OFFICE OF NAVAL RESEARCH

FINAL REPORT

for

GRANT : N00014-94-1-0267

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Date Submitted: January 25, 1997

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Publications and honors

Mark Reed, Yale University

a. Number of papers submitted to refereed journals, but not published: 4


2. “There is plenty of room between two atom contacts”, C.J. Muller and M.A. Reed, Science, in press.


b. Number of papers published in refereed journals: 4


c. Number of books or chapters submitted, but not yet published: 2


d. Number of books or chapters published: none.

e. Number of printed technical reports/non-refereed papers: 1


f. Number of patents filed: none.

g. Number of patents granted (for each, provide a complete citation): 2


h. Number of invited presentations: 6


i. Number of submitted presentations: none

j. Honors/Awards/Prizes for contract/grant employees:

1. Chairman of Electrical Engineering, Yale University, July 1, 1995.


3. Divisional Associate Editor, Physical Review Letters

k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number: 96PR03563

Graduate Students: 4
Post-Doctoral Associates: 0

including the number of:

Female Graduate Students: 2
Female Post-Doctoral Associates: 0
Minority* Graduate Students: 0
Minority* Post-Doctoral Associates: 0
Asian Graduate Students: 2
Asian Post-Doctoral Associates: 0

l. Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

SRA, Evaluation of Denwin Software, 10K, 7/1/95-7/15/96, evaluation of software. No overlap

Hewlett Packard, gift, 50K, quantum structures. No overlap
Program Objective:

Program objective. This work is intended to provide new materials and methods for systems with micrometer and nanometer dimensions that will contribute to microelectronics design and manufacturing. The major components of the programs are:

- Self-assembly, which provides a way of making highly perfect structures with minimal cost and high quality.
- Self-assembled monolayers (SAMs), system of materials that provides a high level of control over the properties of surfaces, and that are also functional in various ways.
- Soft lithography, which provides a technology for patterning in the plane of the surface that is complementary to current photolithography.
- Electronically functional devices from conjugated organic oligomers of precise length and constitution for utilization as interconnects and devices.

Significant Results during the last year:

Self-assembly and SAMs:

1. Development of vertical micro- (~ few microns) and nano- (<100nm) integrated device structures for electrical measurement of SAM and functional device oligomers.
2. Demonstration (with Ralph Nuzzo) of the ability of patterned SAMs to direct the formation of metallic and ceramic structures by CVD and sol-gel processes.
3. Developed molecules for resist structures based on SAMs that should cleave with minimal doses of e-beam exposure, thus permitting patterning in the sub-100 Å regime.
4. Continue to develop molecules for resist technology based on precise control of molecular structure.

Soft lithography

1. The development of a method for very rapid prototyping of complex structures with medium feature sizes (20 microns); these systems are the correct size for use in microreactors, sensors, and related systems.
2. Extension of the techniques of soft lithography to include micromolding and microtransfer printing, and demonstration of the power of these techniques to reproduce structures in the sub-50 nm range of sizes. These methods offer a new class of processes to micro- and nanofabricators, with a number of potentially useful characteristics, including low cost, applicability to non-planar surfaces, and utility with new classes of materials.
3. Development of theoretical treatments for processes such as MIMIC (micromolding in capillaries); these treatments are essential in understanding how to develop processes based on them.
4. Demonstration of the value of microcontact printing for the fabrication of microstructures on curved surfaces. Demonstration systems have included micromagnets for NMR spectroscopy, stents, and stencils for in-fiber diffraction gratings.
5. Transfer of soft lithography process to Yale and demonstration of lithography for device processing.

Electrically functional devices

1. Conductance through a single conjugated oligomer that was isolated from all other conjugated molecules. The two probes were a gold surface and an STM tip. This achievement was listed as the number one contribution (out of the top ten) on MITRE’s web page concerning nanoelectronics.

2. Developed methods for the synthesis of 120 Å long molecules with two end groups attached, suitable for incorporation between patterned probes.

3. Developed methods for the synthesis of greater than 100 Å molecules on a polymer support, thus streamlining the synthetic protocol.

4. Synthesized molecules that may respond as wires with tunnel barriers, wires with quantum wells, and four terminal MOSFET transistor-type arrays. In each case, these possess molecular sized alligator clips for attachment to probes.

5. Developed a route to organic selenols (i.e., using selenium rather than sulfur for thiols) to better approach the Fermi level of metal contacts.

