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X-RAY PHOTOELECTRON SPECTROSCOPIC STUDIES OF ELECTRODE SURFACES

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X-Ray Photoelectron Spectroscopic Studies of Electrode Surfaces

Emphasis is on the development of x-ray photoelectron spectroscopy (XPS) in characterizing electrochemical reaction mechanisms. The advantages of XPS to the study of electrode surfaces are the depth sensitivity to most metals is quite high with the escape length of the emitted electrons occurring only through 10-20A of the sample surface. The measured binding energies are sensitive to the oxidation state of the metal atom. Underpotential deposition for silver and copper on platinum electrodes have been examined by both XPS and Auger.
spectroscopy. A combination of XPS and secondary ion mass spectrometry (SIMS) was designed and connected with two satellite vacuum systems via a set of magnetically driven transfer device. This configuration allowed each technique to have its own chamber for electrode preparation. High energy ion beams were investigated for use in the ion implantation of various substrates aimed at creating new materials with unusual properties. Initial studies were focused on use of copper, silver, and gold ion beams directed toward silicon dioxide and graphite.
I. Introduction

The basic objective of our AFOSR research has emphasized the development of x-ray photoelectron spectroscopy in characterizing electrochemical reaction mechanisms. During the last several years, we have focused our attention on developing XPS as a mechanistic aid in following electrode reactions, primarily those whose surfaces can be altered by the formation of oxide layers. In addition, the method has proved valuable in examining the surface chemistry of metal electrodes where monolayers of foreign metal ions can be deposited at underpotential. These studies are particularly relevant to electrocatalysis since trace metals interacting with an electrode surface can drastically alter the electrode characteristics. Finally, we have exploited the idea that the information gleaned about surfaces by XPS can be greatly enhanced by coupling this spectroscopy with other types such as secondary ion mass spectrometry (SIMS). Examples of the accomplishments relative to these specific objectives will not be discussed in more detail.

II. Results and Discussion

The major advantages of XPS to the study of electrode surfaces are that the depth sensitivity to most metals is quite high with the escape length of the emitted electrons occurring only through 10-20Å of the sample surface. In addition, the measured binding energies are sensitive to the oxidation state of the metal atom. Using our specially
designed apparatus for transferring the electrode into the vacuum system (1), we have successfully monitored the growth of PtO, Pt(OH)₂ and PtO₂ films on platinum oxidized in acidic media. It was also possible to monitor the thickness of the overlayer by following the intensity of the various peaks. For example, the limiting thickness of the "oxide I" was found to be 8Å (1). Higher acid concentrations also induced anion incorporation into the oxide layer which suggested that these components provided the mechanistic key to control the growth of oxide and to prevent multilayer PtO₂ growth on platinum electrodes.

The sensitivity of XPS makes it ideally suited to examining submonolayer quantities of impurities on electrodes. Certain metal ions, for example, are known to reduce below their thermodynamic potential, in the submonolayer regime. We have examined this underpotential deposition for Ag and Cu on Pt electrodes by both XPS and Auger spectroscopy(2). XPS chemical shifts of -0.65 and -0.95 eV vs. the bulk metal have been observed although no distinction was noted between the various underpotential states present in the cyclic voltammogram. The shifts were identical to vapor-deposited submonolayer films of Ag and Cu on Pt in the low coverage (θ ~ 0.1) limit. A gradual shift with coverage to the bulk metal value for the vapor-deposited films and a constant shift with coverage for the underpotential deposit indicated that islanding was present only in the evaporated films. Measurement of the Cu and Ag Auger spectra gave
results independent of the surface work function when compared to the XPS spectra. Interpretation of this Auger parameter is, however, at present ambiguous. These results provide an excellent beginning in our understanding of the electronic structure of these important electrode surfaces.

Of special recent interest is the incorporation of additional surface analysis methods to our XPS spectrometer. The combination of XPS and SIMS seems particularly appropriate since many of the disadvantages of XPS are offset by the additional capability of SIMS. Its ability to detect hydrogen is such an example. Our instrument design philosophy is to connect two satellite vacuum systems via a set of magnetically driven transfer devices (3). This configuration allows each technique to have its own chamber and allows a separate chamber for electrode preparation. This combined approach has been illustrated in numerous applications (4-8) of the study of metal/oxygen systems.

A final accomplishment in the work is the investigation of high energy ion beams for use in the ion implantation of various substrates aimed at the possibility of creating new materials with unusual properties (9,10). Our initial studies have been focused on the use of Cu⁺, Ag⁺ and Au⁺ ion beams directed toward SiO₂ and graphite. For these systems, the XPS measurements reveal the implanted atoms have atomic-like electronic structures similar to the underpotential deposition procedure discussed earlier. The relevance of these investigations to electrochemical studies is preliminary, but this idea has considerable future potential, since ion implantation methods could be used to
prepare high purity doped electrodes or to prepare corrosion resistance surfaces by implantation of trace quantities of transition metals.

