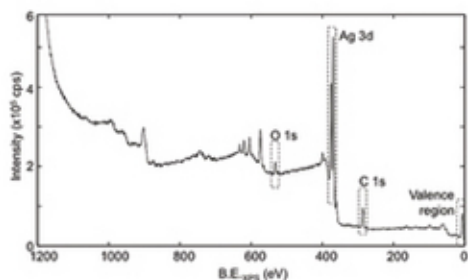
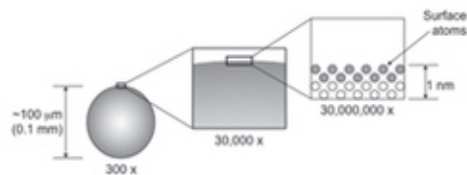


# X-Ray Photoelectron Spectroscopy

An Introduction to Principles and Practices

Paul van der Heide



 **WILEY**



# X-RAY PHOTOELECTRON SPECTROSCOPY



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**PAUL VAN DER HEIDE**

 **WILEY**

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey  
Published simultaneously in Canada

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***Library of Congress Cataloging-in-Publication Data:***

Van der Heide, Paul, 1962–

X-ray photoelectron spectroscopy : an introduction to principles and practices / Paul van der Heide.

p. cm.

Includes index.

ISBN 978-1-118-06253-1 (hardback)

1. X-ray photoelectron spectroscopy. I. Title.

QC454.P48V36 2012

543'.62–dc23

2011028942

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

# CONTENTS

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FOREWORD	xi
PREFACE	xiii
ACKNOWLEDGMENTS	xv
LIST OF CONSTANTS	xvii
<b>1 INTRODUCTION</b>	<b>1</b>
1.1 Surface Analysis / 1	
1.2 XPS/ESCA for Surface Analysis / 5	
1.3 Historical Perspective / 6	
1.4 Physical Basis of XPS / 7	
1.5 Sensitivity and Specificity of XPS / 10	
1.6 Summary / 11	
<b>2 ATOMS, IONS, AND THEIR ELECTRONIC STRUCTURE</b>	<b>13</b>
2.1 Atoms, Ions, and Matter / 13	
2.1.1 Atomic Structure / 14	
2.1.2 Electronic Structure / 15	
2.1.2.1 Quantum Numbers / 16	
2.1.2.2 Stationary-State Notation / 18	

- 2.1.2.3 Stationary-State Transition Notation / 20
- 2.1.2.4 Stationary States / 21
- 2.1.2.5 Spin Orbit Splitting / 23
- 2.2 Summary / 25

### **3 XPS INSTRUMENTATION**

**27**

- 3.1 Prerequisites of X-ray Photoelectron Spectroscopy (XPS) / 27
  - 3.1.1 Vacuum / 28
    - 3.1.1.1 Vacuum Systems / 32
  - 3.1.2 X-ray Sources / 35
    - 3.1.2.1 Standard Sources / 37
    - 3.1.2.2 Monochromated Sources / 39
    - 3.1.2.3 Gas Discharge Lamps / 41
    - 3.1.2.4 Synchrotron Sources / 41
  - 3.1.3 Electron Sources / 42
    - 3.1.3.1 Thermionic Sources / 42
  - 3.1.4 Ion Sources / 43
    - 3.1.4.1 EI Sources / 43
  - 3.1.5 Energy Analyzers / 44
    - 3.1.5.1 CMA / 46
    - 3.1.5.2 CHA / 46
    - 3.1.5.3 Modes of Operation / 47
    - 3.1.5.4 Energy Resolution / 48
  - 3.1.6 Detectors / 49
    - 3.1.6.1 EMs / 50
  - 3.1.7 Imaging / 52
    - 3.1.7.1 Serial Imaging / 52
    - 3.1.7.2 Parallel Imaging / 54
    - 3.1.7.3 Spatial Resolution / 56
- 3.2 Summary / 59

