Dr. C.J. Powell
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Technical Activities 1986 Surface Science Division

C. J. Powell, Chief

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Center for Chemical Physics
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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, ***Secretary***
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Director***

ABSTRACT

This report summarizes technical activities of the NBS Surface Science Division during Fiscal Year 1986. These activities include surface-standards work, experimental and theoretical research in surface science, the development of improved measurement methods, and applications to important scientific and national problems. A listing is given of publications, talks, professional committee participation, and professional interactions by the Division staff.

key words: surface chemistry; surface physics; surface science; surface standards

FOREWORD

This report is a summary of the technical activities of the NBS Surface Science Division for the period October 1, 1985 to September 30, 1986. The report was prepared as part of the Annual Report of the Center for Chemical Physics within the National Measurement Laboratory of NBS.

The technical wok of the Division is separated formally into a task titled "Surface Science - Standards and Measurements" and a Surface Competence task, as outlined briefly in the Introduction. The former task has two principal activities, a Surface Standards Program and a Surface Measurement Program. Work performed for these two programs is reported in Sections 2 and 3, respectively, of the report while work performed for the competence task is reported in Section 4. There are a number of separate technical projects for each activity. Information is given on project objectives, results obtained during the past year, and the nature of planned activities.

Sections 5 and 6 of the report contain listings of papers published, papers submitted for publication, and talks presented during the year. Talks presented at the Division staff on professional committees in shown in Section 8 while internal and external scientific collaborations are described in Section 9. Visiting scientists who have worked in the Division during the year are identified in Section 10 and the Division staff is listed in Section 11.

Further information on the activities of the Division can be obtained by contacting the scientists identified in each project report or by writing Dr. C.J. Powell, Chemistry B-248, National Bureau of Standards, Gaithersburg, MD 20899 (telephone, 301-975-2534).

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SURFACE SCIENCE DIVISION

C.J. Powell, Chief

SUMMARY OF ACTIVITIES

Fiscal Year 1986

1. Introduction

A. Background

Over the last ten years, there has been a dramatic growth of surface science and its applications. This growth and its significance have been documented in detail in two major reports, the Pimentel report to the National Academy of Sciences on "Opportunities in Chemistry" (National Academy Press, Washington, D.C. 1985) and the Brinkman report to the National Academy of Sciences on "Physics Through the 1990s" (National Academy Press, Washington, D.C., 1986).

The Pimentel report identifies chemical catalysis as one of five research frontiers in chemistry. A major recommendation was that modern chemical techniques be applied to obtain a molecular-level and coherent understanding of catalysis that encompasses heterogeneous, homogeneous, photo-, electron-, and artificial enzyme catalysis. For heterogeneous catalysis, in particular, surface science methods can be applied to identify reaction mechanisms and rates important in molecular sieve synthesis and catalysis and in catalysis by metals and oxides. These methods also enable evaluations to be made of the direct effects of catalytic poisons and promoters and can be used to develop new conversion catalysts, catalytic substitutes for precious metals, and catalysts to improve the quality of air and water. In addition, chemistry at solid surfaces is discussed at some length as a prominent example of the intellectual frontiers associated with the national well-being and surface science instrumentation is similarly identified as a significant example of instrumentation needed for modern chemical analysis and research. Other opportunities identified in the Pimentel report include understanding molecular dynamics for the control of chemical reactions, understanding the properties of clusters and of reactions on their surfaces, and the role of surface chemistry in diverse areas ranging from the synthesis of novel materials to energy production, reduction of environmental pollution, increased national security, and improved economic competitiveness.

The Brinkman report identifies surfaces and interfaces as a key area of condensed-matter physics in one of the volumes of the report. Specific topics discussed are the determination of surface-atomic structure, spectroscopy of elementary excitations at surfaces, interactions of atoms and molecules with surfaces, characterization of the interfaces between a solid and either a solid, liquid, or gas phase, and surface theory. Numerous opportunities in these areas were specified including experiments and theory to define the dynamical processes when atoms and molecules interact with surfaces, critical phenomena at surfaces, and measurements of the kinetics of surface processes. Extensive connections of surface and interface science were identified with information processing, speech and data communications, energy generation, transportation, space technology, national security, and medical applications. The significant role of surface and interface characterization was also identified in sections of the volume on Scientific Interfaces and Technological Applications dealing with the physics-chemistry interface, materials science, and microelectronics. Finally, a number of key questions and opportunities in the general area of atomic physics, particularly those dealing with atomic and molecular excitations and dynamics, state-to-state chemistry, laser spectroscopy, and clusters, were described in the volume on atomic, molecular, and optical physics; these issues are also important in surface science and in fully utilizing a number of the surface spectroscopies.

In a third recent report "Research Briefings 1986" (National Academy Press, Washington, D.C., 1986), the science of interfaces and thin films is one of four areas of science and technology identified as having "high-leverage research opportunities." Topics discussed in this report include characterization of "buried" interfaces, the production and characterization of smooth, defect-free epitaxial films, reactivity and catalytic activity of ultrathin films, characterization of processes occurring at biomaterial-tissue interface, mechanical properties of fiber-reinforced composites, and improvement of thin films for corrosion prevention, amongst many others. These topics are vital in the development of improved microelectronic devices, biomaterials, new structural materials, and coatings as well as technologies for new materials and processes.

A large number of techniques are utilized for surface and interface characterization. A choice of one of more techniques is made typically on the basis of the property to be measured, the specimen material, and the specific needs (e.g., spatial resolution, chemical information, sensitivity, degree of difficulty, and cost). The most common type of surface measurement is the determination of surface composition. Most surface analyses now are qualitative but there is a growing demand for quantitative analyses with improved accuracy. At the present time, there are few standard procedures and limited reference data and reference materials. A variety of techniques is employed for the determination of surface atomic structures, surface electronic structure, and for investigations of surface processes such as reactions, diffusion, segregation, etc. Theories of the measurement process need to be developed for the newer techniques. For all techniques, there is a need for relevant procedures, tests to establish measurement reliability, and applicable reference data. In most cases, the measurement science needs to be developed since knowledge of the key concepts and parameters is often extremely limited.

The techniques utilized in surface science have generally been applied to characterize surfaces in an ultrahigh vacuum environment. The solution of many scientific and technical problems often requires removal of liquid- or gas-phase material prior to surface examination and/or the removal of solid-phase material to expose a region of interest. While this approach has often been successful, artifacts of many different types can arise during the removal of one or more phases. There is therefore a growing need for improved measurement methods that can be used for the *in situ* characterization of solid-solid, solid-liquid and solid-gas interfaces with the sensitivity, elemental specificity, and spatial resolution comparable to those attained with the current surface-characterization methods.

B. Goal, Objectives and Division Program

The goal of the Surface Science Division is to improve the quality of existing surface-characterization measurements and to extend the present capability. Specific objectives of the Division are:

(1) Perform experimental and theoretical research in surface science to provide a scientific base for surface-measurement methodology;

(2) Develop measurement methods and provide properties data for the physical and chemical characterization of surfaces and surface processes to meet identified needs of industry, government, and other groups;

(3) Develop standard procedures, calibration data, and reference materials in cooperation with national and international standards organizations; and

(4) Develop expertise in selected new areas of science in order that NBS can provide measurement services where needs are anticipated in the near future.

Objectives (1) through (3) are met organizationally through an NBS task titled "Surface Science-Standards and Measurements" (program codes 155, 156, and 272). The Division's program for this task is divided into two principal activities, a Surface Standards Program and a Surface Measurements Program. Work performed during the year in these two area is reported in Sections 2 and 3, respectively.

Objective (4) is met through the Surface Competence Program (program code 261). This task was established in October, 1984 and represents a new focus by the Division in two areas, "Novel Two-Dimensional Materials" and "State Characterization of Energetic Species Ejected from Surfaces". A separate report on these activities is given in Section 4.

The Division's program is supported financially by other NBS offices and by other Federal Agencies (in addition to the base support allocated by NBS, the National Measurement Laboratory and the Center for Chemical Physics). These arrangements enable the Division to meet NBS objectives and standards needs and also to contribute its expertise and facilities to important national programs. During FY86, support was received from the following offices and agencies:

Office of Standard Reference Data
- Surface Science: Sputtering Yield Data
- Workshop on Quantitative Surface Analysis

Office of Standard Reference Materials
- Characterization of Additional Lots of SRM2135
- Workshop on Quantitative Surface Analysis

NBS Brookhaven Project Coordinator
- Travel to Brookhaven National Synchrotron Light Source

Department of Energy
- Structure and Reactivity of Chemisorbed Species and Reaction Intermediates
- Structure and Reactivity: Applications of Neutron Inelastic Scattering and of Negative-Ion ESDIAD
- Laser Studies of Chemical Dynamics at the Gas-Solid Interface (joint with Molecular Spectroscopy Division)

Air Force Office of Scientific Research
- Laser Studies of Chemical Dynamics at the Gas-Solid Interface (joint with Molecular Spectroscopy Division)

Office of Naval Research
- Use of Synchrotron Radiation to Characterize Oxide Surfaces

U.S.-Spain Joint Committee for Scientific and Technological Cooperation
- Structure and Reactivity in Catalysis by Metals and Oxides

C. Technical Output and Professional Interactions

Sections 5 and 6 of this report contain listings of the publications and talks, respectively, for the past year by Surface Science Division staff and for projects supported by the Division.

Many members of the Division staff hold leadership positions in professional societies and groups, as listed in Section 8. These interactions not only reflect the professional esteem in which these staff members are held but provide useful mechanisms for both disseminating the results of NBS work and for learning of significant measurement problems being faced by those using surface-characterization equipment.

Interest in surface science and surface characterization at NBS continues to grow. The Division has had an active Seminar program, as indicated in Section 7, and these seminars have been attended by other NBS staff. The Division staff also participates in an informal weekly lunch meeting, attended by scientists from a number of NBS organizational units, at which developments in surface science are discussed. Members of the Division staff are frequently consulted on a wide range of NBS problems.

Much of the Division's work is carried out in collaboration with other scientists within the Center for Chemical Physics, within NBS, within the U.S.A., and internationally. The nature of these collaborations is shown in Section 9. These collaborations are considered important because they enable a relatively small Division staff to work synergistically with other experts, they enable us to have access to unique facilities or expertise, and they enable our expertise to be extended to a larger range of important scientific and technical problems.

The Division has been fortunate in having seventeen visiting scientists work at NBS for varying periods during the past year, as indicated in Section 10. These scientists enrich our staff and our projects. A further enrichment of our programs comes from Postdoctoral Research Associates who typically hold two-year appointments; five Postdoctoral Research Associates worked in the Division during FY 1986.

2. SURFACE STANDARDS PROGRAM

G. P. Chambers, W. F. Egelhoff, Jr., N. E. Erickson, J. Fine,
Y. Hashiguchi, R. D. Kelley, R. L. Kurtz, T. E. Madey,
D. Marton, C. J. Powell, R. Stockbauer, and S. Tanuma

The term "surface standards" is intended to cover a broad range of activities that are directed to improving the quality of surface-characterization measurements through: (1) development of needed reference data and standard reference materials; (2) leadership in standards-committee activities, the development of standard practices, and other actions to improve the accuracy and reliability of surface-analysis measurements; and (3) publication of review articles and books that enable scientists to make surface-characterization measurements of the needed quality.

A. Reference Data

We describe here results of projects in which needed reference data are being generated. Section 2.C includes recent review articles by Division Staff that summarize and evaluate data required in a number of surface spectroscopies.

1. Sputtering Yield Data Compilation
(J. Fine and G. P. Chambers)

Sputtering techniques for depth-profile analysis are presently being used in conjunction with a number of surface analytical methods to analyze compositional changes of materials at surfaces and at interfaces. Many of these techniques have now progressed to the point of being able to provide quantitative sputter-depth-profile information yet the necessary sputtering yield data is not readily available in easy-to-use, evaluated form.

We are preparing a compilation of evaluated sputtering-yield data for those parameters that will have specific use in surface analysis and depth profiling. This work is supported by the NBS Office of Standard Reference Data. Our compilation will be in tabular form for those ion species (Ne, Ar, Kr, Xe, O_2, N_2, Cs) and energies (0.5 to 20 keV) and angles of incidence used in surface characterization. The compilation will contain sputtering yields for elemental targets only.

The HP-1000 Data System in the Center for Chemical Physics is being used for the data compilation. Dr. D. Neumann and members of his group have provided guidance as well as technical assistance with the software development.

Two interactive data-base management programs were previously developed to handle the specific needs of the data compilation. The structure developed allows easy data entry into one of these data bases; information can then be transferred to the second data base for rapid access and searching. Additional software has been written to sort and tabulate the searched data in a format suitable for publication. In this past year extensive use was made of our on-line abstract searching capability in order to bring our reference files up to date. Abstract searching has been completed and checked for completeness by making selected author searches. Sputtering yield papers have been identified and compiled, and data has been abstracted and entered into our data base. Work has begun on abstracting certain experimental parameters which will be used to evaluate the reliability of the sputtering yield data.

In the coming year, we intend to make an evaluation of the sputtering yield data available for elemental targets. These data are to be assigned a "quality rating" which will be determined from an evaluation of the measurement method and the conditions under which the measurements were made. This evaluation will include an assessment based on the combined effect of ambient vacuum condition, target reactivity, and rate of sputtering. We will compile this evaluated data in both tabular and graphical form for those parameters of interest to the surface-analysis and sputter-depth-profiling community.

2. Reference Data for the Calibration of the Energy Scales of X-Ray Photoelectron Spectrometers and Auger-Electron Spectrometers

(N. E. Erickson, S. Tanuma, and C. J. Powell)

The energy scales of x-ray photoelectron spectroscopy (XPS) and Auger-electron spectroscopy (AES) instruments need to be calibrated so that measurements of core-electron binding energies (BEs) by XPS or electron kinetic energies (KEs) by AES can be transferred meaningfully from one laboratory to another. The principal motivation of many practical BE and KE measurements is in the determination of the so-called chemical shifts in the energies from which chemical-state information can be obtained. Calibration of the XPS and AES energy scales enables reliable use of the available BE and KE data (if these have been acquired on calibrated instruments). The accuracy required in the calibration of the BE scales in XPS is typically 0.1 eV or better and of the KE scales in AES is typically 1 eV or better. Round robins conducted by NBS staff members about eight years ago indicated that the accuracies of BE and KE measurements then could be appreciably inferior to those required for valid chemical-state identification.

Several years ago, we made preliminary measurements of the BEs by XPS for the principal core levels of Cu, Ag, and Au and of the Auger-electron KEs from the same metals. It was hoped that data of this type would be convenient and satisfactory for the calibration of individual instruments. Unfortunately, the electronics on our instrument were not then as stable as we desired so we have replaced critical power supplies with high-precision programmable power supplies (PPSs) whose outputs can be monitored with high-precision digital voltmeters (DVMs). In the meantime, BE data for Cu, Ag, and Au have been published by the National Physical Laboratory (NPL) and similar AES KE measurements there have recently been concluded. While we believe the NPL measurements to be of high quality, we consider that independent measurements at NBS are important to ensure maximum user confidence, particularly since there are still some discrepancies in some recent high-accuracy measurements.

We give below two reports that summarize work over the past year. First, we have compared the outputs of several high-precision PPSs in our laboratory with several high-precision DVMs. These comparisons indicate that artifacts can occur in these instruments. Artifacts of the type we have found may in fact make an energy-scale calibration of an XPS or AES instrument at a limited number of points (such as with reference data for Cu, Ag, and Au) of doubtful validity since there could be nonlinearities at intermediate energies. If measurements of high accuracy are required, it may be necessary for a user to characterize the performance of the PPS or DVM in more detail. Reference data for Cu, Ag, and Au (and eventually other materials) will then be useful benchmark values. Second, we have analyzed algorithms for locating peak maxima in XPS. Our analysis provides a means for a user to select the conditions for data acquisition so that peaks can be located with a desired accuracy.

We have recently completed the calibration of one PPS and one DVM in collaboration with Mr. T. E. Kiess of the NBS Electricity Division. There were a number of technical problems to be overcome, particularly in extending the calibration to voltages above 1000 volts. These instruments have now been calibrated with an uncertainty of better than 10 mV at voltages close to those to which we will make the BE and KE measurements for Cu, Ag, and Au. We expect to make these measurements soon.

(a) Investigation of Errors in Programmable Power Supplies and Digital Voltmeters

The determination of XPS BEs and AES KEs is usually based on the assumption that the analyzer energy has been incremented uniformly through the energy region selected and that the actual analyzer energy is a continuous and linear function of the programmed value. We checked this assumption in the course of making our new BE and KE measurements. A programmable power supply was used to step the analyzer over the spectral region of interest while a precision digital voltmeter sampled the voltages to verify that no transmission errors had occurred. In the course of checking this agreement with a number of different instruments, a variety of both digital and analog faults were uncovered which are believed to be of a generic nature and hence are likely to be found to greater or lesser degree in virtually all extant instruments.

Fig. 2.1 shows a plot of the voltage difference between a DVM output and the input voltage to a PPS observed for a particular pair of instruments for a sequence of voltages between 10 and 1000 V. Instead of there being a strictly linear deviation between the instruments, which is what might be expected for instruments that had not recently been calibrated, one sees that there are eight discontinuous regions (octades) with a progressively increasing discrepancy between the programmed and measured voltages. This particular set of data indicates, via the steps, that there are bit errors in the resistor decoding network that drives the power supply such that, as one octade is incremented, the supply does not transfer smoothly over into the next higher octade. The number of such discontinuous regions depends on the particular sequencing arrangement that the manufacturer has chosen to use so the number and exact voltages where such discontinuities are apt to occur cannot generally be predicted. It can be predicted, however, that transition regions will occur. In this particular example all the major deviations are of the same sign, but the deviations could be rather variable in both magnitude and sign.

The progressively increasing discrepancy with increasing voltage in Fig. 2.1 is suggestive of a power heating effect in a resistor divider network such that the resistor value increases with the square of the applied voltage. This type of problem can be expected in virtually all high voltage power supplies and can be difficult to detect since many analyzer power supplies have a high impedance and cannot be checked with an ordinary voltmeter because the supply will be loaded. Checking the voltage across the feedback resistor segment of the divider network will, of course, not reveal this particular problem.

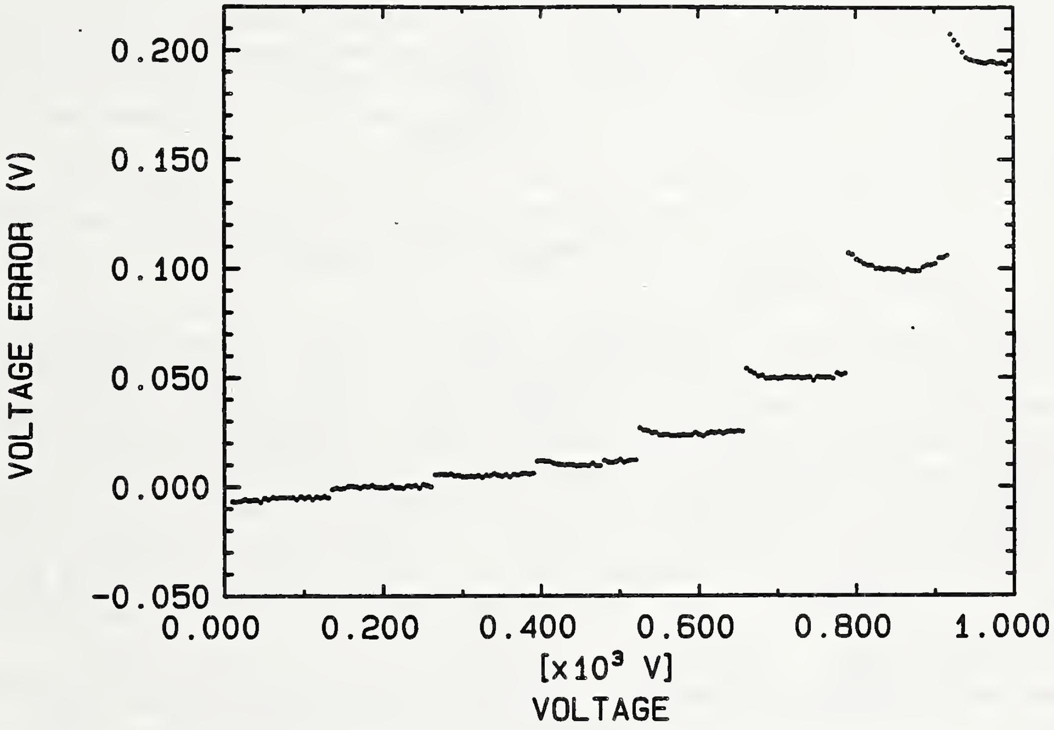


Fig. 2.1 Plot of deviation between a digital voltmeter output and the input voltage to a programmable power supply for a sequence of voltages between 10 and 1000 V.

In other comparisons, we have found appreciable deviations (up to 150 mV) that have occurred over a one volt interval, as illustrated in Fig. 2.2. This fault, which was identified as occurring in a particular voltmeter, is most likely due to a bit decoding error in the circuitry providing communication between an internal counter and the applied voltage. This type of error is expected to be repeated as the same sequence of low- or medium-order bits is repeated at other voltage levels.

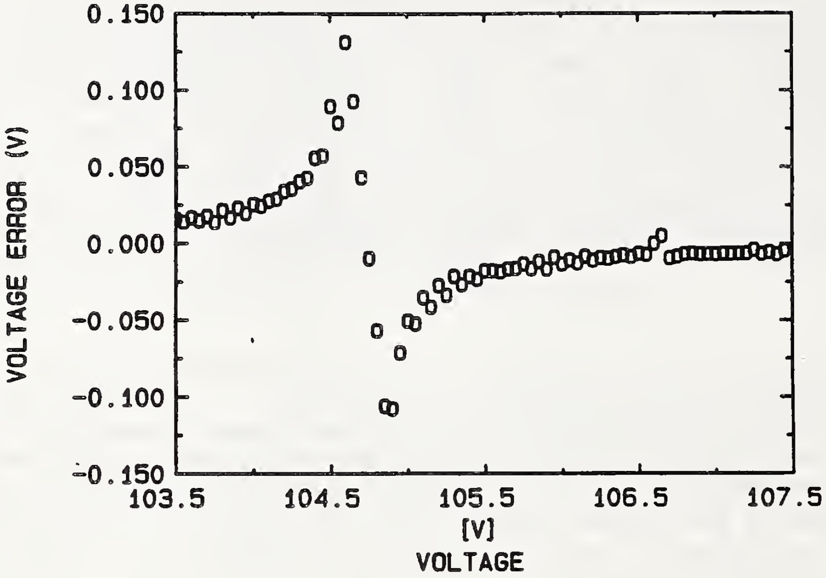


Fig. 2.2 Plot of deviation between a digital voltmeter output and the input voltage to a programmable power supply over a 4 V range of output voltage.

These problems can be extremely difficult for the manufacturer or user to locate since more than a million different combinations of values are possible with high-precision instruments. Fortunately, a modeling and test-point selection method has recently been developed in the NBS Electrosystems Division and it is hoped that analyzer manufacturers will avail themselves of this methodology as it becomes known. This methodology greatly decreases the number of test points that have to be sampled since most logic elements are used in a repetitive fashion as values are incremented. It is also hoped that more complete calibration procedures will be developed by instrument manufacturers for their specific equipment. The errors indicated in the two figures would reflect themselves as shifts in peak positions and possible peak distortions depending upon the relative position of the peak and the transition regions.

(b) Analysis of Peak Location Algorithms

The assertion that a particular electron peak has a certain binding or kinetic energy implies that it is known how to determine the location of the peak. The peak location is usually defined as the position of the peak maximum but a procedure for determining this position is rarely specified. The practical problem is that most real peaks are not symmetric about their center and the location of the maximum is sometimes a matter of subjective evaluation. There are, however, at least two procedures that can be found in the literature although neither seems to have been subjected to any validation checks. The first involves fitting, via a least-squares procedure, a quadratic equation to the top 5% of the peak. The problem with this method is that, in order to get a good fit, one should have a sufficient number of points and good counting statistics since the curvature close to the maximum is not very large. Many electron analyzers, especially older ones, can only step with fairly large energy increments, say 0.05 or even 0.1 eV. With a reasonably narrow peak one may then have only 5 to 10 points to determine the three parameters which describe a quadratic equation. This lack of redundancy in the presence of a small curvature and possibly poor statistics can lead to a fairly large uncertainty in the peak location.

The second procedure is to locate the centers of a sequence of fractional peak heights and to extrapolate these to the top of the peak. The accuracy of this method is limited by the precision with which the centers of the chords can be located.

To study this problem, we have generated a series of synthetic XPS spectra using broadened Doniac-Sunjic line shapes of different widths and with various values of the asymmetry parameter covering the range of values normally encountered. The exact peak maximum location is known from the generating function. We have then determined the accuracy and precision with which least-squares quadratic and quartic fits locate the peak maximum in the presence of various amounts of generated random noise and for various fractions of the peak height in the fit.

It is difficult to summarize this multiparameter space succinctly. In general, a quadratic curve will give good results only if the very top of the curve, say the top 5% to 10%, is analyzed. The difficulty is that noise combined with a small number of data points can make this analysis very unreliable. A quadratic fit over a larger fraction of the peak height leads to a systematic position shift if the asymmetry parameter is substantial. The best solution seems to be to use as small a step size as possible so as to maximize the number of data points, use the top 25% to 30% percent of the peak so that the sides are reasonably well defined even if the data are fairly noisy, and use a fourth order polynomial fit to account for peak asymmetries.

An additional method is also being investigated. This involves applying a Savitzky-Golay smooth to the data and then taking the derivative. Preliminary results indicate that this procedure is competitive in accuracy to the quartic fit method.

3. Reference Data for X-Ray Photoelectron Spectroscopy and Auger-Electron Spectroscopy

(C. J. Powell and N. E. Erickson)

A project was initiated in FY 82 with funding by the NBS Office of Standard Reference Data to prepare compilations and evaluations of core-electron binding energies and of the kinetic energies of selected Auger electrons for a wide range of elements and compounds. In particular, data are being compiled of the "chemical shifts" that can give useful information on the chemical state of a particular element. Data of this type are now scattered throughout the scientific literature but there is a need both for a convenient single source and for evaluation of the sometimes conflicting data. The reference data are being compiled by Dr. C. D. Wagner, a contractor to NBS, and the Surface Science Division is providing technical review.

To date, over 800 references have been examined and more than 11,000 line positions included. The database can be searched for reference, compound, element, spectral line, and physical state of the compound. Work will be completed in the next few months. The reference data will be included in a report for the Journal of Physical and Chemical Reference Data.

4. Comparison of L_3-Shell Binding Energies in Six 3d Metals Measured by X-Ray Photoelectron Spectroscopy, Appearance-Potential Spectroscopy, and Electron Energy-Loss Spectroscopy

(C. J. Powell and N. E. Erickson)

The binding energies (BEs) of core electrons in solids are of importance in a number of electron-spectroscopic methods of surface or thin-film characterization such as x-ray photoelectron spectroscopy (XPS), Auger-electron spectroscopy (AES), appearance-potential spectroscopy (APS), and electron energy-loss spectroscopy (EELS). A frequently made assumption is that BEs measured by one technique are identical to those measured by another (within the common measurement uncertainties), but there have been some indications of systematic differences. The extent to which significant differences occur, however, has been obscured by uncertainties in BE values associated with the particular measurement method, with possible errors in voltage measurements, and with possible specimen impurities.

We have measured L_3-shell BEs for Ti, V, Cr, Fe, Co, and Ni by XPS, APS, and EELS. In order to avoid the more obvious sources of error, we have used the same specimens for each of the three BE measurements and the same reference power supply (whose output is believed accurate to 0.01 V). Our work also differs from most previous comparisons in the following three respects. First, the electron energy scales for the XPS and EELS measurements were calibrated by a method in which electrons from a thermionic source were accelerated to a selected energy, scattered elastically by the specimen, and detected at an energy close to that of the XPS or EELS feature or interest. These calibrations were performed with an uncertainty of about ± 0.1 eV, and the XPS and EELS BEs were determined with a total estimated uncertainty of ± 0.2 eV. Second, we have found that the one-electron model previously used in the analysis of APS data for the 3d metals is invalid for Ti and V (see section 3.H) and is only marginally valid for Fe and Cr. An improved model has been developed that allows us to extract more reliable BEs for these metals. The APS BEs have an uncertainty of about ± 0.3 eV except for Cr for which the uncertainty is estimated to be ± 0.4 eV. Finally, we have made EELS measurements as a function of incident electron ranging from about 50 eV above the threshold for core-level excitation (i.e., the L_3-level BE) to about 1500 eV. These measurements were made to investigate the extent to which the EELS spectral data and the derived BEs changed as the excitation varied from near-adiabatic (as for the APS measurements) to sudden (as for the XPS measurements).

Our BE results are summarized in Fig. 2.3 where we show BE values as a function of excess energy in the excitation. APS is a threshold-excitation method so all APS BEs are shown at zero excess energy. For EELS, the excess energy is the incident energy minus the BE while for XPS, the excess energy is the photoelectron kinetic energy.

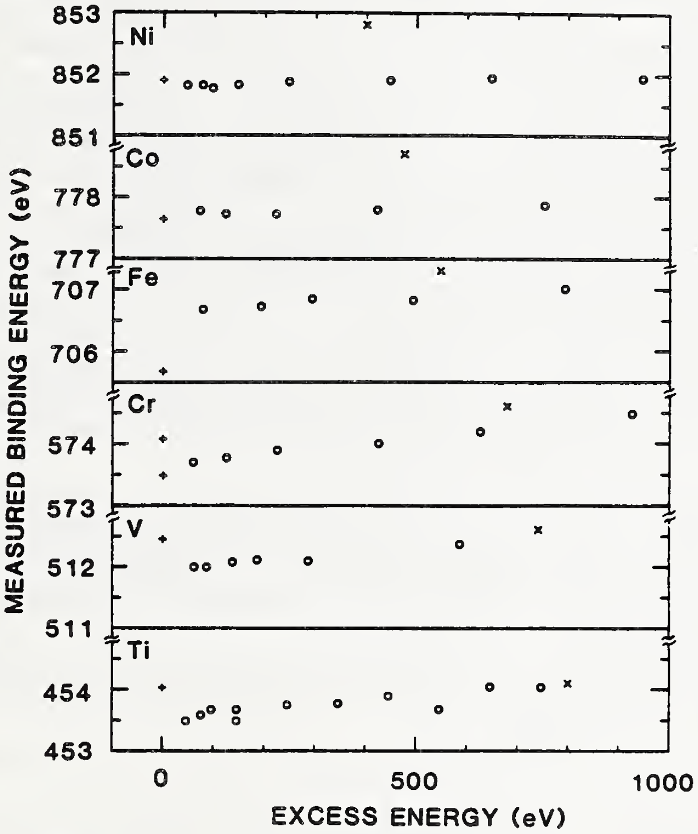


Fig. 2.3 Values of L_3-level binding energies for Ti, V, Cr, Fe, Co, and Ni as determined by three techniques: +, APS; o, EELS; x, XPS. The BE values are shown as a function of excess energy in the measurement, as defined in the text.

The BEs measured by the three methods for Ti and V are very similar although the EELS BEs for both metals appear to be systematically lower than the APS and XPS BEs. The EELS BE values at high excess energies agree with the other values but the non-dipole final states excited at low incident electron energies exhibit lower BEs. For both Co and Ni, the EELS and APS BEs are in good agreement and are appreciably lower than the XPS BEs. The difference between the XPS and APS BE values is 0.9 eV for Ni and 1.1 eV for Co. For Fe, we find a 1.7 eV difference between the XPS and APS BEs, and EELS BEs that are intermediate. For Cr, it was more difficult to determine an APS BE and two values are shown in Fig. 2.3 that represent reasonable limits in our analysis. The average difference between the XPS and APS BEs is then 0.8 eV and the EELS BEs are intermediate between the XPS and APS values, as for Fe.

