holes that have much large positive charges. See Fig. 6 for an artistic depiction of charge neutralization that occurs for valence-holes.

The presence of positive valence-holes in the valence orbitals, where the surface charge neutralization process occurs, is due to three different effects including: (a) normal emission of photoelectrons from valence orbitals, (b) the intra-atomic cascade of electrons jumping from outer mid-core levels inward to deeper core-holes finally producing a valence-hole, and (c) radiationless and Auger transitions that occur simultaneously.

The inelastic mean free path (IMFP)[11] of incoming low voltage (−0.1 to −20 eV) flood gun electrons ranges from 5 to 10 nm, which allows them to tunnel (pass) into the surface of the sample and be captured by low voltage valence-holes that are physically 1–10 nm beneath the surface. This surface charge neutralization process is an important but seldom recognized factor in the total charge neutralization process.

Because electrons have the potential to damage or degrade various materials, especially those with higher oxidation states, the photoemission process and the charge neutralization processes need to be considered as potential sources of damage or degradation. Photoelectrons have the potential to damage (degrade) a material as they travel out of the top 10 nm of the surface before they escape the surface of the sample. The actual current of photoelectrons traveling out of the sample is very low, in the range of 0.01–0.1 μA ($1–100 \times 10^{-9}$ A), which is one reason that electron detectors use amplifiers that multiply a single electron into a million electrons that can be readily counted. For this reason, the current of outgoing photoelectrons does not contribute significantly to electron induced degradation or charge neutralization. Degradation due to electrons is mainly due to the sensitivity of the chemical compounds to the influx (current) of low voltage flood gun electrons. The influx of flood gun electrons depends on flood gun design but is often in the 50–300 μA range, which is 500–30 000 times larger than the 0.01–0.1 μA of the photoelectron current.

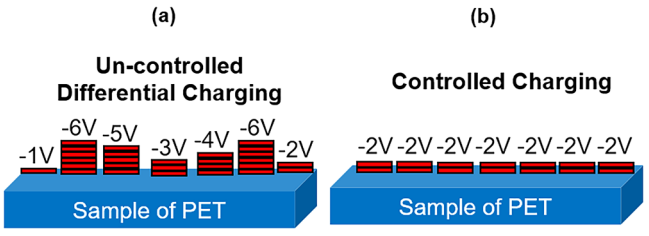


FIG. 7. Schematic examples of: (a) uncontrolled differential charging and (b) controlled charging across a net negative surface.

IV. SURFACE CHARGING, FLOOD GUN, UNCONTROLLED CHARGING, CONTROLLED CHARGING, CHARGING EFFECTS

A. Surface charging

Surface charging (+ or −) is a phenomenon that is normally associated with true insulators, but, in fact, surface charging also occurs for semiconductors, very thin insulating films on metals, native oxides, side-by-side strips made of conductors and insulators, and conductors that are deliberately isolated from the grounding. As a result, >70% of all materials analyzed by XPS can or do suffer from various levels of surface charging.

Surface charging is the accumulation of electrical (voltage potential) charge on the sample surface and/or within the sample near the surface. Surface charging starts when particle or photon bombardment strikes a surface, and that surface retains either a negative or positive charge. Surface charging is often assumed to be uniformly distributed in XYZ, with bulk charging being a similar phenomenon deep within a sample.

In this case, surface charging begins when a monochromatic beam of aluminum K_{alpha} x rays irradiates the surface of a material, causing photoelectrons to be emitted, leaving behind atoms that have positive (+) core-holes within the top 10 nm of the surface. The lifetime of those core-holes is extremely short, typically 10^{-16} to 10^{-18} s because the atom with its core-holes undergoes extremely fast intra-atomic processes that include electrons cascading from filled lower energy orbitals (mid-level or valence-level) into empty higher energy (core) holes, in turn producing mid-level (mid-core) holes (see Fig. 5). This is the major process for charge neutralization in XPS that was discussed in an earlier section.

We all know that materials are electrically neutral, but when monochromatic x rays excite the atoms of any material, a positive charge develops. The uniformity of the resulting positive charges across the surface area being analyzed can be uniform or nonuniform. This uniformity or nonuniformity directly affects the operator's efforts to produce high quality XPS spectra. In some cases, controlled charging is easy to achieve, but in other cases, the surface suffers from uncontrolled differential charging. The concepts and features of "controlled charging" and "uncontrolled differential charging" are introduced in this section (see Fig. 7).

In the case of a properly grounded conductive material being irradiated by monochromatic x rays, the resulting positive core-holes are instantaneously neutralized by electrons that exist in the

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valence band (Fermi sea), free electrons that are 0.0 to −0.1 eV above the Fermi level (~25 °C), and electrons supplied through an electrical ground attached to the instrument. In this case, there is no net charge, so there is absolutely no need to use a flood gun. *As a result, there is absolutely no need to correct any BEs.*

In contrast, when an insulating material is irradiated by a monochromatic x-ray source, the surface area of that insulator will instantly develop a net positive sample charge due to the loss of the photoelectrons that were left behind core-holes and valence-holes with positive charges ranging from +1 eV to as large as +1486 eV. The positive core-hole charges force the atom to undergo various intra-atomic cascades of electrons and other phenomena to neutralize the core-hole charges. In effect, this process forces the positive holes to migrate from the inner core of the atom out to the valence band where the net effective positive charge will range from +1 to +30 eV. When a properly adjusted beam of flood gun electrons overlaps that x-ray irradiated area, that beam of low voltage electrons will quickly neutralize the low voltage positive valence-holes and develop a small net negative charge (−0.1 to −5 eV) within the top 10–12 nm of the surface. Artistic depictions are shown in Figs. 5 and 6.

The buildup of a net negative (−) charge on the surface of an insulator is because insulating materials behave as air-based capacitors (batteries) that collect a pool of flood gun electrons. That pool of electrons can be scattered over an area of the surface that is several times larger than the area irradiated by the x-ray beam.

Based on real-world experience and design testing, the XPS instrument makers design the flood gun electron beam diameter to be 2–5× larger (<2 mm) than the x-ray irradiated area. For that reason, the negatively charged surface area is 2–5× larger (<2 mm) than the x-ray irradiated area (Fig. 8). If we could readily measure beyond that negatively charged area, then we will find a neutral, electron-free surface area, unless that area had been previously exposed to the x-ray beam or the electron beam. This phenomenon reflects the nature of the insulator to behave as a capacitor.

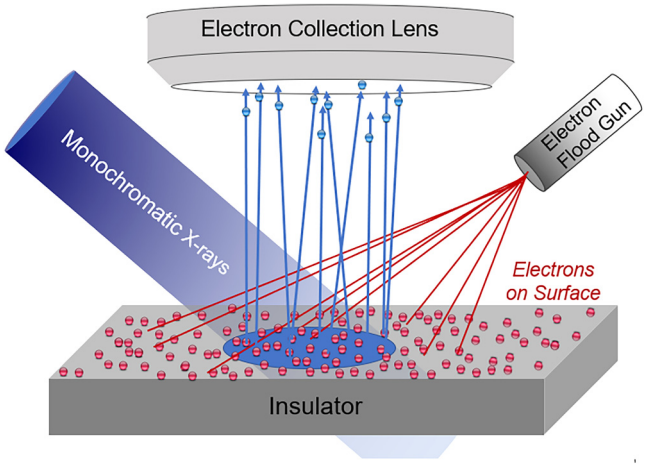


FIG. 8. Artistic depiction of idealized uniform controlled charging. The sample is a thick insulating film. Flood gun electrons fly straight. The surface has a uniform electrical field. Emitted photoelectrons fly straight with original KE values. A flood gun neutralizes all valence-hole charges.

Both types of surface charging (+ or −) produce various electrical field phenomena and problems that distort the shape of the chemical state spectra that cause chemical state signals to appear at erroneous or misleading BEs, which, in turn, degrades the reliability[1] of the BEs used to make chemical state assignments.

The localized micrometer-sized variations in the chemical, electrical, and physical properties (e.g., dielectric nature, roughness…) of the analysis area produce variations in the net negative charge at the surface that are nonuniformly distributed in XY. Highly polar chemical compounds produce a special type of differential charging. Highly polar compounds have strong surface dipole moments that can project, in the Z axis, a positive field several hundred nanometers above the surface.[10] This dipole moment produces unexpected increases in BEs because the surface dipole moments produce preferential retardation of the KE of the photoelectrons. We will report on this phenomenon in a later publication.

As explained, surface charging can be either controlled or uncontrolled. Uncontrolled differential charging is more commonly known as **differential charging** [Fig. 7(a)], which produces one or more types of distortion in XPS peaks. **Controlled charging** [Fig. 7(b)] produces distortion-free XPS peaks. A simple schematic in Fig. 7 displays the basic difference between controlled charging and uncontrolled differential charging.

Differential charging normally occurs horizontally, but it can also be a vertical phenomenon, which is discussed in more detail later.

B. Flood gun beam of low voltage electrons

As stated before, a low voltage beam of electrons is commonly used to control the surface charging that occurs when a monochromatic beam of x rays produces positive core-holes and valence-holes within the surface of insulating materials.[12–20]

Under optimum conditions, the beam of low voltage electrons emitted from the flood gun will fly in a straight line path and land on the surface of the insulator (see Fig. 8). By design, the surface area covered by these low voltage electrons is roughly 2–5× larger (<2 mm) than the area irradiated by the x-ray beam. The electron flux (emission current) in that flood gun beam is normally sufficient to allow the valence-holes to be neutralized fast enough that a slight excess of electrons remains on the surface to produce a small negative electrical field, which may or may not be uniformly distributed across the surface. To be useful, this charge-balance system needs to retain a slight excess of negative charge on the surface.

If the surface of all insulating samples was perfectly smooth, and the dielectric nature of the surface was uniform, and the x-ray beam width was an orthogonal step-function, and the surface was perfectly clean, then it is possible to produce a charge-balance that is uniform. In this near perfect situation, the spectra would have no distortions, peak-fitting would be easy, and the measured BEs would be easy to correct (see Fig. 8).

However, in the real world, real-world samples produce nonuniform electrical fields within the surface and just above the surface. An excessive flood of low voltage electrons can replicate the nonuniform electrical field of the surface. The resulting

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irregular nonuniform field causes emitted photoelectrons to be deflected, slightly accelerated, or to have various KEs as they escape the surface and fly toward the electron collection lens. The irregular nonuniform field also causes incoming flood gun electrons to be deflected or to lose some KE. An artistic depiction of this situation is shown in Fig. 9.

Instrument operators have developed different methods (see Table IV) to minimize the nonuniform irregularity of the voltages on the surface of insulators depicted in Fig. 9.

In Secs. IV C and IV D, we describe the differences between "uncontrolled differential charging: and 'controlled charging'. These sections include tables and example spectra to compare the key features of both types of surface charging.

C. Uncontrolled differential charging

The most common type of surface charging problem is uncontrolled "differential charging." Differential charging means that there is a nonuniform distribution of charge across the surface of the area being irradiated and above the surface as depicted in Figs. 7(a), 9, and 10. Differential charging can be horizontal (across the surface) or vertical (into the Z aspect of the sample). Differential charging is usually due to an irregular distribution of negative voltages (or in rare cases, positive voltages) over the area being irradiated. A summary of the causes of differential charging is given in Table V.

Distortion of the uniformity of the electric field on a surface, also known as Differential Charging, can occur above or within the surface of the analysis area. Differential charging distorts the **true** shape of the peak(s) in a high energy resolution, chemical state spectrum. Differential charging often produces anomalous shoulders or sloping charge tails at the low BE side for each high resolution spectrum obtained from the same sample. An example of this problem is shown here for the C (1s) spectrum obtained from a dirty piece of PET (Fig. 10).

Differential charging can also produce false doublets, and peak broadening with FWHM 3–4× larger than the true FWHM. Differential charging can produce unexpected shifts in binding energies which, in turn, degrade the reliability of the binding energies used to make chemical state assignments. A list of the possible features caused by uncontrolled differential charging is presented in Table VI. Examples of spectra having differential charging features are presented throughout the remainder of this publication. These spectra will have labels that highlight the problem type or feature that distorts the peak-shapes in those spectra.

A typical example of "uncontrolled differential charging" is shown in Fig. 11. The sample is a polyacrylate adhesive on the back side of a paper label. The chemical state spectrum is from the C (1s) signal. This spectrum shows the data that were initially measured. After looking at this spectrum, we suspected that there was a charging problem. The peak-shape features that indicate there is a problem are: (a) the sloping charge tail on the low BE side and (b) the non-Gaussian shape of the main carbon peak on the low BE side. Because we had analyzed this adhesive many times before and had a "reference spectrum" (shown as Fig. 12), we also knew that the peak at 278 eV was not real (a ghost peak), and we knew that the valley at 288 eV should be deeper. By comparing Fig. 12 with Fig. 11, it is easy to see the differences. This is the advantage of having high quality XPS reference spectra.[2] Unfortunately, we sometimes do not have reference spectra, so we must learn to

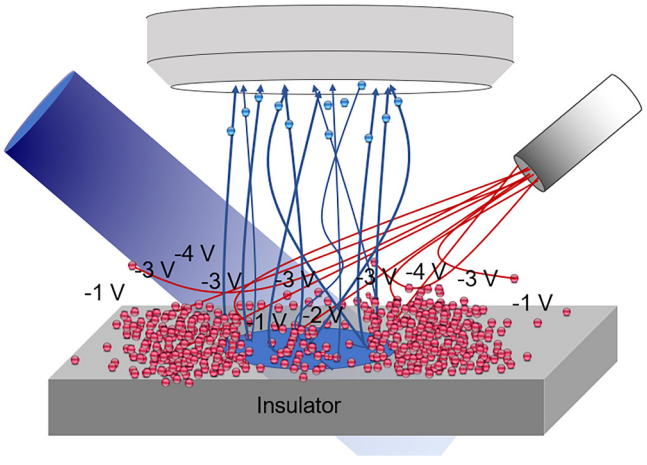


FIG. 9. Artistic depiction of uncontrolled differential charging. The sample is a thick insulating film. Flood gun electron flight paths are irregular due to irregular surface voltage. Emitted photoelectrons' flight paths are irregular due to irregular surface voltage. Using a standard flood gun system, the C (1s) peak would have a sloping charge tail at lower BE or maybe a shoulder. The FWHM is >2 eV.

TABLE IV. Operator's methods used to minimize irregular charging on the surface of insulators.

- Select analysis area ~1–2 mm away from a ground path near the sample edge or corner of a conductive stage,
- Place a thin, grounded conductive washer over the analysis area.
- Use silver paint to draw a conductive circle close to the analysis area with the paint being grounded.
- Float the sample on double-sided tape or another insulator.
- Flood the analysis chamber with argon gas.
- Direct a beam of neutral argon gas to the analysis area.
- Turn on an argon ion gun using the lowest voltage, low current, and a large raster area.
- Bias the sample stage as positive or negative—with low voltages.
- Irradiate the chamber with a UV light source,
- De-ionize the sample just after mounting on the stage.
- Select the smoothest region as seen in the on-board microscope.
- Select an area that looks uniform in the microscope.
- Select an area ~1 mm away from dark spots, fibers, or particles.
- Defocus the largest x-ray beam size available.
- Decrease the x-ray flux or use a smaller beam size.
- Increase the beam voltage to higher voltages.
- Select a lower emission current for the flood gun.
- Add a second flood gun having a different geometry.
- Press powders into flat pellets.
- Freshly grind powder to homogenize chemistry.
- The newest method is the dual use of electrons and argon ions.

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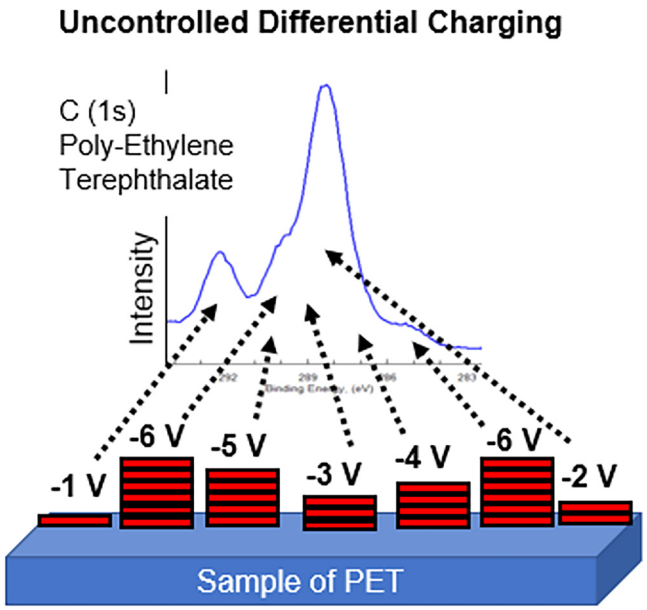


FIG. 10. Example of uncontrolled differential charging due to a nonuniform distribution of negative electron voltages. Potential effects from differential charging include shoulder, sloping charge tail, broad FWHM (>1.5 eV).

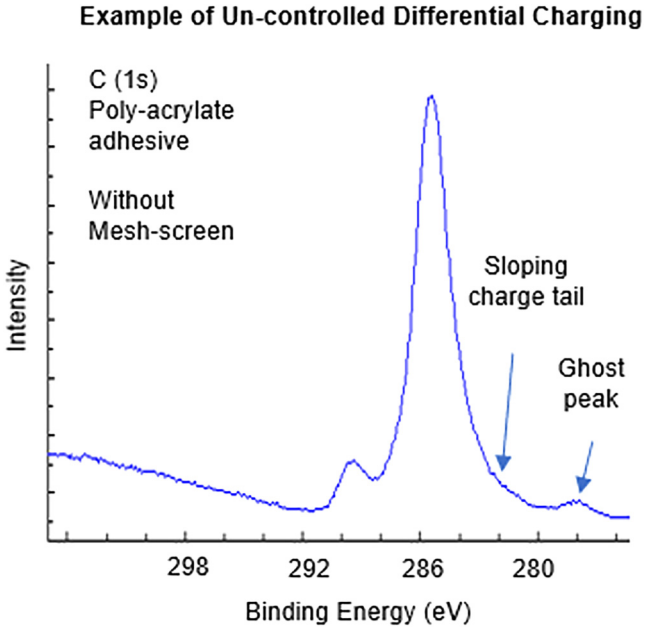


FIG. 11. This C (1s) spectrum from an acrylate adhesive on the backside of a paper label shows a sloping charge tail and a small peak at the low BE side of the C (1s) spectrum, which are typical of uncontrolled differential charging.

TABLE V. Main causes of uncontrolled differential charging.

- Flood gun is misaligned—not optimized.
- Flood gun voltage or emission current—not optimized.
- Differences in x-ray flux due to the Gaussian shape of the x-ray beam.
- Nonuniform electrical, chemical, or physical nature of the surface area being analyzed.
- Irregular electrical grounding of the sample, the sample stage, or the instrument itself.
- Bottom of the sample has irregular conductivity.
- Due to vertical differential charging, the main causes are surface dipole moments and irregular capacitorlike behavior of different surface layers.

recognize peak-shape features that indicate the probable presence of uncontrolled differential charging. This guide is designed to teach the instrument operator and the data analyst how to recognize differential charging.

In addition to the shoulders and sloping tails that might appear when a surface is suffering uncontrolled charging, other differential charging features include peak broadening that can be small but sometimes produces FWHM that are >3–4× the normal FWHM. Such large broadening is easy to notice, but weak broadening is easily overlooked unless you have experimented with your flood gun system and know how to optimize the flood gun settings. By analyzing simple commonplace materials having well-known FWHM, the operator will learn which flood gun setting directly affects their samples. In this guide, we list several commonplace materials that have a single chemical state, and one commonplace material (a water bottle) that has three well-known chemical states (PET).

Later in this guide, there are numerous example spectra that help you to see and to learn which flood gun settings are important for your samples.

Differential charging makes it exceedingly difficult to generate useful and reliable[5] chemical state spectra, which are the key spectra used to produce information. In certain cases, differential charging will also affect the shape of survey spectra. Sometimes the effect on a survey spectrum is small, and we do not see an obvious

TABLE VI. Possible features of uncontrolled differential charging visible in chemical state spectra.

- Obvious "sloping charge tails" spread over a 2–6 eV range on the lower BE side of each high resolution spectrum.
- Shoulders (10%–30% intensity) on the lower BE side of all high resolution spectra that might be a different chemical state.
- Peak broadening—FWHM > 2× larger than typical (the normal range of FWHM for main XPS peaks is: 1.0–1.5 eV).
- Weak broadening of true peak-shape with BE shifting.
- Distortion of peak-shapes due to flood gun effects on nonconductive native oxides—grounded vs insulated—aka vertical differential charging.

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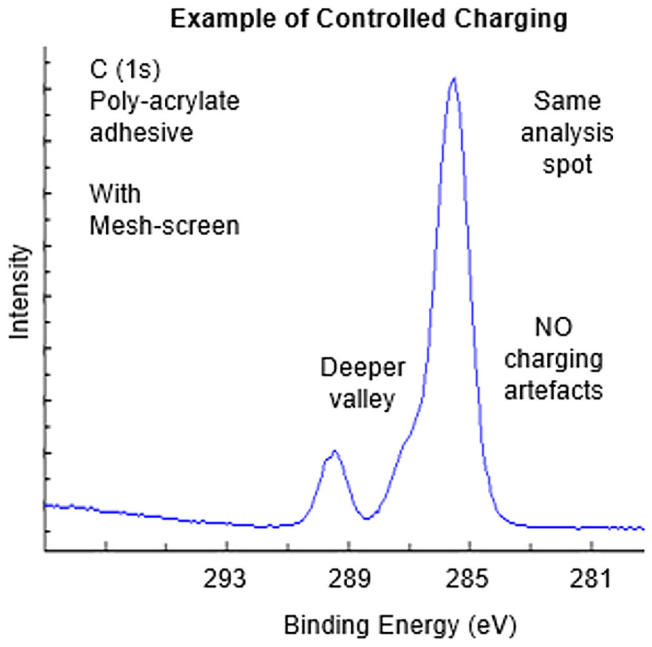


FIG. 12. This C (1s) spectrum shows the true peak-shape after the differential charging is replaced by controlled charging by using a charge-control mesh-screen. The main peak has a Gaussian shape on the low BE side. There are no sloping charge tails.

effect on the survey spectrum. In such a case, we may not see charging problems until we collect chemical state spectra.

Other times, differential charging is easy to notice because the usual survey spectrum peaks that appear near 530 and 285 eV are

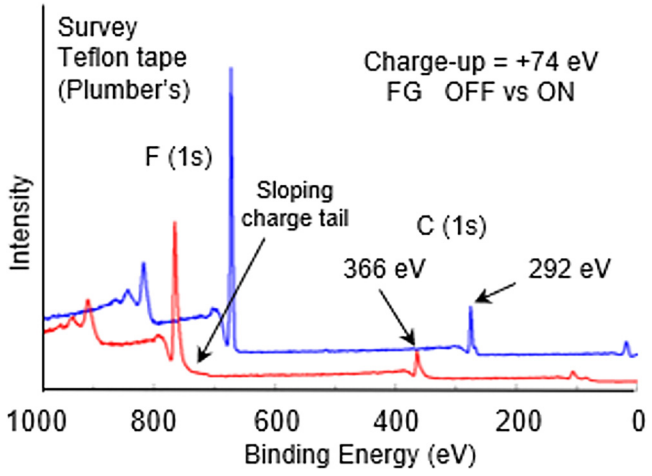


FIG. 13. These survey spectra show controlled charging and uncontrolled (differential) charging from Teflon when the electron flood gun was ON, turned OFF, and then immediately run again.

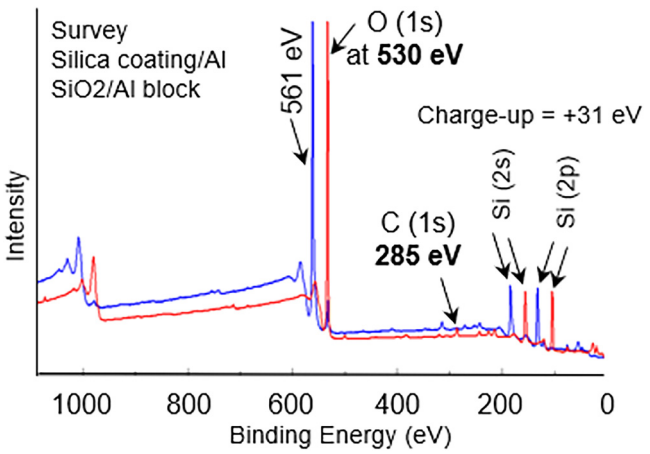


FIG. 14. These survey spectra show controlled charging and uncontrolled (differential) charging from silica glass. The electron flood gun was ON, turned OFF, and then immediately run again.

gone (Fig. 14). Instead of seeing the usual survey peaks near 530 and 285 eV, we see survey peaks at higher BEs. Maybe we see survey peaks that are close to 561 and 316 eV, which might belong to other elements. These two peaks are due to the normal carbon and oxygen contamination that exists on all materials, but the BEs

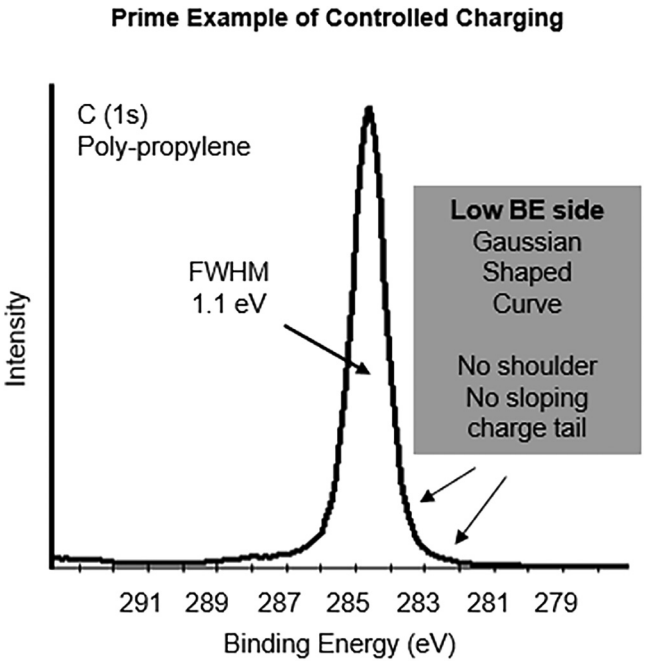


FIG. 15. Prime example of peak-shape having controlled charging. Gaussian shaped peak, no sloping charge tail, no shoulders. Narrow FWHM (<1.2 eV). The peak-shape is symmetrical.

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are higher due to much stronger differential charging. The effects of strong differential charging on survey spectra are shown in Figs. 13 and 14. In this guide, we focus on differential charging that affects high energy resolution, chemical state spectra, because they are expected to provide chemical state information.

Differential charging usually does not affect the quantitative results measured from the survey spectrum unless the effect is extreme. Differential charging problems have, however, likely produced errors in the BEs listed in the free NIST SRD-20 XPS database of BEs. This online database has thousands of BEs derived from insulators, but this type of problem makes it difficult to trust the reliability of the NIST BEs to be used to make reliable[5] chemical state assignments from insulating materials. To make reliable chemical state assignments, the data analyst needs reliable monochromatic spectra[2,3] from the same or related chemical compounds, and FWHM if available.

D. Controlled charging

The C (1s) XPS spectrum shown in Fig. 15 is from a simple nonconductive insulator, polypropylene ($-CH_2-CHCH_3-$). The measured spectrum has a single, fully symmetrical peak. Polypropylene is a pure hydrocarbon polymer that has just one chemical (state) type of carbon that has sp^3 hybridization. For this reason, the C (1s) signal from clean, pure polypropylene is expected to appear as a single symmetrical peak.[12–20]

This spectrum displays a C (1s) chemical state signal, measured from polypropylene, that is free from any obvious distortions. It is a prime example of controlled charging. There are no shoulders. There is one single peak. There are no sloping tails on the low BE side. The peak-shape is Gaussian.

The FWHM of the C (1s) peak is ~1.1 eV, which is typical for C (1s) peaks from a clean, pure organic material when the sample has "controlled charging." The features observed for spectra having "controlled charging" are listed in Table VII.

TABLE VII. Features of XPS peaks having controlled charging for insulating samples.

