

CHAPTER 1

INTRODUCTION

1.1 SURFACE ANALYSIS

We interact with our surroundings through our five senses: taste, touch, smell, hearing, and sight. The first three require signals to be transferred through some form of interface (our skin, taste buds, and/or smell receptors). An interface represents two distinct forms of matter that are in direct contact with each other. These may also be in the same or different phases (gas, liquid, or solid). How these distinct forms of matter interact depends on the physical properties of the layers in contact.

The physical properties of matter are defined in one form or another by the elements present (the types of atoms) and how these elements bond to each other (these are covered further in Section 2.1). The latter is referred to as *speciation*.

An example of speciation is aluminum (spelt aluminium outside the United States) present in the metal form versus aluminum present in the oxide form (Al_2O_3). In these cases, aluminum exists in two different oxidation states (Al^0 vs. Al^{3+}) with highly diverse properties. As an example, the former can be highly explosive when the powder form is dispersed in an oxidizing environment (this acted as a booster

rocket propellant for the space shuttle when mixed with ammonium perchlorate), while the latter is extremely inert (this is the primary form aluminum exists within the earth's crust).

Aluminum foil (the common household product) is primarily metallic. This, however, is completely inert to the environment (air under standard temperature and pressure) since it is covered by a thin oxide layer that naturally reforms when compromised. This layer is otherwise referred to as a *passivating oxide*. Note: Aluminum metal does not occur naturally. This is a man-made product whose cost of manufacture has decreased dramatically over the last 200 years. Indeed, aluminum metal was once considered more precious than gold, and it is reputed that Napoleon III honored his favored guests by providing them with aluminum cutlery with the less favored guests being provided with gold cutlery.

Like aluminum foil, most forms of matter present in the solid or liquid phase exhibit a surface layer that is different from that of the underlying material. This difference could be chemical (composition and/or speciation), structural (differences in bond angles or bond lengths), or both. How a material is perceived by the outside world thus depends on the form of the outer layer (cf. an object's *skin* or *shell*). The underlying material is referred to as the bulk throughout the remainder of this text. Also, gases are not considered due to their high permeability, a fact resulting from a lack of intermolecular forces and the high velocity of the constituents (N_2 and O_2 in air travel on average close to 500 m/s, with any subsequent collisions defining pressure).

Reasons as to why the physical properties of a solid or liquid surface may vary from the underlying bulk can be subdivided into two categories, these being

- (a) *External Forces (i.e., Adsorption and/or Corrosion of the Outer Surface)*. Pieces of aluminum or silicon are two examples in which a stable oxide (passivation layer) is formed on the outer surface that is only a few atomic layers thick (~ 1 nm). Note: Air is a reactive medium. Indeed, water vapor catalyzes the adsorption of CO_2 on many metallic surfaces (both water vapor and CO_2 are present in air), and so forth.
- (b) *Internal Forces (i.e., Those Relayed through Surface Free Energy)*. These are introduced by the abrupt termination of any long-range atomic structure present and can induce such effects as elemental segregation, structural modification (relaxation and/or reconstruction), and so on. This too may only influence the outer few atomic layers.

Some of the physical properties (listed in alphabetical order) that can be affected as a result of these modifications (notable overlaps existing between these) include

- (a) Adhesion
- (b) Adsorption
- (c) Biocompatibility
- (d) Corrosion
- (e) Desorption
- (f) Interfacial electrical properties
- (g) Reactivity inclusive of heterogeneous catalysis
- (h) Texture
- (i) Visible properties
- (j) Wear and tear (also referred to as tribology)
- (k) Wettability, and so on

If the surface composition and speciation can be characterized, the manner in which the respective solid or liquid interacts with its surroundings can more effectively be understood. This, then, introduces the possibility of modifying (tailoring) these properties as desired. From a technological standpoint, this has resulted in numerous breakthroughs in almost every area in which surfaces play a role. Some areas (listed in alphabetical order) in which such modifications have been applied include

- (a) Adhesion research
- (b) Automotive industry
- (c) Biosciences
- (d) Electronics industry
- (e) Energy industry
- (f) Medical industry
- (g) Metallurgy industry inclusive of corrosion prevention
- (h) Pharmaceutical industry
- (i) Polymer research, and so on

Indeed, many of these breakthroughs have resulted from the tailoring of specific surface properties and/or the formulation of new materials that did not previously exist in nature. Like aluminum foil, these are all man-made with examples ranging from the development of plastics to synthesis of superconducting oxides, and so on.