Our results clearly show that BEs measured by different methods can have significant differences; for the L_3-levels of the 3d metals, these differences were up to 1.7 eV. The larger differences occurred to the right of the series where the XPS BEs of Fe, Co, and Ni exceeded the APS BEs by 0.9-1.7 eV. The reasons for the differences are not known in detail but are believed to be associated with the different relaxation and screening responses of each metal for each type of spectroscopy. For APS, a core hole is created adiabatically together with two slow electrons, while for XPS a core hole is created suddenly with a relatively fast (400-800 eV) photoelectron in our experiments. In the EELS experiments, a core hole is generated together with an excited electron above the Fermi level (which may be localized in the presence of the core hole) together with another electron with energy here of ≈ 50-1000 eV. It is therefore not considered surprising that BEs determined by spectroscopies with different excitation mechanisms are different. Only for chromium, however, do the EELS BEs interpolate approximately between the APS and XPS BEs, the limits for adiabatic and sudden excitations, as might naively be expected. Finally, our work clearly indicates that BEs determined by one spectroscopic method should not be used for the energy calibration of another type of instrument unless the extent of systematic differences is known.

We plan to explore the origins of the BE differences by making similar measurements with other materials (e.g., non-transition metals), alloys, adsorbates, and for implants (e.g., of rare-gas ions) into different solids.

5. Inelastic Mean Free Paths and Attenuation Lengths of Low-Energy Electrons in Solids

(W. F. Egelhoff, Jr., R. L. Kurtz, C. J. Powell, and R. Stockbauer)

Values of inelastic mean free paths (IMFPs) and attenuation lengths (ALs) of low-energy electrons are required in quantitative surface analysis by Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) for correction of so-called matrix effects. These parameters also define the surface sensitivity of these and other electron-spectroscopic methods of surface characterization. The AL is distinguished from the IMFP by the fact that AL values are usually derived from overlayer-film experiments on the basis of a model in which elastic electron scattering has been assumed to be insignificant. The IMFP, on the other hand, is usually obtained from theory.

Accurate values of IMFPs and ALs are urgently required for a range of materials and for electron energies of practical interest in AES and XPS. AL measurements of high accuracy are generally difficult since the values are typically in the range 3 to 30A and specimen characterization on this scale (morphology, thickness, homogeneity, uniformity, etc.) is difficult.

Calculations of IMFPs are also difficult since approximations, particularly for electron energies below about 200 eV, may not be valid. Useful formulas are needed to enable useful predictions to be made of AL or IMFP values in materials for which no measurements or calculations have been made. Reliable predictions of this type require knowledge of the dependence of AL or IMFP on electron energy and on material parameters (e.g., density, atomic or molecular weight). Finally, knowledge is needed of the extent to which concepts (and data) developed for polycrystalline or amorphous materials break down in single-crystal materials.

Our accomplishments of the past year have been in the following three areas.

(a) Energy Dependence of Electron Inelastic Mean Free Paths

Comparisons of the AL and IMFP data are often made through plots of AL and/or IMFP values versus electron energy. While these plots are very useful for assessing the relative magnitudes of AL and IMFP values and their trends as a function of energy, they are not well suited to a detailed examination of the energy dependence. A particularly convenient and appropriate method of examining the dependence of AL or IMFP values on electron energy is the Fano plot. The product of a particular inelastic cross section (which in the simplest cases could be for a discrete excitation, ionization, or total inelastic scattering in a gas) and electron energy is plotted versus electron energy on a logarithmic scale. At sufficiently high electron energies, this plot is expected to be linear with a slope that can be derived from appropriate optical data. Such behavior is expected quite generally from the Bethe theory for inelastic electron scattering in matter. Since the Bethe theory is well established, use of the Fano plot is a simple and effective means for analyzing the internal consistency of experimental cross-section data with optical adsorption measurements, and for determining the minimum incident electron energy for which the Bethe theory is valid.

An analysis has been made of the energy dependences of calculated IMFPs for Al, Cu, Ag, and Au from four recent sources of data. Linear Fano plots were obtained for each metal using data from the calculations of Ashley _et al_. and Powell but the Fano plots with the data of Szajman _et al_. had distinct curvature. Fano plots with the data of Penn showed linearity over two separate energy ranges, typically from 80 to 500 or 1000 eV and from 1000 or 1500 eV to 10000 eV. These variations were attributed to different treatments in the calculations of exchange and correlation and of the dependence of the differential inelastic scattering cross section on momentum transfer.

There were significant variations in the slopes of the Fano plots for each material using the four sources of IMFP calculations. The expected slope of the Fano plot can be calculated from optical absorption data and thus can be used as a guide in selecting a preferred data set. Values of the Fano-plot slopes from three of the data sets generally agreed well with the optical values but the slope values based on the data of Szajman _et al_. exceeded the optical values by 9 to 40%.

It was found that the slopes of Fano plots using AL data for Al, Cu, and Au, were larger than the optical values by 29 to 54%. A similar result has been obtained in other analyses of inelastic-scattering cross-section data and is believed due to the electron energies not being high enough to be in the asymptotic Bethe region. A separate analysis of the optical data showed that the minimum electron energy for which linear Fano plots can be expected is about 400 eV for Al and about 1000 eV for Cu, Ag, and Au. Experimental AL measurements in different types of materials over a wide electron energy range are required to define more clearly the energies where the Fano plots attain their asymptotic slopes.

Calculations are in progress of IMFPs from experimental optical data using an algorithm developed recently by Dr. D. R. Penn of the NBS Electron Physics Group. Since optical data are available over a sufficiently wide photon-energy range for a limited number of materials, it is of interest to compute IMFPs and to search for possible systematics in the dependences on electron energy and material parameters.

(b) Measurements of Electron Attenuation Lengths in Condensed Molecular Solids

During the past year we expanded our efforts to measure electron attenuation lengths in condensed molecular solids by performing experiments on the X-24C beam-line (a joint effort of NBS and the Naval Research Laboratory) at the Brookhaven National Synchrotron Light Source. The goal of this experiment is to measure electron attenuation lengths over a wider electron energy range than is possible at the NBS SURF-II storage ring. Films of molecular solids of variable thickness are condensed on a cooled copper substrate and the intensity of substrate valence-band photoemission measured as a function of film thickness. These experiments were conducted with different photon energies and attenuation lengths measured for corresponding photoelectron energies. At Brookhaven, we can make the attenuation-length measurements over the range of about 50 to about 1200 eV which is the range of practical interest for Auger-electron spectroscopy and x-ray photoelectron spectroscopy. Furthermore, careful attenuation-length measurements over a wide electron energy range should enable more accurate determination of the energy dependence.

Films of the molecular solids are prepared by the technique of microcapillary-array dosing, the method we developed in our previous experiments at SURF-II. The Brookhaven surface science chamber was modified to include an in-situ photon intensity monitor, the microcapillary array dosing system (with gas-handling manifold), and an additional cryopumping block for reduced operating pressure. Preliminary measurements were made with water at an electron kinetic energy of 155 eV; however, several experimental snags developed. These complications, coupled with erratic machine operations, precluded the completion of these measurements. Most problematic was that the grating installed in the extended-range monochromator had been manufactured with an improper blaze angle; this mistake resulted in usable photon flux with a maximum photon energy near 160 eV. This grating is being replaced and beryl crystal diffracting elements are presently being prepared also. These elements should be in place for the next run.

The electron attenuation-length measurements will continue in the next available time-slot and will include measurements on condensed films of water, methanol, and cyclohexane (materials for which attenuation-length measurements were made earlier in the energy range 18-68 eV).

(c) Layer-By-Layer Analysis of the Effects of Forward Scattering of Electrons in Attenuation Length Measurements with Single Crystals

Attenuation lengths have been frequently measured from the characteristic decay of an AES and XPS signal as a film of increasing thickness is deposited on a substrate. This decay is generally monotonic for amorphous or polycrystalline samples. For single- crystal samples, however, a fundamental complication for such measurements is the enhancement of an AES or XPS peak intensity along crystal axes. These enhancements along nearest-neighbor directions are due to forward scattering of the emitted electrons by lattice atoms (see Fig. 2.4(b)).

As part of an effort to characterize and elucidate the influences of forward scattering on AL measurements, several simple model systems have been studied. Figure 2.4(a) presents data on such a system. The substrate consists of a monolayer (ML) of Cu epitaxially grown on Ni(100). The attenuation of the Cu AES signal is measured as epitaxial layers of Ni are grown on the Cu. Extreme departures from monotonic decay are observed. At the angles at which the strongest forward scattering is expected, 45° and 0°, the Cu AES signal is actually increased by overlayers and is not reduced to below the clean-Cu levels until more than 4 ML of Ni has been deposited.

Certain types of electron analyzers (e.g., the cylindrical-mirror analyzer) may integrate XPS and AES signals over a wide range of angles and still recover a monotonic decay. Other types of analyzers (e.g., the hemispherical analyzer) often select small solid angles and in such cases, as here, it is clear that the simple concept of exponential electron attenuation breaks down in single-crystal materials. In such cases, quantitative surface analysis by XPS and AES will have large uncertainties unless corrections can be made for the effects of forward scattering. Data of the type shown in Fig. 2.4(a) can be used to select the polar angles and solid angles for which the current simple models for quantitative AES and XPS are more likely to be valid.

Figure 2.4 also provides insight into the layerwise breakdown of the angular distribution of pure Cu(100). Summing the spectra shown in Fig. 2.4 from 0 to ~ ∞ ML of Ni (including those not shown) produces a result essentially identical to the pure Cu(100) angular distribution. This result is reasonable since Ni overlayers scatter electrons in very nearly the same manner as Cu overlayers. Thus, Fig. 2.4(a) makes it possible to see the layerwise contributions to the angular distribution of the Cu AES signal from pure Cu(100).

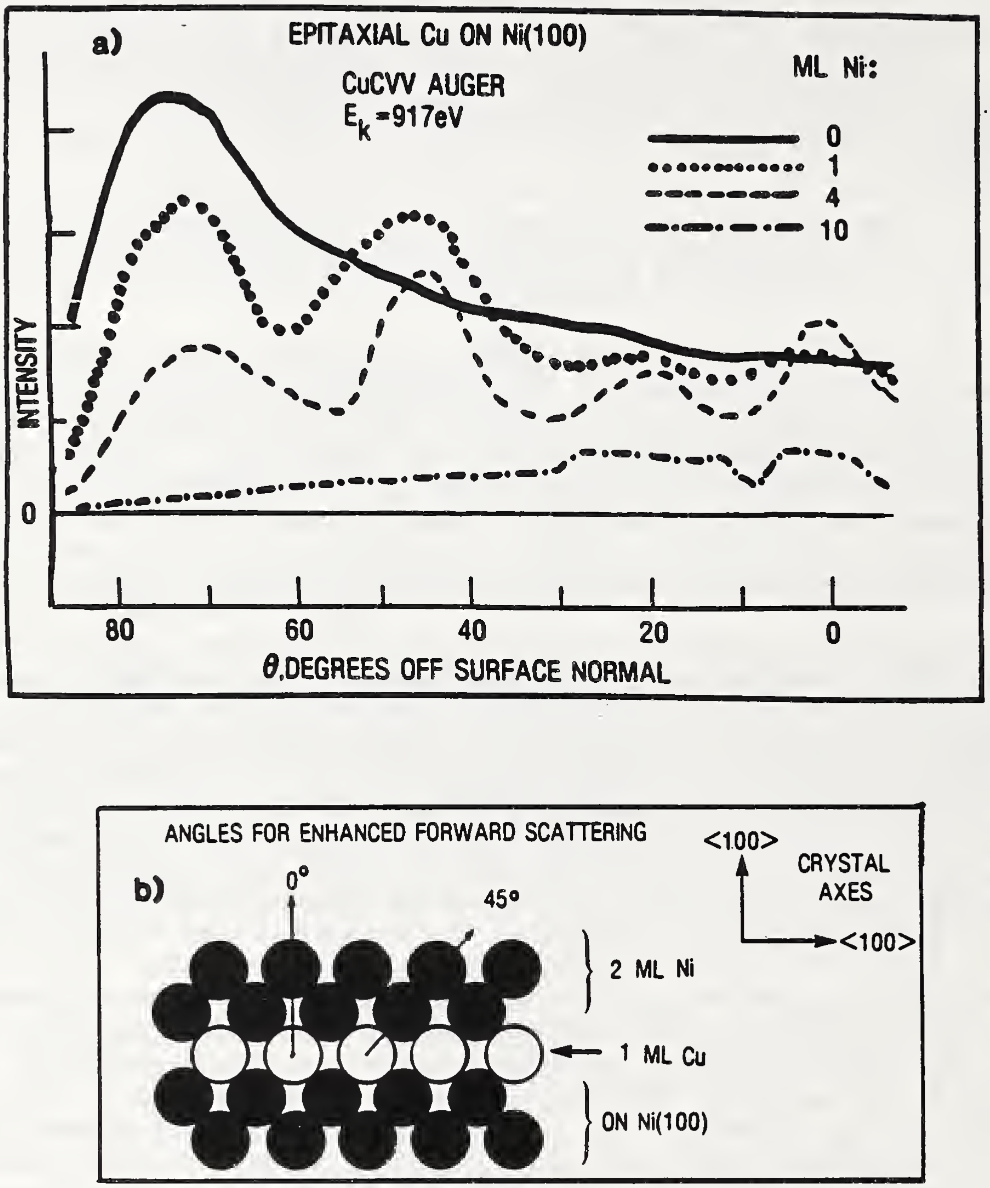


Fig. 2.4(a) Changes in the angular distributions of Auger electrons from an epitaxial Cu monolayer for the indicated number of nickel overlayers.

(b) Illustration of the atomic geometry for these sandwich structures

6. Algorithm for Fitting Sputter-Depth Profiles at Interfaces (J. Fine, G. P. Chambers, and D. Marton)

The determination of interface widths from sputter-depth-profiles is presently accomplished by means of graphical methods. Since the shapes of such interface profiles are generally not symmetric and since there is no accepted method of measuring interface widths, accurate width determination as well as intercomparison of results is often difficult to accomplish. One solution to this problem is to fit numerically the interface profile shape to an appropriate analytical expression from which one can obtain a factor proportional to different definitions of the interface width.

In collaboration with Dr. W. H. Kirchhoff of the NBS Chemical Thermodynamics Division, a fitting analysis for Auger-electron sputter-depth profiles has been developed using a logistic function of the form:

$$I = [A + a(T-T_0)]/(1 + e^{-t}) + [B + b(T-T_0)]/(1 + e^{t})$$

where I is the peak intensity of the Auger spectrum of the sputtered atom as a function of the time T. A is the intensity from a totally covered surface, B is the background intensity from a completely uncovered surface, and a and b empirical parameters which can account for additional time dependence or instrumental effects. T_0 is the apparent midpoint of the transition region and t is a dimensionless, reduced time defined as $(T-T_0)/D$. The scaling factor, D, is the characteristic time for sputtering through the interface region. Asymmetry in the depth profile can be accommodated by allowing D to vary with time.

A least-squares fitting program has previously been written to fit measured Auger spectral intensities to the above equation for completely resolved interfaces (i.e., where component X goes from 100 to 0% and component Y goes from 0 to 100%). We showed that this logistic function could be fitted to Auger data for the NBS multilayered Ni/Cr thin-film structure SRM2135 to within the experimental error of a few percent.

This past year, extension was made of this fitting using the logistic function to interfaces which are not fully resolved. This situation occurs when sputter profiling a very thin layer of material (less than, say, 5 nm) in between two thick layers of another material. By making use of the derivative of the above equation, we have shown that remarkably good fits can be made to high-resolution sputter profiles obtained in our laboratory. The fits were made to depth profiles of a multilayer Ni/Ag thin-film structure which had thin Ag layers (≈ 4 nm) and thick Ni layers (≈ 50 nm). These fits to the analytical logistic function give functional parameters from which we have been able to make quantitative determinations of layer thickness for such very thin films.

A limited distribution has been made during the year of the fitting program and its documentation. The program has been written in Fortran 77 and can be run on IBM-compatible personal computers. Packages containing the program on a floppy disc, a program listing, a detailed description of the program, and examples of its use (with corresponding test data on the disc) were distributed at the spring meeting of ASTM Committee E-42 on Surface Analysis and at the Applied Surface Analysis Symposium in Dayton. At the latter meeting, a demonstration was also given of the program. The purpose of the distribution was to enable further tests and evaluations of the program to be made. We are currently exploring mechanisms for wider dissemination of the program that will enable a larger number of people to make use of this software.

7. Adsorbate Surface Coverage Measurements
(T. E. Madey)

An important parameter in surface science measurements is the coverage (surface density in atoms/unit area) of atoms or molecules which are adsorbed on a given surface. In many instances, there is a factor of two or three uncertainty in measurements of coverage. Such large uncertainties provide major problems in data interpretation, modelling of surface structures, determination of surface kinetics, etc. During the last few years, several experimental methods have been developed which have the potential for providing absolute measures of surface coverage, with a substantially smaller uncertainty (~ ± 25%). Such methods include molecular-beam reflection techniques, high-energy ion backscattering, radiotracer measurements, and nuclear reactions induced by ion bombardment. We expect shortly to initiate a comparative study of these methods with the goal of preparing a critical review of absolute coverage data and of relevant measurement methods.

B. Reference Materials

1. Developments and Production of Standard Reference Materials for Sputter-Depth Profiling)
(J. Fine, Y. Hashiguchi, and D. Marton)

The objective of this project is to develop standard reference materials (SRM's) that will allow convenient determinations of ion-beam sputter-removal rates in commonly used surface-analysis instrumentation. Thin-film reference materials of known thickness will be used to calibrate ion-gun current densities for particular operating conditions. This information together with sputtering-yield data for a range of materials will establish depth scales in the measurement of depth profiles.

Prototype thin-film structures were initially fabricated in order to evaluate their usefulness as depth profiling SRM's and to develop appropriate characterization techniques. These structures were made by sputter deposition as part of a joint US/Yugoslavia program between NBS and Dr. B. Navinsek at the J. Stefan Institute in Ljubljana. Analyses of these prototype materials at NBS and by members of ASTM Committee E-42 on Surface Analysis were done using Auger-electron spectroscopy (AES), x-ray fluorescence, secondary-ion mass spectroscopy (SIMS), Rutherford backscattering spectroscopy, and proton-induced x-ray emission. The results were satisfactory and a stock of similar thin-film SRM's were fabricated in 1982 using the sputter deposition facility at the J. Stefan Institute in Ljubljana. Production and characterization of the Ni-Cr thin-film SRM was supported by the NBS Office of Standard Reference Materials.

Preliminary analyses obtained on the nickel-chromium multilayered thin-film structures indicated that this material should be of considerable benefit as a depth-profiling SRM. It has been characterized and calibrated in order to determine the uniformity and periodicity of the thin-film layers, absolute film thicknesses, sputtered interface depth resolution, and structural stability. The results of these measurements indicated that this Ni/Cr structure could be accurately calibrated for depth profile analysis; it was issued as NBS Standard Reference Material 2135 in the fall of 1985.

Sales of the SRM through the NBS Office of Standard Reference Materials were greater than we anticipated and by the spring of 1986 our initial stock of 80 specimens was sold. An additional stock of 25 specimens, which we had previously calibrated, was issued as NBS SRM 2135a and these, too, were sold by the summer of 1986.

Two additional batches of Ni/Cu structures (about 200 specimens) were characterized by Auger sputter-depth profiling and by neutron activation analysis. These should be ready for issue in the fall of 1986 and should be sufficient to maintain our stock of SRM 2135 for about another year. We are now making arrangements with Dr. Navinsek for the fabrication of about 600 Ni/Cr structures.

Future work includes characterizing and certifying "marker" layer-type sputter-depth-profile SRM which we have recently fabricated in production quantities. This material also was fabricated in Dr. Navinsek's laboratory and consists of eight Cr layers (~ 40 nm each) separated by about 2 monolayers of Cr_2O_3. Preliminary experiments have been carried out to characterize these structures by Auger depth profiling. This is a difficult test since the Cr_2O_3 marker layers are very thin and since the oxygen Auger peaks nearly overlap those of chromium. We have been able to detect the oxygen Auger signal after developing a special background subtraction program. In some experiments, we were able to detect all seven oxide layers in a structure (even the one that was 280 nm deep) after very careful instrumental alignment and with a low-energy (1 keV) argon ion beam. Accurate determination of the position of the marker could be achieved by fitting a theoretical curve to each of the seven oxygen peaks in the depth profile. The theoretical curve was the same as that used to describe the Ag/Ni depth profiles (section 2.A.6) and had terms that described surface-roughness development and radiation-enhanced diffusion occurring during the sputtering of the specimen. In other experiments, we were unable to detect the deeper oxide layers, presumably because of the higher interface broadening associated with roughness development and radiation-enhanced diffusion.

We plan to perform additional characterizations of the Cr/Cr_2O_3 structures. We will measure depth profiles for a wider range of experimental conditions and will calibrate the chromium total film thickness by neutron activation analysis. It is possible that the material may not be suitable for routine use in Auger depth profiling (except perhaps as a stringent test of operating conditions). We expect, however, that it will be useful as a depth-profile standard in SIMS since this technique is more sensitive than AES and does not suffer from the problem in AES for Cr and O of peak overlap in energy. We anticipate that this structure can be issued as an SRM next year.

2. Quantitative Sputter Depth Profiling of Interfaces
(J. Fine, D. Marton, Y. Hashiguchi, and G. P. Chambers)

Determination of composition-versus-depth at virgin solid/solid interfaces is at present difficult to achieve with current sputter-depth-profiling techniques. This is due, to a large extent, to a lack of understanding of the effects of the various bombardment conditions (i.e., ion beam energy, species, angle of incidence, current density, and sputtered depth) on interface resolution. A consistent set of measurements obtained for various ion beam parameters, all done on the same material, would significantly enhance our ability to assess the abruptness of interfaces before sputter-profile analysis took place and would be of value in determining optimum sputter-profile conditions.

Our development of multilayer thin-film structures with known layer thickness and periodicity (as described above) makes it both possible and practical to examine systematically the dependence of interface resolution on ion beam parameters. Use of the computer- controlled, sequential-mode N(E) Auger data system which has been previously developed allows us to obtain reliable and accurate Auger measurements while the fitting of this data to particular functions results in quantitative determination of the interface width and the asymmetry of the interface profile.

Our principal objective in the past year has been to investigate interface broadening mechanisms in depth-profile measurements and to define the limits on the use of layered structures as sputtering-rate reference materials. Two important processes occurring during sputtering have been selected for these studies: the development of surface roughness and radiation-enhanced diffusion. Silver/nickel multilayered samples, fabricated in the laboratory of Dr. B. Navinsek (Ljubljana, Yugoslavia) and consisting of five thin (~ 4 nm) Ag layers embedded between six thicker (50 nm) Ni layers and sputter-deposited on Si wafers have been used as test materials for these measurements.

(a) Surface roughness development during sputter-depth profiling

Both theoretical and experimental studies have been carried out. A simple statistical model has been developed to explain the phenomenon of increasing surface topography (roughness) during ion sputtering of solid targets. The square-root depth dependence of the surface roughness, which has been observed in some cases, is explained by assuming that the roughness increase is caused by the differences in sputtering rates obtained on differently oriented crystallographic surfaces, and that the distribution of the sputtering rates is fully random. Deviation from the random distribution of the sputtering rate leads to different types of depth dependences for the surface roughness.

A light-scattering experiment has been set up in conjunction with the Auger depth-profiling apparatus to measure the surface roughness changes in-situ (i.e. without breaking the vacuum). Stylus measurements with a Talystep instrument (in collaboration with Dr. T. Vorburger of the NBS Precision Engineering Division) have been utilized as calibrations. The light source used in this experiment is a 5 mW unpolarized 630 nm He-Ne laser, and the scattered light is collected by an ellipsoidal reflector. The opening angle of the reflector is about 45° which limits the maximum surface wavelength that can be measured to about 1.85 μm. This experiment is far from the ideal arrangement in which the total scattered light intensity could be measured and thus only relative roughness values can be measured here. This is, however, the first known experiment to measure surface roughness changes in situ following sputtering.

Preliminary experiments carried out with this set-up at 1 keV argon ion energy showed that the surface roughness increased from the starting value for the unsputtered surface of 1 nm to about 6 nm at 50 nm depth and to about 12 nm at 250 nm depth. These results are consistent with the assumption of a square-root depth dependence of the roughness increase and with semi-empirical results obtained from the Auger depth profiles described below.

(b) Radiation-enhanced diffusion during sputter-depth profiling.

Earlier studies in this laboratory have shown that ion bombardment of Ag/Ni multilayer thin-film structures similar to those used in the present experiments lead to a segregation of Ag at the same surface. This phenomenon was explained by assuming that radiation-enhanced diffusion (RED) was responsible for the Ag transport. This process has now been investigated in more detail by sputtering through all Ag and Ni layers and by describing all peaks in the Ag Auger depth profiles in terms of a distortion of the initially ideal step-like concentration profile. Such Ag-layer profiles become Gaussian-like as a result of surface roughening and are made asymmetric by the RED. The equation describing this modified Ag profile is:

$$c = \frac{c_o}{(4Dt+\Delta z_R^2/2)^{1/2}} \exp\left[-\frac{(St-z_o)^2}{4Dt+\Delta z_R^2/2}\right]$$

where c is the Ag concentration, t is the diffusion time, D is the RED rate, S is the sputtering rate, c_o is a constant depending on the Ag layer thickness, Δz_R is the RMS surface roughness, and z_o is the propagation range of the sputter-induced defects.

A computer program has been developed for fitting the above equation to the experimental data. One example of such a fit is shown in Fig. 2.5. The fit is excellent, and both diffusion rate and roughness data can be easily obtained. The same approach seems to be useful for the interpretation of oxygen depth profiles in Cr/Cr_2O_3 multilayers (see section 2.B.1).

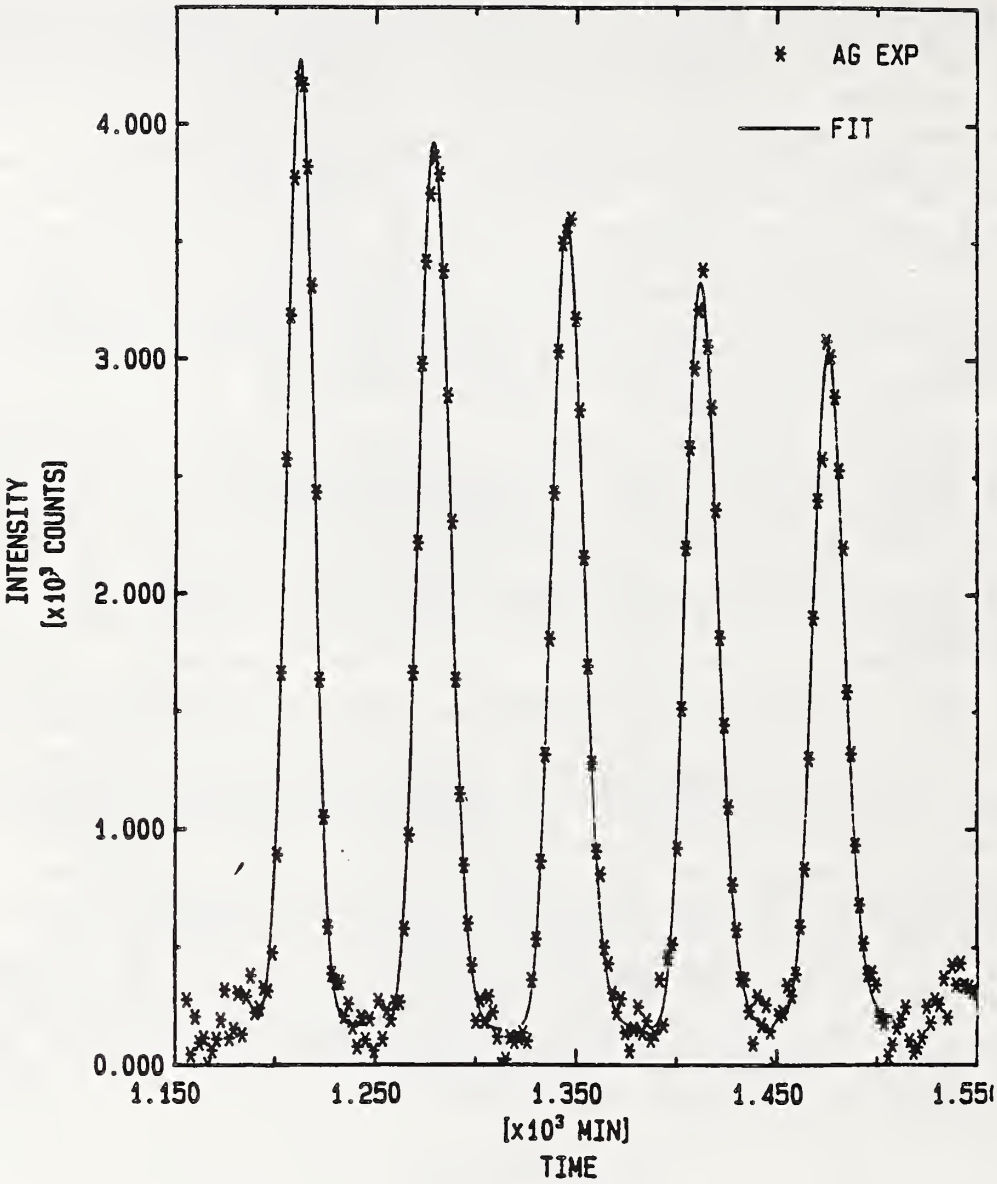


Fig. 2.5 Plot of the Ag Auger-electron signal as a function of sputtering time for an Ag/Ni multilayer thin-film structure consisting of five Ag and six Ni layers on a Si substrate. The points are the experimental intensity measurements and the line is the fit based on the equation given in Section 2.B.2(b).

RED rates have been determined for 1 keV argon ions as a function of current density. It was expected that at low current densities of the ion beam, the sputtering rate would be smaller, the diffusion process would take longer time, and thus wider interfaces would be obtained. This is correct, but the RED rates also decrease for smaller current densities, presumably because of the partial recombination (healing) of the radiation-induced defects. This process decreases the number of defects which then reduces the RED rates. If this process of defect healing is assumed to be exponential, a lifetime or about 250 minutes is obtained. For high sputtering rates, D is found to be 4×10^{-17} cm^2/s for 1 keV ions and around 1×10^{-15} cm^2/s for 4 keV ions. These values for the RED rate are very much larger (by orders of magnitude) than the normal diffusion coefficients for similar systems. The values are strongly dependent on ion energy and therefore appear to be related to defects (probably point defects) caused by the ion bombardment.

These studies of interface layer broadening are to be completed in the next year by obtaining more detailed information on the dependence of these phenomena on the energy of the incident ions. Another important aspect concerns the Ni/Cr standard reference material (see section 2.B.1). Both roughness effects and RED may be applicable to this system; in particular, RED may explain the asymmetry observed in Auger depth profiles of the Ni/Cr multilayers. A rather extensive set of interface measurements obtained on Ni/Cr multilayered structures is now being analyzed to determine the dependence of interface width and asymmetry on the ion bombardment energy and current density as a function of sputtered depth.

C. Review Articles and Books

1. Review Articles

The Division Staff authors many review articles and book chapters that provide information on measurement methods, relevant reference data, reference materials, theories of the measurement process for many surface spectroscopies, and surface standards.

Division staff members have authored 23 review articles recently. The titles and abstracts of review articles published since 1985 are listed below:

(a) "The Thermal Desorption of Adsorbed Species," J. T. Yates, in Methods of Experimental Physics, Vol. 22, Solid State Physics: Surfaces, R. L. Park and M. G. Lagally, eds. (Academic Press, N.Y.), 425 (1985).

The experimental and theoretical basis of thermal desorption spectroscopy as a tool for surface characterization is described. Methods of analysis of thermal desorption spectra to obtain kinetic information (desorption energies, desorption order, coverages of adsorbed species) are included, together with numerous examples of desorption on small molecules from single-crystal metal surfaces.

