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APPLIED SURFACE ANALYSIS

Barr/Davis, editors

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Foreword

The symposium on Applied Surface Analysis was held on 28 Feb.-1 March 1978 in conjunction with the 29th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in Cleveland, Ohio. The symposium was jointly sponsored by the Pittsburgh Conference and by the American Society for Testing and Materials through its Committee E-42 on Surface Analysis. T. L. Barr, UOP Inc., and L. E. Davis, Perkin-Elmer Corp., served as cochairmen of the symposium and coeditors of this publication.

Related ASTM Publications

Surface Analysis Techniques for Metallurgical Applications, STP 596 (1976), \$15.00, 04-596000-28

Adhesion Measurement of Thin Films, Thick Films, and Bulk Coatings, STP 640 (1978), \$39.25, 04-640000-25

Quantitative Surface Analysis of Materials, STP 643 (1978), \$21.50, 04-643000-39

Report on Available Standard Samples, Reference Samples, and High-Purity Materials for Spectrochemical Analysis (1963), DS 2 (1964), \$4.50, 05-002000-39

A Note of Appreciation to Reviewers

This publication is made possible by the authors and, also, the unheralded efforts of the reviewers. This body of technical experts whose dedication, sacrifice of time and effort, and collective wisdom in reviewing the papers must be acknowledged. The quality level of ASTM publications is a direct function of their respected opinions. On behalf of ASTM we acknowledge with appreciation their contribution.

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Contents

Introduction	1
Application of Surface Analysis for Electronic Devices—P. H. HOLLOWAY	5
Electron Spectroscopy in Catalyst Research—J. S. BRINEN	24
<i>In Situ</i> AES and ESCA Analysis of Iron Oxides Formed by a Galvanic Cell—D. A. STOUT, G. GAVELLI, J. B. LUMSDEN, AND R. W. STAEHLE	42
Comparative AES, ESCA, and SIMS Investigation of Oxide Films on Iron-Nickel-Chromium Alloys—G. R. CONNER	54
Surface Composition of Copper-Nickel Alloys—D. T. LING, I. LINDAU, J. N. MILLER, AND W. E. SPICER	66
New Developments in Secondary Ion Mass Spectrometry—H. W. WERNER	81
Ion Scattering Spectroscopy—E. TAGLAUER AND W. HEILAND	111
Data Treatment in Electron and Ion Spectroscopy—W. L. BAUN	125
Energy Calibration of Electron Spectrometers—C. D. WAGNER	137
Application of a Vacuum Transfer Device for Exchange of Surface Standards—J. P. HOBSON AND E. V. KORNELSEN	148
Digital Data Acquisition and Processing in an Auger Electron Spectrometer—Y. E. STRAUSSER	158
Application of XPS Analysis to Research into the Causes of Corrosion—J. E. CASTLE	182
Summary	199
Index	203

Introduction

This volume contains papers read at a symposium held in Cleveland, Ohio, on the 28th of February and the 1st of March 1978. The symposium, entitled "Applied Surface Analysis," was part of the 29th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy and was sponsored jointly by that conference and the American Society for Testing and Materials. Five sessions of invited and contributed papers on a wide variety of topics dealing with surface analysis were presented. Because of conflicts, not all of the papers presented are contained in the present volume; however, the selections contained herein are representative of the presentations given. The meeting was widely attended, and it was apparent from the response that, although many of the presentations were quite detailed, the attendees (ranging from specialists in surface analysis to industrial research managers) generally benefited from the symposium.

The objectives of the symposium placed heavy stress on the word "applied." Thus, it was the intention of the symposium organizers and ASTM that this meeting would concentrate on the applications, rather than the principles, of surface science. This was not done to belittle the fundamental importance of the latter area but, rather, to provide, for the first time, a forum devoted solely to the discussion of the technology and problems inherent in, and in some cases unique to, applications of surface analysis. For this reason, scientists from industrial and governmental research laboratories were encouraged to participate actively, as well as to attend. In this vein, the organizers hoped that the attendees (and the eventual readers of this volume) would gain some knowledge, not only of surface science itself, but also of the present level and direction of the science in its more applied areas.