6. Measurement (using the vertical microfabricated structures) of alkanethiols (insulators) and phenylene-ethynylene-phenylene-disulfur-phenylene-ethynylene-phenylene (abbreviated PEPDSPEP). Both types show no significant length dependence of tunneling current, and resistivities of; for the PEPS film (1000 x1000 Å²) 3000 Ω-cm; and for an alkanethiol (CH₃(CH₂)₁₇SH, film 4 by 5 μm²) is 4x10⁹ Ω-cm.

7. Surface analytical experiments showing validity of cleaved thioacetate molecule absorption mechanisms, and compatibility of microfabricated structures with self-assembly of functional oligomers.

8. Demonstration of a fully integrated break junction in silicon.

9. Measurement of a single molecule in a break junction, with the observation of room temperature Coulomb blockade and the determination of the single molecule resistance (for a phenyl dithiol, ~22MΩ and a gap of ~0.7V)

Graduate students and postdoctoral fellows currently supported.

Reed
Graduate students: Jia Chen, Rachel Lombardi, Chong-Wu Xhou, Gabel Chong, Mandar Deshpande.
Postdocs: none
Undergraduates: Daniel Green
Technical results:
Reed and Tour groups have been working toward a self-assembled molecular electronic device for the past five years. Tour group has synthesized a rigid rod thiophene ethynylene (TE) oligomer disfunctionalized with thioacetates. The device embodiment relies on the thioacetate cleaving to the thiol and self assembling to gold electrodes fabricated by Reed group. The gold-thiol assembly mechanism has been well studied, however, the bulk of the work has been on n-alkanethiols, which are shorter, more labile molecules than these oligomers. The van der Waals interaction between alkyl chains contributes to the driving force for the formation of the n-alkanethiol SAM, this interaction is missing with the TE oligomers. An additional concern with the TE is the presence of sulfur in the backbone, which may provide a competing assembly mechanism. In order to verify the self-assembly of thioacetate functionalized conjugated oligomers, a series of experiments were performed at Pennsylvania State U.with Prof. Allara's group. Thiophene ethynylene copolymers were self assembled onto gold surfaces. The oligomers varied in length from monomer to octomer, with either no functional endgroup or one functional (thioacetate) endgroup. Grazing angle infrared (IR) spectroscopy and ellipsometry were used to study their assembly. Those oligomers with no functional endgroup chemisorbed to the surface via the sulfur in the thiophene backbone. The (base promoted) cleaved thioacetate molecules formed well-ordered monolayers for the shorter molecules. The films become disordered as the molecule length increases. Further experiments were done to test the compatibility of the self assembly with the processing history of the gaps devices. The active surfaces of the gaps devices should be suitable for self assembly.

Experimental Procedure
Substrates were clean silicon wafers with 10 nm chromium adhesion layer and 200 nm gold deposited by thermal evaporation. All molecule depositions discussed here were done under nitrogen in a glovebag, with the exception of the (not deprotected) thioacetates. Solutions of approximate concentration 0.1mM in tetrahydrofuran (THF) were used whenever possible; due to shortages of molecules, some solutions were of lower concentration. For the monofunctionalized oligomers, ~6 µl of NH₄OH was added to the solution to cleave the thioacetate in situ, forming a free thiol. Two of the monofunctionalized molecules, the monomer and the tetramer, were deposited without base as well (thioacetates). Depositions were continued for 1.5 to 6 days. Upon completion, the wafers were removed from solution, rinsed with THF, acetone and methanol, and spun dry. Ellipsometry and IR spectroscopy were done promptly thereafter. After completing analysis of the pure ML, the wafers were submerged into a 1mM solution of octanethiol (herein C8). The displacement of the TE molecules by the C8 was monitored as a function of time by ellipsometry and IR.
Monolayer Results and Discussion
Monolayers were prepared from the unfunctionalized dimer, tetramer and octomer. These compounds stick tenaciously to the gold surface, standing up to the normal cleaning procedures used for the thiol terminated oligomers including sonication. Ellipsometric thicknesses of the three unfunctionalized molecules □ TE₂, TE₄ and TE₈ □ were 8.6, 8.4, and 14.3 Å respectively. XPS analysis was done on the TE₄ monolayer (ML). There is some preliminary indication of two distinct sulfur peaks separated by approximately 2 eV, corresponding to two distinct binding energies. There is only one kind of sulfur in that molecule- in the thiophene ring. This shift is consistent in direction and approximate magnitude with the shift in binding energy seen by XPS for free thiols to gold-bound thiolate. A possible interpretation of this result is that the thiophene sulfur gains energy by chemisorbing to the gold substrate. However, due to steric hindrance, not all of the sulfurs can orient themselves to take advantage of this binding, hence the two separate states. Samples for XPS analysis were also prepared from the other unfunctionalized molecules. Data analysis is not yet complete.