### **4 DATA COLLECTION AND QUANTIFICATION**

**61**

- 4.1 Analysis Procedures / 61
  - 4.1.1 Sample Handling / 62
  - 4.1.2 Data Collection / 64



4.1.3	Energy Referencing / 65	
4.1.4	Charge Compensation / 69	
4.1.5	X-ray and Electron-Induced Damage / 71	
4.2	Photoelectron Intensities / 72	
4.2.1	Photoelectron Cross Sections / 74	
4.2.2	The Analyzed Volume / 75	
4.2.2.1	Electron Path Lengths / 76	
4.2.2.2	Takeoff Angle / 79	
4.2.3	The Background Signal / 80	
4.2.4	Quantification / 81	
4.3	Information as a Function of Depth / 83	
4.3.1	Opening up the Third Dimension / 84	
4.3.1.1	AR-XPS and Energy-Resolved XPS / 84	
4.3.1.2	Sputter Depth Profiling / 87	
4.4	Summary / 97	
<b>5</b>	<b>SPECTRAL INTERPRETATION</b>	<b>101</b>
5.1	Speciation / 101	
5.1.1	Photoelectron Binding Energies / 102	
5.1.1.1	The $Z + 1$ Approximation / 106	
5.1.1.2	Initial State Effects / 107	
5.1.1.3	Final State Effects / 118	
5.1.1.4	The Auger Parameter / 133	
5.1.1.5	Curve Fitting / 135	
5.2	Summary / 138	
<b>6</b>	<b>SOME CASE STUDIES</b>	<b>141</b>
6.1	Overview / 141	
6.1.1	Iodine Impregnation of Single-Walled Carbon Nanotube (SWNT) / 142	
6.1.2	Analysis of Group IIA–IV Metal Oxides / 145	
6.1.3	Analysis of Mixed Metal Oxides of Interest as SOFC Cathodes / 151	
6.1.4	Analysis of YBCO and Related Oxides/Carbonates / 156	
6.2	Summary / 163	

<b>APPENDICES</b>	<b>167</b>
<b>APPENDIX A PERIODIC TABLE OF THE ELEMENTS</b>	<b>169</b>
<b>APPENDIX B BINDING ENERGIES (<math>B.E_{\text{XPS}}</math> OR <math>B.E_{\text{XRF}}</math>) OF THE ELEMENTS</b>	<b>171</b>
B.1 1s-3s, 2p-3p, and 3d Values / 171	
B.2 4s-5s, 4p-5p, and 4d Values / 175	
<b>APPENDIX C SOME QUANTUM MECHANICS CALCULATIONS OF INTEREST</b>	<b>177</b>
<b>APPENDIX D SOME STATISTICAL DISTRIBUTIONS OF INTEREST</b>	<b>181</b>
D.1 Gaussian Distribution / 182	
D.2 Poisson Distribution / 182	
D.3 Lorentzian Distributions / 183	
<b>APPENDIX E SOME OPTICAL PROPERTIES OF INTEREST</b>	<b>185</b>
E.1 Chromatic Aberrations / 186	
E.2 Spherical Aberrations / 186	
E.3 Diffraction Limit / 186	
<b>APPENDIX F SOME OTHER SPECTROSCOPIC/ SPECTROMETRIC TECHNIQUES OF INTEREST</b>	<b>189</b>
F.1 Photon Spectroscopies / 191	
F.1.1 IR, RAIRS, ATR, and DRIFTS / 191	
F.1.2 Raman, SERS, and TERS / 192	
F.1.3 EDX and WDX / 193	
F.1.4 XRF and TXRF / 194	
F.2 Electron Spectroscopies / 195	
F.2.1 UPS / 195	
F.2.2 AES / 195	
F.2.3 EELS, REELS, and HREELS / 196	

