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13. ABSTRACT (Maximum 200 words) This final technical report for AFOSR Grant No. F49620-94-1-0113, entitled Laterally Defined Nanoscale Structures: Film Growth, Chemistry, and Transport, summarizes the work performed on this grant. The research aims were to investigate film growth, chemistry, and electronic and atomic transport on laterally defined nanostructures. The objective of this research was to develop methodologies for creating nanoscale patterns in surfaces using scanned-probe techniques, either through assembly of molecules on surfaces or by the removal of atoms or molecules from an existing structure. because of initial success in our laboratories in increasing the speed of operation of scanned probes, the emphasis changed in the last 1½ years to explorations of the viability of high-speed parallel nanolithography for creating patterns.			
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**Laterally Defined Nanoscale Structures: Film Growth,
Chemistry, and Transport**

**AFOSR Grant No. F49620-94-1-0113
Final Technical Report
30 Sep 97**

**Max G. Lagally
University of Wisconsin-Madison
Dept. of Materials Science and Engineering
Madison, WI 53706
Lagally@engr.wisc.edu**

Introduction and Objectives

This final technical report for AFOSR Grant No. F49620-94-1-0113, entitled **Laterally Defined Nanoscale Structures: Film Growth, Chemistry, and Transport**, summarizes the work performed on this grant. The research aims were to investigate film growth, chemistry, and electronic and atomic transport on laterally defined nanostructures. The objective of this research was to develop methodologies for creating nanoscale patterns in surfaces using scanned-probe techniques, either through assembly of molecules on surfaces or by the removal of atoms or molecules from an existing structure. Because of initial success in our laboratories in increasing the speed of operation of scanned probes, the emphasis changed in the last 1 1/2 years to explorations of the viability of high-speed parallel nanolithography for creating patterns.

Technological driving forces for such studies are numerous. The importance for semiconductor devices of the combination of thin-film growth with the fabrication of laterally defined structures has been obvious for many years. An understanding of mechanism of growth has always been of tremendous importance in the progress of this technology. As lateral dimensions become smaller, their influence on transport and growth mechanisms, as well as electronic and chemical properties, becomes more and more significant. For nanometer and subnanometer lateral dimensions, essentially nothing is known about these properties. The same argument can be made for understanding many other technological processes; for example, our understanding of tribology and lubrication, corrosion, and catalysis, which all depend on local chemical properties, can gain immensely from fundamental studies of chemical processes on surfaces at the nanoscale.

There are both scientific and technological rationales for such studies. In the limit, all chemical processes take place between individual entities: molecules and atoms. If we are to understand what controls reaction rates and reaction paths, what the energetic states of clusters are, and how atoms and molecules self-organize to form crystalline films or other geometries, we must explore their properties at the ultimate size scale. As self-organization usually takes place on some sort of substrate or template, we need to investigate properties of molecules on surfaces. Finally, one wishes to affect reaction rates and other kinetic processes. Scanned probes offer the opportunity to do so in a very controlled manner, both through mechanical action and through electric fields, and possibly even through optical and magnetic means.

Because of budgetary cutbacks and changes in program emphasis, AFOSR chose not to provide the final increment of funding under this grant, but agreed to a no-cost extension until September 30, 1997. This time was used to complete aspects of the work described below.

Accomplishments/New Findings

STM-based fabrication of nanoscale structures in Si (001). We used STM to remove in a controlled fashion individual dimers on clean Si (001) surfaces to make regular structures, like islands and bridges, that are as little as one monolayer deep and 2 to 20 nm long or wide. We have developed the methodology for approaching the sample with the tip and applying the correct size voltage pulse to remove selectively just one dimer. We can therefore make any rectangular shape of island or bridge between two larger regions. We are routinely able to make regular structures successfully. This work was published in *Science* 265, 502 (1994). We have extended it to make patterns that consist of a narrow stripe connected to a large pad (the shape that is left behind when atoms in the shape of the letter U are removed). Efforts to make single-atom high "wires" of Si on Si and to use scanning tunneling spectroscopy to measure the "current" in these wires due to the surface states in the single layer were not successful.

In our theoretical studies of the thermal stability of small nanostructures we have discovered that it is likely possible, by judicious use of STM fabrication techniques, to create structures with greater stability, by making sure that only one type of step occurs (non-rebonded). It is possible to do so because simple geometry controls what steps form after the first removal of dimers by the STM. This work has been published [*Surface Sci.* 370, L213 (1996)].

Molecular assembly at room temperature. We have been able to assemble and move small Sb clusters on Si(001) using the STM tip. We have found that it is possible to pick up and redeposit Sb dimers on the surface. It is to our knowledge the first example of room-temperature assembly. We performed scanning tunneling spectroscopy on these clusters and determined that they had locally (on the nanoscale) quite different electronic properties, including metallic behavior at the center of a cluster. The work has been published [MRS Proceedings 448, 205 (1997)].