A solid or liquid's surface can be defined in several different ways. The more obvious definition is that *a surface represents the outer or topmost boundary of an object*. When getting down to the atomic level, however, the term boundary loses its definition since the orbits of bound electrons are highly diffuse. An alternative definition would then be that *a surface is the region that dictates how the solid or liquid interacts with its surroundings*. Applying this definition, a surface can span as little as one atomic layer (0.1–0.3 nm) to many hundreds of atomic layers (100 nm or more) depending on the material, its environment, and the property of interest.

To put these dimensions into perspective, consider a strand of human hair. This measures between 50 and 100 μm (0.05–0.1 mm) in diameter. The atoms making up the outer surface are of the order of 0.2 nm in diameter. This cannot be viewed even under the most specialized optical microscope (typical magnification is up to $\sim 300\times$) since the spatial resolution is diffraction limited to values slightly less than 1 μm (see Appendix E). The magnification needed ($\sim 30,000,000\times$) can only be reached using a very limited number of techniques, with the most common being transmission electron microscopy (TEM). These concepts are illustrated in Figure 1.1.

TEM being a microscopy, however, only reveals the physical structure of the object in question. To reveal the chemistry requires spectroscopy or spectrometry (the original difference in terminology is discussed in Appendix F). Although a plethora of spectroscopies and spectrometries exists, few are capable of providing the chemistry active over the outermost surface, that is, that within the outermost 10 nm of a solid. Of the few available, X-ray photoelectron spectroscopy (XPS), also referred to as electron spectroscopy for chemical analysis (ESCA),

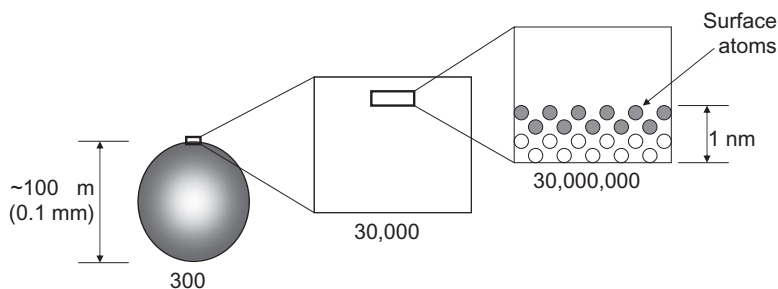


Figure 1.1. Pictorial illustration of the cross section of a strand of human hair at the various magnifications listed whose surface may have been modified to add or remove specific properties, that is, dryness, oiliness, cleanliness, and sheen, through, for example, the application of a specific shampoo.

has over the last several decades become the most popular. Some comparable/complementary microanalytical techniques are discussed in Appendices F and G.

1.2 XPS/ESCA FOR SURFACE ANALYSIS

XPS, also referred to as ESCA, represents the most heavily used of the electron spectroscopies (those that sample the electron emissions) for defining the elemental composition of a solid's outer surface (within the first 10 nm). The acronym XPS will be used henceforth in this text since this more precisely describes the technique. The acronym ESCA was initially suggested by Kai Siegbahn when realizing that speciation could be derived from the photoelectron and Auger electron emissions alone.

The popularity of XPS stems from its ability to

- (a) Identify and quantify the elemental composition of the outer 10 nm or less of any solid surface with all elements from Li–U detectable. Note: This is on the assumption that the element of interest exists at >0.05 atomic % (H and He are not detectable due to their extremely low photoelectron cross sections and the fact that XPS is optimized to analyze core electrons).
- (b) Reveal the chemical environment where the respective element exists in, that is, the speciation of the respective elements observed.
- (c) Obtain the above information with relative ease and minimal sample preparation.