F.3 Ion Spectroscopies/Spectrometries / 196	
F.3.1 SIMS / 196	
F.3.2 TAP / 197	
F.3.3 Ion Scattering Methods / 197	
<b>APPENDIX G SOME MICROSCOPIES OF INTEREST</b>	<b>199</b>
G.1 SEM / 200	
G.2 HIM / 201	
G.3 TEM / 201	
G.4 SPM (AFM and STM)-Based Techniques / 202	
<b>APPENDIX H SOME REFLECTION/DIFFRACTION TECHNIQUES OF INTEREST</b>	<b>205</b>
H.1 XRD / 206	
H.2 GID / 206	
H.3 XRR / 207	
H.4 LEED / 207	
H.5 RHEED / 207	
<b>TECHNIQUE ABBREVIATIONS LIST</b>	<b>209</b>
<b>INSTRUMENT-BASED ABBREVIATIONS</b>	<b>213</b>
<b>GLOSSARY OF TERMS</b>	<b>215</b>
<b>QUESTIONS AND ANSWERS</b>	<b>221</b>
<b>XPS VENDORS</b>	<b>229</b>
<b>REFERENCES</b>	<b>233</b>
<b>INDEX</b>	<b>237</b>



## FOREWORD

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X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), and other related spectroscopies that obtain information about atoms, molecules, compounds, and surfaces by measuring the kinetic energies of electrons ejected from materials have developed rapidly over the past three decades. With their inception in the 1960s at the University of Uppsala, Sweden, under the direction of Professor Kai Siegbahn, these techniques rank as some of the most important advances in surface science and chemical physics in general. Information derivable from these techniques is of vital importance in understanding the electronic structure of solid materials and atoms, molecules, and ions in general.

Dr. Paul van der Heide's book, *X-ray Photoelectron Spectroscopy: An Introduction to Principles and Practices*, treats the phenomenon of photoionization and its consequences by means of modern quantum mechanical methods. The process of ionization, spectroscopic classification of the ionic states, and the subtle spectral vibrational, rotational, vibronic, and spin orbit structure observed in the spectra are discussed in detail. The book serves both a pedagogic need and a research need. It will be of major interest to scientists who use electron spectroscopy in their research and to students majoring in the physical sciences, particularly in the fields of chemistry, physics, and chemical engineering. The book contains a large and valuable collection of references on electron spectroscopy, allowing readers to readily access the original publications. The many examples allow readers to obtain an

understanding of some of the subtle and sometimes not so subtle complexities of the photoionization process. It will be particularly useful to senior undergraduates, graduate students majoring in chemistry, physics, and engineering, and scientists and engineers who wish to apply photoelectron techniques in their work.

*Department of Chemistry  
Lamar University  
Beaumont, Texas*

PROFESSOR JOHN WAYNE RABALAIS

# PREFACE

---

*To know XPS is to know the atom.*

X-ray photoelectron spectroscopy (XPS), otherwise known as electron spectroscopy for chemical analysis (ESCA), represents the most heavily used of the electron spectroscopies for defining the elemental composition and/or speciation of the outer 1–10 nm of any solid substrate. This is of importance since it is the solid's surface that defines how the solid is perceived from the outside world. (Note: The composition and/or speciation over the surface region often differs from that of the underlying material) The information content provided by XPS is, however, heavily limited to the untrained eye.

The inspiration for this text arose when teaching the fundamental and practical aspects of XPS. More precisely, this arose on realizing how the collective works and experiences could be used in preparing a text that would further facilitate this transfer of knowledge. The underlying premise used in putting together this book was *easily attainable answers to all of the questions asked over the years*. For example, “Why is XPS so effective in analyzing all the elements except for hydrogen or helium,

when all it is doing is kicking out electrons?"<sup>1</sup> (Hydrogen and helium have electrons too.)

In adhering to this premise, all aspects associated with XPS are introduced from a practitioners perspective; all sections are prepared such that they can be read independently of each other; all equations are presented using the most commonly used units; and all fundamental aspects are discussed using classical analogies, where possible, over the more correct quantum mechanics descriptions. Note: Although XPS has its foundations in quantum mechanics, knowledge of this is not needed to understand XPS.

