REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	8-20-96	Final 1 Jul 93 - 30 Jun 96

4. TITLE AND SUBTITLE

Parallel Molecular Nanofabrication

5. FUNDING NUMBERS

DAAH04-93-G-0295

6. AUTHOR(S)

Dr. Kenneth Douglas

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Coloardo
Dept. of physics
Campus Box 390
Boulder, CO 80309

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

US Army Research Office
PO BOX 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

ARO 31068.1 PH

11. SUPPLEMENTARY NOTES The view, opinions and/or findings contained in this report are those of the author and should not be construed as an official Department of the Army positions, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release: distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Low energy electron enhanced etching (LE4) has been used to transfer a triangular lattice of 10 nm diameter holes, with lattice constant 22 nm, into (100) silicon with minimal etch damage to the silicon lattice. Fabrication of the hole pattern is guided by a protein crystal template. The periodically heterogeneous surface chemistry of the nanopatterned silicon facilitates the self-aggregation of an electron beam-deposited titanium film to form an ordered array of metal nanoclusters. The titanium aggregates are positioned in register at the LE4-determined hole sites.

14. SUBJECT TERMS

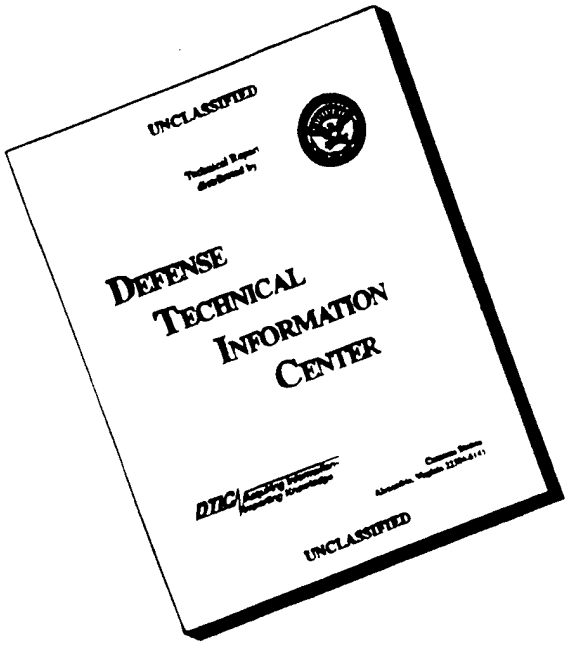
low energy electron enhanced etching (LE4), high resolution cross sectional transmission electron microscopy (HRXTEM)

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	UL

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

FINAL REPORT

1. ARO proposal number: P-31068-PH

2. Period covered by report: 1 Jul 93 - 30 Jun 96

3. Title of proposal: Parallel Molecular Nanofabrication

4. Contract or grant number: DAAH04-93-G-0295

5. Name of institution: University of Colorado at Boulder

6. Author(s) of this report: Dr. Kenneth Douglas

7. List of manuscripts submitted or published under ARO sponsorship during this period, including journal references:

"Parallel Nanofabrication Using Microbial S-Layers," K. Douglas, J.T. Moore, T. A. Winningham, S. Levy, I. Frithsen, J. Pankove, P. Beale, H.P. Gillis, D. Choutov, and K.P. Martin, submitted to FEMS Microbiology Reviews (to appear, Spring 1997).

"Controlled Morphology of Biologically Derived Metal Nanopatterns," J.T. Moore, P.D. Beale, T. Andrew Winningham, and Kenneth Douglas, submitted to *Science*.

8. Scientific personnel supported by this project and degrees awarded during this reporting period: Graduate Research Assistant Jon Moore (no degree awarded during this time period)

9. Report of inventions (by title only):

K. Douglas, J. Pankove, and G. Moddel, "Silicon Quantum Dot Laser"-- U.S. Patent Application Serial No. 08/612,021 filed 5 March 1996.

Brief Outline of Research Findings

We report nanocluster array formation by low energy electron enhanced etching (LE4) of biologically derived patterning masks. We have used LE4 to transfer a triangular lattice of 10 nm diameter holes, with lattice constant 22 nm, into (100) silicon with minimal etch damage to the silicon lattice. Fabrication of the hole pattern is guided by a protein crystal template. Moreover, the periodic alteration of the silicon surface chemistry nucleates the growth of a titanium nanocluster array from a titanium film evaporated onto the surface. The titanium aggregates are positioned in register at the LE4-determined hole sites.

Two-dimensional protein crystals (~1 μm in diameter) are isolated from the bacteria *Sulfolobus acidocaldarius* and are deposited from an aqueous suspension onto (100) crystalline silicon substrates. Prior to protein crystal deposition, the silicon substrates were cleaned in a 3:7 solution of H_2O_2:H_2SO_4 at 60°C or higher for 15 minutes ("piranha cleaning"). Since the LE4 process etches SiO_2 more slowly than Si at room temperature, it is desirable to minimize the thickness of the SiO_2 layer prior to etching. Consequently, we removed the SiO_2 with a buffered oxide etch and then placed the samples in an O_2 plasma for 2 minutes at 20 mA. This creates a new hydrophilic SiO_2 surface suitable for the attachment of the protein crystals, but with a thinner oxide layer than that which is left after piranha cleaning.