In conclusion, our work has focused on the development of modern surface analysis methods, particularly XPS and SIMS, for the characterization of metal or electrochemically modified surfaces. The chemical specificity and surface sensitivity of these methods clearly provides a new dimension to our ability to characterize these systems. It will be particularly interesting in the future to extend these systems to more complex surfaces such as alloys and metals covered with organic films, since the electrochemical properties of these assemblages are only barely known.
References


III. Lectures and Travel Related to the Grant

Nicholas Winograd


5. University of Uppsala, Uppsala, Sweden, August 26, 1976, "Detection of High Mass Cluster Ions Sputtered from Bi Surfaces". (invited lecturer)


15. Shell Development Company, Houston, Texas, March 8, 1977, "X-ray Photoelectron Spectroscopy (ESCA) and Secondary Ion Mass Spectrometry (SIMS)". (invited lecturer)

16. University of Houston, Houston, Texas, March 9, 1977, "X-ray Photoelectron Spectroscopy (ESCA) and Secondary Ion Mass Spectrometry (SIMS)". (invited lecturer)

17. University of Pittsburgh, Pittsburgh, Pennsylvania, March 17, 1977, "X-ray Photoelectron Spectroscopy (ESCA) and Secondary Ion Mass Spectrometry (SIMS)". (invited lecturer)

18. Society of Electron Spectroscopy, Purdue University, West Lafayette, Indiana, March 31, 1977, "X-ray Photoelectron Spectroscopy (ESCA) and Secondary Ion Mass Spectrometry (SIMS)". (invited lecturer)


23. VII Annual Symposium on the Analytical Chemistry of Pollutants, Lake Lanier, Georgia, April 26, 1977, "ESCA and SIMS: A Multi-technique Approach to Surface Analysis". (invited lecturer)


27. VII International Vacuum and III International Conference on Solid Surfaces, Vienna, Austria, September 12-16, 1977, "Quantitative Surface Studies with X-ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectroscopy (SIMS)".


31. IBM, San Jose, California, December 5, 1977, "Low Energy Ion Impact Phenomena on Single Crystal Surfaces". (invited lecturer)


34. Naval Postgraduate School, Monterey, California, March 17, 1978, "Ion Impact Phenomena on Single Crystal Surfaces". (invited lecturer)


36. Surface Science and Catalysis Seminar, University of California and Lawrence Berkeley Laboratory, Berkeley, California, April 26, 1978, "Ion Impact Phenomena on Clean and Reacted Single Crystal Surfaces". (invited lecturer)


41. 4th Pennsylvania State Read Conference on Electrodeposition, University Park, Pennsylvania, August 7-11, 1978, "ESCA and Its Use in the Study of Electrodeposition". (invited lecturer)


43. Foster Lecture Colloquium, Department of Chemistry, University of New York at Buffalo, Buffalo, New York, November 1, 1978, "Close Encounters of Another Kind: Ion Solid Interactions". (invited lecturer)


45. Pennsylvania State University, University Park, Pennsylvania, January 14, 1979, "Understanding the Role of Solid Surfaces in Chemical Processes: Analysis by XPS and SIMS". (invited lecturer)

46. Department of Chemistry, Northwestern University, Evanston, Illinois, February 9, 1979, "Surface Structure Determination by Ion Bombardment of Single Crystals". (invited lecturer)

47. Colloquium, Upjohn, Kalamazoo, Michigan, February 20, 1979, "Surface Analysis by ESCA". (invited lecturer)


49. National Science Foundation, Washington, D.C., February 27, 1979, "Determination of Surface Structure with Ion Beams". (invited lecturer)

51. 177th American Chemical Society Meeting, Honolulu, Hawaii, April 1-6, 1979, "Surface Structure Determinations by Ion Bombardment of Single Crystals". (invited lecturer)

52. General Motors Technical Center, Research Laboratory, Warren, Michigan, April 16, 1979, "Surface Structure by Ion Bombardment of Single Crystals". (invited lecturer)

53. American Chemical Society, Midwest Regional Meeting, Columbus, Ohio, May 7-9, 1979, "SIMS and the Surface Analysis Problem". (invited lecturer)

54. Physical Electronics Conference, College Park, Maryland, June 19, 1979, "Surface Structure from Angle-Resolved SIMS".


57. Expo-Chem, Houston, Texas, October 22-25, 1979, "Surface Analysis with Ion Beams". (invited lecturer)

58. Analytical Chemistry Seminar, Texas A & M, College Station, Texas, October 26, 1979, "Determination of Surface Structure with Ion Beams".

IV. PUBLICATIONS


8. Formation of Small Metal Clusters By Ion Bombardment of Single Crystal Surfaces, B. J. Garrison, N. Winograd, and D. E. Harrison, Jr.,


V. HONORS AND AWARDS

Alfred P. Sloan Foundation Fellow 1974–1978

J. S. Guggenheim Memorial Foundation Fellow 1977–1978

VI. RESEARCH PERSONNEL

Principal Investigator: Professor Nicholas Winograd

Postdoctoral Associates: Dr. Theo Fleisch
                          Dr. Kwang Kim
                          Dr. Vaniecia Young

Research Assistants: Stephen Gaarenstroom
                     Richard Gibbs
                     Richard Hewitt
                     John Holland
                     John Brace
                     John Hammond