Invited, Review

Growth and Trends in Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy

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Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) have been productive tools for a large variety of scientific and technological purposes since commercial instruments became available almost 40 years ago. A brief overview of the early history of AES and XPS is given and subsequent instrumental advances summarized. Advances made in quantitative AES and XPS to calibrate instruments, assess surface sensitivity, determine film thicknesses, evaluate elastic-scattering effects, and determine sample morphology are described together with analytical resources that are now available. Information is given on a new database for the Simulation of Electron Spectra for Surface Analysis (SESSA) and its use to assess the distinguishability of different N composition profiles in SiON films on Si by angle-resolved XPS. Finally, some remarks on the future of AES and XPS for surface analysis are presented.

1. Introduction

Auger-electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are commonly used techniques for surface chemical analysis. Figure 1 shows the numbers of published AES and XPS papers per year from 1991 through 2006 based on a keyword search [1]. Two sets of data are shown in Fig. 1, one based on the use of AES in the search and the other without AES in the search. The former data set is an overcount (because AES is also an abbreviation for atomic emission spectroscopy), while the latter data set is an undercount (since some Auger papers with AES in the title or abstract would be missed). While the number of published Auger papers in Fig. 1 is roughly constant or slowly declining with time, it is clear that there has been substantial growth in the number of published XPS papers. This growth is no doubt due to the fact that XPS can be successfully applied to a great variety of materials [2]. While numbers of published papers are a relatively simple guide to the relative popularity of different techniques, they do not take into account applications and economic impacts of surface analyses (e.g., in industry) that are not normally published. Nevertheless, Fig. 1 alone indicates that many thousands of people have contributed to the development and application of AES and XPS since commercial instruments became available roughly 40 years ago.

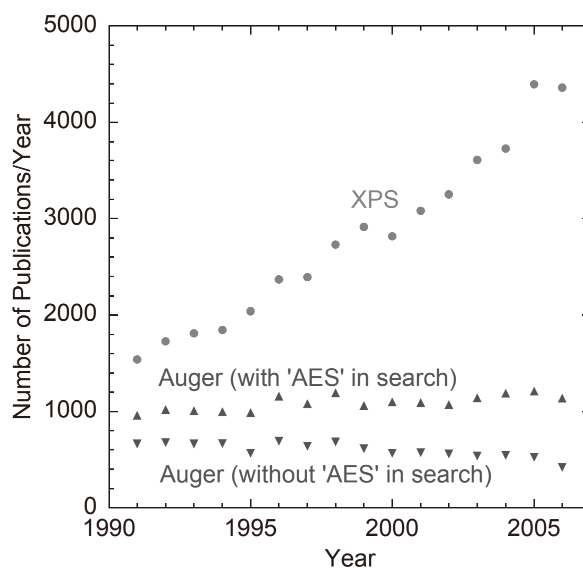

Fig. 1. Plot of numbers of papers published per year on AES and XPS from 1991 through 2006 based on a web search using abbreviations and key phrases for these techniques [1] (see text).

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This review contains a brief history of early AES and XPS experiments and the development of modern AES and XPS instruments during the past four decades. Brief mention is given to growth in the quality of quantitative AES and XPS through the calibration of instruments, assessment of surface sensitivity and evaluation of elastic-scattering effects, and determination of sample morphology. Information is then provided on analytical resources that are now available to guide analysts. A new NIST Database for the Simulation of Electron Spectra for Surface Analysis (SESSA) is briefly described and an example given of its use for angle-resolved XPS. Finally, an outlook is given on areas of possible future growth for AES and XPS.

2. Early Observations of AES and XPS

The history of XPS from 1900 to 1960 has been documented by Jenkin *et al*. [3,4]. An early XPS pioneer was Robinson who, in a 1923 paper [5], used Cu Kα X-rays, a magnetic energy analyzer, and photographic detection in a brass box "closed air-tight by a greased brass plate." He published a diagram showing photoelectron lines observed from Bi, W, Sn, Mo, Cu, Ni, Ca, K, S, Al, Mg, Na, and O as a function of electron energy.

