Eighth International Summer Institute in Surface Science (ISISS 1987)

EIGHTH INTERNATIONAL SUMMER INSTITUTE IN SURFACE SCIENCE
(ISISS 1987)

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The academic goals of ISISS were outlined in the editorial comments of "Surface Science: Recent Progress and Perspectives (ISISS 1975)":

"The favorable acceptance of ISISS was gratifying, but did not exactly come as a surprise. During the recent decade, advanced ultrahigh vacuum technology has made the achievement of pressures $< 10^{-10}$ Torr a routine operation so that surfaces, once freed from impurities, can be kept clean over a sufficient length of time and adsorbates then can be admitted at well-dosed amounts. Techniques for surface analysis were more and more refined; with the atom probe we are now able to analyze even single surface atoms or chemical complexes. Progress in the theory of the solid state subsequently allowed some fruitful dealing with the theoretical aspects of solid surfaces. All these developments combined with the demand for data by vital branches of our modern technology, caused an increasing flood of publications especially in the field of gas-solid interfaces. It became hard to catch up with the literature in one's own narrow area and it appeared nearly impossible to keep track of the developments in neighboring fields. As in other fast developing parts of the natural sciences, one consequently observes some isolationism and the appearance of communication problems. It is quite clear that such a tendency, where one no longer learns from progress or setbacks in neighboring areas, would be very much to our disadvantage. To counteract this tendency, ISISS was organized. Leading experts from various subdivisions of surface science - we chose to restrict the topics to gas-solid interfaces - presented tutorial review talks in which recent progress was summarized and future trends were pointed out."

In order to keep ISISS 1987 at a level of highest quality, all former ISISS speakers were invited to suggest names of suitable lecturers. To avoid duplication, none of the lecturers of the 1985 Summer Institute were invited to present a paper. The final list showed twenty-one internationally known experts in the field of gas-solid interfaces. The speakers came from Canada, Germany, The Netherlands, and from the U.S.A.

The following list shows their names, their affiliations, topics, and short summaries of the papers presented.
T. Baker, Auburn University, Alabama

**Electron Microscopy in the Study of Strong Metal-Support Interaction**

High resolution transmission electron microscopy has been used to compare the structure and growth characteristics of platinum on a number of supports. Many unique features are exhibited by the metal particles supported on titania when the system is treated in hydrogen at temperatures in excess of 500°C. Along with changes in the morphological characteristics of the particle, the support itself was found to transform to a lower oxide, Ti₄O₇. In-situ scanning transmission electron microscopy studies have shown that the metal facilitates the reduction of the titania, which leads to the creation of pits in the support. It is believed that the reduced-titania species removed from the support migrate onto the surfaces of the metal particles. The presence of titania species on the metal surface is thought to be responsible for the occurrence of so-called "strong metal-support interactions".

H.P. Bonzel, Institut für Grenzflächenforschung und Vakuumphysik, Jülich, Germany

**Relationship Between Anisotropy of Surface Energy and Surface Reconstruction**

From general considerations it is clear that the surface free energy of a reconstructed surface should be lower than that of the non-reconstructed form. A somewhat more subtle statement says that surfaces reconstruct if the anisotropy of the surface free energy in the orientational range involving the non-reconstructed surface is high. Measurements of surface self-diffusion on Pt(110) in the [001] direction have recently provided support for this latter statement [1,2]. Another source of information on surface energy anisotropies are measured surface core level shifts (SCLS) [3]. These have been obtained for several surface orientations of metals, for clean reconstructed, non-reconstructed and adsorbate covered surfaces [4]. It will be shown how these measured data can be used to estimate surface energy anisotropies for clean and adsorbate covered surfaces. The changes in these anisotropies due to reconstruction and/or adsorption of molecules can then be utilized for explaining or predicting structural changes. These relationships will be illustrated by the example of the clean and CO covered Pt(110) surface. Recent theoretical calculations of surface energies in connection with surface reconstruction [5] will also be reviewed.

Y. J. Chabal, AT&T Bell Laboratories, Murray Hill, New Jersey

IR Spectroscopy of Semiconductor Surfaces

1. Introduction and Motivation
   Introduce questions pertinent to semiconductor surfaces and expected role that IR spectroscopy will play.