(b) "Experimental Methods in Electron and Photon Stimulated Desorption," T. E. Madey and R. Stockbauer, in Methods of Experimental Physics, Vol. 22, Solid State Physics: Surfaces, R. L. Park and M. G. Lagally, eds. (Academic Press, N.Y.), 465 (1985).

We review experimental techniques and applications of electron stimulated desorption (ESD) and photon stimulated desorption (PSD) of atomic, molecular, and ionic species from surfaces. The physical principles of these methods, as well as details of experimental measurements and data analysis are discussed. We close with a discussion of beam damage in surface analysis.

(c) "Innershell Ionization Cross Sections," C. J. Powell in Electron Impact Ionization, T. D. Märk and G. H. Dunn, eds. (Springer-Verlag, N.Y., 198 (1985).

A review is presented of cross sections for the ionization of inner-shell electrons by electron impact. Calculations, measurements, and empirical formulas are described and compared. Recommendations are given for the selection of cross-section data. Finally, applications of inner-shell ionization cross-section data to materials and surface analysis problems are described.

(d) "The Coordinated Development of Standards for Surface Chemical Analysis", M. P. Seah and C. J. Powell, NBS Internal Report NBSIR 85-3120 (March, 1985).

This report is based on a proposal to the Steering Committee of the Versailles Project on Advanced Materials and Standards (VAMAS) for the coordinated development amongst the VAMAS member states of standards for surface chemical analysis. VAMAS was established following a meeting of the Heads of State or government at Versailles, France in 1982 that agreed on a number of projects relating to technology, growth, and employment. Specifically, VAMAS was organized to promote international coordination in the development of standards in a wide range of advanced material sectors. Surface chemical analysis was approved as a VAMAS Technical Working Area in June, 1984.

The report describes the growth and diversity of surface analysis in the development of advanced materials in modern technologies and the use of surface analysis for improved films and coatings. The principal techniques of surface analysis in common use are identified and the technical limitations to accurate surface analyses pointed out. Accurate surface analyses require: (i) knowledge of the principles of the measurement method, (ii) knowledge of the behavior of the measuring instrument and the (iii) correct interpretation and expression of the final measured result. Standards for the measurement of surface composition with known accuracy and for the reliable determination of chemical state require: (a) a base of principles, definitions of terms, and suitable equations; (b) reference procedures for the measurement of intensities and spectral features, (c) procedures and data for instrument calibrations, (d) reference data for material parameters such as elemental sensitivity factors, matrix terms, chemical state spectra, ion sputtering rates, etc.; and (e) standard methods for specifying an analysis. Specific needs are identified for the common methods of surface analysis, Auger-electron spectroscopy, x-ray photoelectron spectroscopy, and secondary-ion mass spectroscopy together with needs for ion sputtering which is used to obtain composition versus depth information in films and coatings. Existing standards activities in the member countries of VAMAS are reviewed and suggestions are made for additional standards for surface chemical analysis.

(e) "Surface Harpooning", J. W. Gadzuk, Comments on Atomic and Molecular Physics, 16, 219 (1985)

The principles involved in charge transfer/harpooning collisions between atoms or molecules and surfaces are presented in terms of concepts drawn from gas-phase atomic and molecular collision theory. As specific examples, the charge state of atoms and the vibrational excitation or dissociation of molecules which have experienced harpooning while scattering from a surface are considered.

(f) "The Uses and Limitations of ESDIAD for Determining the Structure of Surface Molecules", T. E. Madey, in The Structure of Surfaces, Springer Series in Surface Science 2, M. A. van Hove and S. Y. Tong, eds. (Springer-Verlag, N.Y.), 264 (1985).

The principles and mechanisms of electron-stimulated desorption (ESD) and photon-stimulated desorption (PSD), as well as the utility of the electron stimulated desorption ion angular distributions (ESDIAD) method as a tool for determining the structure of surface molecules, have been described in a recent book and several review articles. The present short paper is intended to provide a guide to the relevant literature, and to describe briefly some recent work relating to the uses and limitations of ESDIAD for determining the structure of surface molecules.

(g) "Recent Advances Using ESDIAD: Applications to Surface Chemistry", T. E. Madey, C. Benndorf, N. D. Shinn, Z. Miskovic, and J. Vukanic, DIET-II, Desorption Induced by Electronic Transitions, Springer Series in Surface Science 4, W. Brenig and D. Menzel, eds. (Springer-Verlag, N.Y.,), 104 (1985).

Recent applications of ESDIAD (electron stimulated desorption ion angular distributions) to surface chemistry are described. Examples include the influence of catalytic promoters and poisons on surface structure and reactivity, the evidence for a new structural form for adsorbed H_2O (i.e., H_2O dimers on Ni(110)), and the characterization of a new bonding mode for CO on Cr(110). Calculations of the perturbing influence of image force and reneutralization effects in ESDIAD are described.

(h) "Recent Developments in Quantitative Surface Analysis by Electron Spectroscopy", C. J. Powell, J. Vac. Sci. Tech. A 4, 1532 (1986)

An overview is given of recent developments in quantitative surface analysis by x-ray photoelectron spectroscopy and Auger-electron spectroscopy. The two major tasks of an analysis are the identification of the surface phases that are present and the determination of the concentrations of particular elements or compounds. Methods for accomplishing both tasks will be described together with the pitfalls and problems that remain. Particular attention is given to the following topics: identification of surface phases and reference data for the calibration of instrumental energy scales; reference data on inelastic mean free paths and attenuation lengths; effects of specimen crystallinity; intensity measurements; measurement of the imaging properties of electron energy analyzers; and the intensity-energy response functions of different instruments.

(i) "Surface Chemical Analysis - Report on the VAMAS Project", C. J. Powell and M. P. Seah, Surf. Interface Anal. 9, 79 (1986)

The VAMAS project on surface chemical analysis is a multi-national cooperation for the provision of standards data and materials for surface chemical analysis measurement and for the provision of the basic understanding necessary for these activities. This project is one of a rapidly growing suite of projects initiated as a result of decisions following the 1982 Versailles Summit Meeting of the Heads of State or Government of Canada, France, Germany, Italy, Japan, UK, USA and the Representatives of the Commission of the European Community. During the past year national representatives to this VAMAS project have been appointed and national committees established. This article summarizes the philosophy, scope, and organization of the project and describes specific activities that have been initiated. Information is given on how individuals, both within and outside the group of member states, may participate.

(j) "Dynamics of Molecular Processes at Surfaces: Vibrational Lineshapes and Spectra", J W. Gadzuk, J. Electron Spectroscopy 38 233 (1986).

Extremely useful connections exist between the dynamics of adsorbed molecule vibrations, as revealed in spectroscopic lineshapes, and the dynamics of molecular processes at surfaces because in both cases, the constituent atoms of a molecule, solid, or combination of the two execute multi-dimensional motion over the same potential energy surfaces, undoubtedly sampling different regions of it.

In this paper, recent insights and advances in surface dynamics will be applied to the problem of vibrational lineshapes. Classical particle and semi-classical wavepacket dynamics will be used to address the issues of energy decay (T_1) vs. pure dephasing ($T_2{}'$) overtones, and non-linear dynamics as they apply to lineshape analysis.

(k) "Electron Stimulated Desorption and its Relation to Molecular Structure at Surfaces", T. E. Madey, J. Vac. Sci. Tech. A 4, 257 (1986).

Recent examples of the use of electron stimulated desorption ion angular distributions (ESDIAD) in determining the structures of molecules on surfaces are discussed. These include the adsorption and decomposition of NH_3 on Fe(100), and the stabilization of H_2O on Ag(110) by impurity O and Br atoms. ESDIAD evidence for "lying down" CO on several surfaces is presented, and the influence of beam damage in producing new surface structures for H_2O on Ni(100) is discussed. Calculations of the influence of the surface image potential and reneutralization effects on ion trajectories are described briefly.

2. Review Articles in Publication

We list below the titles and abstracts of review articles in the course of publication.

(a) "The Chemisorption of Carbon Monoxide by the Transition Metals", J. T. Yates, Jr., T. E. Madey, and J. C. Campuszano, The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis", D. A. King and D. P. Woodruff, eds. (Elsevier, N.Y.)

A comprehensive review of the adsorption of carbon monoxide by transition and noble metals is presented. The systematics of CO adsorption and dissociation are discussed, along with detailed examinations of the surface structures, electronic and vibrational spectra, and kinetic behavior of adsorbed CO.

(b) "Final-State Resolved Studies of Molecule-Surface Interactions", D. S. King and R. R. Cavanagh in New Laser and Optical Investigations of Chemistry and Structures at Interfaces, (Verlag Chemie)

Quantum state-specific diagnostics as applied to surface dynamics are discussed. The NO molecule is used as an illustration of the experimental determination of gas-surface interactions. Topics reviewed included beam-surface scattering, thermal desorption, vibrational accommodation, Doppler profiles, and Fourier-transform infrared emission spectroscopy.

(c) "Core-Level Binding-Energy Shifts in Solids at Surfaces", W. F. Egelhoff, Jr., Surface Sci. Reports.

This review presents an overview of the theory and of various successful approaches to the interpretation of core-level binding-energy shifts observed in photoelectron spectroscopy. The theoretical background is presented at a level readily accessible to the general reader. Particular attention is paid to the relative merits of two basically different conceptual frameworks for interpreting core-level binding-energy shifts, the initial-state--final-state approach and the equivalent-core Born-Haber cycle approach.

(d) "Excitation Mechanisms in Vibrational Spectroscopy of Molecules on Surfaces", J. W. Gadzuk, in Vibrational Spectroscopy of Molecules on Surfaces, J. T. Yates, Jr., and T. E. Madey, eds., Vol. 1 of Methods of Surface Characterization (Plenum, N.Y.).

An introduction to the theoretical basis of vibrational excitation mechanisms and processes relevant to vibrational spectroscopy of adsorbed molecules is presented.

(e) "Neutron Inelastic Scattering: Vibrational Spectroscopy of Adsorbed Molecules on Surfaces:, R. R. Cavanagh, J. J. Rush, and R. D. Kelley, in Vibrational Spectroscopy of Molecules on Surfaces, J. T. Yates, Jr., and T. E. Madey, eds., Vol. 1 of Methods of Surface Characterization (Plenum, N. Y.).

An introduction to neutron scattering as a probe of adsorbates at surfaces is presented. Emphasis is placed on experimental aspects of triple-axis and time-of-flight techniques along with a single-phonon model for the spectral features. Wilson FG methods for constructing molecular force fields relevant to the molecular modes of the adsorbate are presented. The applicability of neutron scattering for exploring rotational diffusion and adsorbate torsions is also examined.

(f) "Field Emission Microscopy - Trends and Perspectives", A. J. Melmed, Chemistry and Physics of Solid Surfaces VI, Springer-Verlag

The author's view of the role of surface microscopies, in particular the field emission microscopies, is given. Brief outlines of the historical development and nature of field-electron emission microscopy (FEEM) and field-ion microscopy (FIM) are given and selected examples are presented to illustrate the scope of research in FEEM and FIM. Research trends are described and some projections for the future are made.

(g) "Electron and Photon Stimulated Desorption: Probes of Structure and Bonding at Surfaces", T. E. Madey, Science

Techniques for analyzing the structure and composition of solid surfaces using electron and photon beams often suffer from difficulties due to radiation damage. Damage-producing processes compete with information-producing events during measurements, and beam damage can be a serious perturbation in quantitative surface analysis. However, there are also substantial benefits of electron and photon stimulated damage processes for studying molecules adsorbed on surfaces. Direct information about the geometrical structure of surface molecules can be obtained from measurements of the angular distributions of ions released by electron- or photon-stimulated desorption. The directions of ion emission are determined by the orientation of the surface bonds which are ruptured by beam irradiation. Moreover, photon-stimulated desorption studies using synchrotron radiation are revealing the fundamental electronic excitations which lead to bond-breaking processes at surfaces. These measurements are providing new insights into radiation-damage processes in areas as diverse as x-ray optics and semiconductor electronics.

(h) "Mechanisms and Applications of Electron Stimulated Desorption in Surface Science", T. E. Madey, Vacuum (TAIP)

The principles and mechanisms of electron-stimulated desorption and the utility of the electron-stimulated desorption ion angular distributions (ESDIAD) method as a tool for determining the structure of surface molecules have been described in several recent books and review articles. The present article is intended to provide a guide to the relevant literature, and to outline briefly some recent work relating to the uses of ESDIAD for determining the structure of surface molecules.

(i) "The Interaction of Water with Solid Surfaces", P. A. Thiel and T. T. Madey, Surface Sci. Reports

The purpose of this review is to compare and discuss recent experimental and theoretical results in the field of H_2O-solid interactions. Emphasis is placed upon adsorption studies performed on well-characterized, single-crystal surfaces of metals, semiconductors and oxides. We discuss the factors which influence dissociative vs. associative adsorption pathways. When H_2O adsorbs molecularly, it tends to form three-dimensional hydrogen-bonded clusters, even at fractional-monolayer coverages, because the strength of the attractive interaction between the two molecules is comparable to that of the substrate-H_2O bond. The template effect of the substrate is important in determining both the local and long-range order of H_2O molecules in these clusters. The influence of surface additive atoms (e.g., O, Br, Na, K) on the surface structure and chemistry of H_2O is examined in detail. Results on single crystal substrates are compared with earlier available measurements of H_2O adsorption on high-area materials.

(j) "Core Level Spectroscopy: A Dynamics Perspective", J. W. Gadzuk, Physica Scripta

Various aspects of the dynamics of time-dependent localized potentials and interactions in solids and at surfaces, as they might relate to the fundamental screening and relaxation processes involved in core-level spectroscopies, are explored.

(k) "Dynamics of Molecular Collisions with Surfaces: Excitation, Dissociation, and Diffraction", S. Holloway, M. Karikorpi, and J. W. Gadzuk, Nuclear Instruments and Methods B

Aspects of molecular collisions are discussed which are important in the chemically relevant energy range of ~ 1-10 eV. In particular, the role of charge transfer, potential-energy-surface topology, and intra-molecular ground- and excited-state potential curves are investigated as they pertain to internal vibrational excitation, dissociative adsorption or scattering, and diffractive scattering. The modeling and analysis are based on classical trajectories and semi-classical wavepacket dynamics, both for intra-molecular and translational motion.

(1) "Neutron Scattering Studies of Hydrogen in Catalysts", in Hydrogen in Catalysis: Theoretical and Practical Aspects, Z. Paal and P. G. Menon, eds. (Marcel Dekker, N.Y.).

Neutron scattering studies of hydrogen in catalysis are reviewed. Techniques applicable to catalysis studies (incoherent inelastic neutron scattering (IINS), quasielastic neutron scattering (QNS), and powder neutron diffraction) are introduced. Selected examples are presented with an emphasis on illustrating the utility of these neutron scattering techniques for probing the vibrational, diffusive, chemical, and structural behavior of hydrogen on catalyst surfaces.

3. Books
(S. M. Girvin, C. J. Powell, and T. E. Madey)

Division staff have been active on two book projects during the past year.

(a) The Quantum Hall Effect

The quantum Hall effect is among the most important discoveries in condensed-matter physics in recent years. There has been a great deal of experimental and theoretical activity in the area since its discovery in 1980 by Klaus von Klitzing. Professor von Klitzing received the 1985 Nobel Prize in Physics in recognition of the importance of this phenomenon. While the original experimental discoveries of the integer and fractional effects were quite surprising and unexpected, recent theoretical progress has led to a fairly well-established standard picture of the physical basis of the effects and the field has reached at least the preliminary stages of maturity. However to date, there have not appeared any extensive review articles on the subject. To remedy this, S. M. Girvin in collaboration with Prof. R. E. Prange of the University of Maryland organized a ten-part lecture series on the quantum Hall effect. The lectures were held at the University of Maryland during the 1985 Fall semester. The attendance was extremely gratifying, averaging 70-75 people for the introductory portions and 35 for the last few advanced lectures. In addition to students and faculty members from the University of Maryland, the audience contained people from other local universities and from area industrial and government laboratories. After extensive editing of the notes, we are publishing a book based on these lectures through Springer-Verlag, New York. This will be the first major review of the field to be published and we anticipate that it will be well received. We have already received a request for permission to translate the book into Russian for publication through Mir, Moscow.

(b) Methods of Surface Characterization

While there are many books and review articles on different aspects of surface science and its applications, there is a dearth of information on how to make reliable surface-characterization measurements. There is, in essence, a large information gap between review articles in which the latest scientific advances are discussed and manufacturers' handbooks in which the operation of commonly used surface-characterization equipment is described. Arrangements have been made with a commercial publisher to produce a series of books, "Methods of Surface Characterization," which will address this need. Two Division staff members (Powell and Madey) and three other scientists (A. W. Czanderna at the Solar Energy Research Institute; D. M. Hercules and J. T. Yates, Jr., at the University of Pittsburgh) constitute an editorial board that will oversee the production. A series of four volumes is currently planned which will describe the principles, techniques, and methods considered important for surface characterization. It is intended to describe how important surface-characterization measurements are made and how to ensure that the measurements and interpretations are satisfactory (to the greatest extent possible). The approach of the series will be pedagogical or tutorial.

Two volumes of the book series will describe the techniques and methods for electron spectroscopy and ion spectroscopy, respectively, which are in widespread use for surface analysis. These volumes will be concerned largely with techniques for which commercial instrumentation is available. Writing for both volumes is close to completion.

A third volume will describe techniques for specimen handling and depth profiling. For specimen handling and treatment, this volume will provide a compilation of methods that have been proven useful. This volume will also address the common artifacts and problems associated with the bombardment of solid surfaces by electrons and ions. Finally, a description will be given of methods for depth profiling. It is hoped that writing for this volume will be completed in 1987.

A fourth volume brings together a description of methods for vibrational spectroscopy of molecules on surfaces. Most of the techniques are currently under active development; commercial instrumentation is available for some techniques but this situation could change in the next few years. Writing of this volume has been completed and manuscripts sent to the publisher.

D. Standards-Committee Activities

Three staff members of the Division hold offices on two ASTM Committees, the E-42 Committee on Surface Analysis and the D-32 Committee on Catalysts, and on the recently established Surface Chemical Analysis Working Party organized under the auspices of the Versailles Project on Advanced Materials and Standards. Participation in the activities of these groups provides an opportunity for leadership, for dissemination of NBS expertise, and to learn of significant measurement problems in relevant areas.

1. ASTM Committee E-42 on Surface Analysis
(C. J. Powell, J. Fine, and N. E. Erickson)

The ASTM Committee E-42 on Surface Analysis, founded in 1976, now has some 120 members; in addition, a larger number of non-members, both within the U.S. and throughout the world, participate in Committee activities. The purpose of the Committee is to advance the field of surface analysis and the quality of surface analyses through the development of appropriate standards, standard practices, reference data, reference materials, round robins, symposia, workshops, and publications.

During the past year, we have drafted a proposed Standard Practice for Determination of the Specimen Area Contributing to the Detected Signal in Photoelectron Spectroscopy and Auger-Electron Spectroscopy for consideration by the ASTM E-42 Committee. This practice describes methods for determining the active specimen area for different conditions of instrument operation, for verifying adequate specimen alignment, and for characterizing the imaging properties of the electron energy analyzer. The practice is restricted to instruments in which the specimen is excited by x-ray or electron beams with widths at the specimen much larger than the specimen dimensions viewed by the analyzer. This draft standard is based in part on recent work at NBS in which extensive measurements were made of the imaging properties of a double-pass cylindrical-mirror analyzer for various operating conditions. The XPS and Auger Subcommittees of the E-42 Committee are currently ballotting the proposed standard.

Committee activities of the past year have included development of the following documentary standards (which are at varying stages of review and approval):

- Additional definitions of terms for AES, XPS, SIMS, and Energetic Ion Analysis
- Guide to Depth Profiling in Auger Electron Spectroscopy
- Practice for Reporting Spectra in XPS
- Method for Calculating Data-Gathering Speed in XPS
- Guide to Steady-State Charge-Referencing Techniques in XPS
- Practice for Reporting Sputter Depth Profile Data in SIMS (secondary-ion mass spectroscopy)
- Guide for Specification of Ion Beams for Use in Surface Analysis
- Procedure for Sample Positioning with Cylindrical Mirror Analyzers in ISS (ion-scattering spectroscopy)
- Procedure for Approximate Energy Scale Calibration with Cylindrical Mirror Analyzers Used in ISS
- Proposed Guide for Data Reporting in ISS
- Proposed Guide for the Measurement of X-ray Flux in XPS Instruments
- Proposed Guide for Establishment of Data Bases in Surface Spectroscopies

An E-42 round robin to compare depth-profile measurements of ^{11}B in Si by secondary-ion mass spectroscopy is being concluded. The study was designed to allow participants to compare the accuracy of analysis, background signal levels, detection limits, and artifacts of their instruments and methods. Each participant received three implanted specimens, a standard implanted to a peak concentration of 2.0×10^{20} atoms/cm^3 and two other specimens implanted with different, but unreported, concentrations of ^{11}B. Each participant was asked to determine the concentration of ^{11}B in the two unknown specimens. The results determined by 12 participants using 6 different instrument types showed very good agreement. One specimen implanted to 5.0×10^{20} atoms/cm^3 was determined to have a peak concentration of $4.9 \times 10^{20} \pm 0.3 \times 10^{20}$ atoms/cm^3; and the other specimen implanted to 3.0×10^{19} atoms/cm^3 was determined to have $3.4 \times 10^{19} \pm 0.6 \times 10^{19}$ atoms/cm^3. These and other results including values for the dynamic range, detection limit, and sputtering yield of Si for each instrument type will be tabulated in a paper being prepared for publication.

The Committee has prepared a booklet of E-42 surface analysis standards which is about to be published by ASTM. It is believed that many users of surface-analysis equipment will find the booklet to be a convenient compilation of terminology, guides, and recommended practices. The booklet will be updated roughly every two years and should be an effective means of disseminating E-42 standards. Arrangements have also been concluded during the year by which E-42 standards will be republished in the journal "Surface and Interface Analysis" on a timely basis.

The Committee arranges a half-day symposium at the annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in the spring. The Committee had also been active through 1985 in arranging sessions at the National Symposium of the American Vacuum Society in the fall but this responsibility will now be taken by the newly formed Applied Surface Science Division of the AVS. The E-42 Committee arranges evening workshops at these meetings to discuss common measurement problems. The topic at the 1985 AVS Symposium was "Analysis of Buried Solid-Solid Interfaces".

2. Surface Chemical Analysis Working Party of the Versailles Project on Advanced Materials and Standards (VAMAS)
(C. J. Powell)

The "Versailles Agreement" arose from a meeting of the Heads of State or Government (Economic Summit) of industrialized nations at Versailles in 1982. The participants represented Canada, the Federal Republic of Germany, France, Italy, Japan, the United Kingdom, the United States of America, and the Commission of the European Communities (CEC). A Summit Working Group on Technology, Growth, and Employment was established consisting of government science advisers. This group established international committees in eighteen areas such as photovoltaic solar energy, food technology, advanced robotics, biotechnology, high speed trains, remote sensing from space, and advanced materials and standards.

The Versailles Project on Advanced Materials and Standards (VAMAS) consists of a Steering Committee with representatives from the seven nations above and the CEC. VAMAS supports international trade through projects aimed at providing the technical basis for drafting Codes of Practice and Specifications in Advanced Materials. The scope of the collaboration embraces all agreed aspects of enabling science and technology--data bases, test methods, design methods, materials technology--which are required as a precursor to the drafting of standards in advanced materials. VAMAS activity emphasizes collaboration on prestandards measurement research, intercomparison of test results, and consolidation of existing views on priorities for standardization action. Through this activity, VAMAS fosters the develpment of internationally acceptable standards for advanced materials by the various existing standards agencies.

The overview of VAMAS and the other international committees was concluded recently at the Tokyo meeting of Heads of State. VAMAS will, however, continue as an independent international collaboration through a VAMAS Memorandum of Understanding now being signed by the founding governments.

The Surface Chemical Analysis (SCA) Working Party of VAMAS is one of twelve such groups that have been approved to date. The main objective of the SCA working party is to produce, by coordinated effort, the reference procedures, data, and materials necessary to establish standards for surface chemical analysis. This effort is expected to lead to the international coordination of standards-related activities before national standards are adopted and to the development of standards on an international level.

The SCA Working Party was approved by the VAMAS Steering Committee in June, 1984. National representatives to the SCA Working Party have been appointed with C. J. Powell as Chairman for a three-year period. The most urgent needs for surface analysis pertain to the use of Auger-electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), secondary-ion mass spectroscopy (SIMS) and sputter-depth profiling (SDP). As projects in these areas become established and as other techniques come into greater use, it is expected that the project will broaden. The general requirements are as follows:

- an agreed based of principles, definitions of terms, and equations to relate the techniques and procedures to the measurement;
- reference procedures specifying how to measure intensities and spectral features;
- reference procedures, reference data, and reference materials for calibrating instruments, determining instruments functions, and inter-relating instruments of different designs;

- reference data of elemental sensitivity factors, matrix terms, information depths, libraries of chemical-state spectra, information on ion-sputtering rates, radiation damage, etc.; and

- standard methods of specifying an analysis.

Details of standard needs for AES, XPS, SIMS, and SDP have been identified.

Suitable infrastructures have been developed in most VAMAS states for the SCA project. In the U.S., the ASTM Committee E-42 on Surface Analysis has agreed to participate and cooperate in VAMAS SCA projects. Standards already developed by the E-42 Committee will be disseminated to the other VAMAS states; standards developed later in the other states will be considered for adoption by the E-42 Committee. Suitable projects at NBS and other U.S. laboratories also contribute to the VAMAS SCA activity.

The first meeting of the SCA Working Party national representatives took place in October, 1985 during a conference in The Netherlands. Three international projects were approved at that time and their current status is as follows:

- Development of thin oxide films as reference materials. Work is nearing completion between laboratories in the UK, France, Canada, and Belgium to define the accuracies of different methods for determining the atomic thickness of a tantalum pentoxide on tantalum material developed earlier in the UK. The material is available with two oxide thicknesses and will be useful as standards for calibrating ion-beam fluxes in sputtering experiments and in high-energy ion-beam reaction and scattering experiments.

- Development of calibration data for the energy scales of Auger-electron spectrometers. Traceable calibrations have been established in the UK for Cu, Ag, and Au Auger peaks with an accuracy of ± 0.02 eV. Similar but independent measurements are nearing completion in the USA (at NBS).

- Procedures for quantitative x-ray photoelectron spectroscopy. Test materials prepared in Canada and Germany have been identified as candidates for a proposed round robin to give information on measurements of film thickness and film stoichiometry. A round robin will be designed following test measurements in the USA.

A number of additional international projects have recently been proposed and are currently under review by the national representatives. These projects are listed below together with the countries expected to be interested in participation.

- Correction Methods for Backscattering in Auger-Electron Spectroscopy (FRG, France, Italy, Japan, UK, USA)

- Measurement of Spatial Resolution in Auger-Electron Spectroscopy (Canada, France, UK, USA)

- Tests of Algorithms and Software for Data Processing (Canada, FRG, France, Italy, Japan, UK, USA, CEC)

- Tests of Channeling Effects in Auger-Electron Spectroscopy (Canada, FRG, France, UK, USA, CEC)

- Reference Data for Electron Attenuation Lengths and Inelastic Mean Free Paths (UK, USA)

- Development of Reference Materials Prepared by Ion Implantation (FRG, Italy, UK); this project could be carried out in collaboration with IUPAC Working Group on Surface Analysis

- Development of Reference Materials for the Measurement of Depth Resolution in Depth-Profile Analysis (Canada, FRG, UK, USA)

- Development of Methods for Instrument Alignment and Calibration (Canada, France, Italy, Japan, UK, USA)

- Development of Reference Materials for the Surface Analysis of Polymers (Italy, USA)

- Reference Data for Ion Sputtering Rates in Oxides (FRG, UK, USA)

- Intercomparison to Assess the Reproducibility of Preferential Sputtering in Surface Analysis (UK, CEC)

- Intercomparison to Assess the Reproducibility of Auger-Electron Energy and Intensity Measurements (UK, CEC)

- Multitechnique Characterization of Vacancies in Alumina (France)

- Evaluation of Sensitivity Factors for Secondary-Ion Mass Spectroscopy (Canada, UK, USA)

It is expected that some of these topics will be initiated following discussion at a meeting of the national representatives scheduled for London on November 17, 1986.

The organization of the SCA Working Party has stimulated the initiation of new national activities related to and supportive of the Working Party objectives. Information on these activities is exchanged twice a year and it is anticipated that a number of these will lead naturally to new multilateral activities. Some examples of projects of this type are:

- Development of a standard data transfer format. Initial work has been done in the UK and a draft should be ready for Working Party consideration shortly.

- Calibration of the intensity scale of Auger-electron spectrometers. Methodology is under development in the UK (with CEC support) and it is expected that interlaboratory tests will be conducted in member states next year.

- Development of reference materials by ion implantation. Some research materials have been prepared in the UK and there is interest in calibrating these and other implanted materials in FRG and other countries.

The VAMAS SCA Working Party has aroused a considerable amount of interest and enthusiasm in many of the VAMAS states. Many scientists believe that VAMAS has already provided and will continue to provide a considerable stimulus to the development of standards for surface chemical analysis in each state. Furthermore, through cooperation via VAMAS, national standards will be developed more efficiently and, it is hoped, without conflicts. The specific areas where international cooperation through VAMAS will be most effective are believed to be: (1) the development of data banks and preferred data formats; (2) the development of reference materials; (3) the development of documentary standards for instrument operation and calibration; and (4) the development of recommended procedures for data acquisition, data reduction, and expression of final results.

3. Workshops on Quantitative Surface Analysis
(C.J. Powell)

Two Workshops on Quantitative Surface Analysis will be held in the autumn of 1986. The first Workshop will be held at NBS on October 24 and is co-sponsored by the ASTM Committee E-42 on Surface Analysis, the Surface Chemical Analysis (SCA) Working Party of the Versailles Project on Advanced Materials and Standards (VAMAS), the Applied Surface Science Division of the American Vacuum Society, and NBS (Surface Science Division, Office of Standard Reference Data, and Office of Standard Reference Materials). The second workshop will be held at the National Physical Laboratory (NPL) in London on November 17 and is co-sponsored by NPL and the VAMAS SCA Working Party. Each workshop will precede a major international meeting and will have discussions on reference data, reference materials, reference procedures, and instrument calibration in surface analysis. In a workshop format with ample time for audience participation, it is hoped that recent advances in these areas will become better known, important problem areas and possible solutions will be identified, and opportunities for new national and international (VAMAS) projects will become apparent.

4. ASTM Committee D-32 on Catalysts
(R. A. Haines and R. D. Kelley)

The activities of the ASTM Committee D-32 on Catalysts are concerned with the physical and chemical properties of commercial catalysts and with developing suitable procedures for catalytic activity measurements. The membership of the Committee numbers approximately 130 representatives of the major producers and users of catalysts including a significant international component. The technical activities are carried out in four sub-committees: Physical/Chemical Properties which has 6 task groups; Physical/Mechanical Properties - 6 task groups; Chemical Analysis - 2 task groups; Catalytic Properties - 5 task groups. In general, the work of the Committee has moved into areas that involve complex and often controversial measurements. Examples of these are the measurement of catalyst acidity, of the sensitivity of cracking catalysts to metallic impurities, and of multi-element chemical analysis by atomic absorption.

The Subcommittee on Chemical Analysis is chaired by R. D. Kelley. The precious metals task group continues to be involved with the Standard Test Method for platinum in reforming catalysts which has been submitted for a Main Committee ballot--the final step in establishing a standard. This platinum standard has involved eleven draft procedures, many round-robin analyses and about ten years of effort. An analytical method for palladium--Standard Test Method for Palladium in Molecular Sieve Catalysts--has also been submitted for Main Committee ballot. The palladium procedure is interesting in that it has involved two negative votes on the subcommittee level and at least one on the Main Committee ballot. All of these negative votes are concerned with the fact that commercial contracts call for greater accuracy than has been possible in the several round-robin tests conducted with the participation of a large number of companies. This issue will continue to enliven future task group meetings. The base metals task group is proceding with the development of a satisfactory test method for determining several base metals by optical atomic spectroscopy.

