OFFICE OF NAVAL RESEARCH

FINAL REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

Grant #N00014-91-J-1630

R&T Code 413s002

“Surface Chemistry and Diffusion of Single Molecules”

This grant is jointly funded by the National Science Foundation as NSF #CHE-9020273

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Submitted: 28 December 1993

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PART I
Objectives, Approach, Scientific Conclusions

1. Objectives

We study the motion and dynamics of atoms and molecules on surfaces in order to assess the roles played by active surface sites such as steps, defects, and phase boundaries in this motion. Surface mobility is critical in such areas as surface chemistry, film growth, etching, corrosion, and the creation and stability of nanoscale structures. We seek atomic level information on the specific rates and mechanisms of this motion, and to determine the nature of the interactions which determine these.

2. Approach

Our understanding of surface motion is developed using a unique variable low temperature ultrahigh vacuum scanning tunneling microscope which can operate using a dc tunneling current when studying conducting and semiconducting substrates, and using a microwave frequency ac tunneling current when studying insulators. The tunable microwave frequency modulation allows chemical differentiation, investigations of the motion of surface charge, and local “electrochemical” measurements of the gas–solid and vacuum–solid interfaces. We also use an ultrastable low temperature ultrahigh vacuum scanning tunneling microscope. All instruments are equipped with a complement of surface analytical tools so as to enable comparison and relation to more conventional macroscopic measurements.

3. Scientific Conclusions

We have demonstrated the first direct measurement of nonzero accommodation lengths upon adsorption, in this case for Xe on Pt\{111\} at 4K. By showing that surface diffusion is slow on the time scale of our experiments (hopping rates < 1/hour), we have shown that the distribution of atoms on the surface is due to motion upon adsorption. Thus we have been able to show that Xe atoms travel hundreds of Ångstroms across the surface upon adsorption. See highlighted publication.

We have discovered a new surface diffusion mechanism in which diffusion occurs via motion of substrate–adsorbate complexes. We used the STM to record a series of “stop–action movies” of self-assembled monolayers of alkanethiols on Au\{111\}. The rate of motion was determined by the reduction in the substrate–substrate bond strengths balanced by the attractions between the adsorbate molecules. This mechanism leads to a means of controlling the rates of motion of the complex by tuning the attractive interactions between the complexes. See highlighted publication.

We have extended atomic resolution imaging and spectroscopy to insulator surfaces using a newly developed microwave frequency tunable alternating current scanning tunneling microscope. We have recorded the first atomic resolution images in this frequency range. We have also shown that we can differentiate between closely related molecules based on their microwave frequency AC tunneling spectra. See highlighted publication.
PART II
Publications, Presentations, Patents, Reports, and Personnel

1. Papers submitted to refereed journals, but not yet published


2. Papers published in refereed journals


3. **Books or chapters submitted, but not yet published**
   None.

4. **Books or chapters published**

5. **Printed technical reports and non-refereed papers published**
   None.

6. **Patents**
   None.

7. **Invited Presentations**


8. Contributed Presentations


9. Honors/Awards/Prizes

Michael J. Abrams, Undergraduate Coworker — CRC Freshman Award (top freshman in the Chemistry Department).

Michael J. Abrams, Undergraduate Coworker — Eberly College of Science Alumni Society Award (top freshman in the Eberly College of Science).

Joseph A. Meyer, Postdoctoral Associate — Alexander von Humboldt Foundation Fellowship.

Stephan J. Stranick, Graduate Research Assistant — Wheeler P. Davey Fellowship of the Penn State Eberly College of Science.

Stephan J. Stranick, Graduate Research Assistant — First Prize for the Physical Sciences, Eighth Annual Graduate Research Exhibition.

Stephan J. Stranick, Graduate Research Assistant — Kenan Analytical Award of the Union Carbide Corp.

Stephan J. Stranick, Graduate Research Assistant — Shell Foundation Graduate Fellowship.

Stephan J. Stranick, Graduate Research Assistant — Sigma Xi Graduate Research Award.

Stephan J. Stranick, Graduate Research Assistant — American Physical Society, Divisions of Chemical Physics Travel Award.

Paul S. Weiss, Assistant Professor — National Science Foundation Presidential Young Investigator Award, 1991–1996.


Paul S. Weiss, Assistant Professor — Chosen by NAS/NRC Board on Chemical Sciences and Technology as U.S. Observer at the IUPAC Meeting on Chemical Research Applied to World Needs, Lisbon, Portugal.

10. Post-doctoral Associates Funded Through the ONR/NSF Contracts

Joseph A. Meyer, Ph.D. in Physics, Brown University (currently a Humboldt Fellow at the University of Ulm)

Michael G. Youngquist, Ph.D. in Chemistry, Cal Tech.

11. Graduate Students Funded Through the ONR/NSF Contracts

James H. Ferris, III
Marilyn M. Kamna
Stephan J. Stranick

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12. Undergraduate Students Funded Through the ONR/NSF Contracts

Michael J. Abrams
Renée M. Itle
Abner Mintz (currently a graduate student in chemistry at Cal Tech)
PART III
Transitions

AT&T Bell Laboratories

AT&T Bell Laboratories has provided substantial research support ($75,000) and has followed with interest each of the projects in our laboratory. The PI has given a series of seminars there and is now beginning a collaboration with Dr. Eric Betzig and Dr. Steven Burratto (near-field optical microscopy).