- Isolated single peak is symmetrical, Gaussian shape.
- For contamination type, adventitious hydrocarbon, the C (1s) peak should be <1.6 eV (FWHM is typically 1.4–1.6 eV for adventitious hydrocarbon).
- For pure organics, the C (1s) FWHM ranges from ~1.0 to 1.4 eV.
- Peak-shapes and FWHM do not change after the flood gun voltage is increased from 0.1 to 2.0 eV.
- Shoulders, tails, or small peaks at a **higher** BE are real and due to higher oxidation states.
- BE of the C (1s) hydrocarbon peak is ~285 eV or slightly smaller (never greater than 285.5 eV, or smaller than 284.5 eV). Carbide BEs range between 281 and 284 eV.
- When you have two or more XPS signals (e.g., C 1s and O 1s) and only one signal shows a shoulder at a lower BE, that shoulder is a real species. (If all high resolution signals have similar shoulders on the low BE side, then they are due to differential charging.)

The C (1s) chemical state spectrum shown in Fig. 16 shows a C (1s) complex chemical state spectrum measured from a freshly scraped film of PET. By comparison to published reference spectra for PET, this C (1s) spectrum has the same four (4) peaks and is free from any obvious distortions. The FWHM of the C (1s) peak produced by the ester (COOR) type carbon is ~0.9 eV, which is typical for C (1s) peaks from a clean, sample of PET. There are no obvious shoulders or sloping tails on the high BE side of this spectrum, which means that we have produced a useful C (1s) spectrum from PET. Because the FWHM of the ester type carbon is <1.0 eV, we consider this spectrum to be free from differential charging, which means that this surface charging of this sample is "well" controlled. To keep terms consistent, we say that this sample has "controlled charging."

PET has become the reference material that is recommended to check on the charge-control performance of the flood gun system sold with brand new XPS instrument. The key feature that defines that charge-control performance is the FWHM of the ester peak. To pass instrument performance tests, the FWHM from the C (1s) ester peak at ~289 eV BE must be <0.9 eV.

PET is readily available because it is used to make various plastic bottles, including soft-drink bottles and water sold in bottles. PET can be cut with a clean razor blade to expose fresh clean bulk or scraped with a clean razor blade. PET can be safely cleaned with various alcohol solvents.

The C (1s) peak-shape of PET is complex and has three well resolved peaks, which is why it is useful to check charge-control performance. But, to learn about charge control and how to

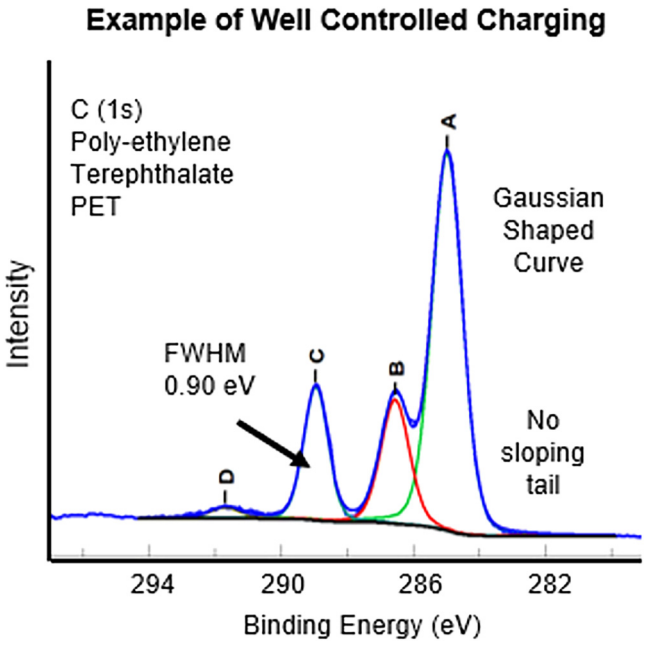


FIG. 16. Peak-fit of a complex XPS chemical state spectra from an insulator (PET) having controlled charging. Gaussian shaped curves, no sloping tail, no shoulders. Narrow FWHM (<1.0 eV).

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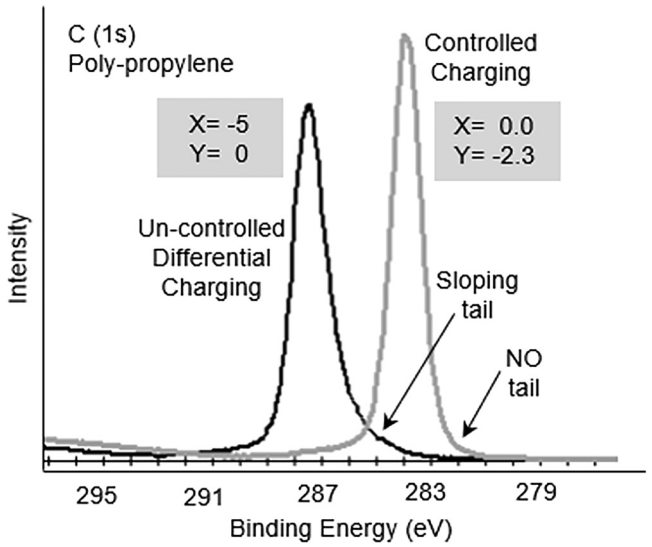


FIG. 17. C (1s) signal from polypropylene sheet having "controlled charging" vs "uncontrolled (differential) charging" due to differences in XY positions of the electron flood gun.

operate a flood gun, we use pure polypropylene, which is available as plastic cups. Look for the initials "PP." Polypropylene is not transparent. It is translucent.

The features observed for spectra having "controlled charging" are listed in Table VII.

E. Charging effects on XPS peak-shapes, FWHMs, and BEs

Surface charging effects on XPS peak-shapes are determined by: (a) flood gun misalignment, (b) flood gun voltage or emission current too low or too high, (c) nonuniform Gaussian shaped flux intensity of the focused x-ray beam, (d) nonuniform electrical, chemical, or physical nature of the surface area being analyzed, (e) irregular electrical grounding of the sample, the sample stage, or the instrument itself, or (f) strong surface dipole moments in highly polar compounds (see Table V).

These interactions produce "surface charging effects," which are due to the electrical potential in or on the surface that are produced by particle or photon bombardment. The total charge on a sample can be either negative or positive depending on the overall density of the charges.

Examples of charging effects on XPS peak-shapes, FWHM, and BEs are presented in Figs. 17 and 18. A sloping charge tail is highlighted by an arrow in Fig. 17. This sloping charge tail is due to the misalignment of the flood gun beam. This misalignment caused the C (1s) peak to move to higher BE and lose electron counts.

The O (1s) spectra shown in Figs. 18(a) and 18(b) are from the same polyacrylate adhesive on the paper labels shown in Figs. 11 and 12. A more significant distortion of an O (1s) chemical state spectrum is presented in Fig. 18(a). To understand the extent of this distortion, we compare Figs. 18(a) and 18(b), the same O

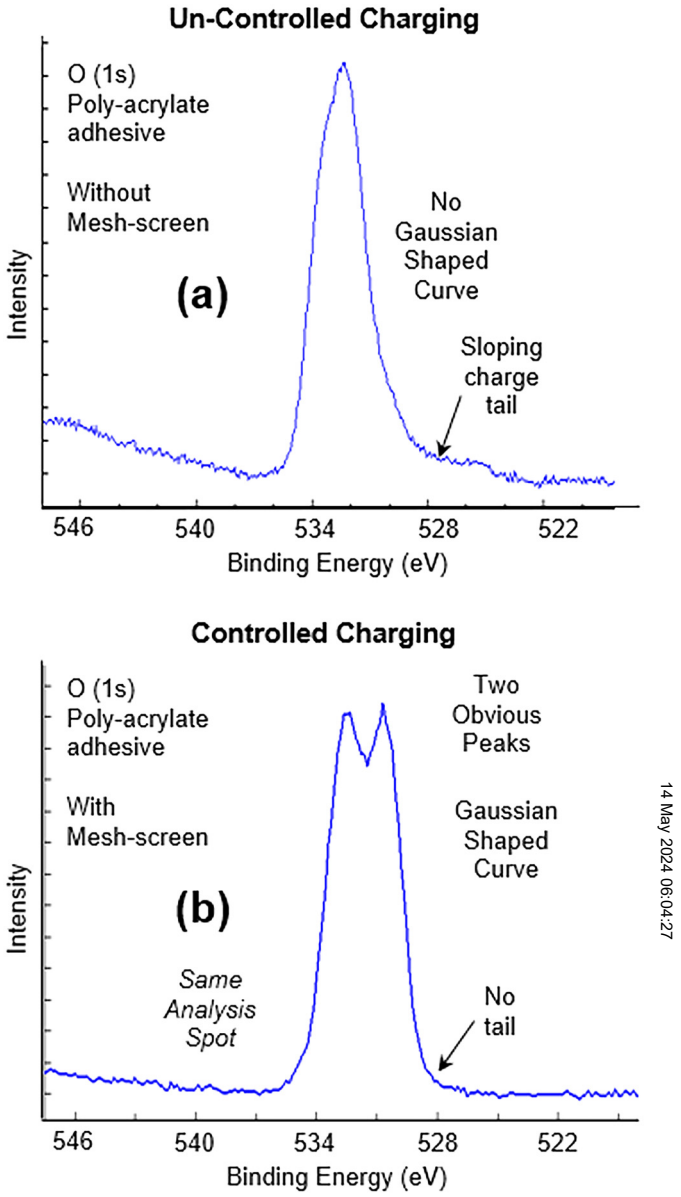


FIG. 18. Example of "uncontrolled (differential) charging" (a) vs "controlled charging" (b) from the same sample of polyacrylate adhesive on the backside of a paper label. The spectrum on the top (a) shows differential charging effects on the low BE side of the O (1s). A charge-control mesh-screen was then placed ~1 mm above the same sample to produce the O (1s) spectra on the right. Note the symmetry and valley in the O (1s) spectrum at the bottom (b).

(1s) spectra but with controlled charging. The O (1s) spectrum in Fig. 18(b) has controlled charging, has no sloping tail, and has a smooth Gaussian shaped curve on the low BE side of the O (1s) spectrum, and reveals the presence of two distinct O (1s) peaks.

The positive valence-hole charges that produce this type of surface charging can range from +1 to +10 eV, which, after the

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flood gun is turned on, becomes a surface charge that is negative and ranges from −0.1 to −10 eV.

In the following five sections, we discuss:

1. Simple peak-shapes from insulating surfaces.
2. Complex peak-shapes from insulating surfaces.
3. Peak-fits of complex peak-shapes of insulators.
4. Undesired peak-shape features caused by differential charging.
5. Advantage of using a charge-control mesh-screen system.

1. Simple peak-shapes from insulating surfaces having controlled charging

The XPS spectra shown as Figs. 19 and 20 are from the non-conductive insulators, polypropylene and manmade SiO_2. The XPS signals produced by these materials have only one chemical state for each XPS signal. When surface charging is controlled, these peak-shapes should be a single peak, fully symmetrical, having a Gaussian shape, and no sloping tails, which is the shape seen in all three (3) chemical state spectra—Figs. 19 and 20.

These measured spectra have peak-shapes that are symmetrical and have no charging tail because the charging was fully controlled, so we say that these samples have "controlled charging."

The features observed for spectra that have controlled charging are listed in Table VIII.

2. Complex peak-shapes from insulating surfaces that have controlled charging

The high energy resolution, chemical state spectra shown in Figs. 21(a)–21(c) have (3d) and (2p) spin–orbit couplings that have and are good examples of "controlled charging" as noted by the absence of shoulders or sloping tails on the lower BE side of the more intense peak and the smooth Gaussian shaped curve on the low BE sides of each set of signals.

Figure 21(a) shows smooth Gaussian shaped curves on both high and low BE sides of the 3d peak-shape that indicate good

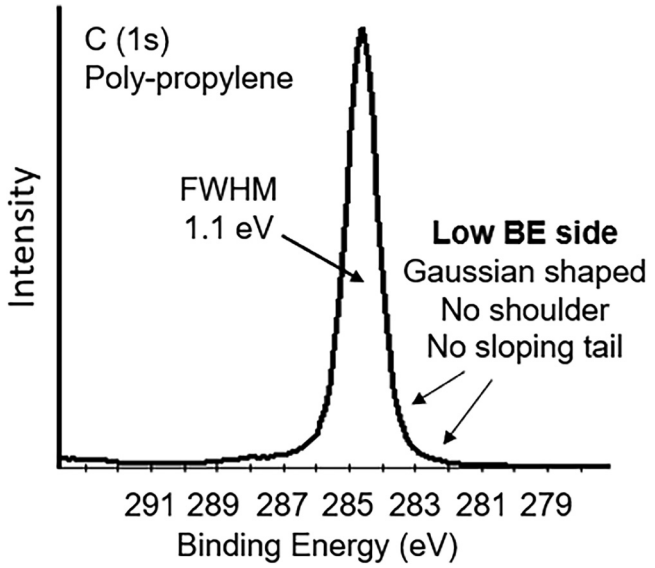


FIG. 19. Peak-shape of a properly charge controlled XPS signal. This C (1s) spectrum from clean polypropylene is symmetrical. It does not have a sloping charge tail or shoulder on the low BE side, which is characteristic of differential charging. The FWHM for polypropylene C (1s) peak is ~1 eV.

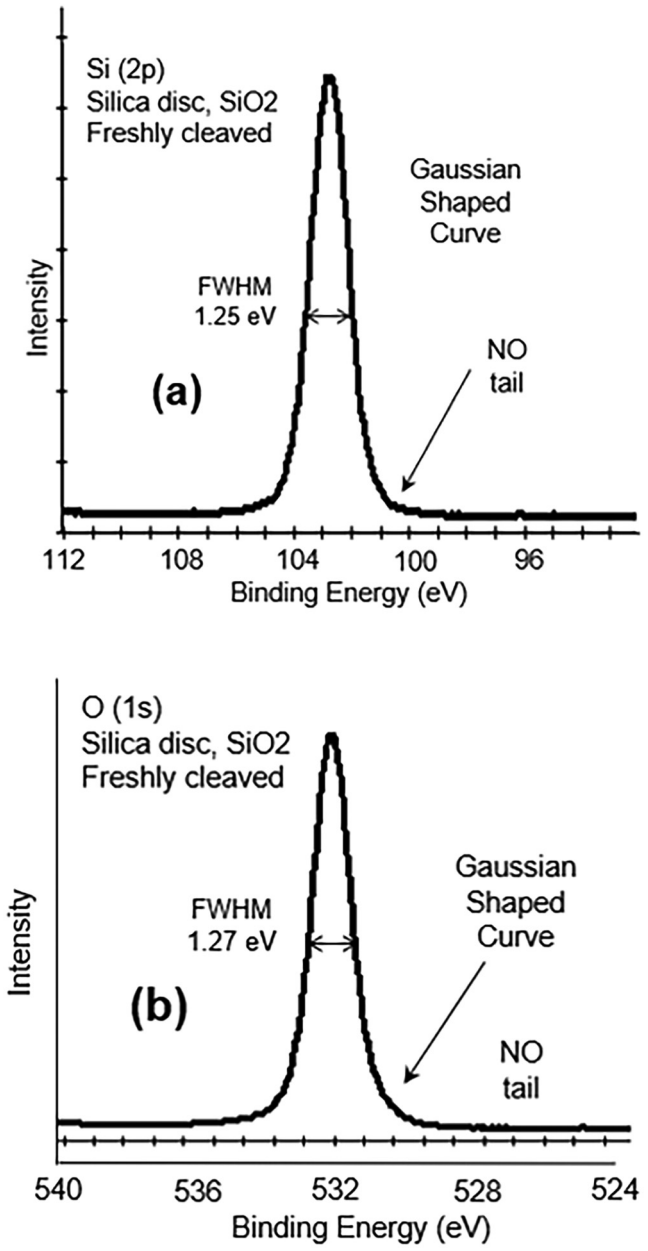


FIG. 20. O (1s) and Si (2p) spectra from pure SiO_2 freshly cleaved to expose the bulk. The symmetry and absence of tails or shoulders on the lower BE side of both (a) and (b) spectra is typical of a material that is fully charge controlled in the surface area being analyzed.

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charge control. Spectra in Figs. 21(b) and 21(c) are more complex but, very importantly, show Gaussian shaped curves at the low BE side, which is also free from any sloping tails or shoulders, allowing us to label these spectra as having "controlled charging."

The two 3d peaks in Fig. 21(b) have shoulders on the higher BE side of both 3d spin–orbit peaks, which are due to the second chemical state present in that sample. The two peaks in Fig. 21(b) have smooth Gaussian shaped curves at the low BE side that indicate good charge control. The spectrum in Fig. 21(c) is from the (2p) spin–orbit signal of a pure metal oxide that has three obvious peaks in the lower BE signal, which are due to multiplet splitting (MS).

The three chemical state spectra shown in Fig. 21 have peak-shapes that are **free** from "differential charging" and are categorized as having "controlled charging."

So, what is the definition of a "native oxide"? Native oxides are thin oxides of pure metals or metal alloys that have formed naturally at room temperature and pressure while sitting in the normal lab air or in a work area for many weeks or months. The native oxides that form are assumed to be the most thermodynamically stable metal oxide.

After analyzing a set of >40 native oxides of pure elements, the thickness of native oxides was found to range from 1 to 5 nm with 2–4 nm of adventitious carbon on top. A few elements formed thicker oxide films and some formed oxide that include carbonate films that were more than 20 nm thick, but most elements formed native oxides that are <5 nm thick. An interesting observation from using XPS to analyze these native oxides is that >80% of them behaved as though the metal oxide layer was conductive, which matches the rumor that native oxides behave as though they are conductive. Based on our experience, much more work is needed to understand the surface physics of native oxides. In general, there

TABLE VIII. Features of spectra having controlled charging.

- Single, isolated (1s) peaks are fully symmetrical and are nearly 100% Gaussian shaped.
- Spectra from spin–orbit coupled signals (e.g., 2p, 3d, 4f) have smooth Gaussian shaped slopes at the low BE side.
- FWHM of the main peaks [e.g., main metal peak or O (1s) on the same sample] range between 1.0 and 1.5 eV.
- FWHM of the adventitious hydrocarbon C (1s) peak on the same sample should range between 1.2 and 1.6 eV.
- For polymers, the hydrocarbon type C (1s) FWHM should range between 0.9 and 1.2 eV.
- Peak-shapes and FWHM do not change when flood gun voltage is increased from 0.1 to 2.0 eV.
- BE of C (1s) hydrocarbon peak max is 285 eV or smaller (never greater than 285.2 eV, except due to vertical charging).
- Shoulders, tails, or small peaks on the higher BE side of 1s, 2p, 3d, or 4f spectra are real and are due to higher oxidation states.
- When you have two or more XPS signals (e.g., C and O) and only one shows a shoulder at a lower BE, that shoulder is a real species. (If all high resolution signals have similar shoulders on the low BE side, then they are due to differential charging.)

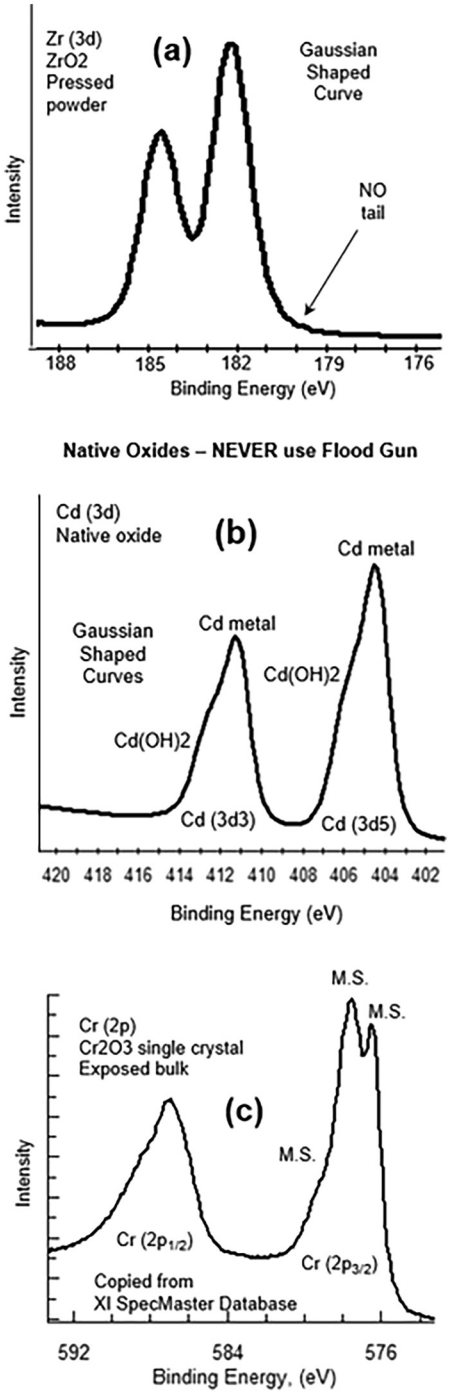


FIG. 21. These spectra are more complicated because they show spin–orbit coupled peaks, peaks with a second chemical state, and peaks have MS. The Zr (3d) spectrum (a) from ZrO_2, Cd (3d) spectrum (b) from native oxide of Cd metal, and Cr (2p) spectrum (c) from freshly exposed bulk of a single crystal of Cr_2O_3 show excellent charge-control characteristics. Narrow FWHM, smooth Gaussian shaped curve on the low BE side indicating no differential charging.

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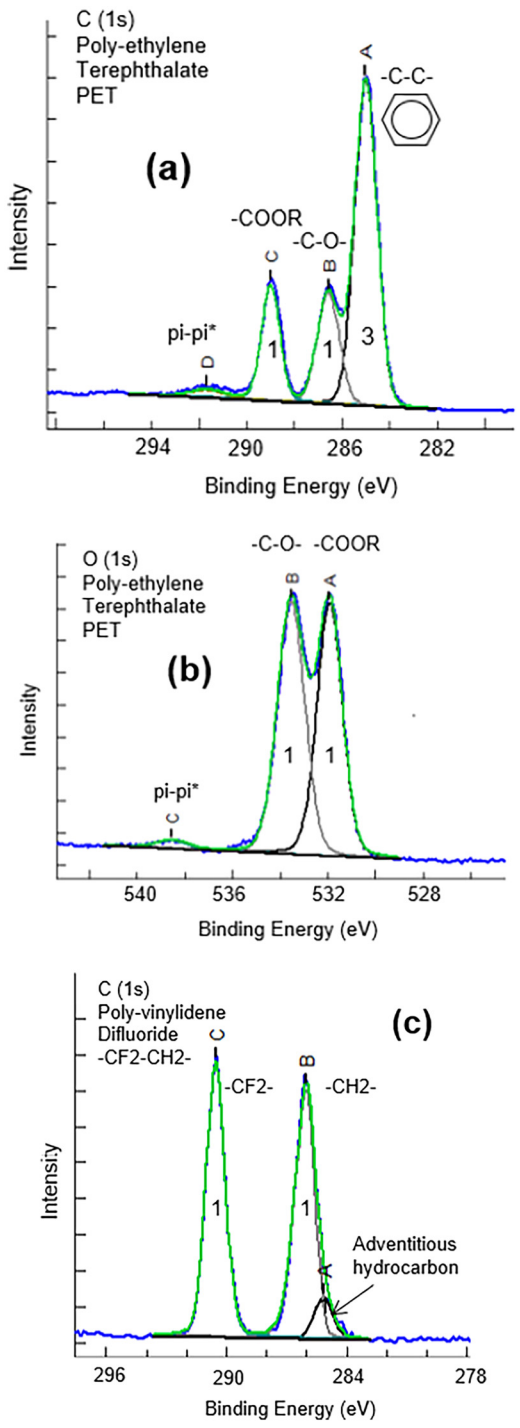


FIG. 22. C (1s) spectrum of PET (Mylar) (a), O (1s) of PET (Mylar) (b), and C (1s) of polyvinylidene difluoride (PVdF) (c). The hydrocarbon C (1s) peak from PVdF has a small shoulder at a low BE, which is due to adventitious hydrocarbons. If that was due to charging, then the CF_2 peak would have the same small shoulder. There is no tail, which means that charge is well controlled.

is a significant number of rumors that say native oxides should be properly insulated, not exposed to flood guns. For this reason, many researchers do not turn on the flood gun when analyzing any type of native oxide.

3. Peak-fits of complex peak-shapes from insulators with controlled charging

The following examples of complex, high energy resolution, chemical state spectra have good peak-fit results between the synthetic peaks and the raw peak envelop because surface charging is well controlled. For these peak-fits of C (1s) and O (1s) from PET, shown in Figs. 22(a) and 22(b), there are no shoulders or sloping tails on the lower BE side of the peaks. This defines controlled charging.

The C (1s) spectrum in Fig. 23(c) does have a small peak on the low BE side of the hydrocarbon peak in addition to the two main peaks. This small peak is attributed to the adventitious carbon that is loosely adhered to the surface of that sample. With a little cleaning, that peak can be eliminated.

Again, there are good fits between each set of synthetic peaks and the experimental peak envelope. This was easy to achieve because these spectra are from 100% pure materials, not real-world samples that have various forms of adventitious carbon, miscellaneous salts, and silicone oil transferred from handling.

These three peak-fits display most of the features listed in Table VIII, such as symmetric, Gaussian shaped slopes, no sloping charge tails, narrow FWHM (<1.4 eV), good fit between raw signals, and synthetic peak envelop.

4. Undesired peak-shape features caused by uncontrolled differential charging

Distortion of the uniformity of the electric field at the surface, known as differential charging, can occur above or within the surface of the analysis area of an insulator during XPS analysis. Differential charging can be horizontal (across the surface) or vertical (into the Z aspect of the sample).

Differential charging is due to a mixture of effects described in Table V. Differential charging when using a monochromatic x-ray source and an electron flood gun is mainly due to an irregular distribution of negative voltages over the area being irradiated that can reduce the voltage, the flux, or deflect flood gun electrons. See Figs. 7 and 9 for artistic depictions.

As a result, differential charging distorts the **true** shape of the peak(s) in a high energy resolution, chemical state spectrum, which makes peak-fitting difficult. Differential charging often produces anomalous "sloping charge tails" or "shoulders" at the low BE side of each high resolution spectrum obtained from the same sample. When sloping charge tails appear on all high energy spectra from the same sample, those sloping tails are due to differential charging. An example of this effect is shown in Figs. 23(a)–23(c) for three chemical state spectra obtained from an irregular, crumbling pellet of Y2O3 powder. After collecting these spectra, a fresh sample was prepared, and the flood gun needed to be tested.

Differential charging can produce peak broadening with an FWHM 3–4× larger than the true FWHM. Differential charging can and does produce unexpected shifts in binding energies toward higher BEs, which degrades the reliability of the binding energies,

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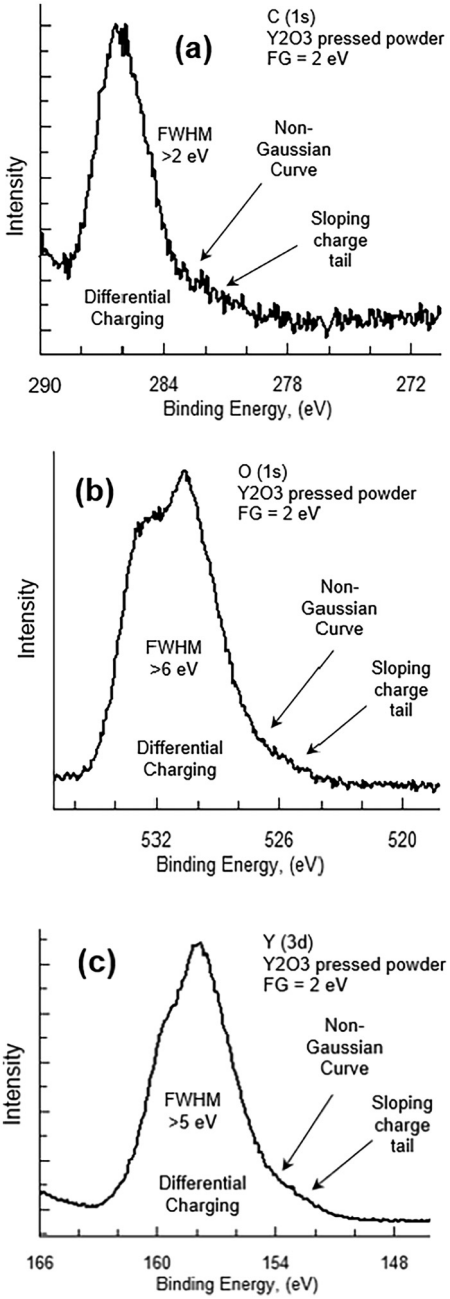


FIG. 23. Examples of uncontrolled differential charging from the pellet of Y_2O_3. (a) C (1s) spectrum, (b) O (1s) spectrum, and (c) Y (3d) chemical state spectra from Y_2O_3 powder pressed onto double side tape with the flood gun set to 4 eV. BE positions look reasonable when comparing them to handbooks and numerical BE databases, but there are obvious sloping charge tails on the low BE sides of all three high resolution spectra, which is a strong indicator of uncontrolled differential charging. The O (1s) and Y (3d) spectra show a peak and a shoulder. If we compare these experimental spectra to reference spectra from cin a database of actual spectra, then we know that both the O (1s) and Y (3d) spectra have two sharp peaks with a valley between them.