The Office of Standard Reference Materials (OSRM) is finalizing an agreement with ASTM Committee D-32 to distribute catalyst reference materials. R. A. Haines serves as a liaison between the two groups. The Committee has preserved the catalysts, catalyst carriers and feed stocks used in their round robins. The 1986-1987 SRM catalog already lists three high-surface-area powders for which the Committee has extensive round robin data using a static BET technique. Material is at NBS awaiting packaging which has been characterized for particle-size distribution and reactivity via gas-oil conversion microactivity tests. A series of zeolites is also available for which diffraction intensity, unit cell dimensions and zeolite areas have been determined. Other materials for which the Committee has data include supported metal catalysts (metal content) and formed catalysts (crush strength). Demand for these materials, once available, will be used as a guide for NBS catalyst standards work.

3. SURFACE MEASUREMENTS PROGRAM

D. R. Burgess, Jr., R. R. Cavanagh, H.-H. Chen, N. E. Erickson,
J.W. Gadzuk, T. J. Jach, A. L. Johnson, R. D. Kelley, R. L. Kurtz,
C. V. S. Larsson, T. E. Madey, J. M. Nicol, C. J. Powell,
D. E. Ramaker, N. D. Shinn, R. Stockbauer and P. D. Szuromi

A. Reaction Kinetics at High Pressures over Single-Crystal Catalysts (P.D. Szuromi, R. D. Kelley, and T. E. Madey)

The overall objective of this research has been to provide a molecular understanding of heterogeneous catalytic chemistry on well-characterized single-crystal surfaces. Among the areas studied are the catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen on metal surfaces, the mechanism of catalytic poisoning and promotion, and the reforming of alkanes over model supported Pt catalysts. The apparatus employed for these studies contains high-pressure reactors contiguous to ultrahigh vacuum surface analysis chambers. This work is supported, in part, by the Office of Basic Energy Sciences of the Department of Energy.

Progress during the last year included studies of the hydrogenation activity of single-crystal W catalysts, as well as the poisoning effect of adsorbed sulfur and oxygen on the W substrates. A surprising result involved the poisoning of W by S. In contrast to the poisoning of Ni by S, where a long-range interaction was observed, there is an apparent short range effect of S on W(110). Details are given below.

1. Sulfur Inhibition of Methanation Over W(110)

Sulfur inhibition of methanation ($CO + 3H_2 \rightarrow CH_4 + H_2O$) over an active W(110) catalyst has been studied. Reaction rates were measured for realistic conditions (P = 100 Torr, $H_2/CO = 100$, 600-750K), while sulfur coverages (θ_s) and carbon and oxygen coverages on the working catalyst were determined by Auger-electron spectroscopy (AES). This work demonstrated that: (1) E_a is not changed by sulfur; (2) For $\theta_s \cong 0.22$ (approximately saturation of the S p(2x2) structure), the rate decreases fourfold, and at higher θ_s decreases slowly by site blocking; (3) Sulfur has almost no effect on postreaction carbon ($\cong$ 0.3 ML), but oxygen coverages decrease from $\cong$ 0.4 ML at $\theta_s = 0$ to $\cong$ 0.05 ML at $\theta_s = 0.4$; (4) Below $\theta_s \cong 0.07$ inhibition is strong ($\cong$ 40% at $\theta_s = 0.05$) and the effect appears long-range, but at higher θ_s it is weaker and the effect appears short-range. In contrast, earlier work in this laboratory showed that long-range effects dominate for all θ_s for methanation over Ni. Model thermal desorption studies of the decrease in saturation coverages of β-CO and H_2 at 90 K due to sulfur show good agreement with decreases in the methanation rate for $\theta_s \geq 0.22$, but below this θ_s the coverages drop linearly, as for a short-range effect. However, addition of coadsorbed oxygen (0.05-0.10 ML, the average oxygen coverage in excess of carbon for the working catalyst at these values of θ_s) caused β-CO and H_2 coverages to decrease in the same way as the methanation rate, i.e., negative deviations from linearity. Long-range effects of sulfur are seen when oxygen disrupts sulfur clustering. Thus deactivation of methanation by sulfur over W(110) is interpreted in terms of oxygen-induced changes in sulfur cluster formation.

2. Effect of Oxygen on Methanation Over Tungsten

Experiments were performed in which oxygen was added deliberately to the H_2+CO reactant mixture in trace quantities (10^{-4} to 10^{-1} Torr at total pressures of 100 Torr). Addition of 10^{-2} Torr of oxygen caused the disappearance of methanation activity even at 700 K. Auger analysis after reaction demonstrated that surface oxidation had taken place. This resembles the inactvity of classical tungsten catalysts toward methanation, which is due to difficulties in fully reducing the tungsten. The inactivity of the oxidized surface in these studies also shows that the reactor has a low blank activity.

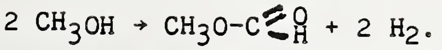
3. Modifications to the Experimental System

Modifications to the sample manipulator used for the near-ambient pressure studies have been completed that will allow low-energy electron diffraction and thermal desorption spectrometry to be used in conjunction with existing capabilities for Auger and ultraviolet photoemission spectroscopies. This manipulator is currently being installed and tested. Also, an x-ray source has become available for our use that will add the capability for x-ray photoelectron spectroscopy (XPS).

During next year, we will expand the scope of our program to different types of reactions (dehydrogenation and partial oxidation) and catalysts (transition metal oxides grown over metals). Such reactions and catalysts are of interest currently for synthesis of important chemical intermediates. Our overall goal remains the same - to understand more clearly fundamental processes in heterogeneous catalysis by: (1) preparing catalysts with well-defined surfaces; (2) studying reaction kinetics under realistic conditions of pressure and temperature; and (3) employing ultra-high vacuum surface science techniques for *in situ* characterization of working catalysts.

Initially, the studies will focus on reactions over copper-based catalysts, for several reasons. Several classes of reactions are catalyzed by copper-based catalysts, so a number of avenues are possible, including rections over metallic copper, copper oxides, and mixed-metal oxide catalysts (examples include methanol synthesis from syngas over copper-zinc oxide catalysts and from methane over copper-molybdenum oxide). In addition, many surface science studies have been conducted for the adsorption of organic molecules on copper surfaces. This body of work will be employed in interpreting our results.

These studies will proceed in two phases. The initial work (during the next year) will focus on the dehydrogenation of methanol to methyl formate over copper. The second phase will concentrate on partial oxidation reactions over cuprous oxide, in this case acrolein synthesis from propylene. Methyl formate synthesis occurs catalytically over copper as



$$2\,CH_3OH \rightarrow CH_3O\text{-}C\overset{O}{\underset{H}{\lessgtr}} + 2\,H_2.$$

Methyl formate has the potential of becoming an important chemical intermediate based on C_1 methanol. Metallic copper is unique in producing both methyl formate and valuable hydrogen using only methanol as a feed. (The other heterogeneous route to methyl formate from methanol involves oxidation and produces water rather than hydrogen as the byproduct.) The Arrhenius and pressure dependence of this reaction over copper will be determined over as wide a range of conditions as possible. The effect of surface geometry on the reaction will be determined by using a Cu(100) crystal in both its well-annealed (cubic close-packed) and sputtered (amorphous) forms, and, for comparison, polycrystalline samples. In addition, the effects of promoters, such as alkali metal oxides, and of inhibitors, which include acidic oxides such as those of Mo and W, will be investigated. The availability of AES and XPS allows the correlation of changes in kinetics with the coverages of such surface modifiers.

Finally, as time and resources permit, other avenues will be explored, including hydrdogenation and hydrogenolysis reactions over model thin-film catalysts (fractional monolayers of metal deposited on crystalline metal or oxide substrates).

B. Molecular Structure and Reactivity on Surfaces as Studied Using ESDIAD AND HREELS

(T. E. Madey, A. L. Johnson, N. D. Shinn, and C. U. S. Larsson)

A continuing challenge in surface science is to determine the structures of molecules on surfaces, particularly in the absence of long-range order. The goals of this project are to provide a direct determination of the structures of adsorbed molecules using the Electron Stimulated Desorption Ion Angular Distribution (ESDIAD) method, and to characterize the structures and reactivity of surface species using High-Resolution Electron Energy Loss Spectroscopy (HREELS). These techniques, both singly and in combination, are powerful tools for surface structural characterization.

The thrusts of this project during the last year were (a) to determine the influence of surface additives (e.g., catalyst promoters and poisons) on the local structure and reactivity of small molecules (CO, NH_3, H_2O) on surfaces, (b) to determine the structures of those molecules on initially-clean surfaces, particularly in controversial cases, and (c) to develop a digital imaging ESDIAD system to improve the measurements of surface molecular structure. This work has been supported, in part, by the Office of Basic Energy Sciences of the Department of Energy.

During the last year, progress has been made in the following areas:

1. Structure of CO on Surfaces of Catalytic Interest: Is it Standing Up, Lying Down, or Inclined?

We have used ESDIAD in combination with HREELS and other surface spectroscopies to study the adsorption of CO on three transition-metal surfaces. In each case, there were indications from our own measurements (as well as from measurements made in other laboratories) that the CO may be strongly inclined or "lying down", rather than the more widely-reported "standing up" configuration. In three cases, CO on Cr(110), CO on Fe(100) and CO on K-dosed Ru(001), it has been found using HREELS that the CO stretching frequencies are abnormally low, in the frequency range 1150 to 1460 cm^{-1}; these stretches are strongly down-shifted from the typical frequency range (~ 1800-2050 cm^{-1}) for CO adsorbed in a standing-up fashion, bonded via the C atom. It has been proposed that the low CO stretching modes are associated with strongly-inclined or lying-down species coordinated to the substrate via both C and O atoms. We performed ESD and ESDIAD studies in all three cases, and confirm that there is little or no O^+ or CO^+ ion emission at any desorption angle from the CO characterized by the low-frequency stretching modes. For CO on the clean Cr(110) and Fe(100) surfaces, this is the expected result for strongly inclined or lying-down CO, and confirms the structural assignments. For CO + K on Ru(001), the influence of reneutralization effects on ion yields is highly probable due to the CO-K interaction, and the configuration of CO (standing up or lying down) remains controversial.

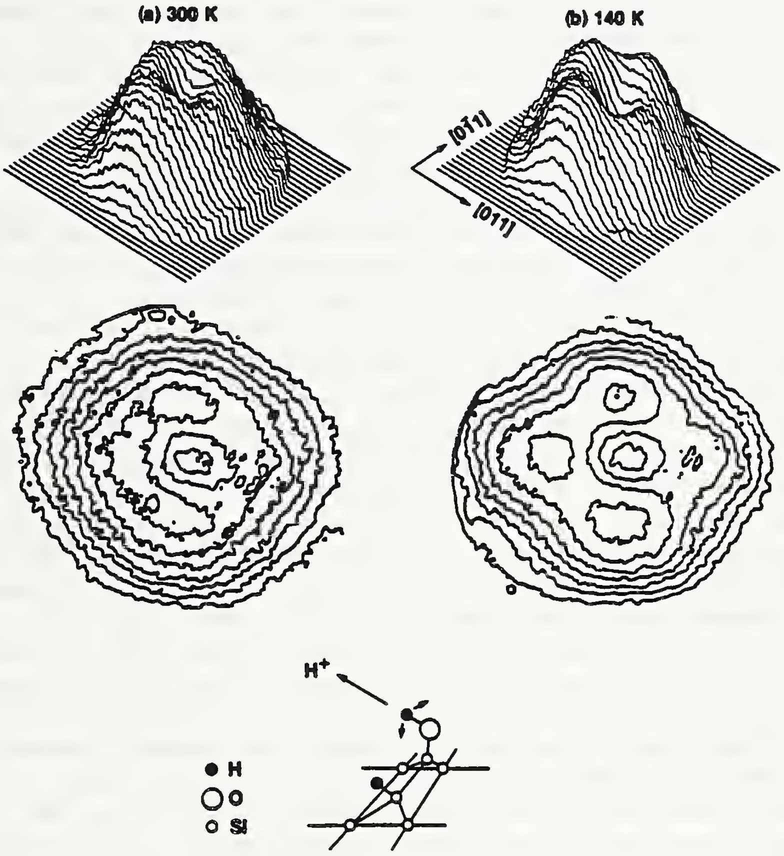
2. Evidence for Molecular O_2(ads): Chemisorption of Oxygen on Cr(110)

In most studies of oxygen interacting with transition metals, it is reported that oxygen dissociates rapidly to form a monolayer of atomic oxygen; subsequently, an oxide layer forms. We have found a strikingly different behavior for the adsorption of oxygen on Cr(110) at 120 K. At low coverages, dissociative oxygen adsorption dominates, while at higher coverages, HREELS and ESDIAD data provide evidence for a co-existing minority molecular O_2 state. An O_2(ads) vibrational frequency of 1020 cm^{-1} and a six-beam ESDIAD pattern are suggestive of super-oxo O_2(ads) bonding at local sites, each with the O-O molecular axis tilted away from the surface normal. Molecular O_2(ads) has been seen previously on less reactive surfaces (Ag, Cu, Pt, Pd), but this is the first time that O_2(ads) has been reported on such a reactive surface having a high heat of oxygen adsorption.

3. New Digital ESDIAD System

Up to the present time, all of our ESDIAD data have been obtained by photographing the two-dimensional patterns displayed on a fluorescent screen. In order to permit more quantitative determination of ion angular distributions, desorption angles (and, by inference, surface bond angles), we have constructed a new digital imaging system based on a high-sensitivity video camera for detecting the ESDIAD images on the fluorescent screen.

The digital imaging system is composed of a laboratory computer with a hard disk, a color monitor, a video camera and hardware boards for video data acquisition and arithmetic processing. The hardware allows the acquisition of live images or the digitization of photographs, the formation of histograms and contour plots, digital image manipulation (such as background subtraction, smoothing, and feature recognition/-enhancement/removal), and plotting. We have demonstrated the ability to do single-ion counting as well as image integration to form ESDIAD patterns. These abilities are crucial for allowing the ESDIAD pattern to be quantified, and for when angle and time-resolved spectra (i.e., negative ion spectra) are acquired. Several digitized ESDIAD patterns obtained using this system are shown in Fig. 3.1; these are described in the following paragraphs.



H^+ ESDIAD from OH on Si(100)

(a) 300 K

(b) 140 K

Fig. 3.1 H^+ ESDIAD and schematic model illustrating the bonding of OH to a Si(100) surface. The data were obtained using the new digital ESDIAD system. Column (a): H^+ ESDIAD (perspective and contour plots) for T = 300K; column (b): H^+ ESDIAD at 140K. A schematic bonding model in which H and OH are bound to both ends of a Si(100) dimmer is shown below. The four H^+ beams resolved in column (b) are due to ESD from degenerate dimer configurations. The decrease in resolution of ESDIAD at 300K is due to increased vibrational motion of the OH.

4. Structure of H_2O Adsorption on Planar and Stepped Surfaces of Silicon

Despite the extensive interest in the surface chemistry of H_2O, there have been relatively few structural studies of H_2O on surfaces having high heats of M-O bond formation where dissociation is likely to occur. We have recently applied the new digital imaging ESDIAD system to the study of H_2O on surfaces of Si; this is the first ESDIAD study ever reported for adsorption on a semiconductor surface!

The adsorption of water on the reconstructed planar (100)2x1 and single domain-stepped (100) 2x1 (cut 5° towards (011)) surfaces of silicon was studied using LEED and digital-imaging ESDIAD as a function of temperature (160-650 K) and coverage. Water has been shown by Chabal and Christman to chemisorb dissociatively to form surface OH groups. At 300K, the H^+ ESDIAD pattern for the planar surface is a nearly symmetric halo (see Fig. 3.1), indicating that OH is oriented with its bond vector inclined away from the surface normal, while at low temperature ($\lesssim$200K) a four-lobed pattern preserving substrate symmetry is observed. This reversible temperature dependence is related to librations and rotations of the OH complexes. ESDIAD from the stepped surface exhibits two-fold symmetry, with enhanced emission towards the steps, consistent with bonding of OH to single-domain terrace sites. An interpretation based on the dimer model of the Si(100) reconstruction has been formulated.

Plans for next year are centered on three areas. First, a major new thrust is to develop the technology for measuring ESDIAD of negative ions, and to apply the new methodology to challenging problems in surface chemistry of adsorbed molecules. There are several reasons for these proposed experiments. First, ESDIAD of positive ions has proven so useful in surface chemistry that we anticipate new structural information about adsorbed molecules whose ion fragments include negative ions. Certain classes of molecules (e.g. halogen-containing species) generate high yields of atomic negative ions (F^-, $C\ell^-$) under electron bombardment. Other candidates include H^- and O^- from H_2O, CO, etc. Second, these studies will provide new insights into the basic mechanisms of ion fragmentation and the influence of surface parameters on ion trajectories, etc. In a few special cases, we expect to compare directly negative- and positive-ion ESDIAD from the same surface species (e.g. H^+ and H^- from NH_3, H_2O). Third, this is a new scientific and technical challenge. Such measurements have never been made before, and there may be unanticipated benefits; e.g., the technology necessary for negative ion detection will permit the first mass-resolved, two-dimensional ESDIAD measurements.

Test molecules for ESDIAD of negative ions include HF, F_2, PF_3, the completely fluorinated analogue of acetone [$(CF_3)_2CO$], di(trifluoromethyl) ether [$(CF_3)_2$ O], and fluorine-substituted pyridine. In all cases, we will combine kinetic measurements with measurements of local structure. Strong repulsive interactions between the electron-rich fluorine-containing portions of the adsorbed molecules may well lead to a rich assortment of local structures. Of particular interest will be the search for adsorbate/substrate systems where ESDIAD of both positive and negative ions can provide complementary structural information.

Second, we will continue our studies of the structure of small molecules on clean metal surfaces, and the influence of surface additives (such as catalyst promoters and poisons) on the structure and chemistry of adsorbed molecules. Examples will include several controversial cases, e.g., the structure of acetylene on Cu(100), and the effect of impurity O and Br on the structure and chemistry of H_2O on Cu(110).

Finally, we will expand our effort in the surface chemistry of electronic materials by applying ESDIAD to the study of semiconductor surfaces, in particular, to characterize the surface structures formed on Si surfaces during adsorption and reaction of small molecules. Despite the technological importance of semiconductors in catalysis and electronics, there have been no published studies of adsorbate structures on semiconductors using ESDIAD.

We intend to characterize the surface chemistry of atomically stepped and planar Si surfaces interacting with small molecules (H_2O, H_2O_2, CH_3OH, NH_3, CH_3OH, HF, F_2) of importance in semiconductor device processing (wet oxidation, plasma etching, reactive ion etching, etc.). A promising new area is the adsorption and decomposition of transition metal carbonyls ($Fe(CO)_5$, $Cr(CO)_6$, etc.) on Si. A study of thermal desorption, electron beam-induced desorption, ESDIAD and HREELS of adsorbed carbonyls will provide valuable insights into the physics and chemistry of metal deposition and silicide formation on Si surfaces.

C. Neutron Scattering Studies of Catalysts
(J. M. Nicol, R. R. Cavanagh, and R. D. Kelley)

Neutron scattering techniques applied to adsorbate systems on high-area catalytic surfaces are providing new insights into catalytic science. NBS has played a lead role in this effort having a unique combination of neutron physicists and surface chemists with an interest in catalysis. During the past year, work has focused on inelastic incoherent neutron scattering (IINS) studies of the interaction of hydrogen with palladium and quasielastic scattering (QNS) studies of the ammonium ion in zeolite rho. This work has been carried out at the NBS research reactor with support, in part, from the Chemical Sciences Division of the Office of Basic Energy Sciences, Department of Energy.

1. Adsorbate Dynamics in Zeolites

Quasieleastic neutron scattering has been used to characterize the diffusive motions of NH_4^+ in zeolite rho. This work reflects a collaborataive effort between the Surface Science Division (R. R. Cavanagh and J. M. Nicol) and the Reactor Radiation Division (T. J. Udovic and J. J. Rush) at NBS, and E. I. DuPont de Nemours (D. R. Corbin), W. R. Grace (M. J. Wax), and the University of California at Santa Barbara (G. D.

Stucky). By measuring the influence of neutron momentum transfer on the elastic incoherent structure factor (EISF), it has been possible to determine the reorientational motions of the ammonium. We have been able to demonstrate that the NH_4^+ groups undergo essentially three-fold reorientational motions. However, the fourth (and "anchoring") proton periodically changes roles with one of the rotating protons. Figure 3.2 shows the data recorded at the NBS reactor along with the predictions of three different reorientational models (120° rotation about a single fixed 3-fold axis, 120° rotations at random about all four 3-fold axes, and rotation about a two-fold axis). Two points should be made regarding these data. The value of Q where the minimum in the EISF is observed provides a measure of the applicability of any model to the observed data. Clearly, one of the models predicts a Q_{min} value (~3 $Å^{-1}$) which is inconsistent with the data (2.3 $Å^{-1}$). The second point is related to the

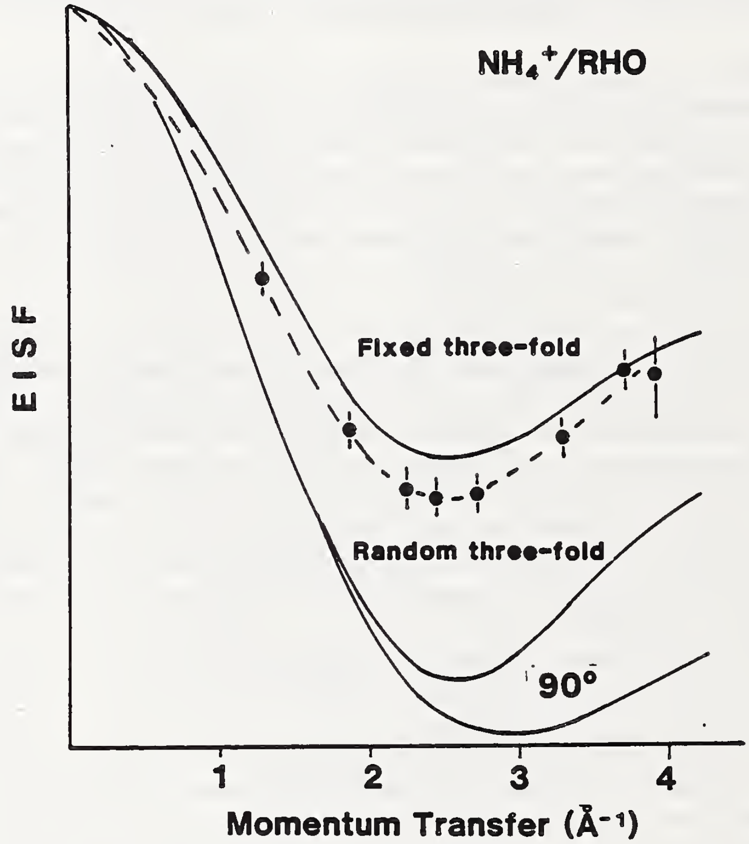


Fig. 3.2 Elastic incoherent structure factor as a function of neutron momentum transfer (Q) between 1 and 4 $Å^{-1}$. The points correspond to data taken at the NBS reactor on NH_4^+ in zeolite rho. Three models of the reorientational motion are indicated: Fixed three-fold (120° rotations about a single fixed 3-fold axis), random three-fold (120° rotations at random about all four 3-fold axes), and 90° (90° rotation about a two-fold axis with each proton sampling four different positions).

depth of the modulation in the EISF. Since deammoniation of the NH_4/rho generates the protonated form of the zeolite (H-rho), there will be a non-zero contribution to the EISF at all Q from the H-rho in the specimen. Thus, the observation of a deeper minimum in the EISF than predicted by an anchored 3-fold rotor (despite the intensity contributed from H-rho) clearly establishes the random 120° model as the best model for the reorientational motion.

The activation energy for this mode has also been estimated from the temperature dependence of the Lorentzian component of the quasielastic scattering signal. An exceptionally low activation energy (~20 meV) is obtained. This barrier is comparable to the lowest observed activation energies for NH_4^+ in molecular solids, and represents the first direct measurement of such dynamics in zeolites.

Futher work is in progress to examine the reammoniation of zeolite H-rho, starting with an ammonia loading equivalent to one NH_4^+ ion per unit cell. In addition to characterizing the diffusive motions of the NH_4^+ ions by quasi-elastic scattering, vibrational spectroscopy of the ammonium modes in the 5 to 20 meV range is being investigated by inelastic neutron scattering. By collecting data over the temperature range 4 to 300 K, a more detailed picture of site geometries and bonding interactions will be obtained.

2. Interaction of Hydrogen with Palladium

IINS is being used to characterize the adsorption and absorption of hydrogen by small particles of palladium (Pd black), with particular emphasis on the identification of subsurface hydrogen. This work is a collaborative effort between the Surface Science Division (J. M. Nicol, R. D. Kelley, and T. E. Madey) and the Reactor Radiation Division (J. J. Rush). The data indicate that bulk β-hydride forms readily following high doses of hydrogen at temperatures as low as 77 K. At lower hydrogen doses, spectral features have been associated with vibrational modes of both surface and subsurface hydrogen. The subsurface species appears to be associated with a vibrational mode at ca. 58 meV, consistent with hydrogen bonded in octahedral sites in the Pd lattice. Evidence for the subsurface hydrdogen is the broad lineshape which is quite distinct from the more narrow linewidth of the β-hydride, and the reactivity with chemisorbed oxygen (measured in oxygen-titration experiments).

Experiments are underway to generate and characterize a hydrogen-free Pd sample and to examine the dynamics of the surface-subsurface equilibrium. Force-constant calculations and other experimental work is being undertaken to try to establish site geometries for the H-Pd system.

In the next year, in addition to the continuing work with zeolites and with palladium black, we will prepare a Raney nickel sample using ^{60}Ni. The low incoherent cross-section of this isotope makes the substrate nearly invisible and provides an unusual opportunity to study the structure and dynamics of an adsorbed hydrogeneous species in great detail.

D. Surface Characterization Using Synchrotron Radiation
(R. Stockbauer, R. L. Kurtz, N. D. Shinn, H.-H. Chen, D. E. Ramaker, and T. E. Madey)

Major goals of this effort are (a) to determine the electronic structure of surfaces and adsorbates using variable-wavelength synchrotron radiation and ultraviolet photoelectron spectroscopy (UPS), and (b) to identify the electronic excitations which result in the photon-stimulated desorption (PSD) of ions form molecules adsorbed on surfaces as well as from condensed molecular films. When possible, PSD ion yields are correlated with UPS of both valence states and core-electronic states of the surface species. These measurements provide tests of recent theoretical models of electron- and photon-stimulated desorption, and provide new insights into the bond-breaking processes induced by ionizing radiation incident on surfaces. The work has been supported in part by the Office of Naval Research.

Accomplishments during the past year were in six areas: (1) electron- and photon-stimulated desorption on ions from oxide surfaces; (2) electronic structure of molecules adsorbed on surfaces; (3) instrumentation of a new beamline at the NBS synchrotron radiation facility SURF-II; (4) construction of a new display analyzer; (5) progress at the Brookhaven National Synchrotron Light Source (NSLS); and (6) theory of stimulated desorption.

1. Electron and Photon-Stimulated Desorption of Ions from Oxide Surfaces

Recent efforts in our laboratory to understand the mechanisms involved in stimulated desorption have forced a re-evaluation of the factors that influence surface stability under ionizing radiation. Our experimental results in desorption from different surfaces of TiO_2 have shown that the local surface atomic arrangements can be as important in determining ion desorption probability as the electronic structure. To expand our efforts in further elucidating the fundamental processes involved in desorption induced by electronic transitions (DIET), we have begun to study different materials and (using synchrotron radiation) to probe deeper core levels.

During the past year, we pursued these two efforts on BL-1 of the NBS SURF-II synchrotron storage ring as well as at the Deutsches Electronen Synchrotronen (DESY) in Hamburg by studying DIET from single-crystal surfaces of MgO. At DESY we used the wiggler beam-line coupled to the Flipper monochromator to measure ion emission from MgO with photon energies spanning all of the electronic energy levels. Excitations spanning the O 1s level produced striking results.

These measurements are the first observation of a fundamentally new excitation producing desorption: core-exciton production whose subsequent decay induces the desorption of O^+ and H^+. The H^+ signal originates from surface contamination on the MgO from the ambient vacuum. We found evidence for the contribution of several excitonic states to the desorption of O^+ and the data show that these states are different from those giving rise to H^+ desorption. Electron yield data from partially oxidized Mg imply that these excitations are localized in the near-surface region.

Core excitons consist of a bound conduction-electron/core-hole pair and, with a deep core-hole such as the O 1s, are localized on a single atomic site. The obvious signature of an excitonic state is the observation of excitations that result from photon absorption at energies below the binding energy. In the case of an insulator such as MgO, this corresponds to absorption of a photon that places the photo-excited electron at an energy in the bulk band-gap.

In Fig. 3.3 the O^+ and H^+ ion yield curves are shown near the onset in O 1s excitation. The onset in O 1s core excitation to unoccupied

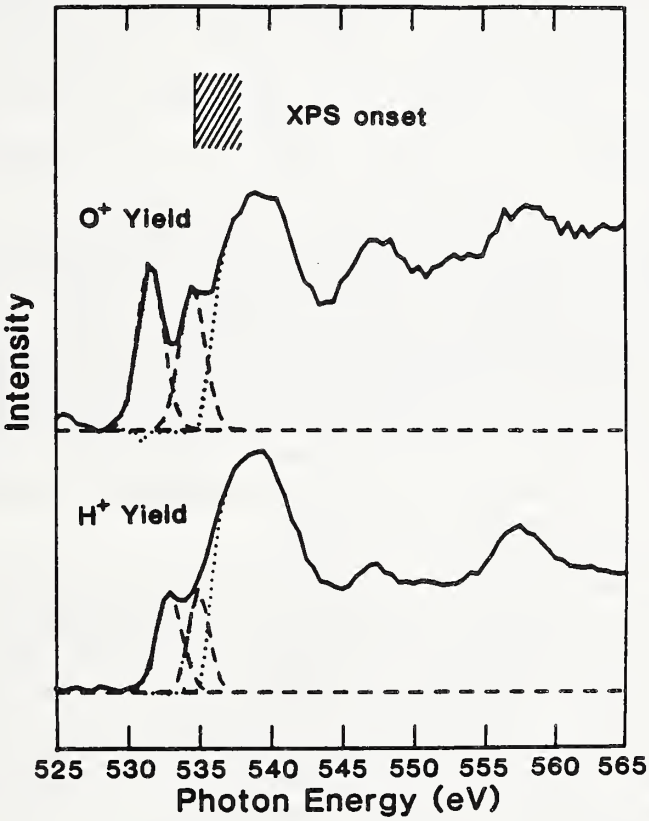


Fig. 3.3 O^+ and H^+ ion yields from MgO(100) versus incident photon energy. The spectra are decomposed into the excitonic desorption contribution given by the Gaussian peaks. When the Gaussians, given by the dashed curves, are subtracted from the spectrum, the dotted curve is obtained.

conduction band states in the bulk is indicated by the shaded bar. Clearly, the excitation producing O^+ desorption at 531.6 eV involves photon energies that place the photoelectron in the 7.8 eV bulk band-gap, an excitonic state. When the ion yield curves are compared with fluorescence and electron energy-loss (ELS) measurements, one finds structure essentially identical to that for photon energies above 535 eV in Fig. 3.3. Using the usual dipole-selection rules, we therefore identify the two Gaussian peaks in the O^+ desorption as $1s^1 2s^2 2p^6 3p^1$ and $1s^1 2s^2 2p^6 4p^1$ excitons and the feature in the H^+ desorption at 532.9 eV as due to a $1s^1 2s^2 2p^6 3p^1$ exciton of OH^-. The observation of H^+ desorption at the O 1s level is not surprising since hydrogen is stable on MgO surfaces in the form of OH^- radicals.