Aside from ultraviolet photoelectron spectroscopy (UPS), which can be thought of as an extension of XPS since this measures the valence band photoelectrons, Auger electron spectroscopy (AES) is the most closely related technique to XPS in that it displays a similar surface specificity while being sensitive to the same elements (Li–U). Its strength lies in its improved spatial resolution, albeit at the cost of sensitivity (for further comparisons of related techniques, see Appendix F).

Wavelength-dispersive X-ray analysis (WDX) and energy-dispersive X-ray analysis (EDS or EDX) are also effective for defining the elemental composition of solids. Indeed, when combined with scanning electron microscopy (SEM), these are more popular than XPS, with the moniker electron probe microanalysis (EPMA) often used. These,

however, are not considered true surface analytical techniques, at least not in the strict sense, since they provide average elemental concentrations over a depth that extends $\sim 1 \mu\text{m}$ or more below the surface.

This difference in depth is important since nearly all the surface chemistry that takes place between different forms of matter is dictated by the chemical composition, speciation, and/or electronic structure present over the outer few atomic layers of the respective solid. These can differ substantially from those noted 1 nm or more below the surface. Note: A surface film of 1 nm equates to three to four atomic layers. Thus, the examination of aluminum foil via EDX reveals spectra heavily dominated by aluminum peaks. This would not reveal the presence of a surface oxide.

1.3 HISTORICAL PERSPECTIVE

Historically, XPS can be traced back to the 1880s whereupon Heinrich Hertz noted that electrically isolated metallic objects held under vacuum exhibited an enhanced ability to spark when exposed to light (Hertz, 1887). This effect, termed the *Hertz effect*, also allowed the derivation of the ratio of Planck's constant over electronic charge (h/e) and the work function (ϕ) of the respective metal object when altering the energy of the irradiation source (frequency, wavelength, and energy are all related).

In 1905, Albert Einstein explained this effect as arising from the transfer of energy from photons (in the form of light) to electrons bound within the atoms making up the respective metallic objects. In other words, he showed that this induced electron emission from metallic objects if the energy transfer was greater than the energy that binds the electron to the respective metal atom/solid (Einstein, 1905). For this and the introduction of the concept of the *photon* (a package of energy with zero rest mass), Einstein was awarded the 1921 Nobel Prize in Physics.

The above-mentioned spark can thus be understood as resulting from the net positive charge that builds on photoelectron and Auger electron emission from electrically isolated objects. Note: Photoelectron emission is also accompanied by Auger electron emission or fluorescence (emission of photons). Auger emission is named after Pierre Auger (1925) but was first reported by Lisa Meitner (Meitner, 1922), while fluorescence was named by George Stokes, who was first responsible for bringing about a physical understanding underlying this phenomena (Stokes, 1852).

The capabilities of XPS were, however, not fully recognized until Kai Siegbahn and his coworkers constructed an instrument capable of analyzing core photoelectron emissions to a sufficiently high energy resolution to allow speciation analysis to be carried out (Siegbahn, 1967, 1970). For this, Kai Siegbahn was awarded the 1981 Nobel Prize in Physics. Following Siegbahn's initial success came a rapid succession of studies and instruments (for a brief synopsis, see Shirley and Fadley, 2004) that resulted in a firm understanding of XPS. The primary reason for this relatively recent development can be traced back to the inability to attain the necessary vacuum conditions required when analyzing such surface regions (the need for vacuum is discussed in further detail in Section 3.1.1). Note: The requirement for vacuum generally limits the application of this technique to the analysis of solid surfaces. Gases and liquids can be analyzed but only when using highly specific instrumentation and/or sample preparation procedures.