Steinhardt and Serfass [6,7] appear to be the first authors to suggest (in 1951) that XPS could be used for the chemical analysis of surfaces. They used Mo Kα X-rays, a magnetic analyzer, and a Geiger-Müller detector in a conventional high-vacuum apparatus to observe characteristic spectra with broad structures for metals such as Cu, Zn, Rh, Ag, and Au, and to make a quantitative analysis of an Ag-Au alloy. They were also able to measure changes in photoelectron intensity from an Au substrate following deposition of monolayers of barium stearate to obtain an estimate of surface sensitivity.

Siegbahn *et al*. [8,9] also used a Mo Kα X-rays and a Geiger-Müller detector but employed a magnetic analyzer having a much higher energy resolution ($\approx$ 10 eV). In 1957, they observed the K-shell XPS spectrum of copper and could distinguish small peaks due to inelastic scattering [8], and later observed a 4.4 eV chemical shift of the Cu 1s line following surface oxidation [9].

Harris has briefly described the early history of AES [10]. In 1935, Haworth investigated the energy distribution of secondary electrons from Mo excited by 150 eV primary electrons [11]. His magnetic analyzer was inside a glass tube that was baked at 500° C for more than 500 hours. The sample was outgassed for 3500 hours, the last 1000 hours above 2100 K. He observed weak features at low energies in the secondary-electron spectrum that did not vary in position with change of the primary energy. It is likely that an observed peak at 25 eV was due to the Mo N_{23}VV Auger transition (although this was not identified as such in the Haworth paper).

Lander reported Auger spectra of Be, C, Al, Ni, NiO, Cu, Ba, and Pt in 1953 that were obtained with a spherical electrostatic energy analyzer and incident energies up to 1212 eV [12]. Lander was the first to suggest that Auger peaks could be utilized for surface analysis.

As a beginning graduate student at the University of Western Australia (UWA) in 1956, I was aware of Lander's work. In my first paper, published in 1958 [13], I described use of the C Auger peak to monitor the amount of carbonaceous contamination that grew on a previously cleaned W sample following exposure to a conventional high-vacuum environment.

By an unlikely coincidence, the head of the Physics Department at UWA while I was a graduate student was C. J. B. Clews who had worked with Robinson, the XPS pioneer, in the late 1930s [3,4]. My research advisor (J. B. Swan) had experience in β-ray spectroscopy and was interested in measurement of core-electron binding energies. We followed the early XPS work of Siegbahn *et al.* but did not attempt any XPS experiments. Clews was an aloof person, and I and probably Swan were unaware at the time of his XPS background.

3. Development of Modern AES and XPS Instruments

The development in the 1960s of ultra-high-vacuum (UHV) components and technology together with gauges to measure ambient pressures in the UHV range stimulated the development of the modern era of surface science. It was then possible to construct demountable UHV systems and to obtain relatively rapid results without the extremely long baking and sample-processing times that were needed previously (as exemplified by the work of Haworth [11].

In 1967, Harris [14,15] showed that a small modulation voltage applied to the plates of a 127°

electrostatic analyzer and in-phase detection of the analyzer current was a useful method for obtaining the derivative of an electron energy distribution. This technique allowed the convenient detection and display of the relatively weak Auger peaks, and enabled new studies of surface segregation and diffusion. Weber and Peria [16] utilized the Harris modulation technique with a low-energy electron diffraction (LEED) system to observe Auger peaks and to detect sub-monolayer coverages of K and Cs on Ge and Si substrates. Although the Harris papers [14,15] were published after the Weber and Peria work [16], publication of the former papers was delayed by an extended disagreement with referees [10].

At this time, LEED was being used to characterize the structures of single-crystal surfaces and of these surfaces with various adsorbates. Inferences were made from LEED patterns that particular surfaces were clean, but AES enabled much more definitive statements of surface cleanliness to be made.

A major event in 1967 was the publication of the first book from Siegbahn's group that described a broad range of XPS experiments [17]. This book also documented the chemical shifts that occurred for an atom in different binding states in molecules and solids.

