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11. Studies on Ions and Neutrals Desorbed from Solid Surfaces by Ion and Electron Bombardment

19. This project was aimed toward increasing our fundamental knowledge of the details of the interaction of energetic particles with solid surfaces. These studies included the measurement of the angular and energy contributions of the yield of desorbed ions by secondary ion mass spectrometry (SIMS). In addition, we developed a novel angle and energy resolved detector capable of measuring for the first time the yield of neutral particles desorbed from monolayers. This detector utilized multi-photon resonance ionization of the ejected atoms which occur at efficiencies approaching 100%. The results of the experimental measurements were coupled to classical dynamics calculations of the ion impact event.

This approach has been pursued to utilize ion beams to examine the structure of surface layers through anisotropies observed in the angular distributions. A variety of materials including alloys, semi-conductors and organic monolayers on metals were candidates as model system. The experiments have opened new avenues for using ion beam methods for the trace analysis of important electronic materials at unprecedented sensitivity limits.

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COMPLETED PROJECT SUMMARY

TITLE: Studies of Ions and Neutrals Desorbed From Solid Surfaces by Ion and Electron Bombardment

PRINCIPAL INVESTIGATOR: Professor Nicholas Winograd
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INCLUSIVE DATES: November 1, 1984 to October 31, 1988

CONTRACT/GRANT NUMBER: AFOSR-85-0028

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William Kay
Robert Levis
Geoffrey Malafsky
Dave Pappas
Brad Weaver

Cumulative List of Publications Since 1984 Acknowledging AFOSR Support

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37. C. C. Chang, N. Winograd and B. J. Garrison, "Model Studies of Particle/Solid Interactions", *Surface Sci.*, **202**, 309 (1988).

FINAL SCIENTIFIC REPORT

for

Period Ending 31 October 1988

*Studies of Ions and Neutrals Desorbed From Solid Surfaces
by Ion and Electron Bombardment*

Grant No. AFOSR-85-0028

Principal Investigator

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ABSTRACT

This project is aimed toward increasing our fundamental knowledge of the details of the interaction of energetic particles with solid surfaces. These studies will include the measurement of the angular and energy contributions of the yield of desorbed ions by secondary ion mass spectrometry (SIMS). In addition, we have developed a novel angle and energy resolved detector capable of measuring for the first time the yield of neutral particles desorbed from monolayers. This detector utilizes multi-photon resonance ionization of the ejected atoms which occurs at efficiencies approaching 100%. The results of the experimental measurements will be coupled to classical dynamics calculations of the ion impact event.

This approach is being pursued to utilize ion beams to examine the structure of surface layers through anisotropies observed in the angular distributions. A variety of materials including alloys, semi-conductors and organic monolayers on metals are candidates as model system. The experiments should also open new avenues for using ion beam methods for the trace analysis of important electronic materials at unprecedented sensitivity limits.

I. SUMMARY OF PROGRESS

Our efforts have been aimed toward experimental and theoretical investigations into the fundamental aspects of the interaction of energetic particles with solids. There have been 5 major phases to our work.

- (1) **Model Studies of Particle/Solid Interactions** by C. C. Chang, N. Winograd and B. J. Garrison published in *Surface Science*, **202**, 309 (1988).

In this study, molecular dynamics calculations of 100 eV to 6 keV incident particles scattering from single crystal surfaces are performed using three particle interaction models. We find that for some incident conditions, a more extended interaction model is needed to produce accurate trajectory simulations than the binary collision model. This extended model takes into account the simultaneous interactions among the primary particle and all the other atoms in the system but not the ones among the substrate atoms. A fair agreement between the calculated results of this extended interaction model and that of the full dynamics model is observed for nearly the entire energy regime studied. The range of primary energies where the binary collision model is adequate is discussed.

- (2) **Energy and Angular Distributions of Rh Atoms Ejected Due to Ion Bombardment From Rh{111}: A Theoretical Study** by B. J. Garrison, C. T. Reimann, N. Winograd, and D. E. Harrison, Jr. published in *Phys. Rev. B* **15**, **36**, 3516 (1987).

Energy and angular distributions of Rh atoms ejected from a Rh{111} surface due to keV ion bombardment are predicted from classical dynamics calculations and are compared to those measured using a multiphoton resonance ionization scheme. The comparison is generally quite favorable. For example, the calculated distributions reproduce the changes in azimuthal anisotropy which occur over an ejected-particle kinetic energy range of 5-50 eV. The new detailed experimental data do, however,

expose deficiencies in the pair potential, which we believe can be overcome with a many-body potential.