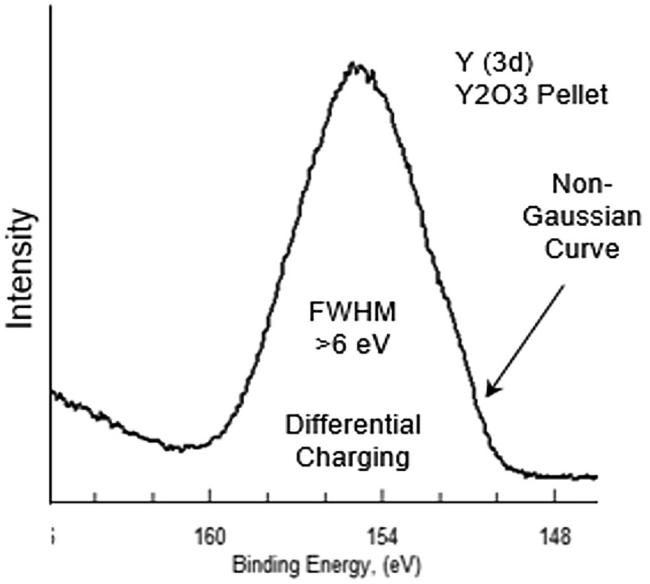


FIG. 24. Uncontrolled differential charging from a crumbling pellet of pure Y_2O_3 powder showing a very broad, nearly symmetrical peak for the Y (3d) signal. The analyst might try to fit this with 3–4 peaks.

BEs, used to make chemical state assignments [see Figs. 24(a)–24(c)]. A list of the observable features of uncontrolled differential charging is presented in Table IX–XI.

XPS spectra shown in Fig. 23 are from a nonconductive insulator that has features due to distortions of the true peak-shape. These distortions can be described as (1) a nonsymmetrical peak-shape with a non-Gaussian shaped curve on low BE side, (2) a very broad FWHM, and (3) a sloping charge tail on the low BE side of the peak. These three features are typical of a surface having differential charging.

These sorts of differential charging problems have likely produced significant errors in the XPS BEs listed in the NIST SRD-20 XPS database of BEs.[1] When we attempt to use BE numbers, in place of valid reference XPS peak-shapes, we have an excessively big risk of making wrong chemical state assignments. Chemical state XPS peak-shapes are often complex, so it is especially important to have valid examples of the actual peak-shapes.

TABLE IX. Observable features caused by uncontrolled differential charging.

- Sloping charge tails spread over a 2–6 eV range on the lower BE side of each high resolution spectrum in that dataset.
- Shoulders (10%–30% intensity) on the lower BE side of all high resolution spectra that were collected at the same time.
- Peak broadening—FWHM > 2–4× indicates differential charging (in contrast to normal FWHM range: 1.0–1.5 eV).
- Weak broadening of the FWHM of true peak-shape with or without charge-induced shifting. Difficult to see.
- C (1s) BE of adventitious hydrocarbons shifts differentially relative to other BEs in the same sample.

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TABLE X. XPS INSTRUMENT DETAILS.

- SSI X-Probe (Cu (2p3) BE at 932.47 eV),
- SSI S-Probe (Cu (2p3) BE at 932.67 eV, Cu (3s) BE = 122.39 eV); Ag (3d5) BE = 368.25 eV; Au (4f7) BE at 83.98 eV,
- PHI 5802 (Cu 2p3) BE at 932.6 eV),
- VG Scientific 220i-XL (Cu (2p3) BE at 932.67 eV),
- Thermo K-Alpha Plus (Cu (2p3) BE at 932.62 eV),
- SSI Charge-Control Mesh-Screen made from Nickel, 90% Transmission, grounded, 0.5-1.0 mm above sample),
- Monochromatic Al K-alpha X-rays (1486.7 eV, 8.338 Å),
- For chemical state spectra, pass energy = 50 eV,
- FWHM of ion etched Ag (3d5) using PE= 50 eV is <0.8 eV,
- FWHM of ion etched Ag (3d5) using PE= 10 eV is <0.6 eV,
- For survey spectra, pass energy = 200 eV,
- Adventitious hydrocarbon C (1s) BE is assigned to occur at 285.0 eV which is used for charge correction,
- Due to the need to show raw spectra, many BEs from insulators were not charge referenced.

Peak-shapes often include spin–orbit coupling, multiplet splittings, shake-up peaks, and vibrational broadening effects not provided in the NIST SRD20 database of XPS BEs. Using simple BE numbers to make chemical state assignments can lead to very serious errors in chemical state assignments that can cost many hours of repeat work or, in some cases, many thousands of dollars in losses.

When data analysts try to make a peak-fit of the spectrum shown in Fig. 24, they might try one broad peak, which would have an FWHM of ~6 eV. Is this too small or too large? What is normal? Other analysts might try to use two peaks; using one peak for the shoulder and one for the main peak. They would probably use different FWHM values for each peak. Even so, the resulting FWHM would be >3 eV for each of those two peaks. This is 2× larger than the average, normal FWHM listed in Table XIII, which is provided to help peak-fitting.

Based on the reference grade XPS spectrum shown in Fig. 25, both choices are wrong. The difference in peak-shapes for the Y (3d) signals from these both spectra Figs. 23(c) and 24 and Fig. 25 is extreme. Such large differences are not so common, but they are possible if charge-control conditions, alignment, and settings were changed significantly by the previous instrument operator.

When data analysts do peak-fitting, it is common practice to use FWHM that are 10%–15% smaller than the expected FWHM of most peaks, and to add a new chemical state peak at 1–1.5 eV steps. If the shape of the peak looks like the peak in Fig. 24, then the analyst might use 5–7 synthetic peaks to fit this peak by using an FWHM in the "normal" range (1.0–1.5 eV). This is an example of the problems that can occur due to differential charging. This is one of the reasons to practice aligning the XY positions of the flood gun using a single peak such as the C (1s) from polypropylene, and peak-fitting the resulting C (1s) spectra.

TABLE XI. Flood gun settings and ranges available to optimize quality and reliability of chemical state spectra.

A. Beam voltage (0–10 V)
B. Extractor voltage (0–25 V)
C. Emission current (1–300 μA)
D. Beam focus voltage (0–25 V)
E. Argon gas cell (0–25 V)
F. Z sample height (1–50 μm steps per motion)
G. X-position (0 to ±5 V)
H. Y-position (0 to ±5 V)

TABLE XII. FWHM of C (1s) and O (1s) indicate quality of charge control for native metal oxides. These FWHM show a rough correlation between all three (3) FWHM. Carbon is a common contaminant. When C (1s) FWHM is small (<1.4 eV), charge control is good. The pass energy (PE) setting for these measurements was normally 50 eV [which produces a 0.75 eV FWHM for the Ag (3d5) peak from elemental silver]. A few results were made using PE = 25 eV (which produces a 0.65 eV FWHM for the signal.).

Native metal oxide	C (1s) FWHM (eV)	Metal FWHM (eV)	O (1s) FWHM (eV)
Ag_2O	1.1	1.04	0.96
Bi_2O_3	1.66	1.48	1.58
Cr_2O_3	1.45	1.33	1.24
Fe_2O_3	1.29	1.32	1.05
Ga_2O_3	1.48	1.37	1.51
HfO_2	1.55	1.4	1.68
HgO	1.16	1.06	0.96
MnO_2	1.21	1.12	1.02
MoO_3	1.48	1.01	1.2
Nb_2O_5	1.35	1.14	1.36
Sc_2O_3	1.45	1.27	1.33
SiO_2	1.27	1.25	1.4
SnO_2	1.36	1.28	1.29
Ta_2O_5	1.56	1.12	1.46
TiO_2	1.34	1.02	1.18
Y_2O_3	1.51	1.25	1.3
Average	~1.4	~1.2	~1.3

The normal range for FWHM for a normal O (1s) peak is between 1.0 and 1.5 eV as listed in Table XIII. However, the O (1s) peaks due to hydroxides or carbonates typically has FWHM that range between 1.4 and 1.8 eV. If you have any peak with an FWHM > 2.0, then you should add a second peak and reduce the FWHM for both peaks to be <1.6 eV (a rule-of-thumb). The FWHM of metal peaks are more challenging due to the possible presence of multiplet splittings and shake-up structure.

As an end to this section, we suggest the following: Each operator, analyst, scientist, manager, and professor needs to know what is "normal" for the FWHM of most insulators because >70% of all samples analyzed by XPS are insulators. Everyone needs to keep in mind that a peak that is due to different chemical state often occurs just 1–1.5 eV higher than the first peak in the series. Everyone should look for a website that provides free access to high quality monochromatic XPS spectra having good charge control with and without peak-fits.

5. Advantage of using charge-control mesh-screen with a flood gun

The charge-control mesh-screen technology was invented and patented by Chuck Bryson in 1986.[4] This mesh-screen provides

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TABLE XIII. FWHM of O main metal peak and the O (1s) peak from metal oxides using charge-control mesh-screen. These FWHM are provided to help data analysts to choose a useful FWHM for peak-fitting pure oxides and other materials. The pass energy (PE) setting for these measurements was normally 50 eV [which produces a 0.75 eV FWHM for the Ag (3d5) peak from elemental silver]. A few results were made using PE = 25 eV (which produces a 0.64 eV FWHM for the signal).

Metal oxide charge referenced to C (1s) at 285.0 eV	Spin–orbit of metal signal	Metal (main peak) FWHM using charge-control mesh-screen (eV)	O (1s) FWHM using charge-control mesh-screen (eV)
Ag_2O	3d5	0.90	1.20
Al_2O_3	2p	1.39	1.60
As_2O_3	3d	1.80	1.71
Au_2O_3	4f7	1.21	1.13
B_2O_3	1s	1.4	1.6
$BaCO_3$	3d5	2.07	1.77
BeO	1s	1.73	1.71
Bi_2O_3	4f7	1.37	1.52
$CaCO_3$	2p3	1.67	1.64
CdO	3d5	1.42	1.28
CeO_2[a]	3d5[a]	3.0[a] (first MS peak at 877.0 eV)	1.5
Co_3O_4[a]	2p3[a]	1.51[a] (first MS peak at 779.5 eV)	1.03
Cr_2O_3[a]	2p3[a]	1.10[a] (first MS peak at 575.6 eV)	1.27
Cu_2O	2p3	1.16	1.00
Fe_2O_3[a]	2p3[a]	1.31[a] (first MS peak at 709.8 eV	1.04
Ga_2O_3	2p3	1.73	1.46
GeO_2	3d5	1.28	1.4
HfO_2	4f7	1.31	1.71
HgO	4f7	1.07	1.00
In_2O_3	3d5	1.33	1.19
IrO_2	4f7	0.84	0.99
K_2O	1s	1.37	1.6
La_2O_3[a]	3d5[a]	2.50[a] (first MS peak at 834.4 eV)	1.66
Li_2O	1s	1.6	1.5
MgO	2p	1.25	1.38
MnO_2[a]	2p3[a]	1.12[a] (second MS peak at 641.4 eV)	1.02
MoO_3	3d5	1.03	1.23
Na_2O	1s	1.78	1.44
Nb_2O_5	3d5	1.12	1.34
NiO[a]	2p3[a]	1.19[a] (first MS peak at 853.7 eV)	1.06
PbO	4f7	1.17	1.09
PdO	3d5	0.98	1.09
PtO_2	4f7	1.09	1.52
Re_2O_7	4f7	1.47	1.49
Rh_2O_3[a]	3d5[a]	0.90[a] (first MS peak at 308.6 eV)	1.09
RuO_2[a]	3d5[a]	0.77[a] (first MS peak at 280.7 eV)	0.95
Sb_2O_5	3d5	1.60	1.6
Sc_2O_3	2p3	1.27	1.30
SiO_2	2p3	1.25	1.27
SnO_2	3d5	1.32	1.14
$SrCO_3$	3d5	1.56	1.9
Ta_2O_5	4f7	1.11	1.47
TeO_2	3d5	1.48	1.42
TiO_2	2p3	1.02	1.20
Tl_2O_3	4f7	1.02	1.07
V_2O_5[a]	2p3[a]	0.99[a] (third MS peak at 517.0 eV)	1.33
WO_3	4f7	1.02	1.28
Y_2O_3	3d5	1.18	1.30
ZnO	2p3	1.43	1.15
ZrO_2	3d5	1.20	1.44

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TABLE XIII. (*Continued.*)

Metal oxide charge referenced to C (1s) at 285.0 eV	Spin–orbit of metal signal	Metal (main peak) FWHM using charge-control mesh-screen (eV)	O (1s) FWHM using charge-control mesh-screen (eV)
Average	—	*1.30*	*1.34*

[a]Due to MS in this spin–orbit, the XPS signal is a complex set of multiple peaks. In this table, we report only the first peak from the set of multiple peaks. For example, CeO_2 (3d5) has multiplet splitting, which produces a complex set of peaks. The FWHM from the first peak in the CeO_2 multiplet splitting is listed as 3.0 eV which is due to the signal at 877.0 eV when charge referencing C (1s) to appear at 285.0 eV. The abbreviation we use is shown here: 3.0 (first MS peak at 877.0 eV). The remaining peaks in the multiplet splitting envelope should also use the same FWHM unless the theory predicts otherwise.

excellent charge control of insulators by producing a flat, uniform electrical field just above the surface of the sample with the electron flood gun is turned on. Optimum height from the surface ranges from 0.5 to 1.0 mm. An artistic depiction of a flat uniform electrical field is shown in Fig. 26.

The handmade charge-control mesh-screen (shown in Fig. 27) is easy to machine and assemble. In place of the metal square, we have also used large-diameter thin brass or SS washers. When you use this mesh-screen you need different heights (spacers) because samples have different thicknesses. The holes in the metal square allow the user to use screws or clips. Be certain to ground the metal square. Warning: Because the mesh-screen is thin and flimsy, it is easy to tear, which is why you may decide to make several as spares.

The mesh can be used on many different XPS systems, but it is not recommended to be used with systems having magnetic immersion lens, which will cause the mesh to deflect upward, which limits its usefulness. The author has used the mesh on a magnetic lens system only once, so it needs testing.

For all other XPS systems, Ni, O, and C that exist on the mesh will **not** be measured because the mesh is, in effect, out of focus of the electron collection lens. This occurs because most focused monochromatic x-ray beams strike the surface at a 35–45 deg angle, with most new systems having a collection lens that is perpendicular to the plane of the surface. That is the reason why the mesh needs to be 0.5–1.0 mm above the surface of the sample. If we accidentally have the mesh closer than 0.3 mm, then a survey spectrum will show a very small Ni (2p) peak with the C (1s) and O (1s) from the mesh being even smaller and hidden under the C and O signals from the actual sample. If you do not object to trace level signals from the mesh, then you can allow the mesh to touch the surface because the mesh has 90 percent transmission (200 × 200 um with 50 um wires). Nickel can be replaced by other metals that have conductive oxides.

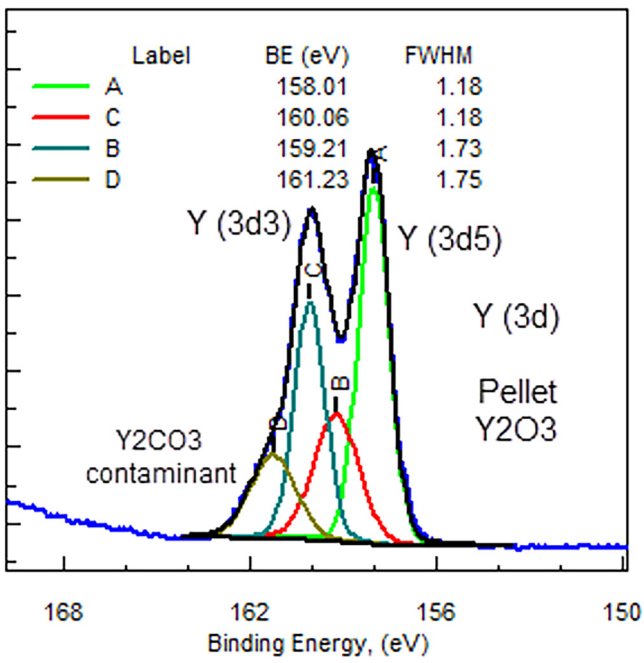
By using the simple handmade version of the mesh-screen (shown in Fig. 27), the author measured the O (1s) FWHM from 40+ metal oxides that ranged from 1.0 to 1.4 eV, and thousands of other materials. The corresponding metal oxide FWHM for the metal signal gave the same range (see Table XIII).

The overlay of C (1s) spectra from PET (Mylar) in Fig. 28 shows that the charge-control mesh-screen removes low levels of horizontal differential charging and that it is difficult to know that it might be present. These two C (1s) spectra were made using a PHI 5802 XPS system that is equipped with a monochromatic x-ray source. Without the mesh, the C (1s) spectrum looked useful. With the mesh, using the same XY position of the flood gun, all three C (1s) peaks have smaller FWHM (Fig. 29).

The charge-control mesh-screen has been used with older monochromatic XPS instruments, newer instruments that use a magnetic lens, and modern XPS instruments including the Thermo K-alpha. When using the mesh-screen on a Thermo K-alpha, the flow of ionized argon needs to be stopped. With the magnetic lens system, we decreased the voltage of collection lens #1. When the magnetic lens was turned on, the nickel mesh was raised up slightly.

V. EXAMPLES OF SIX TYPES OF DIFFERENTIAL CHARGING PROBLEMS

This section provides real-world examples (chemical state spectra) of differential charging for those scientists and engineers



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FIG. 25. Y (3d) spectrum from Y_2O_3 having good charge control. The FWHM are <1.4 eV for peaks A and B. Peak C is due to Yttrium carbonate. These reference spectra were obtained from the SpecMaster database having >70 000 monochromatic XPS spectra (Ref. 2).

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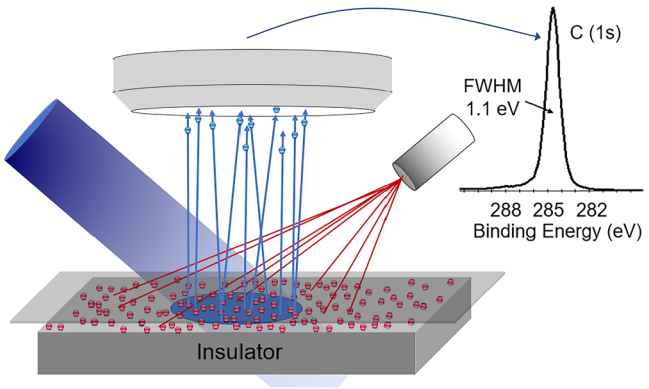


FIG. 26. Artistic depiction of controlled charging that has a flat uniform electrical field with flood gun ON. The flat electrical field is due to the presence of a grounded, 90% transparent metal mesh-screen (colored as dark gray sheet) sitting 0.5–1.0 mm above the surface of the sample. The sample is polypropylene. The C (1s) peak is symmetrical. No sloping charge tail. No shoulder. FWHM < 1.2 eV.

who are learning how to control the differential charging of insulators and need examples. The following example spectra were obtained from real-world samples because they show differential charging. To better understand what differential charging looks like, we provide the same spectrum with uncontrolled differential charging and with controlled charging.

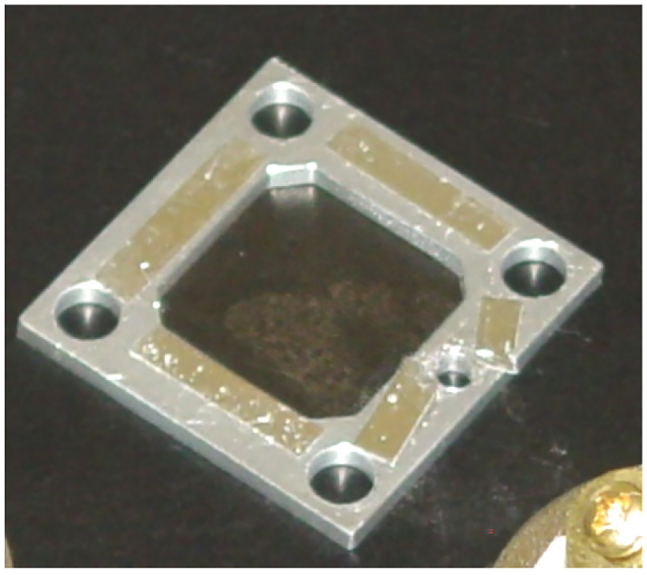


FIG. 27. Handmade charge-control mesh-screen. 25 × 25 mm aluminum square (0.8 mm thick) with a 90% transparent nickel metal mesh taped down by hand using aluminum tape to one side of the square. Holes allow screws to be used if clips are not available. The mesh-screen itself is not perfectly flat. To produce a flat electric field, the aluminum needs to be grounded. Depending on the sample thickness, other mesh-screens or spacers were built using 0.5, 1.0, 1.5, and 2.0 mm thicknesses.

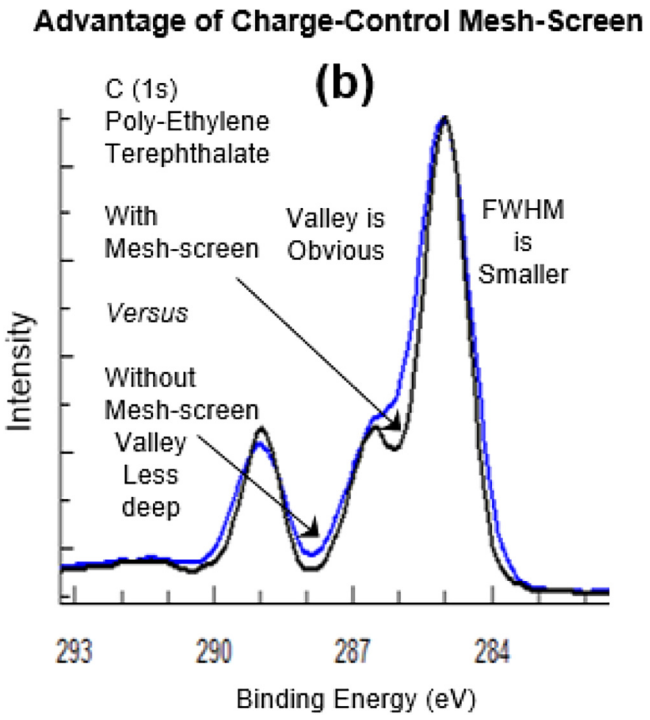


FIG. 28. Difference in energy resolution between these two C (1s) spectra from PET is due to the use of the charge-control mesh-screen. The mesh-screen was ~0.8 mm above the surface of the PET film. The instrument was a PHI 5802 XPS equipped with a monochromatic Al x-ray source and translatable flood gun (see Fig. 29).

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A. Problem type #1

Sloping charge tail that spreads over a 2–6 eV range on the low BE side is shown in Fig. 30(a).

B. Problem type #2

Shoulders (10%–30% intensity of adjacent peak) on the lower BE side are shown in Figs. 31(a) and 31(b).

When differential charging occurs, it is often visible on the low BE side of all the chemical state spectra for a given sample. It can appear as a sloping tail as shown for Problem Type #1. Or, in this case, the differential charging can appear as new peaks or shoulders on the low BE side, which suggests the presence of a new chemical state.

In this example,[21] the Zn (2p3) and O (1s) spectra from a single crystal of ZnO (0001) were compared to the same spectra from nanoparticles of ZnO (mounted on indium foil) that were produced using different levels of *p*H. The peak-shapes in the spectra shown in Figs. 30(a) and 30(b) are complicated and were not expected based on reference spectra from the pure ZnO crystal also shown.

ZnO has a bandgap of 3.3 eV, so it is expected to be nonconductive, which means that the instrument operator had to turn on

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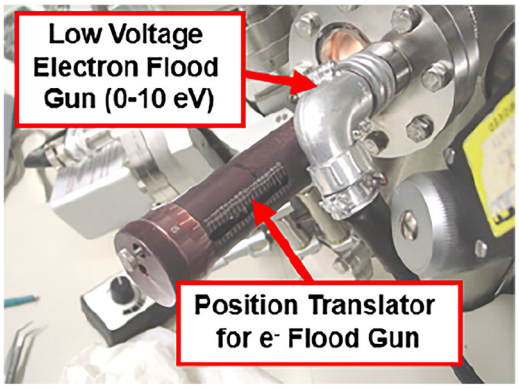


FIG. 29. Translatable flood gun on a PHI 5802 XPS. To use this flood gun, the operator must move the flood gun into the analysis chamber so the electron beam properly overlaps the analysis area.

the flood gun to eliminate surface charging. In this case, the Zn (2p3) spectra were expected to appear as symmetrical peaks with only one component because the Zn (2p3) signal from ZnO has no chemical shift from pure Zn metal, which means that ZnO and Zn metals suffer a direct overlap. Depending on the final chemistry of the reactions, the O (1s) spectra were expected to have either a single peak or more likely two peaks, one due to the oxide and one due to a hydroxide, so seeing two peaks was not unexpected.

From the final set of XPS spectra [Figs. 31(c) and 31(d)], it is obvious that the electrical field within these nanoparticles is complicated when the samples are grounded, and the flood gun is turned on. With the flood gun turned on, the different local electrical environments of the nanoparticles produced a new, unexpected peak for the Zn (2p3) signal, which appears as a shoulder on the low BE side of the true peak. It is a distinct intense shoulder, not a sloping tail.

Due to the unexpected presence of the extra Zn (2p3) signal in Fig. 31(b), the operator decided to cross-check the chemistry by floating the samples on a non-conductor instead of standard mounting of pressing nanoparticles onto indium foil. By floating the sample, the operator learned that the unexpected shoulders were a differential charging artifact (actually, a vertical differential charging artifact.)

The Zn (2p3) and O (1s) spectra (31c and 32d) on the right side of Fig. 31 show the peaks that were expected based on prior experience. The take-home lesson from this set of spectra is that the analyst must be ready to cross-check the results and analyze samples that are truly insulated in case the physical or chemical structure of the material produces some unexpected peaks.

C. Problem type #3

Severe peak broadening (distortion)—FWHM > 3 eV is shown in Figs. 32(a)–32(c).

The three spectra shown here in Fig. 32 from C (1s), O (1s), and Y (3d) signals were collected from the same sample. These spectra [Figs. 32(a)–32(c)] are examples of severe peak broadening caused by differential charging. The beam voltage of the flood gun for this sample was initially set to 2 eV when the first data set was collected. After removing the sample from the instrument, the samples were found to have crumbled, exposing a much rougher surface for analysis.

After the initial data were collected, the measured BE positions were reasonable when compared to the NIST SRD20 database of numerical BEs. Based on an XPS reference spectrum of pure Yttrium metal, the Y (3d) peak of the Y_2O_3 material should have two peaks separated by a valley, but the raw spectrum for the Y (3d) signal of Y_2O_3 appeared as a single wide peak. Why? The C (1s) and O (1s) spectra also show a broad peak and a broad peak with a shoulder. The C (1s) actually looks like two peaks of equal intensity, which is different from the usual C (1s) spectrum from adventitious carbon. It is very useful to remember the typical shape of the C (1s) of adventitious carbon.

When we compare these experimental spectra with actual reference spectra [Figs. 32(d)–32(f)] from Y_2O_3 from a database of actual spectra, we found that both the O (1s) and Y (3d) peaks should appear as two peaks with an obvious valley between them.