2. Theoretical Framework
   2.1 Macroscopic theory (3-layer model)
   2.2 Microscopic model for the active layer
   2.3 Discussion of the assumption of sharp boundaries

3. Experimental Geometries and Techniques
   3.1 Vibrational Modes in substrate gap
   3.2 Vibrational Modes in substrate absorption region
   3.3 Electronic absorption

4. Selected Examples
   4.1 Structure of the Si(100)-(2x1)H system
   4.2 H-saturated Si(100) and Ge(100) surfaces
   4.3 Dynamics of H on Si(100)
   4.4 H\textsubscript{2}O on Si(100)
   4.5 Metallic deposition by photo-enhanced CVD

5. Problems and Future Directions

6. Conclusions

G. Comsa, Institut für Grenzflachenforschung und Vakuumphysik, Jülich, Germany

Inert Gas Layers on Metal Surfaces - Structure and Dynamics

Inert Gas Layers on very smooth {111}-planes of fcc metal crystals have been considered as the closest approximation of the conceptually simplest system, i.e. of inert gas on jellium. Unexpectedly, the periodic corrugation of the inert gas/substrate potential contributes substantially to the orientation and structure of the inert gas layer. The interaction energies within the layer and the amplitude of the potential corrugation being of the same order, the 2-dimensional inert gas layers can exhibit various structures and orientations depending on the actual value of coverage and temperature; even minute amounts of substrate defects and/or impurities may change radically salient layer features.

This behaviour, involving the existence of various 2D-phases and phase-transitions is exemplified in detail especially on the systems: Xe, Kr, Ar/Pt(111) including binary mixtures. Both structure and dynamics of the layers will be discussed. The experimental results are obtained mainly by high resolution thermal He-scattering. An outline of the various He-scattering modes which allow an almost exhaustive characterization of the inert gas layers will be given: specular(elastic) - for coverage; diffuse elastic - for roughness; diffraction - for structure; inelastic - for dynamics and layer completion.
Activated Chemisorption

In the early days of surface studies, in the 1920's, the term activated adsorption was synonymous with chemisorption, but evidence soon accumulated that on clean metals chemisorption could proceed rapidly, and in distinction to reactions in the gas phase, without any apparent activation energy. It is now known, however, that in some instances chemisorption on clean crystal surfaces is indeed activated, and occurs at a finite rate only at elevated temperatures. Recently there has been considerable activity in studying such systems, both because of their intrinsic interest, and for the insights they may afford into the kinetics of chemisorption in general.

After a brief survey of the early work in the field, current efforts will be outlined under the following headings:

1. Activation mechanisms
2. Sticking coefficients in activated chemisorption
   a. Potential diagrams
   b. Dependence on temperature and coverage
   c. Comparison with fast chemisorption
3. Experimental methods for probing the mechanism of activation
4. Case studies in activated chemisorption
   a. Hydrogen adsorption on copper
   b. Simple diatomic gases on low index planes of metals
   c. Chemisorption of saturated hydrocarbons

Critical Phenomena at Surfaces Revisited

I. Review of ISISS-1981 Lecture
II. Monte Carlo simulations of generic structures - structure factors
   A. What can be measured, and with what expected accuracy
   B. How to select data for checks of scaling
   C. Asymmetries of lattice gas models compared to magnetic analogues
III. Specific heat singularity from scattering experiments: energy-like singularity in probes of short-range order
   A. Integrated LEED intensity - Monte Carlo illustrations
   B. Other probes
IV. Other types of measurable behavior
   A. Critical scattering near first-order transitions
   B. Incommensurate melting and chiral Potts model
V. Miscellaneous comments

A. Multiple scattering bugaboo
B. Finite-size behavior and convolution of $T'_c$'s
C. Implications of conformal invariance

VI. Recent experiments

A. Au(110) - (1x2) reconstruction
B. c(2x2) Cl/Ag(100)
C. p(2x1) O/W(112)
D. p(2x2) and c(2x2) Se/Ni(100)

T. Engel, University of Washington, Seattle, Washington

Experiments on Surface Roughening

In recent years, much information has become available on the defect structure of clean surfaces. This research has been motivated by the demonstrated effect of steps on reaction rates, epitaxy, and electronic properties of interfaces. A number of techniques have been used to show the presence of steps on well oriented single crystal surfaces. The temperature dependence of the step density is of particular interest.

