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19. ABSTRACT (Continue on reverse if necessary and identify by block number) We have developed improved substrates and electrochemical methods for deposition of nucleic acids onto substrates for imaging by STM and AFM.  We have also investigated electron transport in nucleic acid polymers using (I vs. V) spectroscopic methods. Our experiments indicate that resonant tunneling probably plays a role in STM images.			
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**ANNUAL PROGRESS REPORT****GRANT No. N00014-90-J-1455****RT CODE xxx001****PRINCIPAL INVESTIGATOR: S.M. LINDSAY****INSTITUTE: ARIZONA STATE UNIVERSITY****GRANT TITLE: BIOLOGICAL APPLICATIONS OF STM AND AFM IN WATER****PERIOD OF PERFORMANCE: January 1, 1990 – June 1, 1990****OBJECTIVE:**

To develop a reliable procedure for imaging biopolymers at an electrochemically controlled interface, and to apply STM and AFM imaging to structural problems in molecular biology.

**ACCOMPLISHMENTS (last 6 months)**

We have continued to improve the reliability of electrochemical methods for depositing biopolymers onto a substrate for imaging in a scanning probe microscope. In particular:

- We have determined optimum conditions for preparation of atomically flat and clean gold substrates.
- We have investigated graphite substrates under potentiostatic control, finding them inferior to gold because of their anisotropic reactivity (steps vs. the basal plane). We have also investigated chemical attachment of DNA to graphite (in collaboration with Yuri Lyubchenko of the Institute of Molecular Genetics, USSR). This project has yielded good results at low resolution (the resolution is limited by the structure of the molecules used for covalent binding of the DNA to graphite).

- We have investigated the effects of salt co-adsorption, concluding that much of the loss of resolution in our early images is a consequence of salt co-deposition.
- We are investigating galvanostatic deposition of low-salt preparations.
- We have carried out initial spectroscopic measurements (I vs. V) over DNA adsorbates, concluding that the current is carried by electrons (tunneling) and that servo-controlled tip pressure effects are important.

## SIGNIFICANCE

Development of probes of the properties of individual molecules is limited by the unreliability of present deposition procedures. All microscopies require an element of 'magic' for biopolymers to be placed onto a surface at an appropriate density while excluding dirt. In practice, uneven depositions are searched for 'good' images. Electrochemical deposition and control can, in principle, remove this element of uncertainty. This would then make STM or AFM a routine tool for analysis. The point is that, once the imaging is routine and not subject to the skills or preferences of the microscope operator, the technique will be useful as a phenomenological tool (like gels).

One important use of reproducible monolayers of biomolecular adsorbate will be studies of the electronic characteristics of individual molecules.

## WORK PLAN (next 12 months)

We will continue to refine deposition methods, and plan to study a number of interesting biomolecular complexes, once we are confident of our electrochemical methods. A high priority is to further quantify the relationship between sequence and nm-scale kinking and bending in nucleic acid fragments.



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We will continue spectroscopic measurements aimed at elucidating the mechanism of electron transport in biopolymers.

We are installing an AFM which we will modify to carry out simultaneous STM and AFM studies of adsorbed molecules.

## **INVENTIONS**

ASU has filed a patent application for a method of sequencing DNA which relies on contrast in an STM image. An application for a patent on improved electrochemical deposition of molecular adsorbates for scanning probe microscopy is being prepared.

## **RELEVANT PUBLICATIONS Last 6 months**

### **Refereed Papers**

"Direct Observation of Bioelectrochemical Processes by Scanning Tunneling Microscopy" T. Thundat, L.A. Nagahara, P. Oden and S.M. Lindsay, *J. Vac. Sci. Technol. A* 8 645-647 (1990).

"Scanning Tunneling Microscopy studies of semiconductor electrochemistry" T. Thundat, L.A. Nagahara and S.M. Lindsay, *J. Vac. Sci. Technol. A* 8 539-543 (1990).

"Pressure and Resonance Effects in Scanning Tunneling Microscopy of Molecular Adsorbates" S.M. Lindsay, O.F. Sankey, Y. Li and C. Herbst, *J. Phys. Chem.*, 94, 4655 - 4660 (1990).