In the decay of these excitonic excitations, the excited electron is less likely to be a participant (which would result in a 1h final state) than it is to remain as a spectator to the decay. A 2h1e state will result from the $1s^1 2s^2 2p^6 3p^1 \rightarrow 1s^2 2s^2 2p^4 3p^1$ decay. Since the radial extent of the 3p wavefunction is large, incomplete screening of the O core by the 3p electron will produce a state that is nonbonding and will influence the stability of the O on the surface. Should the 3p electron escape (and this is assisted by the loss of the exciton binding energy after the Auger decay), the O^+ will clearly be in a repulsive surface Madelung potential.

We plan to continue these studies of ion desorption by expanding our recent work on MgO and TiO_2 to include studies of other isostructural oxide surfaces with varying electronic configurations. An example of such a comparison would be that of $TiO_2(001)$ and $Ti_2O_3(1012)$. We will also begin work on partially-oxidized transition-metal surfaces. These surfaces will allow the application of standard synchrotron radiation techniques that are often unsuccessful when applied to insulating oxides.

2. Electronic Structure of Molecules Adsorbed on Surfaces: Relation to Geometric Structure

Synchrotron ultraviolet photoemission studies of carbon monoxide chemisorption on Cr(110) at 90 K confirm the sequential population of two structurally different molecular binding states. The first state (α_1CO) consists of molecules with both the carbon and oxygen atoms coordinated to the chromium surface; a previously proposed model locates these molecules in the two-fold symmetric surface hollow sites with the intramolecular axis aligned roughly along the $[1\bar{1}0]$ direction. The measured photon energy dependence and limited angular dependence of the α_1CO photoemission peak intensities strongly support this model and are consistent with the proposed local binding site. Only after this binding mode saturates at 1/4 monolayer does the α_2CO binding state appear. For this latter state, the CO molecules are terminally bound to the surface with the C-O axis aligned approximately along the [110] surface normal. A comparison of spectral differences for α_1CO and α_2CO reveals previously unseen binding-mode-dependent effects in the adsorbed CO electronic structure, highlighted by an increase in the CO 4σ orbital binding energy for the lying-down state. These data have been related to previously reported vibrational and stimulated desorption results for Cr(110)/CO.

In parallel experiments in our SURF-II apparatus, electron-stimulated desorption (ESD) experiments using a time-of-flight pulse-counting method were performed for molecular CO chemisorbed on the Cr(110) surface at 80 K. Consistent with previous qualitative observations, negligible CO^+ and O^+ desorption signals were measured from the α_1CO overlayer which saturates at 1/4 monolayer. For $\theta_{CO} > 0.25$, a terminally-bonded (α_2CO) binding mode is populated in addition to the existing α_1CO binding mode and the ion yield sharply increases. For α_2CO, both O^+ and CO^+ ions are observed; the CO^+ ions desorb with characteristically lower kinetic energies than O^+ ions. Near saturation coverages of CO(ads), an observed decrease in the O^+ yield is attributed to adsorbate-adsorbate interactions which reduce the ion desorption probability, as seen in ESD studies of terminally-bonded CO on other metals. These results have been considered in the context of two possible models proposed for the α_1CO binding state, and related ESD observations for CO chemisorbed on potassium-promoted Ru(001) and Fe(001).

3. New Laminar Grating Installed at SURF

A laminar-profile toroidal-grating monochromator has been installed on our dedicated beamline at the NBS SURF-II synchrotron storage ring. This grating is expected to reduce significantly the vexing problem of higher-order contributions to the diffracted light and yet result in good transmission over the 20-100 eV range. Instead of the usual ruled-grating profile, the grooves in this grating have been ion-etched to produce a square-wave profile. The groove-depth has been produced so that destructive interference occurs between the top and bottom faces for all the even orders. Measurements of the relative contributions of all orders through 4th order is presently underway; however preliminary results show significant attenuation of 2nd and 4th order light.

PSD data as well as total secondary-electron emission to which the PSD data are compared are adversely affected by this higher-order radiation. In both experiments, the signals from the different-order radiation are indistinguishable which necessitates removal of the higher-order contribution. By reducing the higher-order radiation from the monochromator, these corrections become smaller allowing us to examine weaker PSD signals and to determine thresholds more accurately.

4. Construction of Angle-Resolving Display Analyzer

A new ellipsoidal-mirror angle-resolving electron- and ion-energy analyzer has been assembled and is undergoing initial testing. This outstanding instrument was designed and constructed at NBS (based on an instrument constructed at IBM by D. Eastman). It is ideally suited for angle-resolved PSD, and will be the only such analyzer in North America used for these measurements. Details and scientific plans are given in section 4.B.3.

5. Resonant Photoemission from Cu Measured at Brookhaven NSLS

During our run this spring at the Brookhaven National Synchrotron Light Source, we were able to make measurements of resonant photoemission from sputtered Cu(100) over the photon energy range spanning the Cu 3p excitation onsets. Photoemission measurements reveal two distinct 3d shake-up satellites at 12 to 14.6 eV apparent binding energy. Interference between these satellites and the Auger decay channels that open up when the photon energy exceeds the 3p excitation onset produce resonances in the satellite intensity. There are two resonant energies (75.5 and 78.5 eV) that correpond to resonances with excitations from $3p_{1/2}$ and $3p_{3/2}$ states. The two distinct satellites are believed to arise from the multiplet splitting of the Cu $3d^8$ configuration. These experiments demonstrate the versatility of the NBS-NRL X24C beam-line with the extended energy range and good resolution of the grating/crystal monochromator.

We also attempted during this run to measure electron attenuation lengths in condensed molecular solids. This work is described in section 2.A.5(b).

6. Theory of Stimulated Desorption

Our work during the last year has addressed an important issue related to the photon-stimulated desorption (PSD) of ions from surfaces. What are the relative roles of direct photoexcitation and indirect excitation via secondary electrons in PSD ion yields? The question of the magnitude of indirect, secondary-electron processes in PSD is an extremely important one. If the ion yield is dominated by such indirect effects, the utility of PSD for the determination of surface structure is severely limited.

Recent reports on the magnitude of secondary-electron contributions in electron/photon-stimulated desorption (ESD/PSD) appear to be contradictory. It has been reported that secondary electrons provide the dominant contribution to the H^+ yield from NH_3/Ni at energies above the N 1s core excitation and this process is called X-ray-induced ESD (XESD). Others have concluded that the XESD process is the dominant mechanism in the PSD of N^+ and O^+ ions from mixed condensed gases such as N_2 and O_2 and in the PSD of H^+ ions from OH/YbO-Sm. On the other hand, large differences are often found between the secondary-electron yield and the PSD ion yield (e.g., O^+ from O/Cr and O/W, H^+ from OH/Ti and Cr, and H^+ from H/diamond) providing strong evidence for the dominance of a direct photon-excitation mechanism. The total absence of ion yield contributions at certain core levels (e.g., the O^+ yields from NO/Pt(110) and CO/Ru(0001) reveal no structure at the N, Ru, or Pt core levels) also indicates that the XESD process is not dominant. Finally, a semiquantitative determination of the secondary-electron contribution to the ESD OH^* yield from OH/TiO_2, where large contributions are expected, indicates that backscattered electrons are responsible for only about 30% of the OH^* desorption.

In this work, we have re-examined the three systems mentioned above, in which dominant XESD effects have been postulated. ESD ion angular distribution (ESDIAD) data on the NH_3/Ni system and a detailed determination of the mechanisms involved in H^+ desorption indicated that all of the features attributed to the XESD effect may, in effect, arise from direct core-level processes. A re-examination of the PSD N^+ and O^+ yields from condensed N_2 and O_2 reveals that the indirect XESD mechanism contributes just one-third of the N^+ yield, but dominates the O^+ yield. This arises because the direct Auger-stimulated desorption (ASD) process following core-hole excitation is inactive for O^+ desorption, but remains active for the N^+. This differences is believed to arise because of $2\pi^*$ electron transfer in condensed O_2 (i.e., electron hopping between neighboring O_2 molecules); the $2\pi^*$ band is, of course, empty in condensed N_2. Finally, a detailed interpretation of H^+ desorption from OH/Ti and Cr, and comparison with the system OH/YbO-Sm indicate that the direct ASD process is also inactive in the latter case. Thus we show for these three systems that either alternate interpretations of the data are possible, indicating that the XESD effect is small, or that the XESD process dominates only because the direct mechanism is suppressed. This makes the results on these three systems consistent with the significantly larger number of papers which indicate that the XESD effect is generally not a major problem.

Plans for the next year include an examination of recent PSD data for MgO (section 3.D.1). The O^+ and H^+ ion yields spectra reveal large excitonic-like features which are not completely understood. Detailed interpretation of these data may also provide information about the role of secondary electrons and the XESD effect in ionic insulators. The extent of these effects in the alkali halides, e.g., LiF and NaCl, has been somewhat controversial. The MgO system is an excellent model system for such studies, since it is more stable than the alkali halides and the electronic processes appear to be simpler. A theoretical examination of the PSD ion yields from condensed and chemisorbed hydrocarbons, and an examination of hydrogen bonding effects, may also be attempted as the data become available.

E. Dynamical Effects Associated with Core-Level Ionization

(T. J. Jach)

The NBS Quantum Metrology Group under the direction of Dr. R. D. Deslattes has developed a program to study the electronic effects associated with core-level ionization in atoms, molecules and at surfaces. Specific effects which are being studied include dynamical effects in inner-shell vacancy production, relaxation of the extra-atomic environment, and production of multiple vacancies, with or without ionization. One member of the Surface Science Division Staff has been working half-time on this project.

For the past four years, this team has designed and built the X-24A Beamline at the National Synchrotron Light Source (Brookhaven National Laboratory). During 1986, the beamline, which is optimized for soft x-ray production in the energy range 800-2000 eV, finished its first full year of operation. The X-24A soft x-ray beamline at Brookhaven has been functioning extremely well, producing the highest flux in the world ($>4 \times 10^{11}$ photons/sec) with an energy resolution of 0.4 eV.

The first round of experiments has been on gas targets, both monatomic and polyatomic; the model systems we are studying will shed light on solids we intend to study in the future. Argon is the "hydrogen atom" of multi-electron atoms since its one-electron excited states are the easiest to calculate using Hartree-Fock-type procedures. Theorists are therefore actively interested in experiments at this level.

An experimental chamber has been built in which the gas is confined to a cell with thin beryllium windows transparent to x-rays entering at the energy range of current interest (about 3 keV) as well as to fluorescent x-rays produced by radiative decays. The emitted x-rays are analyzed by a highly efficient spectrometer consisting of a crystal bent along a Rowland circle and a position-sensitive proportional counter. This state-of-the-art combination allows whole line spectra to be taken simultaneously.

The NSLS x-ray ring is due to shut down for 6-8 months starting in December, 1986 for extensive modifications. As a result, we have concentrated on taking the maximum amount of data, with next year to be devoted to interpretation of the results and preparation of reports. The following experiments have been performed during the past year.

1. X-ray Raman Threshold Behavior Near the Ar K-edge

It is possible to induce fluorescence from the Ar Kα (2p-1s) and Kβ (3p-1s) transitions at incident energies which are too low to excite the 1s electron into the lowest empty bound state. This is accomplished by a Raman process in which an electron is promoted from a virtual state near the 1s state which is then filled by radiative decay of a 2p or 3p state. Using a high-intensity monochromatic x-ray beam and a high-resolution crystal spectrometer, we have been able to directly excite such transitions and measure the amplitudes for fluorescent decay from these states. Theoretical calculations have existed for some time for these amplitudes, but the difficulty in observing the effect with statistically significant count rates has made them difficult to evaluate. We have already obtained data of sufficient quality to allow us to separate out resonant and non-resonant Raman contributions.

2. Energy Dependence of Shake-up Satellites in the Ar Kα and Kβ Lines

The adsorption spectrum of argon (and of more complicated molecules) contains a number of features only resolvable with a highly monochromatic beam above the threshold K-edge. These features are attributed to excitations of one core and one or more valence electrons which are excited by a shakeup process. Similarly, there are satellite lines observed at energies above the fluorescent emission of Kα or Kβ radiation which show an energy dependence near threshold. Because of the high resolution of our monochromator and spectrometer, we have been able to obtain extensive data on the threshold at which these satellites turn on and relate them to specific features in the absorption spectrum. This was possible because of the excellent energy stability of our monochromator over long periods of time. The data allow us to discriminate between various theoretical assignments which have been made for the quantum numbers of the absorption and satellite features.

3. Relative Coherent Elastic and Resonant Elastic X-ray Cross Sections at the Ar K-edge

We have measured the x-rays elastically scattered from argon atoms at energies all through the K-edge, with sensitivity to their polarization. This allows us to separate out the resonant and coherent components and determine cross-sections for each. We hope that this work will be accurate enough to produce absolute cross sections.

4. The Chlorine Fluorescence Spectrum as a Function of Bonding in Multi-atomic (Freon) Molecules

As a start on more complicated molecular spectra, we have observed the K fluorescence lines from chlorine atoms in freon. The chlorine atom is only one electron removed from argon, and can be present as one, two, or three neighboring atoms in freon. This system is therefore appropriate to study the effects of bonding.

5. Photoemission Spectrum of Ar Near the K Edge

In addition to studying the x-ray fluorescence spectra of gases and solids, we need to examine their non-radiative decays and their photoemission spectra. This is important in studies such as of covalent bonding and of post-collisional interactions of the outgoing particles. We are extending the work we have done with gas targets in cells to windowless gas-jet targets. As a step in this direction, we have taken preliminary data with a differentially pumped gas cell connected to a hemispherical electron analyzer. We have measured the photoemission spectrum from argon and hope to extend these measurements in the coming year.

The above experiments were performed in collaboration with Drs. P. Cowan, S. Brennan, and R. LaVilla of the NBS Quantum Metrology Group. The chlorine fluorescence experiment was a collaboration with Dr. Perera of Lawrence Berkeley Laboratory and the photoemission experiment was a collaboration with Dr. S. Banna of Vanderbilt University.

F. Development of Silicon Diode Radiation Detectors for Synchrotron Radiation Research

(T. Jach)

Scientists using x-rays from synchrotron radiation light sources have been traditionally conservative in selecting detection schemes such as gas ion chambers, scintillation counters, film, or Si(Li) detectors. We have developed a new technology over the past four years in which silicon PIN photodiodes, both as-is and with special modifications, have been employed as radiation detectors in experiments. These diodes are manufactured as detectors of radiation, but in fact they are excellent detectors of x-rays over an energy range of 500 eV to 20 keV. Their efficiencies exceed those of ion chambers by an order of magnitude and they offer additional advantages of small size, compatability with ultra-high vacuum systems, and lack of a need for power supplies.

Two experiments were performed during the past year on the Naval Research Laboratory Beamline X-23B. These experiments are part of a continuing (and unique) effort to provide data for synchrotron users on the characteristics of silicon PIN diodes in the x-ray region. As a result of our previous publications, three of the beamlines which use double-crystal monochromators at NSLS now use diode feedback loops which offer much-improved performance. The following measurements have been made recently.

1. Spectral and Spatial Response of Various PIN Photodiodes from 2-7 keV

We have improved upon our earlier measurements by determining the spectral sensitivity and spatial resolution of several commercially available PIN diodes. These measurements were made at the output of a beamline using x-ray mirror optics and a double-crystal x-ray monochromator. The system offered a wider energy range than the tube source used in the previous measurements and allowed us to eliminate corrections for the harmonic and fluorescence contributions which were potential sources of error.

2. Harmonic Rejection in Feedback Loops for Double-crystal Monochromators

Diffraction and EXAFS (extended x-ray absorption fine structure) measurements, among others, are subject to errors due to the fact that crystal monochromators reflect x-rays not only at the fundamental Bragg condition but at higher-order harmonics. One way of eliminating this error is to overlap the rocking curves of the two crystals in the monochromator in such a way as to pass the radiation of the first-order Bragg reflection but not higher orders. This scheme has never been successfully incorporated into the AC feedback loop circuitry which is the best way of electromechanically maintaining the two crystals at the Bragg condition while the energy is scanned. Using PIN diode detectors of differing sensitivity, we have demonstrated a means of solving this problem in a most satisfactory manner. It permits the AC feedback loop to be maintained on the side of the rocking curve in a way which discriminates against the harmonic component to any degree that is arbitrarily selected. The method allows scanning the monochromator through an energy range of 1 keV or more and should prove superior to the DC method which has been used up to this time.

This work was performed in collaboration with Dr. J. Kirkland of NRL and Dr. P. Wolf of Virginia Polytechnic Institute and State University.

G. Production and Characterization of Ultrasmooth Surfaces
(T. J. Jach)

Previous surface science experiments have indicated a need for surfaces which are extremely flat and smooth on an atomic scale. An example of this need is the desire to study photoemission from a metallic thin film at grazing incidence to obtain maximum surface sensitivity. There are also obvious reasons for wanting to make smooth detect-free substrates and thin film such as in the semiconductor industry where device widths of 100 Å are being approached. We have initiated an effort to (a) characterize substrates and thin films for roughness down to a scale of 3 Å; and (b) push the limit of surface smoothness attainable to 10 Å or better for a variety of materials.

Studies are progressing on interpreting gold thin-film deposition on amorphous glass surfaces, as observed by scanning reflection electron microscopy. A wide body of previously unconnected data on the reflectivity, surface roughness, resistivity, etc. of thin films of gold (and other metals) appears to be related to surface growth of microcrystals during deposition. We have observed new whisker growth modes which occur because diffusion kinetics are limited to certain crystal faces by substrate temperature. These results, based on electron microscopy data taken last year, are presently being prepared for publication. This work is being done in collaboration with Dr. L. Holdeman of Comsat and Dr. G. Hembree of the NBS Precision Engineering Division.

H. Electron Spectroscopy of Surfaces
(C. J. Powell, N. E. Erickson and D. E. Ramaker)

A number of electron-spectroscopic techniques are in widespread use for the determination of surface composition, surface vibrational modes, and surface electronic structure. Techniques such as Auger-electron spectroscopy, x-ray photoelectron spectroscopy, and electron energy-loss spectroscopy are useful but the observed spectral lineshapes are often complex. These lineshapes reflect the many processes often involved when electron beams interact with surfaces and when electronic excitations occur. The factors influencing observed lineshapes need to be understood in order that the spectroscopic techniques can be fully utilized and, in particular, so that quantitative intensity measurements can be made (e.g., for quantitative surface analysis).

As part of a project to measure the L_3-shell binding energies of 3d transition metals by different spectroscopic techniques (see section 2.A.4), we have made a detailed examination of the L_3 appearance-potential spectra (APS) of six 3d metals. We measured the so-called Auger-electron APS in which electrons of variable energy bombard the target material and a measurement is made of the derivative of the target current as a function of electron energy in the vicinity of the core-level BEs. Our APS data for Ti, V, Cr, Fe, Co, and Ni are similar to those reported previously but we have established our electron energy scale with greater accuracy and made a more extensive analysis of the data.

In order to determine an APS BE, it is necessary to compare a measured spectrum with one calculated from a model. In the past, APS data have been interpreted in terms of a simple one-electron model in which both the excited core electron and the incident electron have final states near the Fermi level of the target. According to this model, a self-convolution is made of the empty density of states (DOS), obtained from published calculations, and this is convolved with a Lorentizian function to represent core-hole lifetime broadening. A derivative is then taken for comparison with experiment. While this model has long been known to be oversimplified, it has been employed successfully for a number of materials including some 3d metals. We found that this approach gave satisfactory results for the APS data of Co and Ni but there were significant inconsistencies for Ti and V and inconsistencies of a lesser degree for Cr and Fe.

We have interpreted the inconsistencies between measured and calculated APS data in terms of a new Initial-State, Final-State rule in which intensities reflect the initial state, lineshapes reflect the final one-electron DOS in the presence of the core hole, and multiplets reflect electron coupling for the lighter elements of the transition series and hole coupling for the heavier elements. The DOS in the presence of the core hole has been modelled using an expression due to Cini which has been found useful in analogous studies of Auger-electron lineshapes. The modified DOS is given by:

$$N_{mod}(E) = \frac{N(E)}{[1-UI(E)]^2 + [U\pi N(E)]^2}$$

where N(E) is the DOS from the literature for each metal, I(E) is the Hilbert transform of N(E), and U is the effective core-hole, valence-electron attractive energy. Figure 3.4 shows our AP spectrum for vanadium at the bottom and a series of calculated spectra based on $N_{mod}(E)$ for various values of U. As U is increased, the calculated curves become closer in agreement with experiment; although the measured spectrum does not show two clear peaks, there is a weak shoulder at 515 eV. Similar results have been obtained for Ti. Better agreement between experiment and calculation could be obtained by adding more broadening in the calculated spectra (which could be ascribed to the lifetime of the excited two-electron state).

In addition to obtaining better agreement between measured and calculated AP spectra, the initial-state, final-state rule enables satisfactory resolution of apparently contradictory results obtained in the analysis of APS, x-ray absorption spectra (XAS), and electron energy-loss spectra (EELS). Briefly, small values of U are appropriate for the dipole excitations in XAS and in EELS at high incident electron energies, but larger values of U are appropriate for the non-dipole final states excited in APS and in EELS at near-threshold incident electron energies.

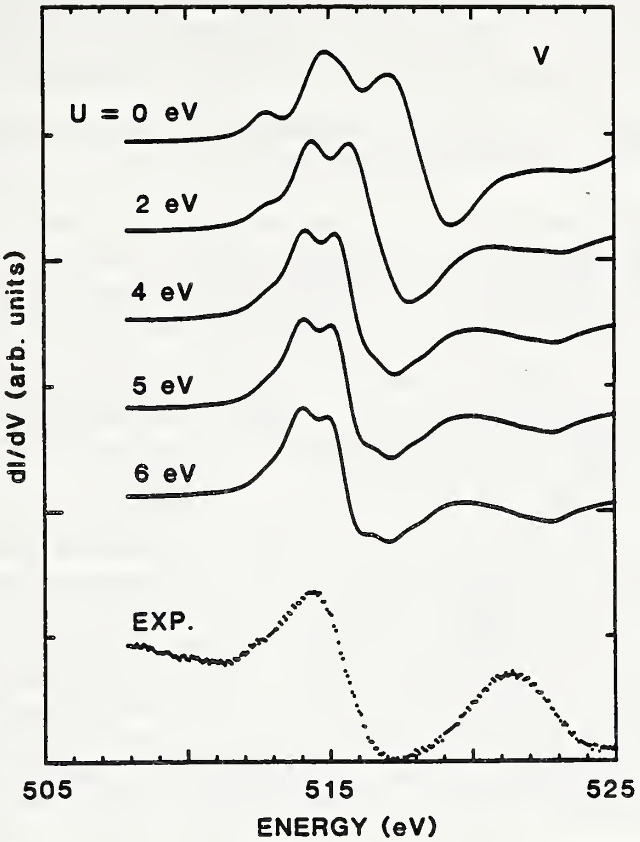


Fig. 3.4 Comparison of measured (bottom) and calculated L_3-shell appearance-potential spectra for vanadium. The top curve (U=0) was calculated with the empty density of states and the other curves with modifications to the density of states due to the core hole. The parameter U is the effective core-hole, valence-electron attractive energy. The calculated spectra were plotted using an L_3-shell binding energy measured by x-ray photoelectron spectroscopy.

We plan to test our model further by examining APS and EELS data of other types of metals.

I. Laser Diagnostics of Surface Dynamics

(D. R. Burgess, Jr. and R. R. Cavanagh)

The pathways and rates of energy transfer at surfaces remain the key unresolved issues for understanding chemical reactions at interfaces. Such information has eluded experiments which rely on conventional surface-characterization technique. A variety of laser-based techniques, however, have recently demonstrated their utility in probing such molecular dynamics in both the gaseous and liquid states. This program utilizes both the temporal and spectra characteristics available in state-of-the-art lasers. Strong collaborations with Drs. M. P. Casassa, E. J. Heilweil, D. S. King and J. C. Stephenson of the NBS Molecular Spectroscopy Division play a vital role in these efforts.

1. Laser-Excited Fluorescence as a Probe of Adsorbate Interactions During Thermal Desorption

Characterization of the mechanisms involved in energy transfer between an adsorbate and a substrate stands as the primary objective of this work. Measurements are made of the translational, rotational and vibrational energy content of desorbed molecules. These population distributions provide an indication of the interaction potentials which are involved in different desorption processes. By measuring the state-specific populations which result from elementary surface processes, it is anticipated that the fundamental steps which influence a variety of surface reactions can be examined.

We have recently completed a series of measurements of co-adsorbed NO and NH_3 thermally desorbed from Pt(111). The co-adsorption system was known to exhibit a strong NO-NH_3 interaction from earlier EELS and TPD measurements. The formation of an NO-NH_3 complex had been suggested by the previous studies. Our measurements of the rotational-state distributions by laser-excited fluorescence (LEF) of the thermally desorbed NO indicate that, despite the concerted desorption of both NH_3 and NO, strong adsorbate interactions are not manifested in the rotational-state distribution. The desorbed NO was found to exhibit a Boltzmann distribution with a rotational temperature 95% of the surface temperature.

2. Laser-Induced Desorption

The nature of the surface processes which can be induced by laser heating has been the subject of recent experiments on a polycrystalline platinum foil. In these experiments, NO was adsorbed on the substrate at 200 K and a laser (532 nm, 3 ns FWHM) was used to induce a temperature jump of 100 K. The NO liberated by this heating processes was detected by a second laser using LEF. Approximately 10^{-5} monolayers were desorbed within the illuminated region of the sample on every heating pulse. By varying the time delay between the heating pulse and the probing (LEF) pulse, a time-of-flight distribution could be measured for individual rovibronic levels. Tuning the wavelength of the LEF probe laser then provided a measure of the population in different rotational states of the desorbed NO.

These measurements have revealed several unexpected results. TOF distributions observed for two experiments, where the only variable is the rotational state probed by the LEF laser, illustrate the observed trends. The TOF data for NO with $J = 19.5$ are characterized by a prompt signal for a time delay between the heating and probe pulses of 0.5 μs. This result is in contrast to the TOF data for NO with $J = 3.5$ where the peak position is shifted to a time delay of about 8 μs. The data have been fitted to the sum of two (non-Maxwell-Boltzmann) velocity distributions. Our results indicate:

- For all rotational states, there is a slow component with a mean kinetic energy of 300 K.

- The rotational temperature for these slow species is ≈ 170 K.

- The mean kinetic energy of the fast component is a function of rotational state, ranging between 1400 K for $J = 3.5$ and 2650 K for $J = 19.5$.

- The population in $v = 1$ is dominated by fast NO molecules, and corresponds to a vibrational temperature of ≈ 900 K and a rotational temperature of approximately 155 K.

These results indicate that it may not be possible to account for the molecular processes induced by ≈ 5 nsec laser-heating pulses by simple thermal heating models. Atom-atom recombination, precursors, transient electron-hole pairs, and exit-channel effects are all consistent with our present data. Still, it should be possible to clarify the source of the two velocity components in future experiments. For instance, in the coming year we anticipate exploring the influence of the laser-heating pulse duration, the sensitivity to surface structure, the influence of co-adsorbates, the role of the heating laser wavelength, and the extent of correlation with surface cleanliness. Initial experiments on Pt(111) are currently in progress as well as work using a laser wavelength of 1.06 µm to heat the platinum foil. In addition, further work is anticipated which will permit direct measurement of the peak temperature jump induced by the heating pulse. This work is supported in part by the Department of Energy.

3. Time-Resolved Measurements of Vibrational Energy Transfer

Direct characterization of the time scales and mechanisms for relaxation and dephasing of vibrational excitation in adsorbed layers is the aim of this work. Such measurements can provide a quantitative understanding of a substrate's ability to quench the energy released upon chemisorption, reaction, or irradiation.

Two new picosecond sources have been developed for probing vibrational relaxation at surface. Both sources are capable of generating picosecond infrared pulses in the frequency range between 1700 and ≈ 4000 cm^{-1}. One system produces pulses of 30 psec duration with energies near 20 µJ. The second system produces shorter pulses (3 ps), but with reduced energy (3 µJ). The extension to longer wavelengths offered by these systems opens the opportunity to study a range of new surface-related problems.

Planned experiments will use pump-probe techniques to generate excited-state populations at surfaces and follow the subsequent time evolution of the excited species. Transmission measurements (on high-surface-area model catalyst systems) and reflection measurements (on single-crystal substrates) are anticipated. However, the reduced energy available in this spectra range (compared to the 300 µJ available at 3 µm), requires a more sensitive detection method than had been employed previously. Not only is the total energy per laser shot reduced, but the transmission (or reflection) transient induced by the laser is expected to be diminished. The first point has required the development of ratiometer techniques based on photoconductive and photovoltaic detectors. The second factor dictated that we improve our ability to measure reflectivities of individual laser shots to better than 1%. This performance must be achieved under conditions where the total energy in sequential shots can fluctuate by a factor of two. We are now able to reproducibly measure changes in transmitted light at the level of 3 parts in 10^3, and anticipate that we will shortly acquire the ability to measure such reflectivities to a few parts in 10^4.

Preliminary measurements have now been made on model compounds [$Cr(CO)_6$, Rh(CO)H(triphenyphosphine)$_3$, and Rh(CO)Cl(triphenyphosphine)$_2$] in preparation for probing the vibrational relaxation rate of CO bound to supported metal particles. The relaxation of the CO ($v = 1$) stretch mode was characterized using 5 μJ pulses with InSb detectors to monitor the relative sample transmission. These preliminary results indicate that the CO ($v = 1$) relaxation time in the hexacarbonyl is significantly longer than that found for OH/SiO_2. In the monocarbonyls, however, the relaxation times are significantly shorter. The applicability of these techniques for adsorbates on supported metal particles will be explored in the coming year. This work is supported in part by the Air Force Office of Scientific Research.

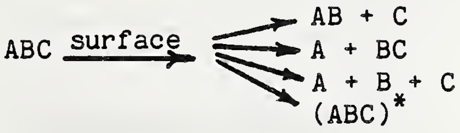
J. Theory of Dynamical Molecular Processes at Surfaces
(J. W. Gadzuk)

This project is part of a continuing effort directed to understanding both the static and dynamic behavior of atoms, molecules, solids, surfaces, radiation and their mutual interactions. This understanding comes from consideration of the microscopic atomic-scale properties of individual entities as well as from larger-scale statistical properties of ensembles. Based upon our studies, phenomenological model theories are constructed which relate to the chemical physics and statistical mechanical behavior and to the intrinsic properties of relevant physico-chemical systems. In addition, a significant effort is invested in the study of the role of an actual measurement process in determining observed quantities in different surface spectroscopies. Ways in which measurement-process-specific quantities such as line shapes, satellite structures, etc. provide additional information on system dynamics are of considerable interest.

Work has remained focused on the role of excited electronic states and intra-molecular vibrational degrees of freedom in reactive surface dynamics. In these situations, energy must be directed in order to break bonds or be extracted to stabilize highly vibrationally excited species formed for instance at curve crossings where electronic rearrangement takes place. There has been significant progress in several different directions in the application of an analytic model describing the dynamics of a diatomic molecular beam incident upon a surface and in which charge-transfer/curve-crossing events takes place. This has been carried out in parallel with numerical trajectory studies over realistic potential-energy surfaces (PES) in order to assess the reliability of the easily-used analytic models.