The surface analysis techniques dealt with in the symposium included: electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy (AES or Auger), secondary ion mass spectrometry (SIMS), ion scattering spectroscopy (ISS), and ultraviolet photoelectron spectroscopy (UPS). Some of the instrument problem areas examined included: energy calibration, multitechnique application, data treatment, and display and vacuum transfer. The areas of use considered were: catalysis, corrosion, metallurgy, polymers, adhesives, identification of intermediate organic substances, alloy composition and segregation detection, trace analysis, oxidation, electrochemistry, and air pollution.

The better-known of the techniques described in this book have, in some instances, reached a state of general acceptance, for example, Auger. However, the versatility and utility of these methods have in the past not been as well publicized as some of their more ostentatious characteristics. One of the purposes of the present study is to present discussions of the techniques that emphasize their broader aspects. In order to accomplish this, interconnected, comparative contributions were sought from prominent scientists in many of the subdisciplines.

The importance of this undertaking is reflected in its originality; however, its total merit extends far beyond novelty. Surface analysis is an unusual branch of the analytical disciplines in that a combination of the apparent "fragility" of the physical and chemical state of a surface, and the sensitivity of the existing techniques have, in the past, led some practitioners to conclude that the methodologies were useful only for the examination of pure, well-characterized materials. This "purest" reputation had, in fact, become a part of the folklore of surface science, particularly for ESCA. A partial refutation of this attitude is one of the general purposes of this publication.

The labels mentioned here for surface science techniques may be unfamiliar to some readers because it has become common to divide surface analysis into categories based upon the various excitation sources employed, rather than use names based upon the particular results. In this manner, the major areas of analysis often are labeled electron, photon, or ion techniques. This type of labeling is not, however, entirely satisfactory because of the misconceptions created when different excitation sources are employed for the same spectroscopy. In any case, explicit designations for areas of surface analysis sometimes promote a disturbing lack of awareness of the common nature of many of the problems faced by all of the spectroscopies. This latter feature is both implicitly and explicitly considered in the following presentations. Thus, for example, although ESCA and Auger are basically different spectroscopies with often different goals, they both have many subareas in common, for example, ultrahigh vacuum and sputter etching. In point of fact, improvements of ESCA in quantitation and of Auger in chemical analysis may eventually make the two disciplines interchangeable. Some presently existing differences are not, in fact, as real as they may at first seem. For example, the fact that sputtering is generally termed depth profiling by practitioners of Auger, and etching by ESCA users, is more a matter of semantics than of reality.

Each of the procedures to be described is endowed with a combination of unique attributes that might constitute a weak point for some other method. This is one of the major reasons for the recent emergence of multitechnique (or combination) analysis. This important development generally results in a system in which several spectroscopies are used in configuration around common vacuum, transfer, and treatment subsystems. Such setups have the virtue of omitting time-consuming, often surface-destructive, sample exchange procedures. As is often the case, however, this approach is not without its unique pitfalls and problem areas. The upkeep of a multitechnique system may, for example, be

more expensive than that for separate systems, since trouble in the multitechnique vacuum system may remove from use three or four expensive techniques, rather than one. In addition, many procedures are, by nature, more surface destructive than others. Thus, when different techniques are to be sequentially applied, the order of analysis becomes an important constraint, and sometimes this prescribed order is not conducive to maximum utilization of the attributes of the separate techniques. However, when multitechnique analysis is used adroitly, all of the potential problems should be overshadowed by the advantages, particularly the significant capital savings involved. In fact, it is becoming more and more apparent that a self-consistent "total" examination of the complex surfaces of materials requires more than one technique, and this can best be accomplished by *careful* application of multitechnique analysis.