1.4 PHYSICAL BASIS OF XPS

Photoelectron production in its simplest form describes a single step process in which an electron initially bound to an atom/ion is ejected by a photon. Since photons are a massless (zero rest mass), chargeless package of energy, these are annihilated during photon–electron interaction with complete energy transfer occurring. If this energy is sufficient, it will result in the emission of the electron from the atom/ion as well as the solid. The kinetic energy ($K.E.$) that remains on the emitted electron is the quantity measured. This is useful since this is of a discrete nature and is a function of the electron binding energy ($B.E.$), which, in turn, is element and environment specific.

A schematic example of the photoelectron emission process from oxygen present within a silicon wafer bearing a native oxide is shown on the left in Figure 1.2a. As covered in Section 2.1.2.2, photoelectron peaks are described using spectroscopic notation. To the right of Figure 1.2a is shown one of the two primary de-excitation processes that follow photoelectron emission, that is, the Auger process. The other process, termed fluorescence, results in photon emission. These are described using X-ray notation. (Note: This can be confusing since the same levels are described.) Since Auger de-excitation also results in electron emission, peaks from both photoelectrons and Auger electrons are observed in XPS spectra. Further discussion on X-ray-induced Auger emission is covered in Section 5.1.1.3.2.4.

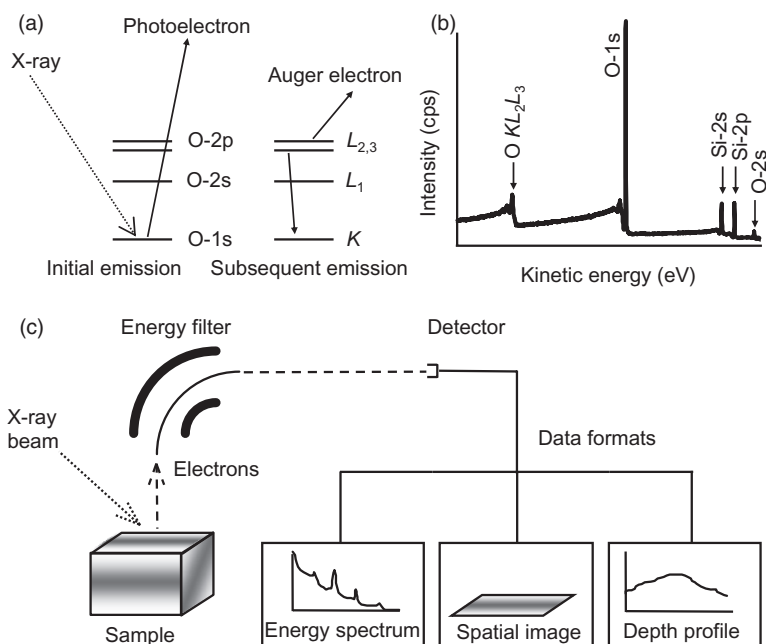


Figure 1.2. Schematic example of (a) the photoelectron process (shown on the left) and a subsequent Auger de-excitation process (shown on the right) with the various electronic energy levels (stationary states) portrayed using either spectroscopic notation (photoelectron peaks) or X-ray notation (Auger electron peaks), (b) XPS spectra collected from a silicon wafer bearing a surface oxide as analyzed under Mg- $K\alpha$ irradiation (as described in the text, this contains peaks from both photoelectron emissions and Auger electron emissions), and (c) the basic components of an XPS instrument along with the data formats that can be implemented. Further discussion on the instrumentation required along with the acquisition of energy spectra along with spatial images is covered in Chapter 3, while depth profiling is covered in Section 4.3.1.2.

In Figure 1.2b, a typical low-resolution spectrum collected from a silicon wafer is shown. This is plotted in intensity (I) versus $K.E.$ (the energy the electron emissions attain on departing the sample). Evident in this spectrum are photoelectrons from electronic levels accessible to the X-ray source used, that is, the O-1s, O-2s, Si-2s, and Si-2p levels (here, the Si-2p_{1/2} and Si-2p_{3/2} contributions overlap) as well as Auger electron emissions resulting from the filling of the O-1s core hole (K level). The latter are, however, described using X-ray notation (see Section 2.1.2.2), that is, as O- KLL emissions or some specific contribution derivative thereof (in this case the KL_2L_3 emissions).