An extensive study has been carried out on the vibrational excitation/dissociative adsorption/dissociative scattering of heavy diatomic molecules such as I_2 incident upon metal surfaces. Classical trajectories for the molecule-surface collision have been calculated as a function of incident energy and for various values of the parameters characterizing the PES. A series of examples illustrating the various outcomes are shown in Fig. 3.5 for incident I_2 oriented parallel to the surface. Here z is the molecule-surface separation and ρ is the intra-molecular stretch coordinate. The low-energy events shown in Figs. 3.5(a) and (b), result in dissociative adsorption. Increasing the energy, as in Fig. 3.5(c) leads to resonance-assisted vibrational excitation. Finally, for energies $\gtrsim 1$ eV, simple in-out scattering with substantial translational to vibrational (T→V) conversion occurs. Calculated values of the energy transfer from translation to vibration versus incident energy, treating the desorption energy parametrically, are shown in Fig. 3.6(a). Results obtained from our analytic modelling are shown in Fig. 3.6(b). It is apparent that for energies greater than ~ 1 eV where in-out trajectories occur, the analytic models provide reasonable representations of reality. This is encouraging and has provided stimulus for new modeling of more complex phenomena in surface chemical dynamics.

One such example is our recent theory on controlling chemical selectivity of reactivity in polyatomic molecule-surface collisions involving the formation of temporary negative-molecular ions due to molecule-surface charge transfer. As a final example, we have considered selectivity in the scattering of a prototypical polyatomic, say ABC, from a surface in which several outgoing channels are possible.



Selectivity is possible if an excited electronic state (negative molecular ion) is used to assist chemistry on the ground electronic state. Creation of a temporary negative ion whose geometry differs from the ground-state neutral permits molecular-ion distortion into configurations which favor one or the other of the outgoing channels when the ion is neutralized. Over the past two years, we have developed theory which shows how the lifetime of such temporary negative ions formed in surface collisions can be easily controlled. Selectivity is achieved by chosing an ion lifetime commensurate with the intermediate-state distortion which leads to the desired outgoing channel (reaction products). Thin exciting prospect has been demonstrated within the context of classical trajectory modeling.

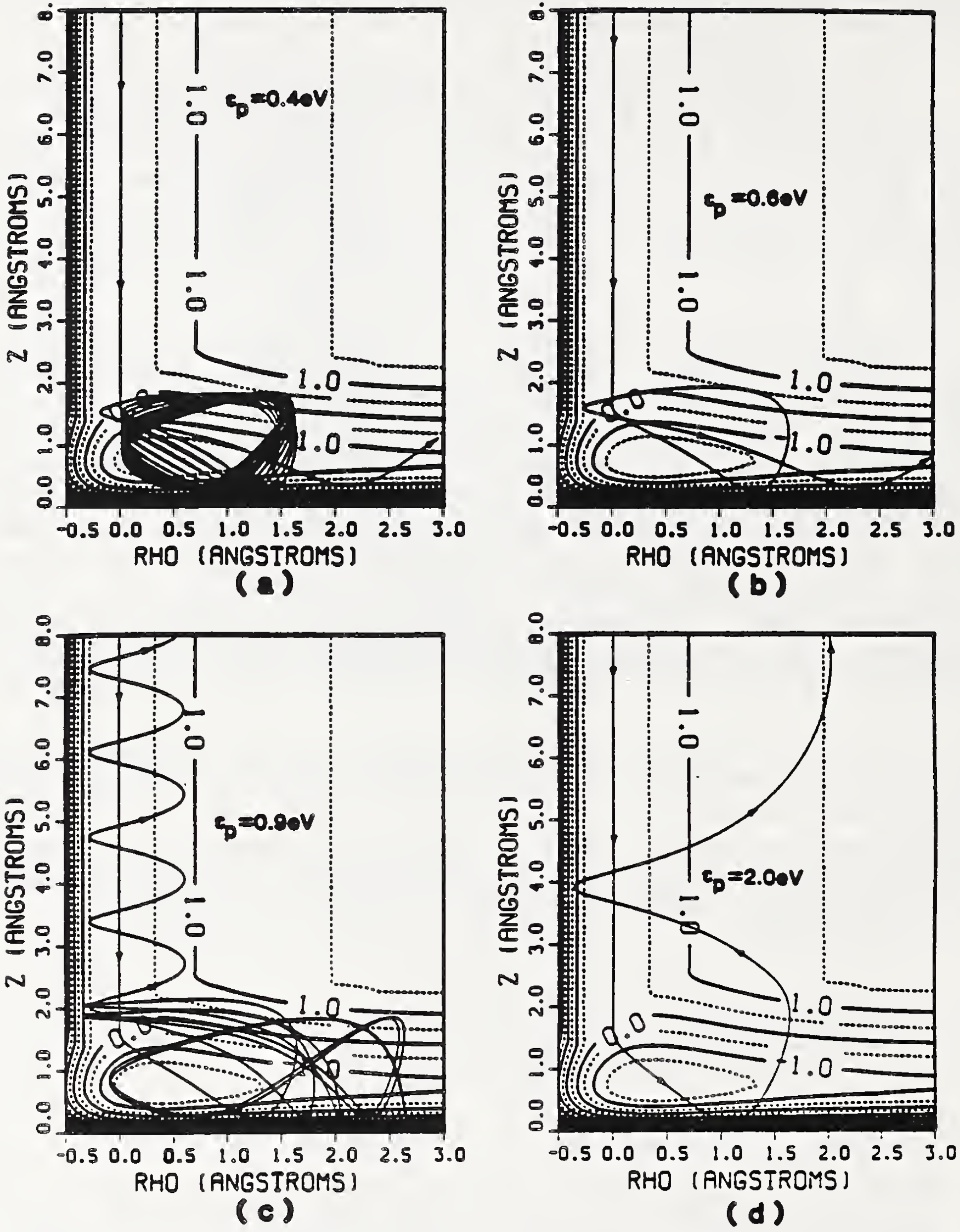


Fig. 3.5 Potential energy surface contours for an iodine molecule incident upon a physical surface in which dissociative adsorption is possible. The z axis is the molecule-surface separation and the ρ-axis is the intra-molecular stretch coordinate. A progression of trajectories for increasing incident translational energy is shown. Figures 3.5(a) and 3.5(b) show dissociative adsorption, Fig. 3.5(c) shows resonance-assisted T→V conversion, and Fig. 3.5(d) the basic in-out behavior leading to substantial T→V conversion.

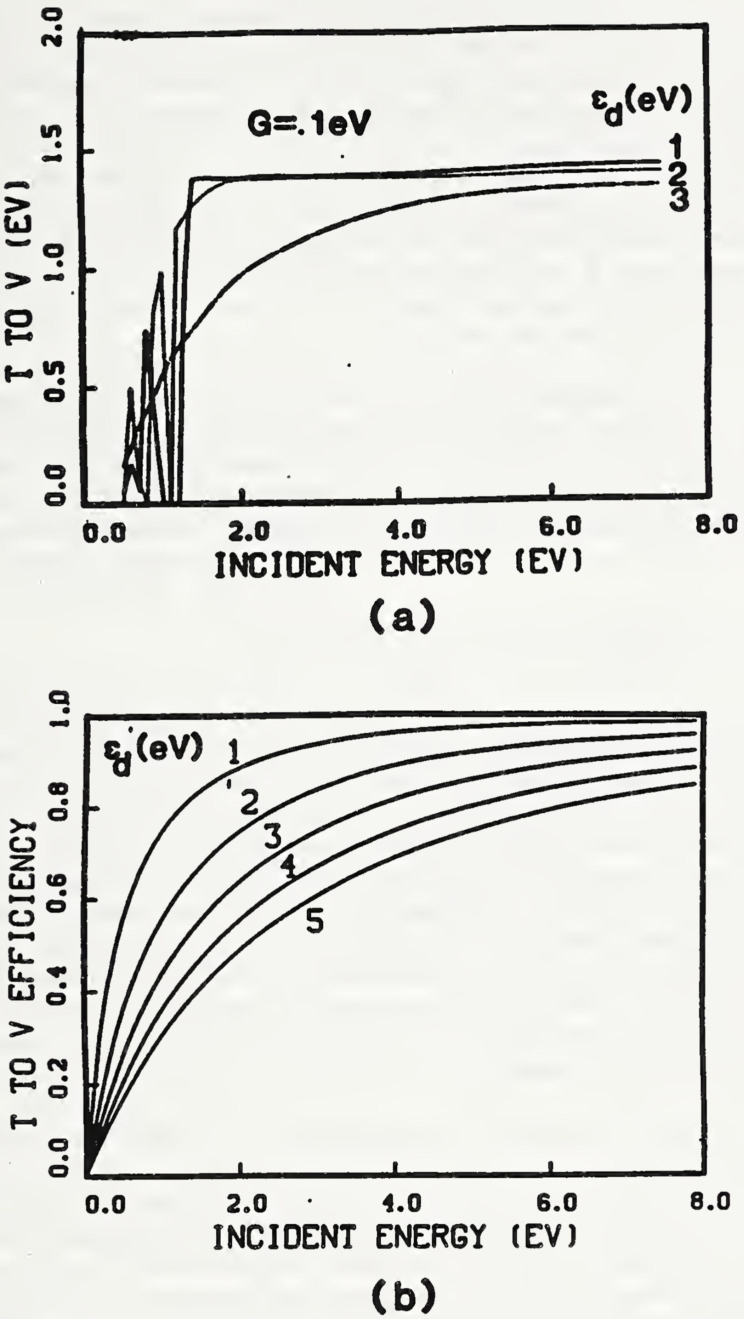


Fig. 3.6 (a) T→V conversion vs. incident I_2 translational energy, obtained from trajectory calculations, treating desorption energy parametrically, as labeled. (b) Ratio of $\Delta\varepsilon_{T\to V}$ to $\Delta\varepsilon_{T\to V}^{max}$ (T to V efficiency) versus incident I_2 energy, obtained from the analytic modeling of Fig. 3.5.

Theory has been worked out for a number of other new molecular-beam experiments, which will be carried out in laboratories, other than NBS, which have beam facilities. Amongst the proposals include scattering of oriented atoms or molecules in which the orientation is achieved by initial preparation of electronically excited states. These experiments should be very useful in providing new information on charge-transfer dynamics. Another proposal has been put forth for the design of neutral molecular beams with kinetic energies possibly up to 1 keV. This development may permit a totally new class of beam scattering experiments outside the extremely limited domain of beams prepared by the current supersonic nozzle-expansion method.

Finally, vibrational lineshapes and spectra of adsorbed molecules have been studied in terms of the quasi-periodic trajectories over a multi-dimensional PES. This is a prudent way to include the anharmonic effects which lead to dynamically interesting lineshapes because one can "see" what the oscillator is doing to acquire the lineshape. The lineshape or vibrational spectrum of an excited oscillator is

$$I(\omega) = \frac{1}{2\pi} \lim_{T\to\infty} \frac{1}{2T} \left\langle \left| \int_0^{2T} y(t)\, e^{i\omega t}\, dt \right|^2 \right\rangle$$

where y(t) is the oscillator displacement as a function of time after initial excitation. A particularly interesting situation exists when the adsorbed molecule can migrate between inequivalent adsorption sites, as in the bridge-3-fold site conversion seen for CO/Pt(111). Questions arise as to how the site conversion affects vibrational lineshapes, or turned around, how one extracts information on site conversion and/or surface diffusion from lineshapes. We have investigated this phenomenen in detail by calculating spectroscopic trajectories and from them, lineshapes. Relationships between the time scales for vibration, anharmonic "damping", and site conversion have been established which enable one to use experimental information such as line widths and shapes to gain additional insights on the surface PES.

We plan to continue work in the area of surface reaction dynamics with near-term emphasis on the determination of self-consistent reaction trajectories, realistic electron-hole pair coupling constants, determination of energy-redistribution patterns amongst translational, vibrational, rotational, and electronic degrees of freedom of "reactant" molecules and electron and phonon modes of surfaces. Analyses are made for controllable dynamic and reactive conditions with synthesis of the various components of the elementary reaction theories into theories of experimentally realizable processes. Special emphasis will be placed on the phenomenon of dissociative surface processes and on the role of non-linear dynamics.

In addition, analysis will be made, whenever possible, of novel experimental results. Current interest includes laser-assisted surface processes and state-to-state analysis, high-resolution surface vibrational spectroscopy, and other experimental probes of non-adiabatic effects.

4. SURFACE COMPETENCE PROGRAM

W. F. Egelhoff, Jr., J. Fine, S. M. Girvin, M. J. DeWeert,
T. E. Madey, A. J. Melmed, D. A. Steigerwald, and R. Stockbauer

The Surface Competence Program is a part of the NBS "Competence Program." The NBS program was introduced to provide long-term support of the establishment and maintenance of areas of excellence in science and technology contributing to the NBS mission and the projected needs of the NBS clientele.

The Surface Competence Program was established October, 1984 with two principal components, "Novel Two-Dimensional Materials" and "State Characterization of Energetic Species Ejected from Surfaces". The initiation of this program represents a new focus on these topics. The principal objectives of each program component are described in the following two main sections together with reports of individual projects.

A. Novel Two-Dimensional Materials

In recent years an increasing awareness has developed of the important modifications in physical properties which occur in materials as they approach the ultra-thin two-dimensional limit. Some examples of unusual behavior discovered in such systems include the enhanced catalytic properties of a gold surface with two monolayers of platinum compared to bulk platinum, superconductivity of a silver monolayer on germanium, the quantum Hall effect, the enhanced magnetism in alternating monolayers of iron and cobalt, the electrical properties of metal-semiconductor junctions (Schottky barriers), and multiple quantum-well systems for optical logic devices. These examples suggest a whole new range of scientifically and technically important chemical and physical properties waiting to be explored in the two-dimensional regime. Concepts and methods developed in surface and interface science have been particularly valuable in many areas of application, and it is believed that these concepts and methods can be further developed and extended to two-dimensional systems with component thicknesses from one to one hundred atomic layers.

There exist major gaps in current understanding of the fundamental principles which govern the chemical and physical properties of layered structures in the two-dimensional limit. In this component of the program, it is planned to synthesize and determine the fundamental chemical and physical properties of ultrathin layered materials with layers so thin (a few atoms thickness) that they exhibit two-dimensional behavior. Knowledge of the factors influencing the growth and properties of ultrathin layered systems is expected to allow optimization of desired chemical and physical characteristics and will thus benefit a number of scientific fields ranging from catalysis to novel semiconductor devices.

We are performing work in three project areas. First, we are planning to develop the techniques needed to synthesize, by alternating monolayer deposition, a new class of materials: non-equilbrium ordered alloys. The structural properties of these materials as grown and during thermal processing will be investigated by x-ray and electron diffraction. The chemical reactivity, catalytic activities, and magnetic properties of these materials will also be investigated. Second, we plan to determine the microstructure and microcomposition of candidate layered structures by atom-probe and field-ion microscopy methods with emphasis on the interface region. These techniques provide composition and structure data with near-atomic spatial resolution. Finally, we are applying modern many-body theoretical techniques to the study of the quantum Hall effect, magnetism and other electronic properties of layered structures and thin films.

1. Surface and Interface Chemical Physics of Ultrathin Films

(W. F. Egelhoff, Jr., and D. A. Steigerwald)

Interest in ultrathin metal films (down to the two-dimensional limit of one atomic layer) on the part of the surface-science community has greatly increased in the past several years as it has become clear than an understanding of such structures will contribute to solving a wide range of problems in surface science. Among these are an understanding of the differences between surface and bulk electronic structure, the changes of surface electronic structure associated with chemisorption, the basis of surface magnetism, the modification of surface-layer properties by the substrate, the relationship between electronic structure and epitaxial growth, and the surface properties of alloys. The experimental program presently underway is using an integrated approach to study single-crystal surfaces, alloys and ultrathin films to contribute to an understanding of all of the above problems.

We have recently developed and applied a technique termed the "searchlight effect" in which enhanced electron intensities in x-ray photoelectron spectroscopy (XPS) and Auger-electron spectroscopy (AES) occur along nearest-neighbor and next-nearest-neighbor axes of single crystals. The searchlight effect is a powerful probe of the short-range order in the near-surface region and is well suited to studies of epitaxial growth, surface segregation, and interdiffusion.

During the past year, the searchlight effect has been applied to the investigation of various surface morphological phenomena as well as studied in its own right to determine how it can be applied with maximum benefit. Progress has been made in the following areas.

- Epitaxial films and sandwich structures of Au and Ag on Ni(100) were studied and found to have cubic short-range order by XPS but hexagonal long-range order by low-energy electron diffraction (LEED). This combination of results implies a very unusual surface reconstruction.

- The rate of Cu surface segregation in Ni-Cu-Ni sandwich structures was investigated as a function of depth of the copper layer. One such structure is illustrated in Fig. 2.4. It was found that different segregation mechanisms operate at different depths of the Cu monolayer.

- The effect of surface contamination on epitaxy was investigated. It was found that, for up to 0.5 monolayers (ML) of carbon or oxygen contamination on Ni(100), the epitaxy of Cu or Ni at 300 K was hardly inhibited. While the top atomic layer was quite disordered (LEED data), the searchlight effect indicated that the deeper layers were well ordered. The carbon and oxygen diffuse rapidly to remain at the growing surface. Even at substrate temperatures of 100 K, many layers of overgrowth (>>10 ML) are required to, in effect, bury the carbon and oxygen.

- A search was made for a theoretically predicted surface-melting phase transition using the searchlight effect [in this case on Hg(111)] but none was found to occur.

- The temperature dependence of the diffusion of a Ni monolayer into a Cu(100) substrate was investigated. This interdiffusion begins around 350 K and is essentially completed by 450 K.

- The effects of multiple scattering on the searchlight effect have been examined. It was found, as predicted theoretically by Tong et al., that the first two or three scattering events enhance the intensity along interatomic axes but that further scattering events break up the searchlight beams. Figure 2.4(a) shows that the peak at 45° is strong for a 4 ML Ni overlayer but vanishes for a 10 ML Ni overlayer. The peak at 0° shows a lesser weakening effect at 10 ML Ni since there are fewer Ni atoms along this axis, as shown in Fig. 2.4(b).

- It was found that multiple scattering events tend to sharpen the searchlight-effect peaks. The peak at 45° in Fig. 2.4(a) is considerably narrower for a 4 ML Ni overlayer than for a 1 ML Ni overlayer.

Much of the experimental work of the past year has been conducted to develop the techniques needed for the next major effort to be undertaken. This will be the synthesis of a new class of materials, non-equilibrium ordered alloys, by epitaxial growth of alternating metal monolayers. This work has the potential for opening up a new area of materials science. The XPS searchlight effect is a near-perfect tool for diagnosing, in real time, any growth processes that interfere with the desired synthesis and should thus aid greatly in recognizing and overcoming barriers. We anticipate the capability of producing novel material properties by tailor-making the lattice structure. Later, we expect to characterize the materials with x-ray diffraction and electron microscopy and to study their chemical reactivity, catalytic activity, and magnetic properties.

During the past year, much effort has gone into upgrading the instrumentation in preparation for the synthesis of the ordered alloys. Changes have been made in the electron optics and in the computer control of the XPS system to improve its operating characteristics. Conversion of the detector system from a single channeltron to a position-sensitive detector is in progress. These changes will permit an increase in the diagnostic power of the searchlight effect.

Another major effort of the past year has been the design, construction, and testing of molecular-beam epitaxy ovens. These ovens produce the stable metal flux that will be required for synthesis of high-quality ordered alloys. The ovens are presently in the final testing stages.

The first alloys to be synthesized will be of the Cu-Fe system. No ordered alloys of Cu and Fe have been produced by conventional metallurgy. However, we believe that our approach of epitaxial growth combined with the XPS searchlight effect (to guide our understanding of how growth parameters affect morphology) will enable us to produce a variety of novel structures. Among these are alternating monolayers of Fe and Cu, monolayers of Fe separated by thicker Cu layers, and alternating bilayers, trilayers, etc. We have a collaboration planned with a group at Simon Frasier University in Canada to study the magnetic properties of these novel materials and we expect to set up other collaborative investigations of other physical properties in the near future.

2. Microcomposition and Microstructure of Thin Films
(A. J. Melmed)

This effort is directed to the measurement of microcomposition in relation to microstructure of thin layers on well-characterized solid substrates and the determination of interfacial diffusion. The methods of investigation for these purposes are field-ion microscopy (FIM), capable of qualitative atomic structural determination, and atom-probe analysis for compositional depth-probing on an atomic scale. Both in situ and ex situ specimen preparation will be used in order to vary widely the layer-formation process parameters.

Further progress was made towards understanding the atomic structure of the recently discovered icosahedral phase of rapidly solidified Al_6Mn, produced in thin ribbon form. Extensive analysis of FIM images obtained last year indicated the presence of a hierachy of cluster or grain sizes from about 1.3 to at least 8 nm in width, and two sizes of discrete pentagonal arrays, each of five atoms. These features agree qualitatively with recently proposed models which describe the structure in terms of an aggregation of small icosahedra (see Fig. 4.1). Furthermore, the unusually irregular appearance of the FIM micrographs is explainable on the basis of such cluster models. Computer simulations of selected areas of the FIM images, based on a cluster model and performed by Dr. H. A. Fowler of the NBS Center for Applied Mathematics, exhibited good qualitative agreement with the experimental images. Additional support for the cluster type of structural model comes from some new transmission-electron-microscopy (TEM) results obtained in collaboration with Dr. M. J. Kaufmann of the NBS Metallurgy Division. We have shown that selected-area electron-diffraction patterns from the icosahedral structure contain diffusely scattered intensity, as well as the well-known sharp diffraction features; we have attributed this diffuse intensity to scattering from atoms filling in the necessary small gaps between clusters. Further low-temperature FIM is underway in an attempt to provide a complete description of the atomic structure of the icosahedral phase.

The composition of the icosahedral phase (i-phase) of rapidly solidified Al_6Mn was determined by our general-purpose atom probe FIM in connection with the FIM structural investigation of this new material. The composition of the i-phase was found to be approximately Al_4Mn, in agreement with recently published analytical TEM results.

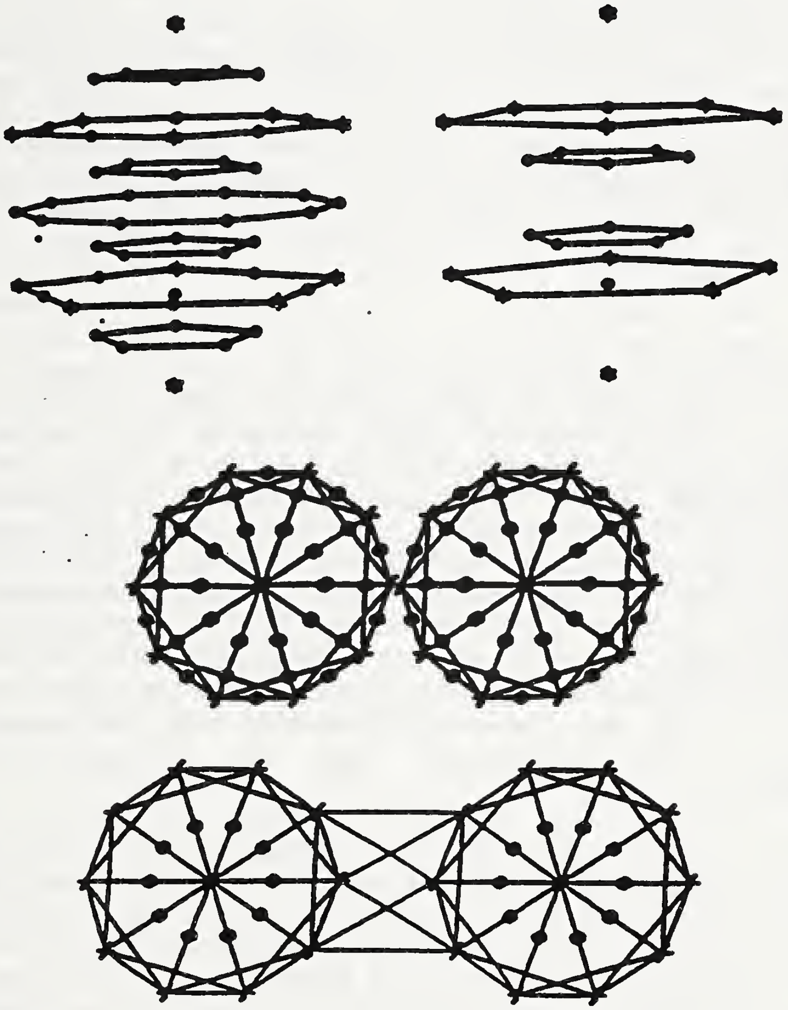


Fig. 4.1 Two proposed cluster models of the icosahedral phase of Al_6Mn. Top: exploded views of the two icosahedral clusters. Middle: top view of one coupling scheme for two icosahedra. Bottom: another coupling scheme. Asterisks indicate Mn atoms and the other symbols indicate Al atoms.

In addition to microcompositional analyses of novel alloys, future efforts will include depth-probing of various layered structures. These will consist of thin film/substrate combinations of metal/metal, metal/semiconductor and metal/glass. The aim will be to determine composition profiles in the films, the interfaces and into the substrates, using the unique analytic capabilities of the atom probe FIM. Initially, specimen preparation for such studies will be done by vapor deposition under well-characterized ambient conditions.

Epitaxial crystal growth of Cr on W and Cr on Re is being studied by field-electron emission microscopy. In both systems, the nucleation and growth, at temperatures sufficiently high to enable rapid surface diffusion of Cr, proceeds as expected, with nucleation occurring at surface steps after about a monolayer of Cr coverage (Stranski-Krastanov growth mode). However, the lateral growth of Cr crystals is inhibited by certain substrate geometries; crystal growth does not extend into (001) planes of W, for example. In addition, a lower-temperature epitaxial growth is found to occur on (001) W, where small 3-D crystals nucleate directly on the clean surface (Volmer-Weber growth mode).

Metal layer deposition on Si is being studied in collaboration with Dr. W. A. Schmidt and Prof. J. H. Block at the Fritz Haber Institut, W. Berlin. Thusfar, we have demonstrated that for thin layers ((3-4 nm) of Au, the method of field-ion appearance spectroscopy can be used to determine the Schottky barrier height for Au/Si. We studied the field ion energy distributions of inert gases (Kr and Ar) for Au-covered n- and p-type Si(111) specimens. Thin layers of Au were vapor-deposited, with the substrate at 78 K, such that diodes were formed and subsequent electrical charging occurred through the bulk Si. The measured field dependence of the ion distribution onset potential was used to calculate a barrier height of about 0.3 eV for the p-type Si, in good agreement with the literature value of 0.34 eV. Similar measurements for n-type Si are presently being completed and the work is being extended to other metals. The method is being considered as a possible route to further understanding of the controversial nature of metal/semiconductor Fermi-level pinning.

The NBS Electrodeposition Group has been producing layered material by controlled alternate deposition of Ni and Cu in layers intended to be uniformly some 10-20 nm thick. There are several questions concerning the resulting material which we have begun to address using FIM and atom-probe methods. These are: (1) uniformity of the layer thickness, (2) composition of the two types of layers, (3) defect densities in the layers, and (4) coherence of layer interfaces. Thusfar, we have developed specimen preparation techniques, done initial FIM studies to address qualitatively points (1) and (4) above, and established feasibility of doing atom probe analysis.

3. Theory of Novel Two-Dimensional Materials
(S. M. Girvin and M. J. DeWeert)

Recent progress in the fabrication of novel two-dimensional materials has generated intense theoretical and experimental activity in several areas of condensed matter physics. The present project is addressing theoretical issues in three of these areas: artificial semiconductor superlattices, thin metallic films, and a new field now being referred to as 'meso-scale' physics. Each of these will be discussed in turn below.

The quantum Hall effect is one of the most remarkable phenomena discovered in recent years. It occurs in the two-dimensional electron gas (inversion layer) which can be formed in artificially layered semiconductor systems. One finds at high magnetic fields and low temperatures that electron transport in the inversion layer becomes nearly dissipationless and that the Hall conductance takes on universal quantized values e^2i/h where e is the fundamental charge, h is the Planck constant and i is an integral or rational fractional quantum number. This discovery has had profound implications for both fundamental physics and electrical resistance metrology.

The theory project has in the recent past focused strongly on the quantum Hall effect. In addition to providing support for the experimental effort in the NBS Electricity Division, recent accomplishments include development of a rather complete and quantitative theory of the collective excitations in the fractional regime (done in collaboration with Dr. A. H. MacDonald, National Research Council, Ottawa and Dr. P. M. Platzman of AT&T Bell Laboratories, Murray Hill) and the editing of a book giving the first major review of the field (done in collaboration with Prof. R. E. Prange of the University of Maryland). The latter is based on a ten-part lecture series which enjoyed a large attendance from academic, governmental and industrial organizations in the greater Washington area (see section 2.c.3(a)).

Theoretical developments in the area of the fractional Hall effect have proceeded rapidly and a general picture of how the effect arises from Coulomb correlations is now in hand. The one remaining area which has been poorly explored is that of the statistical mechanics at finite temperatures and the question of whether the fractional state is reached via a phase transition (and hence whether or not there is an order parameter in the problem). Our work on the collective-excitation spectrum showed that there exists a deep analogy between the fractional Hall effect and superfluidity in helium films. This analogy has been pursued further to develop a phenomenological Landau-Ginsburg theory describing the statistical mechanics and which exhibits, in a natural way, fractionally-charged quantized vortices. In collaboration with Dr. R. B. Laughlin of Stanford University, this phenomenological theory is now being given a microscopic justification.

Until the next generation of experiments arrives to bring new challenges to theorists, it is probably safe to say that theoretical developments in the fractional Hall effect have reached at least a preliminary stage of maturity and it will prove useful to begin exploring other aspects of novel two-dimensional materials. Some new directions which are now getting under way are discussed below.

There has been considerable interest in recent years in the electronic-transport properties of thin metallic films, particularly in connection with weak Anderson localization and the interplay between superconductivity and localization. A related problem is superfluidity in layers of helium adsorbed on a disordered substrate. A fascinating experimental result which has not yet been fully understood has been obtained recently by Goldman et al. at the University of Minnesota. They find in partially-oxidized tin films that if the high-temperature sheet resistance of the film exceeds a critical value R_c of order $h/(2e)^2$, the system becomes insulating at low temperatures. However, if the high-temperature sheet resistance is less than R_c, the system becomes superconducting at low temperatures. This remarkable result is believed to be due to macroscopic quantum tunneling effects in the superconducting grains in the presence of dissipation. These questions are being further explored. A useful spin-off of studies of tunneling in the presence of dissipation will be a greater understanding of how to treat problems such as hydrogen and muon diffusion in metals and at the surface of metals.

A newly developed field known as 'meso-scale physics' is generating intense experimental and theoretical activity. Modern lithographic techniques allow one to produce small one- and two-dimensional structures which are smaller than the inelastic mean free path at low temperatures. This leads to a variety of interesting coherence effects even though the elastic mean free path may be small on the scale of the system size. This is because phase information is scrambled but not destroyed by elastic scattering. One of the most interesting effects is the existence of universal conductance fluctuations in which any small perturbation (displacing a single impurity, adding one quantum of magnetic flux to the sample, etc.) causes a change of order e^2/h in the conductance, independent of the sample size and dimensionality. As an alternative to the usual diagrammatic techniques, this problem will be investigated using replica field theory methods. Another problem of particular interest in one-dimensional structures (quantum well wires) is the nature of Coulomb correlations at low temperatures. This is being investigated in collaboration with Dr. A. H. MacDonald using variational wave functions analogous to those developed for the quantum Hall effect.

B. State Characterization of Energetic Species Ejected from Surfaces

Specific state characterization of desorbed and ejected species from surfaces, whether induced by sputtering or by electron and photon bombardment, is still rare. It is now possible to address such dynamical surface interactions using laser techniques to determine the energy state, velocity, and angular distributions of all the ejected species--especially the neutrals which are the most abundant. Such studies can provide detailed microscopic information concerning energy transfer in these excitation/interaction processes.

The objective in this component of the program is to understand the excitation dynamics by which atoms and molecules are desorbed from surfaces in ion-sputtering processes as well as in electron- and photon-stimulated processes. Detailed characterization of the internal energy, kinetic energy, and desorption thresholds of desorbed species will provide a microscopic understanding of the nature of the electronic excitations leading to desorption due to collisions with electrons, photons, and ions. Angular distributions will provide direct structural information concerning the surface geometry, as well as information concerning energy transfer during the collisional interaction.