- (3) **Many-Body Embedded-Atom Potential for Describing the Energy and Angular Distributions of Rh Atoms Desorbed From Ion-Bombarded Rh{111}** by B. J. Garrison, N. Winograd, D. M. Deaven, C. T. Reimann, D. Y. Lo, T. A. Tombrello, D. E. Harrison, Jr. and M. H. Shapiro published in *Phys. Rev. B*, **37**, 3664 (1988).

We have shown for the first time that many-body interactions are important for describing the energy- and angle-resolved distributions of neutral Rh atoms ejected from keV-ion-bombarded Rh{111}. We compare separate classical-dynamics simulations of the sputtering process assuming either a many-body potential or a pairwise additive potential. The most dramatic difference between the many-body potential and the pair-potential is in the predicted kinetic energy distributions. The pair-potential kinetic energy distribution peaks at ~ 2 eV, whereas the many-body-potential predicts a broader peak at ~ 4 eV, giving much better agreement with experiment. A specific set of parameters has been found which leads to excellent agreement with recent experimental trajectory measurements of desorbed Rh atoms.

- (4) **Shadow-Cone Enhanced Desorption with Angle-Resolved Secondary Ion Mass Spectrometry Detection** by C. C. Chang, G. P. Malafsky, and N. Winograd published in *J. Vac. Sci. Tech. A*, **5**, 981 (1987).

The shadow-cone created by an incident keV bombarding ion is observed to enhance the yield of secondary ions sputtered from the target. This effect may be utilized to determine the bonding configuration of surface atoms in a manner similar to that reported for impact-collision ion scattering spectrometry (ICISS). This new method is utilized to study the bonding of Cl to Ag{110} as the coverage is increased from near

zero to the $p(2 \times 1)$ low-energy electron diffraction structure. The results show that the Ag-Cl bond length is extended by 0.4 Å in the isolated atom limit when compared to the $p(2 \times 1)$ coverage due to a large amount of charge transfer between the Ag substrate and the adsorbed Cl atom. This bond length becomes shorter as the coverage increases due to dipole-dipole repulsions.

- (5) **Detection of Neutral Atoms Sputtered from Ion-Bombarded Single-Crystal Surfaces Rh{111} and P(2x2) O/Rh{111}: Ejection Mechanism and Surface Structure Determinations from Energy- and Angle-Resolved Measurements** by J. Singh, C. T. Reimann, J. P. Baxter, G. A. Schick, P. H. Kobrin, B. J. Garrison, and N. Winograd published in *J. Vac. Sci. Tech. A*, **5**, 1191 (1987).

A temporally sensitive ionization scheme is used in conjunction with a position-sensitive detector to measure simultaneously energy- and angle-resolved distributions of sputtered neutral atoms. We report results for 5-keV Ar⁺ ion-bombarded Rh{111} single-crystal surfaces, both clean and with a $p(2 \times 2)$ overlayer of oxygen atoms. The angular distributions and their variation with ejection kinetic energy are shown to give information about simple collision sequences that produce directionally preferential atom ejection. The changes that occur in the ejection distributions upon O atom adsorption suggest that O atoms occupy the "expected" sites, the sites that would be occupied by Rh atoms in a new monolayer.

II. Cumulative List of Publications Since 1984 Acknowledging AFOSR Support

1. N. Winograd, "Thin Film Electrodes", in *Laboratory Techniques in Electroanalytical Chemistry*, P. T. Kissinger, Ed., Marcell-Dekker, New York, 1984, page 321.
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37. C. C. Chang, N. Winograd and B. J. Garrison, "Model Studies of Particle/Solid Interactions", *Surface Sci*, **202**, 309 (1988).