The growing role that surface analysis will play in future materials studies is apparent when one considers the types of materials involved. Semiconductors, thin-film sensors, and catalysts are entities whose surface properties strongly influence their useful behavior. In view of this, a very important question concerns the extent and the significance of the variances between analytical results obtained by surface methods and those obtained using (more conventional) bulk-oriented techniques. Sometimes the variations discovered are large but relatively unimportant (for example, in the case of air-passivated metal surfaces), in other cases, the differences may be miniscule but significant. In view of the significant disparity in the cost of bulk and surface methods, it is important that the full consequences of these differences be understood. This was one of the goals of this symposium.

The general discipline of surface analysis suffers from a common malady of our age, that is, a mushrooming growth rate. As a result of that growth, a veritable alphabet soup of acronyms has been created, with new techniques appearing in the literature almost monthly. Many of these procedures were too novel to be considered in a symposium devoted to "developing" use areas; however, time constraints and the innate prejudices of the organizers also led to the omission of a number of well-established procedures. The selections here were not meant to imply that the omitted techniques are necessarily less scientifically sound but, rather, that they may be somewhat less useful for general (applied) surface analysis than those described in this volume. Particular apologies are due to surface analysts utilizing EXAFS, Rutherford back scattering, and energy loss spectroscopy for the exclusion of these techniques.

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cochairman and coeditor.

Application of Surface Analysis for Electronic Devices

REFERENCE: Holloway, P. H., "Application of Surface Analysis for Electronic Devices," *Applied Surface Analysis, ASTM STP 699*, T. L. Barr and L. E. Davis, Eds., American Society for Testing and Materials, 1980, pp. 5-23.

ABSTRACT: The principles of Auger electron spectroscopy, X-ray photoelectron spectroscopy, ion scattering spectroscopy, and secondary ion mass spectrometry are discussed, and their applications in the processing of electronic devices are illustrated. Electronic device processing is divided into five areas: (1) substrate and substrate processing, (2) deposited films, (3) patterning, (4) interconnection, and (5) compatibility. Examples are given in each area in which surface analysis has been used to great advantage in solving processing problems and improving technology.

KEY WORDS: surface analysis, electron devices, substrate, deposited films, patterning, bonding, soldering, Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), secondary ion mass spectrometry (SIMS)

Since their inception in the late 1960s and early 1970s Auger electron spectroscopy (AES) [1-4],² X-ray photoelectron spectroscopy (XPS) [5-9], ion scattering spectroscopy (ISS) [7,10,11], and secondary ion mass spectrometry (SIMS) [8,12,13] have proven to be of great value in the electronics industry. This results from their shallow detection depth (generally on the order of 1 nm) which allows analysis to be made of the surfaces of electronic devices. Knowledge of surface composition is essential, since reliability data indicate that 39 percent of device failures are surface related [14]. Another 28 percent of device failures are related to defects in the oxide, metallization, wire, or bonds; these are often surface, near-surface, or interface related, and the surface-sensitive analytical techniques can be combined with mechanical sectioning or ion sputtering to study depth distributions and interfacial regions. In addition to the shallow detection depth, surface-sensitive analytical techniques exhibit good sensitivity for elements of low and high atomic number; this characteristic often

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²The italic numbers in brackets refer to the list of references appended to this paper.

proves valuable in the analysis of devices, as is illustrated further on in this paper by actual applications. However, before discussion of these applications, the principles behind the analytical techniques will be discussed.

Analytical Techniques

The physical phenomena upon which the surface-sensitive analytical techniques are based date back to the early 1900s; however, the rapid development of the techniques to their current status has occurred over the last decade. Developments in ultrahigh vacuum techniques, in energy and mass analyzers, and in data manipulation techniques (for example, potential-modulation differentiation) have contributed to the rapid growth and widespread interest in the analytical techniques. The critical steps in the development of surface analysis have been summarized in Ref. 15.

