

The Contribution of Surface Analysis and Surface Science to Technology*

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Abstract

Surface science is a rapidly growing field offering many scientific and technological challenges. New experimental and theoretical tools have been developed which can be used to probe, at a fundamental atomic and molecular level, the physics and chemistry of complex processes at solid surfaces. Surface characterization, particularly surface analysis, is now an integral part of many technologies and industries (e.g., catalysis, coatings, corrosion, semiconductor devices, computer, automobile and communications) for many different applications (e.g., failure analysis, quality control, process and device development). Characterization of surface properties and processes is similarly important in many areas of public concern (e.g., energy and environment). The concepts and techniques found useful for surface characterization are currently being extended to the characterization of solid-solid, solid-liquid and solid-gas interfaces. It is therefore expected that there will be significant developments in interface science and additional opportunities for technological applications in the coming decade.

1. Introduction

Over the past two decades there has been considerable growth in surface science and in the application of surface-characterization methods, particularly surface analysis, to a wide range of problems of technological interest (Powell 1978). This growth is evident in the large number of local, national and international meetings sponsored by major professional societies and many other groups; the growth is also evident in journal and book publications.

The purpose of this paper is to summarize key features of recent developments and to point out the impact of surface science and surface analysis in technological developments and problems. After a brief historical survey of development up to about 1960 (Section 2), a short description will be given of development in surface science in the past two decades (Section 3). The application of surface analysis to technological problems is reviewed in Section 4. Expected developments in interface characterization are pointed out in Section 5.

2. Historical Perspective

Surface and interface technologies have developed over many centuries in such areas as the separation of minerals, the joining of metals, the development of protective coatings, and the creation of many art forms. In the present century, the

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history of surface science and surface technology is interwoven with major discoveries and developments in other branches of science and technology: the discovery of thermionic-, photo-, field- and secondary-electron emission; the development of valves (tubes) for radio, television, computing and electronic equipment; the development of X-ray sources; the discovery of electron diffraction, electron microscopy and other electron-optical instrumentation; the development of vacuum science and technology; the investigations of discharges in gases; the development of lamps; the development of semiconductor devices; investigations of oxidation and corrosion; the studies of the interactions of electrons, ions, atoms and molecules with surfaces; and the development of catalysts.

In a review published ten years after the discovery of electron diffraction in 1927, Finch and Wilman (1937) wrote that 'the new technique is being successfully applied to such varied surface problems as thermionic and photoelectric emission, conduction of electricity in thin films, surface catalysis, electrodeposition, crystal growth, the colloidal state, corrosion, wear, and lubrication.' Although there is no doubt that electron diffraction was of considerable value in a variety of studies of practical interest, many problems could not be solved due to inadequate surface sensitivity, lack of elemental specificity, or to the lack of other required surface characterizations (see Section 3).

A number of techniques with a high degree of surface sensitivity were developed in the period 1930–60. These techniques included ellipsometry, field-electron microscopy, field-ion microscopy, and the measurement of work function changes with which a high degree of surface sensitivity could be realized. Much useful information about surface properties and processes could be obtained in controlled experiments with these methods but they could not be used to investigate a wide range of practical problems because elemental species in an 'unknown' sample could not be identified. In addition, the field-emission methods were restricted then to the refractory metals.

3. Recent Development of Surface Science and Technological Applications

The growth of surface science since the early nineteen sixties is due to a number of concurrent developments: the routine attainment of ultrahigh vacuums (pressure of 10^{-7} – 10^{-8} Pa) in experimental chambers; the development of more sensitive and specific techniques; the growing availability of commercial surface-characterization instrumentation, particularly for surface analysis; extension of solid-state, atomic and molecular theory to surface properties and processes; synergistic interactions between theory and experiment so that surface phenomena could be interpreted on a microscopic scale; and the successful use of surface analysis to solve a wide range of practical problems.

A principal objective of surface science is to understand the physical and chemical properties of surfaces in relation to bulk properties and external forces (e.g., changes of temperature, chemical environment and interactions with radiation). It is useful to define a surface phase as that region of a sample surface which has properties different from the bulk (Powell 1980). The distinguishability of a surface phase thus depends on the observation of a specific property (e.g., composition or structure) and can in practice be a function of the material and the measurement technique. In many situations of scientific interest, the surface phase may be the 'outermost' layer of atoms. Specific regions of a surface phase (e.g., atomic steps and domains of

adsorbed atoms or molecules) may be of importance. It is convenient to classify surface properties into two groups. The first group consisting of basic properties includes the surface composition, the surface atomic structure, the surface electronic structure, the motions of surface atoms (e.g., vibrations, diffusion and evaporation), surface defects and surface topography. The second group consisting of applied properties includes electrical and optical properties, adhesion, bonding, catalytic activity, plating, durability, corrosion, decoration, leaching, segregation, lubrication, reactivity, oxidation and passivation, amongst others.