D. Problem type #4

Weak broadening of true peak-shape is shown in Figs. 33(a) and 33(b).

In this example, PET was analyzed by using a PHI 5802 XPS with a translatable flood gun.

After optimizing the flood gun voltage to 2 eV, the C (1s) spectrum from PET [in Fig. 33(a)] gave a BE at ~283.5 eV, which matches the 2 eV offset from the flood gun voltage. Based on the reference peak-shape for the C (1s) spectrum of PET (Fig. 17), the C (1s) peak-shape looked Gaussian shaped, but the valley between the C–C peak and the C–O peak was missing when looking at the reference C (1s) spectrum.

After placing a handmade charge-control mesh-screen ~0.8 mm above the surface of the sample, a new C (1s) spectrum revealed the missing valley. The BEs shifted 2 eV lower, which indicates better charge control due to the mesh-screen. Visually, we found peaks with smaller FWHM. The overlay in Fig. 33(b) reveals the improvement in peak-shapes. If we had tried to peak-fit the original C (1s) spectrum, then we might have added an extra synthetic peak to explain the total peak envelope or we might have used FWHMs that are broader than normal. The improved charge-control peak-shape provided by the charge-control mesh-screen result helped us to avoid misinterpreting this spectrum.

E. Problem type #5

Vertical differential charging of native oxides—grounded versus insulated— is shown in Fig. 34.

Most naturally formed native oxides are thin, having oxide layers with thickness ranging from 10 to 50 Å (1–5 nm). These thin layers are usually colorless to the human eye. Some metals form relatively thick layers of native oxides or carbonates that can spall off as a form of corrosion.[2]

In general, thin films of many metal oxides behave conductively when they are grounded to the sample stage. In powder form, metal oxides that behave conductively are brown or black in color, but some are green or red.

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In powder form, nonconductive metal oxides are white or pale yellow. Unfortunately, we cannot see any color from native oxides because they are so thin.

Thin layers of various nonconductive metal oxides on metals can suffer from **vertical differential charging**, which becomes obvious when a flood gun beam of electrons is applied at various voltages [see Figs. 34(a) and 34(b)].

Most naturally formed nonconductive native oxides are thin enough that Fermi level electrons (at 295 K) from the underlying metal can and do migrate (tunnel) along grain boundaries to neutralize the valence-holes (*not* core-holes) formed by XPS. For many native oxides, there is no obvious need to use a flood gun beam of electrons to neutralize nonconductive native oxides if the sample is grounded.

However, various nonconductive native oxides can and do produce adventitious hydrocarbon C (1s) BEs that range from 285.5 to 286.5 eV, with the metal oxide BEs being 0.5–1.2 eV higher than the BEs reported in various handbooks and the NIST SRD-20 database of numerical BEs. Why? Based on our research, the answer involves the presence of strong surface dipole moments produced by highly polar metal oxides, which is the topic of our next paper.

When instrument operators find larger than expected BEs for the C (1s) and the main metal oxide peak for a thin native oxide of a metal, those operators then imagine that the larger BEs are due to a charging effect and so turn on the flood gun to compensate for the charging. When they try a small flood gun beam voltage, there might be almost no change in BEs. However, when they use larger voltages (5, 10, or 15 eV), they find significant BE shifts for the metal oxide peak, the oxygen peak, and the C (1s) peak [Figs. 34(a) and 34(b)].

In this figure, we see peak broadening, and sloping charge tails for the C (1s), O (1s), and metal oxide peak, but the pure metal peak does not shift. Why? The pure metal peak does not shift because the metal is properly grounded due to contact with the sample stage that is properly grounded. The pure metal peak BE is true. Only the upper layers of the surface (the carbon and the metal oxide layers) suffer vertical differential charging.

What produces this type of vertical differential charging and how do we deal with it? The vertical differential charging can be attributed to two factors. One factor is the vertical *charge* gradient that develops as soon as we turn on the flood gun. The charge gradient begins at the metal–metal oxide interface, which is the start point for a natural dipole moment. The dipole moment, due to the interface, produces a charge gradient, extending upward into the adventitious carbon layer. The positive end of the dipole moment retards (decreases) the KE of the emitted C (1s) photoelectron, in turn causing the C (1s) BE to appear at a higher than expected BE. The second factor that contributes to vertical differential charging is the capacitive nature of the nonconducting native oxide and the interface layer between the metal and the native oxide. These two factors are due to natural surface chemistry, surface physics, and electrical properties of the two interfaces and the resulting two dipole moments.

We can eliminate this vertical charging phenomenon by insulating (floating) the same sample to produce the spectra shown in Fig. 34.

Figures 35(a) and 35(b) show that floating the native oxide of aluminum produces an almost linear response to the flood gun voltage. After charge referencing the spectra in Figs. 36 and 37 based on the Al (2p) pure metal BE, we see an almost perfect overlap of the peak-shapes, and BE shifts. Figures 36 and 37 show us that

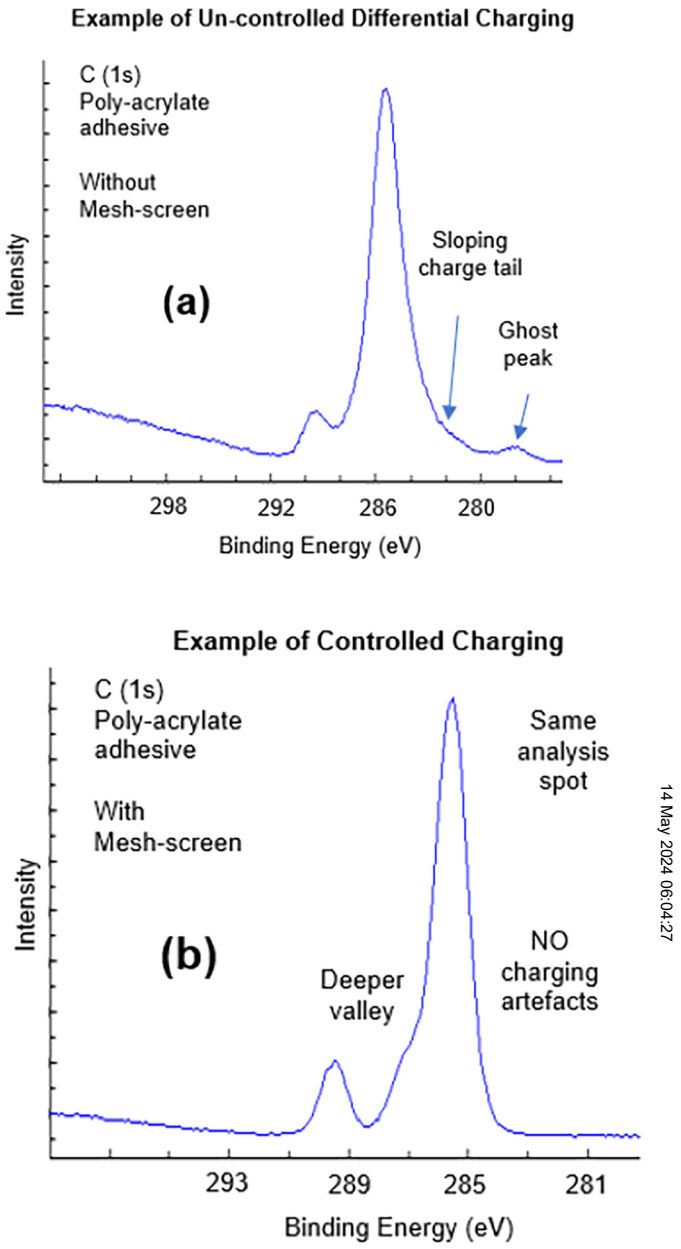


FIG. 30. Adhesive surface of a paper label was analyzed (a) without a charge-control mesh-screen and then (b) with a charge-control mesh-screen keeping the flood gun at the same conditions. After a charge-control mesh-screen was installed ~0.8 mm above the surface, the shapes of the C (1s) and O (1s) changed from being distorted to normal peak-shapes having no sloping charge tails on the low BE side.

differential shifting and broadening seen in Figs. 34(a) and 34(b) are eliminated by floating the sample [see Figs. 35(a) and 35(b)].

By using the Al (2p) BE of pure aluminum (72.9 eV) to charge correct both Al (2p) and C (1s) spectra, we know that the correct

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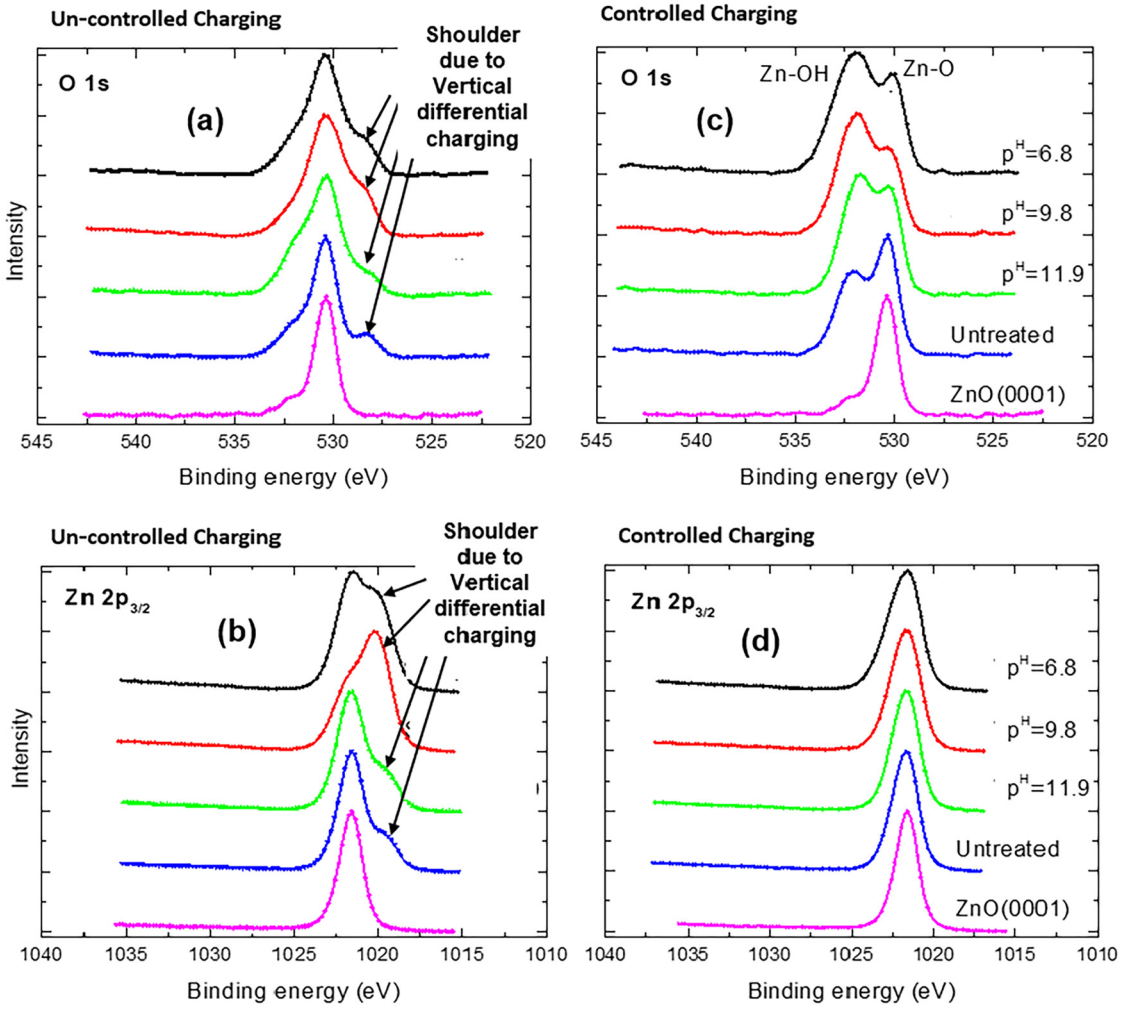


FIG. 31. Nanoparticles of ZnO were exposed to different levels of *p*H to change their conductivity. The different nanoparticles were pressed onto Indium metal foil and then analyzed by XPS. Because the nanoparticles had developed levels of conductivity, they caused vertical difference charging shoulders [(a) and (b)] highlighted by arrows pointing at the shoulder that is a charging artifact. After mounting the nanoparticles onto nonconductive adhesive tape, the differential charging was replaced by true insulation producing one electrical potential for each sample.

Al (2p) BE for Al_2O_3 is 75.8 eV, which matches the synchrotron work done in 1978.[28] This Al (2p) BE is a particularly important BE for anyone working with Al_2O_3.[22–24]

1. True BE of Al_2O_3

Based on oxidation studies performed at a synchrotron facility in 1978, the true Al (2p) chemical shift for Al_2O_3 is 2.7, and the true Al (2p) BE for Al_2O_3 is ~75.9 eV (Fig. 38). The BE difference between pure aluminum (Al 2p = 72.9 eV) and Al_2O_3 is 2.7 eV, which gives an Al (2p) BE at 75.9 eV for Al_2O_3.

This synchrotron based Al (2p) BE is 1.7 eV larger than the 74.2 eV BE published in the PHI Handbook of XPS in 1992[25] and the 74.3 eV BE in Surface Science Spectra in 1998.[26]

This difference is due to a surface dipole moment,[10,27] an effect that preferentially retards the KE of the C (1s) photoelectrons in adventitious carbon on top of the aluminum native oxide by ~1.7 eV. This effect is common for elements in columns 2 and 3 of the periodic table. The size of this effect depends on the dipole moment, which is related to the bandgap of the oxides.

F. Problem type #6

1. Effect of sample size and distance from ground

When a large insulating sample is irradiated with an x-ray beam, the exposed area develops a positive surface charge. When the electron flood gun is then turned on, that positive charged area

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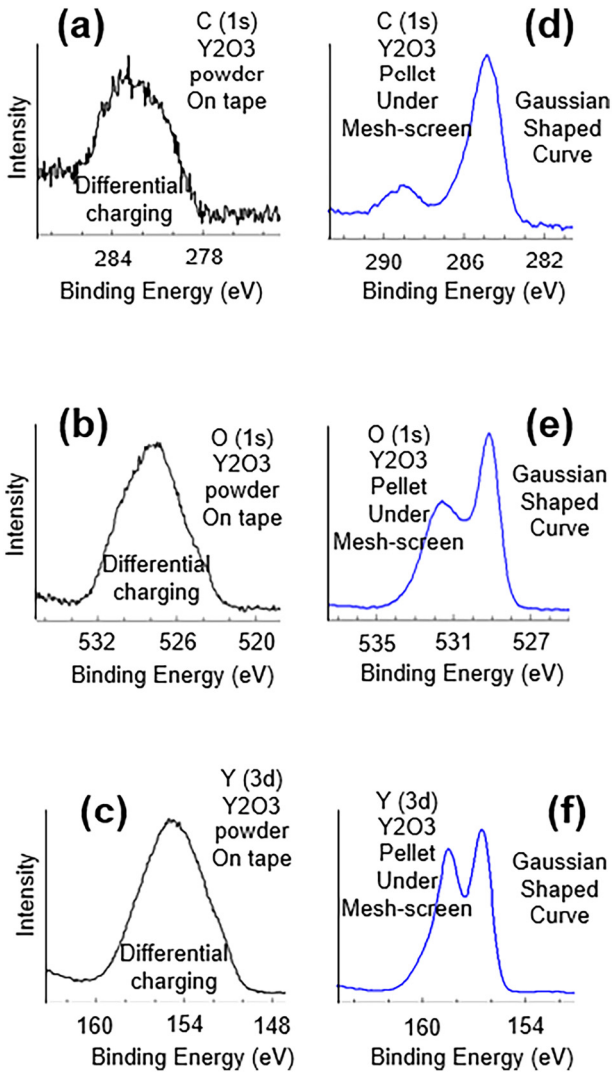


FIG. 32. Examples of uncontrolled differential charging from the Y_2O_3. The C (1s), O (1s), and Y (3d) chemical state spectra [(a)–(c)] from 99.99% pure Y_2O_3 powder pressed onto double-sided tape. The BE positions look reasonable when comparing them to the PHI handbook and NIST numerical BE database, but there is an obvious sloping tail on the low BE sides of all three spectra, which is an indicator of uncontrolled differential charging. By comparing these spectra to reference grade spectra (Ref. 2) [(d) and (e)] from as-received 99.99% pure Y_2O_3 pressed into a pellet and covered with the charge-control mesh-screen, we understand how strong the differential charging can be. The right-hand side of each peak has a nice Gaussian shape, which is typical of controlled charging. [The reference spectra (Ref. 2) are from the XPS International SpecMaster database of >70 000 spectra.]

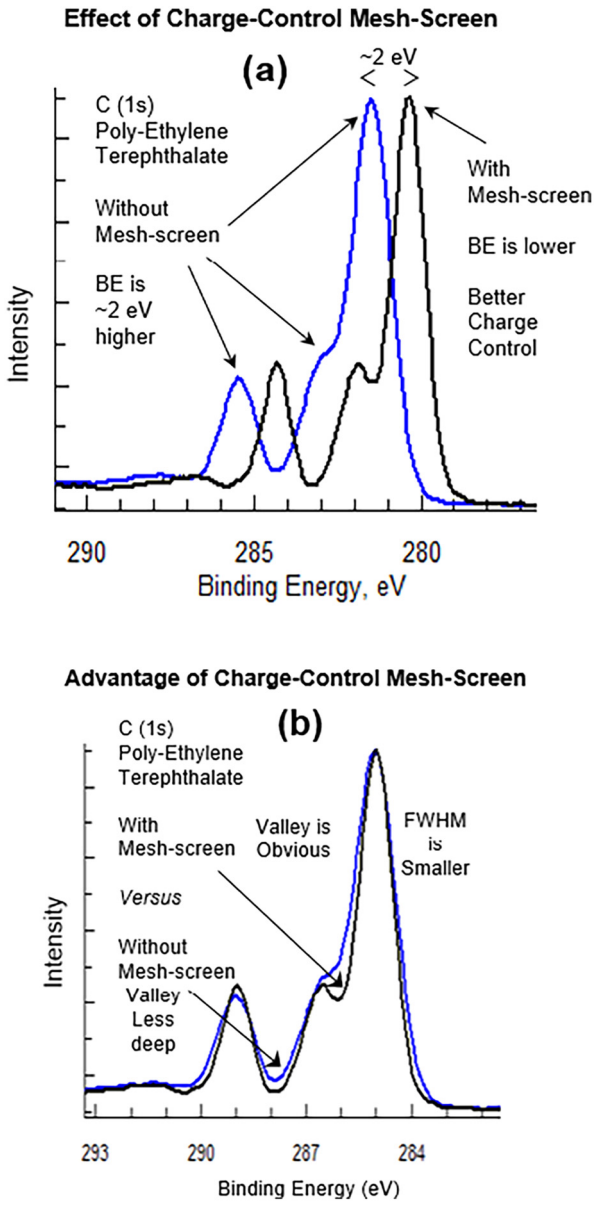


FIG. 33. FWHM of C (1s) from PET appears at normal BE values, but the FWHM is slightly broader and the peak valley is missing. This effect was revealed by placing a charge-control mesh-screen above the same sample and collecting the same spectra. (a) shows some of the effect of using the mesh-screen. After shifting BEs to align, (b) clearly reveals the improved charge control provided by the charge-control mesh-screen.

should develop a net negative charge if the voltage and emission current of the flood gun are high enough. Before we spend a lot of time collecting data from a large area with a ground point that is distant, we need to confirm that the area will produce high quality chemical state spectra.

An example of the effects of horizontal differential charging was found by analyzing a large piece of aluminum nitride ceramic (Fig. 39). Chemical state spectra [Figs. 40(a)–40(c)] were obtained from the center of the aluminum nitride ceramic and from an area that was ~1 mm from the grounded copper clip holding the sample.

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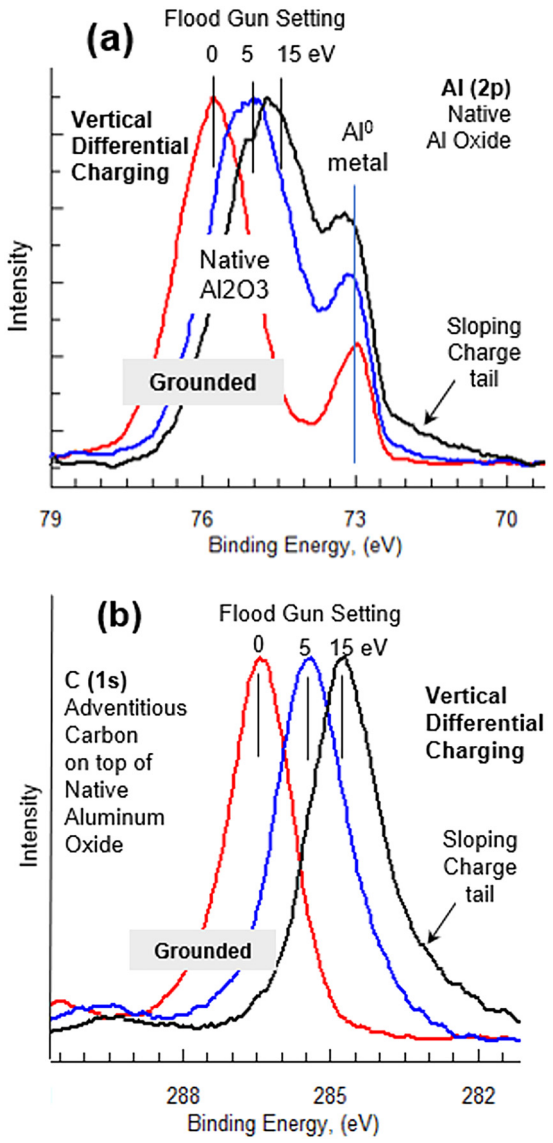


FIG. 34. (a) is an overlay of Al (2p) spectra exposed to 0, 5, and 15 eV flood gun voltages. 34(b) is an overlay of C (1s) spectra exposed to 0, 5, and 15 eV flood gun voltages. Example of vertical differential charging for a naturally formed, native oxide of aluminum when the flood gun beam voltage is increased. This type of differential charging occurs when a nonconductive native oxide is irradiated with a low voltage beam of electrons varied from 0 to 5 to 15 eV. It is important to notice that the carbon peak shifted more than the aluminum oxide peak.

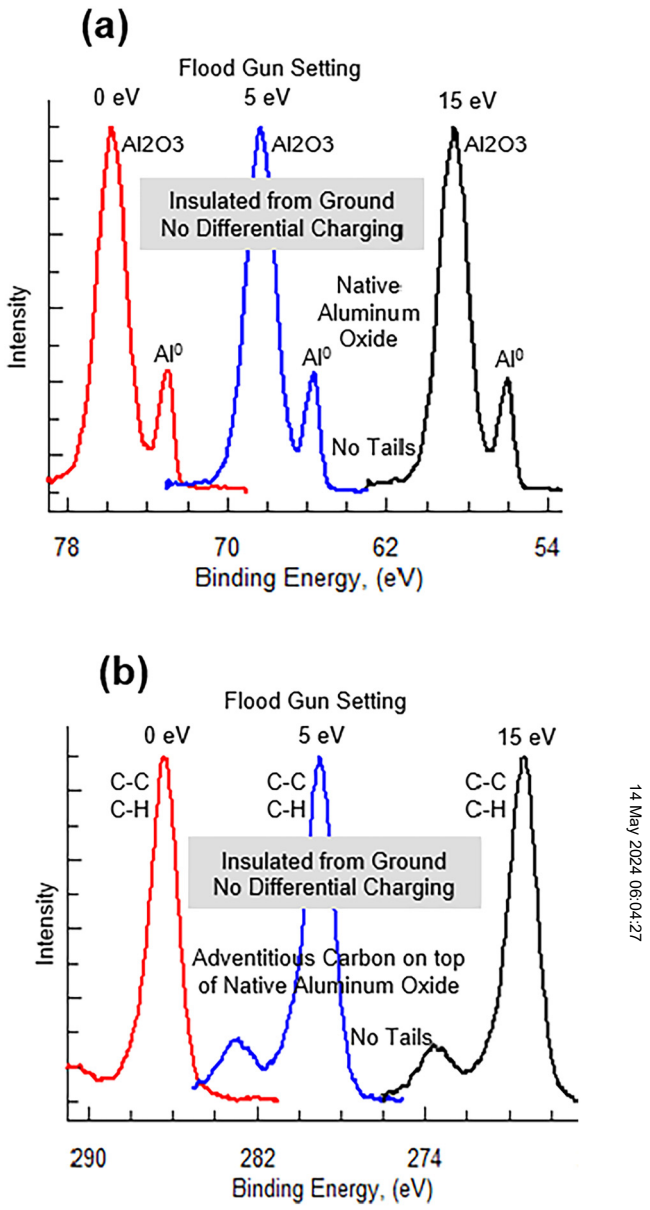


FIG. 35. Native oxide of an aluminum sample was insulated, and the flood gun was turned on using 0, 5, and 15 V settings. These Al (2p) and C (1s) peak-shapes look reasonable, and there is no obvious distortion due to differential charging.

To minimize the effects of differential charging for the data obtained from the center area, the sample was moved in X and Y to allow electrons to build up on neighboring areas.

After making overlays of the chemical state spectra from the two areas, the spectra from the center were found to be shifted by ~3 eV to higher BE and to suffer peak broadening [Figs. 40(a)–40(c)].

The spectra from the area that was ~1 mm from the copper clip produced symmetrical signals that have Gaussian tails on the low BE side that were more intense with slightly smaller FWHM. This difference is attributed to the nearness of the copper clip. We suggest that electrons from the grounded clip were able to migrate across the 1 mm distance of the surface to

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provide better charge control. The mechanism for this involves the monolayer level of water and various gases that are trapped on many surfaces.

VI. EFFECTS THAT LOOK LIKE CHARGING

XPS work on insulators often involves the use of different pass energies, argon ion etching, and a flood gun on materials having different degrees of surface roughness, electrical irregularities, etc. In some cases, the industrial customer does not know how the sample was last treated, or the customer may have accidentally contaminated the surface.

Industrial samples and samples from suppliers are sometimes extremely dirty, having as much as 6–9 nm of organic contamination, which usually requires the unexpected use of the flood gun. For these reasons, the operator needs to be able to distinguish between differential charging, sample treatments, and analysis conditions that can produce spectra that appear to have differential charging.

In this section, we present examples of normal chemical state spectra that might appear to suffer the effects of differential charging. Figure 41 is an artistic depiction of the chemistry of a typical native oxide.

Because XPS typically measured ~100 angstroms (10 nm) depth and reports quantitation as a total of 100 atom %, we developed a **rule-of-thumb** where a 1 atom % of any element is approximately equal to 1 Å (0.1 nm) of that element. There are equations that can produce a more accurate value, but for practical work, this rule-of-thumb is useful.

The drawing in Fig. 41 indicates that the adventitious carbon layer is typically 3–4 nm thick on most native oxides. This is based on many years of experience. Using our rule-of-thumb, the atom % amount of carbon is 30–40 atom %. This depiction includes a monolayer or two of water, which is enough to enable solutions and conductivity.

A. Misleading effects of different pass energy settings on FWHM

Low levels of differential charging can produce peak broadening that makes the operator or analyst consider decreasing the pass energy to get a better energy resolution. However, when your peak-fit has large FWHM, (>1.5 eV), you should consider that there can be two difference causes. One cause can be pass energy setting while the other can be differential charging. It is sometimes faster to check on flood gun settings instead of decreasing your pass energy setting and running a complete set of chemical state spectra. In either case, you should run just one of your chemical state spectra if you decide to decrease the pass energy. Be careful not to waste your time by jumping to the smallest possible pass energy. The smallest pass energy produces smaller FWHM and a very large loss in signal intensity.