The Auger electron and X-ray photoelectron processes both involve the identification of elements by measurement of the energy of an ejected electron, as shown in Fig. 1. For either spectroscopy, the process is started by the ejection of a core-level electron from a surface atom. Since characteristic X-rays are used as the probe in XPS, the ejected photoelectron has a very well defined energy, as shown in Fig. 1. Beyond simple elemental analysis from the unique energy of

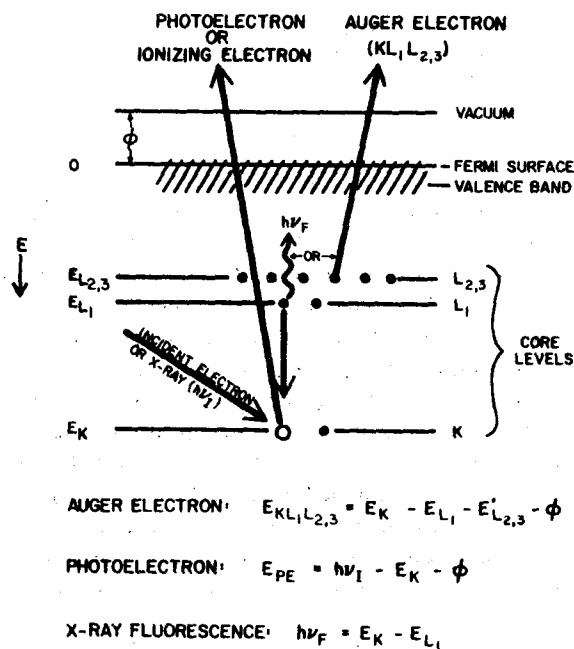


FIG. 1—Schematic representation of the photoelectron and Auger electron processes, showing the energy level transitions.

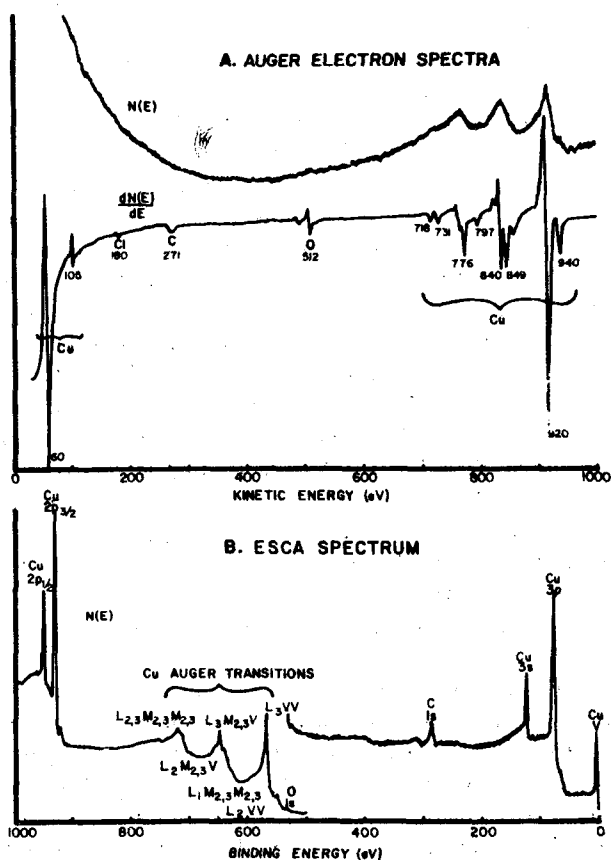


FIG. 2—Typical electron (AES) and X-ray-excited (XPS or ESCA) spectra from copper contaminated with chlorine, carbon, and oxygen (from Ref 15).

photoelectrons, changes in the valence band cause small but detectable shifts in the core levels, which can be used to determine the chemical state of the element (and hence the acronym ESCA—electron spectroscopy for chemical analysis). A typical ESCA spectrum from contaminated copper is shown in Fig. 2.