Dow Corp.

The PI has visited the analytical group and others at Dow’s Midland, MI research facility. We have identified scientifically and technologically interesting samples to study with the ACSTM, but have not yet found a way to clear these for shipment to our laboratory.

Dupont Co.

We collaborate with two scientists, Dr. Don Coulman and Dr. Sau Lan Tang. These collaborations involve understanding imaging using STM, AFM, and ACSTM. A graduate student, Jim Ferris, spent the summer at Dupont Experimental Station in Wilmington, DE working with Don Coulman and supported by Dupont. Several samples of scientific and technological importance have been sent to us for examination. Don Coulman will be coming to our laboratory for an extended visit. He has previously visited two times; Sau Lan Tang has visited once. The PI has made two visits to Dupont and has presented seminars both times.

Eastman Kodak

Eastman Kodak has provided direct research support ($30,000) and has followed several of the projects in our laboratory. Their interests are in understanding STM imaging, in the ACSTM, in the dynamics we have observed, and also in self-assembled monolayers. They have provided key information on some of their technologies and suggested a number of interesting experiments.

Galileo Electro-Optics Corporation

Galileo is interested in our field emission and field ion microscopy work and has provided two detectors for this.

Hewlett-Packard

(directly and through a consortium of American Cyanamid, Amoco, Dow, Ecogen, Hewlett-Packard, International Minerals & Chemical, Agricultural Research & Development called Biotechnology Research and Development Corporation)

Support has been in microwave equipment and in grants ($450,000). This support has been instrumental in developing the tunable ACSTM. This grant support is expected to continue in another three year cycle. In addition, we have been given access to all HP Labs facilities, expertise, and personnel. We have had a two day visit from three experts from HP Labs in the area of microwave engineering, scanning probe microscopy, and analytical techniques. We have regular communication and reciprocal visits.

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IBM

Theory supporting our experimental STM images of adsorbates has been provided by Dr. Norton Lang of IBM Yorktown Heights in a continuing collaboration and by Peter Blöchl and his group at IBM Zürich. In addition the PI is part of a five-member team recently awarded a parallel processing IBM SP-1 for computational support of our molecular imaging.

Shell Development Co.

The PI visited Shell Development Co. Westhollow Research Center twice in order to keep them current in STM and ACSTM research. Casual contact with their analytical group, especially Dr. David Denley, is maintained.

Union Carbide

The PI and one student have both visited the West Virginia research facilities of Union Carbide. Contact with the analytical group and the catalysis research group is maintained. The main interests of Union Carbide are in understanding STM images, in the ACSTM, and in surface dynamics on the atomic scale.
PART IV
Administrative Information, Project Description and Highlights

1. Administrative Information
   a. Principal Investigator
      Paul S. Weiss
   b. Current Telephone Numbers and Electronic Mail Address
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   c. Cognizant ONR Scientific Officer
      John Pazik
      Cognizant NSF Program Directors
      Steven Bernasek and Henry Blount

2. Project Description
   We study the motion and dynamics of atoms and molecules on surfaces in order to assess the roles
   played by active surface sites such as steps, defects, and phase boundaries in this motion. Surface
   mobility is critical in such areas as surface chemistry, film growth, etching, corrosion, and the
   creation and stability of nanoscale structures. Our understanding of surface motion is developed
   using a unique variable low temperature ultrahigh vacuum scanning tunneling microscope which
   can operate using a dc tunneling current when studying conducting and semiconducting substrates,
   and using a microwave frequency ac tunneling current when studying insulators. The tunable
   microwave frequency modulation allows chemical differentiation, investigations of the motion of
   surface charge, and local “electrochemical” measurements of the gas–solid and vacuum–solid
   interfaces.

3. Highlighted Publications
   S. J. Stranick, A. N. Parikh, D. L. Allara and P. S. Weiss, A New Mechanism for Surface Diffusion:
   Motion of a Substrate–Adsorbate Complex, submitted to Physical Review Letters.
   We have discovered a new surface diffusion mechanism in which diffusion occurs via motion of
   substrate–adsorbate complexes. We recorded stop–action movies of self–assembled monolayers on
   Au{111}. We monitored the motion of the underlying Au substrate through the monolayer films and
   showed that the Au motion was dramatically reduced by the attachment of the thiols and that the
   observed rates were consistent with the motion of the complex. In a related publication (Stranick et
   al., submitted to Journal of the American Chemical Society), we showed that mixed composition
   self–assembled monolayers phase segregate on the nanometer scale. These observations are
   extremely important in the application of self–assembled monolayers to nanotechnology.

We have measured the (unambiguous) first non-zero accommodation lengths — the distance that surface adsorbates travel after trapping on a surface but before accommodating to the surface temperature (a related publication on this subject by Abrams and Weiss is in revision for *Surface Science*). We showed that even for rare gas atoms, step and defect sites are the most reactive on the surface.


We showed the apparent chemical sensitivity of our tunable microwave frequency alternating current scanning tunneling microscope. This was done by imaging and recording AC tunneling spectra on self-assembled monolayers of alkanethiols where the terminal groups of the thiols was varied.