Figures 42(a)–42(c) are examples of differences in pass energy settings that produce only modest improvement in FWHM for a nonconductive material. Due to the natural limit of FWHM of nonconductive chemical compounds, the smallest FWHM that can be measured ranges between 0.9 and 1.4 eV. Decreasing to a smaller pass energy will not produce a meaningful smaller FWHM,

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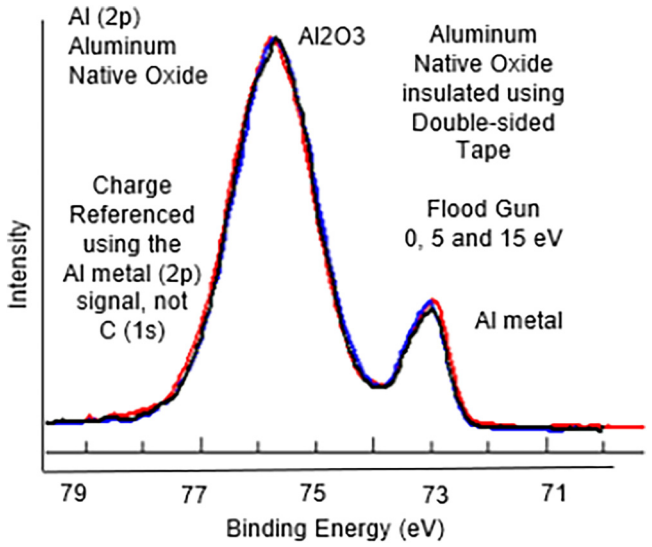


FIG. 36. Three Al (2p) spectra from the native oxide of aluminum (shown in Fig. 34) were deliberately insulated using double-sided tape and corrected by using the Al (2p) BE of pure aluminum metal. The Al_2O_3 peak still shows almost no differential charging. Please note that the Al (2p) BE of the Al_2O_3 native oxide is 75.8 eV, not 74.4 eV as published in the NIST SRD20 database and PHI handbook.

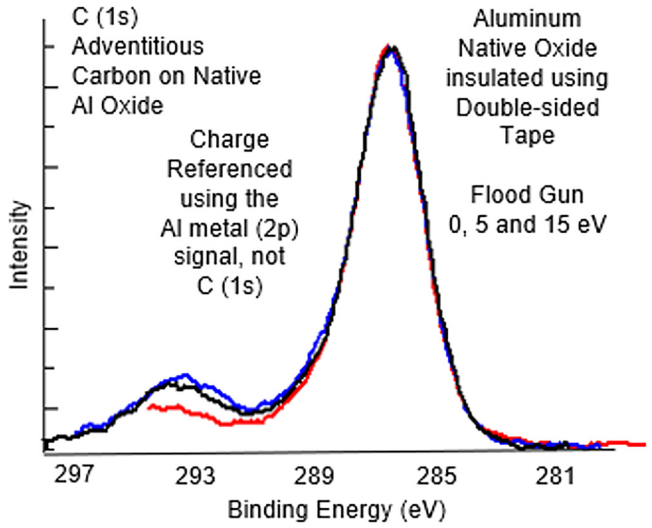


FIG. 37. Three C (1s) spectra [Fig. 34(b)] from the native oxide of aluminum that were deliberately insulated using double-sided tape and corrected by using the Al (2p) BE of pure aluminum metal. Because carbon is on the very top, it still suffers differential charging. Please note that the C (1s) BE is ~286.5 eV, not 285.0 eV, which is due to a surface dipole moment effect that preferentially retards the KE of the C (1s) photoelectrons by ~1.5 eV.

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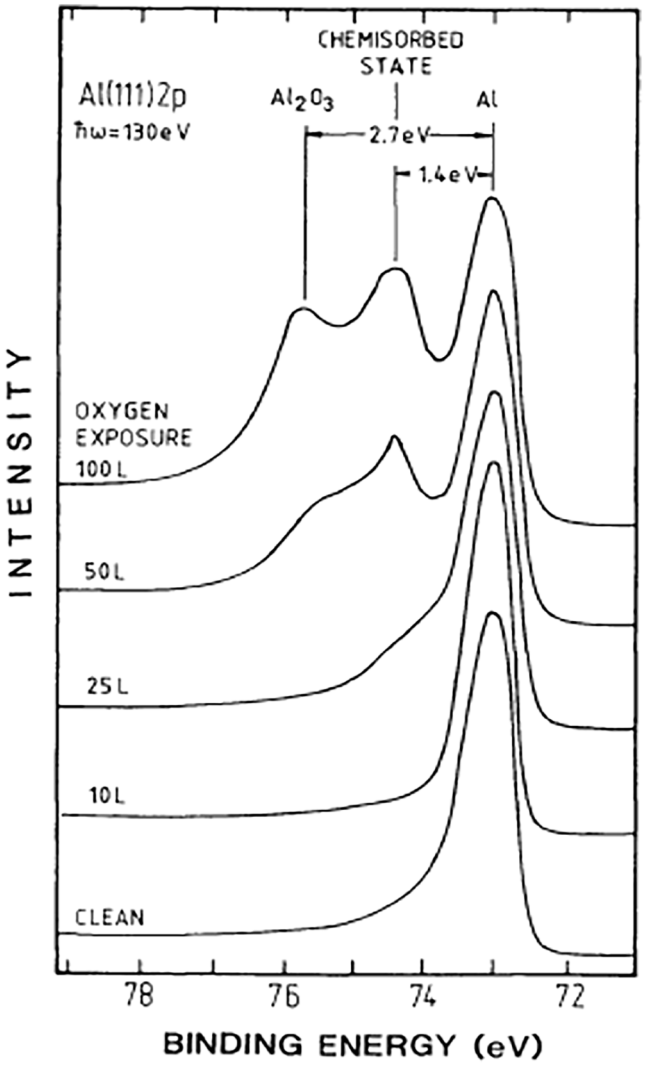


FIG. 38. Oxidation of a (111) surface of aluminum monitored using h-bar omega = 130 eV synchrotron radiation published in 1978. The conversion of the chemisorbed state into the subsequent Al_2O_3 is shown. The BE difference between pure aluminum (Al 2p = 72.9 eV) and Al_2O_3 is 2.7 eV, which gives an Al (2p) BE at 75.9 eV for Al_2O_3. This Al (2p) is 1.5 eV larger than the 74.6 eV published in the PHI Handbook of XPS and 74.5 eV in Surface Science Spectra in 1998. The adventitious hydrocarbon C (1s) BE is adjusted to give a C (1 s) BE = 285.0 eV. This difference is due to a surface dipole moment effect that preferentially retards the KE of the C (1s) photoelectrons by ~1.7 eV. Reproduced with permission from Flodstom *et al.*, Phys. Rev. Lett. 40, 907 (1978). Copyright 1978, APS.

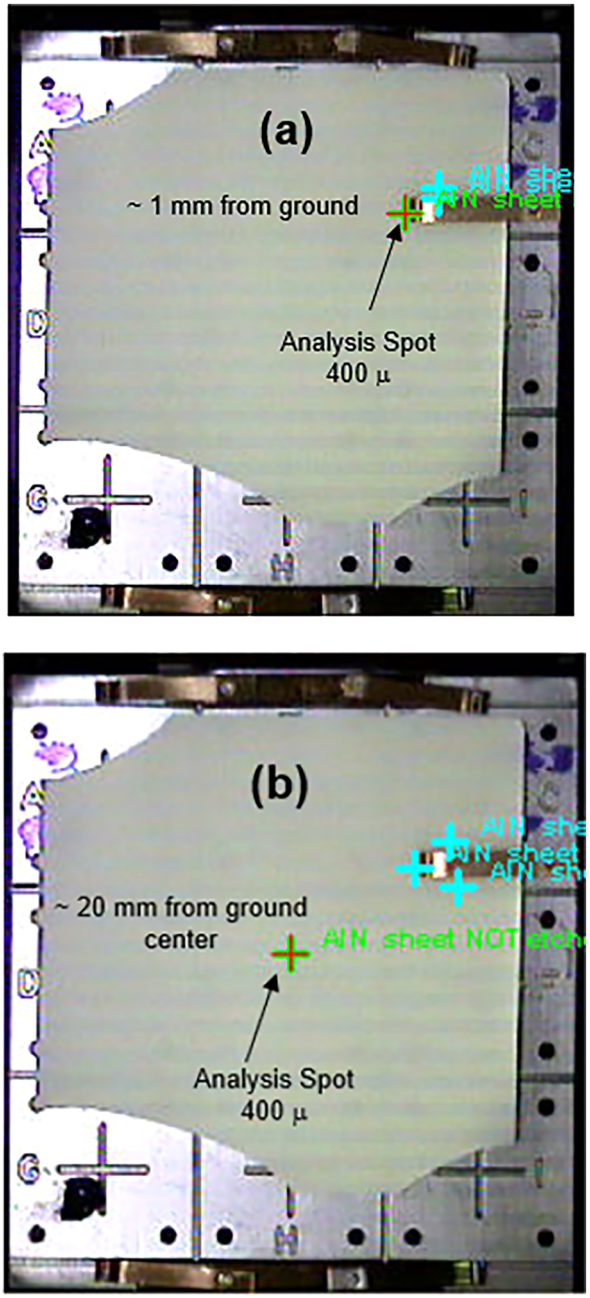


FIG. 39. Aluminum nitride sample. 400 μ analysis spot changed from being ~1 mm away from a copper grounded clip to the center of the 50 × 50 mm sample far from the grounding, where the grounding was 20 + mm away.

and to achieve the same S/N ratio, the number of scans and time used must increase by 50–100×.

Large pass energy settings provide the most intense XPS signals, which allows the operator to quickly measure the presence or absence of any element, but large pass energy settings provide a poor energy resolution that is not useful when we need chemical state information. Small pass energy settings are used when we want to measure the presence or absence of different chemical states. Small pass energies produce a better energy resolution but a

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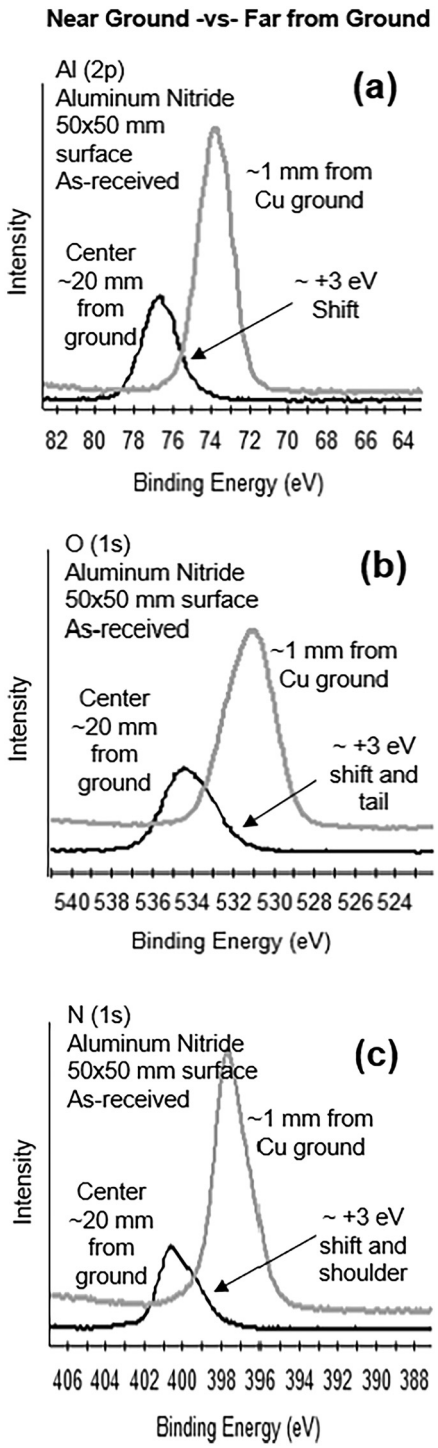


FIG. 40. Overlays of (a) Al (2p), (b) O (1 s), and (c) N (1 s) chemical state spectra from two different locations on a large (50 × 50 mm) insulating sample. One position was ~1 mm from a grounded clip. The other analysis position was in the center ~20 mm from the grounded clip.

weaker signal, causing us to spend more time collecting more spectra. It is a tradeoff.

There is a natural limit to the FWHM of peaks obtained from pure elements, conductive chemical compounds, and nonconductive chemical compounds [see Figs. 42(a)–42(c)]. These examples show that conductive materials can produce small FWHM, while nonconductive materials do not. This difference is important to remember because the time required to produce spectra having useful signal/noise (S/N) ratios grows exponentially as we decrease the pass energy to measure higher and higher energy resolutions. There is a "middle-ground" for Pass Energies when measuring nonconductive chemical compounds. If your instrument provides pass energies ranging from 5 to 200 eV, then the most effective use of your time, to analyze chemical states from nonconductive compounds, is to use a pass energy setting of 50–100 eV.

B. Effects of argon ion etching

Argon ion etching removes contamination from pure elements and chemical compounds. Ion etching is useful to remove adventitious carbon contamination and native oxides from pure metals to reveal a pure metal signal that has a narrow FWHM, but argon ion etching can cause peak broadening for XPS peaks from chemical compounds. This section shows the effects of using argon ion etching, which can be confused with differential charging.

The analyst needs to be careful when considering using argon ion etching to clean any material. Argon ion etching can and does degrade the chemistry in various materials, which destroys the chemical state information that we are trying to measure.

Ion etching of various oxides, polymers, and other chemical compounds can cause BE shifts, degradation of chemical states, and preferential loss of one element, and the end effect is usually

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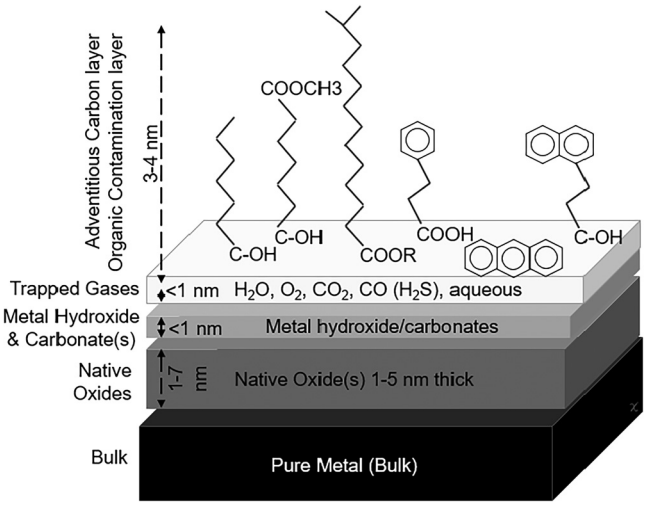


FIG. 41. Artistic depiction of a typical native oxide having adventitious carbon and monolayers of trapped gases, water, hydroxides, or carbonates, and the native oxide(s) on a pure metal bulk.

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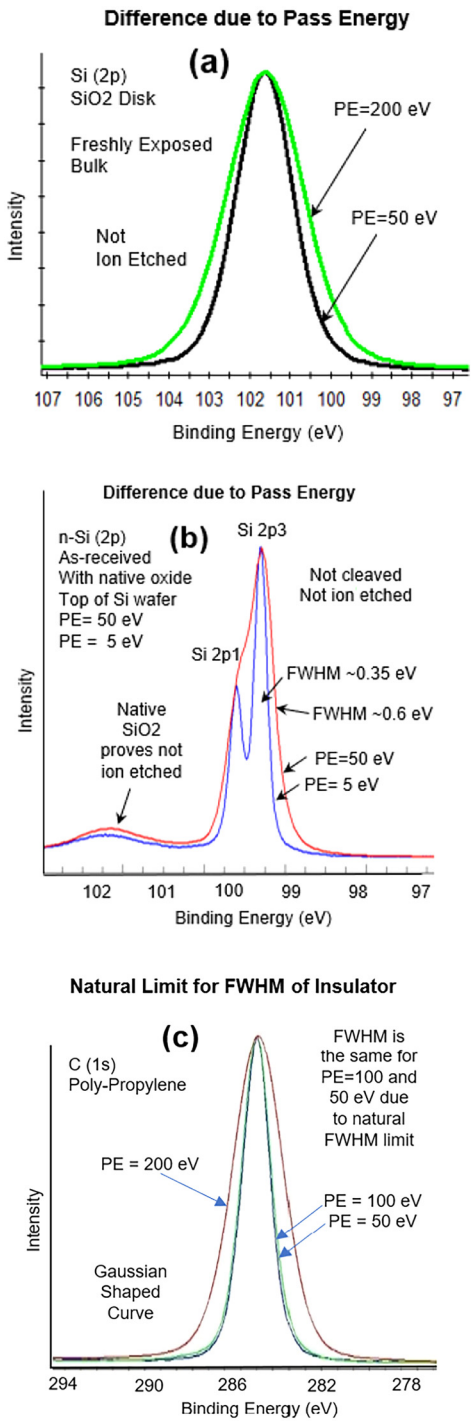


FIG. 42. (a) Pure SiO_2 (silica)— freshly exposed edge of an SiO_2 disc. PE = 50 and 200 eV. Not ion etched. (b) Si wafer with native oxide. Measured at PE = 50 and 5 eV. (c) Polypropylene, PE = 200, 100, and 50 eV. FWHM did not change after PE was decreased from 100 to 50 eV because this is natural FWHM of the C (1s) in polypropylene.

peak broadening. The following spectra show chemical state spectra before and after a few seconds (5–30) of argon ion etching using only 500–1000 V argon ions.

The metal signal of most metal oxides will have a larger FWHM after being ion etched because the chemistry or physical structure has been degraded. There are only a few metal oxides that are only modestly affected by argon ion etching, such as Al_2O_3 or SiO_2. Figure 43 shows the effect of lightly ion etching the freshly exposed bulk of pure SiO_2 (silica). This broadening could be confused with differential charging. Pure SiO_2, when ion etched, degrades to Si_2O_3, which has a lower BE.

Crystalline Silicon ⟨100⟩ in wafer form (n-Si) suffers a significant change in peak-shape because argon ion etching damages the crystalline structure of the top few nanometers, introduces defects, and changes the conductivity as illustrated in Fig. 44.

As-received, many chemical compounds, such as Cr_2O_3 powder and crystals, produce chemical state spectra that show a fine structure due to MS [see Fig. 45(b)]. After we lightly argon ion etch the Cr_2O_3 powder, the fine structure is gone due to chemical degradation (e.g., lower oxidation states), and the fine structure due to multiplet splitting is gone [Fig. 45(a)]. These types of changes in the peak-shape are not due to differential charging effects. These are chemical degradation due to ion induced reduction and the loss of one or more elements as ions or gases.

It is very often worthwhile to analyze an insulator after optimizing charge-control conditions and before any argon ion etching, even light ion etching. New style, cluster argon ion gun systems, when used correctly, do not degrade the chemistry of many materials as they remove overlayers, but they are extremely slow to remove the damaged overlayers that were produced by very light monoatomic argon ion etching (10 s at 1 kV).

Chemical state spectra of the freshly exposed bulk of an amorphous silica (SiO_2) sample were analyzed soon after fracturing in air and then after argon ion etching. The C (1s), Si (2p), and O (1s) spectra (Fig. 46) shown here reveal that the ion etching removes surface contamination, which increases the intensity of the Si (2p) and O (1s) signals but has no obvious effect on the FWHM of these signals.

Due to the light argon ion etch, one charge related change did occur. The Si (2p) and O (1s) BEs increased by ~1 eV, but the C (1s) BE of the remaining carbon did not shift. Why? This change can be attributed to a change in the static charge of the SiO_2 bulk. This is a bulk charging effect, not a surface charging effect.

C. Degradation due to electrons from a flood gun

In general, there are very few materials that are degraded by being irradiated with low voltage electrons from a flood gun. Two materials that are exceptions to that statement are the polyacrylic acid (PAA) polymer film and sodium thiosulfite, $Na_2S_2O_3$.

Damage (degradation) due to total x-ray flux is a concern that can distort peak-shapes, produce new chemical states, or cause preferential loss of one element. Even so, the rate of damage by x rays is small for most materials. The same is true for damage due to flood gun electrons.

The rate of damage by x rays and flood gun electrons is low, but it does exist for various materials, such as polymers with acid

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groups, chlorine, fluorine, and esters. Today's x-ray beams have enough flux to degrade various polymers during the time spent analyzing them. For this reason, the operator should run a single scan survey at the start and the end of the analysis run. Other materials that can be degraded by high x-ray flux include high oxidation state metals (e.g., CrO_3, $KMnO_4$, $K_2Cr_2O_7$, Au_2O_3) and carbonates, which can lose CO_2. Again, these types of degradation are few, flux-dependent, and usually slow, unless you are using a synchrotron beam line.

For both materials, the analysis area was changed after the first spectrum was recorded to avoid any damage due to the x rays. Before turning on the x rays, the flood gun was turned on for the specified time lengths shown in the figures. The x rays were then turned on and the second spectrum was recorded. This method minimized any significant damage due to the x-ray beam itself.

The two overlaid C (1s) spectra for PAA (Fig. 47) were from two fresh regions of the same film. The signal at ~289 is due to the acid group (RCOOH). The time difference between the two spectra is 15 min while using a 10 eV beam of electrons. The loss in intensity is due to the loss of CO_2 as a gas.

The two overlaid S (2p) spectra for sodium thiosulfite (Fig. 48) were obtained from the same region. The signal at 166 eV is attributed to the loss of oxygen from the SO_3 group. The time difference between the two spectra is 60 min using a 2 eV beam of electrons.

There are two catalyst materials (MoO_3/Alumina and Pt/Alumina) that are known to be sensitive to electron flood gun electrons (personal observations, not published).

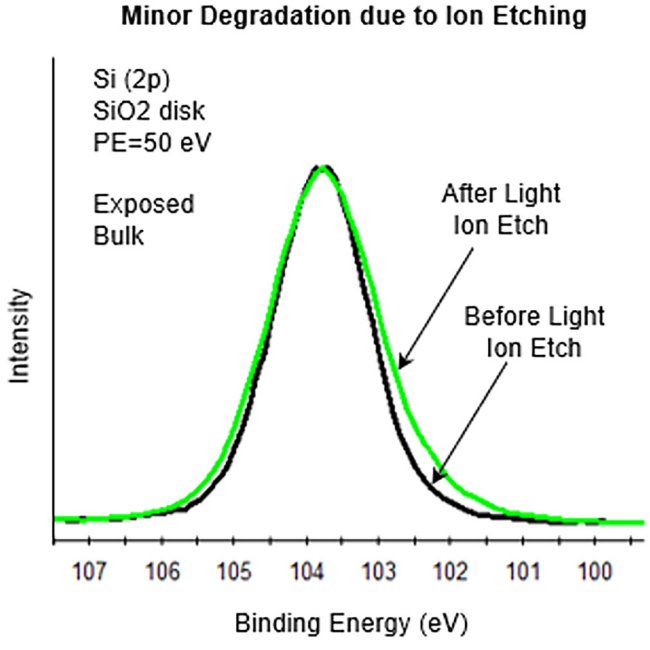


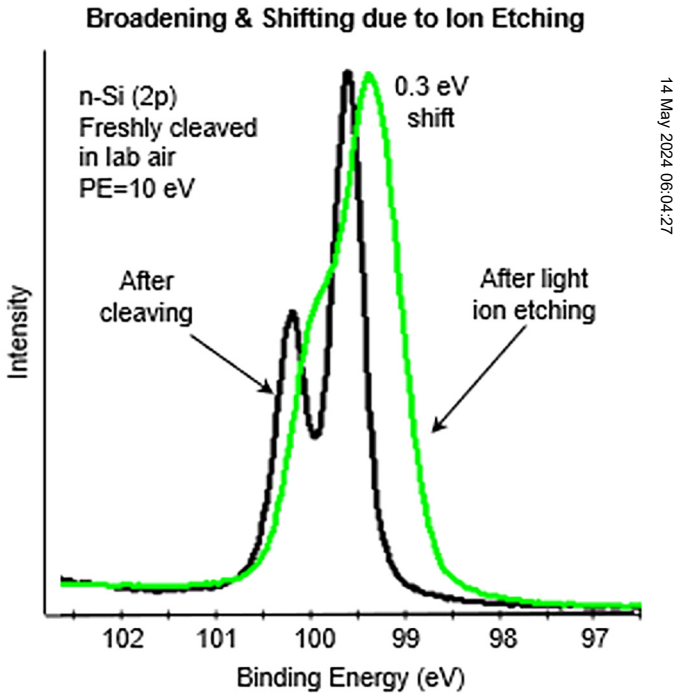
FIG. 43. Pure SiO_2 (silica)—freshly exposed edge of SiO_2 disc. PE = 50 eV. Before and after light ion etching. Only minor degradation.

D. Effect of surface roughness

A KBr pellet hand-press was used to produce a 3.0 mm diameter disc with ~0.5 mm thickness from pure Y_2O_3 powder. Chemical state spectra from the Y (3d) signal were collected from: (a) a powder firmly pressed onto double-sided tape (DST) (green line) and (b) powder hand-pressed into a 3 mm diameter disc (black line). To make sure the surface of the pellet disc was clean, a fresh piece of aluminum foil was placed between the powder and the anvil to stop transfer of any contamination from the steel anvil.

Due to the added smoothness of the pressed pellet disc, the resulting Y (3d) spectrum has a slightly better peak-shape indicated by the arrow in Fig. 49. This is attributed to a more uniform surface charge.

We conclude that when we need to analyze a powdered sample, we have three options for sample preparation, (1) drop powder into a cup to avoid any chance to contaminant the surface of the powder, (2) use a clean spatula to firmly press the loose powder onto double-sided tape or indium metal foil, or (3) compress the powder into a thin pellet by using a hand-press or a high pressure pellet press. Option 1 is acceptable if you do not need spectra with the best FWHM values. Option 2 gives smaller



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FIG. 44. Si (2p) measured with ultrahigh energy resolution. After ion etching, the freshly exposed bulk of an n-type silicon wafer, the BE of n-type silicon, decreased by ~0.3 eV as shown in this overlay. The BE shift is not due to differential charging but is due to doping of the semiconductor with argon ions. The peak broadening is due in part to the defects produced by the ion etching and is attributed to crystal structure degradation at the surface.

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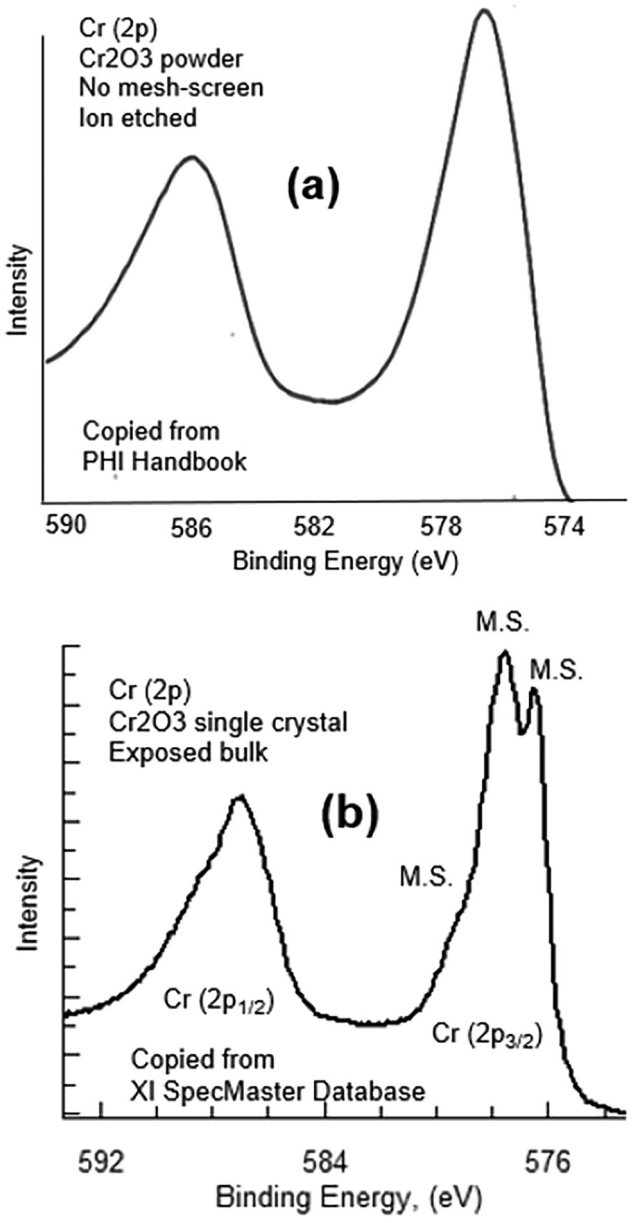


FIG. 45. Cr (2p) spectra from Cr_2O_3. The smoothed Cr (2p) spectrum in (a) is from the well-known XPS PHI handbook. The other spectrum in (b), which shows a little noise, is from a single crystal of Cr_2O_3 measured using a 50 eV pass energy. The multiplet splitting shoulders and peaks are obvious when charging is well controlled and the sample has not been argon ion etched. MS is the abbreviation for a multiplet splitting signal.