When primary electrons are used for ionization instead of X-rays, the energy transferred to the ionizing electron varies over the range between the binding energy of K-shell electrons, E_K , and the kinetic energy of the primary electron, E_p , and the ionizing electron is generally not used for material analysis. Whether X-rays or electrons are used for creating the core hole, the surface atom is left in an excited state by the event and will return to a state nearer to the ground state by the decay of an upper-shell electron (for example, an L-shell electron in Fig. 1) into the K core hole. The excess energy from this transition either is released as a characteristic fluorescent X-ray, or can be transferred to another

electron (either an L-shell or a valence electron in this example), which is ejected as an Auger electron. Since the released energy ($E_K - E_{L_1}$) and the binding energy of the Auger electron ($E_{L_{2,3}}$ in Fig. 1) are related to atomic energy levels, the energy of Auger electrons is unique and useful for elemental identification. The Auger transitions are designated by the three letters in the sequential step; therefore, the Auger electron in Fig. 1 is designated as a $KL_1L_{2,3}$ transition. Auger electron and fluorescent X-ray emission are complementary processes (that is, the sum of their probability is unity), but for transitions with an energy $\lesssim 2000$ V, the probability of Auger emission is near unity. Auger electrons can be detected for all elements (except hydrogen and helium) by using KLL, LMM, MNN, and NOO Auger transitions, depending upon the atomic number of the element of interest. Electron- and X-ray-excited Auger peaks are both shown in Fig. 2. The XPS spectrum containing Auger transitions is plotted as the number of electrons with an energy, $N(E)$, versus that energy. Note that the background intensity is low for XPS in relation to the $N(E)$ spectrum for electron-excited AES (by convention AES refers to electron-excited Auger electron spectroscopy) because X-rays generate fewer electrons. To suppress the high background in AES and thereby allow signal enhancement, the technique of potential modulation differentiation [16] is often used. The $dN(E)/dE$ curve in Fig. 2 is the result of such a differentiation and is the common form of AES data.

In ISS a surface is bombarded with noble gas ions (usually helium or neon) at a fixed angle of incidence. A small fraction of the ions will be elastically scattered from surface atoms, with the amount of energy loss being defined by the expression in Fig. 3a. Thus the energy scale can be converted to a mass scale for elemental analysis. Essentially only the outermost atomic layer is analyzed since the probability of neutralization is extremely high if the primary ion penetrates beyond the first atomic layer.

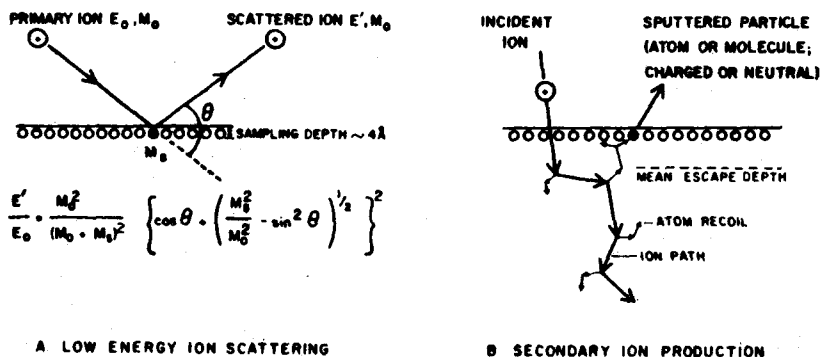


FIG. 3—Schematic representation of the primary phenomena in low-energy ion scattering (ISS) and the production of sputtered particles (SIMS). In SIMS the sputtered ions are analyzed.

SIMS utilizes a primary beam of ions to sputter material from a sample. A small fraction of the sputtered atoms and molecules will leave the sample as ions, which are usually detected with a quadrupole mass analyzer. The sputtering process is very complicated (Fig. 3b) [17], and the ability to predict secondary ion yields, which vary with the element and chemical states over several orders of magnitude, is very poor. However, because of the high sensitivity of modern mass analyzers, in some instances SIMS can detect extremely small concentrations of elements. Spectra from ISS and SIMS are shown in Fig. 4 for a gold film partially covered with chromium oxide and other contaminants. The SIMS data