Development of a schema for rapid nanolithography. During the extension period we continued to develop a methodology that was invented earlier in our laboratories using other funds, namely a way to increase the speed and throughput of scanned-probe microscopes using a controller/driver for the piezoelectric positioner incorporating a novel feedback system. The follow-on work has been to develop a viable prototype to incorporate into our STMs. Higher speed and throughput are tremendously important in any nanolithography or nanopatterning, the central tenet of the work on this grant. We were able to complete this task by August 1997. Initially we simulated the performance of a piezo positioner under a variety of feedback schemes, both in an ideal noise-free environment and with added noise. We were able to show that our observer-based scheme equalled the performance of a feedback system with an ideal velocity sensor even in the presence of noise, the best possible performance. We then attempted to measure the resonant frequency and other necessary parameters of different piezo tubes, in order to design the feedback circuit. We decided that a better way was simply to measure the total

response of the system to a step function input and then to fit the measured response function with a second-order polynomial. The resultant "model" of the piezoelectric driver provides state estimates for the feedback system. We then constructed a prototype circuit that performed as expected. We are presently implementing this circuit in an STM. It is likely that there will be many STM applications for rapid-scan instruments, including for rapid surface chemical modification, as well as further applications beyond STMs for this feedback system, for example in precision machining, nanoscale-precision motion, and metrology. It is likely that this technology will eventually be commercialized.

A postdoc worked with partial grant support to complete the above task.

Personnel Supported by this Grant

M.G. Lagally

Craig Salling (postdoc)

Ivan Kravchenko (postdoc)

Brad Garni (student)

Zhenyu Zhang

Feng Liu

Adam Li (student)

David Olson (student)

Nobuyoshi Kitamura (student, later postdoc)

In addition, Jim MacKay (postdoc) provided effort in support of this project, but had other support.

Publications

1. "Fabrication of Atomic-Scale Structures on Si(001) Surfaces", C.T. Salling and M.G. Lagally, *Science* **265**, 502 (1994)
2. "Atomic Manipulation for Patterning Ultrathin Films", C.T. Salling, in Fabrication and Patterning at the Nanoscale, Materials Research Society Symp. Proc., Materials Research Society, Pittsburgh, PA (1995).
3. "Atomic Manipulation for Patterning Ultrathin Films", C.T. Salling, I. Kravchenko, and M.G. Lagally, *J. Vac. Sci. Technol.* **B13**, 2828 (1995).
4. "Unique Edge Structure and Stability of Fabricated Dimer Islands in Si(001)", Feng Liu, C.T. Salling, and M.G. Lagally, *Surface Sci.* **370**, L213 (1996).
5. "Antimony Cluster Manipulation on the Si(001) Surface by Means of STM", I.I. Kravchenko, C.T. Salling, and M.G. Lagally, *MRS Proceedings* **448**, 205 (1997)

6. "STM Studies of the Initial Growth of Sb on Si(001)", B. Garni, I.I. Kravchenko, C.T. Salling, and M. G. Lagally (in preparation).
7. "Optimum State Feedback Controller for the Piezoelectric Actuator", N. Kitamura and M.G. Lagally (in preparation).

Interactions/Transitions

a. Presentations at meetings. A number of invited papers were presented by Craig Salling, Zhenyu Zhang, and Max Lagally. The ones by Salling were all specifically on the work supported by this grant. The ones by Zhang and by Lagally were more general lectures that included highlighting the AFOSR work as a demonstration of deliberate nanopatterning in the larger picture of nanoscale structure formation. The paper by Salling at the American Chemical Society was highlighted in *C&E News* in April 1995.

1. "The Scanning Tunneling Microscope Looks at Crystal Growth", M. G. Lagally, CAM94 (Joint Meeting of the Canadian, American, and Mexican Physical Societies), Cancun, Mexico, September 1994.
2. "Scanning Tunneling Microscope Studies of Nanometer-Scale Pattern Formation at Surfaces", Zhenyu Zhang, Midwest Conference on Electron Microscopy, Evanston, IL, November 1994.
3. "Atomic-Resolution Measurements of Diffusion and Thermal Fluctuations at Si Surfaces", M. G. Lagally, Joint Japan/USA Gordon Research Conference on "Excitations at Semiconductor Surfaces: Fundamental Concepts and Applications in Semiconductor Processing", Oahu, Hawaii, November 1994.
4. "Strange and Wonderful Two-Dimensional Structures in Epitaxial Growth", Materials Research Society Fall Meeting, Boston, MA, November-December 1994 (MRS Medal Award Lecture).
5. "Theoretical and STM Studies of Nanometer-Scale Pattern Formation at Surfaces", Zhenyu Zhang, International Colloquium on Scanning Tunneling Microscopy, Kanezawa, Japan, December 1994.
6. "The Effect of Surface Structure on Atomic-Scale Patterning of Si(001)", C.T. Salling, 1995 Joint Research Center for Atom Technology International Symposium and Workshop, Tsukuba, Japan, February 1995.
7. "Insights from Nanoscale Structure and Morphology of Surfaces and Interfaces", M. G. Lagally, American Physical Society March Meeting, San Jose, CA, March 1995 (Davisson-Germer Award lecture).