The ordering of the text is as follows: Since XPS derives information on the elemental composition and speciation by probing the electronic structure of the system in question (this is first covered in the introduction), an overview of the electronic structure of atoms is presented. Following this, the practical aspects of XPS from basic analysis procedures to instrumentation are covered. An overview of spectral interpretation is then presented followed by several illustrative case studies. Lastly, various complementary techniques and related concepts are covered in the Appendix.

In preparing this text, it also became apparent that this could be used as an effective stepping stone to some of the more extensive publications available, some of which contain a wealth of useful information that can otherwise be inaccessible to the uninitiated. What separates this text from other introductory texts is the greater emphasis placed on spectral understanding/interpretation. This is considered important since therein lies the ability of XPS to define speciation.

PAUL A.W. VAN DER HEIDE

<sup>1</sup> Hydrogen and helium within solids are not detectable by XPS because their photoelectron cross sections (yields) are below XPS detection limits. This arises from a combination of effects, namely, that

- (a) Photoelectron cross-sections (these govern intensities) from stationary states of a specific principal quantum number decrease with decreasing atomic number.
- (b) XPS is not highly sensitive to valence electrons (hydrogen and helium only have valence electrons, while XPS analysis is optimized toward core electrons).

In addition, since all of their electrons are within the valence region, there is nothing characteristic about their binding energies (*B.E.s*); that is, these participate in bonding.

Note: The increased sensitivity of ultraviolet photoelectron spectroscopy (UPS) to valence electrons can allow for the detection of hydrogen and helium in the gas phase.



## ACKNOWLEDGMENTS

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Although this book has profited from many people, there are three in particular whose names deserve mention. These are Professor John Wayne Rabalais, Dr. David Surman, and Kim van der Heide for the invaluable assistance, encouragement, and/or comments provided in preparing this text. Thank you.

*P.V.D.H.*



# LIST OF CONSTANTS

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Boltzmann constant or in units of eV/K	$k_B$	$1.381 \times 10^{-23}$ J/K $8.616 \times 10^{-5}$ eV/K
Charge of electron	$e$	$1.602 \times 10^{-19}$ C
Mass of electron	$m_e$	$9.109 \times 10^{-31}$ g
Mass of neutron	$m_n$	$1.675 \times 10^{-27}$ g
Mass of proton	$m_p$	$1.673 \times 10^{-27}$ g
Planck constant or in units of eV·s	$h = \hbar \cdot 2\pi$	$6.626 \times 10^{-34}$ J·s $4.136 \times 10^{-15}$ eV·s
Speed of light	$c$	$2.98 \times 10^8$ m/s



# 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 ( $\text{Al}_2\text{O}_3$ ). In these cases, aluminum exists in two different oxidation states ( $\text{Al}^0$  vs.  $\text{Al}^{3+}$ ) 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 ( $\sim 1$  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

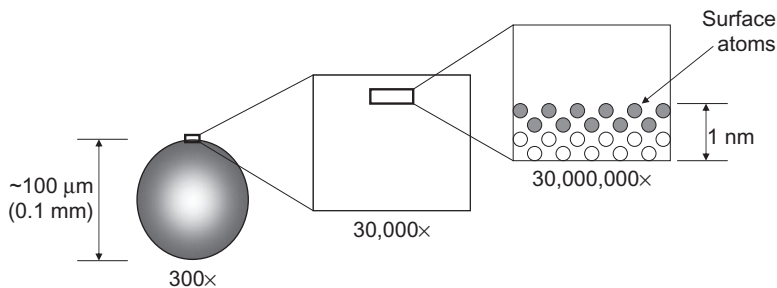
- (a) Adhesion research
- (b) Automotive industry
- (c) Biosciences
- (d) Electronics industry
- (e) Energy industry
- (f) Medical industry
- (g) Metallurgy industry inclusive of corrosion prevention
- (h) Pharmaceutical industry
- (i) Polymer research, and so on

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  $\mu\text{m}$  (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  $\mu\text{m}$  (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 ( $\phi$ ) 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.