As the surface temperature increases, the equilibrium step density will also increase due to the gain in configurational entropy by the system. As was first proposed by Burton and Cabrera [1] a surface may undergo a phase transition from a smooth to a rough phase. In the smooth phase, the height fluctuations about a reference plane are bounded whereas they would become unbounded for a hypothetical surface of infinite extent. This transition has been first observed for solid helium in equilibrium with its superfluid [2,3] and has also been shown to occur on vicinal nickel [4] and copper [5] surfaces. In this talk the roughening transition and dependence of the roughening temperature on the surface orientation will be discussed for the metal surfaces. In addition, the differences in configuration of the surface somewhat below and somewhat above the roughening temperature will be discussed.

Surface Kinetics with Near Edge X-ray Absorption Fine Structure

Near Edge X-ray Absorption Fine Structure (NEXAFS) in the soft x-ray region has developed rapidly as a tool for characterizing adsorbed monolayer. The resonant transitions observed between adsorbate core levels and the lowest unfilled molecular orbitals have been used successfully to characterize both the orientation and bonding in carbon, nitrogen, oxygen and sulfur containing adsorbates on metal surfaces. In general terms, NEXAFS combines the chemical and structural sensitivity of a valence level method with the element specificity of a core level method. Because of this ability to distinguish between chemically similar adsorbed species, NEXAFS offers real advantages as a method for measuring reaction rates on surfaces. Rates of desorption, reorientation and dehydrogenation have been characterized on metal single crystal surfaces in vacuum using partial electron yield detection of the transient NEXAFS signal. Recently we have developed fluorescence detection as a method for detecting X-ray absorption above the carbon K edge (285 eV); this detection method allows NEXAFS spectra to be obtained rapidly even in the presence of reactive gaseous environments. Recently we have found that chemisorbed CO is displaced from the Ni(100) surface by more weakly adsorbed hydrogen above 10^-3 Torr. This unexpected result highlights the utility of surface methods which can be used to characterize surface reaction rates under reaction conditions.

H.D. Hagstrum

Surface Electron Interaction Underlying Ion Neutralization and Metastable De-excitation Spectroscopies (INS, MDS)

1. The two types of surface electronic transition involving atoms that carry potential energy: resonance and Auger processes
2. Quantum-mechanical tunneling as the basis for the surface specificity of INS and MDS
3. Energy limits of resonance and Auger processes
4. Variation of atomic energy level and potential energy as an atom approaches a surface
5. Two types of "two-stage" electronic transition process involving atoms near a solid surface
6. The INS and MDS regimes as determined by work function, atomic level crossing of the Fermi level, and the character of wave function projection from the surface
7. The possibility of using fast (~10 eV) or slow (52 meV) ions or metastables
8. The characteristics of metastable de-excitation (Penning ionization) spectroscopy
9. The characteristics of ion neutralization spectroscopy
Interpretation of the NEXAFS Spectra of Adsorbates Using Multiple Scattering Calculations

The multiple scattering Xα molecular orbital technique will be described, and a brief history of calculations of photoabsorption cross sections for transitions to discrete and continuum states using this technique will be given. A procedure for using the multiple scattering Xα technique for calculations of the X-ray absorption spectra of adsorbates, based on a cluster model, will be outlined. The results for cluster models representing CO on Ni(100) and O₂ on Ag(110) will be discussed.

A number of examples of the application of this method to the interpretation of experimental NEXAFS spectra of adsorbates will be given. First, the resolution of an apparent anomaly in the NEXAFS spectrum of ethylene on Pt(111) will be described. Then the interpretation of the NEXAFS spectra of more complex molecules will be discussed, with particular reference to the benzene molecule and saturated cyclic hydrocarbons. The relationship of the observed resonances to antibonding states of these molecules will be discussed, including both C - C and C - H antibonding states. Finally, the application of this technique to the interpretation of the NEXAFS spectra of unstable surface reaction intermediates will be illustrated by a calculation of the spectrum of the proposed Pt metallacycle intermediate in the desulfurization of thiophene on Pt(111).