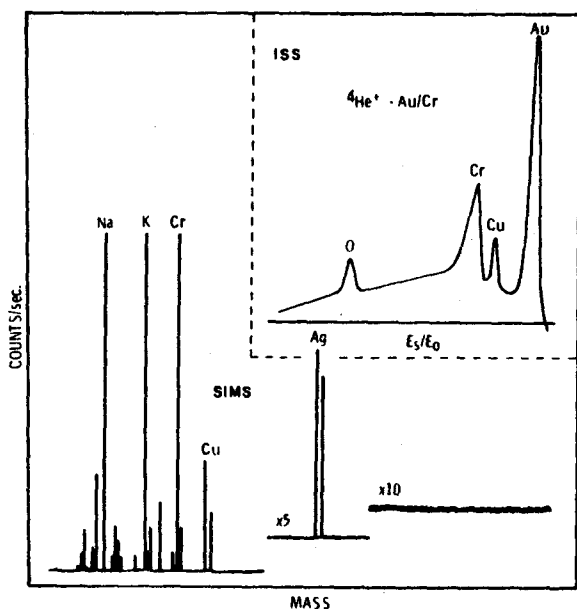


FIG. 4—Typical ISS (upper right) and SIMS (bottom) spectra from gold contaminated with Cr_2O_3 , sodium, potassium, copper, and silver (from Ref 15).

exhibit low background, good sensitivity to trace impurities, and good isotopic mass resolution, but total insensitivity to the dominant species—gold. The ISS data clearly show the presence of gold, but cannot detect the trace elements. The mass resolution is poor for ISS, especially at higher masses; the silver detected by SIMS is hidden in the broad gold ISS peak.

All four of the techniques just mentioned have shallow detection depths. For AES and XPS (ESCA), the mean free path of electrons in solids, λ , is energy dependent, but ranges from ~ 0.5 nm at ~ 100 eV to ~ 3 nm at ~ 2000 eV; 99 percent of the AES or XPS signal originates within 3λ of the outer surface. The previous discussion indicates that ISS is very sensitive to the top atomic layer,

and data for SIMS suggest that 67 percent of the signal arises from the outer 2 to 3 nm. The equipment requirements for these techniques and other details on sample requirements, surface alteration, lateral distribution, etc., are given in Ref 15.

Applications in Device Processing

Deal [18] has discussed the processing of integrated circuits and particularly those areas where surface analysis could be used to improve device reliability and processing yield. The specific processing scheme listed by Deal will not be followed in the present discussion. Instead, five general areas of concern in the processing of any electronic device will be considered: (1) substrate and substrate processing, (2) deposited films, (3) patterning, (4) interconnections, and (5) compatibility. The sequence just listed does not correspond to the actual processing of a device, but indicates general classification areas, several of which may be involved in any processing stage. The substrate and substrate processing area deals with the cleaning, etching, etc., of silicon, germanium, compound semiconductors, or ceramics for hybrid microcircuits, and the oxidation, dopant diffusion, or implantation, etc., of semiconductor substrates. In the deposited film area we are concerned with deposition of oxide, nitride, and metallic films and their structure, impurities, and subsequent diffusion and reaction. The residues left during pattern definition and their removal are of concern in the area of patterning, and the bonding or soldering of integrated and hybrid microcircuits to connect them into an assembly are of interest in the interconnection area. Finally, compatibility is concerned with the transfer of material from the processing or packaging environment to the device. Surface analysis has provided insight into new technology and processing procedures for each of these areas, as will be illustrated by selected examples.

Substrate and Substrate Processing

AES has been used by Yang, Koliwad, and McGuire [19] to study various methods for cleaning silicon substrates prior to oxidation, dopant diffusion, and metal deposition. Their data show that carbon and oxygen are the most common impurities, and that chemical cleaning still leaves a large amount of carbon-containing impurities unless a strong oxidizing reagent is also used. Sputtering was unsatisfactory for cleaning since it activated the wafers towards rapid adsorption of atmospheric impurities upon their removal from the sputtering chamber. Plasma cleaning was the most effective procedure, as long as the proper gases were used in the plasma. Oxidizing gases lowered the carbon concentration to near the detection limits.

With respect to clean silicon surfaces, Rowe and co-workers [20] have used high-resolution electron spectroscopy to identify surface electronic states on clean silicon wafers. Subsequent theoretical calculations by Hamann [21] and