We are combining ultrahigh-vacuum surface-science techniques with state-of-the-art spectroscopy in several experiments involving electron-stimulated desorption (ESD), photon-stimulated desorption (PSD), and ion sputtering. Specifically, we propose to use multiphoton ionization and other laser-spectroscopic techniques to detect and analyze neutral species released from crystalline surfaces by electron, photon, and ion bombardment. These measurements will provide unique insights into the mechanisms of desorption induced by both electronic transitions and by direct momentum transfer. Measurements of neutral angular distributions will be compared directly with ion angular distributions using a new two-dimensional display analyzer, thus providing a detailed description of competing desorption pathways.

We are performing work in three project areas. First, we are designing an experiment in which laser-spectroscopic techniques will be used to determine the energy states of neutral atoms and molecules sputtered from surfaces by ion bombardment. Second, we are collaborating with scientists at Vanderbilt University on a similar experiment in which neutral species desorbed from surfaces by electron or photon excitation will be detected and characterized. This experiment may lead later to similar work at NBS. Finally, we are constructing a new type of display analyzer to measure angular and energy distributions of charged species desorbed from surfaces by electrons or photons to obtain surface-geometry information and to test theories of ejection mechanisms. Close contact is made with the related experimental and theoretical projects in the Division described in Sections 3.B, 3.D, 3.I and 3.J.

1. Energy States of Neutral Species Sputtered from Surfaces (J. Fine)

Energetic ion-surface collisions generate extensive near-surface collision cascades in a solid. The energy transfer and atomic excitations that take place as a result of such collisions are not well understood in part because, until rather recently, the primary method for monitoring these collision phenomena was to measure macroscopic effects such as the total sputtering yield. The collision cascade causes the ejection of atoms, ions, electrons, and photons from the surface but it has only been in the past few years that measurements of the ejected particles or radiation have been utilized to obtain detailed information on specific atomic collisions that take place in condensed materials.

In recent experiments in which aluminum or silicon targets were bombarded by argon ions, we have shown that the Auger decay of collisionally excited Al or Si atoms can take place outside the solid depending on the distance from the surface (within the material) at which the excitation occurred, the atom's velocity, and the lifetime of the atomic excitation. As a result of our Monte-Carlo calculation to analyze these experiments; we expect that such sputtered atoms will have rather high kinetic energies - extending up to hundreds of electron volts. Collisions capable of transferring this much energy and creating inner-shell (2p) excitation can generate sputtered atoms (ions) which are in highly excited states. Such energy-transfer and excitation mechanisms are basic to our enhanced understanding of collisional processes in condensed materials. Information is required of those atomic processes which lead to electron promotion, excitation and ionization, and particle ejection. It is now possible to obtain this type of information by: (1) probing specific ejected (sputtered) atoms via resonant, multiphoton laser techniques; (2) monitoring the Auger-electron de-excitation of ejected atoms as well as those which decay inside the solid; (3) analyzing the emitted secondary-electron energy distributions. Progress made during the first year of this project in each of these areas is described below.

(a) Laser Spectroscopy of Sputtered Atoms and Ions

In collaboration with Drs. J. D. Fassett (NBS Inorganic Analytical Research Division) and Dr. J. Boulmer (NBS Inorganic Analytical Research Division and Université Paris, France), a new series of experiments has been designed to determine the kinetic energy distributions of specific sputtered atoms (ions) and their states of excitation. Measurements have been planned of: (1) the kinetic energy distributions of all the sputtered ions as a function of charge state, (2) the kinetic energy distributions of emitted electrons, (3) the collisional excitation of Rydberg states, (4) excited-state decay by photon emission, and (5) the kinetic energy distributions of sputtered atoms in specific excited sates. Resonance multiphoton laser-ionization schemes have been developed to detect sputtered atoms in specific excited states.

Construction began on a new instrument this past year. A stainless steel ultrahigh vacuum (uhv) chamber was constructed at NBS to contain a sample manipulator, pulsed ion gun, pulsed time-of-flight (TOF) extraction optics and detector, Auger-electron spectrometer, and windows for the two ultraviolet laser beams. Some of this instrumentation is described below.

The UHV sample manipulator incorporates the usual XYZ translations and rotation about the Z axis, as well as a special sample holder which permits rotating the sample about an axis in the plane of the surface (the laser beams are parallel to this axis). This sample rotation, in conjunction with the two ion gun ports directed at different angles with respect to the target surface, will allow us to vary the ion beam angle from near-grazing to near-normal incidence.

The ion gun used can produce a 1 mm wide beam with about 0.5 μA current in the 1-5 keV energy range. We have designed and built an additional high-speed beam switcher that can turn the bean on and off in about 50 ns (rise time). The complete pulsed ion gun can be mechanically aligned with the target.

The TOF analyzer, which we designed and built, was optimized for maximum collection efficiency; it is short (about 5 inches long) and has apertures 1.2 inches in diameter. The extraction and collection grids are spherical and operate as a modified Pierce lens in order to increase the collection of sputtered ions which are ejected with a cosine-type distribution from the surface. Pulsed fields are applied to these spherical grids to accelerate those sputtered ions produced by the incident pulse of ions from the gun. Electrons also can be measured with this TOF analyzer using reversed fields. Both ions and electrons, as well as x-rays, are detected by a microchannel plate TOF detector.

Data acquisition of TOF spectra is accomplished with a transient digitizer oscilloscope with internal signal averaging that permits spectra with high time resolution (10 ns) to be acquired over periods of many microseconds.

The completed system as described above was put into operation in early July, 1986. Using a polycrystalline magnesium target with pulsed ion beam and TOF extraction, we have observed the three Mg ion isotopes, MgO^+, virtually no Mg^{++}, and ejected electrons. The system seems to work very well with high sensitivity and good time resolution; calculated flight times are in good agreement with those measured. Work is in progress to characterize and understand the details of the spectra observed.

(b) Auger-Electron De-Excitation of Sputtered Atoms

In collaboration with Drs. C. Le Gressus and J. P. Duraud (Centre d'Etudes Nucleaires de Saclay, France), a series of measurements were begun to investigate the Auger-electron emission from ion-bombarded single-crystal aluminum surfaces. Aluminum (100) and (111) surfaces were bombarded with argon ions and the dependence of atomic-like and band-like Auger-electron emission was monitored as the crystals were rotated about an axis normal to the surface. Preliminary results indicate a very marked change in the total Auger-electron emission intensity as a function of azimuthal angle. Intensity minima correspond to geometrical conditions where the incident ion beam is aligned with a string of atoms (i.e., there is a shadowing of underlying atoms by the outermost surface atom of a given string).

An example of our results is shown in Fig. 4.2 where we show the total Auger yield and the ratio of the atomic-like and band-like Auger-electron emission as a function of azimuthal angle. Both the total signal and the ratio show minima at the same angles. This result strongly suggests that most of the collisional inner-shell excitation, for an ion beam aligned with an atom string, occurs deep below the surface so that the probability of an atom being sputtered before it can deexcite is low.

Measurements of this phenomena are still in progress in Saclay; we anticipate extending this investigation of collisional excitation processes in single-crystal solids at NBS.

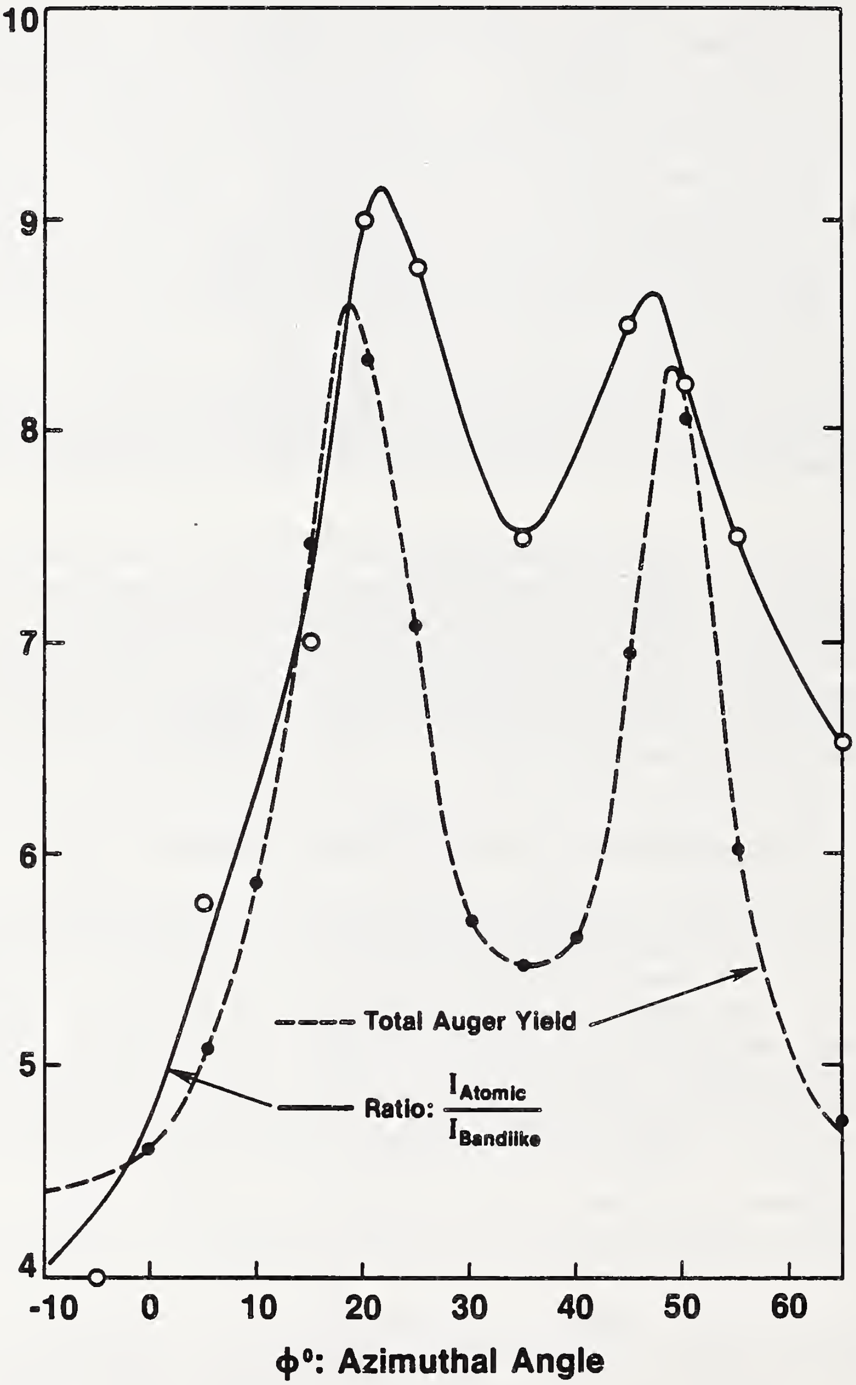


Fig. 4.2 Plot of the total Auger yield and the ratio of atomic-like and band-like Auger-electron emission from an Al(100) surface bombarded by 4 keV argon ions as a function of the angle of rotation of the sample about its normal.

(c) Secondary-Electron Energy Distributions Due to Ion Bombardment

In collaboration with Dr. I. Terzic (Boris Kidric Institute, Belgrade, Yugoslavia), an experiment has been designed to study the secondary-electron energy distributions that result from Ga^+-Ga collision at ion energies from 20 to 60 keV. Previous measurements at NBS indicate that collisional excitation may account for the high energy (> 100 eV) emitted electrons observed. An apparatus is presently under construction in Belgrade which will enable us to examine inner-shell excitation thresholds in this system.

2. Electron- and Photon-Stimulated Desorption of Neutral Species Using Laser Detection Techniques

(T. E. Madey)

In a collaborative effort with Prof. N. Tolk at Vanderbilt University, we have initiated measurements to characterize the mechanisms by which neutral species are excited and desorbed from surfaces using electron- and photon-stimulated desorption (ESD/PSD).

The majority of species removed from surfaces via ESD and PSD are neutral atoms and molecules. However, virtually all measurements of the energy and angular distributions of desorbing species have been of the more-easily-detected minority ionic species; only recently have laser techniques been applied to the detection of neutral species. Most measurements made to data have concentrated on radiation-induced decomposition of bulk solids (e.g., alkali halides).

Our experiments are designed to search for and characterize the ESD of both ground-state and excited Li and Na atoms desorbed from fractional-monolayer films of Li and Na adsorbed on both clean and oxygen-covered W(100) surfaces. We will employ laser-induced fluorescence to detect the ground-state neutrals, and light emission following metastable deexcitation to detect excited neutral species. Depending on signal levels, a later stage of the measurements involve the use of synchrotron radiation to determine the threshold energies for desorption via photon-stimulated desorption. The choice of experimental systems for these first studies (Na, Li on O/W(100)) is based on previous related experiments involving ion desorption and the theoretical interest in these conditions.

3. Angular and Energy Distributions of Desorbed Ionic Species

(R. Stockbauer and T. E. Madey)

We have designed a special analyzer to measure simultaneously the angular, energy, and mass distributions of ions desorbed from surfaces. The analyzer will in addition be used for angle-resolved photoemission.

The construction and assembly of a new angle-resolving, display-type ion and electron energy analyzer is completed. This instrument is based on the IBM design of Dr. D. Eastman. The analyzer is undergoing initial testing in the laboratory using an electron impact source. The video processing software which will display the two-dimensional data in an appropriate form is also being developed during this initial testing. Similar software is being used to process two-dimensional data from a video display system installed for our ESDIAD project (section 3.B).

The initial test experiments using the new analyzer will be a series of quantitative ESDIAD (Electron Stimulated Desorption Ion Angular Distributions) studies of small molecules adsorbed on metal surfaces. The test systems will include NH_3 and H_2O on Ni(111), as well as the coadsorption of each of these molecules with electronegative (O, S, Br) and electropositive (K, Na) additives. Some of these systems have been studied previously but a number of longstanding and important fundamental questions remain for which the new analyzer can provide quantitative answers. Experiments are planned to address the following questions.

- What are the angular profiles of the ion beams?
- Is there quantitative structural information in individual ESDIAD beam shapes?
- How do the angular profiles of individual ion beams vary with adsorption coverage and the presence of coadsorbates?
- How do the ESDIAD patterns vary as a function of electron excitation energy?
- Are the ion energy distributions a function of desorption angle?
- How do measured ion trajectories compare with theory?

In later experiments at the NBS synchrotron radiation source SURF-II, the analyzer will be used in angle-resolved photon-stimulated desorption studies of clean and adsorbate-covered oxide surface. Desorption thresholds and energy dependences will be correlated with angle-resolved electron spectroscopic measurements (ultrviolet photoelectron spectroscopy, constant-initial-state, constant-final-state measurements). These measurements will be the first detailed, angle-resolved mechanistic studies of photon-induced bond-streaking processes at surfaces.

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c) Recent Publications of New Staff Members Resulting From Previous Positions (Burgess, DeWeert, Johnson and Steigerwald)

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6. TALKS

Burgess, Jr., D. R. F., "Calculations of the Surface Temperature Rise and Desorption Temperature in Laser-Induced Thermal Desorption," American Vacuum Society Meeting, Houston, TX, November 20, 1985.

Burgess, Jr., D. R. F., "Laser-Excited Fluorescence Measurements of Rotational and Translational Energy Distributions of NO Desorbed from Platinum by Laser-Induced Thermal Desorption," American Vacuum Society Meeting, Houston, TX, November 21, 1985.

Burgess, Jr., D. R. F., "Laser-Excited Fluorescence Measurements of Rotational and Translational Energy Distributions of NO Desorbed from Platinum by Laser-Induced Thermal Desorption," American Physical Society Meeting, Las Vegas, NV, April 2, 1986.

Burgess, Jr., D. R. F., "Dynamical Interactions of Molecules with Surfaces," Applied Physics Division Seminar, U.S. Army Harry Diamond Laboratories, April 22, 1986.

Burgess, Jr., D. R. F., "Dynamical Interactions of Molecules with Surfaces," Materials Science Group Seminar, Johns Hopkins University Applied Physics Laboratory, May 1, 1986.

Burgess, Jr., D. R. F., "Dynamical Interactions of Molecules with Surfaces," Laser Group Seminar, National Bureau of Standards, Gaithersburg, MD, May 12, 1986.

Burgess, Jr., D. R. F., "Dynamics of the Laser-Induced Thermal Desorption of Nitric Oxide from Platinum," 46th Annual Conference on Physical Electronics, University of Texas, Austin, TX, June 16, 1986.

Burgess, Jr., D. R. F., "Dynamical Interactions of Molecules with Surfaces," Chemistry Division Seminar, Naval Research Laboratory, July 31, 1986.

Burgess, D. R. F., "Laser-Induced Thermal Desorption: Characterization of Rotational, Virbrational, and Translational Energy," 192nd American Chemical Society, Anaheim Convention Center, Anaheim, CA, September 10, 1986.

Cavanagh, R. R., "Time-Resolved Measurements of Vibrational Energy Transfer on Surfaces," Davison Division, W.R. Grace & Co., Columbia, MD, November 20, 1985.

Cavanagh, R. R., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," University of Chicago, Chicago, IL, February 11, 1986.

Cavanagh, R. R., "Neutron Scattering as a Probe of Surfaces: Adsorbate Bonding and Dynamics," National Measurement Laboratory Review Panel, Gaithersburg, MD, March 6, 1986.

Cavanagh, R. R., "Energy Transfer to Chemical Bonds on Surfaces," Gordon Research Conference on Chemistry of Electronic Materials, Concord, NH, August 20, 1986.

Chambers, G. P., "An Analytical Expression for Auger Sputter Depth Profiles," American Vacuum Society Meeting, Houston, TX, November 21, 1985.

DeWeert, M., "Magnetic Field Dependence of Superconducting Quasi Particle Interface States," American Physical Society Meeting, Las Vegas, NV, April 1, 1986.

DeWeert, M., "Theory of Magnetically-Induced Quasiparticle Bound States at Super Conductor-Ferromagnet Interfaces," Washington Area Statistical Physics Symposium, Gaithersburg, MD May 6, 1986.

Egelhoff, Jr., W. F., "Photoelectron Forward Scattering," American Vacuum Society Meeting, Houston, TX, November 21, 1985.

Egelhoff, Jr., W. F., "Auger and XPS Forward Scattering," American Physical Society Meeting, Las Vegas, NV, March 31, 1986.

Egelhoff, Jr., W. F., "Forward Scattering in XPS as a Tool for Studying Surface Segregation and Interdiffusion in Thin Films," Eastern Electron Spectroscopy Society, W.R. Grace & Company, Columbia, MD, May 8, 1986.

Erickson, N. E., "Study of the Performance Characteristics of Programmable Power Supplies & DVMs: Possible Relevance to Electron Energy Measurements," Eastern Electron Spectroscopy Society, W. R. Grace & Co., Columbia, MD, May 8, 1986.

Erickson, N. E., "Effects of Operational Faults of Programmable Power Supplies and DVMs on Measured Line Positions," Physical Electronics Users' Meeting, Hagerstown, MD, September 23, 1986.

Fine, J., "Characteristics of NBS Standard Reference Material 2135 for Sputter Depth Profile Analysis," European Conference on Applications of Surface and Interface Analysis, Veldhoven, The Netherlands, October 15, 1985.

Fine, J., "Collisionally Excited Auger Electron Emission from Al(100): Dependence on Azimuthal Orientation," Thirteenth Symposium on the Physics of Ionized Gases," Sibenik, Yugoslavia, September 1, 1986.

Gadzuk, J. W., "Common Ground in Surface Science and Electrochemistry," Summary talk at "Fourth Electrochemical Study Group, Fritz-Haber-Institute, Berlin, W. Germany, September 27, 1985.

Gadzuk, J. W., "Dynamics of Molecular Processes at Surfaces: Vibrational Excitation and Dissociation," Solid State Physics Seminar, Institut für Festkörperforschung der KFA Julich, Julich, West Germany, January 22, 1986.

Gadzuk, J. W., "Molecular Dynamics at Surfaces: Harpooning, Vibrational Excitation, and Dissociative Adsorption," Chemistry Department, University of Toronto, Toronto, Canada, February 13, 1986.

Gadzuk, J. W., "Molecular Dynamics at Surfaces: Harpooning, Vibrational Excitation, and Dissociative Adsorption," Physics Department Colloquium, University of Waterloo, Waterloo, Canada, February 14, 1986.

Gadzuk, J. W., "Exciting Vibrations: Scattering and Spectroscopy at Surfaces," Rutgers University, Piscataway, NJ, February 26, 1986.

Gadzuk, J. W., "Dynamics of Molecular Processes at Surfaces: Vibrational Lineshapes and Spectra," American Physical Society Meeting, Las Vegas, NV, March 31, 1986.

Gadzuk, J.W., "Site Conversion, Chaos, and Vibrational Lineshapes of Adsorbed Molecules," Institute of Theoretical Physics Seminar, Chalmers University, Goteborg, Sweden, April 22, 1986.

Gadzuk, J.W., "Exciting Vibrations: Scattering, Spectroscopy, and Wavepackets at Surfaces," Physics Department Colloquium, Rice University, Houston, TX, May 19, 1986.

Gadzuk, J.W., "Exciting Vibrations: Spectroscopy and Scattering at Surfaces," Solid State Seminar, Georgia Institute of Technology, Atlanta, GA, May 21, 1986.

Gadzuk, J. W., "Core Level Spectroscopy: A Dynamics Perspective," Adriatico Research Conference, "Dynamical Screening and Spectroscopy of Surfaces," International Centre for Theoretical Physics, Trieste, Italy, June 25, 1986.

Gadzuk, J. W., "Theoretical Aspects of Electronic, Vibrational, and Rotational Energy Flows in Molecular-Surface Interactions," Sixth International Workshop on Inelastic Ion-Surface Collisions, Argonne National Laboratories, Chicago, IL, August 27, 1986.

Girvin, S. M., "Introduction to the Quantum Hall Effect," University of British Columbia, Vancouver, B.C., Canada, October 17, 1985.

Girvin, S. M., "Wave Functions for the Fractional Quantum Hall Effect," Department of Physics, University of Maryland, College Park, MD, October 28, 1985.

Girvin, S. M., "The Quantum Hall Effect," Physics Department, University of Maryland, College Park, MD, October 29, 1985.

Girvin, S. M., "Collective Excitations in the Fractional Quantum Hall Effect," Physics Department, University of Maryland, College Park, MD, November 11, 1985.

Girvin, S. M., "Unsolved Problems in the Quantum Hall Effect," Physics Department, University of Maryland, College Park, MD, November 18, 1985.

Girvin, S. M., "Collective Excitations in the Fractional Quantum Hall Effect," Institute of Theoretical Physics, Chalmers University, Gothenburg, Sweden, December 4, 1985.

Girvin, S. M., "The Fractional Quantum Hall Effect: Superfluidity, Rotons and Fractionally Charged Vortices", Physics Department, University of Virginia, Charlottesville, VA, February 28, 1986.

Girvin, S. M., "Collective Excitations in the Fractional Quantum Hall Effect: Superfluidity, Phonons, Rotons, and Fractionally Charged Vortices," American Physical Society Meeting, Las Vegas, NV, March 31, 1986.

Girvin, S. M., "The Fractional Quantum Hall Effect: Superfluidity, Phonons, Rotons and Fractionally Charged Vortices," Department of Physics, Massachusetts Institute of Technology, Cambridge, MA, June 3, 1986.

Girvin, S.M., "Collective Excitations in the Fractional Quantum Hall Effect," Fourth Summer Institute of Theoretical Physics, Queen's University, Kingston, Ontario, Canada, July 15, 1986.

Girvin, S.M., "Collective Excitations in the Fractional Quantum Hall Effect," NORDITA Conference on Fundamental Effects in Semiconductors, Copenhagen, Denmark, August 7, 1986.

Girvin, S. M., "Collective Excitations in the Fractional Quantum Hall Effect," Physics Department, University of Notre Dame, IA, September 17, 1986.

Jach, T., "Dynamical Diffraction of X-rays from Crystal Surfaces at Grazing Incidence", Eidigenossiche Technische Hochschule, Zürich, Switzerland, October 15, 1985.

Jach, T., "Dynamical Diffraction of X-rays from Crystal Surfaces," Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Universite Paris-Sud, Orsay, France, November 4, 1985.

Jach, T., "Dynamical Diffraction of X-rays from Crystal Surfaces and Its Use in Surface Science", University of California at Berkeley, Physics Department, Berkeley, CA, November 13, 1985.

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Jach, T., "Dynamical Surface X-ray Diffraction and its Requirements of a High Brightness Source", Advance Light Source Workshop, Lawrence Berkeley Laboratory, Berkeley, CA, November 15, 1985

Jach, T., "Determination of Dispersion Surfaces by Surface Dynamical Diffraction at Grazing Incidence," American Physical Society Meeting, Las Vegas, NV, April 1, 1986.

Jach, T., "Energy-Dependent Intensities of the Kβ Fluorescent Line and its Satellites in Ar Gas," American Physical Society Meeting, Washington, DC, April 30, 1986.

Jach, T., "PIN Diodes as Detectors of X-Ray Reflectivity from Optical Surfaces," Brookhaven Workshop on X-Ray Optics, Brookhaven National Laboratory, Upton, NY, June 2, 1986

Jach, T., "PIN Diodes as X-Ray Detectors for Synchrotron Experiments," National Synchrotron Light Source Annual User's Meeting, Brookhaven National Laboratory, Upton, NY, June 5, 1986.

Jach, T., "Dynamical Diffraction of X-Rays from Crystal Surfaces at Glancing Incidence--A New Surface Science Technique," AT&T Bell Laboratories, Murray Hill, NJ, July 21, 1986.

Johnson, A. J., "Small Particles Chemisorbed on Si(100) Studied by ESDIAD: Water," Gordon Research Conference on Chemistry of Electronic Materials," Concord, NH, August 18, 1986.

Johnson, A. J., "Small Molecules Chemisorbed on Si(100) Studied by ESDIAD: Water," Chemistry Department, Harvard University, Cambridge, MA, August 22, 1986.

Kelley, R. D., "Surface Science and Catalysis," Chemical Engineering Department, Auburn University, Auburn, AL, May 22, 1986.

Kelley, R. D., "Oxygen Atom-Olefin Reactions in Low Temperature Films: Relation to Catalytic Epoxidation of Ethylene," Gordon Research Conference on Catalysis, New London, NH, June 26, 1986.

Kurtz, R. L., "The Influence of Surface Structure on Ion Emission from TiO_2," American Vacuum Society Meeting, Houston, TX, November 20, 1985.

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Kurtz, R. L., "Measurements of Electron Attenuation Lengths on Condensed Molecular Solids," Georgia Institute of Technology, Atlanta, GA, May 9, 1986.

Madey, T. E., "Mechanism of Applications of Electron Stimulated Desorption in Surface Science," Joint Vacuum Congress of Hungarian, Yugoslavian and Austrian Vacuum Societies, House of Debrecen Committee of the Hungarian Academy of Science, Debrecen, Hungary, October 7, 1985.

Madey, T. E., "The Influence of Surface Additives on the Structure and Chemistry of NH_3 and H_2O on Metal Surfaces," Josef Atilla University, Dept. of Chemistry, Szeged, Hungary, October 10, 1985.

Madey, T. E., "Recent Advances in Electron and Photon Stimulated Desorption," American Vacuum Society Meeting, Houston, TX., November 21, 1985.

Madey, T. E., "Recent Applications of Electron Stimulated Desorption in Surface Structure Determination," Physics Department Colloquium, Cornell University, Ithaca, NY, December 4, 1985.

Madey, T. E., "The Surface Chemistry of Water," Gordon Research Conference on Electrochemistry, Santa Barbara, CA, January 20, 1986.

Madey, T. E., "Uses of Electron Stimulated Desorption in Surface Science," Materials Research Division, University of California at Berkeley, Berkeley, CA, January 23, 1986.

Madey, T. E., "Mechanisms and Applications of Electron and Photon Stimulated Desorption," Joint Institute for Laboratory Astrophysic, NBS, Boulder, CO, January 28, 1986.

Madey, T. E., "Mechanisms and Applications of Electron and Photon Stimulated Desorption," Physics Department, University of Pennsylvania, Philadelphia, PA, February 5, 1986.

Madey, T. E., "Early Applications of Vacuum Science and Technology," American Vacuum Society Symposium on Ion Beam Technology and Applications, Anaheim, CA, March 18, 1986.

Madey, T. E., "The Structure and Chemistry of H_2O on Surfaces," Beijing Laboratory of Vacuum Physics, Beijing, China, April 9, 1986.

Madey, T. E., "Advances in Electron and Photon Stimulated Desorption," Beijing Laboratory of Vacuum Physics, Beijing, China, April 9, 1986.

Madey, T. E., "History of Vacuum Science and Technology," Beijing Laboratory of Vacuum Physics, Beijing, China, April 10, 1986.

Madey, T. E., "The Use of Electron Stimulated Desorption to Determine the Structures of Surface Molecules," Fudan University, Shanghai, China, April 17, 1986.

Madey, T. E., "Secondary Electron Effects in Photon Stimulated Desorption," Sixth International Workshop on Inelastic Ion-Surface Collisions, Argonne, IL, August 16, 1986.

Madey, T. E., "Influence of Electronic and Geometrical Structure on Desorption Kinetics of Isoelectronic Polar Molecules: NH_3 and H_2O," Joint Workshop on Interface Phenomena, 'Kinetics of Interface Reactions,' Campobello International Park, ME, September 26, 1986.

Melmed, A. J., "Field Ion Appearance Spectroscopy of Gold Overlayers on Silicon," 33rd International Field Emission Symposium, W. Berlin, Germany, July 10, 1986.

Melmed, A. J., "Effects of a Gold Shank-Overlayer on the Field Ion Imaging of Silicon," 33rd International Field Emission Symposium, W. Berlin, Germany, July 10, 1986.

Melmed, A. J., "Progress in Understanding Atomic Structure of the Icosahedral Phase," 33rd International Field Emission Symposium, W. Berlin, Germany, July 11, 1985.

Melmed, A. J., "Atomic Structure of the Icosahedral Phase in AlMn," University of Erlangen-Nurnberg, Erlangen, W. Germany, July 14, 1986.

Powell, C. J. "Overview of Surface Analysis Techniques," New England Section of the Society for Applied Spectroscopy, Newton, MA, October 9, 1985.

Powell, C. J. "Surface Chemical Analysis - Report on the VAMAS Project," European Conference on Applications of Surface and Interface Analysis, Veldhoven, The Netherlands, October 17, 1985.

Powell, C. J. "Characterization of the Imaging Properties of a Double-Pass Cylindrical-Mirror Analyzer," European Conference on Applications of Surface and Interface Analysis, Veldhoven, The Netherlands, October 17, 1985.

Powell, C. J. "L_3-Level Binding Energies and Excitation Spectra of 3d Transition Metals by Different Techniques," Physical Chemistry Department, University of Nijmegen, Nijmegen, The Netherlands, October 18, 1985.

Powell, C. J., "Recent Developments in Quantitative Surface Analysis by Electron Spectroscopy," American Vacuum Society Meeting, Houston, TX, November 19, 1985.

Powell, C. J., "Imaging Properties and Energy Aberrations of a Double-Pass Cylindrical-Mirror Electron Energy Analyzer," American Vacuum Society National Symposium, November 19, 1986.

Powell, C. J., "Lectures on Surface Science and Surface Analysis," Short Course of the Mexican Vacuum Society, Mexico City, Mexico, March 17-18, 1986.

Powell, C. J., "Auger Electron Spectroscopy," Short Course on Microanalytical techniques in Materials Science, Washington Chapter of the American Society for Metals, NBS, Gaithersburg, MD, April 22, 1986.

Powell, C.J., "Comparison of L_3-Shell Binding Energies in 3d Metals by XPS, APS, and EELS," IBM Almaden Research Center, San Jose, CA, May 20, 1986.

Powell, C.J., "Comparison of Measured and Calculated Appearance-Potential Spectra of 3d Metals," Physical Electronics Conference, University of Texas at Austin, Austin, Texas, June 16, 1986.