Growth Kinetics of Si Molecular Beam Epitaxy

Molecular beam epitaxy utilizes the condensation of various molecular beams of matrix and dopant materials on the clean surfaces obtained by special substrate preparation techniques and under ultrahigh vacuum process conditions. The talk emphasizes the important role of the equilibrium adatom properties and of the monatomic surface steps on the growth kinetics. Adsorption, desorption and segregation govern the incorporation of dopant atoms from neutral beams. Ionization of either matrix atoms or dopant atoms is frequently used to influence the doping. Heteroepitaxy, strain influence on growth mode, pseudomorphism, misfit dislocation generation is discussed on the example of Si/SiGe superlattices.
E. Kay, IBM Almaden Research Center, San Jose, California

Surface and Interface Magnetic Characterization During Film Growth

A. Brief discussion of need for surface versus bulk magnetic measurements during film growth

B. Available techniques for measurement of surface versus bulk magnetic measurements during film growth with emphasis on:
   1. Longitudinal Kerr Magneto-optics
   2. Spin Polarized Electron Spectroscopies
      a. Secondary Electron Emission
      b. Threshold Photoemission
      c. Auger Spectroscopy

C. Description of U.H.V. thin film synthesis apparatus with in situ Kerr and spin polarized electron spectroscopy facility.

D. Application of the above characterization techniques to a variety of problems encountered during multilayered thin film growth
   1. Study of magnetic coupling mechanism at interface of two dissimilar magnetic materials, e.g. ferromagnet/antiferromagnet
   2. Magnetic consequences of oxidation driven surface segregation in 3d4f amorphous alloys
   3. Cation valence state and site coordination information in sputtered ferrite films by threshold spin polarized photoemission.
   4. Effects of ion milling artifacts on magnetic depth profiling techniques.
   5. Non-destructive magnetic depth profiling.

H.J. Kreuzer, Dalhousie University, Halifax, Nova Scotia, Canada

Desorption Kinetics

We will briefly review the master equation approach to physisorption kinetics (H.J. Kreuzer and Z.W. Gortel, Physisorption Kinetics, Springer Series in Surface Science, Vol. 1, Springer-Verlag, Berlin, 1986). We will then develop a systematic approach to the adsorption-desorption kinetics of two-phase adsorbates based on the Onsager approach to non-equilibrium thermodynamics, discussing in detail isothermal and temperature-programmed desorption from such adsorbates. This will be followed by a more detailed model for the kinetics of a two-phase adsorbate developed along the lines of the Becker-Döring theory of nucleation and droplet growth.
A. A. Maradudin, University of California, Irvine, California

**Surface Phonons - Theory**

A survey is presented of some of the significant discoveries and advances in the theoretical study of surface phonons during the 1980's. Both clean and adsorbate covered surfaces are considered. Some directions in which the field can go in the next few years are suggested.

H.J. Maris, Brown University, Rhode Island

**The Surface of Solid Helium**

The interface between liquid and solid helium is the only liquid-solid boundary which can exist down to absolute zero temperature. It has several remarkable properties as a result of the highly quantum nature of helium. We will review these properties and also describe how helium provides unique opportunities for the observation of several important effects in surface physics.

P. Pfeifer, University of Missouri, Columbia, Missouri

**Fractals in Surface Science**

1) Fractal concept (introduction, surface vs. mass vs. pore fractals)

2) Experimental determination of fractal dimension (monolayer capacities, porosimetry, electronic energy transfer, X-ray/neutron diffraction)

3) Thermodynamic properties of adsorbed films (Henry's law, fractal BET isotherm, Bose-Einstein condensation)

4) Anomalous diffusion on fractals (spectral dimension, kinetics, quasi-elastic scattering)