O- KLL emissions arise from the filling of the K level core hole produced on photoelectron emission by an electron from some L level,

with the energy difference between these two levels carried away in the emission of a third electron, also from some L level. The most intense of the peaks actually arises from KL_2L_3 and KL_3L_2 transitions collectively referred to $KL_{2,3}L_{2,3}$ emissions. The remaining peaks arise from KL_1L_1 , KL_1L_2 , and KL_1L_3 emissions with the latter two collectively referred to as $KL_1L_{2,3}$.

In Figure 1.2c is shown a schematic example of an XPS instrument, along with the three most common means of relaying the data, namely,

- (a) Energy distributions of any electron emissions falling within some predefined energy range
- (b) Spatial distributions of specific electron emissions noted across a surface (this allows the elemental or speciation distributions to be mapped)
- (c) Depth distributions of specific electron emissions to some predefined depth (this can extend from less than 10 nm to several micrometers)

Analysis is usually carried out by first collecting energy spectra over all accessible energies and then concentrating on particular photoelectron signals. This ensures that all elements are accounted for during quantification and that the data are collected in a time-effective manner.

Although $K.E_{XPS}$ is the quantity recorded in XPS, it is the derived $B.E_{XPS}$ that is used to construct the energy spectrum. Note: The XPS subscript is applied henceforth to denote the fact that the value obtained is not exactly equal to that expected in a ground-state atom; that is, the introduction of a core hole during photoemission effectively alters $B.E$ values from that exhibited by a ground-state atom/ion, albeit by a small amount. This effect, referred to as a *final state effect*, is discussed in Section 5.1.1.3.

The $B.E_{XPS}$ derived is used to construct a spectrum since the $K.E_{XPS}$ is dependent on the X-ray energy, whereas the $B.E_{XPS}$ is not. Values of $K.E_{XPS}$, $B.E_{XPS}$, and the initiating photon energy (E_{ph}) are related through the expression (Einstein, 1905)

$$K.E_{XPS} = E_{ph} - \phi_{XPS} - B.E_{XPS}, \quad (1.1)$$

where ϕ_{XPS} is the work function of the instrument, not the sample. This is included since it represents the minimum energy necessary to remove an electron from the instrument on the assumption that a conductive sample in physical contact with the instrument is analyzed (the use of this as opposed to that of the sample is discussed in Section 4.1.3).

Note: Equation 1.1 does not apply to Auger emissions noted in XPS spectra. This is realized since Auger electron energies are not directly related to the incoming photon energy (E_{ph}); rather, these represent the difference between two energy levels once electronic perturbation effects are accounted for (Auger emission is discussed further in Section 5.1.1.3.2.4). Applying Equation 1.1 to spectra obtained under different X-ray energies thus yields different values for Auger electrons. Indeed, this can be useful when there exists confusion as to whether an observed peak is a photoelectron peak or an Auger electron peak; that is, this effectively shifts the Auger peaks along the $B.E._{\text{XPS}}$ scale as discussed in Section 4.1.2.

Representative $B.E._{\text{XPS}}$ values for all the elements can be found in Appendix B.

1.5 SENSITIVITY AND SPECIFICITY OF XPS

Two parameters that describe the ability of XPS to identify and quantify the elemental composition and speciation present over the outer 10 nm or less of any solid surface, on the assumption that the element of interest exists at >0.05 atomic %, are

- (a) Surface specificity or the ability to separate the signal from the surface region relative to that of the underlying region
- (b) Sensitivity or the ability to detect the signal of interest given the constraint of the reduced volume from which the signal emanates

Surface specificity arises from the limited flight path an electron has within a solid before it loses some fraction of its energy (this is generally less than 10 nm as discussed in Section 4.2.2.1). Note: X-rays can penetrate micrometers below the surface. If energy is lost, the signal will disappear within the spectral background (see Section 4.2.3). This occurs for almost all photoelectrons produced from atoms/ions situated at some depth greater than ~ 10 nm below the surface. Hence, the discrete signals that remain (those that result in the spectral peaks observed) are from the surface region alone. The presence of an adsorbed surface layer of some thickness will thus act to quench, to some degree, all signals from the underlying substrate. This otherwise reduces the sensitivity of XPS to these elements. These concepts are illustrated in Figure 1.3.