FWHM and makes charge control easier. Option 3 is best, but it requires more time and requires the use of clean aluminum foil or glycine paper as an interface to stop the transfer of rust from the anvil to the pellet.

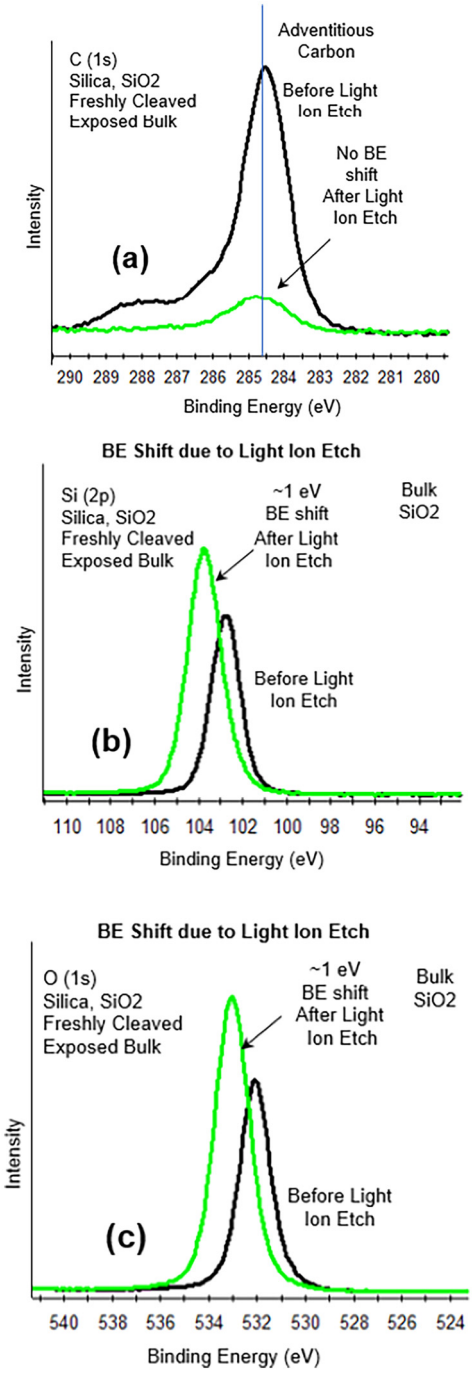


FIG. 46. C (1s), O (1s), and Si (2p) spectra from a freshly cleaved natural crystal of SiO_2 as cleaved and after light argon ion etching. After light ion etching, the amount of carbon decreases, but the hydrocarbon C (1s) BE does not change (a). After light ion etching of the O (1s) and Si (2p), the intensity of these signals increases as expected, but the BEs of both signals increase by ~1 eV [(b) and (c)]. This situation reveals one reason why it is difficult to use adventitious hydrocarbon (AdC) to correct the charge shifted BEs.

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VII. MODERN FLOOD GUN SETTINGS

Modern electron flood guns have digital controls built into the instrument operating software. The spectra shown in this section were obtained by analyzing the center of a large piece (20 × 20 mm) of polypropylene (Fig. 50) in a Thermo K-alpha XPS. The grounded copper clip was ~7 mm from the analysis area. The flood gun exists on the right side in the analysis chamber.

Using the flood gun menu in Thermo software (Fig. 51), the operator can change beam voltages, extractor voltage, beam current, beam focus, and XY positions of the flood gun shown here in this list and in Fig. 51. The Z sample height is adjusted on the normal user's computer screen.

The choice to use a pure hydrocarbon polymer (polypropylene) to test or choose a flood gun setting is due to the simplicity of chemistry and the knowledge that the C (1s) signal must be symmetrical because there is only one chemical state and because the FWHM of the C (1s) peak is small, roughly 1.0 eV.

By changing the XY positions of the electron beam, the user can normally optimize the charge-control conditions of each sample. In general, the user seldom needs to use the other settings. However, when the operator must analyze materials that have different degrees of surface roughness or strong dielectric constants, the operator may need to increase the Beam Voltage and/or the Emission Current. This author prefers to use a 1 V beam voltage to make sure the surface is slightly negative in voltage. This author also prefers to use a higher emission current, which provides more than enough electrons to neutralize most samples, although a higher current shortens the lifetime of the filament and risks electron induced reduction.

Based on the author's personal experience to operate different XPS instruments and their flood guns, the best results for peak-shapes, FWHM, and charge control are produced when changing the XY positions of the flood gun causes the peak C (1s) BE to move to a smaller and smaller BE value. Depending on the instrument, XY adjustments can move the C (1s) BE for polypropylene by as much as 2–3 eV. As the C (1s) BE moves to a smaller BE, you should find FWHM decreasing, and the sloping charge tail will disappear.

Figures 52–57 show the effects of changing from a default flood gun value to other values, which might be necessary as your flood gun filament gets older or becomes dirty due to outgassing samples (depending on use, the flood gun filament can last 2–3 years).

These figures are mainly for teaching purposes. We strongly recommend that you first record your default settings (screen grab image), and then test the effect of changing each parameter to improve your ability to control charging. Record each image. Please note that when you change any setting, the charge conditions on the sample may or may not change if you make only a small change. Larger steps are more revealing and useful.

Based on the author's experience, the major objective of changing any of these settings is to move the C (1s) or O (1s) peak to as small a BE value as possible, which normally gives the smallest FWHM, eliminates sloping tails or shoulders, gives a 20%–40% stronger signal, and produces optimum charge control.

A. Beam voltage settings

The beam voltage control (Fig. 51) provides a linear response to increases in beam voltage. Increasing to 1 eV causes BE to

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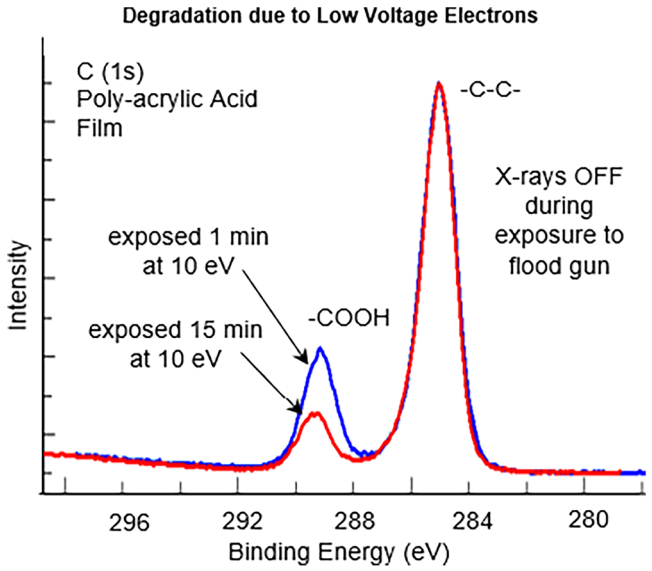


FIG. 47. Overlay of the C (1s) chemical state spectra of polyacrylic acid. The decrease in the C (1s) acid chemical group at 289 eV is due to reduction by the flood gun electrons.

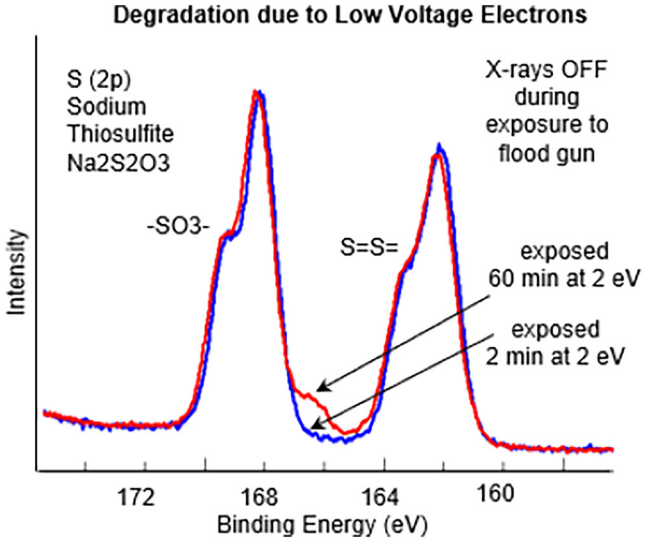


FIG. 48. Overlay of S (2p) chemical state spectra of sodium thiosulfite ($Na_2S_2O_3$). The production of a new SOx species at 166 eV is due to electron induced reduction of the SO_3– chemical group at 168 eV.

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decrease by 1 eV as shown in Fig. 52. In new instruments, the upper limit for beam voltage can be 5 V. In older instruments, the upper beam voltage can be as high as 20 V.

The flood gun in the Thermo K-alpha XPS instrument can be set to −0.1 eV, which provides good charge control for smooth surfaces. Based on 10+ years of use, it is better to use a −1.0 eV setting to produce a truly negative surface.

B. Extractor voltage settings

The extractor voltage control for the Thermo K-alpha is normally set to 40 V. This voltage of the extractor pulls and accelerates electrons out of the heated W (ThO_2) filament and downstream. If the extractor voltage is decreased from its optimum value, then the measured C (1s) BE increases, and the spectra will have a sloping charge tail. The optimum value is between 30 and 40 V (see Fig. 53).

C. Emission current settings

The emission current for different flood guns ranges from a low of 1 μA to a maximum of 350 μA. If your sample has a rough surface, then you might want to increase the current to increase the number of electrons deposited on the surface, but you increase the chance of chemical damage by reduction. High oxidation states and polymers might degrade under a higher emission current. This author used 200–300 μA because the samples had many different dielectric constants. When you use a higher emission current, you decrease the lifetime of the flood gun filament. The normal lifetime is 1–3 years. An example of the change produced is shown in Fig. 54.

D. Beam focus settings

Beam focus controls the size of the electron beam. The electron beam size is <2 mm in diameter. The normal beam voltage is 25 V. A smaller beam voltage, ~5 V, produces a smaller BE with a smaller FWHM, which indicates better charge control. The smaller beam voltage probably produces an electron beam area larger than 1 mm and smaller than 5 mm. An example of the change produced is shown in Fig. 55.

E. Argon gas setting

In the argon gas ionization chamber, the pressure is of the order of 10^{-1} Pa. The pressure downstream is 10^{-4} to 10^{-5} Pa, which results in a 2×10^{-7} Torr pressure in the main analysis chamber.

The default setting for the gas cell is 25 V. Based on the patent, the voltage can be dropped to 1 V with the resulting ion beam flux current being 10–100 nA. When the voltage is turned to 0 V, the argon ion beam is turned off and there are no argon ions that react with electrons sitting on the surface. The dual nature of

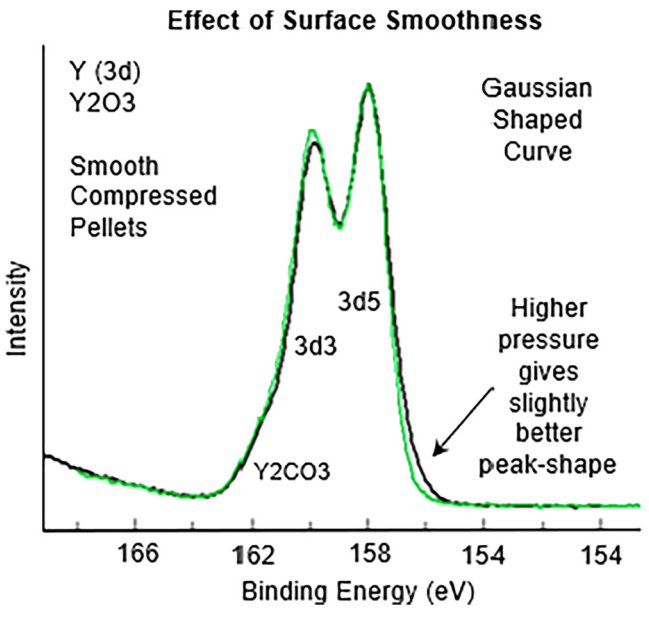


FIG. 49. Overlay of chemical state spectra of Y (3d) from the pellet made from powdered Y_2O_3, pressed pellet, and firmly pressed powder. The difference in the slopes at 155 eV is due to less charging that results when a surface is smoother. The difference was produced by using a simple hand-press. A layer of glycine weighing paper or aluminum foil was used to stop the transfer of contaminants from the steel anvil.

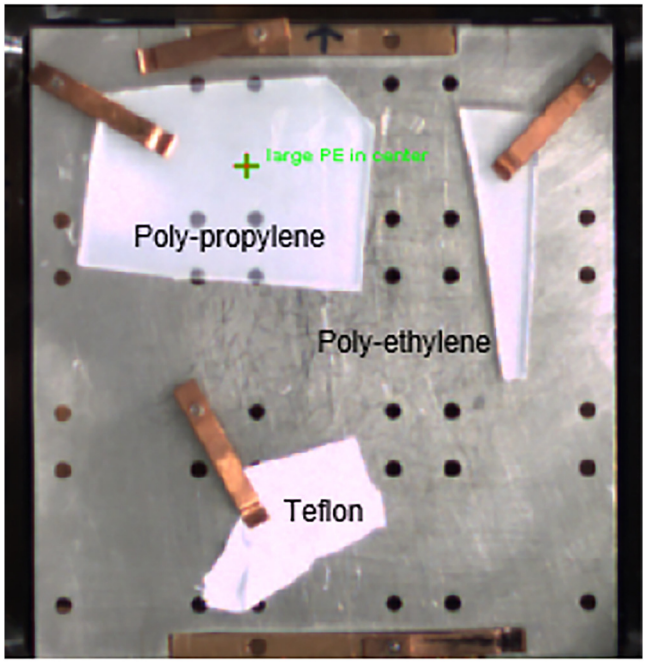


FIG. 50. This photo displays three different materials used to study the effects of changing the electron flood gun settings. The materials include: polypropylene, polyethylene, and Teflon™ tape. The narrow wedge sample (top-right) was used to study the effect of sample size. The electron flood gun is located at the far right.

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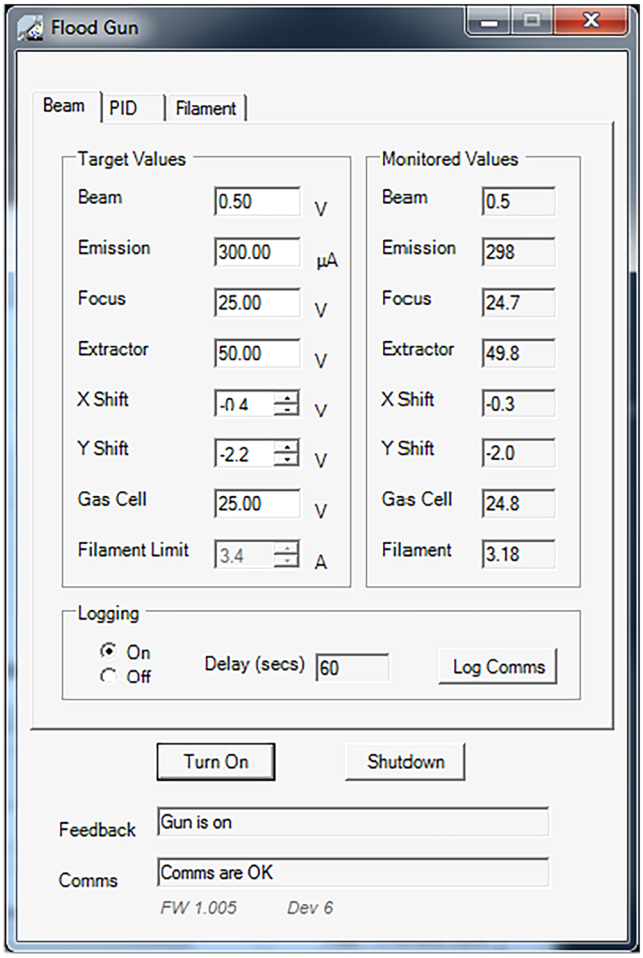


FIG. 51. Pop-up screen showing the flood gun menu for the Thermo K-alpha XPS. This menu displays the dual-beam flood gun parameters that can be varied to improve the charge-control conditions of the active sample. The monitored values are the actual (readback) values that result when the target values are changed.

this gun is changed to being only an electron flood gun. The presence of the argon ions removes a significant number of free electrons sitting on the surface, which can cause differential charging. The voltage needed to ionize the argon gas does not have any obvious effect on charge compensation except when there are no argon ions.

The argon ionization voltage can range from 1 to 25 V.

The approximate size of the argon ion beam used in the thermo dual-beam flood gun is <3 mm).

F. Z position of a sample

The Z position of a sample naturally affects the XPS signal intensity for all focused x-ray systems. But the maximum counts and best Z position for charge control and data collection are often

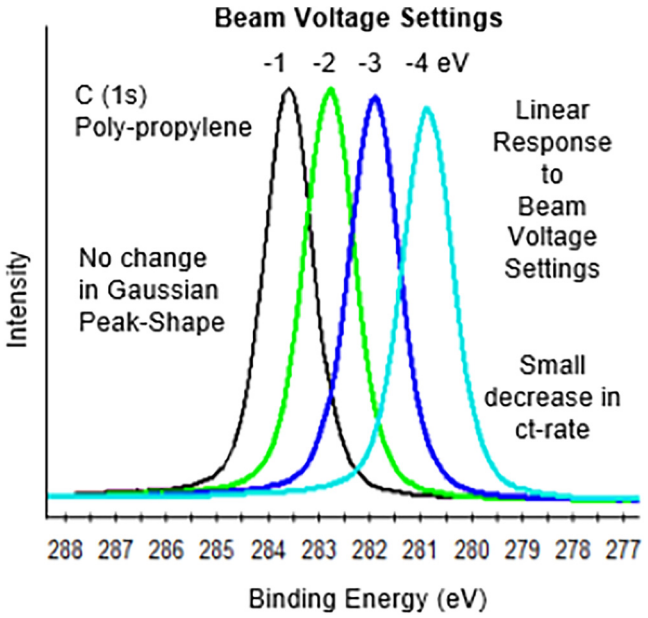


FIG. 52. Peak shifts when the beam voltage varies from −1, −2, −3, to −4 V. A linear response. As the negative voltage is increased, the measured BE moves to a smaller BE. (The lowest possible voltage is 0.1 eV, which is the default setting. The maximum voltage is 5.0 eV.)

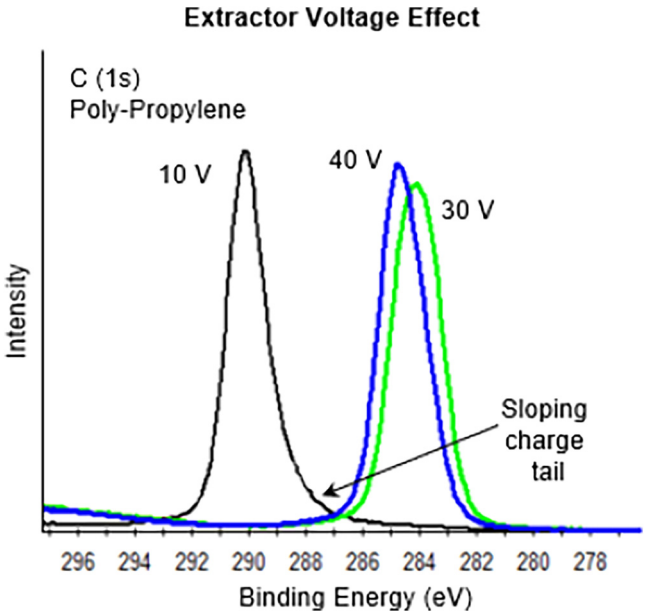


FIG. 53. Extractor voltage. The normal setting is 40 V. Using 30 V causes a small shift to a lower BE. Using 10 V causes a large 6 eV shift to a higher BE and produces a sloping tail. Lower BE results are better.

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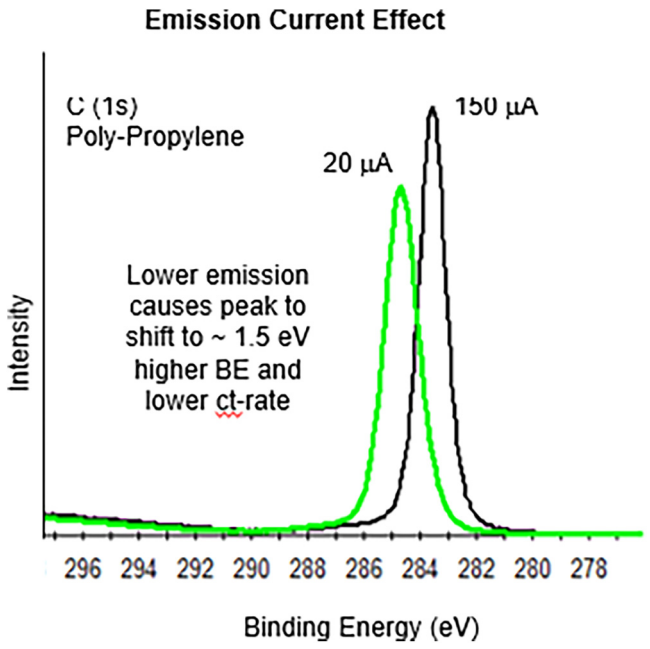


FIG. 54. Emission current. The normal setting is 150 μA. Using 20 μA causes BE to increase and decrease the signal intensity and causes peak broadening. Lower BE results are better.

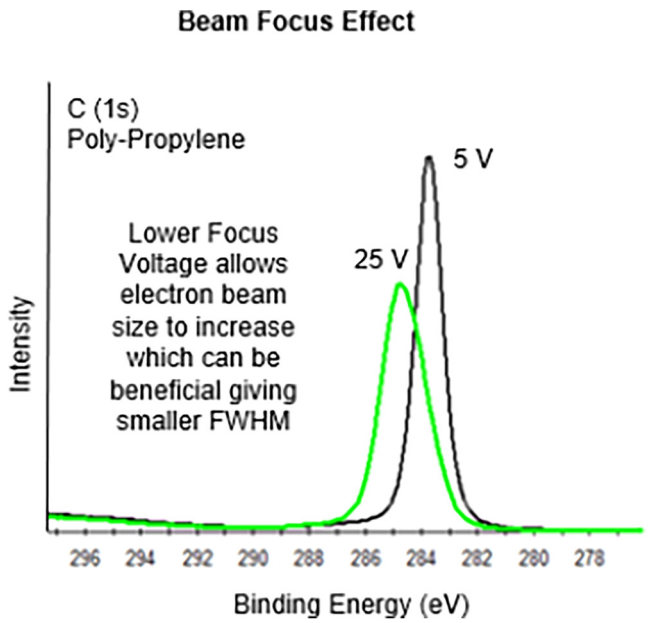


FIG. 55. Beam focus voltage. The normal setting is 25 V. Using a 5 V setting allows the electron beam size to grow, which is beneficial in this example. Lower BE results are better.



FIG. 56. Argon gas ionization setting. The normal setting is 25 V.

not the same as the optical focus of the sample surface as provided by optical cameras on XPS instruments. If you have Snap-shot™ or unscanned mode capability, then you can use that to determine the optimum Z position for collecting XPS data. The optimum Z position for electron counts is not necessarily the same as the optimum optical focus of the sample surface. Figure 57 shows the variation in electron count-rate for the Thermo K-alpha when the Z position is dropped vertically. As the Z position drops, the count-rate drops. Optical focus may or may not change until the Z position is changed by >200 μm. This behavior probably occurs on other systems equipped with optical cameras.

G. X-Y position settings of a "focused" flood gun beam

Based on the author's efforts to produce high quality, high energy resolution, chemical state spectra, the first objective is to change the XY positions of the flood gun so that the C (1s) BE or O (1s) BE are as small as possible, which normally gives the smallest FWHM, eliminates sloping tails or shoulders, and produces best charge control.

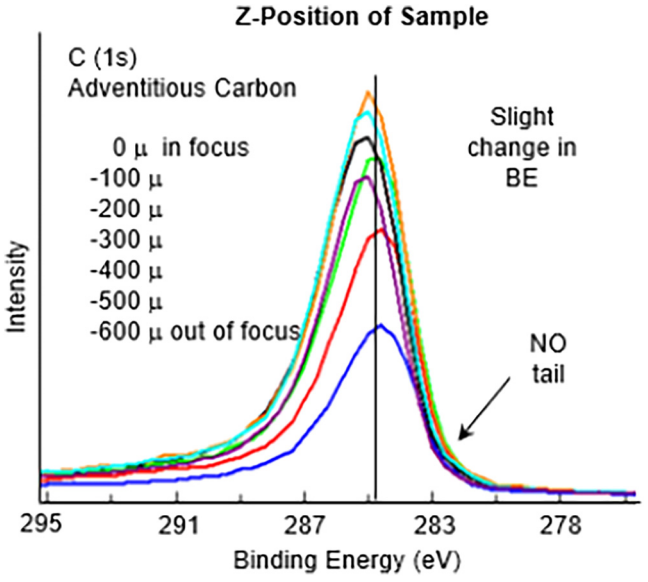


FIG. 57. Z position of sample height. The sample height was decreased in 100 μm steps to 600 μm from the max counts position. This produced a 75% decrease in signal intensity, which is due to x-ray focus. Focus based on high electron count-rate is often different from focus based on the optical microscope due to misalignment of the camera focus.

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For that reason, Sec. VIII is dedicated to "optimizing XY positions of focused low voltage beam of electrons." There are three subsections dedicated to this topic because optimizing XY has been a reoccurring necessity when optimizing any flood gun system on different XPS instruments.

Figure 58 gives a quick overview of what happens when the XY positions are **not** optimized for the sample currently being prepared for XPS analysis.

Brand new XPS instruments and their electron flood gun systems are normally installed by engineers from the maker. Nowadays, those engineers initially adjust the flood gun settings to a default set of values. The engineers finalize the electron flood gun settings based on the C (1s) FWHM of the ester signal (at ~289 eV) from a piece of freshly cleaned polyethylene terephthalate (PET, Mylar) which has dielectric properties that are unique to PET. Their PET sample is usually a smooth film or sheet that was cleaned with alcohol, acetone, or scraped to expose the fresh bulk. A smooth clean surface is much easier to use to find optimum flood gun settings. Making the sample small also helps. Ask them if you can keep that PET sample.

VIII. OPTIMIZING XY POSITIONS OF THE FOCUSED LOW VOLTAGE BEAM OF ELECTRONS

A. Test method useful to optimize XY positions

Because different insulating samples have different shapes, dielectric properties, roughness, contamination, etc., the operator may need to optimize one or more of the electron flood gun settings. The questions are: Which ones to adjust, why, and how much? Real-world experience indicates that optimizing the XY position of the flood gun should be your first effort.

Before spending an hour or more to collect chemical state spectra that might have differential charging features, the instrument operator should test if the current flood gun settings are optimized for the *sample currently being analyzed instead of the previous sample*. This objective is one of the main reasons for this publication.

Because each material can have different charging effects due to differences in chemistry, dielectric constant, roughness, etc., the operator may need to change the flood gun settings for each individual sample if the operator or the customer needs or wants the best peak-shapes for each sample. If the operator or customer is not looking for the best FWHM to help resolve the presence of or the absence of various chemical state components, then there may be no need to adjust the flood gun settings for each individual sample on the sample stage. The needs of the customer determine the design of the experiment and the time spent optimizing the flood gun settings.

Because oxygen is present in most materials, it is easy to use the O (1s) signal to optimize the XY positions of your flood gun settings for your real-world samples.

However, for learning purposes, the C (1s) peak from freshly scraped polypropylene is used. Figures 60 and 61 show the effects of changing XY flood gun positions after collecting data using the normal "scanning mode" of data collection. For these learning measurements, the flood gun beam voltage was set to −2 eV.