J. Stöhr, IBM Almaden Research Center, San Jose, California

**X-Ray Absorption Fine Structure Studies of Molecules, Molecular Chains and Thin Polymer Films on Surfaces**

The use of the near edge x-ray absorption fine structure (NEXAFS) technique is discussed for the study of the interaction of low-Z molecules with and on surfaces. The origin of the observed NEXAFS structures, their energy position and their polarization dependence reveal the hybridization of the intramolecular bond, the intramolecular bond length and the molecular orientation on the surface. Using these concepts we discuss examples of the determination of the bonding and structure of simple chemisorbed molecules (e.g. $\text{O}_2$ or $\text{C}_2\text{H}_2$) on various metal surfaces. With increasing size and complexity of the molecules, even for molecular chains and polymers, NEXAFS spectra are
found to be characteristic of the individual functional groups of the molecules. As examples we discuss complex alcohols and acids chemisorbed on Si(111) and Ag(110), Langmuir-Blodgett chains on Si(111), and thin polymer films such as polybutadiene, polystyrene or PMMA. As for simple molecules the polarization dependence of the resonances can be used for the determination of the orientation of the different functional groups on the surface.

R. Tromp, IBM Thomas J. Watson Research Center, Yorktown Heights, New York

Recent Developments in Scanning Tunneling Microscopy

Scanning Tunneling Microscopy (STM) has developed from a simple technique with which one measures surface corrugations into a multifaceted real space spectroscopic technique. Recently extensive studies have been performed on the real space surface electronic structure of solid surfaces, both clean and covered with various adsorbates. Inelastic tunneling spectroscopy has also been demonstrated. In my talk I will discuss these and other recent advances in scanning tunneling microscopy.

J.F. van der Veen, FOM-Instituut voor Atoom-en Molecuulfysica, Amsterdam, The Netherlands

Surface Melting

The possible role of the surface in initiating the melting of a solid has long been debated. Since the beginning of the twentieth century there have been numerous attempts to observe a surface melting effect. Many of the early experiments, however, produced ambiguous results, because they were performed under ill-defined conditions or lacked sufficient surface sensitivity.

In recent years there has been a surge of renewed interest in the phenomenon of surface melting. In part this is related to the availability of novel probes of surface structure, but it also reflects a general need to understand order-disorder transitions in systems of reduced dimensionality.

The most direct probe of surface melting is high-resolution Rutherford backscattering of protons in conjunction with the use of shadowing and blocking effects. This technique enables a quantitative determination of the degree of disorder at a surface on an atomic scale. Evidence for surface-initiated melting has also come from neutron scattering experiments and from precise measurements of the specific heat and the optical emissivity at temperatures in the vicinity of the bulk melting point $T_m$. Also on the theoretical side significant progress has been made. Furthermore, molecular dynamics simulations performed on various model systems have contributed substantially to our understanding of the thermodynamics of melting at a crystal boundary.
Our present state of knowledge can be summarized as follows: Surface melting is an intrinsic effect, present in pure substances. It involves a positional disordering of the lattice in the surface region just below $T_m$. At such, it is to be distinguished from 'surface roughening', which involves the formation of steps, ledges, kinks, etc., while the positional lattice order is left intact. As the temperature $T$ approaches $T_m$, the disordered layer thickness $d$ is predicted to diverge as $\ln(T_m - T)/T_m$ or as $(T_m - T)^{-1}$, depending on whether the acting forces are of short or long range. The disordered layer is not a true liquid but a quasi-liquid, i.e., it has some crystalline order which is induced by the underlying lattice.

Finally, Rutherford backscattering measurements have revealed a strong dependence of the disordering or the crystallographic orientation of the surface. For example, the loose-packed (110) face of a Pb crystal melts, whereas the close-packed (111) face does not.

The above results will be discussed in the light of recent theories of surface melting.

M.A. Van Hove, University of California, Berkeley, California

Solving Complex and Disordered Surface Structures with Electron Diffraction

The past of surface structure determination with low-energy electron diffraction (LEED) will be briefly reviewed, setting the stage for a discussion of recent and future developments. The aim of these developments is to solve complex and disordered surface structures. Some effective solutions to the experimental and theoretical problems will be presented. Since the theoretical problems dominate, the emphasis will be on theoretical approaches to the calculation of the multiple scattering of electrons through complex and disordered surfaces.