Many techniques are in use for the measurement of basic and applied surface properties (Powell 1978). The large number of techniques and acronyms is confusing to those who are unfamiliar with the field, but it may be helpful to point out that the variety of techniques is associated with the large number of basic and applied properties to be measured and the different optimizations (e.g., sensitivity, specificity, spatial resolution, sample heterogeneity, chemical information and cost) required for different types of samples and problems. The diversity of experimental configurations is exemplified by the fact that electron beams can be used to bombard sample surfaces, and scattered or secondary electrons can be detected in ways that will yield composition information (Auger-electron spectroscopy), atomic-structure information (low-energy electron diffraction), electronic-structure information (Auger-electron spectroscopy, electron energy-loss spectroscopy and secondary-electron spectroscopy), and surface topography (scanning electron microscopy).

For scientific applications, it is often necessary to determine the surface composition, surface atomic structure, and the surface electronic structure of carefully prepared surfaces (e.g., single-crystal samples, single-crystal samples with steps, small clusters or particles, or surfaces with various amounts of adsorbed gases of deposited atoms or molecules) and to evaluate the physical and chemical properties in terms of current theory and other knowledge. The objective of the work may be to test a theory, to examine the validity of a particular surface-characterization method, or to gain fundamental understanding of a particular applied property or process. One of the key developments of the past two decades is that many surface properties can be interpreted in terms of microscopic (i.e., atomic and molecular) interactions and properties. While measurements of ellipsometric parameters and work functions could be modelled in terms of atomic and molecular properties, for example, only recently has it been possible to identify surface species unambiguously and to interpret particular properties in terms of specific orbitals or surface states.

Surface science has advanced beyond the stage of testing a particular (new or improved) measurement method with a well-studied sample (e.g., carbon monoxide on tungsten). While many interesting and worthwhile scientific problems remain to be tackled on such classic sample surfaces (e.g., two-dimensional phase transitions, the nature of bonding and reactions at atomic steps, and the identification of 'active sites' and intermediate species in surface reactions), the recently developed surface-characterization methods (and the related concepts) are being utilized in scientific studies of technological interest. Examples of such studies include the following:

(1) Auger-electron spectroscopy (AES) has been applied to identify surface species on a model single-crystal catalyst used in the reaction to produce methane from carbon monoxide and hydrogen (Goodman *et al.* 1980). The reaction rate could be correlated with the concentration of active carbidic carbon on the surface over a wide range of reaction variables.

(2) Photoelectron spectroscopy (PES), AES and low-energy electron diffraction (LEED) have been utilized in investigations of the chemical effects of very thin layers of one metal deposited on another. Sachtler *et al.* (1980) have shown a fivefold enhancement in the rate of cyclohexene dehydrogenation to benzene when one monolayer of gold is deposited on a Pt (100) surface. An Au (100) surface is inactive for this reaction but the deposition of two monolayers of platinum increased the reaction rate to a value about six times higher than that for a clean Pt (100) surface. In other work, monolayer quantities of Pd deposited on Nb or Ta enhanced the hydrogen uptake by over an order of magnitude (El-Batanouny *et al.* 1981).

(3) Submonolayer quantities of Al deposited on CdS and CdSe and then covered by overlayer contacts of 15 nm Au have been used to tune the effective Schottky-barrier heights for these rectifying contacts over the available range (Brucker and Brillson 1981). Parallel studies with LEED and PES of thin Al layers on GaAs have shown profound modifications of structure and composition in the interface region (Duke *et al.* 1980).

(4) The structure and coordination of dispersed monometallic and bimetallic cluster catalysts have been investigated with the extended X-ray absorption fine structure (EXAFS) method (Via *et al.* 1981). Bimetallic clusters of Ru and Cu have been shown to consist of a Ru core surrounded by Cu.

In these and similar investigations, novel insights have been obtained. This knowledge can and has been applied to predict, design, optimize and control surface properties or processes.

4. Technological Applications of Surface Analysis

Several techniques of surface analysis (Czanderna 1975) utilizing charged particles (AES, X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA), secondary-ion mass spectroscopy (SIMS), and ion-scattering spectroscopy (ISS)) are now in widespread use for a variety of technological purposes (Barr and Davis 1980; Casper and Powell 1982). Optical methods are also employed (Casper and Powell 1982), although there is a current emphasis on the charged-particle methods. For the more applied investigations, it is often necessary to determine the surface composition and surface morphology (i.e., distribution of surface phases) of a wide range of samples (e.g., catalysts, polymers, semiconductor devices, metal parts, ion-implanted materials, composite materials, compounds, coatings, thin-film devices, laser windows, display devices, solar devices, memory devices, electrical contacts, biomaterials, adhesives, seals, wear surfaces, energy-storage devices, walls of controlled-fusion reactors, building materials and flyash) and to relate the measured surface properties to other characteristics of the sample or its history. In many instances, other types of surface and bulk characterization may be needed to solve a particular technical problem.