III. Recent Invited Talks by Nicholas Winograd

133. Sixth International Summer Institute in Surface Science, Milwaukee, WI, "Angle-Resolved SIMS", August 22-26, 1983.
134. Fourth International Conference on Ion Mass Spectrometry, Minoo, Osaka, Japan, "Detection of Sputtered Neutrals by Multiphoton Resonance Ionization", November 13-19, 1983.
135. Symposium on Atomic and Surface Physics, Hintermoos, Austria, "Ion Beam Studies of Surfaces by Multiphoton Resonance Ionization of Sputtered Neutrals", January 29-February 4, 1984.
136. Electronics Institute, Prague, Czechoslovakia, "Ion Beam Studies of Surfaces by Multiphoton Resonance Ionization of Sputtered Neutrals", February 6, 1984.
137. Brookhaven National Laboratory, Long Island, NY, "Ion Beams, Lasers and X-rays! Some Aspects of the Current Renaissance in Surface Science", February 14, 1984.
138. Chemistry Departmental Colloquium, Seton Hall University, Orange, NJ, "Ion Beams, Lasers and X-rays! Some Aspects of the Current Renaissance in Surface Science", February 28, 1984.
139. Chemistry Departmental Colloquium, University of California, Berkeley, CA, "Ion Beams, Lasers and X-rays! Some Aspects of the Current Renaissance in Surface Science", April 3, 1984.
140. Second International Symposium on Resonance Ionization Spectroscopy and Its Applications, Knoxville, TN, "Ion Beam Studies of Surfaces by Multiphoton Resonance Ionization of Sputtered Neutrals", April 16, 1984.
141. Gordon Research Conference on Particle-Solid Interactions, Plymouth, NH, "Emitted Particles and Lasers Excitation", July 13, 1984.
142. National ACS Meeting, Symposium on Photochemical and Electrochemical Surface Science: Techniques for the Characterization of Electrode Surfaces, Philadelphia, PA, "Ion Beam Studies of Metal Surfaces", August 26, 1984.
143. National ACS Meeting, Symposium on Techniques for the Characterization of Electrode Surfaces, Philadelphia, PA, "Ion Beam Studies of Metal Surfaces", August 28, 1984.
144. Amoco Research Center, Naperville, IL, "Ion Beam Studies of Solids and Surfaces", September 25, 1984.
145. Chemistry Departmental Colloquium, University of Cincinnati, Cincinnati, OH, "Ion Beam Spectroscopy of Solids and Surfaces", September 26, 1984.
146. Symposium on SIMS and FAB Mass Spectrometry: An Interdisciplinary Discussion, St. Paul, MN, "Angle-Resolved SIMS", October 8, 1984.

Invited Talks continued

147. Optical Society of America, San Diego, CA, "Detection of Sputtered Neutrals by Multiphoton Resonance Ionization", California, October 29, 1984.
148. Greater New York Chapter of the American Vacuum Society, Symposium of Surface Modification by Directed Deposition of Energy, Yorktown Heights, NY, "Multiphoton Ionization of Sputtered Atoms", IBM Laboratories, November 9, 1984.
149. Chemistry Departmental Colloquium, Ohio University, Athens, OH, "Renaissance of Surface Science", November 9, 1984.
150. 31st National Vacuum Symposium of the American Vacuum Society, Reno, NV, "Angle-Resolved Studies of Neutrals Desorbed from Single Crystals by Ion Bombardment", December 12, 1984.
151. National Bureau of Standards, Gaithersburg, MD, "Surface and Solids Characterization by MPRI of Sputtered Atoms", February 11, 1985.
152. Physics Departmental Colloquium, Cornell University, Ithaca, NY, "Ion Beam Studies of Solids and Surfaces", February 20, 1985.
153. SRI International, Menlo Park, CA, "Ion Beam Studies of Solids and Surfaces", February 26, 1985.
154. IBM Corporation, San Jose, CA, "Ion Beam Studies of Solids and Surfaces", February 28, 1985.
155. 3rd Annual Texas A&M Chemistry Department Industry-University Cooperative Chemistry Program Symposium, College Station, TX, "Ion Beam Techniques", April 1, 1985.
156. Symposium on High Resolution Scanning Ion Microscopy (SIM) and Secondary Ion Mass Spectrometry (SIMS) at Scanning Electron Microscopy/1985, Las Vegas, NV, "Fundamental Aspects of Energetic Particle/Solid Interactions", April 4, 1985.
157. Texas Instruments' Foundation, Dallas, TX, "Ion Beam Studies of Solids and Surfaces", May 17, 1985
158. American Society for Mass Spectrometry Symposium on Inelastic Ion-Surface Interactions, San Diego, CA, "Multiphoton Ionization of Sputtered Particles", May 30-31, 1985.
159. American Society for Mass Spectrometry Symposium on Inelastic Ion-Surface Interactions, San Diego, CA, "Solid Analysis Using Energetic Bombardment and Multiphoton Resonance Ionization with Time-of-Flight Detection", May 30-31, 1985.