M. Wortis, University of Illinois, Urbana, Illinois

Equilibrium Crystal Shapes

I. Introduction
   Equilibration
   Recent experimental observations of equilibrium shapes
   The Wulff construction of the ECS (equilibrium crystal shape)

II. Review:
   Rough versus smooth interfaces
   Facetting and roughening
   Andreev's relation: the ECS as a free energy
   $T = 0$ crystal shapes
   Marginality/degeneracy of edges and corners at $T = 0$
III. Thermal Evolution of the ECS: Phase Transitions:
   Type A behavior ($^4\text{He}$, metals)
   Type B behavior (NaCl)
   Phase diagrams, global (nonuniversal) properties
   Universal Properties:
      \( y \sim x^{3/2} \) (Pokrovsky-Talapov)
      facetting (Kosterlitz-Thouless)
      curvature jump at \( T_R \)
      corner rounding

IV. Models and Calculations:
   Models: Mean-field theory (phase diagrams)
      SOS roughening models (\( T_R \))
      Restricted SOS models (phase diagrams, \( T_R \))
      Tilted SOS models (phase diagrams, facet shapes)

   Examples: $^4\text{He}$ and NaCl (comparison with experiment)
   Effect of adsorption on crystal shapes

V. Summary, Discussion, Conclusion:
Since the discussions are an essential part of ISISS, the Session Chairmen play an important role. At ISISS 1987, the following surface scientists served as Chairmen:

Professor Jose Fripiat  
Laboratory for Surface Studies  
University of Wisconsin-Milwaukee  
Milwaukee, Wisconsin

Dr. Albert Cassuto  
Laboratoire Maurice Letort  
CNRS - BP 104  
54600 Villers  
Nancy, France

Dr. Robert Gomer  
The James Franck Institute  
University of Chicago  
Chicago, Illinois

Professor Maurice B. Webb  
University of Wisconsin-Madison  
Dept. of Physics  
Madison, Wisconsin

Professor Carolyn Aita  
Laboratory for Surface Studies  
University of Wisconsin-Milwaukee  
Milwaukee, Wisconsin

Professor Kenneth Watters  
Laboratory for Surface Studies  
University of Wisconsin-Milwaukee  
Milwaukee, Wisconsin

Professor S. Y. Tong  
Laboratory for Surface Studies  
University of Wisconsin-Milwaukee  
Milwaukee, Wisconsin

Professor Max Lagally  
Materials Science Center  
University of Wisconsin-Madison  
Madison, Wisconsin

Professor Menachen Steinberg  
Dept. of Inorganic and Analytical Chemistry  
The Hebrew University of Jerusalem  
Jerusalem, Israel
One hundred and thirty-one scientists from all parts of the U.S.A., from Belgium, Canada, France, Germany, Israel, Japan, New Zealand, The Netherlands, and the People's Republic of China participated. They came from universities (82%), from industry (14%), as well as government institutions (4%). The educational value of the conference is demonstrated by the fact that again about 48% of the participants were Graduate Students and Post-Doctoral Fellows. Especially for that reason, the registration fee was kept as low as possible.

The following registration fees were requested:

Registration before 17 July 1981:
- $100.00 Regular
- $40.00 Graduate Students and Post-Doctoral Fellows

Registration after 17 July 1987:
- $120.00 Regular
- $50.00 Graduate Students and Post-Doctoral Fellows

Students in the UW-System paid a nominal fee.

Besides the scientific program, a number of social programs were arranged. They included dinner tours, a reception for speakers and participants from foreign countries, and a banquet. Many participants used the opportunity to visit the facilities of the Laboratory for Surface Studies at UWM. In connection with the Summer Institute, an exhibition of surface science books was organized.

International scientific societies and journals announced the conference. About 2700 scientists were contacted directly.

As in the case of former ISISS, the lecturers also wrote review papers which are published collectively in the form of a single volume book. Volume VII of "Chemistry and Physics of Solid Surfaces" is printed by Springer Verlag, Berlin-Heidelberg-New York-Tokyo.
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Dr. Ralf Vanselow
Director of ISISS
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