To observe the BE shifts in the C (1s) spectrum as we test different XY positions, we place a transparent ruler on the computer

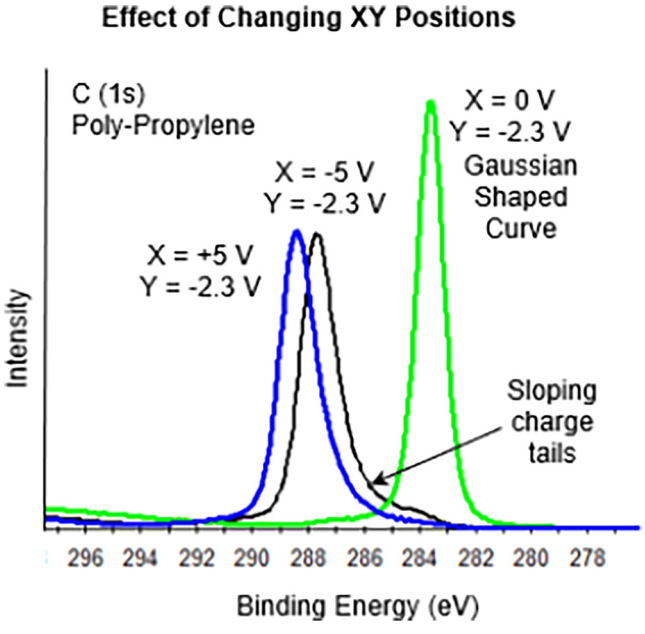


FIG. 58. For this test, the X-position was varied from −5, to 0, to +5 V. The Y-position was fixed at −2.3 V because it had already been optimized. Notice that the optimum position has the lowest BE, a Gaussian shape, the highest count-rate, smaller FWHM, and no sloping tail.

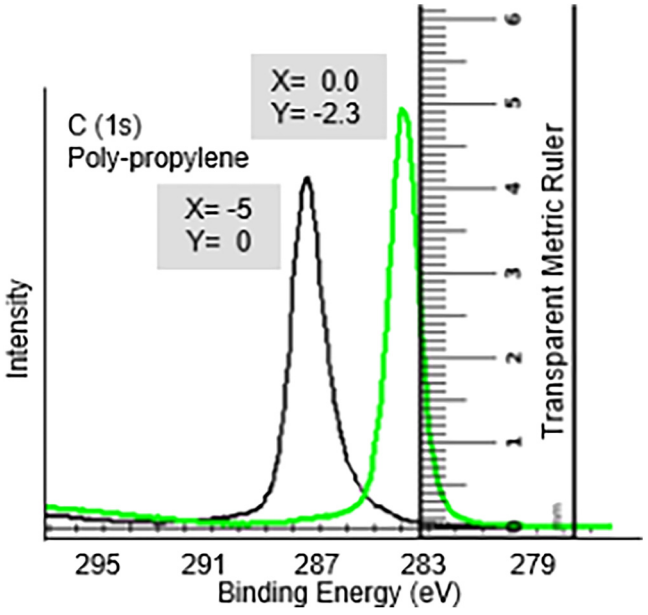


FIG. 59. Transparent ruler, shown here, should be placed on the ledge of the computer monitor to serve as a reference point when testing different X and Y flood gun positions.

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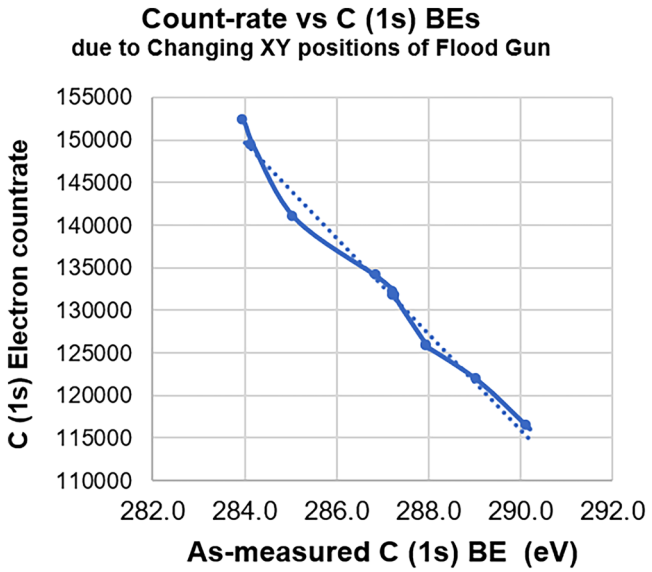


FIG. 60. After recording the effects of choosing different XY positions of the flood gun, we discovered that the raw as-measured C (1s) BE correlates linearly with the electron count-rate. Smaller C (1s) BEs give higher count-rates. When the flood gun is properly aligned in X and Y, the smallest C (1s) BE correlates with a 40% increase in count-rate. Scanned mode C (1s) spectra revealed that the FWHM is smaller by ~20% at the XY position that produces the smallest C (1s) BE. If XPS makers automate this routine into their software, then users would be able to measure spectra with less distortion, higher count-rate, and smaller FWHM. These measurements were performed by using the fast snapshot (unscanned) mode while measuring ~20 eV wide C (1s) spectra from polypropylene. The dashed trendline shows linearity.

monitor, which can sit on the edge of the monitor. As an example, look for the reference to Fig. 59. Watch the relative position of the peak max BE.

The normal scanning mode of data collection was used to produce Figs. 60 and 61 because the operator needs to know what happens to the BE and intensity of the chemical state spectra when XY flood gun positions are varied.

Later in this section, the snapshot (unscanned) mode results are presented. Please remember that energy resolution is low for snapshot mode, but data collection is fast, so snapshot mode is used to watch the BE and the peak-shape change as the XY positions are changed. The effects of using the snapshot or unscanned mode are shown in Figs. 61 and 62.

As the C (1s) peak BE moves to smaller and smaller BE, you have made an improvement in charge control, which will provide an improvement in FWHM and peak-shape and minimize any differential charging.

Align the edge of a transparent ruler with the current position of the peak maximum from C (1s). While observing the peak max, change either the X or Y settings by 25%–50% and start the next recording. If a large movement in C (1s) BE is observed in the new spectrum, then decrease the size of the changes by 2×. The size of these steps depends on the chemistry, the analysis position, roughness of the sample, and the settings used by the previous operator.

As the C (1s) BE becomes smaller and smaller, the operator should notice an increase in counts or count-rate. The chart shown in Fig. 59 is the result of changing XY positions (10 positions) until the BE was as small as possible. If adjusting XY positions does not produce a measurable change, then increase the beam voltage by 1 eV and start over. By increasing the beam voltage, the C (1s) will have moved to a lower BE by 1 eV. Once more, adjust XY positions to try to move the C (1s) peak BE even lower. If there is no change, then the next option to improve charge control is emission current. Increase the current by 10%–50% and again test BE or FWHM.

In the past, analysts were trained to increase the beam voltage as the first step to getting better results. You should test both methods.

Based on the author's experience, it is best to document what happens when any of the flood gun settings are changed by 10%–20% from the default setting by recording the C (1s) spectra of polypropylene exactly as presented in Secs. VII and VIII in this report. It is very convenient to use a Screen-Capture software to record the changes made as we change XY positions, current or voltage. The operator should save those spectra and write up a small report to share with all users and customers, so they know the extra work that is needed to get the best result for them. Figures 60 and 61 were produced from polypropylene by changing the XY positions of the flood gun beam using 10 different settings and recording the C (1s) spectra that result. Figures 60 and 61 summarize the results of those peak-fits.

After recording the effects of choosing different XY positions of our dual-mode flood gun, we discovered from scanned mode spectra that the raw as-measured C (1s) BE correlates inversely with the electron count-rate. In other words, smaller C (1s) BEs have higher count-rates (Fig. 60). The graph in Fig. 60 clearly shows the direct correlation between electron count-rate and peak BE when XY positions are varied. This indicates that every effort should be made to adjust the flood gun settings to produce lower BEs that correlate with higher electron count-rates.

This observation is based on the scanned mode results shown in the graph shown in Figs. 60 and 61.

When the flood gun is properly aligned in X and Y, the smallest C (1s) BE correlates with an ~40% increase in count-rate (Fig. 60). Scanned mode C (1s) spectra in Fig. 61 reveal that the FWHM is smaller by ~20% at the XY position that produces the smallest C (1s) BE.

The scanned C (1s) spectra from a piece of polypropylene (Fig. 61) demonstrate what happens when the XY positions of a modern flood gun are changed from a position that produces good peak-shapes to other potentially better or less useful XY positions. The electron beam voltage for this set of spectra was set to −2 eV. Only the XY positions were varied. All BEs are "as-measured" and were not corrected. The middle two spectra [Figs. 61(b) and 61(e)] show **symmetrical** peak-shapes, have the smallest FWHM values, and have the smallest BE values.

As a rule-of-thumb for charge control: *adjust XY positions to produce the lowest BE for the test peak.* This series of spectra shows that the lowest BE spectra do *not* have sloping tails and have smaller FWHM values. For most real-world samples, O (1s) is the most intense signal. For that reason, it might be useful to repeat

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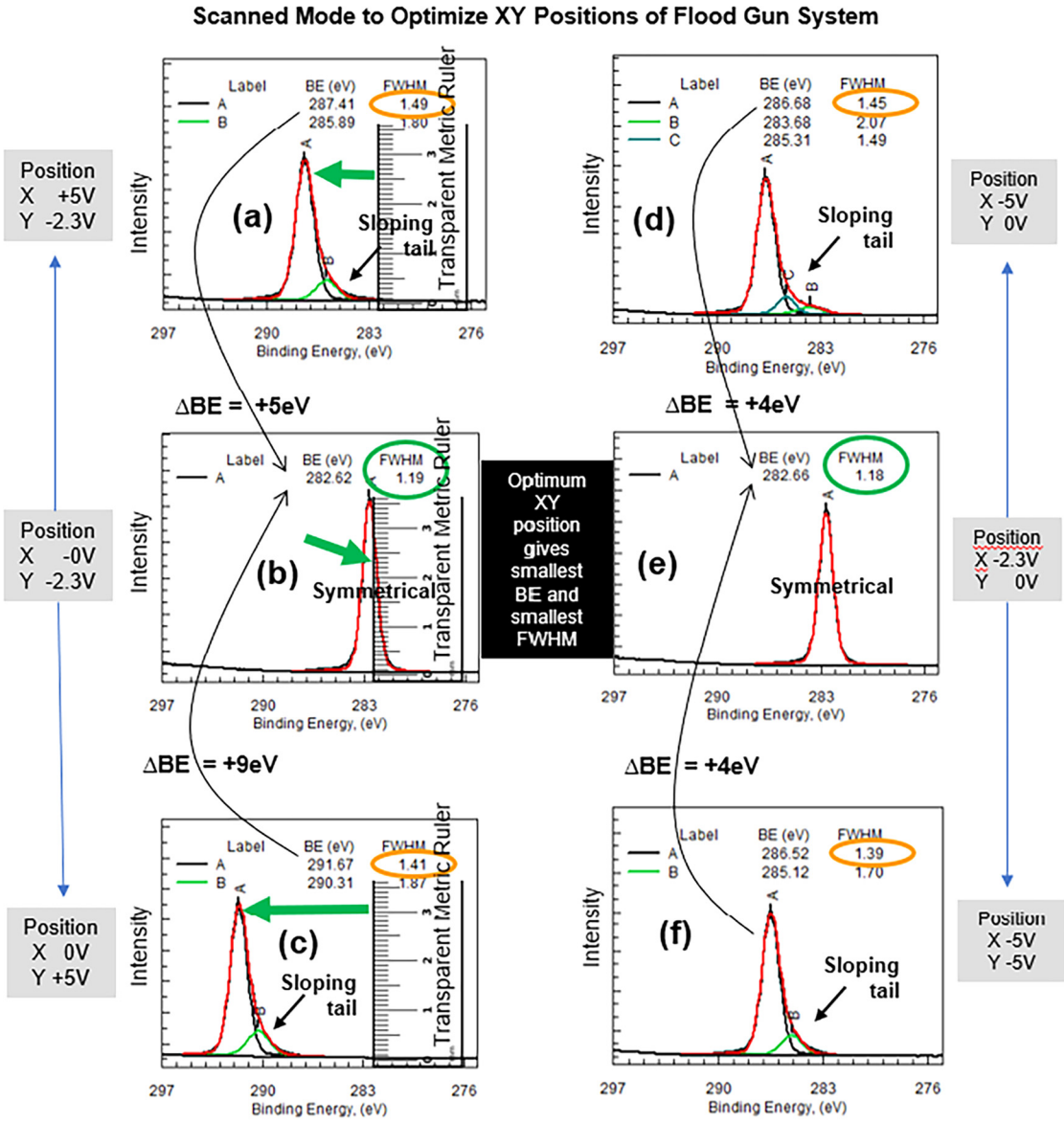


FIG. 61. This set of scanned C (1s) spectra from a piece of polypropylene serves as an example guide showing what happens when the XY positions of a modern flood gun are changed from a position that produces good peak-shapes to other potentially better or less useful XY positions. The electron beam voltage for this set of spectra was set to −2 eV. Only the XY positions were varied. All BEs are "as-measured" and were not corrected. The middle two spectra [(b) and (e)] show symmetrical peak-shapes, have the smallest FWHM values, and have the smallest BE values. As a rule-of-thumb for charge control: *adjust XY positions to produce the lowest BE for the test peak*. This series of spectra shows that the lowest BE spectra do *not* have sloping tails and have smaller FWHM values. For most real-world samples, O (1s) is the most intense signal. Repeat this series of XY position changes of the flood gun beam on your real-world sample using the O (1s) signal because it is usually the most intense and it usually appears as a single peak.

this series of XY position changes of the flood gun beam on your real-world sample using the O (1s) signal.

If XPS makers would automate this charge-control test routine into their software, then operators and users would be able to quickly optimize the flood gun settings that would help operators to collect spectra with less distortion, higher count-rate, and smaller FWHM. These measurements were performed by using the scanned mode for data collection using a 20 eV window, pass energy of 50 eV, and the C (1s) spectra for polypropylene. Other high-purity materials that produce single symmetrical peaks, such as SiO_2, Al_2O_3, poly-styrene, or high density poly ethylene (HDPE), are readily available in many labs, and can be used in place of polypropylene.

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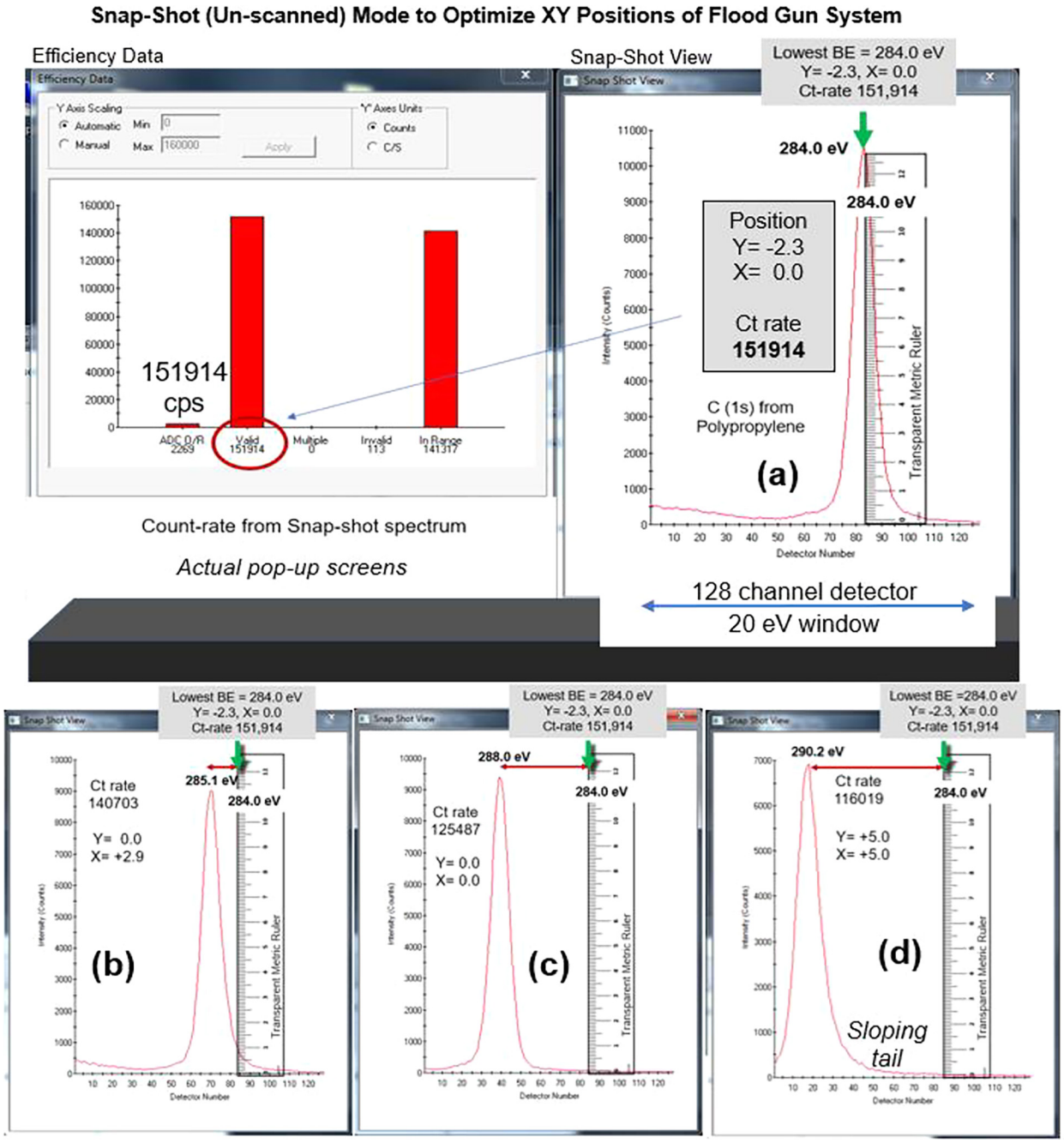


FIG. 62. This set of screenshots shows the pop-up windows that were used to determine the effects of changing the XY positions of the flood gun while using the snap-shot (unscanned) mode to measure the C (1s) spectra from polypropylene. The ~20 eV size window (from a 150 eV pass energy) shown here is useful for this test of finding which XY positions are best for collecting normal Scanned mode spectra with optimized peak-shapes. The pop-up panel on the top left gives the count-rate obtained from the pop-up screen on the top-right, which shows the snapshot (parallel mode) spectrum. To simplify the work, a transparent plastic ruler is placed on the ledge of the computer screen [see Fig. 61(a)]. After the first spectrum is measured, the left edge of the ruler is aligned with the peak max position. The operator then changes either X or Y position and remeasures the spectrum, noting if the peak maximum moved to the left or the right [as indicated in (b)–(d)]. Best spectra peak-shapes are obtained when the peak maximum BE moves as far to the right as possible to the lowest BE. In this figure, we only show four of the ten spectra used to decide that the best XY position is Y = – 2.3 and X = 0.0. In Fig. 60, we present a correlation between the count-rate and the C (1s) BE, which shows that the lowest BE value has the highest count-rate.

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Figure 62 shows a set of screen-shots captured from the software pop-up windows that were used to determine the effects of changing the XY positions while using the Snapshot™ (unscanned) mode to measure the C (1s) spectra from polypropylene. The objective is to locate the optimum XY positions that produce the best peak-shapes for measuring chemical state spectra from this sample. The ~20 eV size snapshot (unscanned) mode window shown here is used for determining which XY positions are best for collecting normal Scanned mode spectra with optimized peak-shapes. The pop-up panel on the top left (*Efficiency Data*) gives the electron count-rate obtained from the spectrum shown in the pop-up screen on the top-right, which is the *Snap-shot View* (parallel mode) spectrum. To simplify the work, a transparent plastic ruler is placed on the ledge of the computer monitor. After the first spectrum is measured, the left edge of the ruler is aligned with the peak position. The operator then changes either X or Y positions and remeasures the spectrum, noting if the peak maximum moved to the left or the right. The best results are obtained when the peak maximum moves as far to the right as possible, producing the lowest BE. In this figure, we only show four of the ten spectra used to determine the optimum XY position for this sample.

B. Using C (1s) or O (1s) peak FWHM and BE to optimize and check the quality of charge control

The FWHM of the C (1s) of adventitious hydrocarbons on the active sample from *scanned mode* spectra can be used as an indicator of the quality or goodness of charge compensation. Smaller FWHM indicates better charge control. Therefore, if the FWHM of the adventitious hydrocarbon peak in your C (1s) spectrum is >1.5 eV, you should consider that the sample might suffer from differential charging. If the FWHM of the O (1s) and main metal signals are also >1.5 eV, then you have more evidence that the sample might suffer from differential charging.

Based on this understanding, a rule-of-thumb was developed to guide charge-control quality by measuring the FWHM of C (1s) and O (1s).

The rule-of-thumb for best peak-shapes and charge control is: *Adjust XY positions to produce lowest O (1s) BE (or C 1s) with highest count-rate. This corresponds with smaller FWHM.*

Our experimental results in Table XII show that when the FWHM of the adventitious hydrocarbon C (1s) signal is small, the FWHM of the main metal peak and the O (1s) peak are also small. In a similar manner, when the FWHM of the C (1s) is large, the metal and O (1s) peaks are large (Table XII). This means that the C (1s) FWHM and BE can be used to check on the quality of the charge control of your current sample.

One of the goals of this publication is to guide the instrument operator and the data analyst on methods that can be used to obtain high energy resolution spectra with excellent peak-shapes that have little or no differential charging that might broaden FWHM or produce unexpected shoulders. The next goal is to provide the operator and data analyst with a useful set of FWHM values to be used to peak-fit raw spectra.

To derive as much useful information as possible from peak-fitting, data analysts need not only true peak-shapes free from distortion and reliable[5] BEs, but also useful or reliable FWHM to maximize the information derived from peak-fitting. Differential charging can produce peaks that are falsely broad, leading the data analyst to use an FWHM that is not useful or meaningless. By providing data analysts with a useful set of FWHM, they can improve their efforts to properly peak-fit complex chemical state spectra by using FWHM derived from high quality XPS reference spectra. With this goal in mind, Table XIII presents a list of FWHM from the main metal XPS peaks and O (1s) peaks for a list of 48 commercially pure binary metal oxides and two metal carbonates. These FWHM were obtained from peak-fitting spectra from commercially pure binary oxides published in the XPS International SpecMaster database[2] and The XPS Library.[3]

In Table XIII, the metal oxides that have multiplet splittings for the metal signal are highlighted with the abbreviation M.S. The FWHMs shown for these metal oxides are due to the initial peak belonging to the splitting. The remaining peaks in that peak-fit use the same FWHM. This style produced a reasonable fit between the first peak and the peak envelop.

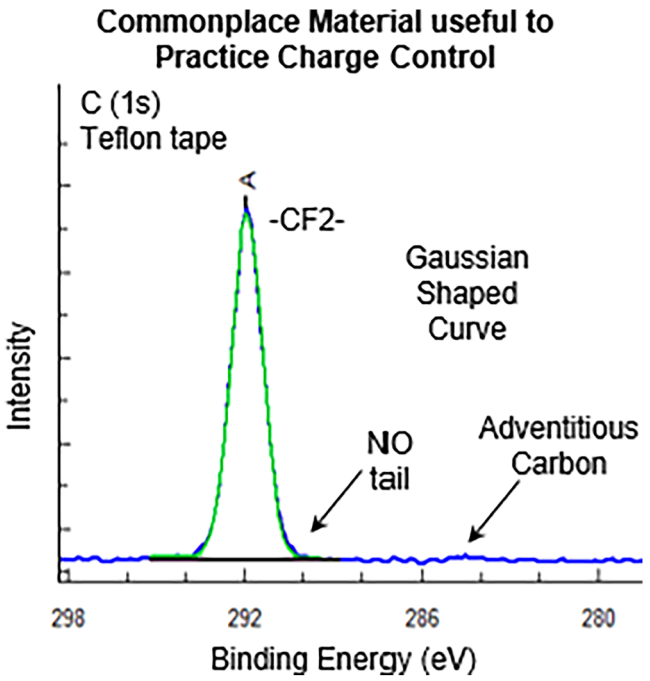


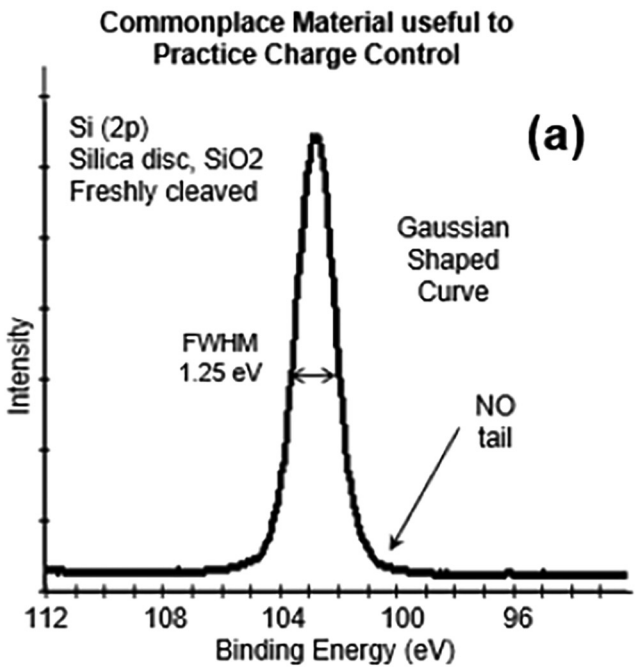
FIG. 63. C (1s) spectrum from Teflon tape (Plumber's tape). The -CF_2- signal is symmetrical without a tail. Adventitious hydrocarbon is highlighted with an arrow because the -CH_2- signal is small. This example spectrum of the C (1s) peak-shape and BE is expected when you use Teflon tape to test flood gun settings.

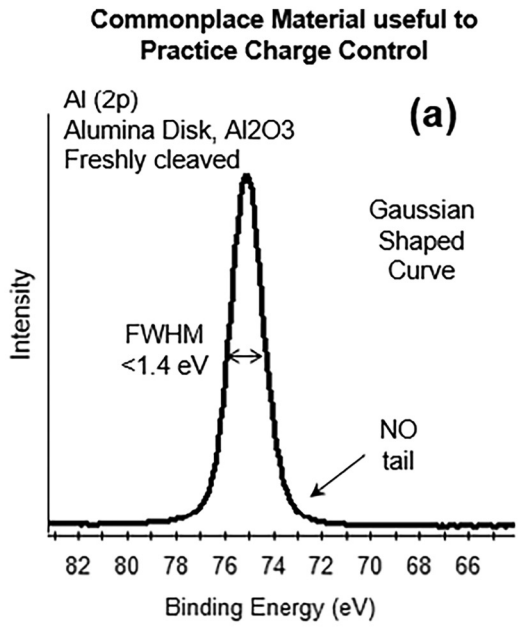
C. Commonplace materials used to optimize XY positions and charge-control settings

Nonconductive commonplace materials are extremely useful to practice how to optimize the peak-shape and FWHM of your high energy resolution, chemical state spectra. The following materials—polypropylene, HDPE, Teflon, PET, SiO_2, and Al_2O_3—are

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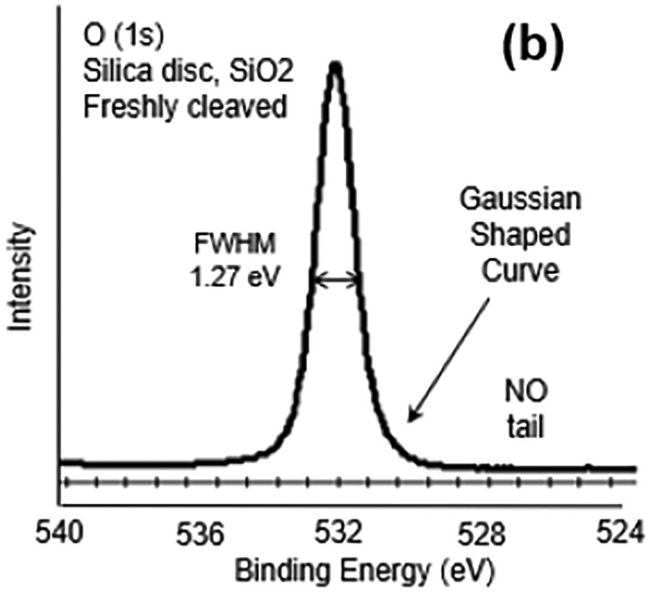


FIG. 64. O (1s) and Si (2p) spectra [(a) and (b)] from freshly fractured SiO_2 (silica or quartz). Both signals are symmetrical, which means that the surface has controlled charging. No tails. FWHM < 1.4 eV. The peak-shapes shown here show what is typical for good charge control. This material, freshly fractured, is useful to learn how to operate the flood gun settings and learn how to locate optimum XY positions.