Invited Talks continued

160. 5th International Conference on Surface and Colloid Science and 59th Colloid and Surface Science Symposium, Potsdam, NY, "Ion Beam Studies of Solids and Surfaces", June 24-28, 1985.
161. Owens-Corning Fiberglass Corporation, Granville, OH, "Surface Analysis with Ion Beams", September 9, 1985.
162. University of Pittsburgh, Pittsburgh, PA, "Multiphoton Resonance Ionization of Atoms and Molecules Desorbed from Surfaces", September 19, 1985.
163. Fifth International Conference on Secondary Ion Mass Spectrometry, Washington, D.C., "Multiphoton Resonance Ionization of Emitted Particles", September 29 - October 4, 1985.
164. Air Force Surface Science Research Conference, Dayton, OH, "Studies of Ions and Neutrals Desorbed from Solid Surfaces by Ion and Electron Bombardment", November 6, 1985.
165. American Vacuum Society, Houston, TX, "Angular Distributions of Sputtered Particles", November 20, 1985.
166. First International Laser Science Conference, Dallas, TX, "Multiphoton Resonance Ionization of Atoms Desorbed from Surfaces by Energetic Particle Bombardment", November 21, 1985.
167. Chemical Physics Seminar, California Institute of Technology, Pasadena, CA, "Ion Beam Spectroscopy of Solids and Surfaces", November 26, 1985.
168. Chemistry Department Colloquium, Texas A&M University, College Station, TX, "Ion Beam Spectroscopy of Solids and Surfaces", December 10, 1985.
169. Physical Chemistry Colloquium, University of California at Irvine, Irvine, CA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", February 4, 1986.
170. Physical Science Colloquium, Naval Weapons Center, China Lake, CA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", February 13, 1986.
171. Physical Chemistry Colloquium, University of California at Los Angeles, Los Angeles, CA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", March 3, 1986.
172. Chemistry Colloquium, University of Georgia, Athens, GA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", March 19, 1986.

Invited Talks continued

173. Chemistry Colloquium, Georgia Institute of Technology, Atlanta, GA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", March 20, 1986.
174. Chemistry Colloquium, University of Florida, Gainesville, FL, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", March 21, 1986.
175. Chemistry Colloquium, Emory University, Atlanta, GA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", March 24, 1986.
176. Physics Colloquium, California Institute of Technology, Pasadena, CA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", May 1, 1986.
177. Chemistry Colloquium, California State University, Fullerton, CA., "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", May 2, 1986.
178. Chemistry Colloquium, University of California, Riverside, CA "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", May 7, 1986.
179. Chemistry Colloquium, Harvard University, Boston, MA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", May 21, 1986.
180. Sohio, Cleveland, OH, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", June 19, 1986.
181. Gordon Conference on Analytical Chemistry New Hampton, NH, "New Approaches to the Studies of Solids and Surfaces Using Particle Beams", August 11, 1986.
182. Gordon Conference on Electronic Materials, Concord, NH, "Secondary Neutral Mass Spectrometry", August 21, 1986.
183. Third International Symposium on Resonance Ionization Spectroscopy and Its Applications, Swansea, UK, "Surface Studies Using Particle Beam Induced Desorption and Multiphoton Resonance Ionization", September 7-12, 1986.
184. American Vacuum Society, Malibu CA, "Secondary Ion Mass Spectrometry", September 25, 1986.
185. Akron ACS Award Symposium, Akron, Ohio, "Ion Beam Studies of Solids and Surfaces", October 16, 1986.
186. University of Akron, Akron, Ohio, "Ion Beam Studies of Solids and Surfaces", October 17, 1986.