Monolayers were formed from the deprotected monofunctionalized monomer, tetramer, and octomer. All appear to have formed well organized MLs. All of the IR features and the ellipsometric thicknesses remain essentially unchanged on repeated sonication in THF. Transmission IR measurements were done on an isotropic distribution of the molecule dispersed in KBr where quantity allowed to determine the optical constants for modeling purposes. From the results of the transmission IR, the angular orientation of the molecules in the self assembled monolayer can be modeled. Self assembled monolayers were also formed without base promoted cleaving of the thioacetate for two of the thioacetate terminated oligomers: the monomer, and the tetramer. It has been suggested that these molecules would form surface bound thiols similar to the cleaved species. Depositions were done for approximately 4 days with TE₁SAc and TE₄SAc. Ellipsometry and IR spectroscopy results indicate that the final product is very similar for either chemistry. For the tetramer, the only obvious difference in the IR spectra is the presence of the thioacetate stretch in the 1675-1715 cm⁻¹ region, as can be expected. However, there is a significant difference in the displacement time constant measured. This variation is inconsistent with the hypothesis that the thioacetates assemble the same as the thiols.

Microfabrication Process Compatibility with Self Assembly
The eventual goal of this collaboration is the self-assembly of the difunctionalized TE oligomers on a microfabricated chip in order to explore their electrical properties. Therefore, it is important to verify that the standard microfabrication processes will not inhibit assembly. A series of
experiments were performed to explore the compatibility of the two resist processes involved with gaps device fabrication done at Yale: photolithography and electron beam (e-beam) lithography. These processes are performed sequentially in the gaps device fabrication. The first features defined are large (100 + 100 μm²) squares (bonding pads) with ~10 μm lines leading from the pads to the central 100+100 μm² region of the chip. The features are formed by photolithography using a lift-off technique. When using lift-off to form metal structures, the final metal pattern is exposed to the resist only during the actual solvent dissolution of the resist. The definition of the smaller central lines (and gaps) is accomplished by e-beam lithography. This sequence means that while the e-beam written features are only exposed to the e-beam resist (poly methyl methacrylate, PMMA) during lift-off, the larger photolithographically defined features have a dual exposure: first to photoresist during lift-off, second to PMMA as it is spun onto the wafer and baked before e-beam exposure. In these experiments, the conditions for both lift-off and resist spin and bake were mimicked, after which the wafers were put through the usual procedure to form a SAM. In some cases, a monofunctionalized oligomer (TE4) was used, in others, a simple n-alkanethiol (n = 16). Analysis included ellipsometry before and after each step, and grazing angle IR reflectance spectroscopy. The ellipsometry and IR results indicate that although lift-off leaves some residue on the gold from both resists, this residue is insufficient to inhibit self assembly. Even the residue left from a baked on photoresist, regardless of the removal process, did not prevent ML formation. However the baked PMMA residue was tenacious, completely resisting sonication in acetone and only somewhat susceptible to sonication in 1,2,4-trichlorobenzene (loss of ~20Å in 20 minutes). Since the active surfaces for the gaps devices are only exposed to PMMA during lift-off, they should be suitable for self assembly.

To confirm these results on the actual devices of interest, a deposition of monofunctionalized TE4 was done at Yale with a microfabricated chip for elemental analysis by Auger Electron Spectroscopy (AES). Detection of the element sulfur was interpreted as indicative of the gold-thiol bond as well as the presence of the TE backbone. Data were collected for S, C and Au. The AES spot size was of order tens of microns, therefore the only suitable features for analysis on the real devices were the photolithographically defined bonding pads. The largest ebeam written structure was only 10μ wide. The ebeam written structures had the relevant surfaces, so for this test piece, the electron beam patterning was modified. A 200+200 μm² square in the central region of the chip replaced the usual <10μ lines and small gaps. The process history was kept the same as that of the real devices. On the large electron-beam written square, a level of sulfur was detected that was consistent with the pure MLs formed on the fresh gold substrate. On the bonding pads, however, the S measured was near noise level. Also note that while the gold signal was quite strong on the e-beam written sites, it was near the noise level on the photolithography
sites. This is consistent with the detection by ellipsometry of a much thicker overlayer on the photolithographic features attenuating the 68 eV electrons.

**Summary**

The sulfur in the backbone of the TE oligomers chemisorbs to gold. However, if one thioacetate group is present, the (endgroup) thiol-gold interaction dominates, at least for shorter molecules. The films become disordered as the molecule length increases. The effect of the difunctionalization on assembly has not been thoroughly addressed due to lack of molecules. The compatibility of the self assembly with the processing history of the gaps devices has been verified.