Powell, C.J., "Comparison of Measured and Calculated Appearance-Potential Spectra of 3d Metals," Gordon Research Conference on Electron Spectroscopy, Wolfeboro, NH, July 14, 1986.

Powell, C.J., "Energy Dependence of Electron Inelastic Mean Free Paths," Physical Electronics Users' Meeting, Hagerstown, MD, September 23, 1986.

Shinn, N. D., "Dossier of a Molecular Precursor to Dissociation: The Cr(110/CO) Case," Department of Chemistry, University of Texas, Austin, TX, November 19, 1985.

Shinn, N. D., "Synchrotron Photoemission Evidence for Lying-Down CO on Cr(110)," American Vacuum Society Meeting, Houston, TX, November 19, 1985.

Shinn, N. D., "Synchrotron Photoemission Study of π-Bonded CO on Cr(110)," American Chemical Society Meeting, New York, NY, April 16, 1986.

Shinn, N. D., "Alkali Overlayer Ordering on the Atomically Corrugated Cu(311) Surface," American Chemical Society Meeting, New York, NY, April 17, 1986.

Stockbauer, R. L., "Photon and Electron Stimulated Desorption of Ions from Surfaces," Department of Physics, Lehigh University, Bethlehem, PA, October 17, 1985.

Stockbauer, R.L., "Use of Synchrotron Radiation in Studies of Adsorbed H_2O: Surface Chemistry and Radiation Damage," American Chemical Society Meeting, New York, NY, April 16, 1986.

Szuromi, P. D., "Sulfur Poisoning of CO Hydrogenation over a Tungsten Catalyst," Chemistry Department, George Washington University, Washington, DC, February 7, 1986.

Szuromi, P. D., "Inhibition by Sulphur of Catalytic CO Hydrogenation over Tungsten," Inorganic Materials Division Seminar, National Bureau of Standards, Gaithersburg, MD, March 25, 1986.

Szuromi, P. D., "Inhibition by Sulfur of Catalytic CO Hydrogenation over Tungsten," Surface Chemistry Branch, Naval Research Laboratory, Washington, DC, April 7, 1986.

Szuromi, P. D., "Effect of Sulfur and Oxygen on the Hydrogenation of CO over W(110)," American Chemical Society Meeting, New York, NY, April 17, 1986.

Szuromi, P.D. "Effects of Metallic Surface Structure on Molecular Dissociation," Physics Department, Stevens Institute of Technology, Hoboken, NJ, April 28, 1986.

Szuromi, P. D., "Sulfur Inhibition of Methanation over W(110)," Gordon Research Conference on Catalysis, New London, NH, June 24, 1986.

7. SURFACE SCIENCE DIVISION SEMINARS

Adelman, S. A., Purdue University, West Lafayette, IN, "Some Concepts in Condensed Phase Chemical Kinetics," October 30, 1985.

Behm, R. J., University of Munich, Munich, W. Germany, "Local Surface Processes Detected by Scanning Tunneling Microscopy," Joint Seminar with Electron Physics Group, December 2, 1985.

Bono, J., Pennsylvania State University, University Park, PA, "Free-Electron Theory of Scanning Tunneling Microscopy," November 13, 1985.

Bonzel, H. P., KFA, Jülich, Germany, "Morphological Changes of Periodic Surface Profiles on Pt(110): Surface Self Diffusion, Anisotropy of Surface Energy, and Surface Reconstruction," June 26, 1986.

Burgess, Jr., D. R. F., "Laser-Induced Thermal Desorption as a Probe of Surface Processes," Surface Science Division Seminar, Gaithersburg, MD, October 23, 1985.

Ceyer, S. T., Massachusetts Institute of Technology, Cambridge, MA, "Dynamics of Molecular Chemisorption, Site Conversion and Activated Dissociative Adsorption on Ni(111)," May 29, 1986.

Chabal, Y., AT&T Bell Laboratories, Murray Hill, NJ, "Structure and Dynamics of Hydrogen on Si(100) and W(100) - An Infrared Study," January 6, 1986.

Chambers, G. P., Nuclear Engineering Dept., Univ. of Maryland, and Guest Worker, Surface Science Division "Design of an Interactive Sputtering Yields Database Using Commerical and In-House Software", October 25, 1985.

Davenport, J., Brookhaven National Laboratory, Upton, NY, "Surface Relaxation in Gold (110)," September 11, 1986.

Demmin, R. A., University of Pennsylvania, Philadelphia, PA, "Methanation Reaction Kinetics over Model Pt Catalysts," September 5, 1986.

Eesley, G., General Motors Research Laboratories, Warren, MI., "Energy Relaxation in Metals on the Picosecond Timescale", October 18, 1985.

Einstein, T. L., University of Maryland, College Park, MD, "Informal Lecture Series on Phase Transitions at Surfaces: I. General Introduction to Concepts in Critical Phenomena," April 8, 1986.

Einstein, T. L., University of Maryland, College Park, MD, "Informal Lecture Series on Phase Transitions at Surfaces: II. Application to Surfaces," April 9, 1986.

Einstein, T. L., University of Maryland, College Park, MD, "Informal Lecture Series on Phase Transitions at Surfaces: III. Chemisorbed Systems and Universality Classes," April 10, 1986.

Einstein, T. L., University of Maryland, College Park, MD, "Informal Lecture Series on Phase Transitions at Surfaces: IV. Transfer Matrix and Monte Carlo Methods," May 28, 1986.

Einstein, T. L., University of Maryland, College Park, MD, "Informal Lecture Series on Phase Transitions at Surfaces: V. Aspects of Roughening on Surfaces, How to Measure It, and How It Relates to Other Models", June 5, 1986.

Gallagher, A., Joint Institute for Laboratory Astrophysics, NBS, Boulder, CO, "Issues Concerning Hydrogenated Amorphous Silicon Surfaces", June 6, 1986.

Glaus, U. W., University of Maryland, College Park, MD, "Adsorbed Phases with Impurities and the Random Field Ising Model," June 11, 1986.

Heller, E., University of Washington, Seattle, WA, "Chaos, Quantum Mechanics, and the Mexico City Earthquake," February 18, 1986.

Holloway, S., Liverpool University, Liverpool, England, "Surface Dynamics: The Liverpool Perspective," January 15, 1986.

Hall, R., EXXON Research & Engineering Co., Annandale, NJ, "Surface Chemistry Induced by Pulsed Lasers--Competition Between Desorption and Reaction", May 16, 1986.

MacDonald, A. H., National Research Council of Canada, Ottawa, Canada, "In Defense of Normalcy: Why Potassium Ought Not to Have a Charge-Density-Wave Ground State," April 14, 1986.

Marton, D., Technical University of Budapest, Budapest, Hungary and Guest Scientist, Surface Science Division, "Depth Resolution in Sputter Depth Profiling," January 15, 1986.

Mitchell, G. E., University of Texas, Austin, TX, "The Surface Chemistry of Ketene on Pt(111)," September 9, 1986.

Netzer, F., University of Innsbruck, Innsbruck, Austria, "Angle Resolved Photoemission of Aromatic Molecules Adsorbed on Transition Metals," Joint Seminar with Photon Physics Group, July 11, 1986.

Nicol, J. M., "Infrared Studies of Zeolite--Adsorption Complexes," Surface Science Division Seminar, Gaithersburg, MD, January 30, 1986.

Nordlander, P., Chalmers University, Goteborg, Sweden, "Potential Energy Surfaces for Atoms and Molecules Near Metal Surfaces," March 21, 1986.

Pfluger, P., BBC Brown, Boveri & Company, Ltd., Baden, Switzerland, "Electronic Processes in Organic Dielectrics Under High Electrical Fields", October 18, 1985.

Sanche, L., Universite de Sherbrooke, Sherbrooke (Quebec), Canada, "Electron Spectroscopy of Molecular Solids Condensed on Metal Surfaces", February 14, 1986.

Sarma, S. D., Physics Department, University of Maryland, College Park, MD, "Molecular Statics and Dynamics Studies of Epitaxy", June 10, 1986.

Sass, J. K., Fritz-Haber-Institute, Berlin, Germany, "Tuneable Laser Radiation and Surface Plasmon-Polariton Excitation in Infrared Spectroscop at the Metal-Electrolyte Interface", October 21, 1985.

Schuetzle, D., Ford Motor Company Research Laboratories, Dearborn, MI, "Recent Advances in ESCA and SIMS: Applications to Materials Science," Joint Seminar with Center for Analytical Chemistry, May 15, 1986.

Snowdon, K., Vanderbilt University, Nashville, TN and University of Osnabruck. Osnabruck, Germany, "Surface Neutralization of Low Energy Atomic and Molecular Ions", June 9, 1986

Stiles, M., Cornell University, Ithaca, NY, "Inelastic Molecular Hydrogen Surface Scattering," February 21, 1986.

Tobin, R., University of California, Berkeley, CA, "Infrared Spectroscopy of Molecules Adsorbed on Metal Surfaces," March 17, 1986.

Umbach, E., Technical University of Munich, Munich, W. Germany, "Photoemission and Auger Spectroscopy as Probes for the Investigation of Adsorbate Systems," April 24, 1986.

8. TECHNICAL AND PROFESSIONAL COMMITTEE PARTICIPATION AND LEADERSHIP

Cavanagh, R. R.

Surface Science Division Safety Officer (through 1/86)

Treasurer, General Committee of the Physical Electronics Conference

Erickson, N. E.

Member, ASTM Committee E-42 on Surface Analysis

Fine, J.

Chairman, Subcommittee E-42.09 on Standard Reference Materials of ASTM Committee E-42 on Surface Analysis

Gadzuk, J. W.

Member, Editorial Advisory Board, "Progress in Surface Science"

Member, International Steering Committee, 5th International Conference on Vibrations at Surfaces, Garmisch-Partenkirchen, FRG, September, 1987

Girvin, S. M.

Member, Program Committee, 7th International Conference on the Electronic Properties of Two-Dimensional Materials (Sante Fe, July 1987)

Jach, T.

Invited participant, Workshop on an Advanced Soft X-Ray and Ultra-violet Synchrotron Source, Berkeley, CA, Nov. 13-15, 1985

Participant, Workshop on X-Ray Optics, Brookhaven National Laboratory, June 2-4, 1986

Kelley, R. D.

Chairman, Subcommittee D-32.03 on Chemical Analysis of ASTM Committee D-32 on Catalysts

Kurtz, R. L.

Member, Local Arrangements Committee, 10th International Vacuum Congress, 6th International Conference on Solid Surfaces, 33rd National Symposium of the American Vacuum Society, Baltimore, MD, October, 1986

Madey, T. E.

Member, American Institute of Physics Subcommittee on Electronic Publishing

Program Chairman, 10th International Vacuum Congress/6th International Congress on Solids Surfaces/33rd National Symposium of the American Vacuum Society, Baltimore, MD, October, 1986

U.S. Representative to Surface Science Division of the International Union of Vacuum Science, Technique and Applications (IUVSTA) and Secretary of Committee

Member, Program Advisory Committee for the Synchrotron Radiation Center of the University of Wisconsin, Madison, Wisconsin

Member, International Advisory Committee, Beijing Laboratory of Vacuum Physics, Peoples Republic of China

Member, Advisory Committee for Laboratory of Surface Science and Technology at the University of Maine, Orono, ME

Chairman, Committee for Foreign Interactions, American Vacuum Society

Member, International Advisory Committee, Second International Conference on the Structure of Surfaces, Amsterdam, The Netherlands, June, 1987

Member, International Advisory Committee, Workshop on Desorption Induced by Electronic Transitions, DIET-III, Long Island, NY, May, 1987

Member, ASTM Committee E-42 on Surface Analysis

Member, Editorial Board, "Methods of Surface Characterization"; co-editor of two volumes in series

Melmed, A. J.

President (from 7/86) and Secretary, International Field Emission Society

Division Safety Officer (from 2/86)

Powell, C. J.

Chairman, ASTM Committee E-42 on Surface Analysis (through 12/85) and International Liaison (from 1/86)

Chairman, Surface Chemical Analysis Working Party, Versailles Project on Advanced Materials and Standards

Chairman, Board of Trustees, Gordon Research Conferences

Chairman, American Vacuum Society Applied Surface Science Division

Chairman, American Vacuum Society Scholarships and Awards Committee

Member, Ad Hoc Committee on Topical Conferences, American Vacuum Society

Chairman, Applied Surface Science Division Steering Committee, International Union of Vacuum Science, Technique, and Applications

Member, Board of Visitors, Research Advisory Board, Physics Program, Office of Naval Research

National Representative, Commission I.6 on Colloid and Surface Chemistry including Catalysis, International Union of Pure and Applied Chemistry

Member, Editorial Board, "Applications of Surface Science"

Member, Editorial Board, "Surface and Interface Analysis"

Member, Editorial Board, "Methods of Surface Characterization"; co-editor of one volume in series

Stockbauer, R.

Assistant Program Chairman, 10th International Vacuum Congress/6th International Conference on Solid Surface/33rd National Symposium of the American Vacuum Society, Baltimore, MD, October, 1986

Member, Office Automation Committee, American Vacuum Society

9. PROFESSIONAL INTERACTIONS, CONSULTING AND ADVISORY SERVICES

Cavanagh, R. R.

Collaborating with Dr. D. S. King of the NBS Molecular Spectroscopy Division on state-specific diagnostics of molecular desorption processes

Collaborating with Drs. M. P. Casassa, E. J. Heiweil and J. C. Stephenson of the NBS Molecular Spectroscopy Division on real time measurements of vibrational relaxation processes at surfaces

Collaborating with Drs. T. J. Udovic and J. J. Rush of the NBS Reactor Radiation Division on neutron inelastic scattering studies of adsorbates on high-surface-area transition metals

Collaborating with Dr. J. J. Rush of the NBS Reactor Radiation Division, Dr. G. D. Stucky of the University of California at Santa Barbara, and Dr. M. J. Wax of W. R. Grace Co. on vibration and diffusion properties of hydrogen and ammonia in zeolite H-rho

Collaborating with Drs. T. J. Udovic and J. J. Rush of the NBS Reactor Radiation Division and Dr. B. J. Tatarchuck of Auburn University on neutron inelastic scattering measurements from adsorbates on dispersed ruthenium catalysts

Egelhoff, Jr., W. F.

Collaborating with Dr. J. E. Rowe of AT&T Bell Laboratories in studies of semiconductor surface reconstructions by the technique of X-ray photoelectron forward scattering

Collaborating with Dr. B. Henrich of Simon Frasier University (Canada) on the synthesis and characterization of metallic superlattices

Erickson, N. E.

Collaborated with Mr. T. E. Kiess of the NBS Electricity Division on the calibration of a high-precision digital voltmeter and a high-precision programmable power supply.

Fine, J.

Collaborated with Prof. B. Navinsek of the J. Stefan Institute, Ljubljana, Yugoslavia on the effect of surface topography on measurements of sputtering yields, on depth resolution at interfaces, and on the fabrication and characterization of standard reference materials for surface analysis. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology

Collaborating with Dr. I. Terzic of the Boris Kidric Institute, Belgrade, Yugoslavia on electronic excitation and electron emission for ion-bombarded surfaces. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technolgoy.

Colloborating with Drs. L. and N. Tanovic of the University of Sarajevo, Yugoslavia on characterizing surface topography changes that result from ion bombardment. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Dr. T. Nenadovic of the Boris Kidric Institute, Belgrade, Yugoslavia on the surface topography effect of both particle and laser-beam interactions with thin solid films. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Dr. J. D. Fassett of the NBS Inorganic Analytical Research Division and Dr. J. Boulmer of the Universite Paris, France and guest scientist in the NBS Inorganic Analytical Research Division on the use of laser multiphoton ionization techniques to identify sputtered atoms and to determine their kinetic energies.

Collaborating with Dr. W. Kirchhoff of the NBS Chemical Thermodynamics Division on a data analysis procedure for sputter-depth-profile interface characterization.

Collaborating with Dr. R. F. Fleming of the NBS Inorganic Analytical Research Division on thin-film thickness measurements of standard reference materials for surface analysis.

Collaborating with Drs. C. Le Gressus and J. P. Duraud of the Centre d'Etudes Nucleaires de Saclay, France on the colloisional excitation and electron decay of atoms at single-crystal surfaces.

Gadzuk, J. W.

Collaborating with Prof. M. Sunjic of the Rudnor Boskovic Institute and the University of Zagreb, Yugoslavia on theories of electron spectroscopies and dynamics of molecular processes at surfaces. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Dr. S. Holloway, University of Liverpool, England on classical trajectory theories of molecular processes at surfaces. This collaboration is assisted by a grant from the NATO Scientific Affairs Division.

Collaborating with Dr. E. Hood, Montana State University on a theory of high-energy neutral-molecular beams.

Collaborating with Dr. N. Satyamurthy, Indian Institute of Technology, Kanpur, India, and serving as monitor for a project "Chemical Dynamics and Laser Spectroscopy", under the auspices of the India-U.S. Materials Science Program funded via the provisions of PL-480.

Consulted with Dr. J. K. Sass, Fritz Haber Institute, W. Berlin on problems of spectroscopy at electro-chemical interfaces (Nov. 25-30, 1985).

Consulted with Dr. J. Harris and other members of the Solid State Theory Group, KFA (Nuclear Research Organization) Julich, W. Germany on problems associated with molecular dynamics at surfaces.

Consulted with Professors S. Andersson and B. Lundqvist of the Chalmers University of Technology, Gothenburg, Sweden on molecular dynamics at surfaces.

Invited lecturer and participant at Adriatico Research Conference, "Dynamical Screening and Spectroscopy of Surfaces", International Centre for Theoretical Physics, Trieste, Italy (June 23-27, 1986).

Invited lecturer and participant at Sixth International Workshop on Inelastic Ion-Surface Collisions, Argonne National Laboratory (August 25-29, 1986).

Invited discussion leader at Gordon Research Conference on Electron Spectroscopy, Wolfeboro, NH (July 14-18, 1986).

Girvin, S. M.

Collaborated with Drs. A. H. MacDonald, (National Research Council, Ottawa) and P. M. Platzman (AT&T Bell Laboratories, Murray Hill) on the study of collective excitations in the fractional quantum Hall effect.

Completed a collaboration with Drs. D. R. Penn and S. P. Apell of the NBS Electron Physics Group on a theory of spin-polarized secondary electron cascades in ferromagnets.

Collaborated with Prof. R. E. Prange (University of Maryland) in organizing a ten-part lecture series on the quantum Hall effect and in editing the lecture notes for publication.

Jach, T. J.

Collaborating with Drs. P. Cowan, S. Brennan, and R. Lavilla of the NBS Quantum Metrology Group on gas-phase x-ray fluorescence experiments at the Brookhaven National Synchrotron Light Source.

Collaborating with Dr. R. Perera, Lawrence Berekely Laboratory on gas-phase x-ray fluorescence experiments at the Brookhaven National Synchrotron Light Source.

Collaborating with Dr. S. Banna, Vanderbilt University on gas-phase x-ray photoemission experiments at the Brookhaven National Synchrotron Light Source.

Collaborating with Dr. J. Kirkland, Sachs Freeman Associates on measurements of silicon photodiode yields at x-ray energies at the Brookhaven National Synchrotron Light Source.

Collaborating with Dr. J. Kirkland and P. Wolf, Virginia Polytechnical Institute and State University on harmonic detection and elimination in double-crystal monochromators at the Brookhaven National Synchrotron Light Source.

Collaborating with Dr. L. Holdeman, Comsat Corp., and Dr. G. Hembree, NBS Precision Engineering Division on measurement at the surface morphology of thin films.

Advised Mr. C. E. Bouldin of the NBS Semiconductor Electronics Division on the use of silicon photodioides for the measurement of extended x-ray absorption fine structure in a beamline to be set up at the Brookhaven National Light Source.

Kelley, R. D.

Collaborating (with J. M. Nicol) with Drs. T. J. Udovic and J. J. Rush of the NBS Reactor Division on neutron inelastic scattering measurements of adsorbates on high-surface-area transition metals.

Working on detail as a Program Manager with the Department of Energy, Office of Energy Research, Division of Chemical Sciences. This detail is on a 80% part-time basis for a two-year period that began June, 1985.

Kurtz, R. L.

Collaborating with Prof. V. E. Henrich and members of his group at Yale University in studies of the electronic structure and the influence of adsorbates on transition-metal oxide surfaces.

Collaborating (with R. Stockbauer) with Dr. V. Bermudez of the Naval Research Laboratory in a study of the influence of adsorbates in promoting phase transitions in the surface conductivity of oxides.

Collaborating (with R. Stockbauer) with Dr. A. Flodström of the Royal Institute of Technology, Stockholm, Sweden in studies of the mechanisms involved in stimulated desorption of ions and in studies of the influence of surface structure on ion angular distributions.

Collaborating (with T. E. Madey and R. Stockbauer) with Drs. W. R. Hunter, J. Rife, and M. Kabler of the Naval Research Laboratory and Dr. R. Williams of Wake Forest University in experiments at the x-ray ring of the Brookhaven National Light Source. This work includes the instrumentation of the double-grating monochromator designed by the NRL group and implementation of a surface science chamber that will be used for studies of the mechanisms of stimulated desorption of ions as well as extended-energy measurements of electron attenuation lengths in condensed molecular solids.

Collaborating (with T. E. Madey and R. Stockbauer) with Dr. J. L. Pena of the National Polytechnic Institute, Mexico City in studies of molecular chemisorption and ion desorption from TiO_2 surfaces.

Collaborating (with T. E. Madey and R. Stockbauer) with Prof. J. L. de Segovia of the Instituto de Fisica de Materiales, in Madrid, Spain in studies of the structure and reactivity in catalysis by metals and oxides. This work is conducted under the auspices of the U.S.-Spain Joint Committee for Technical Cooperation.

Madey, T. E.

Collaborating with Drs. I. Terzić, J. Vukanić and Z. Mišković of the Boris Kidrić Institute, Belgrade, under the auspices of the U.S.-Yugoslav Agreement for Cooperation in Science and Technology, on theoretical and experimental studies of electron-stimulated desorption and scattering of alkali ions from surfaces.

Collaborating (with R. L. Kurtz and R. Stockbauer) with Drs. W. R. Hunter, J. Rife and M. Kabler of the Naval Research Laboratory and with Dr. R. Williams of Wake Forest University on the design and instrumentation for a beamline and chamber at the Brookhaven National Synchrotron Light Source to study chemisorbed molecules on clean metal surfaces, mechanisms of photon-stimulated desorption of ions, and electron attenuation lengths in condensed molecular solids.

Collaborating with Dr. N. Tolk of Vanderbilt University on studies of electron-stimulated desorption of excited-alkali neutral atoms from surfaces.

Collaborating with Dr. C. Benndorf of the University of Hamburg, under the auspices of a NATO grant, on studies of the influence of surface additives on local molecular structure.

Collaborating with Prof. P. A. Thiel of Iowa State University in writing a comprehensive review article on the interaction of water with solid surfaces.

Collaborating with Dr. J. L. de Segovia of the Instituto de Fiscia de Materiales, in Madrid, Spain, under the auspices of the U.S.-Spain Joint Committee for Technical Cooperation on experimental studies of adsorption on metals and oxides using electron-stimulated desorption and synchrotron radiation methods.

Collaborating (with R. Kurtz and R. Stockbauer) with Prof. J. L. Pena of the National Polytechnic Institute, Mexico City in synchrotron studies of oxide surfaces.

Melmed, A. J.

Collaborating with Dr. W. A. Schmidt and Prof. J. H. Block of the Fritz Haber Institute, Berlin on properties of semiconductors in electric fields and effects due to metallic overlayers.

Collaborating with Dr. R. D. Arollia of the General Electric Company and Prof. H. Fraser of the University of Illinois to investigate atomic structure and chemical microcomposition for a series of nickel-based superalloys.

Collaborating with Mr. J. Smith and Prof. H. Fraser of the University of Illinois on studies of three related nickel-based superalloys using field ion microscopy, transmission electron microscopy, and atom-probe analysis.

Collaborating with Dr. M. J. Kaufman of the NBS Metallurgy Division on comparative studies with atom-probe field-ion microscopy and transmission electron microscopy of nickel-based superalloys and a series of Al-Li-Cu alloys.

Collaborating with Dr. N. Shinn of the Sandia National Laboratories on the growth of chromium crystal layers by expitaxy from the vapor phase.

Powell, C. J.

Collaborating (with S. Tanuma) with Dr. D. R. Penn of the NBS Electron Physics Group on calculations of inelastic mean free paths of low-energy electrons in solids.

Collaborating with Dr. M. P. Seah of the National Physical Laboratory, London on the development of plans and programs for the Surface Chemical Analysis Working Party of the Versailles Project on Advanced Materials and Standards.

Adjudicator for the Science Prize of the UK ESCA and Auger Users Group

Stockbauer, R.

Collaborating (with R. L. Kurtz) with Drs. C. Kunz and F. Senf of the German Synchrotron Laboratory DESY, Hamburg and Drs. R. Nyholm and A. Flodström of the Royal Institute of Technology, Stockholm, Sweden in studies of the mechanisms of the photon-stimulated desorption of ions from surfaces.

Collaborating (with R. L. Kurtz) with Dr. A. Flodström of the Royal Institute of Technology, Stockholm, Sweden on experiments at the NBS Synchrotron Radiation Facility SURF-II to investigate (1) mechanisms of photon-stimulated desorption of ions from a non-maximal-valent oxide and (2) ions desorbing from adsorbates on semiconductors.

Collaborating (with R. L. Kurtz) with Dr. V. Bermudez of the Naval Research Laboratory on studies at the NBS SURF-II facility of the influence of adsorbates in promoting phase transitions in the surface conductivity of oxides.

Collaborating (with R. L. Kurtz and T. E. Madey) with Drs. W. R. Hunter, J. Rife, and M. Kabler of the Naval Research Laboratory and with Dr. R. Williams of Wake Forest University on the design and instrumentation for a beamline and chamber at the Brookhaven Synchrotron Light Source to study chemisorbed molecules on clean metal surfaces, mechanisms of photon-stimulated desorption of ions, and electron attenuation lengths in condensed molecular solids.

Collaborating (with T. E. Madey and R. L. Kurtz) with Dr. J. L. Pena of the National Polytechnic Institute, Mexico City in studies of molecular chemisorption and ion desorption from TiO_2 surfaces.

Collaborating (with T. E. Madey and R. L. Kurtz) with Prof. J. L. de Segovia of the Instituto de Fisica de Materiales, in Madrid, Spain in studies of the structure and reactivity in catalysis by metals and oxides. This work is conducted under the auspices of the U.S.-Spain Joint Committee for Technical Cooperation.

Collaborating with Dr. A. C. Parr of the NBS Radiation Physics Division and with Dr. D. Holland of Daresbury Laboratory, England on measurements of the fragmentation of molecules using photoelectron-photoion coincidence techniques.

Interacting with Drs. A. C. Parr, J. Hardis, and D. L. Ederer of the NBS Radiation Physics Division, Dr. J. L. Dehmer of Argonne National Laboratory, and Drs. J. B. West and D. Holland of Daresbury Laboratory, England on measurements of photoelectron angular distributions as a function of photon energy in gas-phase molecules.

10. VISITING SCIENTISTS

The Surface Science Division has been host during the past year to a number of scientists who have worked with the Division staff on problems of mutual interest.

Barak, D., Head of the Electronic Design Department of the Israeli Nuclear Research Center-Negev, worked at NBS for one year beginning August 1985. He interfaced an x-ray photoelectron spectrometer to a computer system and developed new software for this instrument and for a new digital ESDIAD system.

Bermudez, V. M., of the Naval Research Laboratory worked one month at NBS in early 1986 performing photoemission experiments on vanadium oxide surfaces at the SURF-II synchrotron radiation facility.

Chambers, G. P., a graduate student at the University of Maryland, has worked at NBS this past year under a cooperative agreement. He has been involved in the development of a data base system for the compilation of evaluated sputtering yield data and in quantitative sputter-depth-profiling of interfaces.

Chen, H.-H., of the National Science Council in Taiwan is spending a year at NBS, beginning in July 1986, working on applications of synchrotron radiation to the characterization of surfaces.

Clinton, W. L., of Georgetown University spent eight months at NBS on an intermittent basis performing theoretical studies related to electron- and photon-stimulated desorption of ions and neutrals from surfaces.

Einstein, T. L., of the University of Maryland worked at NBS for about five months on an Intergovernmental Personnel Assignment on studies of surface critical phenomena.

Hashiguchi, Y., of the Nippon Steel Corporation, Japan worked at NBS since March 1985 on a one-year assignment involving measurements of sputter-depth profiles of multilayer thin-film reference materials.

Holloway, S., of the University of Liverpool, visited NBS for two weeks during the winter of 1985-86 and one week during the summer of 1986 to work on theoretical modeling of reactive molecular processes at surfaces.

Hylden, J. L., of the Naval Research Laboratory spent one month at NBS in early 1986 performing photoemission experiments on vanadium oxide surface at the SURF-II synchrotron radiation facility.

Jansen, W. R., a graduate student of the Twente University of Enschede, The Netherlands worked at NBS for three months in the fall of 1985. He extended software for automated x-ray photoelectron spectroscopy measurements in a timesharing mode and for data reduction.

Larsson, C. U. S., of the University of Lund, Sweden, is spending about 4 months per year at NBS, starting December 1985, performing ESDIAD studies of the surface chemistry of silicon.

Marton, D., of the Technical University of Budapest, Hungary, is a Fulbright Scholar who is spending sixteen months at NBS, beginning September, 1985, on studies of the surface topography of ion-bombarded surfaces and characterizing multilayer thin-film structures.

Nicol, J. M., of the University of Maryland is spending two years at NBS, beginning November 1985, using neutron scattering methods to characterize adsorption on surfaces of high-area metallic and zeolite catalysts.

Polak, M., of the Ben Gurion University of the Negev, Isarel, is spending one year at NBS beginning August 1986, performing studies of molecular structure on semiconductor and metal surfaces using high-resolution EELS and ESDIAD.

Shinn, N. D., of Sandia National Laboratory, spent four months at NBS during the fall of 1985 performing synchrotron radiation studies of small molecules adsorbed on single-crystal chromium surfaces.

Tanuma, S., of the Nippon Mining Company is working at NBS on a two-year assignment that began in August 1985. He is participating in measurements of core-level binding energies by different electron-spectroscopic methods, in calculations of electron inelastic mean free paths in solids, and in analyses of algorithms for x-ray photoelectron spectroscopy.

Wei, J., a graduate student at the University of Maryland from the People's Republic of China, spent two months at NBS during the summer of 1986 performing studies of catalysis over well-characterized copper surfaces.

11. SURFACE SCIENCE DIVISION STAFF

As of September 30, 1986 the Surface Science Division was staffed as follows:

C. J. Powell, Chief
L. M. Johnson, Secretary
D. R. F. Burgess, Jr.[*]
R. R. Cavanagh
M. J. DeWeert[*]
W. F. Egelhoff, Jr.
N. E. Erickson
J. Fine
J. W. Gadzuk
S. M. Girvin
T. J. Jach[**]
A. J. Melmed
D. A. Steigerwald[*]

Surface Structure and Kinetics Group

T. E. Madey, Group Leader
B. E. Stewart, Secretary
P. M. Connelly[#]
A. L. Johnson[*]
R. D. Kelley
R. L. King[+]
R. L. Kurtz
E. O. Neitzel[#]
D. E. Ramaker[@]
R. L. Stockbauer

[*] NBS-NRC Postdoctoral Research Associate
[@] Faculty Appointment, Part-Time
[#] Engineering Technician
[+] Electronics Technician
[**] Half time with Quantum Metrology Group

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11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

This report summarizes technical activities of the NBS Surface Science Division during Fiscal Year 1986. These activities include surface-standards work, experimental and theoretical research in surface science, the development of improved measurement methods, and applications to important scientific and national problems. A listing is given of publications, talks, professional committee participation, and professional interactions by the Division staff.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

surface chemistry; surface physics; surface science; surface standards

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