Commercial instruments designed specifically for AES and XPS became available in the late 1960s. Since then, there has been a steady growth in instrumental capabilities:

- Improved cathodes for scanning Auger microscopy
- Improved X-ray monochromators
- Improved electron detectors
- Improved X-ray sources (and synchrotron radiation) for XPS
- Improved electron energy analyzers, with higher transmissions for a given energy resolution
- Angle-resolved XPS
- Improved methods for specimen handling (e.g., 300 mm Si wafers) and treatments
- Improved methods for charge control and charge correction
- Sputter-depth profiling for thin-film analyses
- Improved lateral resolutio (imaging and spectro-microscopy)
- Computer-controlled systems
- Extensive software for instrument control, data acquisition, and data analysis

These instrumental developments have enabled many thousands of applications of AES and XPS for the development of new materials and processes, failure analysis, and quality control (Fig. 1).

4. Growth in Quality of Quantitative AES and XPS

A brief summary is given here of growth in the quality of quantitative AES and XPS. More details have been published elsewhere [2,18].

(a) Calibration of Instruments

Early interlaboratory comparison of AES and XPS energies showed much greater dispersion than had previously been suspected [19,20]. Extensive work at the National Institute of Standards and Technology (NIST) [21] and particularly at the UK National Physical laboratory (NPL) [22,23] provided data and procedures for calibration of the binding-energy (BE) and kinetic-energy (KE) scales of XPS and AES instruments, respectively. This work culminated in the adoption of formal procedures for the calibration of BE scales of XPS instruments and the calibration of KE scales of AES instruments by the International Organization for Standardization (ISO) [24] and ASTM International [25]. Other ISO and ASTM standards for surface analysis are described below.

The AES and XPS comparisons also showed spreads in the ratios of peak intensities from cleaned samples of Au and Cu of up to a factor 10 for XPS and 120 for AES [19,20]. Extensive work at NPL identified the factors responsible for these variations [26]. Software is available from NPL for the calibration of the intensity scales of individual AES and XPS instruments [27].

(b) Surface Sensitivity and Elastic-Scattering Effects

The basic material parameter describing the surface sensitivity of AES and XPS measurements is the inelastic mean free path (IMFP). Tanuma *et al*. [28] have reported an extensive series of IMFP calculations, and Powell and Jablonski [29] have reviewed these and other IMFP determinations.

Commonly used expressions for the signal-electron intensities in AES and XPS are based on the assumption (now known to be mistaken) that elastic-scattering effects can be neglected. Modified expressions are

available that take these effects into account [30]. Information depths and mean escape depths are also generally different from the values expected on the basis that elastic scattering can be neglected [31]. For measurements of film thicknesses, it is necessary to use the effective attenuation length (EAL) instead of the IMFP [32]. For XPS, the EAL depends on the instrumental configuration.

(c) Determination of Sample Morphology

Tougaard showed from model calculations that XPS peak intensities differed appreciably for different sample morphologies [33]. He has developed software with which information on sample morphology can be derived from analyses of AES and XPS spectra [34].

5. Growth in Analytical Resources for AES and XPS

While AES and XPS are conceptually simple, there can be many complications in experimental design, data acquisition, data analysis, and data interpretation. The International Union of Vacuum Science, Technique, and Applications sponsored a Workshop in 2002 to develop the structure and initial content of a possible future expert system for XPS [35]. These discussions led to many recommendations for elements of an expert system and constitute a valuable source of best practices for XPS.

NIST has developed five databases to support AES and XPS measurements [36]:

- XPS Database
- Electron Elastic-Scattering Cross-Section Database
- Electron Inelastic-Mean-Free-Path Database
- Electron Effective-Attenuation-Length Database
- Database for the Simulation of Electron Spectra for Surface Analysis (SESSA)

An example of a SESSA application is given in the following section.

Reference spectra and related analytical data are available from a number of sources [2,37]. Data-analysis software is available from various vendors [37]. Documentary standards for terminology, sample preparation and handling, data transfer, and instrument performance are available from ISO and ASTM International for AES and XPS as well as other surface-analysis methods [24,25].

6. Distribution of N in SiON Films on Si by Angle-Resolved XPS

The NIST SESSA database [36,38] was designed for two main purposes. First, data are provided for the parameters needed in quantitative AES and XPS. Second, AES and XPS spectra can be simulated for thin-film structures with user-specified layer compositions and thicknesses. The compositions and thicknesses can then be adjusted to find maximum consistency between simulated and measured spectra.