8. "Point Defects on Semiconductor Surfaces", Zhenyu Zhang, Symposium on High-Performance Computing, 1995 SMC Simulation MultiConference, Phoenix, AZ, April 1995.
9. "Direct Nanoscale Patterning by Atomic Manipulation with the STM", C.T. Salling, Spring Meeting of the Materials Research Society, San Francisco, CA, April 1995.
10. "Fabrication of Regular Structures on Si(001) Surfaces by Removing Atoms with the STM", C.T. Salling, American Chemical Society Symposium, Anaheim, CA, April 1995.
11. "Structural Probes", M. G. Lagally, Virtual MBE Workshop, Hughes Research Center, Malibu, CA, June 1995.
12. "Atomic-Scale Fabrication on Semiconductor Surfaces at Ordinary Temperatures", C.T. Salling, Fifth International Conference on the Formation of Semiconductor Interfaces, Princeton, New Jersey, June 1995.
13. "Direct Patterning of Si(001) Surfaces by Atomic Manipulation", C.T. Salling; Eighth International Conference on Scanning Tunneling Microscopy, Snowmass Village, Colorado, July 1995.
14. "Energetics and Dynamics of Surface Atoms", M. G. Lagally, 40th International Field Emission Symposium, Madison WI, August 1995.
15. "Energetic and Dynamics of Surface Atoms", M. G. Lagally, ASPRONC Workshop on Nanoscale Technologies, Hakone, Japan, August 1995.
16. "Energetics and Dynamics of Self-Assembled and Manmade Nanoscale Structures on Si(001)", M. G. Lagally, International Symposium on the Science and Technology of Atomically Engineered Materials, Richmond, VA October 1995.
17. "Surfaces, Interfaces, and Thin Films", M.G. Lagally, NRC Workshop on Condensed Matter and Materials Physics, Washington, DC, June 1996

Contributed papers included ones associated with publications #2 and 5 above and the following:

1. "Investigation of the Mechanism for Removing Atoms from Si(001) with the STM", C.T. Salling and M. G. Lagally, 41st Annual Symposium of the American Vacuum Society, Denver CO, October 1994.
2. "Atomic Manipulation for Patterning Ultrathin Films", C.T. Salling, I. I. Kravchenko, M.G.Lagally, 39th International Conference on Electron, Ion, and Photon Beam Technology and Nanofabrication, Scottsdale, AZ, May 1995.

3. "The Topology and Stability of a Single-Dimer-Row Trench on Si(001)", F. Liu, C. Salling, and M.G. Lagally, APS March Meeting, St. Louis, MO, March 1996.

b. Consultative and advisory functions. During the first two years of the grant we worked with Dr. Michael Capano of Wright-Patterson AFB to determine the surface morphology of diamond-turned GaAs. We use a unique soft-x-ray diffraction facility that we have developed at the Synchrotron Radiation Center, as well as AFM. We have found a novel surface nanopattern that we believe may be useful as a template for multilayer coating gratings for x-ray focussing and monochromatization. A manuscript is in draft form but has not been completed.

We acted as a consultant on scanned probe microscopy and AFM tip fabrication to Lynntech, a small company that is supported by AFOSR under an SBIR Phase II grant. We have been helpful to the company in their search for appropriate tips and AFM tip coating technology that may be useful to the company.

c. Transitions. The work with WPAFB may eventually lead to a functional x-ray optical focussing element. We believe the work with Lynntech may lead to improved tip coating technology for localized corrosion investigations.

The work on scanners/controllers for piezoelectric actuators is of interest to PIE-ZOMAX Technologies, a local small company.

New Discoveries

Scientific discoveries as above; no patents or patent applications; development of concept discovered in the group but supported by other funds at the time of discovery.

Honors/Awards

M. G. Lagally was the 1994 recipient of the **MRS Medal**, awarded by the Materials Research Society in December 1994, the 1995 recipient of the **Davisson-Germer Prize** of the American Physical Society, awarded at the March 1995 APS meeting, and the recipient of the **Outstanding Science Alumnus Award** of the Pennsylvania State University in October 1996. The research supported by AFOSR is part of the body of work that was recognized by these awards. In the recent past Lagally has also received the **Adler Lectureship Award** of the American Physical Society and the **Welch Award** of the American Vacuum Society.