After the protein crystal masks are deposited on the prepared silicon surface they are coated with titanium (1 Å/sec) at an oblique angle of incidence (40° from normal incidence) by electron beam deposition. Average titanium thickness was measured (in vacuo) to be 1.2 nm, as determined by a quartz crystal monitor. The titanium film subsequently oxidizes when exposed to air. The titanium oxide thickness was measured to be 3.6 nm by atomic force microscopy (AFM) and independently confirmed by spectroscopic ellipsometry. The metal oxide/protein crystal composite is then etched by LE4 in a dc plasma configuration in 100 mTorr of H_2 at room temperature. Samples were thinned by tripod polishing and examined using high resolution cross-sectional transmission electron microscopy (HRXTEM). Figure 1(a) shows a low

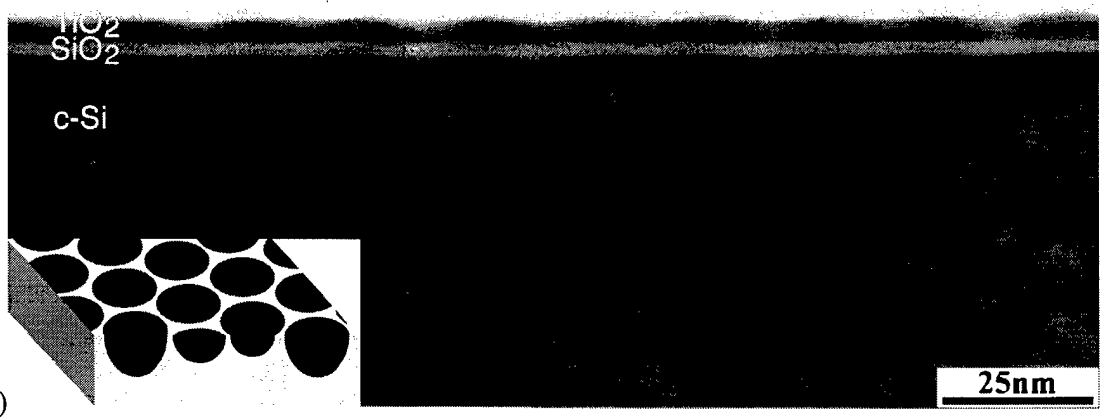
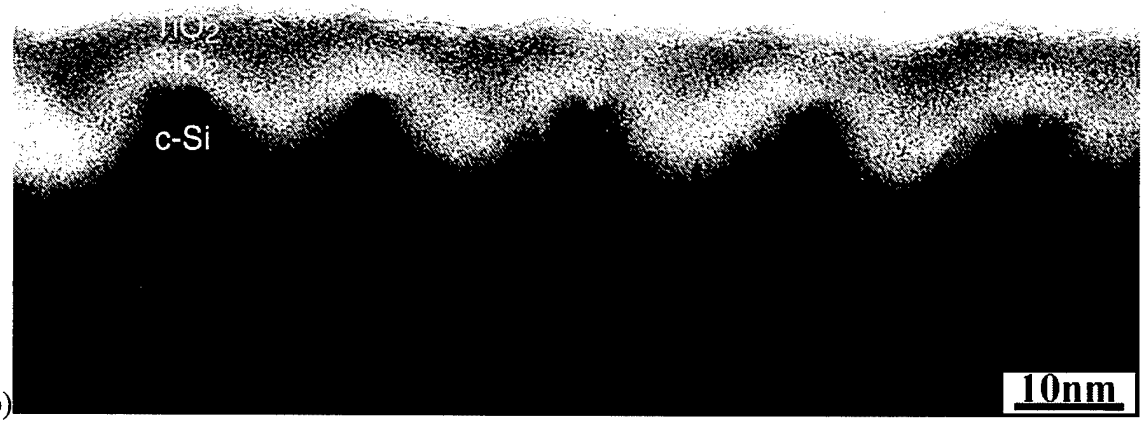


Figure 1(a)



1(b)

magnification view of an area of the sample exposed to LE4. The periodic nanometer-scale pattern of the protein crystal mask has been etched into the Si lattice to a depth of 10 nm. Because the cross-section occurs at an arbitrary orientation with respect to the rows of etched holes, inhomogeneities in the pattern and even missing holes in the image may arise as represented schematically in the inset to Figure 1(a). Etched features appear fairly isotropic. However, in previous experiments, Si(100) which has been LE4 patterned on a micron length scale with metal and with dielectric masks has shown etch directionality of various degrees, from nearly vertical sidewalls to classical isotropic etching. The extent of undercut increases with hydrogen partial pressure in all cases. Substantial improvement in the results reported here should be possible through process optimization. Figure 1(b) shows a high magnification view of an area etched by LE4. Lattice fringes are evident surrounding the holes indicating that the holes were etched through the native SiO_2 and into the crystalline Si and with an absence of the lattice damage typically seen with conventional ion beam and plasma etch methods.