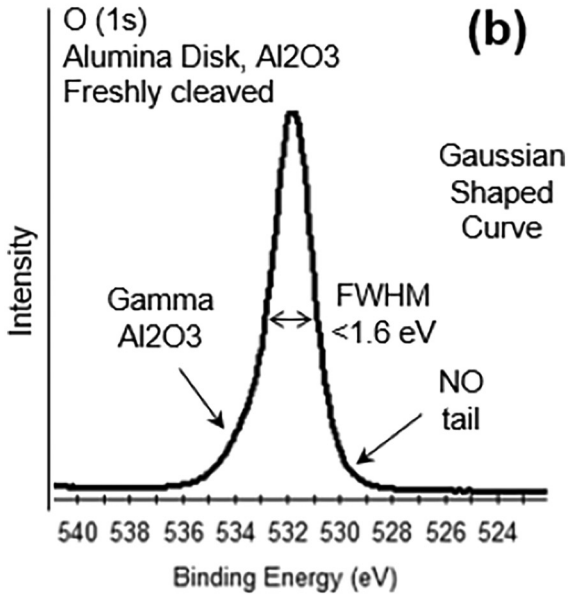


FIG. 65. Al (2p) and O (1s) spectra [Figs. 65(a) and 65(b)] from a freshly fractured Al_2O_3 sheet. The Al (2p) signal is symmetrical, while the O (1s) signal has a tail on the high BE side. The question you may ask: Is that tail due to charging? The answer is: No. Charging tails only appear on the low BE side of the complete set of chemical state spectra for a material. Neither of these two peaks have tails on the low BE side. The O (1s) peak at ~534 eV is most likely due to gamma-type Al_2O_3, but this is speculation.

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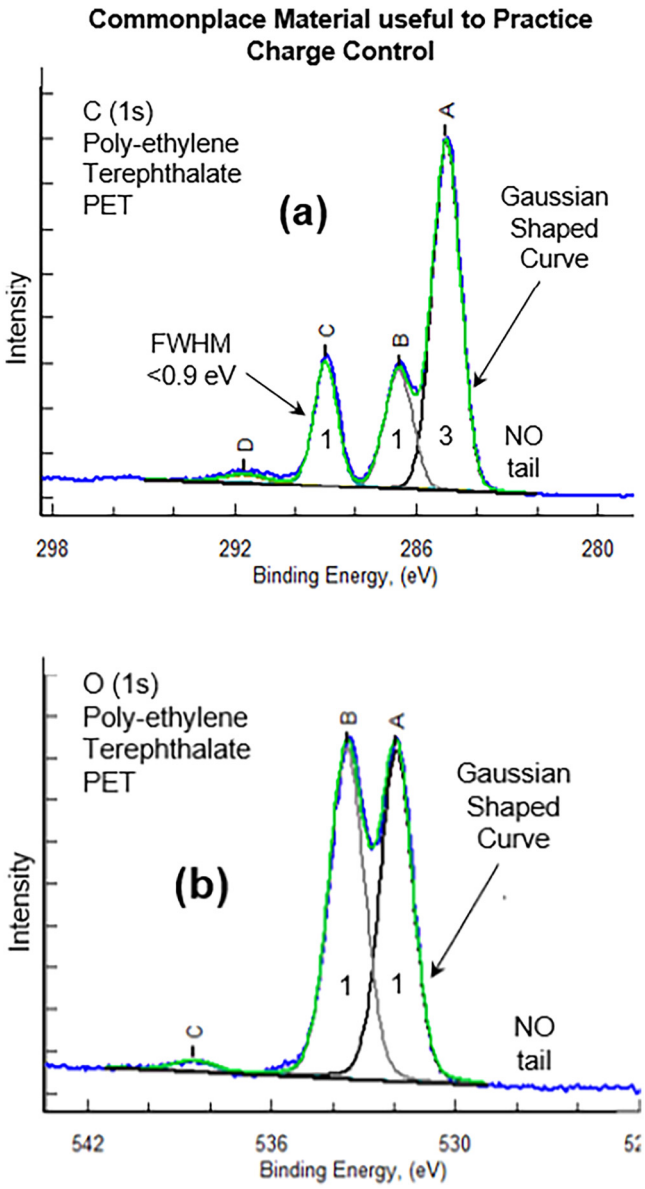


FIG. 66. C (1s) and O (1s) spectra [Figs. 66(a) and 66(b)] from freshly scraped PET. PET (Mylar™) produces more complicated peak-shapes that will test not only your charge-control skills but also your peak-fitting skills. PET has become the reference material used to check on the performance of modern flood gun systems in an XPS instrument. Peak area ratios are shown as numbers inside each peak-shape. The three peaks for C (1s) should have a 3:1:1 ratio for the three species shown. If your peak-fit produces a ratio = 4:1:1 or 4:2:1, then the surface is contaminated and needs to be cleaned. You can add an extra constrained peak to learn how much contamination is present. The most likely contaminants are hydrocarbons and organic alcohols.

useful to practice optimization. Figures 63–66 are chemical state spectra from these commonplace materials. The simple symmetry of the XPS signals in the chemical state spectra from Teflon, SiO_2, and Al_2O_3 make them easy to use when testing flood gun settings.

Three (3) hydrocarbon polymers [e.g., polypropylene, HDPE, low density poly ethylene (LDPE)] that are useful for these tests are commonly used to make plastic boxes, trays, and wrapping films. These materials are translucent and are easily cut. Each of these hydrocarbon polymers produces a single symmetrical C (1s) peak. If you use one of these products, you should wipe the surface clean using 90% isopropyl alcohol (IPA) or acetone. Or, if you have a polymer sheet, you can use a clean single-edged razor blade to scrape or expose the bulk, which is free of surface contaminants. Exposing the bulk of any sample helps you to learn what is the true chemistry of the bulk of that material (Table XIV).

By adjusting XY positions of the flood gun, and sometimes Z focus, we can reproduce the symmetrical peaks shown below in Figs. 63–66. If adjusting XY of the flood gun does not produce a symmetrical C (1s) signal, then adjust other flood gun settings, such as beam voltage, or focus, or extractor, or emission current. (Maybe the flood gun is not fully inserted to the proper translation position.) If you can bias your stage, then try a small positive bias to attract more flood gun electrons. Maybe you need a smaller sample. Maybe you should analyze near one of the corners of your sample. By testing the effects of changing these different variables on a simple symmetrical peak, we can more easily learn more about our flood gun system and how to optimize it. A list of variables that might help improve the peak-shape and FWHM is shown later.

Please keep in mind that different materials have different dielectric constants, surface roughness, and mixed chemistry, which requires you to adjust one or more of the flood gun settings when you need optimum peak-shapes that can yield a bit more chemical state information. Very often, we only need to adjust the XY positions of the flood gun or the beam voltage, but not always.

Clean Teflon produces a single symmetrical C (1s) peak as well as a single symmetrical F (1s) peak; both can be used to develop your expertise to producing charge controlled spectra. Teflon with its higher dielectric constant will provide a bit more challenge than the pure hydrocarbon polymers (see Fig. 63).

TABLE XIV. Commonplace materials, available in labs, that are useful to practice charge control by adjusting XY positions of the flood gun and to learn how to adjust other settings.

- Polypropylene (translucent) after wiping with 90% IPA or after scraping with a clean single-edged razor blade,
- Polyethylene (HDPE/LDPE) after wiping with 90% IPA or after scraping with a clean single-edged razor blade.
- Polyethylene terephthalate, PET (transparent soft-drink bottles). After wiping with 90% IPA, or scraping with a clean razor blade.
- Teflon tape (Plumber's tape) but has a static charge.
- Teflon sheet (1–2 mm thick). Cut to expose bulk, or scrape surface with a clean razor blade.
- Silica (quartz) glass (amorphous SiO2 disc, not soda-lime microscope slide). Expose fresh bulk by fracturing.
- Alumina glass (amorphous Al2O3). Wipe with 90% IPA or expose fresh bulk by fracturing.

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There are two commonplace amorphous glasses that provide single symmetrical peaks from O (1s), Si (2p), and Al (2p). The Si (2s) and Al (2s) peaks are also symmetrical peaks, but they have FWHM that are broader due to differences in core-hole lifetimes (see Figs. 64 and 65).

If, by chance, you need to also check your sensitivity factors or atom % quantitation, then you can use the pure freshly exposed bulk of SiO_2, Al_2O_3, PET, and Teflon.

The following spectra (Figs. 63–65) show the true peak-shapes from a few commonplace (lab) materials, which serve as a tool to help you to practice optimizing your flood gun system.

IX. TABLES (A-I) PROVIDING GUIDANCE

Stepwise instructions to produce quality XPS spectra are given in Table XV. Typical flood gun settings are given in Table XVI. Potential causes of surface charging problems are given in Table XVII. Sample size, preparation, and mounting (in lab air) are given in Table XVIII. Table XVIII explains the various issues or parameters to consider as you prepare each sample for mounting onto the sample stage. Confirm quality of charge control after analysis is done and is given in Table XIX. Potential problems with instrument design, flood gun, sample, sample stage are given in Table XX. Other methods useful to improve charge compensation are given in Table XXI.

A. Advice to obtain good charge control

Based on many years of experience, a user-controlled, steady state, uniformly distributed, negative voltage potential, having a slight excess of electrons, provides the least amount of differential charging such that chemical state peak distortions BEs do not form. The voltage range for best results is between −0.1 and −5 eV. When the voltage is raised higher than −5 eV, there is a chance for electron induced degradation of materials and differential charging. It is best to float all samples to minimize the chance of differential charging (Table XXII).

TABLE XV. Stepwise instructions to produce quality XPS spectra.

- Float all samples and use the flood gun.
- X rays off, move to the desired analysis area.
- Adjust XYZ to give good optical focus of the analysis area.
- Select an analysis area ~1–2 mm from the edge or corner.
- 1–2 mm away from the ground.
- On top of the smoothest region.
- On top of an area that looks uniform,
- ~1 mm away from dark spots, fibers, or surface particles.
- Select the largest x-ray beam size available and turn ON the x rays.
- Select a voltage of 1–2 eV for the new, dual-beam flood gun or repeller system. (4–5 eV for older flood guns).
- Select a current emission for the flood gun that is between 100 and 300 μA (1 mA for old gun).
- Turn ON the flood gun source.
- Open snapshot (unscanned) mode view of the spectrum.
- Set pass energy to produce a 20–22 eV wide spectrum using PE = 150–200 eV,
- Select KE (BE) to show the O (1s) signal or C (1s) signal.
- Start data collection—Snapshot (unscanned) view.
- You should see a signal in the middle of the view.
- Place a transparent ruler on screen—align to peak max.
- Select a 1–2 s refresh rate.
- Adjust Z height up and down until the count-rate is maximized.
- Also check the X-Y position if desired.
- Now adjust the X- or Y-position of the flood gun beam to make peak max move to lower BE.
- Use large steps first, then smaller X-position steps.
- We want the O (1s) BE [or C (1s)] to decrease to a minimum value. It might move 1–2 eV.
- We do not want to see a shoulder on the right side of the O (1s) peak [or C (1s)], which is often due to differential charging. (While adjusting X and Y, we might see a shoulder or separate peak at higher BE. Ignore those.)
- Peaks at higher BE are real peaks, not charging.
- Adjust the X- or Y-position to give the lowest possible BE, which should have the smallest FWHM and no shoulders.
- Repeat X adjustment and Y adjustment until you have smallest BE and FWHM, and no low BE slope or shoulder.
- If you need to analyze the center of a large sample, then move to the center and move the stage in XY 3–5 mm in X and Y directions.
- This big motion spreads electrons over the areas near to our analysis area to minimize differential charging.
- Now you are ready to collect normal scanned data.
- If you worry about a change in charging during a long data collection run, then you should program a C (1s) [or O (1s) spectrum] at the start and again at the finish to check for any change in charge control during the time used to collect all the other spectra.

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TABLE XVI. Typical flood gun settings.

- Beam voltage for older, traditional flood guns: −1 to −20 eV (voltage onset is typically −2 eV).
- Dual-beam flood guns beam voltages: −0.1 to −5 eV.
- "Repeller" style flood guns produce beam voltages: −0.1 to −5 eV.
- Filament currents to the actual filament: 1–4 A.
- Typical emission currents produced: 50–300 μA.
- For the PHI 5802 XPS flood gun, the settings should be: 1.2 A, stage bias +6 V. Extractor 75 V, XY positions − + 20, −20.

1. Automated data collection sequence to check for change during data collection

To check if surface charging has changed during data collection, collect survey spectrum first, then measure C (1s) and O (1s), then measure all other high res spectra, repeat survey spectrum to check for any x-ray induced degradation, and finally run C (1s) and O (1s) again to check for any change in charge control or degradation.

The best-known method (BKM) is given in Table XXIII.

X. XPS INSTRUMENT DETAILS

- SSI X-Probe [Cu (2p3) BE at 932.47 eV].

TABLE XVII. Potential causes of surface charging problems.

- Flood gun is not turned ON.
- Flood gun emission current is too low.
- Flood gun voltage is too low.
- Sample size is too large.
- Flood gun is broken or contaminated with carbon.
- Differential charging because too thick.
- Conductive sample is having an unexpected ground.
- Flux density of the small x-ray beam.
- Surface roughness is too high.
- Irregular contamination on the surface.
- Nearby tall sample is blocking half of the electron beam.
- Geometry (angle) between the sample and flood gun.
- Stage ground is bad.
- Ball bearings, surface, spring, or clip are oxidized.
- Differential charging of highly polar native oxide.
- Repeller plate is not On or set at the wrong voltage.

- SSI S-Probe [Cu (2p3) BE at 932.67 eV, Cu (3s) BE = 122.39 eV]; Ag (3d5) BE = 368.25 eV; Au (4f7) BE at 83.98 eV.
- PHI 5802 (Cu 2p3) BE at 932.6 eV).
- VG Scientific 220i-XL [Cu (2p3) BE at 932.67 eV].
- Thermo K-Alpha Plus [Cu (2p3) BE at 932.62 eV].

TABLE XVIII. Guide to sample size, preparation, handling, and mounting (in lab air).

- Near corner or edge, but still 1–2 mm away.
- Float all samples, if possible.
- Place sample 1–2 mm away from the ground to the instrument.
- On top of the smoothest region.
- On top of an area that looks uniform.
- 1–2 mm away from dark spots, fibers, or surface particles.
- Small sample size is best (5 × 5 mm or a 5 mm sliver).
- Clean tweezers or cutting edge of the knife or razor blade with acetone or alcohol.
- Lightly sandpaper the single-edged razor blade before use.
- If the sample does not fit on the stage, then the sample size must be reduced to fit on the stage. Small is best.
- Verify that the top and bottom of the stage provide good ground.
- Verify that the sample is grounded or floating—use a voltmeter.
- If the sample cannot be cut, then put the sample inside a clean plastic bag and use a hammer to break the sample.
- If the sample must be cut with a metal blade, then do not use any oil while cutting. Cut dry. Use a diamond blade if available.
- If the sample is a powder, press the powder into small thin pellets having a smooth surface using a spatula or a hand-press. (Pellet is best. Use Al foil to protect surfaces. A smooth surface is best for controlling charging and giving higher counts.)
- Grab the sample using clean tweezers or grab corners of the sample while wearing clean gloves.
- Trap the sample onto the surface of the stage using nonconductive double-sided tape, metal clip, metal mask, or indium foil to hold the sample.
- Verify that the x-ray beam and flood gun beam can irradiate the analysis area effectively with no obstructions.
- If available, gently spray the sample with de-ionizing air spray to remove excess charge.
- Plan to analyze the corner or edge of the sample that is nearest the flood gun and nearest the metal stage. This minimizes charge buildup that causes differential charging.
- If you use a metal mask, then, after the sample is inside the instrument, you must test different areas inside the mask to find the smallest BE and smallest FWHM of the C (1s) or O (1s) signal. The area near the bottom is usually best for charge control.
- If you use a mesh, then make sure the mesh is grounded and is less than 0.5–1 mm above the surface of the sample. Due to geometry, the mesh is normally out of focus of the collection lens.
- Confirm that the x-ray beam and flood gun beam can irradiate the analysis area effectively.

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TABLE XIX. Confirm quality of charge control.

- Run normal, high resolution scans (not snapshot) of C (1s) and O (1s) spectra as the first two high resolution spectra.
- If you see shoulders at low BE side on both C (1s) and O (1s), stop. Fix the problem.
- If there are no shoulders, then data may be good.
- Does carbon (1s) appear below 285 eV?
- Do quick peak-fits or use a ruler. FWHM should be <2.0 eV.
- If FWHMs are <1.5 eV, then you have good charge control.
- Important! Run C (1s) and O (1s) once again at the very end to confirm that charge control did not change during analysis.

- SSI Charge-Control Mesh-Screen made from Nickel, 90% Transmission, grounded, 0.5–1.0 mm above sample).
- Monochromatic Al K-alpha x rays (1486.7 eV, 8.338 Å).
- For chemical state spectra, pass energy = 50 eV.
- FWHM of ion etched Ag (3d5) using PE = 50 eV is <0.8 eV.
- FWHM of ion etched Ag (3d5) using PE = 10 eV is <0.6 eV.
- For survey spectra, pass energy = 200 eV.
- Adventitious hydrocarbon C (1s) BE is assigned to occur at 285.0 eV, which is used for charge correction.
- Due to the need to show raw spectra, many BEs from insulators were not charge referenced.

Photos of standard flood gun components are given in Fig. 67. Photo of charge-control mesh-screen is given in Fig. 68.

XI. SOURCES OF XPS REFERENCE GRADE SPECTRA

XPS is rapidly growing, being used in hundreds of different research fields because it is extremely useful to identify different chemical states at the surface of any solid material. Researchers that need XPS results use central research centers that provide raw XPS spectra without chemical state assignments. To help them to process and peak-fit their raw spectra, these researchers use the NIST XPS database and a free standalone peak-fitting software, CasaXPS.[2,3]

TABLE XX. Potential problems with instrument design, flood gun, sample, sample stage.

- X-ray beam size (flux) is too high—causes charging.
- Grounding of the base of the stage or the sample is poor.
- Surface of the stage or the sample is dirty or oxidized.
- Bearings or gears are dirty or oxidized.
- Grounding spring or brush oxidized.
- Sample is not truly grounded.
- Stage or instrument not grounded.
- Flood gun filament too old—almost broken.
- Flux from the flood gun filament is too low—increase.
- Angle between sample plane and flood gun beam is bad.
- Geometry problem—beam is partially blocked.
- Electron beam does not overlap analysis area—adjust XY.
- Surface is too rough—flood gun beam is blocked.

TABLE XXI. Other methods useful to improve charge compensation.

- Float the sample to get a linear voltage response from the flood gun.
- Clean sample stage—remove nonconductive oxides or oils.
- Clean the bottom of the sample—to improve the electrical connection.
- Clean or sandpaper stage or sample mounts or sample clips.
- Use charge-control mesh-screen to produce a uniform flat field of electrons on the surface.
- Add a second flood gun with a different angle.
- Use a thin grounded mask or silver paint (thin washer).
- Improve grounding (earth) to instrument.
- Bias stage (positive) using 9-V battery.
- Irradiate with laser (large beam, low power).
- Irradiate with UV light (large beam).
- Heat sample (>300 °C) while analyzing.
- Tilt the sample so x rays or electrons graze the surface plane.
- De-ionize the sample using an Alpha particle beam 5 cm from the sample.
- Press powder into a smooth pellet (use Al foil to protect the pellet).
- Press the top of the sample with DST to make it uniform.
- Freshly grind powder to homogenize chemistry.

The NIST database supplies XPS BEs but no actual spectra, only numbers. These simple numbers[2] have been found to have various problems with reliability. Calibration in the NIST database is usually limited to BEs from silver or gold, but never copper. The scientific literature that publishes XPS data normally only publishes two to three raw or processed chemical state spectra even though the research analyzed various chemicals. Data analysts need actual reference XPS spectra to cross-check spectra obtained from central

TABLE XXII. Advice for obtaining good charge control.

- Float all samples on nonconductive DST or thin ceramic.
- Decrease size of all samples down to 5 × 5 or 10 × 10 mm.
- Float sample stage, if possible.
- Press all powders into a smooth pellet using a hand-press.
- Confirm all stage parts are conductive (clean or sandpaper).
- Place analysis beam near the sample ground (clip).
- Add a second flood gun.
- Add a low power, defocused green or blue laser.
- Bias stage to attract flood gun electrons.
- Float samples to be depth profiled—do not ground the top of the sample.
- Use a monochromatic x-ray source to avoid problems and improve data quality.
- X-ray damage is possible, run single scan survey and single scan of main elements at start, then run longer scans, and finish with single scans of survey and main elements at the end.
- Multiplex data collection is not recommended because if damage occurs, then that method hides it or averages it over time.

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TABLE XXIII. Best-known method.

- Float sample stage, if possible.
- Or place all samples together with HOPG on top of the insulator and use true BE of HOPG to charge correct all BEs.
- Analyze area near the corner or edge, but still 1–2 mm away.
- Choose area 1–2 mm away from the ground.
- Select the smoothest region.
- Select an area that looks uniform.
- Stay 1–2 mm away from dark spots, fibers, or surface particles.
- Test snapshot spectra to get lowest C (1s) BEs (<285 eV).
- Look for FWHM 1.0–1.4 eV for scanned high resolution peaks of C (1s), O (1s), and main metal.
- Make sample small in XY size (5 × 5 or 10 × 10 mm).
- Make double-sided adhesive tape same size as sample.
- Move sample to spray electrons onto nearby areas.
- Press a thick gold dot pressed onto surface to help check calibration BEs.
- Do not trust adventitious hydrocarbon C (1s) BE for charge referencing. It is a useful guide but can cause errors.
- Au coating on surface is NOT a solution—migration occurs.
- Gold islands creep and cause work function to change.
- For best BEs, mount sample on a thin insulator. Mount HOPG on the same insulator. Record HOPG C (1s) BE. Use charge shifted HOPG BE for charge correction.

labs. These reference XPS spectra allow the data analyst to more accurately and more reliably peak-fit their raw spectra.

To help data analysts and instrument operators, two groups have been publishing *complete sets of actual monochromatic XPS spectra*. Actual spectra are extremely helpful and valuable guides to processing raw spectra and checking on the presence or absence of differential charging. The products offered by these groups are:

1. XPS International, SpecMaster Database[2,3] with >70 000 Monochromatic XPS Spectra from pure materials, natural crystals, single crystals, polymer films, polymer beads, etc.
2. B. Vincent Crist, Handbook of Monochromatic XPS Spectra, The Elements and Native Oxides, Wiley, (2000) ISBN: 978-0-471-49265-8.[29]

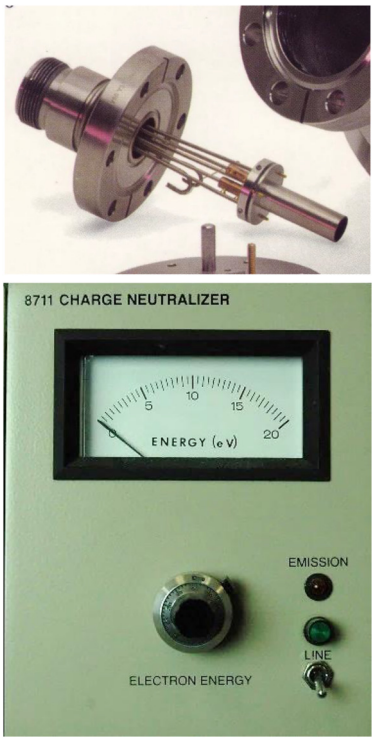


FIG. 67. Photos of the S-Probe flood gun system (rf Service-Physics LLC).

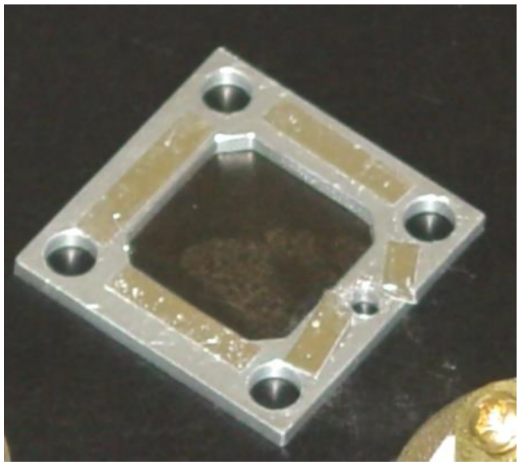


FIG. 68. Handmade charge-control mesh-screen. 25 × 25 mm aluminum square (0.8 mm thick) with 90% transparent mesh taped down by hand using aluminum tape to one side of the square. Holes allow screws to be used if clips are not available. The mesh-screen is not perfectly flat. To produce the flat electric field, the aluminum needs to be grounded. Depending on the sample thickness, other mesh-screens were built using 1.0, 1.5, and 2.0 mm thicknesses.

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3. B. Vincent Crist, Handbook of Monochromatic XPS Spectra, Semiconductors, Wiley, (2000) ISBN: 978-0-471-49266-5.[30]
4. B. Vincent Crist, Handbook of Monochromatic XPS Spectra, Polymers and Polymers Damaged by X-rays, Wiley (2000).[31,32]
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6. J. Surface Science Spectra (Am. Vac. Soc.) with >1500 monochromatic XPS spectra, Editors: J. E. Castle and R. Haasch.

XII. SUMMARY AND CONCLUSIONS

Current day XPS instrument makers have made significant advances in charge-control systems over the last 20 years, which makes it easier to analyze insulators, but samples still have many differences in chemistry, dielectric properties, sizes, surface roughness, etc. that force instrument operators to tweak flood gun settings if they want or need to obtain high quality chemical state spectra that provide the most information.

Current day data analysts and researchers, who use XPS spectra, have little if any experience with the difficulties of preparing samples for XPS analysis and various problems that can and do occur when running an XPS instrument, maintaining that instrument, and calibrating that instrument. As a direct result, these researchers do not recognize differential charging problems because they have no idea what differential charging looks like. If the data analysts would run the instrument, then they would learn what good spectra look like and what bad spectra look like.

This guide teaches what differential charging looks like by showing a significant number of example spectra together with spectra from the same sample that are free from differential charging.

This paper discusses the origins and types of charging, charge neutralization within the atom, and how the atom deals with the loss of a photoelectron.

To help learners and mid-level users to learn which flood gun variables to check, we present tables showing the effect of changing those variables. Learning how to optimize electron flood gun settings by presenting high energy resolution, chemical state spectra makes learning easier and faster.

By focusing on the XPS measurement of insulators—nonconductive metal oxides and polymers this paper reveals what happens to >70% of all materials analyzed by XPS. This guide shows that by measuring commonly available polymers (polypropylene and PET) or ceramic materials (SiO_2 and Al_2O_3), the operator can easily characterize the good and bad effects of XY position settings and other settings provided by modern electron flood gun systems.

Many original, never-before-published peak FWHMs are provided that will greatly assist peak-fitting efforts. This guide reveals a useful direct correlation between electron count-rate, measured BEs, and best charge-control settings that should be a common phenomenon.

This guide discusses the FWHM and BE of C (1s) or O (1s) spectra produced from the sample currently being analyzed that can be directly used to decide if charging has or has not been minimized. A list of other charge control methods is provided along with advice and the BKM.

A short list of large extensive databases of *actual XPS spectra* is extremely beneficial to users who need real-world examples of high quality chemical state spectra to guide their in-house efforts to collect high quality spectra and to interpret valuable information from the peak-fits of those spectra.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

B. Vincent Crist: Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Resources (equal); Validation (equal); Visualization (equal); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request. All XPS spectra, data, data tables, and images were produced by B. Vincent Crist, the author. There are no funding agents as the author paid for all materials and analyzed all materials. All spectra are part of The XPS Library and The SpecMaster Database of XPS Spectra, which are commercially available from XPS International LLC. The software "SDP v8" was used to process all spectra. SDP v8 is produced by XPS International LLC (https://xpsdata.com). All spectra and images are copyrighted by the author and available free-of-charge. https://xpslibrary.com/charge-control-guide-JVST-2020.

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