Surface analysis is utilized for failure analysis, quality control, and process and device development in the semiconductor, petrochemical and metals industries and in a variety of other areas. The interface region between two solid phases (e.g., of a thin-film device) can be probed by sequential removal of surface material followed by characterization of the new surface. The interface between a solid and a fluid can be similarly probed by the removal of the fluid and analysis of the exposed

solid surface. A few illustrations of recent applications of surface-analysis methods follow:

(1) *Semiconductor devices.*—Devices of increasing density and complexity are being developed, and this trend has exacerbated problems of reliability, quality, yield and cost. Surface analysis has become essential in the development and monitoring of cleaning processes, while thin-film profiling (i.e., the variation of composition as a function of depth) has been invaluable in the study of the composition of dielectric films, dopant profiles, intermetallic diffusion and other thin-film interactions (Ryan and McGuire 1982). Surface analysis has provided valuable information in the development of plasma and chemical vapour deposition techniques, thermal oxidation, plasma oxidation, plasma etching and ion implantation (Holloway and McGuire 1980).

(2) *Catalysts.*—The XPS technique in particular has been utilized extensively in measurements of the chemical composition of catalyst surfaces, studies of catalyst deactivation, and chemical bonding on catalyst surfaces (Brinen 1980; Briggs 1980). Numerous studies have been made of the effects of poisons and promoters, support interactions, sintering, and of correlations of reaction rates with surface composition; Kugler and Steffgen (1979) gave illustrative examples for the specific case of Fischer-Tropsch synthesis.

(3) *Corrosion.*—AES and XPS have both been used to identify the nature of corrosion products formed on metals in gaseous and aqueous environments (Castle 1980; Baer and Thomas 1982). Parallel studies have been made on the growth and integrity of passive films. Solute segregation to grain boundaries in alloys with resultant fracture has been investigated successfully with AES (McMahon and Marchut 1978; Hench and Clark 1982). AES, XPS and SIMS have been utilized in studies of the chemical durability of glasses (Hench and Clark 1982) and of leaching phenomena in nuclear-waste packages (McIntyre 1982).

(4) *Polymers.*—XPS has been used in numerous investigations of polymer surfaces (Clark 1977; Andrade *et al.* 1977; Briggs 1980). Changes in surface properties (e.g., adhesion), chemical structure and morphology have been studied following chemical-derivatization reactions and plasma treatment (Clark 1977; Briggs 1980). Measurements have also been made of the effects of different treatments on the surfaces of polymers intended for biomedical applications (Andrade *et al.* 1977).

Most surface analyses that have been made to date have been qualitative, not quantitative. It seems intuitively clear, however, that the full potential of the various surface-analysis techniques will not be realized until surfaces analyses can be made with known accuracy (Powell 1980).

5. Concluding Remarks: Growing Importance of Interface Characterization

A brief survey has been given of recent applications of surface science and surface analysis to problems of technological interest. The charged-particle techniques in common use for surface science and surface analysis require that the sample be analysed in an ultrahigh or high-vacuum environment. While a great deal of significant information has been obtained, it is becoming clear that the solution of many scientific and technical problems requires the characterization of the interface region between two phases (see e.g. Czanderna and Gottschall 1982).

Interfaces have been investigated with the available surface-science and surface-analysis techniques in an ultrahigh vacuum after one of the phases has been removed, but changes often occur in interface composition and morphology during the removal of one phase. Non-destructive or *in situ* interface characterization is therefore to be preferred, and effort is currently being devoted to the development of new methods which can be used to characterize solid-solid, solid-liquid and solid-gas interfaces with the sensitivity, specificity, spatial resolution, etc. now achieved with surface-characterization methods. Promising techniques for interface characterization include EXAFS and infrared spectroscopy (Pfnur *et al.* 1980; Mahaffy and Dignam 1980), neutron inelastic scattering (Kelley *et al.* 1980), surface-enhanced Raman scattering (Furtak and Reyes 1980), analytical electron microscopy (Hren *et al.* 1979), Rutherford backscattering spectroscopy, ion channelling, ion-induced X-ray emission and nuclear reaction analysis (Wolicki *et al.* 1978), atom-probe field-ion microscopy (Ng *et al.* 1979), and inelastic electron tunnelling spectroscopy (Wolfram 1978).

It is believed that the next decade will show substantial growth in interface science and interface analysis. The impact on technology should be as significant as the impact over the past two decades of surface science and surface analysis.

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