Following pattern transfer by LE4, the TiO_2/protein crystal mask was stripped off with a 1:1 solution of H_2SO_4:H_2O at 130°C. XPS measurements performed at this juncture showed that the TiO_2 was completely removed within the sensitivity of XPS. In order to remove the SiO_2, the sample was then dipped in buffered HF for 30 seconds, rinsed with dH_2O, and blown dry with N_2. AFM of the bare Si surface revealed an array of holes on a triangular lattice with lattice constant 22 nm, identical to the protein crystal lattice used for patterning the surface. Then an LE4 patterned sample with the mask removed but with the SiO_2 layer still present was cleaved into two pieces. One piece was oxygen plasma cleaned for 30 seconds at 1 keV and ~8 mA. The second piece was not exposed to the oxygen plasma. 12 Å of titanium was then deposited by electron beam evaporation at normal incidence on both pieces. Upon AFM examination, the sample that was exposed to the oxygen plasma revealed ordered arrays of nanoclusters displaying the same symmetry and lattice constant as the protein crystal lattice used for patterning the surface (Figure 2; inset to figure shows Fourier transform). We hypothesize that the difference in the morphology of the TiO_2 arises, in part, from the presence or absence of an SiO_2 layer in the etched holes. As LE4 etches, it leaves behind a

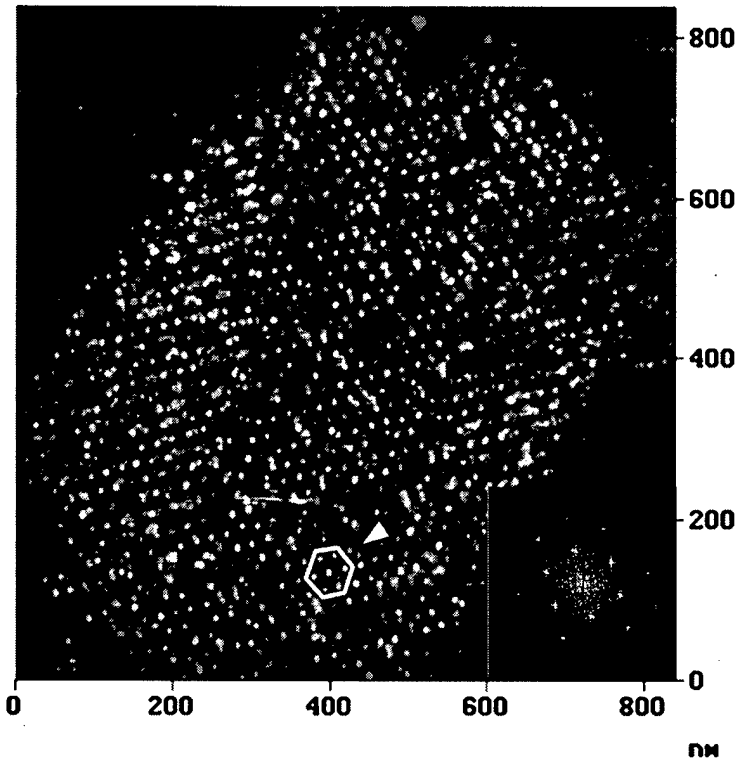


Figure 2

hydrogen-terminated Si layer which exhibits resistance to oxidization. The oxygen plasma treatment removes this layer after which the exposed silicon oxidizes and nanocluster formation can proceed. This interpretation is supported by the observation that LE4 processed samples which are allowed to age in ambient air for long periods of time (~2-3 months) will, following mask removal, also reveal nanocluster formation upon titanium evaporation.

A greater understanding of the mechanism of nanocluster formation may be obtained by the use of alternatives to titanium as the adsorbate. Metals with known islanding tendencies, such as silver, may be revealing and could possibly yield an array of interest for surface inhanced Raman scattering (SERS) investigation. Semiconductor nanocluster arrays are of interest for their optical properties, for example, and attempts at using germanium as the adsorbate are currently underway.

Low energy electron enhanced etching (LE4) has been used to transfer a triangular lattice of 10 nm diameter holes, with lattice constant 22 nm, into (100) silicon with minimal etch damage to the silicon lattice. Fabrication of the hole pattern is guided by a protein crystal template. The periodically heterogeneous surface chemistry of the nanopatterned silicon facilitates the self-aggregation of an electron beam-deposited titanium film to form an ordered array of metal nanoclusters. The titanium aggregates are positioned in register at the LE4-determined hole sites.