Invited Talks continued

187. University of Wisconsin, Madison, WI, "Multiphoton Resonance Ionization of Particles Desorbed from Surfaces by Ion Bombardment", October 21, 1986.
188. Eastern Analytical Symposium New York City, NY, "Ion Beam, Lasers and X-Rays! Some Aspects of the Current Renaissance in Surface Science", October 23, 1986.
189. 10TH International Vacuum Congress, Baltimore, MD, "Energy and Angle Resolved Studies of Sputtered Particles", October 24, 1986.
190. Vanderbilt University, Nashville, TN, "Energy and Angle Resolved Studies of Sputtered Particles", November 7, 1986.
191. University of Virginia, Charlottesville, VA, "Ion Beam Studies of Solids and Surfaces", November 21, 1986.
192. Rensselaer Polytechnic Institute, Troy, NY, "Novel Approaches to the Study of Surface Reactions", December 4, 1986.
193. Indiana University, Bloomington, IN, "Ion Beam Studies of Solids and Surfaces", December 10, 1986.
194. American Physical Society New York City, NY, "Ion Beam/Surface Interaction", March 18, 1987.
195. University of Houston, Houston, TX, "Surface Studies Using Ion Beams Induced Desorption and Multiphoton Resonance Ionization", March 30, 1987.
196. University of Texas, Austin, TX, "Surface Studies Using Ion Beams Induced Desorption and Multiphoton Resonance Ionization". April 2, 1987.
197. Case Western Reserve University, Cleveland, OH, "Surface Chemistry Studies with Ion Beams and Lasers", April 25, 1987.
198. CLEO/IQEC '87, Baltimore MD, "Surface Studies Using Particle Beam Induced Desorption and Multiphoton Resonance Ionization", April 29, 1987.
199. Rochester Section ACS, Rochester, NY, "Surface Analysis and Laser Ionization of Sputtered Neutrals", May 13, 1987.
200. III Workshop on Biomolecular and Environmental Mass Spectrometry, Laghi di Sibari, ITALY, "Energy and Angle Resolved SIMS", July 20, 1987.
201. AFOSR Contractors Conference, U.S. Air Force Academy, Colorado Springs, CO, "Surface Characterization and Modification using Energetic Particle Beams.", September 18, 1987.
202. Chemistry Department Colloquium, Iowa State University, Ames, IO, "Surface Studies with Ion Beams and Lasers", October 22, 1987.

Invited Talks continued

203. Analytical Chemistry Seminar, Iowa State University, Ames, IO, "Is It Possible to Count Single Adoms on Surfaces?", October 23, 1987.
204. Lilly Research Laboratories Seminar, Indianapolis, IN, "Ion Beam Studies of Biomolecules", November 16, 1987.
205. Analytical Science Symposium, Hercules Incorporated Research Center, Wilmington, DE, "Surface Studies Using Ion Beams and Lasers", January 22, 1988.
206. Lawrence Berkeley Laboratory Seminar, Berkeley, CA, "Surface Studies Using Ion Beams and Lasers", March 16, 1988.
207. Allied-Signal, Inc., Corporate Technology, Morristown, NJ, "Surface Studies Using Particle Beam Induced Desorption and Multiphoton Resonance Ionization", March 24, 1988.
208. Fourth International Symposium on Resonance Ionization Spectroscopy and its Applications, Gaithersburg, MD, "Surface Studies using Ion Beams and MPRI", April 12, 1988.
209. Texas Instruments Technology Day, Dallas, TX, "Texas Instrument Founders Prize Update", May 11, 1988.
210. ACS Summer Symposium on Lasers in Analytical Chemistry Stanford, CA, "Surface Studies Using Ion Beams and MPRI", June 26-29, 1988.
211. 7th International Workshop on Inelastic Ion Surface Collisions, Kraków, Poland, "Energy and Angular Distributions of Desorbed Atoms and Molecules", September 19-23, 1988.
212. Chemistry Department Colloquium, University of Tennessee, Knoxville, TN, "Surface Studies Using Ion Beams and Lasers", November 3, 1988.
213. Chemistry Department Colloquium, Oak Ridge National Laboratory, Oak Ridge, TN, "Surface Studies Using Ion Beams and Lasers", November 4, 1988.
214. Analytical and Physical Chemistry Seminar Series, University of Delaware, Newark, DE, "Surface Studies Using Ion Beams and Lasers", November 14, 1988.
215. Electrochemistry Gordon Conference, Ventura, CA., "Interaction of Energetic Particles with Solid Surfaces", January 15-20, 1989.

V. Awards and Prizes - Nicholas Winograd

1. Texas Instruments Foundation 1984 Founders Prize

This prize consisting of a cash award of \$50,000 (tax free) recognizes Winograd's work in fundamental studies of the bombardment of solids with energetic particles. The award is presented each year to a single individual to recognize achievement in the fields of physical science, health science, management science, engineering or mathematics. According to the Foundation, the award is made "for past achievement that would indicate even greater potential for accomplishment in the future".

2. Penn State Faculty Scholar Medal

This Medal is awarded for outstanding achievement in recognition of a single contribution or series of related contributions to a Professor in the Physical Sciences or Engineering. The recipient's contribution must have occurred within the last three years of the nomination.

3. Evan Pugh Professorship

In 1985 Winograd was named an Evan Pugh Professor, the highest honor that Penn State bestows on a faculty member. Evan Pugh Professorships are awarded to faculty members whose "research publications or creative work or both have been of the highest quality over a period of time". The award has been given to 33 faculty members during the history of Penn State. There are currently 17 Evan Pugh Professors in residence.