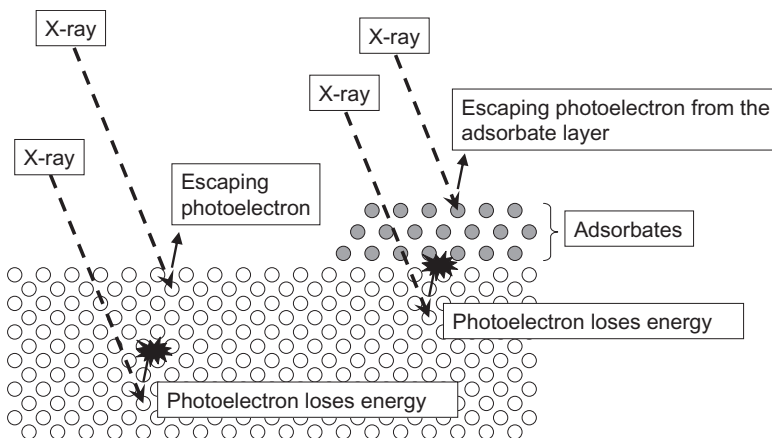


Figure 1.3. Pictorial illustration of photoelectron emission (those with a $K.E._{XPS}$ of ~ 100 eV) from a solid material (represented by the hollow circles) and the surface adsorbate layer (represented by the gray circles).

Sensitivity is primarily a function the photoelectron cross section and the spectral background level (these are discussed further in Sections 4.2.1 and 4.2.3, respectively). The photoelectron cross section describes the yield of electrons produced as a function of the impacting photon energy. Indeed, the low photoelectron cross sections from H and He under X-ray irradiation are the primary reason why these elements are not detectable when present within solids. The ambient pressure, or more precisely the vacuum under which the analysis is carried out, can also affect sensitivity since this controls the density of molecules in the gas phase and, thus, the flight path of any photoelectrons emanating from the surface. In other words, this acts to restrict the passage of electrons from the sample to the detector. Contaminant overlays also form within analysis timescales if the pressure under which the analysis is being carried out is too high. Pressure and its impact in XPS are discussed in greater detail in Section 3.1.1.1.

1.6 SUMMARY

The properties of a solid or liquid as viewed from the outside world are primarily dictated by the physical properties of the outermost layer. Indeed, this region, termed the surface, can differ in composition and/or structure from that of the underlying bulk material. As a result, much

effort has been expended in the understanding of this region. To complicate matters, this region can span as little as a few atomic layers (1 nm or less) to many hundreds of atomic layers (up to 100 nm).

With the advent of the technology necessary to produce the vacuum conditions required to effectively analyze a solid's surface came the ability to measure the surface chemistry. This culminated in the 1960s in the development of a technique that has since become the most popular and heavily used of the microanalytical techniques for examining the chemistry active on or within solid surfaces. This technique, termed XPS, is now the mainstay of almost all surface analysis labs worldwide, whether in academic or industrial settings. Attributes that have lent to the popularity of XPS include

- (a) Elemental identification and quantification of any element from Li to U
- (b) Sensitivity (concentrations down to 0.1 atomic %)
- (c) Surface specificity (less than 10 nm)
- (d) Ease of analysis (minimal sample preparation is required)

As first explained by Einstein, XPS derives this information by directing an energetic photon beam (X-rays) to induce the emission of core-level electrons. The energy of the electron emissions is then measured since this provides insight into the specific type of atoms/ions the electrons emanated from (the elements), the amount or ratios of the respective atoms/ions (the composition of the volume analyzed), and, in many cases, the manner in which the element was bound (the speciation of the atoms/ions within the volume analyzed), all with relative ease.