"Electrical, spectroscopic and Morphological investigations of chromium diffusion through thin gold films" Q. Bo, M.A. George, I. Sorenson, W.S. Glaunsinger, T. Thundat and S.M. Lindsay, *Thin Solid Films*, in press (1990).

"STM Tip field induced surface modification of Ta surfaces in aqueous solutions" T. Thundat, L.A. Nagahara, S.M. Lindsay, M.A. George and W.S. Glausinger, *J. Vac. Sci. Technol.*, in press (1990).

"Thermally induced changes in electrical and topographical properties of thin gold films" Q. Bo, M.A. George, I. Sorenson, W.S. Glausinger, T. Thundat and S.M. Lindsay, *J. Vac. Sci. Technol.*, in press (1990).

"Electrochemical Deposition of Molecular Adsorbates for In Situ Scanning Probe Microscopy" L.A. Nagahara, T. Thundat, P.I. Oden, S.M. Lindsay and R.L. Rill, *Ultra-microscopy*, in press (1990).

"Nanolithography on Semiconductor Surfaces under an Etching Solution" L.A. Nagahara, T. Thundat and S.M. Lindsay, *J. Appl. Phys.* In Press (1990).

"How does the Scanning Tunneling Microscope Image Biopolymers?" S.M. Lindsay, O.F. Sankey and K.E. Schmidt, submitted to *Comments in Molecular and Cellular Biology* (1990).

"Can the Scanning Tunneling Microscope Sequence DNA?" S.M. Lindsay and M. Philipp, submitted to *Genetic Analysis* (1990).

### **Abstracts**

"Contrast and Chemical Sensitivity in STM Images of DNA" S.M. Lindsay, O.F. Sankey, Y. Li, C. Herbst and M. Philipp, *Biophys. J.* **57** 383a (1990).

"A Scanning Tunneling Microscope for Biophysical Research" L.D. McCormick, D. McCormick, U. Knipping and S.M. Lindsay, *Biophys. J.*, **57** 383a (1990).

"Electrochemistry as Molecular Tweezers for Scanning Probe Microscopy" L.A. Nagahara, T. Thundat, P. Oden and S.M. Lindsay, Bull. Am. Phys. Soc. **35** 649 (1990).

"Imaging the Unimagable I: A Tight Binding Theory of a Molecule in a Tunnel Gap" O.F. Sankey and S.M. Lindsay, Bull. Am. Phys. Soc., **35** 484 (1990).

"Imaging the Unimagable II: Location of Molecular Orbitals and the Effects of Pressure in a Tunnel Gap" S.M. Lindsay, Y. Li and C. Herbst, Bull. Am. Phys. Soc., **35** 484 (1990).

"Imaging the Unimagable III: Some Examples" T. Thundat, P. Oden, L.A. Nagahara, R. Hirsch, I. Zweibel and S.M. Lindsay, Bull. Am. Phys. Soc., **35** 484 (1990).

"Tip Induced Surface Modifications of Photo Corroded GaAs in Solution by STM" J.A. DeRose, T. Thundat, L.A. Nagahara and S.M. Lindsay, Bull. Am. Phys Soc., **35** 269 (1990).

## OBJECTIVES

- Achieve complete control of electrochemical deposition of nucleic acid fragments for scanning probe microscopy.
- Understand contrast mechanism of the STM.

## ACCOMPLISHMENTS

- Improvements in reliability of deposition by galvanostatic method.
- Theory for contrast and some experimental support.

## SIGNIFICANCE

- Can make STM/AFM a routine phenomeological tool for molecular biology.
- Probe the electronic properties of individual biomolecules for the first time.

S.M. Lindsay, Arizona State University

ANNUAL REPORT QUESTIONNAIRE

Principal Investigator: S.M. Lindsay

Institute: Arizona State University

Grant title: Biological Applications of STM and AFM in Water.

Period of performance: 1-1-90 to 6-1-90

Number of publications last year: 17

Number of patents/inventions: 2

Total number of students/trainees: 2

How many are female? 0

How many are minority students (e.g. Black, Hispanic)? 0

How many are not US citizens? 1

Awards/Honors to PI and/or to members of PI's research group (please describe):

Members of the group were invited to present a total of 11 talks on this work so far this year.

Equipment purchased (# and description of items >\$1500):

Atomic Force Microscope.

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This address can be reached via Arpanet or Bitnet. We read our mail daily.