The composition of films as a function of depth is frequently determined by analyses of angle-resolved XPS (ARXPS) data. One such application is the determination of the N composition in silicon oxynitride gate-dielectric films as a function of processing conditions. ARXPS data sets are analyzed by various algorithms that are based on a number of simplifying assumptions [39] that include the neglect of elastic scattering and the finite acceptance angle of the analyzer.

SESSA has been utilized to check the distinguishability of computed angular distributions of N 1s and O 1s intensities for a 2.5 nm SiON film on Si with different assumed amounts and distributions of N in the film for a common instrumental configuration [40]. Appreciable dispersion of the intensities was found only for the N 1s peak at an emission angle of 75° with respect to the surface normal. Conventional analyses of ARXPS data that include such large emission angles are unlikely to be valid due to angle-dependent changes of the EAL [40].

Similar SESSA simulations have been made for two models of photoelectron transport in the SiON/Si structure [41]. Model (i) is for elastic scattering switched "on" and an analyzer acceptance semi-angle of 12°. Model (ii) represents the conditions assumed in conventional analyses of ARXPS data (i.e., elastic scattering switched "off" and a very small analyzer acceptance semi-angle, in this case 0.5^o).

SESSA simulations were made for a 2.5 nm SiON film on Si with a linearly decreasing N composition from the surface (where the composition was $SiO_{1.2}N_{0.8}$) to the interface (where the oxide composition was SiO_2) [41]. Figure 2 shows a comparison of the N 1s and O 1s intensities for models (i) and (ii) at four emission angles (representing tilting of the sample). For emission angles of 0°, 30°, and 55°, there is a roughly constant reduction

of intensity that can be empirically represented by an appropriate EAL that is smaller than the corresponding IMFP; note, however, that the fractional intensity reduction is not constant with angle. For the 75° emission angle, where elastic-scattering effects are strongest, the difference between models (i) and (ii) is more pronounced. Qualitatively similar results have been obtained for other assumed N composition profiles in SiON [41].

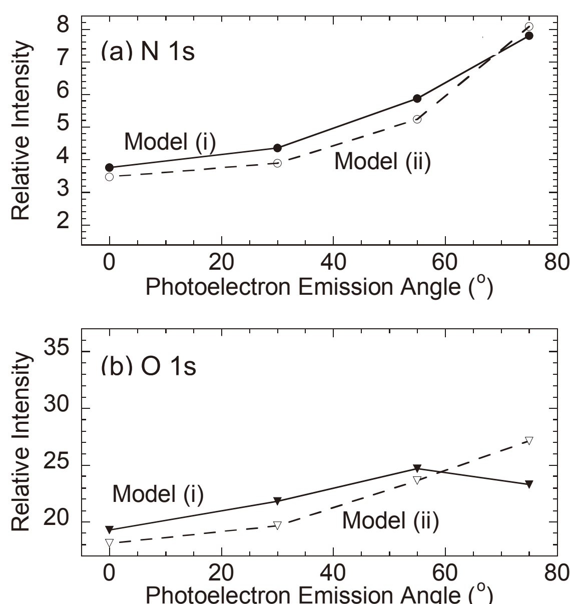

Fig. 2. Relative intensity of (a) N 1s and (b) O 1s peak intensities as a function of photoelectron emission angle for a 2.5 nm SiON film on Si with an assumed linearly decreasing N concentration with depth from the surface using Models (i) and (ii) (see text).

7. Outlook

Further growth of AES and XPS could occur in the following areas:

- Improved lateral resolution for XPS, particularly through greater use of synchrotron radiation. "Compact" sources of synchrotron radiation are expected to be available shortly, and these could provide facilities dedicated to specific types of applications.
- Detection of emitted ions from samples damaged by intense electron or X-ray beams.
- Development of "low-cost" instruments designed for specific applications.
- Development of software with more extensive and better-integrated databases.
- Development of expert systems.
- Characterization of nanometer thin-film materials by surface, bulk, and thin-film analytical techniques.
- Chemical and physical characterization of nanomaterials.

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